SCREENING LEVEL RISK ASSESSMENT TO DETERMINE POTENTIAL HIGH PRIORITY CONTAMINANTS AND NATURAL RESOURCES AT RISK IN BISCAYNE AND EVERGLADES NATIONAL PARKS

Final Project Report

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EXECUTIVE SUMMARY

Ecological risk assessment (ERA) is a process to evaluate the relationship between exposure to stressors and the probability of adverse effects occurring in ecological receptors from such exposures.

Florida International University was retained by Everglades National Park to conduct a 3-year study to monitor stressors such as organic (e.g., pesticides) and inorganic (i.e., trace metals) contaminants in Everglades and Biscayne National Parks (i.e., ENP, BNP) and conduct a screening level ecological risk assessment (SERA) to determine aquatic resources at risk in freshwater ecosystems (e.g., C-111 system) and/or adjoining estuarine sites (i.e., N.E. Florida Bay, and South Biscayne Bay). This SERA is exposure-driven because prior monitoring programs by state and federal agencies have detected the presence of both organic contaminants and metals in surface water and/ or in sediment of south Florida canals and estuarine sites.

The team selected sediments and fish as matrices to assess anthropogenic input of contaminants since they are better integrators of pollution chronology than water and constitute common reservoirs for most important toxic chemicals in environmental settings. The sediment sampling strategy for the project was based on the assumption that regions of ENP located near the Homestead Agricultural area (HAA) are more prone to chemical residue deposition, exposure and biological effects than areas along the Western boundary. Sites were located in a north-south pattern such as Shark River Slough (SRS) and Taylor Slough (TS). Saltwater sampling sites were also located in Biscayne and Florida Bays (BB, FB) to assess the presence of chemical stressors in the estuarine systems adjacent to ENP.

Sediments were collected (in multiple instances) from 26 sites in ENP, 9 sites in BNP and 4 sites in FB. Furthermore, the total 39 sites were divided into 7 regions; 5 in ENP and one each in BB and FB. Analysis of biological tissue was conducted on small fish in a total of 14 sites corresponding to sediment collections and also at 6 sites in Florida Bay. Selection of fish was restricted to species bioaccumulation capacity thus reflecting the occurrence of stressors in a localized area near the potential sources. In order to assess direct responses to environmental stressors acute toxicity tests were also conducted with freshwater benthic invertebrates (*Hyalella azteca*, *Chironomus tentans*) using field-collected sediment from selected sites using standard USEPA methodology.

Based on the most recent U.S.EPA framework for ERA three specific SERAs were produced during the course of the study based on available historical data to develop an understanding of background risk. The three SERAs included: risk associated with pesticides in surface waters from the C-111 system and adjoining estuarine systems (from historical data from South Florida Water Management District (SFWMD), NOAA, USGS), pesticides in sediment from South Florida canals (from historical SFWMD data); and metals in sediment from South Florida canals (from historical SFWMD data). In addition, a complementary SERA was also conducted based on the analytical data generated from the present 3-year contaminant monitoring program.

All four SERAs followed a two-tier approach. Tier 1 ranked impacted sites and identified chemicals of potential ecological concern (COPECs) based on available toxicological information and the occurrence levels through the hazard quotient (HQ) approach. Hazard indices (HIs) were then calculated when multiple chemicals were present at sites. In tier 2, probabilistic risk assessments (PRAs) were conducted with COPECs by

comparing exposure distributions of single contaminants with distributions of toxicity effect values (i.e., LC50s, and chronic no effect concentrations or NOECs) for those contaminants. The overlap of the distributions was used as a measure of risk. When analysis of contaminants was based on sediment concentrations they were converted to predicted pore water exposure concentrations. Distributions of pore water concentrations were then compared to distributions of aquatic toxicity values determined from water only toxicity tests. The similarity between toxic effect concentrations measured in pore water and in water-only exposures supports the use of the latter approach. The primary "exposure benchmark" used for the PRA was the 90th percentile exposure concentration (exceedence of a given value only 10% of the time) and the primary "toxicity benchmark" was the 10th percentile from the species sensitivity distributions (SSDs) of toxicity values (protection of 90% of the species) from acute and chronic laboratory toxicity tests. Protection of 90% of the species 90% of the time (10th percentile) was recommended by the Society of Environmental Toxicology and Chemistry (SETAC) when endangered, threatened, keystone and commercial species are not part of the ecosystem being considered for the ERA or SERA. In tier 2, the distributions of exposure data for organics and metals at sites were also used to determine the probability of exceeding consensus-based sediment effect concentrations (i.e., threshold effect concentrations or TECs, and probable effect concentrations or PECs) that were derived from effects based sediment quality assessment guidelines (SQAGs). Uncertainties in exposure and effects analysis and risk characterization are discussed for each SERA.

From the data obtained from the 3-year chemical monitoring program several key points could be made: several past and present use agrochemicals (i.e., mainly DDT, endosulfan, and their major metabolites; and copper) and urban derived contaminants such as

heavy metals (lead, chromium, nickel and zinc), metalloids like arsenic, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were detected in several areas within ENP and BNP. However, the general concentrations of contaminants in both sediment and fish tissue surveyed in this study from Everglades National Park, Biscayne National Park, and Florida Bay, are generally low in comparison to impacted areas near heavily urbanized and industrialized settings and rather similar to those found in relatively pristine areas. For example, when compared with data generated by the NOAA National Status and Trends Programme (NS&T) the mean levels of organochlorine compounds detected rank well below the national mean pooled concentrations. Despite this fact, the risk analysis did identify a handful of contaminants that will require additional long-term monitoring to assess future trends and insure proper resource management. Within this context, it is clear that anthropogenic activities have resulted in the enrichment of certain contaminants at various locations throughout the study area. Indications of trace metal enrichment, presence of PCBs at Black Point Marina, systematic detection of p,p'-DDE along the canal systems and the nearby marshes and a quasi-ubiquitous presence of endosulfan sulfate residues along the eastern border of ENP are clear examples of increased anthropogenic pressure along the parklands. Compounds of particular concern, based on the observed sediment concentrations and environmental distributions include: lead, chromium, copper, arsenic, nickel, and DDT and its metabolites (mainly p,p'-DDE).

Tissue body burden data show clear indications that currently used pesticides such as endosulfan are accumulating in tissue. Further studies are necessary to assess the effects of long-term chronic exposure particularly to higher trophic level organisms where biomagnification could be important. Endosulfan, and its sulfate have been reported in

multiple matrices (water, sediments and oysters) along the southern portions of Miami-Dade County and Florida Bay in several other monitoring studies. Endosulfan sulfate was detected in 87% of the tissue samples and 64% of the sediment samples analyzed in this study. Although the risk estimation does not point out to endosulfan or its metabolite as chemicals of potential ecological concern (COPEC) this assessment is probably biased due to the lack of benchmark exposure data (or criteria) to fully assess their effects. Because of the reiterative and consistent detection of this agrochemical in protected areas in south Florida it is recommended that increased monitoring and risk assessment be conducted in order to establish protection guidelines for resource management purposes.

Other organochlorine pesticides such as DDT, and its metabolites DDD and DDE, which are no longer in use, were also detected more frequently near agricultural areas, however the presence of these compounds in remote areas is a reflection of past activities and suggests that long-range transport of these compounds could be occurring throughout south Florida environments if sediments and soils are disturbed by modification of the water delivery systems.

The distribution of polychlorinated biphenyls was found to be relatively low and rather uniform throughout the areas sampled with the exception of one station sampled in Biscayne Bay (Black Point Marina), near a municipal landfill, which may be the source of the elevated levels of PCBs detected at that station. The observed concentrations for PCBs in both sediment and fish tissue throughout most of the stations sampled are low and are not expected to be of significant environmental concern. Overall, it appears that PCB distribution in this area is probably due mostly to unavoidable atmospheric deposition from long-range global dispersion.

Polycyclic aromatic hydrocarbon (PAH) concentrations detected throughout the study area are relatively low in comparison to other studies. The distribution of PAHs in sediments show more elevated concentrations at stations located in close proximity to Tamiami Trail and US-1 indicating street runoff as a potential source. An examination of the ratios of Benzo[a]pyrene/Benzo[ghi]perylene also indicate that automobile emissions are a predominant source of PAHs at most stations throughout the study area. The highest concentration of total PAHs detected in this study (912 ng/g) was detected at the BNP station (BBBP 1) located near a landfill and in close proximity to Black Point Marina, all other detections were much lower and usually at background levels. One exception were samples collected from the S-197 and US-1 areas at the lower reaches of the C-111 canal. PAH concentrations in these sediments ranged from 13 to 16 mg/kg. However, clear indication of the presence of creosote coated pilings in the area that may explain the results and makes these results outliers in the overall assessment.

Trace metal data indicate a potential for sediment enrichment above naturally occurring levels for elements including arsenic, chromium, copper, lead, nickel, and zinc at several of the stations sampled within ENP as well as arsenic in BNP. Copper, zinc, arsenic and lead all showed elevated concentrations along the Eastern boundary, and Tamiami Trail. Trace metal distribution in fish tissue show similar trends to the sediment data with the exception of zinc, which had high concentrations at all stations likely reflecting the natural abundance of the element in biological tissue. The reasons for the enrichment of this particular group of metals in ENP are not yet clear, but anthropogenic emissions from the urban areas of south Florida are the most likely source.

Although the presence of contaminants was clearly documented during the monitoring effort, results from the specific SERAs were used to bring these findings into a risk perspective for the probability of potential acute and chronic risks to aquatic organisms. Results from the two sediment SERAs on south Florida canals from SFWMD historical data are summarized below.

DDT and its metabolites (DDD and DDE), chlordane and endosulfan are identified as chemicals of potential ecological concern (COPECs) in sediment from South Florida Canals based on their frequency and magnitude of exceedence of sediment quality standards. Among these compounds p,p'DDE was the most frequently detected COPEC in sediments and chlordane was the least frequently detected COPEC. When the sediment concentrations were converted to exposures from predicted pore water concentrations endosulfan ranked highest and DDT lowest. However, when acute risk was evaluated as the probability of pore water exposures of COPECs exceeding the 10th percentiles for the species sensitivity distributions (i.e., 10th percentile from acute toxicity LC50 distribution) of freshwater arthropods all COPECs ranked <1%, indicating low acute risk based on available acute toxicity data. Endosulfan had the highest potential chronic risk to freshwater arthropods in the C-111 canal system (at structure S-178) based on the probability of pore water exposure concentrations exceeding arthropod chronic NOEC 10th percentile at 41%. Risk at the close-by S-177 structure was only estimated to be 8.1%. These results point out the localization of the stressors as well as the potential for these structures/canals to be sources of COPECs to ENP. The only other compound with similar potential for chronic risk was DDD at structures S-2 (southeast part of Lake Okeechobee), S-3 (southeast part of Lake Okeechobee), S-7 (near

WCA2/3) and at S-6 (on L-15 near WCA1 and 2). In contrast, the parent compound, DDT, presents no acute or chronic risks to freshwater arthropods along the surveyed areas.

The SERA for the SFWMD metal database showed that arsenic, antimony, cadmium, chromium, copper, lead, nickel and zinc were COPECs in sediment of south Florida canals based on their exceedence of sediment quality standards. Arsenic found in the Holey Land tracts and chromium found in the C-111 system were the most frequently detected metal COPECs and antimony, zinc and lead were the least frequently detected COPECs. S-176, S-177, S-178 and S-18C on the C-111 system had some of the highest metal hazard indices. The highest hazard index for metals in the C-111 system out of all sites was at S-178 based on the presence of chromium, copper, nickel and zinc. The highest bulk sediment exposures were for zinc (at S-178) and lead (at S-176) in the C-111 system. The probability of pore water exposures exceeding the acute10th percentile for SSDs was highest for copper at S-178 and S-177. Acute risk estimates were also high for zinc at S-178. The probability of pore water exposures exceeding the chronic NOEC 10th percentile for SSDs was highest for copper at S-178 followed by S-177. The metal with the next highest probability of exceeding the NOEC 10th percentile was lead at S-176. Zinc and nickel were also present at S-178 with low potential chronic risk.

Results of the surface water SERA in the C-111 system indicated possible hazards from surface water exposure concentrations of endosulfan and chlorpyrifos. Malathion concentrations equaled WQC in two samples but detections were generally

infrequent. Surface water concentrations of atrazine and metolachlor did not exceed criteria benchmark values. Therefore, a second tier using probabilistic methods and criteria from field/mesocosm studies was conducted to assess the potential risks of chlorpyrifos and endosulfan on fish and arthropods. The highest 90th centile concentration estimate for endosulfan was found at S-178/Site C. Concentrations of endosulfan at S-178/Site C were generally higher in samples taken at the height of the dry season (February) than the wet season (June). Concentrations of endosulfan decreased downstream of S-178/Site C. The two highest concentrations of chlorpyrifos were found at S-177/Site B, which also had the highest 90th centile concentration estimate for chlorpyrifos. When measured concentrations from all freshwater sites were considered together, the 90th centile concentration estimate for endosulfan was higher in 2000 than in 1999. In addition, the 90th centile concentration estimate for chlorpyrifos and endosulfan were higher at Joe Bay than other estuarine sites. For chlorpyrifos and endosulfan effects, the 10th centile effect concentration estimates were generally lower for saltwater species than for freshwater species. The 10th centile effect concentration estimates for chlorpyrifos in freshwater and saltwater were lower for arthopods than fish. The 10th centile effect concentration estimate for endosulfan was lower for freshwater fish than freshwater arthropods but higher for saltwater fish than saltwater arthropods.

From a review of field and mesocosm studies for both endosulfan and chlorpyrifos, threshold effect concentrations of 0.1mg/L and 1.0mg/L, for each respective compound, were chosen.

Based on joint probability curves that compared the overlap of distributions of measured concentrations and acute effect values, potential risk was higher for arthropods in freshwater or estuarine sites exposed to chlorpyrifos in 1999 over 2000. Furthermore,

potential risk was greater for arthropods exposed to endosulfan in freshwater and estuarine sites for 2000 versus 1999. Joint probability curves for all data from 1999 and 2000 at various sites found the highest potential risk for freshwater arthropods to be from measured endosulfan concentrations at S-178/Site C. Likewise, the highest potential risk for freshwater fish was found at S-178/Site C from measured endosulfan concentrations. Potential risks to freshwater fish and arthropods decreased at a site (S-18c/Site E) directly downstream from S-178/Site C. For the estuarine sites, potential risks appeared to be only slightly higher at Joe Bay for arthropods than at Card Sound and Highway Creek.

Potential risks at all estuarine sites were higher for endosulfan and arthropods than chlorpyrifos and arthropods. The potential risks to estuarine fish were lower than for estuarine arthropods. Potential risks at all freshwater sites were higher in February (dry season) than June (wet season). Potential risks for measured concentrations in estuarine sites were variable. In all scenarios, potential risk increased from single chemical exposures to multiple chemical exposures.

The 1 mg/L NOEC for the effects of endosulfan on aquatic invertebrates and fish from field studies was exceeded once at S-178/Site C on February 16, 2000. The highest measured concentration of chlorpyrifos at S-177/Site B did not exceed a NOEC of 0.1 mg/L from field and mesocosm studies.

Results of the sediment SERA from the 3-year monitoring program showed that among the 135 contaminants measured, p,p'-DDE was the only organic pesticide ranked as a COPEC as a result of the exposure data from Shark River Slough (SRS) and Tamiami Trail (TT). However, not enough data was available to assess its ranking for Biscayne National Park. In addition, the probability of acute and chronic risk from DDE was zero. Shark River

Slough followed by Tamiami Trail had the highest pesticide Hazard Index (HI) of all seven regions. Florida Bay had the lowest pesticide HI. Arsenic, chromium, copper, lead, nickel and zinc were also classified as metal COPECs in multiple regions. Cadmium was the least frequently detected metal. Arsenic was the only metal COPEC present in all seven regions which also had the highest number of sediment quality exceedences. The East Boundary (EB) of Everglades National Park and TT had the highest metal HIs. The metals at EB responsible for the high HI were arsenic, followed by chromium, copper, nickel and lead. The metals at TT responsible for the high HI were arsenic, followed by copper, zinc, lead and nickel. Florida Bay's metal HI was greater than that of Biscayne Bay's. The highest 90th percentile for bulk sediment was for chromium in EB followed by zinc in TT. Copper was found as a COPEC in five regions at a 90th percentile range of 11.64 mg/kg (BB) to 41.98 mg/kg (TT). The highest 90th percentiles for predicted pore water concentrations were for arsenic with a range of 45.53 ug/L in the EB to132.68 ug/L in FB. Risk estimates were only determined for arthropods because they represent the most group to metals.

Probability of copper concentrations exceeding acute toxicity values was highest in TT, followed by EB, SRS, C-111 and BB. These were the highest acute risk estimates of all metal COPECs in all seven regions. Acute risk estimates for copper in the C-111 system were lower than other sites but it was the metal COPEC at C-111 with the highest risk out of six metal COPECs found. Results are similar to the SERA conducted on historical metal data from South Florida Water Management District.

Arsenic was the only metal COPEC in Florida Bay with high potential acute risk. In Biscayne Bay both arsenic and copper showed potential acute risk. The highest potential

chronic risk for a metal COPEC was for copper based on the probability of exceeding chronic NOEC values in TT, followed by EB, SRS, C-111 and BB.

Probability of DDE exceeding the Florida DEP sediment quality assessment guideline (SQAG) threshold effect concentration (TEC) at SRS and TT was high but less than 5% for exceeding the Florida DEP sediment SQAG PEC at these sites. The highest probability of a metal COPEC exceeding the sediment Florida TEC was for lead in TT followed by arsenic in TT. Arsenic also had a high probability of exceeding the Florida TEC in SRS and in FB and BB. The highest probability of a metal COPEC exceeding the
Florida DEP sediment SQAG PEC was for chromium in EB followed by lead in EB. Copper did not appear to be of concern using the TEC/PEC probabilistic approach.

Our SERAs show that when using the historical databases and the three-year analytical monitoring data for contaminant exposures in South Florida, there were a small number of organic (e.g., DDD, endosulfan) and metal (e.g., arsenic, copper, chromium, lead, nickel, zinc) COPECs based on concentrations found in sediment and/or water and their exceedence of numerical criteria. Contaminant distribution of COPECs is however limited to a small number of sites in south Florida. Based on a probabilistic approach with the exposure data and the readily available acute and chronic toxicity data for each COPEC, risks to aquatic receptors in south Florida are also limited to DDD, endosulfan, arsenic and copper. For Everglades National Park and surrounding areas endosulfan, copper and arsenic appear to be the most likely COPECs to present potential risks to aquatic organisms.

Note that although we completed one of the first and more complete ecological risk assessments for Everglades National Park considering the geographic extent of south Florida, the diversity of land uses, the presence of multiple and increasing sources for anthropogenic

loading and, the fact that ENP covers an area of approximately 28,000 km^2 (~11,000 mi^2) in close proximity to sprawling urban settings; we have only monitored a very limited number of sites and ecosystems. Therefore, a more extensive, long-term chemical monitoring and ecological risk assessment effort should be pursued to definitively delineate specific areas of concern, identify native resources at risk and ultimately to provide better management decision tools in support of present and future ecosystem sustainability.

1. INTRODUCTION

1.1 Background

Ecological risk assessment (ERA) "is a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors" (U.S.EPA, 1992; 1998). As stated in the most recent U.S. EPA guidelines for ERAs, it "is used to systematically evaluate and organize data, information, assumptions and uncertainties in order to help understand and predict the relationships between stressors and ecological effects in a way that is useful for environmental decision-making. An assessment may involve chemical, physical, or biological stressors, and one stressor or many stressors may be considered" (U.S.EPA, 1998).

Florida International University under Cooperative Agreement # 1443CA5280-01-007 was retained by Everglades National Park (National Park Service, US Department of the Interior) to conduct a 3-year study (2001-2004) entitled-"Screening Level Risk Assessment to Determine Potential High Priority Contaminants and Natural Resources at Risk in Biscayne and Everglades National Parks: Critical Information Needs for CERP."

In the present context, "adverse ecological effects" are understood to be anthropogenic changes considered undesirable because they could alter valued structural or functional characteristics of ecosystems (USACE, 1996; U.S.EPA, 1998). The "stressors" at issue are considered to be organic chemical contaminants (e. g., pesticides) and/or inorganics (i.e., trace metals) present in freshwater ecosystems and/or adjoining estuarine sites in South Florida. The authors of this assessment recognize that salinity changes (and other chemical

and non-chemical factors) may be direct, indirect, or interacting stressor(s). However, the latter factors are not being considered here because this is a “screening” ERA (or SERA).

This is the first SERA conducted in support of the Comprehensive Everglades Restoration Plan (CERP) and it is being “exposure-driven” (Suter, 1993) because monitoring programs conducted by State (i.e., South Florida Water Management District or SFWMD, West Palm Beach, FL; Department of Environmental Resources Management or DERM, Dade County, Miami, FL) and Federal (i.e., U.S.EPA, NOAA, USGS) regulatory agencies have detected the presence of organic pesticides and metals in water and/or in sediment in South Florida freshwater canals and/or in estuaries/saltwater systems. Presently, there is little evidence that such chemical exposures are eliciting adverse biological effects in aquatic organisms (or ecological receptors) in these systems or on their potential risk. Cause-effect relationships have also not been defined. However, endosulfan concentrations in the C-111 freshwater system and adjoining estuaries have exceeded U.S.EPA acute and chronic numerical water quality criteria for fresh- and salt-water (DeLorenzo et al., 2001). Furthermore, there was a small margin of safety when comparing ambient water exposure concentrations of chlorpyrifos to U.S.EPA water quality criteria for this insecticide. Although the herbicide atrazine is at low concentrations in the freshwater systems in South Florida, it is ubiquitous and frequently present in water (Pfeuffer, personal communication; Gross et al., 2001). The significance of exposure to pesticides by ecological receptors in South Florida in general gains in importance in lieu of the long crop-growing season, frequency of pesticide usage, wide-scale use of pesticides for mosquito and termite control and on golf courses and continuous presence of multiple pesticide residues in sediment and water of receiving systems (Richard Pfeuffer, personal communication). The increase in population

development in South Florida further potentially exacerbates exposures to ecological receptors from PAHs and trace metals.

The SERA presented herein is a "prospective" aquatic assessment where the presence of organic (e.g., pesticides) and inorganic contaminants (i.e., metals) are typically associated with historical activities. It is designed to "predict" the potential risk(s) associated with an alteration of the site landscape (e.g., alteration from agricultural fields to freshwater systems and secondarily to saltwater systems-Northeast Florida Bay and South Biscayne Bay). We have used a variety of toxicity and risk assessment procedures that are presently classified as the best available technology and that are widely accepted by the current scientific community to predict toxicity and risk to ecological receptors.

1.2 Objectives and General Ecological Risk Approach

The four main objectives of the three-year study were to conduct a screening level ecological risk assessment (SERA) in Everglades and Biscayne National Parks and to:

1. review background data on contaminants and their toxicological effects in South Florida aquatic ecosystems and conduct SERAs for these data determining whether risks to aquatic organisms are significant and estimate the magnitude and extent of effects and their associated uncertainties,
2. determine the identity, magnitude, and distribution of contaminant (organic and trace metals) exposures in sediment and whole fish tissue at selected sites in and around Everglades National Park (ENP) and Biscayne National Park (BNP),
3. conduct whole sediment toxicity studies collected from field sites, and

4. conduct an SERA using the sediment chemistry monitoring data for contaminants present from objective 2.

To address objective 1 the project team conducted a review of all existing available literature on contaminants from monitoring programs in South Florida including Everglades and Biscayne National Parks. Chemical monitoring programs are surveys that identify contaminants, their occurrence, geographic distribution and the trends of detections both spatially and temporally. We then conducted screening level aquatic ecological risk assessments (SERAs) according to the U.S. EPA framework (1992, 1998) for:

- contaminants (pesticides) in sediment from South Florida canals on historical data from a monitoring program by South Florida Water Management District (SFWMD).
- contaminants (metals) in sediment from South Florida canals on historical data from a monitoring program by South Florida Water Management District (SFWMD).
- contaminants (pesticides) in surface water from the C-111 system on data from monitoring programs by SFWMD, NOAA and USGS.

The rationale for the first three SERAs were to serve as a baseline of information for the present 3-year study. Historical data from 1990-2002 on pesticides and metals were compiled and analyzed separately using the SFWMD data which is one of the most extensive state sediment and water quality monitoring programs in the U.S. (Miles and Pfeuffer, 1997; Pfeuffer and Rand, 2004). In addition, we conducted a SERA for the C-111 system and

adjoining estuarine areas (NE Florida Bay, South Biscayne Bay). The rationale for the latter assessment is that water from the C-111 basin along with Taylor Slough form the eastern hydrologic boundaries for water delivered to ENP. Furthermore, in the northern and central portion of the C-111 basin is an agricultural area (Frog Pond) which lies at the headwaters of Taylor Slough. This area is a potential source of pesticides to Taylor Slough, ENP (including Florida Bay) and BNP (including south Biscayne Bay). This is the first time analytical data from monitoring programs in South Florida have been compiled, synthesized and evaluated according to the USEPA framework for CERP. These risk assessments will provide information for CERP projects and will identify the following products:

- contaminants (or stressors) of potential ecological concern (COPECs),
- acute and chronic risks of exposure to single contaminants for aquatic organisms based on existing data,
- acute and chronic risks of exposure to the joint action of mixtures of contaminants for aquatic organisms based on existing data,
- the sites (locations) where acute and chronic risks are present to species,
- the sensitive species, and
- relevant data gaps and uncertainties

Relevant background information on contaminant exposures in surface water versus sediment in ecological risk assessments are discussed in the next section.

To address objectives 2 and 3 the project team conducted (a) an analytical chemical monitoring program to define the specific contaminants and their concentrations in sediments and whole fish tissue in ENP and BNP (b) toxicity studies on standard test species with field-

collected sediment from selected sites. To address objective 4 the project team conducted an SERA on the chemistry data we generated from objective 2.

The ultimate goal of the three-year project was to determine the potential probability of toxicological effects/risk resulting from exposure to contaminants in ENP (including northeast Florida Bay) and BNP (including south Biscayne Bay). Exposure (i.e., from monitoring programs) and toxicologically effects (i.e., from the literature) data in freshwater and saltwater environments were considered. Aquatic invertebrates, plants, phytoplankton, and fish were included in the assessment, but reptiles, birds, and mammals were not. Amphibians were only included in the SERA on the C-111 for malathion, endosulfan and atrazine.

Based on the monitoring data, organics and trace metals were considered for single chemical SERAs. Since each chemical is not used in isolation and may co-occur with the others; aquatic risk associated with the joint effects of multiple exposures was also considered in certain cases (i.e., pesticide surface water exposure SERA in C-111). The generic approach for the SERAs conducted for objectives 1 and 4 are discussed below. For more specific details on each assessment refer to Section 5 for the actual SERA.

For risk characterization of single-chemicals, a probability distribution of actual environmental concentrations (AECs) of contaminants in media (i.e., sediment, water) was compared to a probability distribution of species response data (e.g., LC50s, NOECs from chronic studies) as determined from laboratory single-species laboratory toxicity tests, field studies or microcosm studies (Suter, 1993; Solomon, 1996). The overlap of the distribution is a measure of risk for that chemical to aquatic life. The hazard quotient (HQ) approach was also used, based on the water or sediment criteria and the measured environmental

concentrations (MEC) (Suter, 1993). If the quotient of the exposure concentration to the criteria or guideline value (i.e., surface water or sediment) was equal to or greater than 0.5 an adverse effect (i.e., hazard) was expected to occur and was treated as evidence that the contaminant is worthy of concern. The HQ approach was the earliest method used by the U.S.EPA in the pesticide registration process for chemical companies under the Federal Insecticide Fungicide Rodenticide Act (FIFRA) to determine acute and chronic risks and whether a new pesticide should be approved (or not) for registration or be placed under a restricted use classification (Urban and Cook, 1986).

Probabilistic distributions that are used in probabilistic risk assessments (PRAs) are preferred over the use of HQs because they allow a better estimation of the magnitude and likelihood of potential ecosystem level impacts as opposed to using "worst-case scenarios" typically used in the HQ approach (Solomon, 1996; Solomon et al., 2000). PRAs allow the assessor to include estimates of uncertainty as well as stochastic properties of both exposures and responses. The HQ method is useful in the early stage stages of an ERA to rebut the presumption of a potential for adverse effects. It does not estimate the type, level, or probability of effects. Highly conservative assumptions and parameter estimates (i.e., point) are used in the HQ method. It is thus very protective and extremely conservative. Risk is a statistical concept that is defined as the expected frequency (or likelihood) or probability of undesirable effects resulting from specified exposures to known or potential concentrations of a chemical. Therefore, point estimates used in the HQ approach cannot be used to establish risk estimates.

A tiered ecological risk assessment approach was suggested by ARAMDGP (SETAC, 1994) and endorsed by the U.S.EPA (ECOFRAM, 1999) that uses a stepwise approach

progressing from the simple HQ approach to more complex and more resource-intensive methods like probabilistic risk assessments (PRAs). The above approach was endorsed in the SERAs conducted in this program. The results of both approaches are discussed in the individual SERA sections. The line of evidence thus uses concentrations of individual chemicals in environmental media (i.e., measured concentrations in water, sediment) to estimate exposure and results of toxicity test endpoints for individual chemicals to estimate effects. In tier 1 they are combined in two steps. First, they were screened against criteria benchmarks to determine chemical (or contaminants) of potential ecological concern (COPECs) based on HQs ≥ 0.5. The results of the screening assessment are presented as a table listing all chemicals that exceed benchmark criteria indicating which contaminants are COPECs and the sites where they were present. Second, if numerous contaminants were present at potentially toxic concentrations at a site, a Hazard Index (HI) was calculated (Suter et al., 2000). Since there is little to no toxicity data on most mixtures we assumed the combined toxic effect was a result of concentration-addition from the combined effects of individual toxicities of contaminants. The assumption of additivity is accurate for chemicals with the same mechanism of action and is conservative in most cases for mixed mechanisms of action (Konemann, 1981; Alabaster and Lloyd, 1982). The HI is the sum of HQs at a site and is expressed as:

$$\sum (AEC/TBC)$$

It is the quotient of the actual environmental concentration (AEC) or the maximum concentration of the contaminant in a media divided by the toxicological benchmark concentration (TBC) or criteria/guideline (e.g., water or sediment criteria).

The hazard indices are used for comparative purposes rather than to draw conclusions. If the HI equals 1 or more it is predicted that the assessment endpoint (i.e., what is at risk or the environmental value in need of protection) will occur (e.g., survival of fish populations). This prediction is applicable if all the contaminants have the same mechanisms of uptake and mode of action. For heterogeneous chemicals in a mixture, the addition of normalized HQs to predict effects is going to provide a conservative estimate, because the combined effects of chemicals in environmental samples have usually been found to be additive or less than additive and not synergistic (Alabaster Lloyd, 1982). When contaminants act independently a response addition model is applicable. This type of model has not been used much in ecological risk assessments. We however use a response addition model in Tier 2 (Probabilistic Risk Assessment) of our SERA in the C-111 following a procedure similar to Traas et al. (2002). The alternatives to concentration and response addition are interactions like synergism and antagonism. Although synergistic and antagonistic interactions are possible there is little scientific basis for modeling these phenomenon without toxicity tests with mixtures. Therefore, in the absence of specific toxicity information on interactions, concentration-addition is the most appropriate default assumption.

In tier 2 probabilistic risk assessments (PRAs) were conducted for all COPECs by comparing exposure distributions of single contaminants with distributions of toxicity effect values (LC50s, chronic NOECs). Multiple chemical exposures (or joint action) was only considered in the surface water SERA in the C-111 system but it was not considered in any of the sediment risk assessments because of the limited sediment toxicity databases and the number of uncertainties involved. The primary exposure benchmark used for this risk assessment was the 90th percentile exposure concentrations (exceedence of a given value

only 10% of the time) and the primary toxicity benchmarks was the 10th percentile of species sensitivity distributions (protection of 90% of the species) from acute and chronic exposures. Protection of 90% of the species 90% of the time (10th percentile) was recommended by the Society of Environmental Toxicology and Chemistry (SETAC, 1994). It is assumed that with this benchmark protecting a large enough percentage of the population will promote the structure and function of most ecosystems. However, if the unprotected species are endangered, threatened, keystone or of commercial or recreational importance these benchmarks cannot be adequately supported.

In tier 2, the distributions of exposure data for organics and metals at various sites (or regions) were also used to determine the probability of exceeding consensus-based sediment effect concentrations (SECs; Swartz, 1999) that were derived from effects- based sediment quality assessment guidelines (SQAG) (MacDonald et. 2000a). The SQG for the protection of benthic organisms are grouped into two categories-a threshold effect concentration (TEC) and a probable effect concentration (PEC). TECs identify COPEC concentrations below which harmful effects on benthic organisms are expected to occur only rarely (MacDonald et al., 2003; Buchman, 1999). The TEC is calculated as the geometric mean of the 15th percentile concentration of the toxic effects data set and the median of the no-effect data set. Examples of of TECs include threshold effects levels (TELs; Smith et al., 1996; Ingersoll et al., 1996), effect range low levels (ERLs; Long and Morgan, 1991; Ingersoll et al., 1996), and lowest effect levels (LELs; Persaud et al., 1993). PECs identify COPEC concentrations above which adverse effects on benthic organisms are frequently expected. The PEC is calculated as the geometric mean of the 50% of impacted, toxic samples and the 85% of the non-impacted samples. Examples of PECs include probable effect levels (PELs; Smith et al.,

1996; Ingersoll et al., 1996), effect range median values (ERMs; Long and Morgan, 1991; Ingersoll et al., 1996) and severe effect levels (SELs; Persaud et al., 1993).

The consensus-based TECs and PECs are calculated by determining the geometric mean of all SQGs that are included in the TEC/PEC type values. The consensus-based approach has been used to derive numerical SQGs for PAHs in marine systems (Swartz, 1999), PCBs in freshwater/marine sediments (MacDonald et al., 2000b), and for metals, PAHs, PCBs, and pesticides in freshwater sediments (Ingersoll and MacDonald, 1999; MacDonald et al., 2000a). MacDonald et al. (2003) in there document on "Development and Evaluation of Numerical Sediment Quality Assessment Guidelines for Florida Inland Waters" (Technical Report) pointed out the following about concensus-based SECs:

- provides a unifying synthesis of existing SQGs by estimating their central tendency
- reflects causal rather than correlative effects
- accounts for effects of contaminant mixtures in sediment

Consensus-based SECs were evaluated by MacDonald et al. (2000a, 2000b, 2001), Kemble et al. (2000), USEPA (2000a), and Ingersoll et al. (2001). USEPA (2000a) and Ingersoll et al. (2001) concluded that consensus based SECs can be used to accurately predict the presence and absence of sediment toxicity on a regional and national basis. The consensus-based approach appears to be applicable for evaluating sediment quality conditions and establishing effects-based SQAGs for Florida inland waters (MacDonald et al., 2003).

The SERAs were intended to quantify the likelihood and significance of potential ecological effects of the contaminants in water and sediment and not to determine causes of any declines in populations of native invertebrates, fish, plants or amphibians that may be

prevalent in ENP and BNP. Historical water development activities may have altered habitats and impacted populations. Furthermore, other contaminants (e.g., pharmaceuticals) including nutrients are not being investigated in the SERA and may likely also contribute to aquatic impacts in these freshwater/saltwater areas.

1.3 General Considerations for Exposure Assessment in Surface Water and Sediment

Included below is a brief summary of relevant information and some key principles or generalizations on the activity of metals and organics in water and sediment which will be important in not only assessing risk to the aquatic environment but also in the discussion of uncertainties in the individual risk assessments. It is not intended to review all the chemistry, transport and transformation processes that affect the fate and ultimate exposure to metal and organic contaminants in water and sediment systems.

Organisms in water and sediment are primarily exposed to contaminants through the following exposure routes: inhalation/respiration, dermal absorption and dietary (i.e., either through food or ingestion of sediment). Physical and chemical characteristics of both water and sediment affect their quality, and the bioavailability, accumulation and toxicity of metals and organic contaminants.

Metals are naturally occurring in the environment and several play a key role in plant and animal distributions and are potential limiting factors ( ). Certain heavy metals that are essential for life are Cu, Zn, and Fe. Other heavy metals like Cd and Pb have no known biological role, are highly toxic and are therefore considered non-essential. Organisms have therefore developed mechanisms for coping with certain excess metals (e.g., acclimation,

adaptation). Alternatively, there are "background" concentrations of certain "relic" organochlorine compounds (e.g., DDE, DDD, DDT) that are not naturally occurring but are nonetheless present as a result of anthropogenic input and which also may compromise the physiology of organisms. However, there is little information in the literature on the significance of background concentrations of organochlorines to aquatic organisms. It should be noted that we are aware that background concentrations of metals (and organics) in some sampling locations may contribute to and exacerbate toxicological effects and accumulations of contaminants from various exposure routes or conversely they may result in adaptation of organisms to higher contaminant concentrations and result in increased exposure. Since it is difficult to separate "natural background" from anthropogenic concentrations of metals the risk assessments conducted in this report we use "total metal concentrations" in the exposure assessment part of each SERA. Thus far the "added risk" approach has not been widely used (EC Health and Consumer Protection, 2004).

Water

Ecological risk assessments of contaminated waters are typically based on measurements of surface water concentrations of contaminants. Unlike sediment and soil, concentrations of contaminants in water may be highly variable over short time periods. Sampling should therefore include episodes of high concentrations and the frequency and duration of such episodes. Ecological effects assessments require both short- and long-term exposure information to prepare acute and chronic estimates of risk. Most monitoring programs typically are short in duration (e.g., 1-2 years) and do not sample frequently (e.g., 1-2 times/year). The SERAs conducted in this study were based on both long-term monitoring

(e.g., SFWMD) and short-term monitoring programs. The water sampling in the C-111 surface water SERA was based on water column grab samples collected from a boat.

The major issues to be considered by a risk assessor are averaging times for the sampling measurements and the forms of the chemical in water that must be measured.

For example, in aqueous exposures of biota the most controversial issue is the form of metal to analyze in water. In aquatic systems two pools of metals have to be considered. One pool consist of metals that exist as dissolved species, bound to colloids (organic or metal oxides) or dissolved organic matter and those bound to sediment particles through an exchangeable binding process (exchangeable or labile pool). The second pool consists of metals found within the mineral matrix of sediment solids and is mostly unavailable to biota and its release will occur over geological time periods. The exchangeable pool is composed of naturally occurring metals as well as metals released into the environment due to anthropogenic activities. The exchangeable pool of metals is subject to speciation in the aqueous phase (e.g., pore water, see discussion below on Exposure Assessment in Sediment) and sorption to solid phases (adsorption/desorption) (Stumm and Morgan, 1996). Speciation refers to the distribution of metal species in a sample. In water metal reacts or binds with dissolved ligands according to pH, Eh and abundance of ligands. The concentration of metal in the dissolved phase is controlled by sorption to the solid phase. Different forms of the dissolved metal have different bioavailabilities; free metals are the most bioreactive and complex forms are less reactive. Although the link between bioavailability of metals and factors influencing toxicity are of importance other abiotic factors particularly by cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) influence accumulation and toxicity. Dissolved cations competitively inhibit metal uptake ( ). In fact Water Quality Criteria (WQC) developed for aquatic life for several cationic metals to

support the Clean Water Act (CWA) are expressed as a function of water hardness to address the relationship of certain cations on toxicity. In our risk assessment of metals we normalize for water hardness.

The Water Effect Ratio (WER) was also developed in the 1990s to take into account water quality and bioavailability differences by deriving a WER between the metals toxicity in laboratory dilution water and in site-specific water (USEPA, 1994). The WER is then used to adjust the national criterion to reflect site-specific bioavailability.

The USEPA Office of Water recommends that exposure-effects assessments of metals be based on dissolved metal as determined by analysis of 0.45-um-filtered water (Prothro, 1993). However, some States require that total metal concentrations be used for conservatism. Typically dissolved concentrations are also likely to be conservative because they include complexed as well as dissolved metals. Total concentrations of metals are appropriate for screening risk assessments but the dissolved form is appropriate for definitive risk assessments of aquatic organisms. The form of metal in the exposure assessment should also match the form in the effects assessments. Risk assessments of metals should be based on the form that is best correlated with effects. For exposures of aquatic biota to metals this appears to be the free metal ion (Bergman and Dorward-King, 1997).

It must be noted that the use of total metal concentrations are not always conservative. Because the high concentrations of acid-extractable metals may cause analytical interferences, the limits of detection may be higher for total concentration analyses and toxic concentrations of metals may not be detected. When comparing concentrations at contaminated sites to background if the dissolved concentration is small relative to the total concentration, there may be a significant increase in dissolved concentrations relative to

background but no significant increase relative for total. This means that the particle associated background may mask a relatively small but toxicologically significant increase in dissolved concentrations. The solution to this problem is to measure both total and dissolved concentrations and used the dissolved concentrations to estimate risk. Unfortunately, most of the metal analyses data in the literature are for total metal concentrations and therefore most ecological risk assessments are based on total metal concentrations.

Speciation should be considered for both inorganic and organic chemicals that have several ionization states (e.g., valence states) within the range of realistic environmental conditions. In general nonionic forms are more toxic because they partition more rapidly from water to biota. This does not apply to metals particularly those that have multiple ionic species within the range of ambient concentrations. The addition of metal speciation to the analytical budget is an expensive addition. Forms and species of metals in water can be estimated from measurements of total concentration by applying metal speciation models. However, speciation models (e.g., WHAM) are less reliable than analytical chemistry data and are not typically used in regulatory practice.

Bioavailability is an issue which is relevant to organic chemical contaminants as well as metals. Like metals, organic contaminants may bind to dissolved or suspended particulates making them less bioavailable. Organic contaminants are measured directly in water (or modeled) and the parent chemical is typically the form that is measured. Metabolites are measured occasionally. There is no guidance from the USEPA to use filtered water samples of organic contaminants to represent surface water exposures as there is for metals.

Sediment

Ecological risk assessment on contaminants in sediments are typically based on chemical concentrations in whole sediment (i.e., bulk sediment) or sediment interstitial water (i.e., pore water) which usually accounts for over 50%, by volume of surface sediments (Forstner, 1987). Routes of exposure include uptake from pore water and overlying water across body wall walls, respiratory surfaces and ingestion of contaminated sediment particles. The main issues to address are sediment heterogeneity and bioavailability of measured concentrations. It is also important to estimate contaminant uptake and trophic transfer. These and other topics relevant to sediment ecological risk assessments are discussed in Ingersoll et al. (1997). Note that although accumulated metals and organics may serve as a source of exposure and toxicity to predator species the presence of significant burdens in prey does not necessarily mean that this is bioavailable to the predator. For example, bioavailability of accumulated metal in prey to there predators can vary significantly based on the form of the metal in tissues, physiology of the organisms and the tissue in which metal is stored (exoskeleton versus soft tissue). In addition, biomagnification of inorganic forms of metals across three or more trophic levels in an aquatic food web is rare.

Concentrations of contaminants in sediment unlike water, vary spatially (horizontally and vertically) more than temporally. Most sediment organisms generally are exposed to surface sediment in the top 5-10 cm. The burrowing depth of sediment dwelling insects and species of oligochaetes rarely exceeded 10 cm (Charbonneau and Hare, 1998: Lazim et al., 1989; Merritt and Cummins, 2002). Most sediment samples are taken from a top layer of a core or for a surface grab sample and they represent the exposure of the benthic and epibenthic organisms at a site. Some sediment ecological risk assessments do not specify sampling

depth. Sampling in the SERA for the SFWMD data included sediment samples from the top layer (10cm) of sediment using a stainless steel petite Ponar® dredge. Sediment sampling in the present 3-year monitoring study included core samples of the top layer (7.5cm) and diving.

Most benthic (epibenthic and infaunal) organisms are relatively immobile and therefore receive their exposures from a small sediment surface area. Benthic organism exposures from sediment are more reflective of the sampling area than organisms that inhabit water systems because water concentrations are variable and organisms in the water column are more mobile. Contaminant exposure concentrations in sediment vary little at a site for the life cycles of most benthic infaunal species since the life cycles of most benthic infauna insects are short (< 1year) ( ). Estuaries are one exception in which the physical-chemical characteristics of the overlying water vary within biologically significant time scales ( ) which could affect the partitioning of contaminants and consequent exposures. Variations in benthic infaunal exposures should be considered in sampling, collection and analyses of sediment data but they rarely are.

Historical data may provide a conservative estimate of current exposures if scouring events and the rates of sedimentation are limited, and there is a reduction in the source of the contamination. However, this type of data are appropriate for screening level risk assessments but not for definitive risk assessments (Suter et al., 2000). The contaminant monitoring programs in south Florida have been conducted by the South Florida Water Management District , National Oceanic and Atmospheric Administration (NOAA), U.S. Environmental Protection Agency (U.S.EPA), Florida Department of Protection (FDEP), Dade County Environmental Resources Protection (DERM) and U.S. Geological Survey

(U.S.GS). The SERAs conducted in this report are based on historical data from several of these programs. This is the first time this analytical data has been put into a risk perspective.

Concentrations of contaminants in sediment are based on whole sediments and concentrations in pore waters. It is assumed that exposure of benthic organisms is proportional to the concentrations of contaminants in pore waters and that those contaminants associated with the solid phase are largely unavailable ( ). This assumption is supported by the scientific community ( ). Toxic effects to a benthic organism depends on its sensitivity to pore water and particle-bound contaminants (Swartz et al., 1986). In addition, the concentration-response curve for an adverse effect can be correlated not to the total sediment concentration but to the pore water concentration DiToro, 1989). Note that some studies indicate that uptake from overlying water or ingested sediment may also be a significant source of contaminant body burdens for sediment dwellers (Hare et al., 2003; Hare, 1999). Burrowing marine species are typically sediment ingesters, however, in freshwater systems oligochaetes (i.e., worms) and some chironomids are ingesters (Adams, 1987). It should be noted that Chironomids (e.g., *C. riparius, C. tentans*) are one of the main groups used as standard test species in sediment toxicity testing for freshwaters. The selective feeding of *Hyalella azteca* (i.e., freshwater amphipod) another standard freshwater benthic species selectively feeds on smaller food particles which results in a concentration of diet on fine sediments with the highest organic matter and consequently highest contaminant concentration (Landrum and Scavia, 1983). At sites with fine grain sediments the latter taxa may comprise most of the freshwater benthic community and fine grain particles (e.g., clay at <2μm) have more active sites than other grain sizes and are thus more significant in terms of metal and organic binding. Sediment toxicity and risk assessments are therefore, based on

estimating (i.e., through modeling) or measuring pore water concentrations of contaminants ( ). Measuring pore water concentrations for particularly nonionic organics and metals is the preferred approach because pore water-particle partitioning mechanisms are difficult to model. Issues related to chemical form and speciation issues in pore water are similar to those in surface water.

Collection and extraction of pore water from whole sediment has been accomplished by many methods but they are labor intensive, they require large quantities of sediment for chemical analysis and testing, and the form and chemical species may change depending upon the collection and extraction procedure. In our sediment SERAs, concentrations of organics and metals were measured in whole sediment and were then converted to pore water concentrations. It is important to understand that when a probabilistic approach is being used to determine risk of a COPEC, distributions of exposures (e.g., surface water) are compared to distributions of effects from toxicity test results conducted in different media (e.g., surface water). There is a limited database for both whole sediment toxicity tests with single chemicals and with pore water tests with single chemicals. Therefore, we compared distributions of estimated pore water exposures to distributions of effects from toxicity test results conducted in surface waters.

There are several ways to adjust for whole sediment concentrations of organics and metals to account for bioavailability and estimate pore water concentrations. Firstly, for nonionic organic chemicals bulk concentrations are normalized to organic carbon content. For nonionic organics the federal government has supported this approach over direct measurement (USEPA, 1993). The bioavailable concentrations of nonionic organics in pore water are estimated from the organic carbon normalized sediment concentration based on the

EqP approach. This is supported by toxicity data and concentration-response curves which show adverse effects are correlated with interstitial water concentrations (μg chemical / liter of pore water) and not to total sediment-chemical concentration (μg chemical / gram sediment) (DiToro et al., 1991; Berry et al., 1996; Hansen et al., 1996). For example, mortality in toxicity tests correlates with predicted pore water toxic units thus demonstrating the use of pore water concentrations to remove sediment-to-sediment differences. Correlation of effects to contaminant concentrations in pore water suggests that whether you either measure the actual pore water concentration or predict it from the total whole (or bulk) sediment concentration then that concentration could be used to quantify the exposure concentrations for aquatic organisms. In addition, toxic effect concentrations in pore water are similar to those in water-only exposures ( ). The latter points are critical in support of the EqP approach. Estimating pore water concentrations of organics (and metals, see below this section) from whole sediment concentrations is the approach we took in the probabilistic part of our sediment SERAs where we compare distributions of pore water concentrations to toxic effect distributions from water-only exposures.

The EqP approach assumes that pore water and organic carbon in sediment are in equilibrium and concentrations are related by K_{oc} (contaminant specific partition coefficient for sediment organic carbon). Thus hydrophobic interaction (i.e., hydrophobic adsorption) assumes that only organic carbon is active and controls the partitioning of non ionic organic contaminants between sediment particles and pore water. The mass fraction of organic carbon (f_{oc} in kilograms organic carbon per kilogram sediment, or decimal equivalent of percent organic carbon, foc=0.01 if TOC=1%) for the sediment is now the determining factor

of the sorption capacity. Therefore, the partition coefficient K_p (L/kg sediment) between sediment and pore water can be calculated as:

$$Cs \text{ (sediment concentration)}/Cd \text{ (pore water concentration)}$$

and is equal to $f_{oc} * K_{oc}$ so that the predicted pore water concentration is equal to:

$$MC \text{ (whole sediment concentration)}/K_p$$

When there is high dissolved organic carbon and very hydrophobic contaminants the solid phase contaminant concentration provides a more direct estimate of the bioavailable pore water contaminant concentration than does the pore water concentration (USEPA, 1993a). The EqP approach has been used to derive sediment quality guidelines (SQGs) by the USEPA (1997) for a variety of non-polar organics. The New York State Department of Environmental Conservation also developed SQGs for the protection of aquatic life using the EqP approach (NYSDEC, 1999).

For metals we used three approaches to assess exposures. We first used the above EqP approach to estimate pore water concentrations of metals since it is well known that organic carbon is an important metal partitioning phase for soils (Fu et al., 1992; Sauve et al., 2000; Weng et al., 2001; Gustafsson et. al., 2003) and in surface water particulate matter (Lee et al., 1996; Tipping et al., 1998). To estimate predicted pore water concentrations of metals from the above equation metal partition coefficients for sediment/pore water were obtained from USEPA (1999). These metal pore water exposures were then used to prepare exposure distributions for the metal sediment SERAs.

Secondly, for metals we determined the fraction of the bulk metal concentration that is bound to reactive sulfides. Acid volatile sulfide (AVS), and more specifically iron monosulfide (FeS) is a reactive pool of solid phase sulfide (Forstner, 1995a). The availability of sulfide controls metal binding, distribution and solubility and thus renders that portion unavailable. The simultaneously extracted metal concentration (SEM) not the total metal concentration is compared to AVS concentration. AVS is found in freshwater and marine sediments and concentrations range from <0.1 to >50 μmol of AVS/g ( ). In south Florida the AVS in sediment ranges from 1 to 40 μmol (SFWMD). In the presence of AVS as the principal partitioning phase, cationic metals (e.g., cadmium, copper, lead, nickel, silver and zinc) form insoluble metal sulfides that possess low biological availability and thus limit concentrations in pore waters.

Cadmium, copper, lead, nickel and zinc are divalent metals so that 1 mol of each metal can bind 1 mol AVS. Molar concentrations of these metals are compared with AVS on a one to one basis. Silver exists as a monovalent metal so that silver monosulfide (Ag_2S) binds two moles of silver for each mole of AVS. Therefore, SEM Ag represents the molar concentration of silver. When AVS exceeds the sum of the SEMs present ($\sum SEM = SEM_{Cd} + SEM_{Cu} + SEM_{Pb} + SEM_{Ni} + SEM_{Zn} + \frac{1}{2} SEM_{Ag}$) excess sulfides are present in the sediment and all metals are present as insoluble unavailable metal sulfides. Metals act in a competitive manner when binding to AVS to form sulfides in the order of their increasing solubility (silver, copper, lead, cadmium, zinc and nickel) and therefore must be considered together. This EqP approach does not estimate metal pore water concentrations but it predicts the ***lack*** of bioavailability and toxicity of cationic metals in spiked and field contaminated sediments based on AVS (Berry, 1996; Hansen et al., 1996). If there is sufficient sulfide (AVS>SEM),

toxicity of the cationic metals is not expected because of low bioavailability. The literature shows that there is an inverse relationship between sediment toxicity and AVS for freshwater and marine sediments (Ankley et al., 1991; DiToro et al., 1990, 1992) and between pore water concentrations and AVSs (Brumbaugh et al., 1994; Casas and Crecelius, 1994).

The AVS/SEM approach has been used in the development of sediment quality guidelines for metals (Ankley et al., 1996) or what is now called equilibrium partitioning (EqP) derived guidelines or EqP sediment benchmarks (ESBs) (USEPA, 2000; DiToro et al., in Press). However, the approach does not predict toxicity in metal contaminated sediments when AVS is small or zero and it does not consider other phases (e.g., sediment organic carbon) that may influence pore-water sediment partitioning. When using organ carbon normalized SEM and AVS the acute and chronic toxicity of metals can be predicted (DiToro et al., 2002, in press; USEPA, 2000). Acute and chronic toxicity typically occurs at $SEM_{x.oc}$ ~100 μmol/gOC. No acute toxicity occurs when $SEM_{x.oc}$<100μmol/gOC. The AVS/SEM approach with organic carbon normalization was used to determine the presence of potential metal toxicity in the sediment SERAs.

1.4 Literature Review

In 1996, the Department of the Interior (DOI) prepared a report entitled "A Comprehensive Plan for the Restoration of the Everglades" with four main elements: 1) federal legislative authority for restoration activities; 2) accelerated state and federal land acquisition; 3) increased scientific research to guide restoration; and 4) federal, state, private sector cost sharing (http://www.sfrestore.org/tf/otherres/comp.html). In 2000, Congress passed the Comprehensive Everglades Restoration Plan (CERP) as a part of the Water

Resources Development Act (1996). The goal of the CERP is to restore and preserve the hydrology of the pre-drainage Everglades ecosystem, to protect the quality of the remaining habitat, to promote the return of populations of plants and animals and to foster human development compatible with sustaining a healthy ecosystem.

Biological changes in the Everglades have been linked to levels of phosphorus and mercury and to changes in the complex hydrological patterns of the natural system resulting from water management projects to control floods and water distribution (Science Subgroup, 1996). In fact, alterations in the hydrologic system are thought to be the main cause of dramatic declines of fish and wildlife populations because of habitat changes. Therefore, the basic premise behind all restoration activities identified by the Restoration Task Force for South Florida is that hydrologic restoration is a prerequisite to achieve ecosystem restoration and a sustainable South Florida Ecosystem. The restoration plan was thus formulated to reconstruct some key features of the natural hydrologic system in order to restore conditions that support landscape patterns, biodiversity, wildlife abundance and clean and abundant water. Little consideration however has been given in the restoration effort to the role that organic pesticides and other contaminants play in the structure and function of ecosystems although this is clearly a recommendation of the Science Subgroup (1996) in all physiographic regions that comprise South Florida. This was further supported at a workshop "Linking Ecotoxicity and Risk Management to Sustainable Restoration of South Florida Ecosystems" which recommended screening-level ecological risk assessments with retrospective and prospective diagnostic studies (LaPoint et al., 1998). The recent report by the U. S. General Accounting Office to the Department of the Interior on the South Florida ecosystem restoration (US GAO, 2003) stated that there is "no single agency that has primary

responsibility for developing scientific information needed to address problems regarding contaminants" and as a "result system-wide information in this area is difficult to develop". The results of limited studies indicate the need for more system wide working on screening contaminants and the "risks faced by organisms".

It is evident that water quantity rather than water quality issues have dominated the South Florida restoration planning (Scott et al., 2002). However, it is also evident that agriculture represents a major land use in South Florida and pesticide use presents a potential risk, especially to aquatic organisms. Based on a hazard ranking of pesticides by the National Oceanographic and Atmospheric Administration (NOAA) the three top estuarine drainage areas at risk in the U.S. were Rookery Bay, Biscayne Bay and Tampa Bay (Pait et al., 1992). The subtropical climate, long crop-growing season, application frequency, and multitude of uses (e.g., mosquito and termite control, golf courses) renders pesticides particularly hazardous in South Florida ecosystems. The literature review below is divided into two sections-one relevant for Everglades National Park and one for Biscayne National Park.

Everglades National Park (ENP)

The Canal 111 (Aerojet Canal or C-111) freshwater basin is a buffer zone that separates the wetlands of Everglades National Park (ENP) from highly productive subtropical agricultural lands and urban development to the east, and while considerable attention and resources have been allocated to altering the hydrology of the landscape, little effort has focused on understanding water quality issues that may arise from land use practices. Thus far analytical monitoring programs have detected the presence of organic pesticides in surface water of the lower C-111 freshwater canal basin and/or its confluent estuaries/saltwater systems

(Northeast Florida Bay, South Biscayne Bay or South Bay (Figure 1). For example, the South Florida Water Management District (SFWMD) began monitoring pesticides in water and bottom sediment in South Florida canals in the mid-1980's (Pfeuffer, 1985, 1991). Recent sediment and water analyses in South Florida by SFWMD indicates that atrazine, ametryn, bromacil, simazine, diuron, alpha-endosulfan, beta-endosulfan, endosulfan sulfate, ethion, hexazinone and norflurazon were the most frequently detected pesticides in surface water and DDE, DDD, ametryn, atrazine, dicofol, diquat, and endosulfan sulfate were the most frequently detected pesticides in sediment samples between 1991 and 1995 (Miles and Pfeuffer, 1997). Several of the sampling sites were located in the Everglades Agricultural Area (EAA) and others in the Homestead Agricultural Areas (HAA) adjacent to Everglades National Park. For example, detectable endosulfan residues (alpha and beta, and sulfate) in the C-111 (at S178) were consistently present in surface water from 1991-1995 and occasionally exceeded Florida Department of Environmental Protection (FDEP) and U.S.EPA water quality criteria (Miles and Pfeuffer, 1997). Surface water samples collected independently by NOAA from the southern SFWMD sampling sites confirmed these findings (Scott et al., 1994). Residues of endosulfan sulfate were also consistently found by SFWMD in sediment samples at S178 in the C-111 while the alpha and beta isomers were occasionally found. All three endosulfan residues were also found in sediment samples from structures S177 and S18C in the C-111. SFWMD summarized endosulfan sulfate residues in S178 water and found that Florida Department of Environmental Protection Water Quality Criteria were exceeded 11 times from 1996-2000 (two samples were from NOAA; Pfeuffer, personal communication, 2004). Recently, the most common pesticides present in surface water were atrazine and ametryn while DDE and DDD were the most frequently detected in sediment

samples (Pfeuffer and Rand, 2004). The U.S.EPA in 1995 also monitored contaminants in surface water, sediment and biota in C-111 and creeks of Northeast Florida Bay (Goodman et al., 1999). Endosulfan residues were detected in sediments of C-111, and in sediments of Shell and Trout Creeks (in N.E. Florida Bay). Organochlorine contaminants occurred at low concentrations in sediments of canals and creeks and PCBs and PAHs were also at low concentrations but higher in the C-111 than in creeks. At most sampling sites for water and sediment more than one pesticide was detected in each sample.

NOAA conducted a contaminant study of C-111 and Florida Bay from 1993-1997, but it did not evaluate cause (exposure)-effect (toxicity) relationships for contaminants (Scott et al., 2002). It did however; indicate the presence of low levels of the pesticides endosulfan (total), atrazine, chlorpyrifos and chlorothalonil in surface waters of canals adjacent to agricultural areas that drain into C-111 and in Northeast Florida Bay waters. Florida Bay waters occasionally exceeded U.S. EPA marine water quality criterion for endosulfan. Waters from canal sites also contained detectable concentrations of endosulfan that sporadically exceeded U.S.EPA freshwater quality criterion. Detectable endosulfan (total) residues were also found in sediment and oysters while chlorpyrifos was detected in fish tissue. Toxicity tests with in-place sediment and copepods and bivalves indicated potential adverse effects but the causative agent (s) was not determined. Toxicity studies with native species under controlled conditions were not conducted at environmentally relevant concentrations. The highest concentration of endosulfan (total) reached 477 ng/L and 10% of the samples from canal sites exceeded U.S.EPA chronic freshwater water quality criterion (56 ng/L). The highest percentage (40%) of water quality violations, based on U.S.EPA standards was detected in samples from S-178. NOAA in 1999-2000 also found

endosulfan concentrations were highest (mean dry season concentration ~300 ng/L) in the C-111E (Fulton et al., 2004). Data from NOAA's National Status and Trends (N S and T) Program Mussel Watch Project further indicated that the mean annual concentrations of endosulfan (II, β- isomer) residue in tissues (oysters) sampled from Joe Bay in N.E. Florida Bay were higher than the N S and T 85th percentile (i.e., is in highest 15 % of the data set with over 280 sites nationwide) (Cantillo et al., 1999).

Biscayne National Park (BNP)

Biscayne Bay is a subtropical lagoon located on the southeast coast of Florida. The Bay is subdivided into three regions-North Bay (from Broward County in the North to the Rickenbacker Causeway in the South), Central Bay (from the Rickenbacker Causeway south to the boundary of Featherbed Bank) and South Bay (from the Featherbed Bank to Card Bank) (Cantillo et al., 2000). Much of the Central Bay and South Bay encompasses the lower portion of Biscayne National Park (BNP). Extreme South Bay is part of the Biscayne Bay Aquatic Preserve and Florida Keys National Marine Sanctuary. The Bay receives nutrients, metals and organic contaminants via surface runoff, canals and discharges from industrial facilities (SFWMD, 1995). North Bay has been influenced by urban development activities (DERM, 1987; Markley et al., 1990). The main sources of contaminants of this watershed are the Miami River, the Port of Miami, and several canals (SFWMD, 1995). Metals and organic contaminants including pesticides have been found in water and sediment of discharge sites. The Central Bay has industrial and agricultural discharges and leachate from the South Dade landfill (McKenzie, 1983; Shinn and Corcoran, 1987). The southern portion of the Bay which includes Biscayne National Park, the Florida Keys National Marine

Sanctuary, the Card Sound Aquatic Preserve and the Biscayne Aquatic Preserve is influenced primarily by canal discharges from landfills, agricultural lands and a military facility.

As early as the mid 1970s it was determined that the Miami River and other canals were a source of toxic chemicals to Biscayne Bay (Waite, 1976). In the 1980s the lower Miami River was again referenced as the source of contaminants to Biscayne Bay (Corcoran, 1983; Corcoran et al., 1983, 1984). Concentrations of pesticides, metals and PCBs were reported in tributary canals and the northern portion of the Bay. Lower chemical concentrations were found down the central north-south axis of the Bay. Other data have confirmed that the Miami River sediments were more contaminated than other sediment in Florida (DERM, 1993; Gulf Engineers and Consultants, 1993; Seal et al., 1994). Sediments contained metals, pesticides, polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Pait et al. (1992) ranked Biscayne Bay as an estuarine drainage area with one of the highest ratings for intensity of application of the more hazardous pesticides.

Recently, chemical monitoring and toxicity of sediments in Biscayne Bay was conducted by the National Oceanic and Atmospheric Administration (NOAA) in cooperation with the Florida Department of Environmental Protection (FDEP) to characterize the relative degree, geographic patterns, and spatial extent of sediment quality (Long et al., 1999; Long et al., 2002). Toxic conditions occurred in acute and sublethal toxicity tests. Results from toxicity tests indicated that the highest toxicity was from sediment samples from the lower Miami River, Black Creek Canal and other canals adjoining south Bay and in canals and tributaries near Miami and Miami Beach. The causative toxic agents were not determined. Mixtures of metals and organics were present in sediment of the lower Miami River. High toxicity

occurred in southern Biscayne Bay but could not be correlated with the chemistry data. Concentrations of ammonia were high in some samples.

Dade County Department of Environmental Resources Management (DERM) also conducted sediment chemistry and toxicity studies in freshwater canals and determined that sediments from Wagner Creek, Little River and Military Canal showed toxicity and the highest concentrations of metals (e.g., copper, mercury, cadmium) were present in Military Canal. U.S EPA (1999) confirmed these findings in Military Canal. A screening level aquatic ecological risk assessment (SERA) was conducted by Montgomery Watson (1999) for Military canal based on using only the hazard quotient (HQ) method. Chemical compounds detected in surface water and sediment exhibited HQs greater than 1, which indicates need for further assessment using a more definitive probabilistic ecological risk approach. In addition to NOAA a number of monitoring programs by state [Dade County Department of Environmental Resources Management (DERM), South Florida Water Management District (SFWMD)], and federal [U.S. Geological Survey (USGS), U.S. Environmental Protection Agency (USEPA), U.S. Army Corps of Engineers, U.S. Department of Agriculture (USDA)] agencies have provided data on concentrations of contaminants in sediment and water in Biscayne Bay and tributary canals but the potential risk associated with the concentrations of these contaminants in surface water and sediment has not been determined in most of Biscayne Bay.

1.5 Applicable ERA Guidance

There is no formal promulgated, official state guidance for performance of an ERA or SERA at sites in Florida. U.S. EPA has developed general guidance for conducting ERAs

(USEPA, 1998) and one recent draft document more specifically for metals (USEPA, 2004). These are guidelines that "set forth current scientific thinking and approaches for conducting and evaluating ecological risk assessments." However, the U.S. EPA guidelines do not provide detailed information in specific areas and are not highly prescriptive. The U.S. EPA Emergency Response Team (ERT, Edison, NJ) has developed guidance for ecological risk assessments at Comprehensive Environmental Response Compensation and Liability Act (or CERCLA or "Superfund") sites otherwise known as ERAGS (or Ecological Risk Assessment Guidance for Superfund) (U.S.EPA, 1997). This document was more prescriptive and was used when needed.

The U.S. Army Corps of Engineers (U.S.ACE) released "Environmental Quality Risk Assessment Handbook, Vol II: Environmental Evaluation" in 1996 that applies to ERAs for U.S.ACE investigations and studies (U.S.ACE, 1996). Like the U.S.EPA guidance manual, the latter is not intended to be a "how to" protocol but rather to provide the concepts for performing ERAs consistent with good science and accepted regulatory practices. This guidance document was also consulted.

A tiered ecological risk assessment approach was suggested in a document (Aquatic Dialogue Group: Pesticide Risk Assessment and Mitigation) by the Aquatic Risk Assessment and Mitigation Dialogue Group (ARAMDGP) (SETAC, 1994) which consisted of representatives from the government, academia and industry. This tier approach progresses from a simple HQ to PRA. It is summarized in a document by the Ecological Committee on FIFRA Risk Assessment Methods for Aquatic Assessment (ECOFRAM, 1999). The committee was initiated by the USEPA Office of Pesticide Programs (OPP) and was also composed of a diverse group of representatives. The SETAC document and particularly

ECOFRAM (1999) were used as the main sources for guidance on the risk approach used in this study.

As an essential source of information for the ecological evaluation, the Science Subgroup (1996) report on the South Florida Ecosystem Restoration was also used.

2. SAMPLING DESIGN, STRATEGY AND CHEMICAL ANALYSIS

2.1. Everglades National Park Sediment Collections

The sampling strategy for the project was based on the assumption that regions of the Everglades National Park (ENP) located near the Homestead Agricultural Area (HAA) are more prone to chemical residue deposition, exposure and adverse effects than more remote areas along the western boundary. In addition, sites were also located throughout major water delivery routes in a North-South pattern such as Shark and Taylor Sloughs and the C-111 drainage basin. A list of sampling locations and collection dates for ENP is presented in Table 2.1 including the GIS positions. The first sediment-sampling event for Everglades National Park was performed between August and September of 2001 and sampling was completed in March 2004. A map of ENP sediment sample stations is shown in Figure 2.1. In order to aid the data interpretation samples were grouped in five main transects. The first transect follows an east-west direction across the northern boundary of the park which receives water from the Water Conservation Areas to the north of the Park and lies just south of Tamiami Trail, the major highway in this area. The second transect follows a north-south direction across the eastern boundary of the park, this transect lies closest to the Homestead Agricultural Area (HAA) and contains several water delivery modification projects such as the 332B pump station along L-31W. The third transect is located in the drainage basin of the C-111 canal which flows through most of the HAA. One important feature in this drainage basin is the presence of structures S-178 and S-177 which have been routinely monitored for water quality during the last decade (SFWMD, 2005).

Table 2.1.- Everglades National Park sampling stations.

Station	Description	First Collection Date	Last Collelction Date	Latitude	Longitude
332Ba	East Boundary (Chekika)	August 1, 2001		25.5462	-80.5758
332Bb	East Boundary (Chekika)	August 1, 2001	March 24, 2004	25.5460	-80.5743
21	East Boundary (Chekika)	August 1, 2001		25.6471	-80.5724
22	East Boundary (Chekika)	August 1, 2001	March, 24, 2004	25.5794	-80.5764
23	East Boundary (Chekika)	August 1, 2001		25.4995	-80.5755
24	East Boundary (Chekika)	August 1, 2001		25.4180	-80.5888
R158	East Boundary (Park Rd.)	August 1, 2001		25.3963	-80.5937
07	Shark Slough	August 1, 2001	October 01,2002	25.5600	-80.7789
37	Shark Slough	August 1, 2001	October 01,2002	25.4692	-80.8502
50	Shark Slough	August 1, 2001		25.6843	-80.7620
58	Shark Slough	February 1, 2002	October 01,2002	25.6352	-80.6552
63	Tamiami Trail	August 1, 2001	June 21, 2002	25.7608	-80.5527
64	Tamiami Trail	August 1, 2001		25.7607	-80.5910
57	Tamiami Trail	August 1, 2001		25.7404	-80.4979
L67	Tamiami Trail	August 1, 2001		25.7611	-80.6738
53	Taylor Slough	August 1, 2001		25.2554	-80.6675
54	Taylor Slough	August 1, 2001		25.3579	-80.6038
MDA	Taylor Slough	August 1, 2001		25.3216	-80.6443
59	Taylor Slough	September 1, 2001		25.2852	-80.5687
SRS2	Shark Slough	March 24, 2004		25.5497	-80.7852
SRS3	Shark Slough	March 24, 2004		25.4682	-80.8533
55	C-111	September 1, 2001	December 10, 2003	25.3126	-80.5197
60	C-111	September 1, 2001		25.2863	-80.5072
61	C-111	September 1, 2001	December 10, 2003	25.2893	-80.4603
US-1/C-111	C-111	September 16, 2003		25.2895	-80.4448
S-197	C-111	September 16, 2003		25.2857	-80.4415

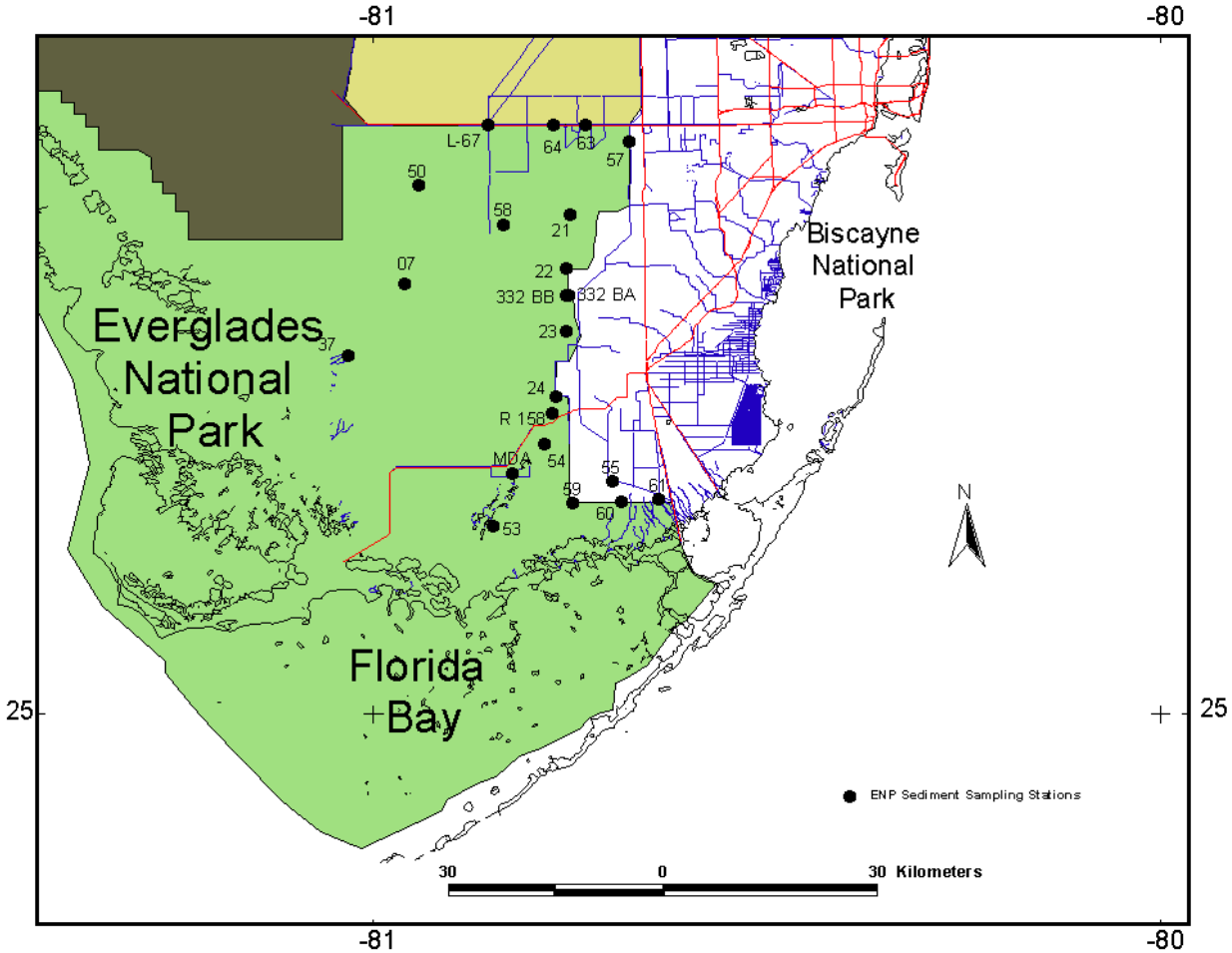


Figure 2.1.-Detailed map of Everglades National Park sampling stations.

In addition, recent modifications on the lower reach of the C-111 canal (berm degradation and removal) have improved water flow into marsh areas south from the main canal. The last two transects follow Shark Slough and Taylor Slough which flow in a south-west direction from the north and east boundaries, respectively.

Either consolidated sediments or surficial soils were collected at every station visited. Because of the variable nature of the sites (dry vs. wet) manual collections were conducted at all sites in ENP. Two (2) feet long push-coring devices were manufactured in house from 2.5” and 4” clear polycarbonate pipe respectively. A threaded end was placed on the top section and the bottom lips were mechanized to provide a sharp penetrating edge. A valve system was fitted to the top of the push-core assembly to allow collections in waters up to 6 feet deep. At least six (6) pre-cleaned exchangeable devices were brought to the collection sites. A total of five (5) cores were retrieved at each site. Cores were collected within a 100 ft2 area centered at the GIS coordinate for the site. All cores were than extruded from the polycarbonate tube using a Teflon plunger and the top 3 inches of consolidated sediment/soil were placed in pre-cleaned, certified, glass jars equipped with TFE lined caps. After labeling and cataloguing all samples the jars were placed in coolers and kept refrigerated until arrival to the analytical laboratory. At the laboratory samples were assigned the appropriate ID numbers, logged into the sample tracking system, combined, carefully homogenized and redistributed into the original collection jars. A ten-gram (10g) sub-sample was taken for the determination of grain size while the rest of the sample was placed in the freezers and held at or below -20°C until the time of analysis. In addition, when required for toxicological testing, a total of

5-liters of sediment/soil were also collected in a similar and transported to the Ecotoxicology Laboratory at FIU North Campus. Several stations from within ENP were chosen for further analysis and sediment collections were repeated during the second and third year sampling events. These stations were representative of three of the regions previously described, the C-111 basin, Shark Slough, and the East Boundary near the HAA, which exhibited clear evidence of anthropogenic enrichment of several contaminants. A total of twenty seven (27) individual sites were developed during the project after consultation with park staff and the COTR. Eight (8) of the original sites were re-visited at least two times and four (4) sites were collected and analyzed between three and five times during the duration of the project.

2.2. Biscayne National Park and Florida Bay Sediment Collections

A list of sampling stations for Biscayne National Park (BNP) and Florida Bay is given Table 2.2. In BNP, samples were collected from 9 stations at areas near land along the channel from Black Point Marina, off the channel from Turkey Point Nuclear Power Plant, near outflows from major canals (Military, Mowry and Princeton), as well as from sites near Elliot Key, a barrier island approximately 8 miles offshore. All these stations were selected to address concerns regarding sediment toxicity reported by NOAA in their 1995 Sediment Quality Assessment Study for Biscayne Bay (NOAA 1998). A detailed map of BNP sediment sample stations is given in Figure 2.2. Sediment samples were also collected at four stations from the eastern area of Florida Bay from areas near the influence of the C-111 drainage basin as well as more remote areas of the Bay receiving

waters from ENP like Joe Bay and the mouth of the Taylor River. A map detailing the location of the Florida Bay sampling stations is given in Figure 2.3. Since most locations in these areas were located at a depth of approximately 6 to 10 ft a different sampling approach was taken. All BNP and FLB samples were hand collected by diving. At each station, 3 samples were collected by directly forcing pre-cleaned, certified glass 500-ml jars into the bottom sediments (2-8 inches). As stated before, samples were labeled and catalogued in the field, refrigerated during transport and combined into a single homogenate upon arrival to the laboratory. After sub-sampling (10g) for grain size determination all samples were stored frozen until prepared for analysis.

Table 2.2.-Biscayne National Park and Florida Bay sampling locations.

Station	Description	Collection date	Latitude	Longitude
BNP				
BBTPC	Turkey Point	November 1, 2001	25.47127	-80.28368
BBICS	Intercoastal south	November 1, 2001	25.39985	-80.25442
BBEKH	Elliott Key	November 1, 2001	25.44533	-80.20655
BBCP	Coon Point	November 1, 2001	25.47385	-80.21605
BBSK	Sands Key	November 1, 2001	25.50983	-80.19680
BBBP2	Black Point 1	November 1, 2001	25.52487	-80.29600
BBBP1	Black Point 2	November 1, 2001	25.53052	-80.31602
BBFP	Fenders Point	November 1, 2001	25.50370	-80.30270
BBMM	Military/Mowry Canals	November 1, 2001	25.47960	-80.30122
Florida Bay				
FB MTJB	Mouth, Taylor River	May 1, 2002	25.21642	-80.53535
FB MTR	Mouth, Joe Bay	May 1, 2002	25.19050	-80.64000
FB LS	Long Sound	May 1, 2002	25.23320	-80.46532
FB LSR	Long Sound Road	May 1, 2002	25.23972	-80.43563

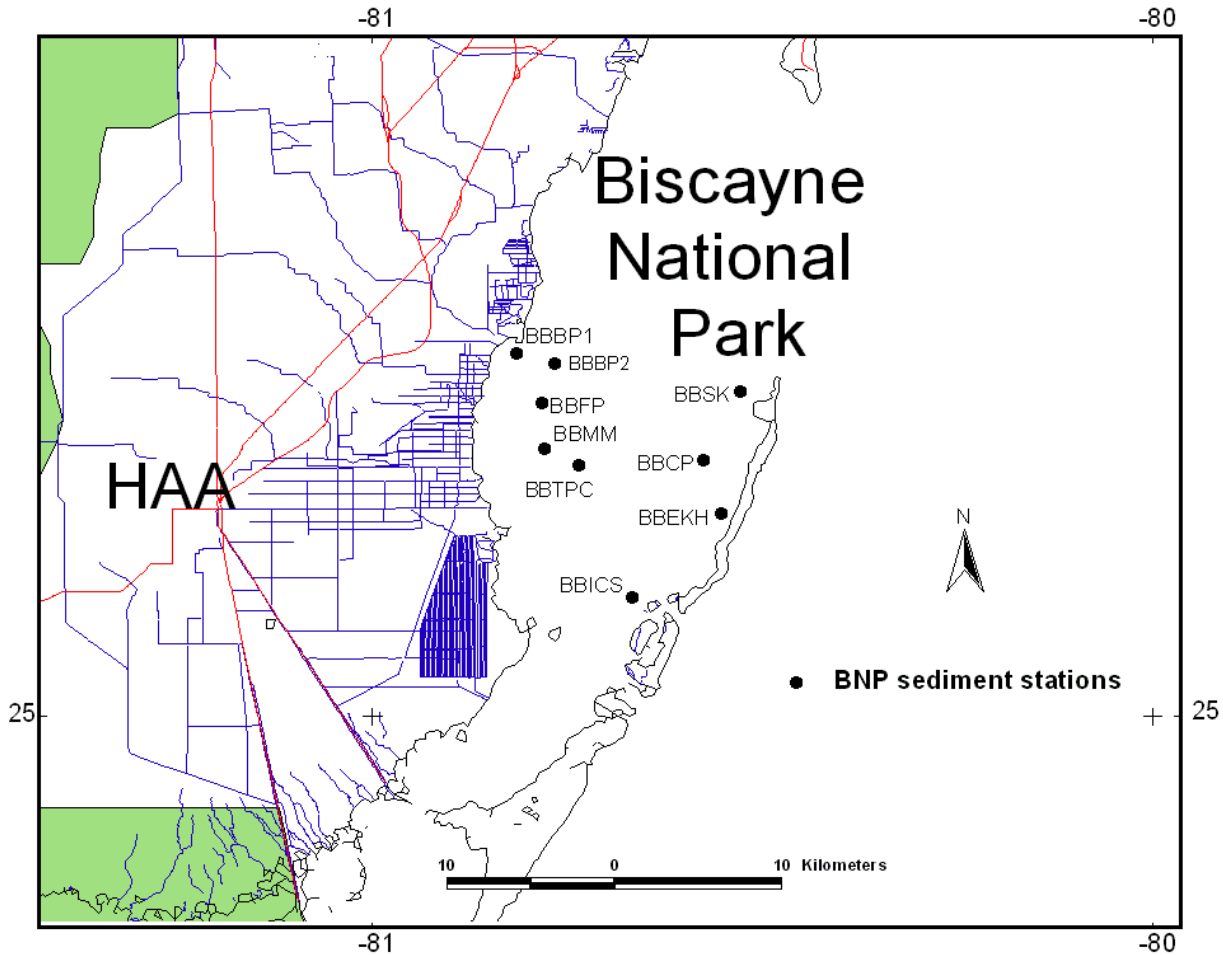


Figure 2.2.-Detailed map of Biscayne National Park sampling stations

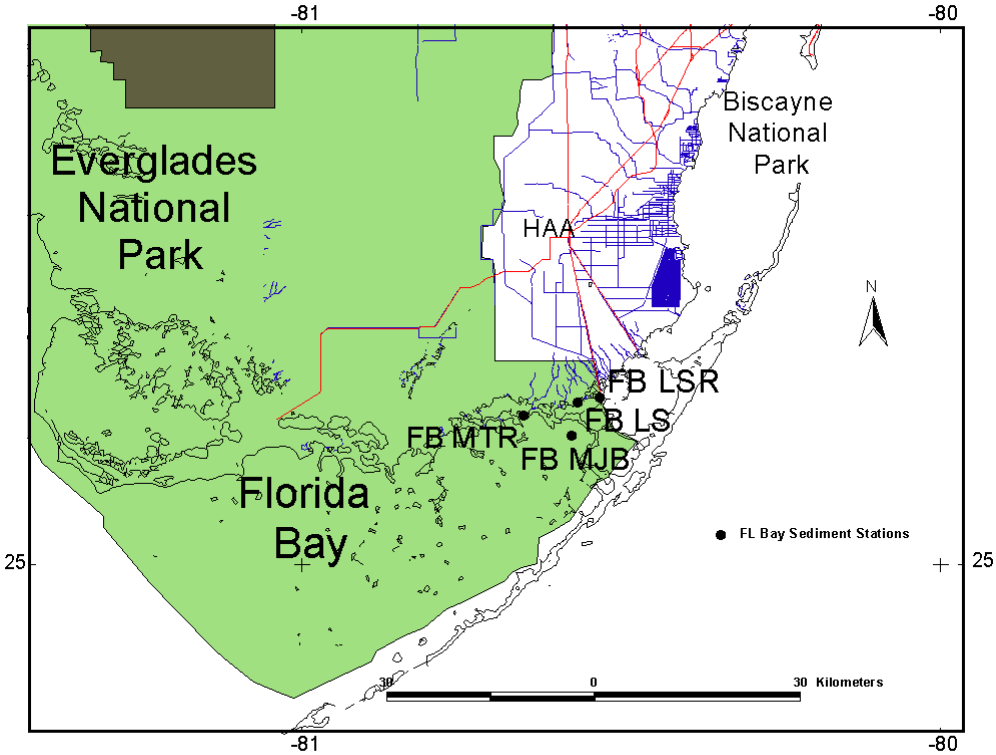


Figure 2.3.-Detailed map of Florida Bay sediment sampling stations.

2.3 Biological Tissue Collections for Everglades National Park.

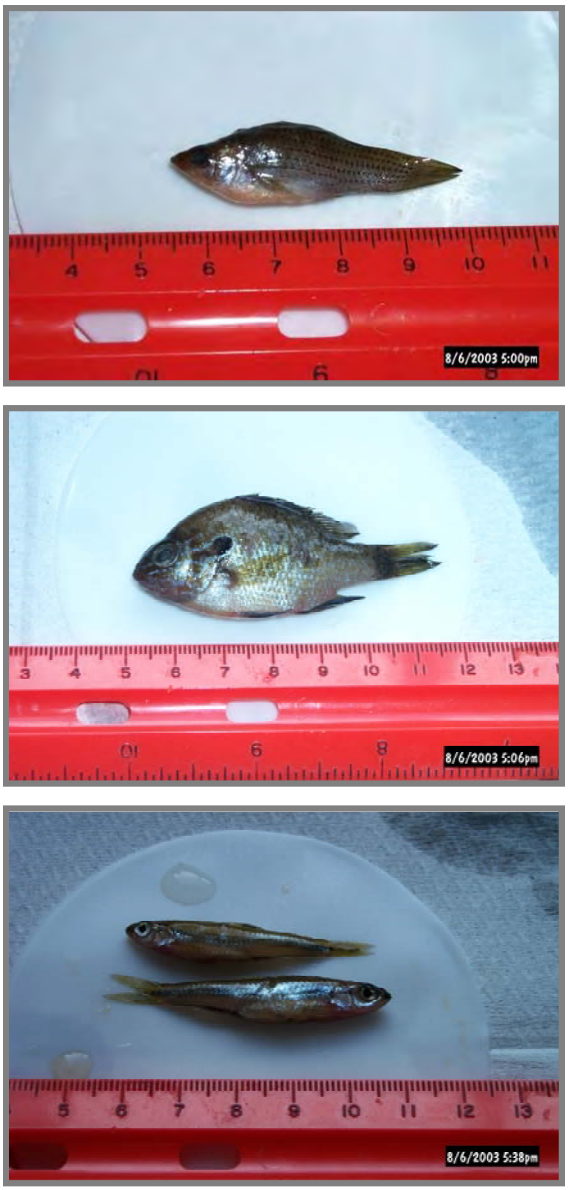
Analysis of biological tissues for body burden was conducted on small fish only. It was the intention of the team to look only at organisms in the lower portion of the Everglades food chain to use them as a worst case scenario and to avoid the variances associated with contaminant depuration with the reproductive cycle of mature individuals. In addition, the selection of small fish provided a limited range of mobility (spatial selectivity) and good accumulation rates for contaminants but limited capacity for biomagnification. Although the original idea was to collect the same specie of fish at every station it was soon realized that multiple analyses of several species was a more

appropriate way to assess the overall exposure levels. Tissue collections started in December 2001 and were completed in September 2003. A total of fourteen (14) sites corresponding to the sediment collections were visited in multiple occasions during the duration of the project. The limiting factor on the fish collections were water level and the presence/absence of predators. Because of their limited mobility and their limited capacity for biomagnification, the fish targeted for collection and analysis included mosquito fish (*Gambusia holbrooki*, marsh killifish (*Fundulus confluentus*), flag fish (*Jordanella floridae*), mayan cichlid (*Cichlasoma urophthalmus*), pike killifish (*Belanesox belizanus*), bluefin killifish (*Lucania goodie*), and sunfish (*Lepomis spp*.). A list of sampling stations for organisms is given in Table 2.3. The collection date given in the table is the first collection date for that station; multiple collections were conducted until an adequate sample size was attained.

Fish were obtained using ¼ and $^{1}/_{8}$" minnow traps deployed 24 hours prior to collection. At any given site ten to twenty (10-20) traps of each mesh size were deployed. Traps were located so that the entrance gates were totally submerged but the top of the traps were exposed to air. In many cases this layout required for the minnow traps to be attached to the surrounding vegetation. Sampling in deep open areas was avoided in preference of marsh areas with abundant vegetation coverage. An initial assessment and collection was conducted after 24 hours of the initial deployment. All organisms present in the traps, with the exception of snakes, were placed in 5-gallon plastic containers containing water from the collection site. Fish were separated from other organisms, identified and sorted in situ. All individuals from the same specie were placed in pre-cleaned aluminum foil, labeled on the outside and placed in a zip-lock bag. All bags were

then placed in ice while in transit to the laboratory. Upon arrival, samples were assigned an identification number, photographed for organism identification, logged into the sample tracking system. All samples with more than 20 individuals were then combined and homogenized using a tissumizer until a fine paste was obtained. The final homogenates were placed in pre-cleaned, certified glass jars with TFE lined caps and stored at or below -10ºC until the time of analysis. Large fish (>10 cm) were grinded using an all metal commercial meat grinder before the final homogenization. In all cases whole body analyses were performed. Pictures of typical species collected in ENP are shown in Figure 2.4.

Fish samples were also collected from 6 stations in Florida Bay using cast nets. Because of the nature of the collection environment these samples included larger species of fish such as mojarra (*Cichlasoma* spp.) and mullet (*Mugil* spp.). A detailed map of the fish sampling stations for this area is given in Figure 2.5.



Code	Common name
MF	Mosquito fish
MKF	Marsh killifish
GTM	Golden top minnow
DSF	Dollar sunfish
MC	Mayan cichlid
FF	Flag fish
WM	Warmouth
PKF	Pike killifish
YBC	Yellow bullhead catfish
Gar	Gar
SF	Sunfish
BFK	Bluefin killifish
MOJ	Mojarra
MUL	Mullet
SIL	Silversides
GKF	Gulf killifish
GSKF	Goldspoted killifish
NF	Needle fish
SHM	Sheepshead minnow
SFM	Sailfin molly

Figure 2.4. Photographs of typical small fish collected using the 1/8” and ¼” minnow traps. The table shows the code name assigned to all fish species used in the project.

Table 2.3.-Fish sampling stations.

Station	Description	First Collection date	Latitude	Longitude
ENP				
21	East Boundary	December 28, 2001	25.64713	-80.57243
22	East Boundary	January 11, 2002	25.57943	-80.57637
332B	East Boundary	January 11, 2002	25.54603	-80.57432
23	East Boundary	December 28, 2001	25.49945	-80.57545
24	East Boundary	January 25, 2002	25.41803	-80.58882
R 158	East Boundary (Park Rd.)	December 28, 2001	25.39625	-80.59368
58	Shark Slough	February 26, 2002	25.63517	-80.65517
A07	Shark Slough	October 2, 2002	25.56000	-80.77883
A37	Shark Slough	October 2, 2002	25.46917	-80.85017
63	Tamiami Trail	February 26, 2002	25.75150	-80.55133
64	Tamiami Trail	February 26, 2002	25.75133	-80.58733
55	C-111	July 31, 2003	25.31233	-80.51450
61	C-111	July 31, 2003	25.29667	-80.47133
61S	C-111	July 31, 2003	25.29000	-80.45183
Florida Bay				
TR 1	Taylor River 1	July 22, 2003	25.21733	-80.58300
LMB	Little Madiera Bay	July 22, 1931	25.18833	-80.62000
JB 1	Joe Bay 1	July 22, 2003	25.53950	-80.25083
JB 2	Joe Bay 3	July 22, 2003	25.21850	-80.53067
HC	Highway Creek	July 22, 2003	25.25100	-80.45650
LS	Long Sound	July 22, 2003	25.44117	-80.32650
TR 2	Taylor River 2	August 21, 2003	25.22083	-80.64900
JB	Joe Bay	August 21, 2003	25.22083	-80.64917

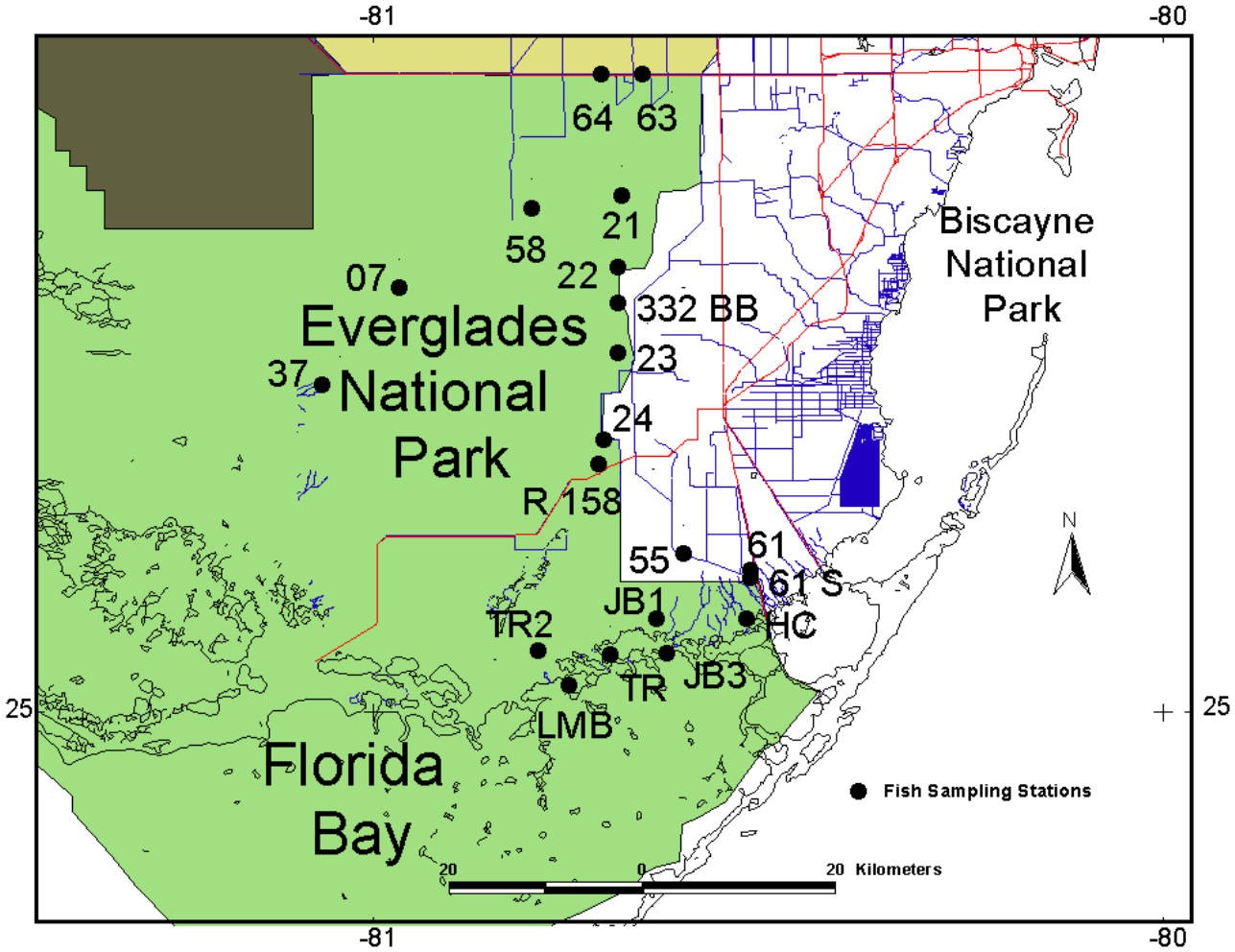


Figure 2.5.-Detailed map of fish sampling stations

2.4 Sample Preparation

2.4.0 Sediment/Soil Samples

2.4.1 Dry Weight Determination of Sediments

In order to express the results of analysis on a dry weight basis for sediments, the dry weight percent of sediments must be determined. A 5 – 10 g sub-sample of the homogenized sediment from each sample was placed in a pre-weighed 40 mL beaker and the "wet" weight recorded. Containers were then placed in a drying oven at 65 °C for 24 hours. The beakers were then weighed and the weight recorded and then placed back in the oven for a two-hour period. This process was repeated for each sample until the difference between two consecutive weights was less than 0.02 g. For each set of 20 samples or less a duplicate was processed with a maximum allowable Relative Percent Difference (RSD) of ± 25%. If the RSD exceeded the criteria, the entire set was reprocessed.

2.4.2 Organic Matter Determination of Sediments (loss of ignition)

Since a significant portion of the organic contaminants in sediments are bound to the organic matter fraction, it is useful to determine the organic matter content of a sediment sample for interpretation of the results of OCP, PCB, and PAH analysis.

In order to conserve the amount of available sample, the sub-samples employed for the determination of percent dry weight were used for total organic matter determination. The beakers containing the dried sediment samples were covered in aluminum foil and placed in a combustion oven at 450 °C for a 24 hr period. The samples were then allowed to

cool to room temperature in a dessicator. The beakers were then weighed and the weight recorded until constant weight was achieved as described in the previous section.

2.4.3 Sediment Grain Size Analysis

Previous studies have shown that sediment contamination concentrations can be correlated to the grain particle size with higher concentrations associated with the smaller sized particles (Thompsom and Eglinton 1978). Therefore, this characterization was performed in this study.

A ROTAP RX-29 automatic sieve equipped with 8" Fisher Brand test sieves was used to determine particle size distribution of sediment samples. The sieves used were: # 10 (2000μm), # 60 (250 μm), # 120 (125 μm), and # 230 (63 μm). 10 – 20 g sub-samples of homogenized sediment were dried in a drying oven at 65 °C for at least 24 hrs. Samples were then placed over the # 10 sieve, were covered and then sieved for 3 – 5 minutes. The top fraction > 2000 μm (large rocks, plant debris and foreign objects) was discarded, and the remaining four fractions were then each collected and weighed to ±0.001 g to determine the percent of medium/ coarse/ v. coarse sand, fine sand, very fine sand, and silt fractions.

2.4.4 Sediment preparation for ICP-MS determination of Metals

The method used for digestion of sediment and soil samples for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is based on EPA Method 3052 for microwave assisted acid digestion of siliceous and organically based matrices. Between 0.2 and 0.5 g of thoroughly homogenized sediment (dry weight basis) was placed in a 100 mL fluorocarbon

(PFA) microwave digestion vessel, and 10 mL of trace metal grade HNO_3 was slowly added. The vessels were sealed and the samples were processed for a total of 15 min. The samples were digested using a microwave digestion system (Mars 5, CEM) at 180 ºC for 9 min (EARL SOP-2000-I-001.1). Although this procedure resulted in the digestion of all metals considered toxic it did not yield a total sample digestion (silicate dissolution). Because of this, the enrichment plots are only a conservative estimate since the true concentration of the normalizing element (Aluminum) could be underestimated. However, because of the nature of South Florida soils (marl and peat) is unlikely that this could impact the observed trends.

After digestion, the samples were quantitatively transferred to 100 ml volumetric flasks, diluted to the mark with DDI water and then transferred to acid cleaned 125 mL Nalgene HDPE bottles for storage prior to analysis. After the particulates settled, 2 ml of the clear solution was placed in a 10 ml plastic test tube and diluted to 10 ml with DDI water. In the case of major elements such as aluminum, the solutions were diluted 100 times before ICP/MS analysis. Fifty microliters of internal standard solution (Y, Sc, In, and Rh 10 ppm) was added, thoroughly mixed, and the samples were ready for ICP/MS analysis. All samples were digested with a duplicate, and for each batch of 10 or less samples, blanks, matrix spikes, and reference materials were processed as part of the QA/QC protocol. Certified reference materials digested for soil/sediment analysis include PACS-2 marine sediment reference material obtained from National Research Council Canada (NRCC) and Buffalo River Sediment 2704 obtained from the National Institute of Standards and Technology (NIST).

2.4.5 Sediment preparation for GC-ECD determination of Organochlorine Pesticides, PCBs, and GC-MS determination of PAHs.

The method used for the extraction and clean-up of sediments for trace organic analysis is based on the standard methods used by NOAA for its NS&T Mussel Watch Program (NOAA, 1998). Approximately 20g of the wet sediment/soil samples were chemically dried using sodium sulfate (Na_2SO_4); soxhlet extracted for 20 hours with 300 mL of dichloromethane in 500 mL flat bottom flasks. Samples were concentrated to 1 ml hexane using a 3-ball Snyder column in a hot water bath at 65 °C followed by a quantitative transfer into a 25 mL concentrator tube with the addition of hexane until final volume was achieved and boiling ceased, solvent cleaned Teflon boiling chips were added at each concentration step. Samples were then purified from potential matrix interferences using a mixed bed silica-alumina chromatographic column.

The chromatographic column was prepared in Pentane with 10g of Alumina previously deactivated with 1% wt./wt. DDI water followed by 20g of Silica deactivated with 5% wt./wt. DDI water. $NaSO_4$ was added on top to prevent humidity in the column and granulated activated copper was added to eliminate elemental sulfur. The sediment extract concentrated to 1 ml of Hexane was then added to the column. The first fraction containing the aliphatic hydrocarbons was eluted with 45ml of pentane at a rate of 1 mL/min. The second fraction was eluted with 250ml of a 1:1 mixture of pentane: dichloromethane. This second fraction contains the aromatic compounds that include PCBs, organochlorine pesticides and PAHs. Approximately 10g of Acid activated (5% HCl) metallic copper (Cu) was added (on the column and on the receiving flask) to eliminate elemental Sulfur that can act as interference in the GC/ECD determination of Organochlorine compounds.

Internal standard surrogate solutions were added to each sample prior to extraction. For Organochlorine pesticide and PCB analysis, A 100 μL solution of

DBOFB (1.035 ppm), PCB 103 (1.039 ppm), PCB 198 (1.014 ppm), and OCN (20.97 ppm) was added to each sample and QC sample. For PAH analysis a 100 μL mixture of 2 ppm Napthalene-d8, Phenanthrene-d10, Chrysene-d12, Acenapthene-d10, and Perylene-d12, were added to each sample and QC sample. A 100 μL spiking solution containing all Organochlorine analytes and a 100 μL spiking solution containing all PAH analytes were added to each matrix spike (MS) and laboratory blank spike (LBS) to assess method performance prior to extraction. All samples are concentrated to a final volume of 1 ml hexane prior to instrumental analysis.

Prior to transfer of the second fraction extract into 2 mL amber glass vials, 100 μL of TCMX (1 ppm) and 100 μL of 2 ppm Flourene-d10 and Benzo(a) Pyrene-d12 were added to each sediment sample and QC sample as external standards for OC and PAH analysis respectively. For the aliphatic fraction, 100 μL of TCMX (1 ppm) was added as an external standard.

2.4.6 Sediment preparation for the determination of Organo-nitrogen herbicides (Triazines).

All Triazine herbicides: Ametryne ($C_9H_{17}N_5S$), Terbutryn ($C_{10}H_{19}N_5S$), Simetryn ($C_8H_{15}N_5S$), Prometryn ($C_{10}H_{19}N_5S$), Atraton ($C_9H_{17}N_5O$), Atrazine ($C_8H_{14}ClN_5$), Prometon ($C_{10}H_{19}N_5O$), Propazine ($C_9H_{16}ClN_5$), Simazine ($C_7H_{12}ClN_5$), Terbutylazine ($C_9H_{16}ClN_5$), were obtained as a neat solution TP-619 Mix of 500 μg/ml, from Chem Service (PA, USA). Solid standards of Irgarol 1051 99.0 % ($C_{11}H_{19}N_5S$), M1 99 % ($C_8H_{15}N_5S$), Desisopropyl atrazine 98 % ($C_5H_8ClN_5$), Desethyl atrazine 97.5 % ($C_6H_{10}ClN_5$) were obtained from Dr. Ehrenstorfer (GmbH, Augsburg, Germany). The internal standard Atrazine D_5 (C_8

$H_{14}N_5D_5Cl$) was obtained as a neat solution of 100 µg/ml from Dr. Ehrenstorfer (GmbH, Augsburg, Germany). Methanol (MeOH), methylene chloride ($MeCl_2$) and Hexane were of optima™ grade and were obtained from Fisher Scientific (Suwannee, GA) and used as received. The drying agent was diatomaceous earth from Recreational Water Products (Scottdale, GA) and was combusted prior to use.

Stock and calibration solutions

Approximately 5 mg of Irgarol 1051 99%, 5 mg of M1 99%, 6 mg of Desisopropyl atrazine 98 %, and 6 mg of Desethyl atrazine 97.5 % were weighed individually in a Cahn-33 microbalance and were added to a 10 ml individual amber volumetric flasks and dissolved with acetone in the case of Irgarol 1051 and M1, and methanol for the Atrazine metabolites to yield a concentration of c.a. 500-600 µg/ml for each standard. Five hundred micro liters of the Irgarol 1051 and M1 stock solutions were taken and added to a 25 ml independent amber volumetric flask and diluted with methanol for a final concentration of approximately 10 µg/ml for each compound (Working Solution A and B). In the case of the atrazine metabolites 390 µl of each stock solutions were added together to a 25 ml amber volumetric flask and diluted with methanol for a final concentration of 10 µg/ml of each metabolite (Working Solution C). Five hundred micro liters of the TP-619 triazine-based herbicides mixture of 500 µg/ml were taken and added to a 25 ml amber volumetric flask with methanol to obtain a final concentration of 10 µg/ml (Working solution D). Five hundred micro liters of 100 µg/ml of Atrazine D_5 neat solution were taken and diluted with methanol in a 5 ml amber volumetric flask for a final concentration of 10 µg/ml. These stock and working solutions were stored in the dark at –20 ºC. The calibration standard solutions were prepared in the range of 0.05 to 2.5 µg/ml by adding increasing amounts of each one of the 10 µg/ml

solutions A, B, C and D, from 50 µl up to 2500 µl (eight calibration points). The concentration of the internal standard (Atrazine-d_5), was kept constant at a concentration of 0.5 µg/ml. (see table 2.4 for details)

Spiking solution

Mixtures of triazine-based herbicides and metabolites the in the range of 20 µg/ml were prepared from stock solutions and diluted with methanol. The internal standard solutions concentration (Atrazine D_5), was kept constant at a concentration of 0.5 µg/ml.

Table 2.4. Preparation of the triazines calibration solutions.

	Calibration Solution							
Stock Solution	**CS 0**	**CS 1**	**CS 2**	**CS 3**	**CS 4**	**CS 5**	**CS 6**	**CS 7**
	Volume Added							
A[a]	0 µl	50 µl	100 µl	250 µl	500 µl	1000 µl	2000 µl	2500 µl
B[b]	0 µl	50 µl	100 µl	250 µl	500 µl	1000 µl	2000 µl	2500 µl
C[c]	0 µl	50 µl	100 µl	250 µl	500 µl	1000 µl	2000 µl	2500 µl
D[d]	0 µl	50 µl	100 µl	250 µl	500 µl	1000 µl	2000 µl	2500 µl
Internal standard	50 µl	50 µl	50 µl	50 µl	50 µl	50 µl	50 µl	50 µl
Final concentration of internal standard (µg/ml)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Final concentration of analytes (µg/ml)	0	0.05	0.10	0.25	0.50	1.0	2.0	2.5

[a] solution A contains ~10000 µg/ml of Irgarol
[b] solution B contains ~10000 µg/ml of M1
[c] solution C contains ~10000 µg/ml of DIA and DEA
[d] solution D contains ~10000 µg/ml of atratone, prometrone, atrazine, simazine, symetrin, ametryn, prometryn, terbutryn, propazine and terbutilazine.
[e] solution E contains ~ 100 µg/ml of atrazine D_5

Wet sediment samples (c.a. 15 g) were mixed with combusted diatomaceous earth. After approximately 15 minutes of mixing, the sample was transferred to a 33 ml stainless

steel ASE extraction cell. The solvents of choice were methanol: water (90:10). The extraction program in the ASE was the following: oven temperature: 100 °C; pressure: 1500 psi; oven heat up time: 5 minutes; static time: 10 minutes; flush volume: 60 % of extraction volume cell; nitrogen purge: 150 psi for 60 seconds. The ASE extracts (ca 45 ml) were centrifuged in 50 ml Teflon centrifuges tubes at 3,500 rpm for 7 minutes. The extracts were later concentrated in a Büchi rotary evaporation unit from Brinkmann (Westbury NY, USA) up to 10 ml. Twenty milliliters of water were added to each concentrated extract to reconstitute the sample to 30 ml before the SPE cleanup step.

The Oasis HLB Plus cartridges were pre-conditioned with 10 ml of methanol follow by 5 ml of water. An aqueous extract of 30 ml was passed through the conditioned cartridge at 1.5 ml/min using a 30 ml polypropylene syringe as support of the sample. A pre-filter unit consisting of a 25 mm filter polypropylene holder with a previously combusted GF/B glass microfibre filter (Whatman Scarborough MN, USA), was used before the SPE cartridge in order to trap the fulvic/humic materials precipitated. The elution solvent was 10 ml of CH_2Cl_2. The eluted fraction from the SPE was concentrated using nitrogen in a heated block (45°C) up to dryness and reconstituted in methanol (for LC/MS analysis) to a final volume of 1000µl. If GC/MS analysis was required the SPE elutates were then evaporated to dryness using a combination of a water bath and a clean stream of purified Nitrogen, fortified with the appropriate amount of the recovery standard (100 µL of a 1 ng/µl TCMX solution) and reconstituted to a final volume of 1 ml using hexane. The final extracts were then transferred to 2–mL amber GC vials and stored at or below -10°C until the time of analysis. This method represents a novel way of recovering slightly polar analytes from organic rich soils and was much more robust that traditional EPA methods in avoiding matrix interferences.

Figure 2.6 shows the final methodology selected for the extraction of triazines from organic rich sediments.

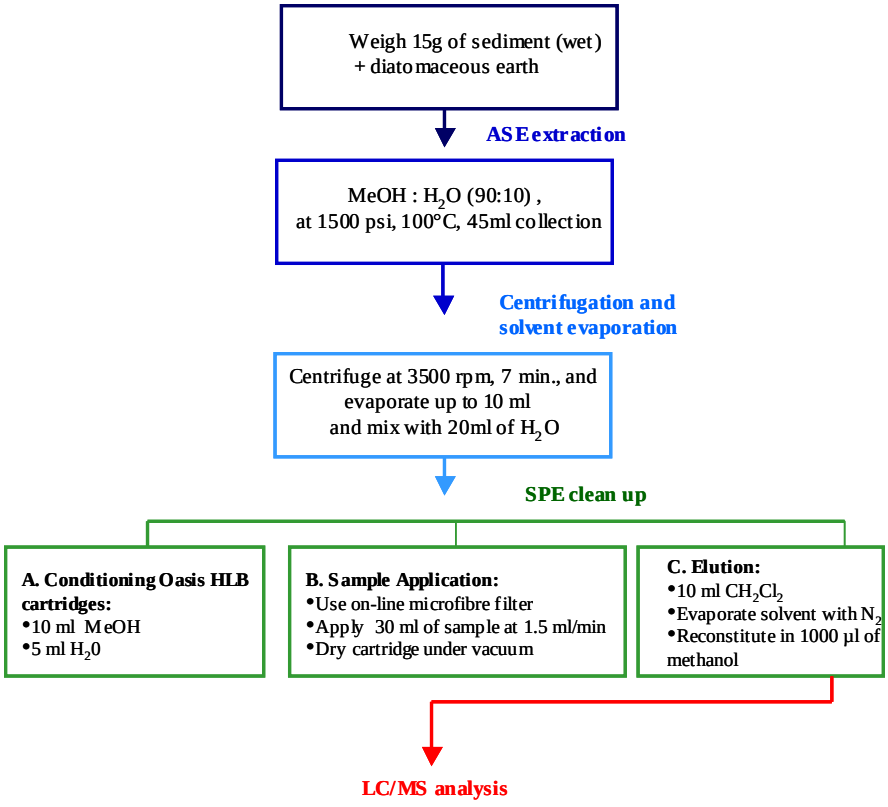


Figure 2.6. Scheme of the analysis of triazine-based herbicides in sediments.

2.4.7 Sediment preparation for the determination of Organo-phosphorous pesticides.

The analytical method is based on extraction of sediment by accelerated solvent extraction (ASE) using a mixture of acetone and methylene chloride. Purification of the sample extracts is achieved by column chromatography clean-up using Florisil and alumina. Determination of target compounds is performed by gas chromatography-mass spectrometry analysis, using the selected ion mode (SIM). All Organo-Phosphorous pesticide standards and the surrogates standards were purchased as neat compounds with a purity of 95% or better from Chem Service (PA, USA) and sued without further purification. The complete list of analytes is presented in Table 2.5.

Stock Standards

Stock solutions (500 to 1000 ppm) of all the target analytes, the surrogate standards (tri-phenyl-phosphate; TPP and tri-butyl-phosphate; TBP) and the internal standard (Tetrachloro-m-xylene; TCMX) are prepared by dissolving 5.00 to 10.0 mg of the appropriate substance in 10 mL of ethyl acetate. The stock standard solutions are stored in vials with Teflon lined screw caps at -20ºC, protected from light. Stock standard solutions are checked frequently for signs of degradation or evaporation, especially immediately prior to preparing calibration standards from them.

Intermediate/ Working Standards

Intermediate and Working solutions at 50, 20, 2, or 1 ppm are prepared by diluting the stock solutions in the appropriate solvent as follow:

Surrogate standard solution (SSS): The surrogate standards used for this analysis are tri-phenyl-phosphate and tri-butyl-phosphate. A surrogate standard spiking solution (20.0

ng/μL) is prepared by diluting 1 mL of the 200 ppm stock in 10 mL of methanol. The surrogate standard spiking solution is stored at 4ºC protected from light. One hundred micro liters (100μL) of the SSS is added to all samples during the sample preparation step before extraction.

***Blank/Matrix spiking solution (MSS)*:** The blank/matrix spiking solution contains all the organophosphorous pesticides present in the calibration at various concentrations. 100 μl of the MSS is added to the fortified blanks and fortified matrix samples.

***Internal standard solution (ISS)*:** The compound 1,2,3,5-tetrachlorometaxylene (TCMX) is the internal standard used for the calculation of surrogate recoveries. An ISS at a nominal concentration of 2 ng/μL is prepared by accurately weighing an appropriate amount of pure TCMX and diluting to volume with ethyl acetate. The working solution is stored at 4ºC protected from light. The ISS is added to each sample to obtain a final concentration of 0.2 ng/μL. The calculations of surrogate recovery however are only advisory since they are dependent of the final extract volume.

Wet sediment samples, approximately 25 g were weighed to the nearest 0.2g, spiked with 100 μL of the SSS and mixed with enough combusted sodium sulfate to fill the 33 ml ASE cell. Multiple cells were used if the sediment dry weight was between 20 and 30 %. After mixing for 15 minutes, the sample was transferred to a 33ml stainless steel ASE extraction cell packed from bottom to top as follows: glass fiber filter (GF/B), sodium sulfate (2 cm), sample, glass fiber filter. The extractions were carried out using a Dionex ASE 200 system using a mixture of acetone: dichloromethane (50:50) under the conditions listed in Table 2.6.

OP pesticide calibration solutions	CS1 (PPM)	CS2 (PPM)	CS3 (PPM)	CS4 (PPM)	CS5 (PPM)	CS6 (PPM)
DICHLORVOS	0.005	0.010	0.020	0.040	0.060	0.195
DEMETON-S+O	0.160	0.320	0.640	1.280	1.920	6.240
DEMETON-O	0.050	0.100	0.200	0.400	0.600	1.950
DEMETON-S	0.100	0.200	0.400	0.800	1.200	3.900
SULFOTEP	0.020	0.040	0.080	0.160	0.240	0.780
TERBUFOS	0.040	0.080	0.160	0.320	0.480	1.560
DISULFOTON	0.040	0.080	0.160	0.320	0.480	1.560
DICHLOFENTHION	0.009	0.018	0.036	0.072	0.108	0.351
PHOSPHAMIDON	0.060	0.120	0.240	0.480	0.720	2.340
METHYL CHLORPYRIFOS	0.009	0.018	0.036	0.072	0.108	0.351
FENTHION	0.030	0.060	0.120	0.240	0.360	1.170
PARATHION	0.060	0.120	0.240	0.480	0.720	2.340
TRICHLORONATE	0.020	0.040	0.080	0.160	0.240	0.780
CHLOFENVINPHOS	0.060	0.120	0.240	0.480	0.720	2.340
CROTOXPHOS	0.080	0.160	0.320	0.640	0.960	3.120
SULPROFOS	0.050	0.100	0.200	0.400	0.600	1.950
FAMPHUR	0.060	0.120	0.240	0.480	0.720	2.340
PHOSMET	0.060	0.120	0.240	0.480	0.720	2.340
LEPTOPHOS	0.060	0.120	0.240	0.480	0.720	2.340
AZINPHOS ETHYL	0.070	0.140	0.280	0.560	0.840	2.730
MEVINPHOS(E) cis isomer 73%	0.014	0.028	0.056	0.112	0.168	0.546
MEVINPHOS (E+Z)	0.020	0.040	0.080	0.160	0.240	0.780
ZINOPHOS	0.050	0.100	0.200	0.400	0.600	1.950
PROPHOS	0.020	0.040	0.080	0.160	0.240	0.780
DIMETHOATE	0.090	0.180	0.360	0.720	1.080	3.510
FONOFOS	0.007	0.014	0.028	0.056	0.084	0.273
DIAZINON	0.008	0.016	0.032	0.064	0.096	0.312
METHYL PARATHION	0.050	0.100	0.200	0.400	0.600	1.950
RONNEL	0.010	0.020	0.040	0.080	0.120	0.390
MALATHION	0.020	0.040	0.080	0.160	0.240	0.780
CHLOROPYRIFOS	0.060	0.120	0.240	0.480	0.720	2.340
ASPON	0.030	0.060	0.120	0.240	0.360	1.170
TETRACHLOVINPHOS	0.020	0.040	0.080	0.160	0.240	0.780
TOKUTHION	0.030	0.060	0.120	0.240	0.360	1.170
DYLOX	0.080	0.160	0.320	0.640	0.960	3.120
FENSULFOTHION	0.060	0.120	0.240	0.480	0.720	2.340
ETHION	0.040	0.080	0.160	0.320	0.480	1.560
CARBOPHENOTHION	0.070	0.140	0.280	0.560	0.840	2.730
EPN	0.050	0.100	0.200	0.400	0.600	1.950
AZINPHOS METHYL	0.050	0.100	0.200	0.400	0.600	1.950
NALED	0.080	0.160	0.320	0.640	0.960	3.120
SURROGATES and INTERNAL STANDARDS.						
TCMX (IS)	0.200	0.200	0.200	0.200	0.200	0.200
TBP (SS1)	0.200	0.200	0.200	0.200	0.200	0.200
TPP (SS2)	0.200	0.200	0.200	0.200	0.200	0.200

Table 2.5.- Composition of the Organophosphorous Pesticides calibration solutions in ng/µL (ppm).

Parameter	Set point
Extraction Pressure	2000 psi
Extraction temperature	100°C (5 minute cycle, 5 minute static)
Solvent	1:1 Acetone/Dichloromethane
Extraction Cycles	2
Flush Volume	60% of cell volume
Purge	Nitrogen, 60seconds

Table 2.6. - ASE conditions for the extraction of organophosphorous pesticides.

Because of the volatile and reactive nature of some Organophosphorous pesticides, the method was optimized so that evaporation steps were conducted under relatively mild conditions. After the ASE extraction, the samples were reduced to a volume of 10 ml, using a gentle stream of filtered nitrogen. The extract was then quantitatively transferred to a concentrator tube and further concentrated to 1 ml. In order to expedite the concentration process, a dry heat incubator set at <50 ºC was used during the final blow down.

Sample Cleanup

Sediment extracts were purified by using a mix-bed Florisil-Alumina chromatography column. Alumina (80-200 mesh), was cleaned by combusting it at 450ºC and deactivated by adding 1% or water (w/w). Florisil (100-200 mesh) was used without purification and was deactivated adding 5% or water (w/w). Chromatography columns ((25 cm length x 8 mm ID,

with a Teflon stopcock and a 125 mL reservoir) were packed using the slurry method as follow:

TOP

Sodium Sulfate (1 cm)

Florisil (3 g, 5% deactivation)

Alumina (1 g 1 % deactivation)

Sand (2 cm)

Glass Wool (1 cm)

BOTTOM

Sample extracts were then loaded to the column and the column was eluted with 10 ml of pentane followed by 6 mL of methylene chloride to recover the analytes. The combined solvents, collected in a KD concentrator tube were then evaporated to a final volume of 1 ml by suing the method described previously. After addition of the GC recovery standard (100 μl, 1 ppm TCMX) samples were transferred to amber GC vials and archived for GC/MS analysis.

2.4.8 Sediment preparation for the determination of Phenoxy-Acid herbicides.

Methanol (CH_3OH), glacial acetic acid ($C_2H_4O_2$), water (H_2O), acetone (C_2H_6CO), and methyltertbutyl-ether (MTBE, $C_5H_{12}O$) of HPLC grade or equivalent quality were

obtained from Fischer Scientific (Suwannee GA, USA). Formic acid (HCOOH) reagent grade was obtained from Fischer Scientific (Suwannee GA, USA).

The acidic herbicides 2,4-D ($C_8H_6Cl_2O_3$), MCPA ($C_9H_9ClO_3$), 2,4,5-T ($C_8H_5Cl_3O_3$), 2,4-DB ($C_{10}H_{10}Cl_2O_3$), Mecoprop ($C_{10}H_{11}ClO_3$), Silvex ($C_9H_7Cl_3O_3$), Dichlorprop ($C_9H_8Cl_2O_3$), Dicamba ($C_8H_8Cl_2O_3$), Dinoseb ($C_{10}H_{12}N_2O_5$), Bentazone ($C_{10}H_{12}N_2O_3S$), Acifluorfen ($C_{14}H_7ClF_3NO_5$) and Picloram ($C_6H_3Cl_3N_2O_2$), were obtained as solids at 99 % purity from Chem Service (West Chester PA, USA). The internal standards used were 2,4-dichlorophenyl acetic acid 99 % (DCAA, $C_8H_6Cl_2O_2$) obtained as solid from Chem Service (West Chester PA, USA) and a solution of 2,4-D $^{13}C_6$ 100µg/ml (Dr. Ehrenstorfer, GmbH, Augsburg,Germany).

Stock, Working and Calibration Solutions

Approximately 6 mg of each one of the solid standards were weighed individually in a Cahn-33 microbalance (Cahn Instruments CA, USA), and were added to a 10 mL amber volumetric flask and dissolved with MeOH. These c.a. 600 µg/ml stock solutions were stored in the dark at –20 ºC. The working standard solutions mixtures were prepared to a concentration c.a. 50 µg/ml by adding 790 µl of each individual stock solution into a 10 ml amber flask. These working standard solutions were used to prepare an 8 level calibration curve between 0.15 and 4 µg/m (see Table 2.7). The internal standard solution of DCAA or 2,4-D $^{13}C_6$ was added to each calibration solution to a concentration of 2 µg/ml. Stock solutions were replaced every 3 months.

Spiking Solutions

Mixtures of phenoxy acid herbicides at 20 µg/ml were prepared by adding approximately 333 µl of 600 µg/ml stock solutions to a 10 ml amber flask and diluted with methanol. The internal standard solutions of DCAA or 2,4-D $^{13}C_6$ were also prepared at 20 µg/ml and added to all samples at a constant concentration of 2 µg/ml.

Table 2.7. Preparation of the phenoxyacid calibration solutions.

Solution	Concentra-tion of working solution [a]	Volume of working solution [a]	Volume of internal standard [b]	Final volume	Final concentration of analytes
CS0	0	0	400 µl	10 ml	0
CS1	50 ug/ml	30 ul	400 µl	10 ml	0.15 µg/ml
CS2	50 ug/ml	50 ul	400 µl	10 ml	0.25 µg/ml
CS3	50 ug/ml	60 ul	400 µl	10 ml	0.30 µg/ml
CS4	50 ug/ml	100 µl	400 µl	10 ml	0.50 µg/ml
CS5	50 ug/ml	200 µl	400 µl	10 ml	1.0 µg/ml
CS6	50 ug/ml	400 µl	400 µl	10 ml	2.0 µg/ml
CS7	50 ug/ml	600 µl	400 µl	10 ml	3.0 µg/ml
CS8	50 ug/ml	800 µl	400 µl	10 ml	4.0 µg/ml

[a]Working solution is a mix of 2,4-D; 2,4,5-T, acifluorfen, silvex, picloram, mecroprop, 2-4,D-B; bentazon, dicamba, dichlorprop, dinoseb and MCPA.
[b] Internal standard solution at 50 µg/ml

Sample Extraction and Cleanup.

Sediment samples (c.a. 15 g) were mixed with combusted diatomaceous earth. After approximately 15 minutes of mixing, the sample was transferred to a 33 ml stainless steel

ASE extraction cell. The extractions were carried out using a Dionex ASE 200 Accelerated Solvent Extractor (Dionex Corporation, Sunnyvale, CA, USA) with 33 ml stainless-steel extraction cells, using a mixture of acetone:5 % HOAc (80:20 %). A system pressure of 2000 psi and an extraction temperature of 100 ºC were used. A static time of 5 minutes, flush volume of 60 % of extraction cell volume; nitrogen purge of 150 psi for 60 s were used to complete the extractions.

The ASE extracts (ca 45 ml) were acidified with 700 µl of concentrated sulfuric acid and centrifuged in 50 ml Teflon centrifuges tubes at 3,500 rpm for 7 minutes. The extracts were later concentrated in a Büchi rotary evaporation unit from Brinkmann (Westbury NY, USA) up to 20 ml. Fifty milliliters of 5 % solution of acetic acid was added to each concentrated extract to reconstitute de sample to 70 ml before the SPE cleaning step.

The SPE procedure was performed with a SPE vacuum manifold VAC ELUT SPS 24 column processor (Varian Palo Alto CA, USA). The Oasis HLB Plus cartridges were pre-conditioned with 5 ml of freshly mixed methyl-tert-butyl-ether (MTBE): methanol (90:10) with 0.01 % of formic acid; followed by 5 ml of methanol (0.01% formic acid); 5 ml of water and finally 5 ml of water (0.25 % sulfuric acid). An aqueous extract of 70 ml was passed through the conditioned cartridge at 1.5 ml/min. A pre-filter unit consisting of a 25 mm filter polypropylene holder with a previously combusted GF/B glass microfibre filter (Whatman Scarborough MN, USA), was used before the SPE cartridge in order to trap the fulvic/humic materials precipitated during the acidification. Analytes were recovered from the cartridge by using a mixture of MTBE:Methanol (90:10) with 0.01 % of formic acid (2 x 6 ml). The eluted fraction from the SPE was concentrated using nitrogen in a heated block (45°C) up to 500 µl and reconstituted in methanol to a final volume of 1000µl. Figure 2.7

summarizes the final extraction procedures selected for the analysis of phenoxy-acid herbicides.

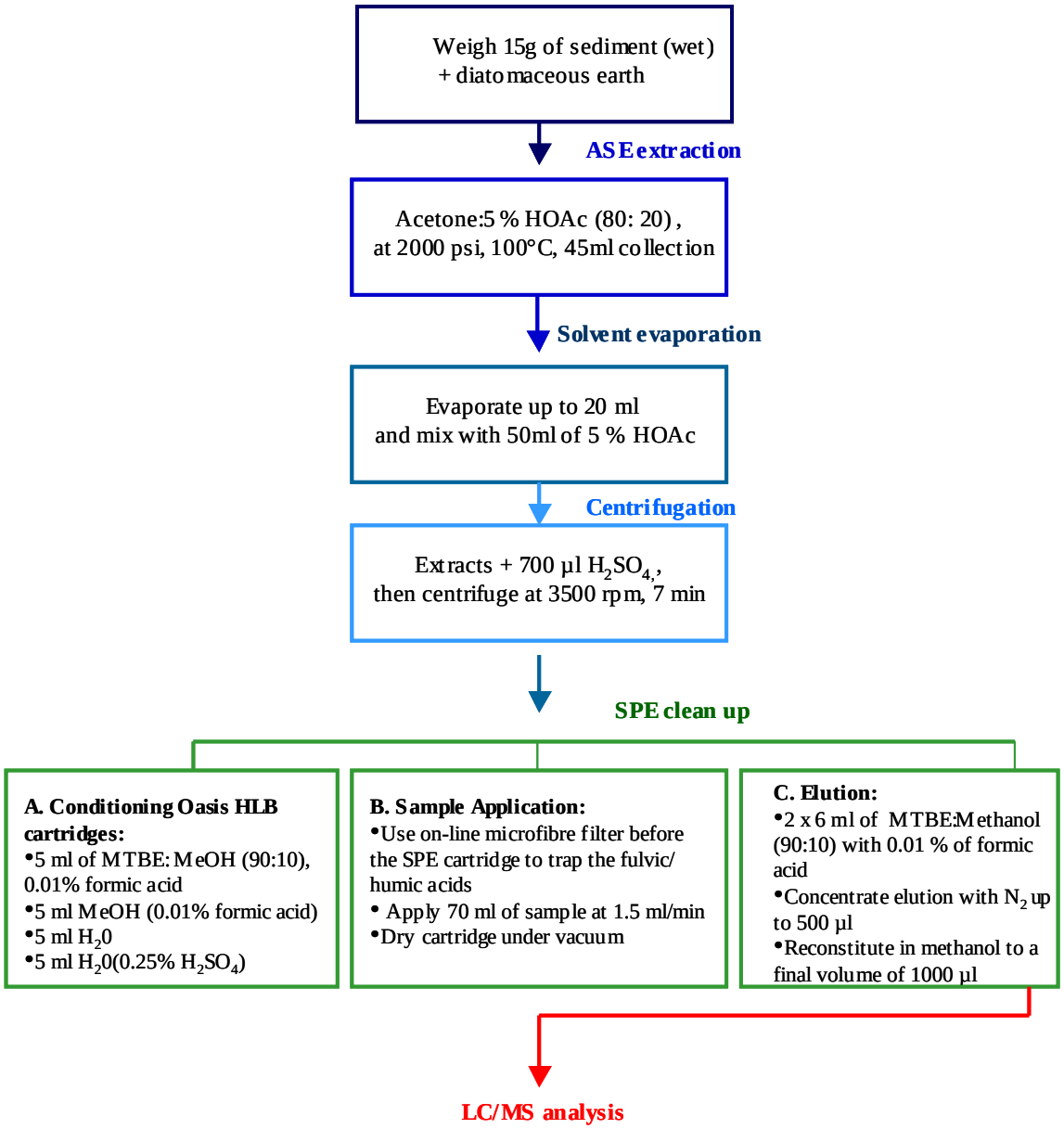


Figure 2.7. Scheme for the analysis of phenoxy-acid herbicides in sediments.

2.5. Biological Tissue Samples

2.5.1 Percent Dry Weight Determination of Tissue

In order to express the results of analysis on a dry weight basis for tissue samples, the dry weight percent of the tissue must be determined. A 3 – 5 g sub-sample of homogenized tissue from each sample was placed in a pre-weighed 40 mL beakers and the weight recorded. The beakers were then placed in Labconco vacuum freeze drier for 3 days. The beakers were then weighed and the weight recorded and then placed back in the freeze drier for a 24 hr. period. The sample set was then reweighed and the weight recorded. This process was repeated for each sample until the difference between two consecutive weights was less than 0.02 g. For each set of 20 samples or less a duplicate was processed with a maximum allowable Relative Percent Difference (RSD) of ± 25%. If the RSD exceeded the criteria, the entire set was reprocessed.

2.5.2 Determination of Percent Lipid in Tissue

Concentrations of organic contaminants are often expressed as a function of the percent lipid content of a tissue sample since most organic contaminants are lipophilic, and therefore tend to accumulate in higher concentrations where the percent lipid is greater. To method applied for determining the percent lipid content of tissue samples is modified from NOAA (1998), a 20 mL aliquot of the dichloromethane extracted tissue was placed in a loosely capped 24 mL vial and allowed to evaporate to dryness. The samples were then reconstituted to 1 mL in dichloromethane. 100 μL was then transferred to a clean, dried, Whatman® GF/C glass microfibre filter paper (1 cm x 2 cm), pre-weighed to 0.001 mg using a Cahn

Electrobalance, and then placed on pleated sheet of heavy duty aluminum foil over a hot plate set at the lowest setting. After 30 minutes the filter paper was weighed and the weight recorded. This was repeated until the difference in weight between two consecutive weighs was less than 5 %. For each set of 20 or less samples, a duplicate sample was processed. If the RPD between duplicates was not within ± 25 %, the entire batch was reprocessed.

Equation 1. Percent Lipids in fish tissue.

$$\text{Percent Lipid} = \frac{\text{TV}}{\text{AV}} \text{ x } \frac{\text{FV}}{\text{VW}} \text{ x } \frac{\text{LW}}{\text{SW}} \text{ x } 100$$

where TV is the total volume of the extract (mL), AV is the volume of the aliquot (mL), FV is the final volume (mL), VW is the volume weighed (mL), LW is the lipid weight (g), and SW is the sample weight (g).

2.5.3 Fish tissue preparation for GC-ECD determination of Organochlorine Pesticides, PCBs, and GC-MS determination of PAHs.

The method used in study for the extraction of fish tissue for trace organic analysis is modified from the method described by NOAA (1998) and has been applied previously for extraction of trace organics from tissues (Gardinali et al, 1996, Gardinali and Wade, 1998). An aliquot of 10 - 12g (wet wt.) of tissue sample was weighed into a 200 mL centrifuge bottle and then the appropriate surrogate and spiking solutions were added. Approximately 40g of anhydrous sodium sulfate and 100 mL of dichloromethane were then added to each bottle. Each sample was then macerated for 3 min using an Ultra Turrax® T18 Basic

tissuemizer. The sample extract was then decanted and filtered through a funnel with a glass wool plug and approximately 40g sodium sulfate pre-wetted with dichloromethane into a 500 mL flat bottom flask. The extraction was repeated two more times with 100 mL aliquots of dichloromethane, after the third extraction, the sample bottles were rinsed 3 times with dichloromethane and poured through the funnel into the flask. The total volume of the flask was then marked with a permanent marker and a 20 mL aliquot removed for lipid content analysis.

Internal standard surrogate solutions were added to each sample prior to extraction. For Organochlorine pesticide and PCB analysis, A 100 μL solution of DBOFB (1.0355 ppm), PCB 103 (1.0385 ppm), PCB 198 (1.0135 ppm), and OCN (20.97 ppm) was added to each sample and QC sample. For PAH analysis a 100 μL mixture of 2 ppm Napthalene-d8, Phenanthrene-d10, Chrysene-d12, Acenapthene-d10, and Perylene-d12, were added to each sample and QC sample. A 100 μL spiking solution containing all Organochlorine analytes and a 100 μL spiking solution containing all PAH analytes were added to each matrix spike (MS) and laboratory blank spike (LBS) to assess method performance prior to extraction.

Prior to transfer of the second fraction into 2 mL amber glass vials, 100 μL of TCMX (1 ppm) and 100 μL of 2 ppm Flourene-d10 and Benzo(a) Pyrene-d12 were added to each sample and QC sample as external standards for OC and PAH analysis respectively. For the aliphatic fraction, 100 μL of TCMX (1 ppm) was added as an external standard.

The sample extract was then concentrated and purified using a mixed bed silica-alumina chromatographic column in manner similar to sediment samples as mentioned above except

the addition of copper turnings, which are not necessary for tissue samples. After silica-alumina cleanup, sample extracts are concentrated to 1 mL of dichloromethane.

2.5.4 Purification of Tissue samples by Gel Permeation Chromatography for Organic analysis.

Sample extracts from biological tissue samples contain large amounts of lipids and high molecular weight components that may interfere with the instrumental analysis of PAHs, OCPs, and PCBs. Sample extracts are purified of these interferences by size exclusion chromatography using a gel permeation chromatographic technique employing a high performance liquid chromatography system consisting of an Acuflow Series I HPLC pump, and a Thermo Separation Products Spectra Series UV 150 ultraviolet detector set at λ 254. Samples were processed through a Phenomonex phenogel 50 x 7.80 mm 10 micron guard column and two Phenomonex phenogel 300 x 21.20 mm 10 micron 100A columns.

Prior to introducing samples, the HPLC is calibrated using a solution containing spiking level concentration of all analytes and surrogates to be analyzed and an appropriate amount of fish oil to achieve a 10 % lipid content in a dichloromethane solution. The calibration solution is introduced to the HPLC system at a rate of 5 mL per minute at an operating pressure of 350 to 450 psi. ELAB chromatographic software is used to determine the retention times of the lipid content and the target compounds to determine the appropriate collection times for each fraction. A dichloromethane blank is also processed to verify no contamination within the system. Total process time for each sample is 40 min with the desired fraction collected from about 21 min to 40 min.

After calibration of the GPC-HPLC system was verified, alumina-silica purified samples pre-concentrated to just under 1 mL dichloromethane were introduced into the

system and the desired fraction collected into 250 mL flat-bottomed flasks. A dichloromethane blank was processed after every five samples and a calibration solution processed after every ten samples. The GPC purified extract was then concentrated to approximately 5 – 10 mL in a hot water bath set a 65 °C in the flat-bottomed flask with a 3-ball Snyder column. The concentrated sample was then quantitatively transferred into 25 mL concentrator tubes and concentrated to 1 mL, exchanging the final solvent to hexane. The appropriate internal standards for GC-ECD and GC-MS analysis were then added before transferring samples into labeled 2 mL amber vials with Teflon lined caps for storage until ready for analysis.

2.5.5 Preparation of fish tissue samples for ICP-MS determination of trace elements.

The method employed for total digestion of tissue samples is an adaptation of EPA Method 3050B using an Environmental Express HotBlock™. An aliquot of approximately 1 gram (wet wt.) was directly weighed into a 50 mL polypropylene digestion vessel. 10 mL of 50:50 trace metal grade (TMG) nitric acid and DDI water was then added to the vessel, swirled to mix well, covered with a watch glass and placed in the HotBlock at 95 °C for 15 minutes. The sample was then removed from the HotBlock and allowed to cool before the addition of 5 mL of concentrated TMG nitric acid and then placed back in the HotBlock. After 60 minutes, the sample was removed from the HotBlock, allowed to cool before the addition of 2 – 5 mL of DDI water, followed by the slow addition of 1 mL of 30% A.C.S. certified H_2O_2, allowing 5 -10 minutes for exothermic reaction to occur before returning sample to the HotBlock. After 30 minutes an additional 0.5 mL of H_2O_2 is added to sample, this step is repeated until no reaction occurs upon addition of H_2O_2. After cooling, the sample is diluted to 50 mL in digestion vessel and is ready for analysis. QA/QC for each

set of 20 or fewer samples included a blank, two blank spikes, and two matrix spikes were processed, whenever possible samples were processed in triplicates, if sufficient sample was not available for all samples, a duplicate was processed with each batch. A 0.25 – 0.5 g aliquot of DORM-2 (CNRC) dogfish muscle reference material was digested with each batch as part of the QA/QC protocol.

2.6 Instrumental Analysis

2.6.1 Organochlorine Pesticide and PCB determination by GC-ECD

Chlorinated hydrocarbons can be determined at trace concentrations (ppb) using gas chromatography with and electron capture detector (ECD), a list of target analytes if given in Table 2.8. Purified extracts were analyzed for chlorinated hydrocarbons in a Hewlett Packard 5980II gas chromatography with electron capture detection (GC-ECD) using a 30-meter, 0.25 mm i.d., 25 μm DB-5 fused silica capillary column from J&W Scientific. The HP 5880II GC is equipped with a split/splitless capillary inlet system with a splitless liner, ultra high purity (UHP) grade helium as a carrier gas (25 psi), and UHP grade nitrogen for make-up gas (40 psi). The initial temperature for the oven is 100ºC, and it reaches a maximum temperature of 300ºC. The injection port has a temperature of 280ºC and the ECD at 325 °C. The run length is about 93.33min.

Internal standard quantitation with a 5-point calibration curve (5 – 200 ng/mL) was used for the analytical determinations. The analysis requires a correlation coefficient of 0.99 for all of the compounds analyzed. Analyte concentrations were calculated based on surrogate standards using PCB 103. Surrogate standard recoveries were calculated using the internal standard TCMX. For each set of samples analyzed, all QA samples including blanks, fortified laboratory blanks, duplicates, and matrix spikes were included

in the sequence. The calibration standards were interspersed throughout the sequence to account for instrument drift of retention times and changes in sensitivity.

Table 2.8.-Organochlorine pesticides and Polychlorinated Biphenyls of interest.

Pesticides	Polychlorinated biphenyls
Chlrorinated Benzenes	Dichlorobiphenyls
Tetrachlorobenzene 1,2,4,5	PCB8/5
Tetrachlorobenzene 1,2,3,4	Trichlorobiphenyls
Pentachlorobenzene	PCB18/17
Hexachlorobenzene	PCB29
Hexachlorocyclohexanes	PCB28/31
Alpha HCH	Tetrachlorobiphenyls
Beta HCH	PCB52
Gamma HCH	PCB44
Delta HCH	PCB66/95
Chlorodane-related Compounds	Pentachlorobiphenyls
Heptachlor	PCB101/90
Heptachlor Epoxide/OCS	PCB87/115
Alpha Chlordane	PCB105
Gamma Chlordane	Hexachlorobiphenyls
Other Cyclodiene Pesticides	PCB153/132
Aldrin	PCB138 /160
Dieldrin	Heptachlorobiphenyls
Endrin	PCB187
Other Chlorinated Pesticides	PCB180
Chlorpyrifos	PCB170/190
Mirex	Octochlorobiphenyls
Endosulfan Sulfate	PCB195/208
Endosulfan II	Nonachlorobiphenyls
DDTs and Related Compounds	PCB206
2,4' DDE/ENDOSULFAN I	Decachlorobiphenyls
4,4' DDE	PCB209
2,4' DDD	
4,4' DDD	
2,4' DDT	
4,4' DDT	

In the event the response for any sample peak exceeded the highest calibration solution, the extract was diluted and a known amount of surrogate solution added. The final concentration was then reported, adjusted for dilution using the ratio between TCMX and the added surrogate concentrations.

2.6.2 PAHs determination by GC-MS.

GC-MS provides sensitive detection of polycyclic aromatic hydrocarbons (PAHs) at low concentrations due to their strong molecular ion response. A list of PAHs analyzed is given in Table 2.9. PAHs were analyzed from the purified extracts using a Hewlett-Packard HP5890II-HP5971 gas chromatography-mass spectrometry system operated in selected ion mode (GC/MS-SIM). Chromatographic separation was achieved in a 30-meter 0.25 mm i.d., 25 μm DB5-MS fused silica capillary column using UHP grade helium as the carrier gas at a flow of 2.0 mL/min. The mass spectrometer was operated at 70 eV electron energy in the electron impact ionization mode. The injection port was held at 300ºC and operated in splitless mode. The oven was set up at an initial temperature of 55ºC and a final temperature of 300ºC at a rate of 6.5 ºC/min. The total run time was 50min.

A 5-point calibration curve (20 ng/mL – 4000 ng/mL) with a correlation coefficient of > 0.99 for all analytes was used to demonstrate the linear range of the detector. Analyte concentrations are calculated based on surrogate standards Napthalene-d8, Phenanthrene-d10, Chrysene-d12, Acenapthene-d10, and Perylene-d12. Surrogate standard recoveries are calculated based on internal standards benzo(a)pyrene-d12 and flourene-d10.

Table 2.9.-Polycyclic Aromatic Hydrocarbons of interest.

Compounds	Quantitation ion	Confirmation ion
Recovery (Internal) Standards		
Benzo(a)pyrene d-12	264	260
Fluorene-d10	176	174
Surrogate Standards		
Perylene-d12	264	260
Naphthalene-d8	136	134
Acenaphthene-d10	164	162
Phenanthrene-d10	188	184
Chrysene-d12	240	236
Target Compounds		
Naphthalene	128	127
2-methylnapthalene	142	141
1-methylnapthalene	142	141
2,6-dimethylnapthalene	156	141
1,6,7-trimethylnapthalene	170	155
C2-Napthalenes	156	141
C3-Napthalenes	170	155
C4-Napthalenes	184	169
Biphenyl	154	153
Acenaphthylene	152	153
Acenaphthene	154	153
Flourene	166	165
C1-fluorene	180	165
C2-fluorene	194	179
C3-fluorene	208	193
Dibenzothiophene	184	152
C1-Dibenzothiophenes	198	184
C2-Dibenzothiophenes	212	197
C3-Dibenzothiophenes	226	211
Phenanthrene	178	176
Anthracene	178	176
Carbazole	167	166
1-methylphenanthrene	192	191
C1-phenan/anthrac	192	191
C2-phenan/anthrac	206	191
C3-phenan/anthrac	220	205
C4-phenan/anthrac	234	219
C1-chrysenes	242	141
C2-chrysenes	256	241
C3-chrysenes	270	255
C4-chrysenes	284	NA
Benzo(b)flouranthene	252	253
Benzo (k)fluoranthene	252	253
Benzo (e)pyrene	252	253
Benzo (a)pyrene	252	253
Indeno[1,2,3-cd]pyrene	276	277
Benzo[g,h,i,]perylene	276	277
Dibenzo(ah)anthracene	278	279
Perylene	252	253

A NIST standard reference material (SRM 1491) at an equivalent concentration of 1.0 ng/g with appropriate surrogates and internal standards is processed with every sequence to verify accuracy of calibration curve. For each set of samples analyzed, all QA samples including blanks, fortified laboratory blanks, duplicates, and matrix spikes were included in the sequence.

2.6.3 Trace and Major Element Determination by ICP-MS

The method used for inductively coupled plasma-mass spectroscopy (ICP-MS) determination of trace and major elements was developed based on EPA Method 6020A (Revision 1, 1998). This method was chosen for its ability to analyze for a wide range of elements at the ppb level in a very short amount of time. The elements chosen for determination in this study and their masses of interest are listed in Table 2.10.

Table 2.10.-Trace and major elements of interest (EPA Method 6020A).

Element	Analyte Masses	IS Massess
Aluminum (Al)	27	45
Arsenic (As)	75	89,103
Beryllium (Be)	9	45
Cadmium (Cd)	111,112,114	103,115
Chromium (Cr)	52,53	45,89
Cobalt (Co)	59	45,89
Copper (Cu)	63,65	45,89
Lead (Pb)	206,207,208	89,103
Nickel (Ni)	58,60,61	89,103
Silver (Ag)	107,109	89,103
Vanadium (V)	51	45,89
Zinc (Zn)	64,66,68	45,89

2.6.3.1 ICP-MS determination of sediment samples

The ICP-MS instrument used for metal analysis of sediments was Model HP 4500 plus (Hewlett-Packard Co., Wilmington, DE) equipped with a Babington-type nebulizer and an ASX-500 autosampler (Cetac Technologies Inc., Omaha, NE). Instrument configuration and general experimental conditions were reported previously (EARL SOP-2000-I-004.1). A set of 9 calibration points was used for minor and major elements (0, 2, 5, 7, 10, 20, 50, 100, 200 ppb). The analysis requires a coefficient of correlation greater than 0.99 for all elements. For each sample, 2 mL of digestate (10% HNO_2) was placed in a 15 mL plastic test tube, then 50 μL of 10 ppm internal standard solution (Y, In, Sc, and Rh) was added to each test tube, and the solution diluted to 10 mL (2% HNO_2). Internal standards were added to all samples, calibration standards, instrument checks, and QA samples to correct for instrument drift and physical interferences present in sample matrices. For analysis of aluminum, samples were diluted 100 times to bring the concentrations within the calibration curve.

The QA/QC protocol for each batch of samples processed includes blanks, blank spikes, matrix spikes, duplicates, and SRM. An instrument check solution, obtained from a source independent of the calibration and stock standards, containing all analytes of interest was processed at 3 concentration levels at the beginning, middle, and end of each sequence to verify accuracy of calibration curve and check for instrument drift.

2.6.3.2 ICP-MS determination of tissue samples

The ICP-MS instrument used for metal analysis of tissue samples was a Perkin Elmer ELAN DRC equipped with a Babington-type nebulizer and an ASX-500 autosampler (Cetac Technologies Inc., Omaha, NE). A 15-point calibration curve (0, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5, 7, 10, 20, 50, 100, 200 ppb) was used for all elements. The analysis requires a coefficient of correlation greater than 0.99 for all elements.

For each sample, 1 mL of digestate (20% HNO_2) was placed in a 15 mL plastic test tube, then 50 μL of 10 ppm internal standard solution (Y, In, Sc, and Rh) was added to each test tube, and the solution diluted to 10 mL (2% HNO_2). Internal standards were added to all samples, calibration standards, instrument checks, and QA samples to correct for instrument drift and physical interferences present in sample matrices. QA/QC protocol for tissue analysis was the same as that for sediment analysis.

2.6.4 Determination of Triazine Herbicides and its metabolites in Sediments/Soils by LC/MS.

Because of their chemical characteristics and the potential need to analyze both the parent compounds and their metabolites a liquid chromatography/mass spectrometry method was develop for triazine absed herbicides. The use of an atmospheric chemical ionization (APCI) interface enabled direct coupling of a Finnigan Navigator aQa quadrupole mass

spectrometer with a TSP liquid chromatograph equipped with a 150 mm x 4.6 mm Luna C-18 reverse phase column working at a flow rate of 0.5 ml/min. The mass spectrometer source was operated in the APCI mode for positive ions (APCI+) with a cone voltage set at 15 volts, the corona pin at 3.5 kV, and the probe temperature at 350°C. The positive ions monitored for the Triazine herbicides are summarized in Table 2.11. It is important to point out that one of the main characteristics of the APCI interface is the production of ions, where the most predominant specie is the $[M+H]^+$. Little fragmentation is normally observed under the conditions of ionization established so quantitation is done based on molecular ions thus reducing the likelihood of interferences.

The total ion chromatogram (TIC) of the mixture is presented in Figure 2.8. At this concentration level (150 µg/ml) all pesticides were easily detected. The initial elution program tested for this set of pesticides involved the use of methanol and acetic acid 1 % with the following linear programming: t=0, 60:40 up to 90:10 in 40 minutes and returning to original conditions at 45 minutes (see Table 2.12).

Table 2.11 Primary ions for Triazine herbicides in APCI +

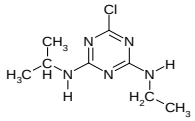
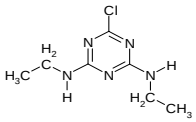
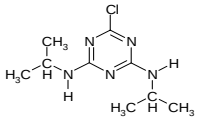
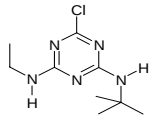
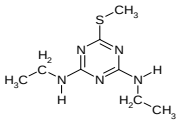
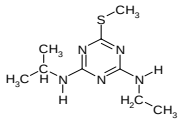
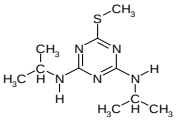
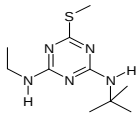
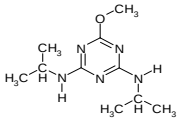
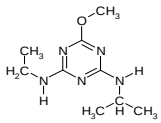
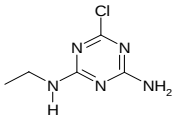
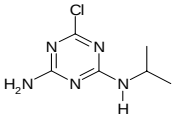
#	Compound	Structure	Exact Mass	Ion [M+H]
1	**Atrazine** $C_8H_{14}ClN_5$ CAS # 1912-24-9		215	216
2	**Simazine** $C_7H_{12}ClN_5$ CAS # 122-34-9		201	202
3	**Propazine** $C_9H_{16}ClN_5$ CASS # 139-40-2		229	230
4	**Terbutylazine** $C_{10}H_{18}ClN_5$ CAS # 5915-41-3		229	230
5	**Simetryn** $C_8H_{15}N_5S$ CAS #1014-70-6		213	214
6	**Ametrin** $C_9H_{17}N_5S$ CAS # 834-12-8		227	228
7	**Prometryn** $C_{10}H_{19}N_5S$ CAS # 7287-19-6		241	242
8	**Terbutryn** $C_{10}H_{19}N_5S$ CAS # 886-50-0		241	242
9	**Prometon** $C_{10}H_{19}N_5O$ CAS # 1610-18-0		225	226
10	**Atratone** $C_9H_{17}N_5O$ CAS # 1610-17-9		211	212
11	**Deisopropylatrazine (DIA)** $C_5H_8ClN_5$ CAS # 1007-28-9		174	175
12	**Desethylatrazine (DEA)** $C_3H_4ClN_5$ CAS # 3397-62-4		187	188

Figure 2.8 - Full scan chromatogram for triazine herbicides mixture

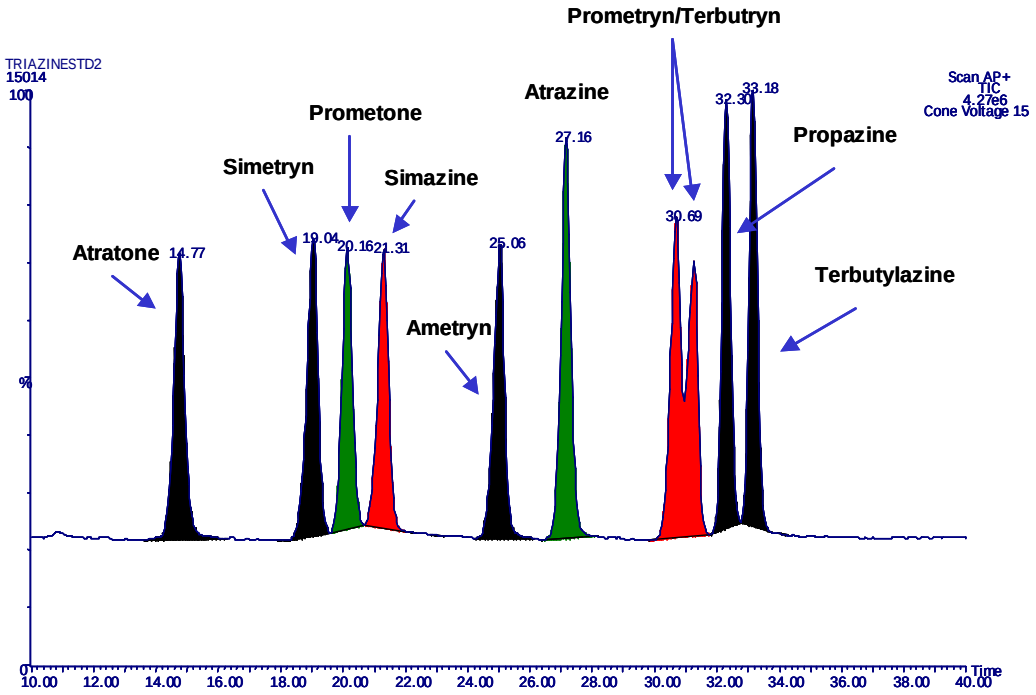


Table 2.12: Gradient elution program for triazine herbicides separation

#	Time (minutes)	% A (Methanol)	%B (HOAC 1%) pH 2.76
1	0	60	40
2	40	90	10
3	45	60	40

The mass spectrum for atrazine and simetryn is shown in Figure 2.9. The predominant $[M+H]^+$ ion is noticed in both spectra. All triazines studied gave mainly protonated molecular ions. It was observed also that none of the herbicides produced major fragmentations even at higher cone voltages.

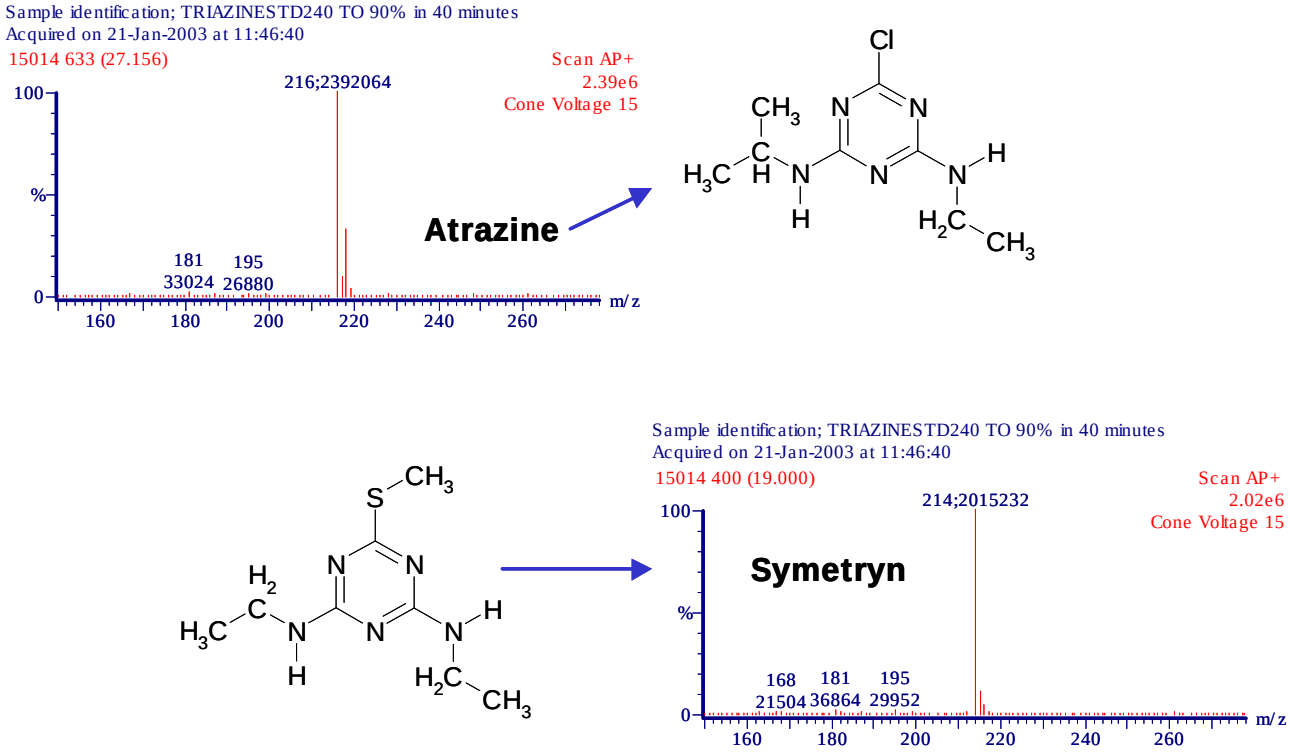


Figure 2.9 - Mass spectrum of symetryn and atrazine herbicides

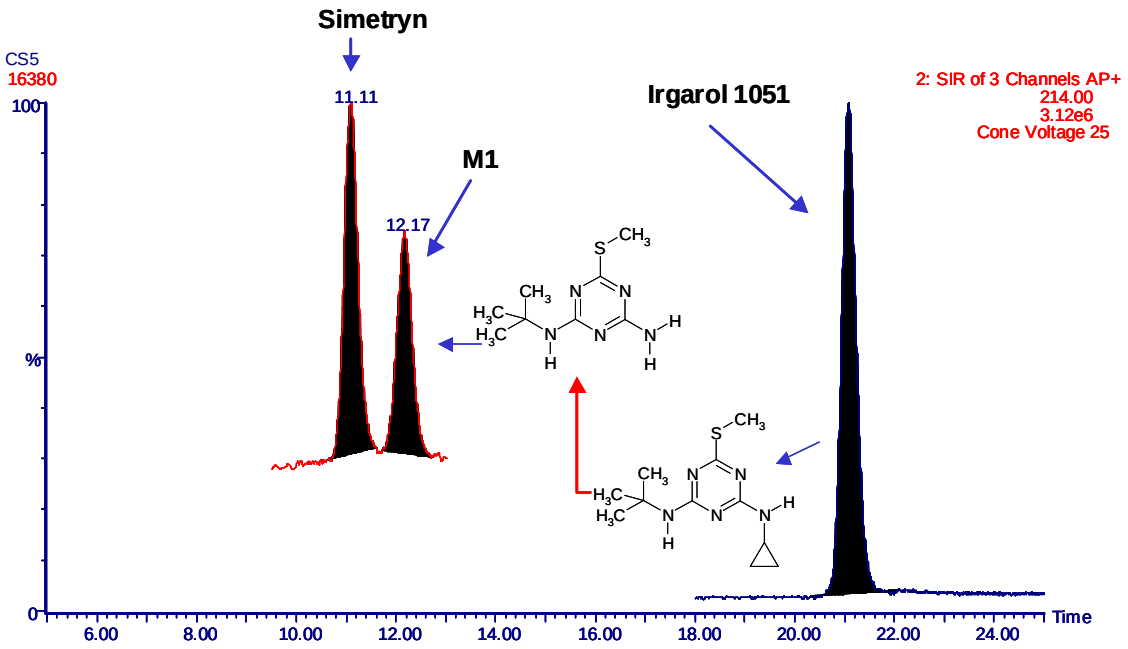


Figure 2.10 - SIR chromatogram for irgarol 1051 and its metabolite M1

In order to obtain an increase in sensitivity and expand the applicability of the analytical method, a single ion-monitoring (SIR) program was created for data acquisition. This program included Irgarol 1051 and its main metabolite called M1 (see Figure 2.10). Even though Simetryn and M1 have the same m/z at 214, they were resolved under the selected conditions. The presence of Irgarol was not expected within the Everglades National Park because it is used an antifouling agent applied mainly in boats, and its presence within the park is not that usual. However, its monitoring is important in the Biscayne Bay National Park, because of the existence of Marinas and the frequent recreational boat activity within this area. At this point is important to mention that the chromatographic separation was optimized in terms of time of analysis. A more rapid elution of the herbicides was achieved without altering the resolution of most of the compounds of interest. The final separation

consisted of an initial composition of 60:40 (MeOH:HOAC 1%) up to 90:10 in 30 minutes, returning to the initial condition in 35 minutes. The cone voltage that gives better sensitivity was found to be 25 volts and the corona discharge voltage of 3.5 kV.

Figure 2.11 shows the complete separation of the triazine herbicides using the single-ion monitoring program.

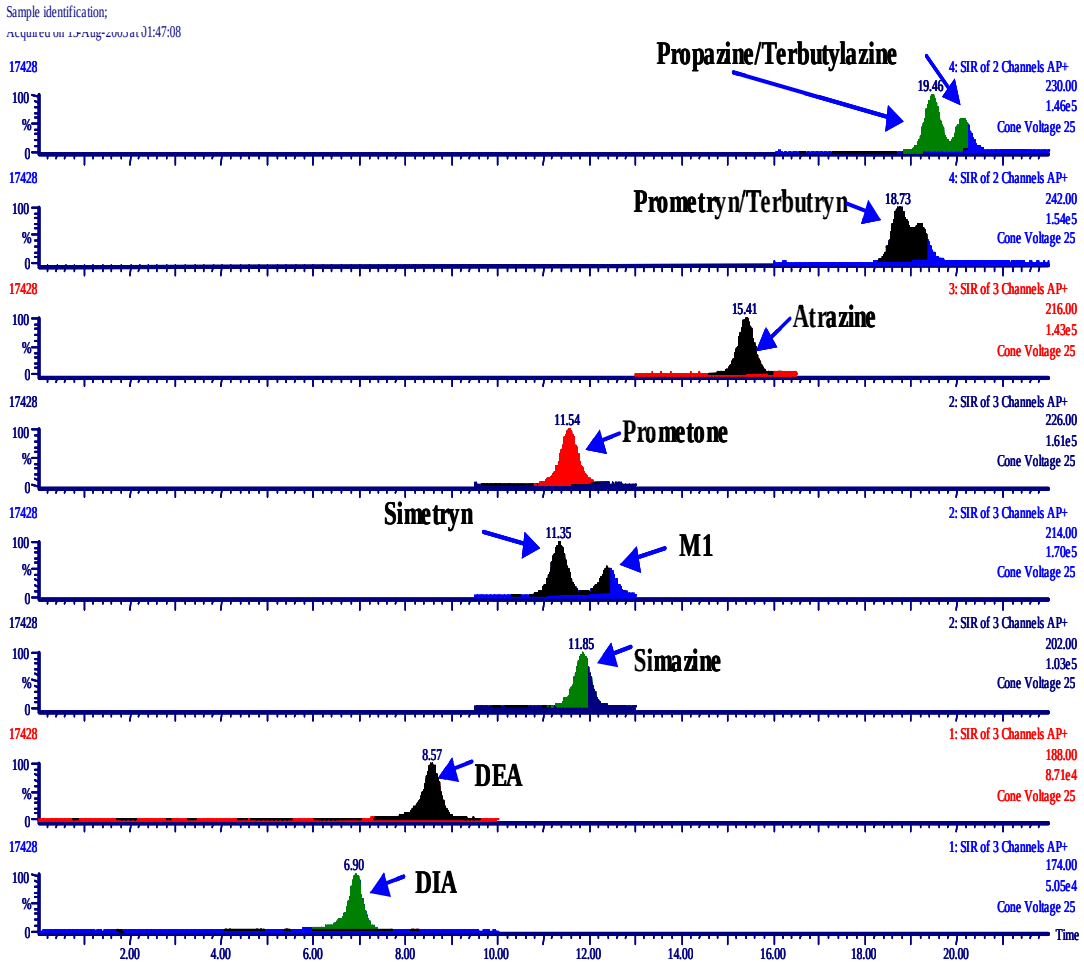


Figure 2.11.-Reconstructed mass chromatogram for triazine herbicides and their major metabolites

The extracted ions shown in this figure demonstrates the capabilities of the mass spectrometer to resolve all the analytes of interest. Included in the SIR program, there are the two of the main metabolites of the atrazine: desethylatrazine (DEA) and desisopropylatrazine (DIA). A close view of these compounds is shown in Figure 2.12. It is worth noting that there are significant differences in polarity between these metabolites and the rest of the triazines. Nevertheless, all compounds were succesfuly separated and analyzed by the HPLC-MS method developed for this study.

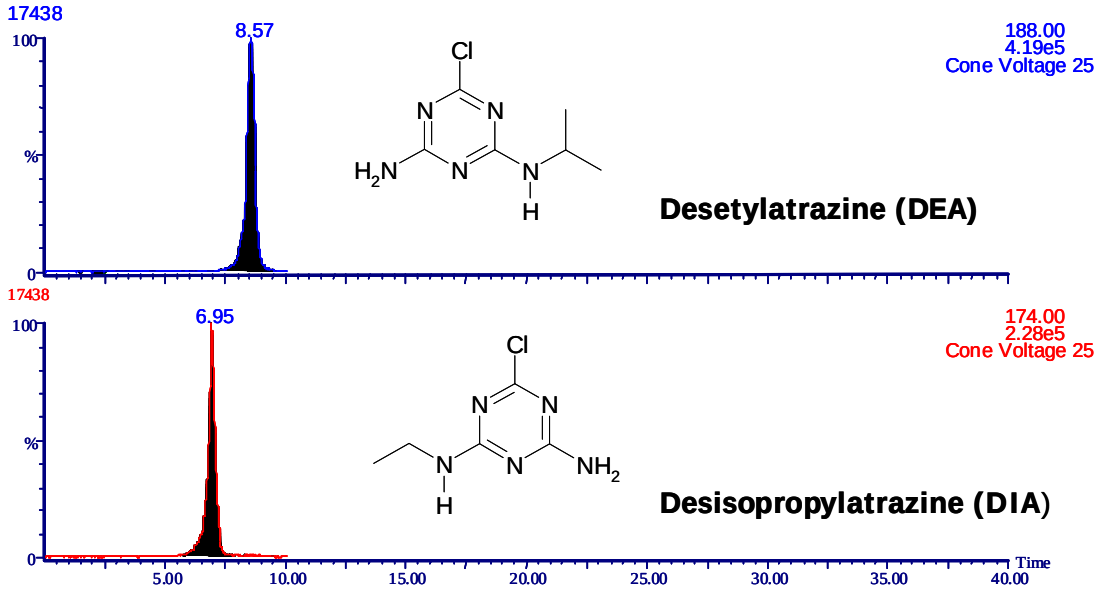


Figure 2.12 - Extracted ion chromatogram for principal metabolites of atrazine.

Analytical Performance for Triazine Herbicides

Calibration graphs were constructed with standard solutions with concentrations between 0.05-2.5 µg/ml. A linear response was observed in the range studied. The correlation coefficients are shown in Table 2.13. All regression coefficients were >0.998 for both the parent compounds and the metabolites tested.

Table 2.13 Correlation coefficients for triazine herbicides

Analyte	r^2	Analyte	r^2
Ametryn	0.999	Terbutylazine	0.999
Prometryn	0.997	Atraton	0.999
Symetryn	0.998	Prometone	0.998
Terbutryn	0.997	DIA	0.999
Atrazine	0.999	DEA	0.999
Simazine	0.999	Irgarol 1051	0.999
Propazine	0.999	M1	0.998

Deuterated atrazine (Atrazine D_5) was used as internal standard. This compound facilitates the quantification of the herbicides because of its similarity with the target analytes. It also shows a strong ionization in APCI interface, condition that helped in the overall results from a quantitative point of view. Other figures of merit for the method such as compound recoveries and the method detection limits are presented in Table 2.14. As in any other

method sued, all samples analyzed included a full set of QA/QC samples with at least a blank, a fortified blank/sample and sample replicates.

Table 2.14.-Sipke sample recoveries and Instrumental Method Detection Limit for triazine herbicides

Compound	Average % Recovery	IMDL (ng/g)
Ametryn	94 (±2)	4
Prometryn	96 (±2)	4
Simetryn	95 (±3)	4
Terbutryn	86 (±4)	4
Atrazine	88 (±2)	4
Simazine	89 (±3)	4
Propazine	88 (±1)	4
Terbutylazine	91 (±2)	4
Atraton	95 (±3)	4
Prometone	95 (±2)	4
DIA	86 (±5)	5
DEA	89 (±4)	5

2.6.5 Determination of Organophosphorous Pesticides by GC/MS

Organophosphorous pesticides (OPs) were analyzed from sediment extracts by gas chromatography mass spectrometry. A list of the OPs analyzed and their diagnostic fragments is given in Table 2.15. OPss were analyzed from the purified extracts using a Thermo Finnigan Ultra Trace DSQ gas chromatography-mass spectrometry system operated in selected ion mode (GC/MS-SIM). Chromatographic separation was achieved in a 30-meter 0.25 mm i.d., 25 μm DB5-MS fused silica capillary column using UHP grade helium

as the carrier gas at a flow of 1.2 mL/min. The mass spectrometer was operated at 70 eV electron energy in the electron impact ionization mode. The injection port was held at 230ºC and operated in splitless mode. The oven program was set up as follows:

50°C/min for 1 min.;
15.0°C/min to 145°C. hold 0 min.;
1.5°C/min to 210°C. hold 1 min.
15.0ºC/min to 300ºC hold 3.33 min
total run time: 60.00 min

The responses of OP's in the mass spectrometer are structure dependent so the calibrations were optimized to detect the least amount possible for every analyte rather than having a fix concentration for all of them. In general a 5-point calibration curve (average 20 ng/mL – 1000 ng/mL) with a correlation coefficient of > 0.99 for all analytes was used to demonstrate the linear range of the detector. Analyte concentrations are calculated based on two surrogate standards TBP, and TPP (Table 2.5). Surrogate standard recoveries are calculated based on an internal standard (TCMX)

This method allowed for the identification of most of the commonly used OP pesticides and some relatively rare ones. However, recovery of analytes was heavily dependent on the analytical procedure and some OP pesticides were inventively lost during the extraction and cleanup procedures or degraded during the GC/MS analysis.

Table 2.15 shows the recoveries of OPs in sediment samples spiked at low level (10-250 ng per sample). To the best of our knowledge this is one of the most comprehensive list of OP's to be determined in sediments where the analytical losses are not substantial.

Organophosphorous Pesticides Ions and SIM windows			
4.0 min.	**Quantitation Ion**	**Confirmation Ion**	**Confrmation Ion**
Dichlorvos	185	109	79
Mevinphos	127	192	109
12.5 min.			
Zinophos	107	97	96
TCMX	244	242	
Demeton 0	88	89	170
Prophos	158	139	126
TBP (Surrogate)	211	99	
Naled	109	145	185
Sulfotep	322	174	202
17.0 min.			
Demeton-S	88	170	126
Dimethoate	125	93	87
Terbufos	231	153	103
Fonofos	246	137	109
Diazinon	179	152	137
Disulfoton	88	97	89
22.5 min.			
Dichlofenthion	279	162	223
Phosphamidon	127	264	138
Methyl chlorpyrifos	286	288	125
Methyl parathion	263	125	109
Ronnel	287	125	285
27.5 min			
Malathion	173	127	125
Aspon	211	210	115
Chlorpyrifos	199	197	97
Fenthion	278	169	125
Parathion	291	97	109
Trichloronate	297	269	109
32.0 min			
Chlofenvinphos	323	269	267
Crotoxyphos	193	127	105
Tetrachlorvinphos	329	331	109
Tokuthion	309	267	162
41.5 min			
Fensulfothion	293	141	125
Ethion	231	121	153
Sulprofos	156	140	139
Famphur	218	125	93
Carbophenothion	157	153	121
50.0 min			
TPP (Surrogate)	326	325	
Phosmet	160	133	77
E.P.N	169	141	157
Leptophos	377	375	171
Azinphos methyl	160	132	77
Azinphos ethyl	160	132	77

Table 2.14.- List of acquisition groups and ions monitored for the determination of target analytes, surrogate standard and internal standard compounds.

Compound	Sediment MDL (ng/g)	Low-level spike recovery (%)
Dichlorvos	not recovered	-
Mevinphos	0.010	49
Zinophos	0.27	58
Demeton-O	0.62	116
Prophos	0.31	118
Naled	not recovered	-
Sulfotep	0.26	95
Demeton-S	0.32	85
Dimethoate	0.53	151
Terbufos	0.059	82
Fonofos	0.11	127
Diazinon	0.041	148
Disulfoton	0.53	76
Dichlofenthion	0.007	94
Phosphamidon	0.11	60
Methyl Chloropyrifos	0.024	97
Methyl Parathion	0.52	84
Ronnel	0.10	115
Malathion	0.089	128
Aspon	0.29	119
Chloropyrifos	3.5	137
Fenthion	0.17	98
Parathion	0.32	56
Trichloronate	0.26	118
Chlofenvinphos	0.65	122
Crotoxyphos	1.5	76
Tetrachlorvinphos	0.24	58
Tokuthion	1.29	146
Fensulfothion	3.02	138
Ethion	0.87	102
Sulprofos	0.24	75
Famphur	0.38	56
Carbophenothion	1.08	121
Phosmet	2.34	105
EPN	0.034	56
Leptophos	0.59	103
Azinphos-Methyl	16.1	58
Azinphos-Ethyl	0.91	74

Sample fortification ranged from 10-250(ng). Average recovery is 92%.

Table 2.15 – Figures of merit for the organophosphate pesticide determinations.

2.6.4 Determination of Phenoxy-Acid Herbicides by LC/MS.

Because of their chemical characteristics, Phenoxy-acid herbicides were analyzed by HPLC coupled to atmospheric pressure ionization mass spectrometry (API) in order to avoid the derivatization steps required for gas chromatography. The chromatographic separation was conducted by using a reverse phase column C_{18} 250 x 4.6 mm x 5 µm, and changing the composition of the mobile phase, the flow rate and the temperature of the column in order to find the best resolution between the peaks of interest in the shortest possible time of analysis. Methanol and acetic acid 1% were chosen as the principal components of the mobile phase. The presence of an acidic modifier in the eluent, helped to avoid the ion suppression of the herbicides in the mass spectrometer source under electrospray conditions. The best ESI performance was achieved at low flow rate of 0.5 ml/min. A gradient elution was optimized to allow the chromatographic separation of the twelve herbicides by LC/MS and it is presented in Figure 2.13. The mobile phase composition consisted of a binary gradient elution of methanol and acidified water with acetic acid 1%. The HPLC gradient program is shown in Table 2.16. The total run time for this separation was less than 30 minutes.

Table 2.16 - Gradient elution program for phenoxy acid separation

#	Time (minutes)	% A (Methanol)	%B (HOAC 1%) pH 2.76
1	0	75	25
2	15	82	18
3	18	75	25
4	30	75	25

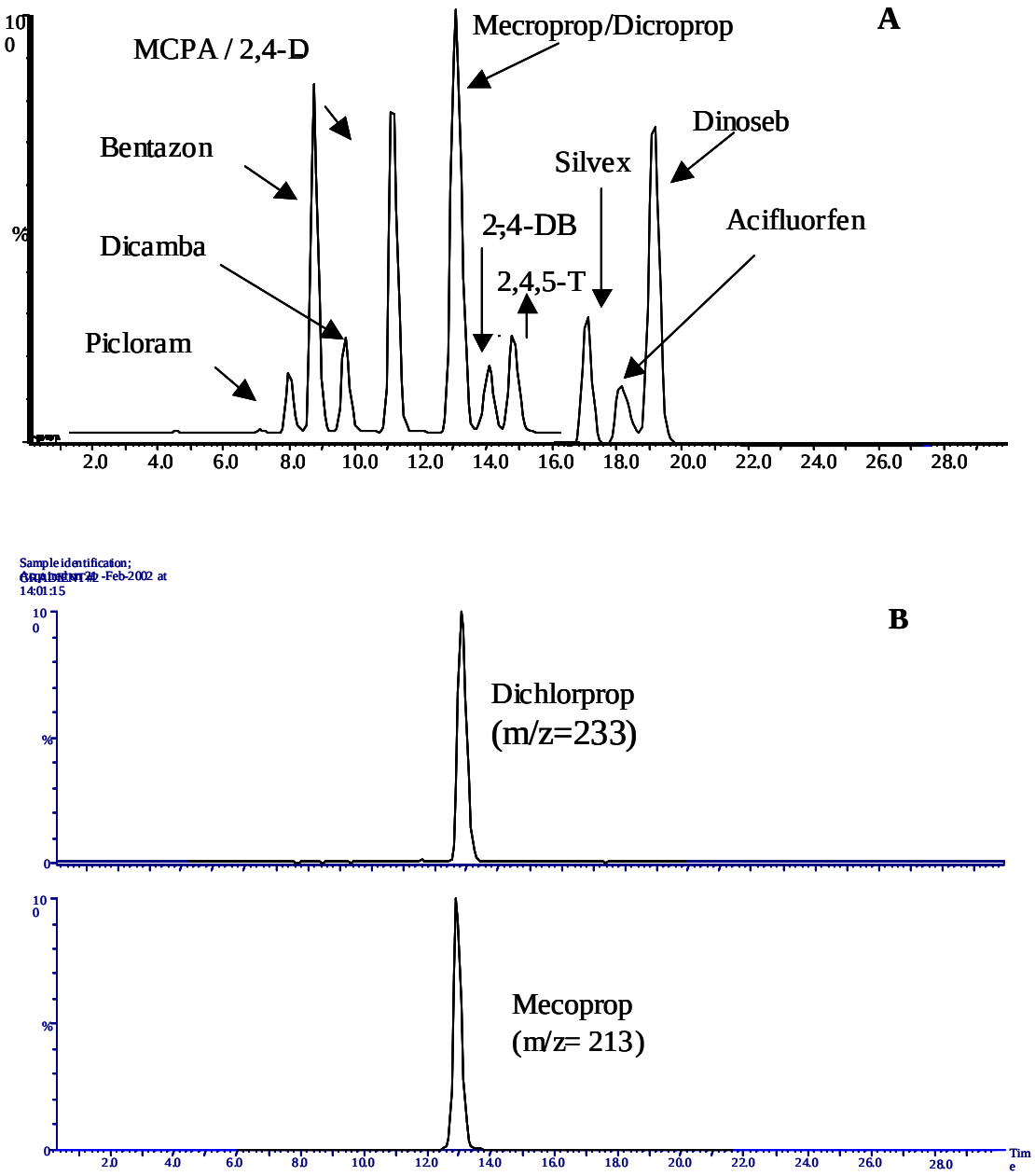


Figure 2.13 - A. Typical chromatogram from an LC-ESP-MS analysis of phenoxy acid herbicides. B. Extracted ion for mecoprop (m/z=213) and dichlorprop (m/z =233)

Although some analytes co-elute (peaks 4,5 and 6,7), they can be easily identified using their specific molecular ion and fragments. This was the case for mecoprop and. dichlorprop (figure 14 B) where their identification is possible by means of the respective negative parent ions $[M-H]^-$ = 213 and $[M-H]^-$ =233, respectively.

Table 2.17 - Single ion monitoring (SIM) program and quantifying ions for phenoxy acid

#	Compound	Formula	SIM #	Retention time (s)	Nominal Mass	Parent Ion $[M-H^{l-}$	$[M-H+1]^-$ (q)	$[M-H+2]^-$ (q)
1				6.9				
	Picloram	$C_6H_3Cl_3N_2O_2$	1		240	239	241	243
2				7.8				
	Bentazon	$C_{10}H_{12}N_2O_3S$	1		240	239	241	-
3				8.0				
	Dicamba	$C_8H_6C_{l2}O_3$	1		220	219	221	223
4				10.3				
	2,4-D	$C_8H_6Cl_2O_3$	3		220	219	221	223
5				10.4				
	MCPA	$C_9H_9ClO_3$	3		200	199	201	-
6				12.6				
	Dichlorprop	$C_9H_8Cl_2O_3$	4		234	233	235	-
7				12.6				
	Mecoprop	$C_{10}H_{11}ClO_3$	4		214	213	215	-
8				13.4				
	2,4,5-T	$C_8H_5Cl_3O_3$	5		254	253	255	257
9				13.6				
	2,4-DB	$C_{10}H_{10}Cl_2O_3$	5		248	247	249	-
10				15.7				
	Acifluorfen	$C_{14}H_7ClF_3NO_5$	6		361	360	362	-
11				16.3				
	(Silvex)	$C_9H_7Cl_3O_3$	6		268	267	269	-
12				18.9				
	Dinoseb	$C_{10}H_{12}N_2O_5$	7		240	239	241	-

In order to improve the sensitivity of analysis, a single ion-monitoring program (SIM) was used. This program includes molecular and isotope ions for the phenoxyacids that are shown in Table 2.17. Seven different SIM functions were selected with an interchannel delay of 0.02 seconds and a dwell time of 0.5 seconds per ion. The SIR monitoring mode allows the elimination of interference background and the proper separation of the 12 peaks of interest using a gradient elution.

Analytical Performance for Phenoxy Acid Herbicides

The linear dynamic range was studied under the chromatographic conditions adopted. The measurement of the response by LC-ESP-MS, was performed by injecting standards solutions of all the target analytes within the range of 0.15 to 4 µg/ml (eight calibration points), and averaging the peaks areas of the extracted ions of interest (n=3). Satisfactory linearity ($r^2 > 0.990$) was obtained for all acidic herbicides. Regression coefficients values are summarized in Table 2.18. The Instrument detection limits (IDLs) as well as the statistical method detection limits (MDLs) calculated by analyzing spiked sediment samples are presented in Table 2.19.

Table 2.18 - Correlation coefficients for target analytes

Analyte	r^2	Analyte	r^2
Picloram	0.996	Dichlorprop	0.994
Bentazon	0.992	2,4,-DB	0.994
2,4-D	0.999	2,4,5-T	0.998
MCPA	0.996	Silvex	0.995
Dicamba	0.993	Acifluorfen	0.995
Mecroprop	0.995	Dinoseb	0.990

Table 2.19 - Instrument detection limits (IDL) and method detection limits (MDL) for phenoxy acid herbicides using LC-ESI-MS.

Herbicide	IDL (ng/g)	MDL (ng/g)
Bentazon	2.00	8.5
Dicamba	5.00	9.1
MCPA	0.34	1.0
2,4D	1.10	3.3
Mecroprop	0.54	1.6
Dichlorprop	0.16	0.5
2,4 DB	5.00	13.8
2,4,5-T	0.55	1.7
Silvex	0.65	1.9
Acifluorfen	2.00	3.2
Dinoseb	0.67	1.6
Picloram	10.00	23
Bentazon	2.00	8.5

Analyte recoveries were assessed during the method validation steps by spiking sediment/soil samples at levels at least 10x MDL. The results shown in Table 2.20 clearly indicate the robustness of the analytical protocol.

Herbicide	Mean Recovery %	% RSD
Picloram	74	15
Bentazon	98	12
Dicamba	77	12
MCPA	102	5
2,4-D	108	4
Mecoprop	105	11
Dichlorprop	93	7
2,4-DB	53	9
2,4,5-T	76	8
Silvex	83	9
Acifluorfen	54	11
Dinoseb	71	15

Table 2.20 - Recovery study for phenoxy acid herbicides in sediments samples (n=7) using the optimized ASE and SPE paramenters.

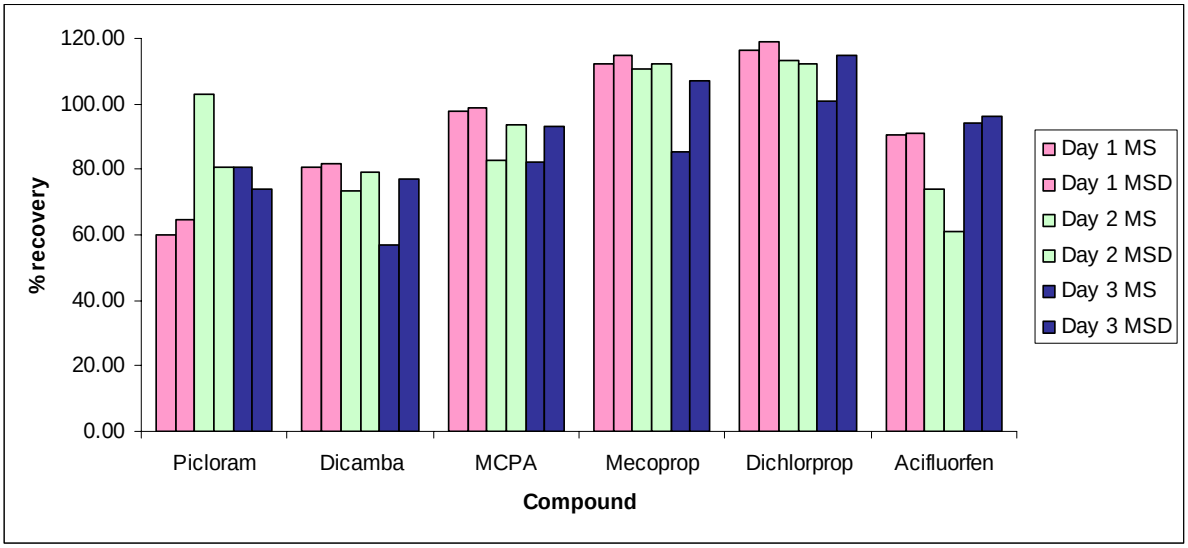


Figure 2.14 -Intra and interday variation for selected phenoxy herbicides spiked in sediment/soil samples collected from the Everglades. (MS:Matrix spike, MSD: Matrix Spike Duplicate)

A summary of the inter-day and inter-batch analyte recoveries from spiked samples and their duplicates processed along with the samples is also presented in Figure 2.14. Based on the results obtained, the precision of the method was below 15 % of RSD for all analytes with the exception of picloram, which showed a slightly higher value (19%). The relative percent difference (RPD%) among duplicates was also below 30 % for all spike samples analyzed. These results clearly show the effectiveness of the method for the analysis of these polar compounds in complex, organic rich Everglades's soils and sediments.

3.0 CHEMICAL ANALYSIS RESULTS AND DISCUSSION

3.1 Sediment Bulk Parameters

The characteristics of sediments have been determined to affect the binding and availability of many contaminants in benthic environments. In general, contaminants are found in higher concentrations in smaller grained particles. For this study all sediment samples were analyzed to determine the fractions of sediment particle size consisting of medium/ coarse/ v. coarse sand, fine sand, very fine sand, and silt. Total organic and carbonate carbon are also important in characterizing sediment contamination. Sediment samples were analyzed to determine total carbon, total inorganic carbon and total organic carbon. Results for these determinations are shown in Table 3.1, 3.2, and 3.3 for ENP, BNP and FB respectively. For brevity, results for stations with multiple collections are omitted from the table and the values given as ranges. Full description of each sample is provided in the Appendix.

In general, sediments/soils form the freshwater dominated environments along ENP are much more productive than the estuarine systems in Biscayne and Florida Bay. A graph comparing the organic matter contents of all sediments/soils collected is also presented in Figure 3.1. Because of the nature of organic rich sediments/soils it is expected that ENP sediments will have a much higher capacity of retaining hydrophobic contaminants while carbonate rich sediments from estuarine environments will be less conducive to contaminant accumulation. In addition, since speciation of contaminants is heavily dependent on grain size distributions soils and sediments collected for the monitoring effort were also classified based on their particle size distributions.

Station	332BA	23	24	22	332BB	21	59		
Geographic Area	East Boundary	East Boundary	East Boundary	East Boundary	East Boundary	East Boundary	East Boundary		
Matrix	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment/Soil		
% Dry Wt	52.15	46.00	42.50	30.05 - 52.25	38.17- 55.79	43.63	30.89		
% Total Organic Matter (ignition loss)	11.57	22.76	8.24	19.88 - 21.24	11.57	19.14	13.15		
% Total Carbon	14.59	12.78	14.37	8.49 - 15.88	12.71 - 12.73	14.78	16.09		
% Total Inorganic Carbon	7.34	12.09	7.96	1.69 - 3.46	1.41 - 8.35	3.64	5.90		
% Total Organic Carbon	7.25	0.70	6.41	6.80 - 12.62	4.38 - 11.29	11.15	10.20		
Particle Size Distribution (%)									
> 250 microns: medium/coarse/very coarse sand	30.3	56.9	36.9	50.00 - 76.91	49.43 - 53.25	60.0	23.3		
126-250 microns: fine sand	14.5	16.7	12.9	12.48 - 26.76	15.28 - 16.04	21.1	14.8		
62.5-125 microns: very fine sand	11.1	8.9	10.0	4.36 - 10.87	8.28 - 10.15	8.2	12.6		
<62.5 microns: silt	44.1	17.5	40.2	6.25 - 14.46	23.19 - 24.39	10.8	49.3		
Station	MDA	A53	R158	A07	A54	A57	63	64	L67
Geographic Area	Taylor Slough	Taylor Slough	Taylor Slough	Taylor Slough	Taylor Slough	Tamiami Trail	Tamiami Trail	Tamiami Trail	Tamiami Trail
Matrix	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment/Soil
% Dry Wt	22.99	26.54	32.51	11.60 - 38.61	27.48	22.21	11.13 - 34.09	18.27	31.40
% Total Organic Matter (ignition loss)	28.31	16.41	21.69	85.04 - 86.05	12.70	48.21	54.39 - 85.81	48.50	24.44
% Total Carbon	24.09	17.28	17.18	18.00 - 44.97	17.30	29.25	24.09 - 41.29	16.09	15.53
% Total Inorganic Carbon	10.59	7.72	5.86	0.63 - 6.48	7.89	8.13	1.03 - 10.59	5.90	4.17
% Total Organic Carbon	13.50	9.57	11.31	11.15 - 44.34	9.41	21.12	13.50 - 40.26	10.20	11.36
Particle Size Distribution (%)									
> 250 microns: medium/coarse/very coarse sand	57.8	41.1	47.7	75.18 - 76.87	54.0	60.8	35.19 - 92.82	52.4	57.5
126-250 microns: fine sand	15.6	16.5	16.3	11.90 - 12.59	15.1	18.4	3.36 - 19.69	20.2	22.9
62.5-125 microns: very fine sand	10.0	13.2	11.0	6.35 - 7.02	14.0	10.4	1.57 - 11.15	15.1	9.1
<62.5 microns: silt	16.6	29.2	25.0	4.42 - 5.91	16.9	10.3	2.25 - 44.93	12.3	10.6
Station	A55	A60	A61	61 S	C111-US1	S197	A50	A37	58
Geographic Area	C111 basin	C111 basin	C111 basin	C111 basin	C111 basin	C111 basin	Shark Slough	Shark Slough	Shark Slough
Matrix	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment/Soil	Sediment	Sediment	Sediment/Soil	Sediment/Soil	Sediment/Soil
% Dry Wt	26.01 - 54.62	38.68	27.18 - 38.75	44.04 - 50.79	30.40	33.92	37.57	10.08 - 28.05	26.60 - 34.13
% Total Organic Matter (ignition loss)	7.32 - 8.46	6.85	9.25 - 17.26	21.90	10.81	6.99	24.32	77.55 - 85.93	21.29
% Total Carbon	13.78 - 14.42	15.68	14.11 - 24.09	13.79 - 16.09	13.07	12.82	17.64	43.33 - 45.41	46.24
% Total Inorganic Carbon	5.27 - 10.50	7.06	4.03 - 10.59	5.22 - 5.90	5.67	6.15	2.41	0.57 - 9.98	0.87
% Total Organic Carbon	3.63 - 8.51	8.61	6.89 - 13.5	8.57 - 10.20	7.40	6.66	15.23	35.43 - 44.49	45.37
Particle Size Distribution (%)									
> 250 microns: medium/coarse/very coarse sand	22.98 - 75.75	22.2	28.59 - 43.71	30.36 - 38.98	55.8	35.8	12.7	67.61 - 75.26	51.73 - 71.96
126-250 microns: fine sand	9.17 - 18.97	11.1	15.21 - 19.51	20.07 - 20.47	15.7	25.8	51.8	10.97 - 17.61	16.17 - 46.24
62.5-125 microns: very fine sand	5.22 - 16.83	10.5	12.20 - 22.38	15.30 - 22.38	10.2	13.7	19.0	6.96 - 9.15	0.87 - 6.68
<62.5 microns: silt	9.86 - 48.19	56.2	26.30 - 42.45	25.66 - 26.80	18.2	24.6	16.5	5.63 - 6.07	5.19 - 45.37

Table 3.1 -Sediment bulk parameters for ENP soils/sediments.

Station Geographic Area	BBTPC Biscayne Bay	BBICS Biscayne Bay	BBEKH Biscayne Bay	BBCP Biscayne Bay	BBSK Biscayne Bay	BBBP2 Biscayne Bay	BBBP1 Biscayne Bay	BBFP Biscayne Bay	BBMM Biscayne Bay
Matrix	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment	Sediment
% Dry Wt	67.87	68.25	75.15	74.02	34.95	60.68	39.84	68.41	68.79
% Total Carbon	2.56	2.26	1.42	1.56	6.73	3.13	6.80	2.44	2.11
% Total Inorganic Carbon	NA	NA	NA	NA	NA	NA	NA	NA	NA
% Total Organic Carbon	NA	NA	NA	NA	NA	NA	NA	NA	NA
Particle Size Distribution (%)									
> 250 microns: medium/coarse/ very coarse sand	42.03	65.17	50.07	61.68	61.63	65.82	27.65	73.40	81.13
126-250 microns: fine sand	36.81	25.45	46.89	30.40	19.30	23.49	28.45	18.39	12.95
62.5-125 microns: very fine sand	13.15	4.23	2.58	3.99	8.62	5.97	18.51	4.91	3.56
<62.5 microns: silt	8.01	5.15	0.46	3.92	10.45	4.71	25.39	3.31	2.35

Table 3.2 – Sediment bulk parameters for BNP sediments.

Station Geographic Area	FL BAY LSR Long Sound Road	FL BAY MJB Mouth, Joe Bay	FL BAY MTR Mouth, Taylor River	FL BAY LS Long Sound
Matrix	Sediment	Sediment	Sediment	Sediment
% Dry Wt	40.55	39.13	29.31	44.64
% Total Carbon	13.59	13.49	19.61	9.74
% Total Inorganic Carbon	NA	NA	NA	NA
% Total Organic Carbon	NA	NA	NA	NA
Particle Size Distribution (%)				
> 250 microns: medium/coarse/very coarse sand	75.9	22.1	37.9	62.7
126-250 microns: fine sand	10.8	19.9	14.5	19.2
62.5-125 microns: very fine sand	5.0	18.2	14.2	8.1
<62.5 microns: silt	8.2	39.8	33.4	10.0

Table 3.3 – Sediment bulk parameters for Florida Bay sediments.

Sediment Contamination Assessment

To date, there are no state or federal standards or mandates concerning contamination of sediments and soils. However, several environmental regulatory agencies, such as the National Oceanic and Atmospheric Administration (NOAA), the U.S. Environmental Protection Agency (EPA), and the Florida Department of Environmental Protection (FDEP) have developed guidelines to be used in assessing the potential hazard of certain pollutants in both freshwater and marine environments as well as in sediments and soils from such systems.

FDEP has established Sediment Quality Assessment Guidelines (SQAGs) in order to evaluate the potential for biological effects associated with sediment-sorbed contaminants (MacDonald 1994, 2003). The SQAGs developed specifically for Florida are based on high quality sediment toxicity databases that relate occurrence (exposure) with potential harmful effects. These databases were used to develop two sets of guidelines for interpreting the effects of contaminants on biological endpoints in both freshwater and coastal (estuarine) environments; these are a threshold effects level (TEL) and a probable effects level (PEL) for assessing coastal systems and a threshold effects concentration (TEC) and probable effects concentration (PEC) for freshwater. The TEL and TEC represent the upper range limit of contamination for which no effects are observed in the majority of toxicity studies done for that contaminant. Below this level, contaminants are not considered to pose a significant hazard to aquatic organisms. The PEL and PEC represent the lower limit of a contaminants concentration, which is usually associated with adverse biological effects to aquatic organisms. Above this level, contaminant

concentrations could potentially be associated with adverse biological effects thus interpreted as a potential for concern. However, levels near the threshold effects (TEL and TEC) should be interpreted with caution since misfits between effects and concentrations have been often reported at these low environmental levels (O'Connor and Paul, 2000). Because these guidelines provide a good management starting point and provide common ground among previously reported data they have been included in the chemical monitoring interpretation section. However, to get a more accurate picture of the risk associated with the presence of these contaminants and other chemicals for which SAQGs are not available we recommend that readers concentrate on the ERA results provided in the latter sections of the report (5.0).

Organic Contaminants in Sediments

Organochlorine Pesticides

A total of 25 organochlorine pesticide (OCP) compounds were chosen for this analysis. A summary of the compounds detected in the sediments and their concentration ranges are given in Table 3.4. The results represent the more frequently detected OCPs and they are compared with the national averages and ranges reported by NOAA from their Status and Trends Mussel Watch program (Cantillo, 1997) where coastal sediments from the continental seaboard were analyzed for the same suite of contaminants. In addition, the 85th centiles concentrations for selected compounds summarized in the Coastal Sediment Database (COSED) (Daskalakis and O'Connor, 1994) are also included in the table. These numbers are not related to effects but rather represent that "high concentrations" based on the national distribution of contaminants. Two main

conclusions could be drawn from the results; OCPs are present in the study area and compounds of both past and present usage were detected in the sediments. However, the concentration ranges and averages rank well below the national means and clearly fall outside of what NOAA has classified as the 85th centile "high" values for occurrence. With the exception of one sample outside of ENP at the US-1 bridge in the C-111 Canal.

Of the OCPs detected in sediments from Everglades National Park, only DDE exceeded of the established TEC criteria. PEC criteria were not exceeded for any contaminant at any of the stations. Ranked concentrations of these contaminants vs. TEC/PEC criteria are shown in figures 3.1 to 3.5. Since organic contaminants tend to accumulate more in sediments with greater total organic carbon (TOC) content, OCP concentrations are also plotted normalized against TOC to account for variations in OM within the study area. It should be noted that concentrations expressed in ng/g organic carbon, are not applicable to the TEC/TEL and PEC/PEL criteria that are expressed in ng/g dry weight.

Table 3.4.-Concentrations of organochlorine pesticides in ENP sediments compared to sediment concentrations detected by NOAA Status and Trends Mussel Watch program.

Parameter	This Study				COSED (Daskalakis and O'Connor, 1995)	NOAA S&T MWP (Cantillo 1997)			
	MIN	MAX	MEAN	Occurrence	85th "High"	MIN	MAX	MEAN	Occurrence
Total DDTs	N.D.	7.16	0.99		22	<0.02	3270	32.0	
Total PCBs	N.D.	42.0	1.78		80	<0.02	3730	55.70	
Dieldrin	N.D.	2.91	0.10	9%	2.9	<0.02	9.47	0.36	43%
Endrin	N.D.	0.74	0.15	17%					
Chlorpyrifos	N.D.	0.84	0.04	3%					
Endosulfan Sulfate	N.D.	2.25	0.19	9%					
β–Endosulfan	N.D.	1.33	0.11	6%					
p-p' DDE	N.D.	6.45	0.61	29%		<0.02	195	3.71	86%

All numbers in ng/g dry weight unless noted, n=55

The spatial distributions of total DDTs and p-p‘DDE in ENP, BNP and Florida Bay sediments are given in figures 3.6 and 3.7.

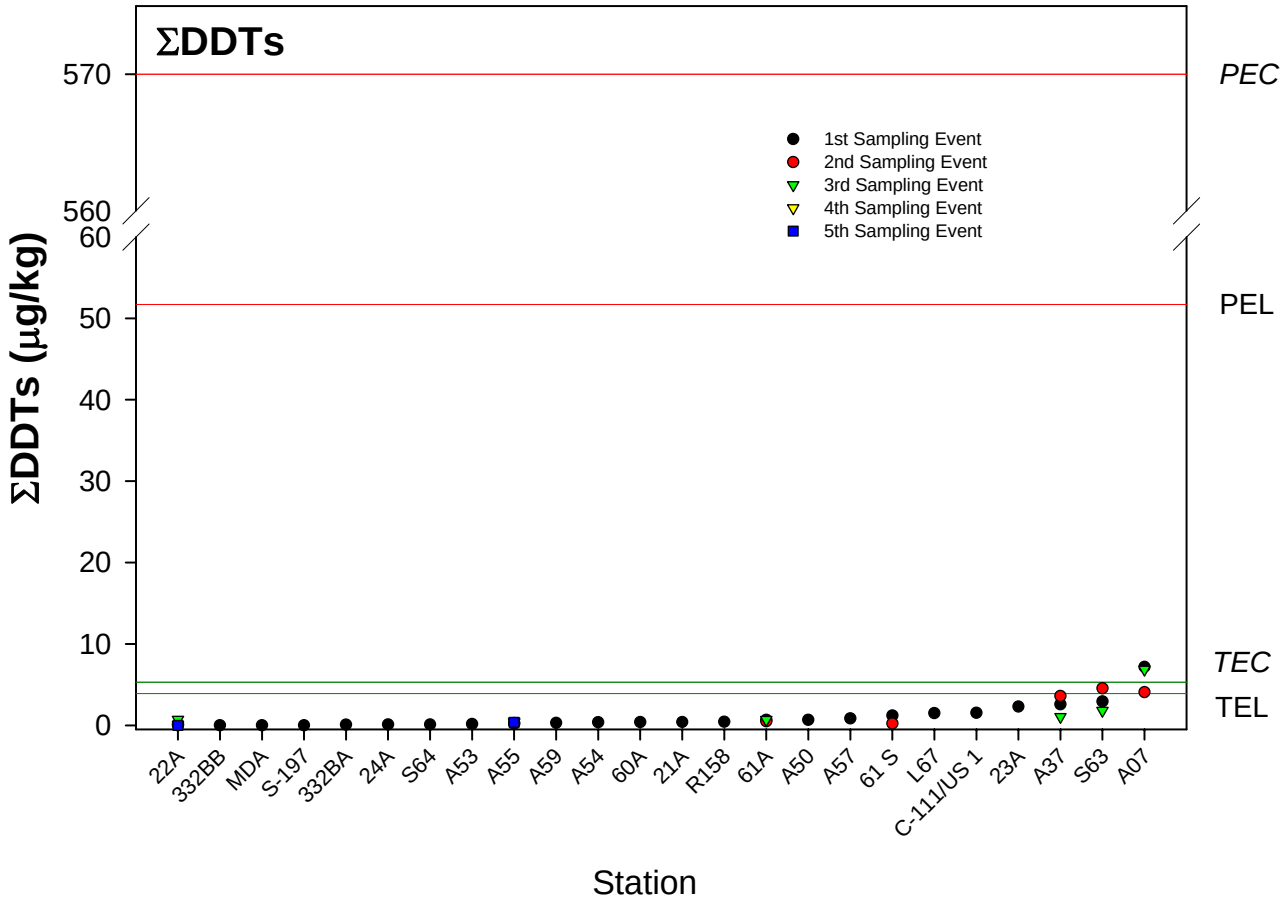


Figure 3.1.-Ranked concentrations of total DDTs in freshwater sediment.

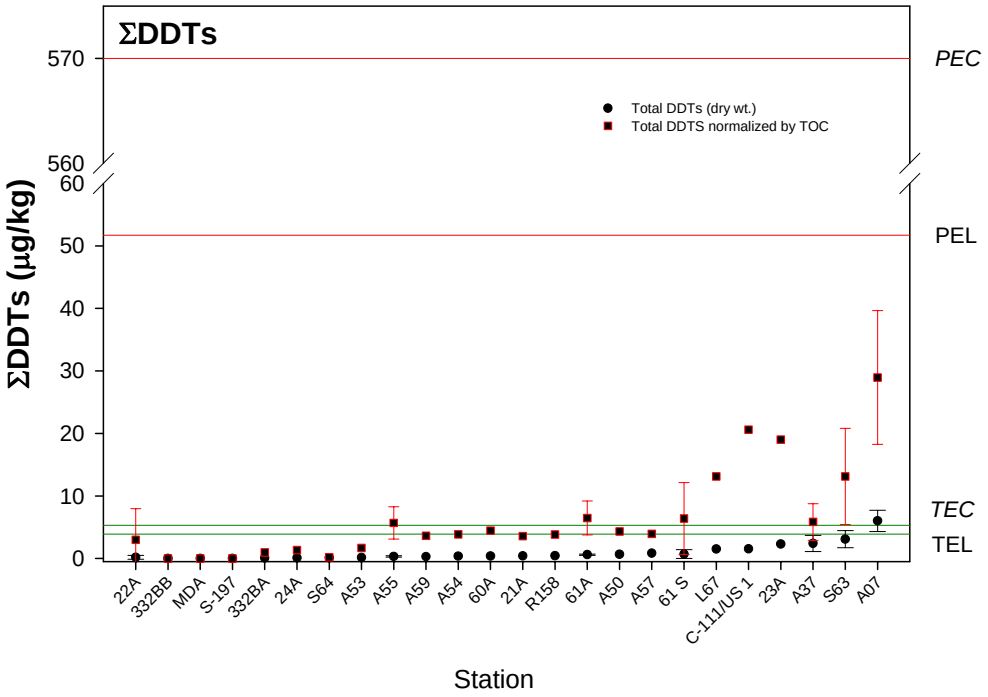


Figure 3.2.-Ranked concentrations of total DDTs in freshwater sediment

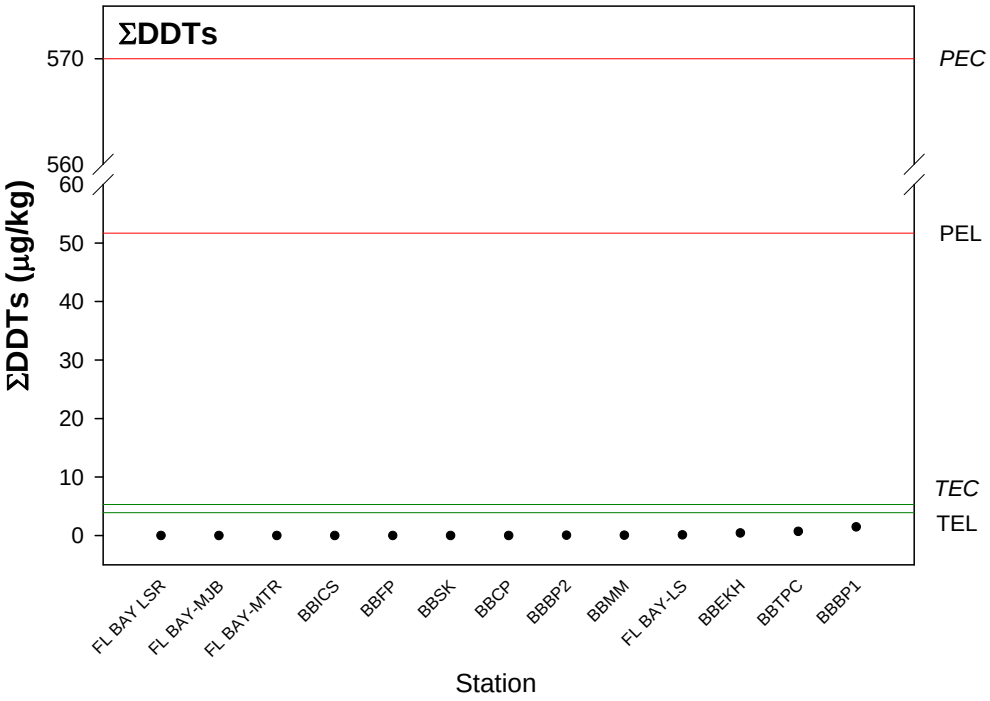


Figure 3.3.-Ranked concentrations of total DDTs in coastal sediments.

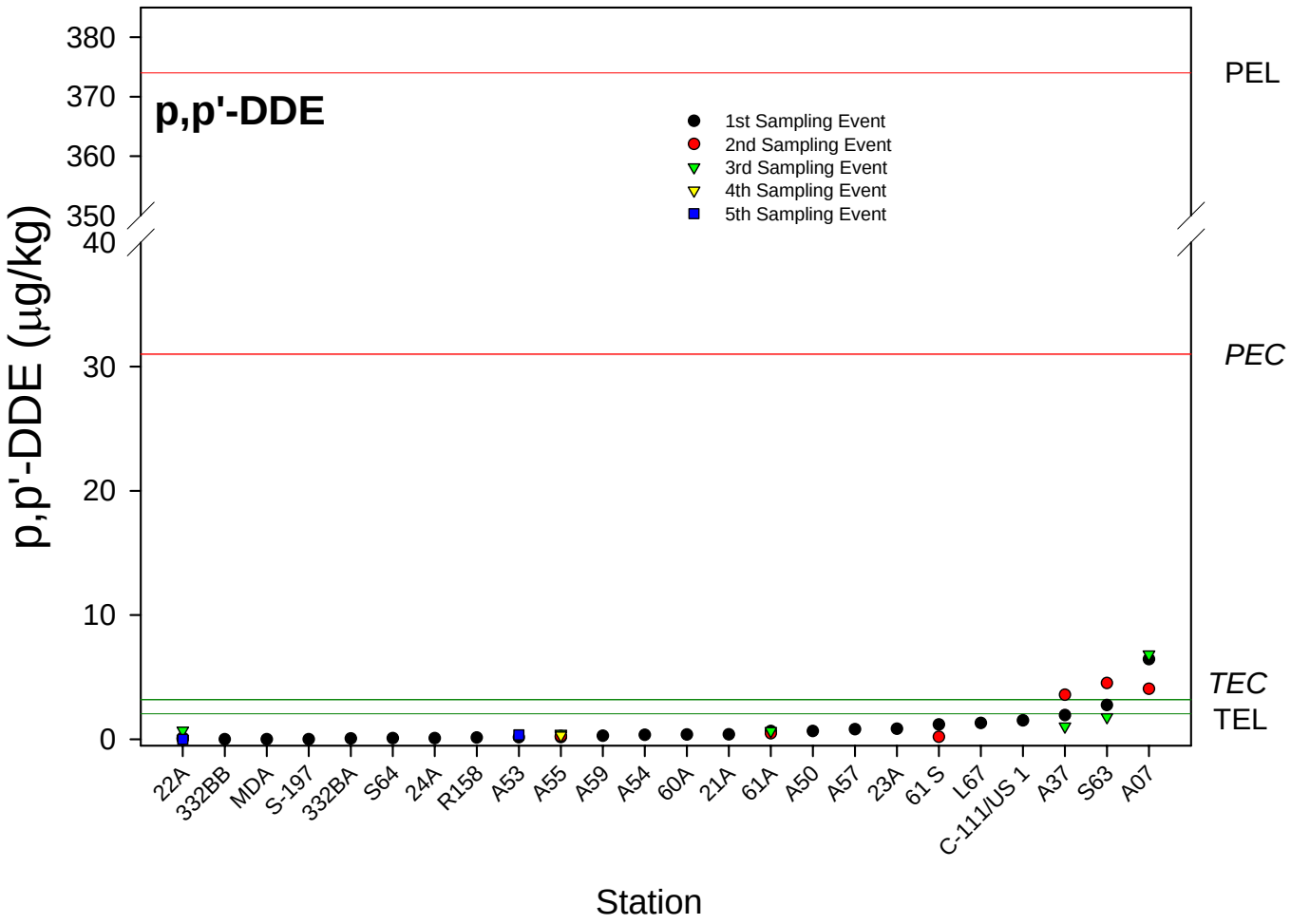


Figure 3.4.-Ranked concentrations of p-p'DDE in freshwater sediments.

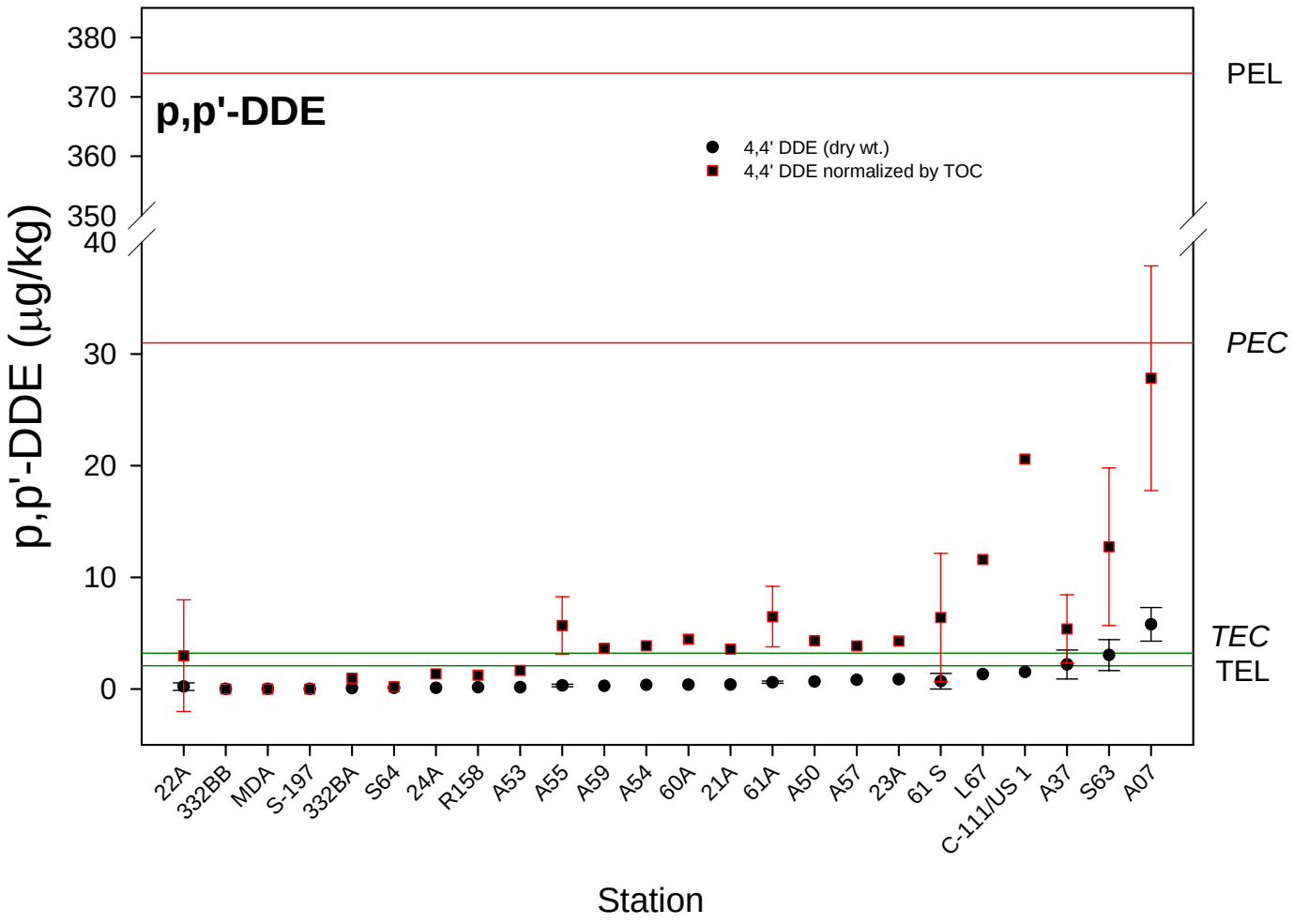


Figure 3.5.-Ranked concentrations of p-p'DDE in freshwater sediments.

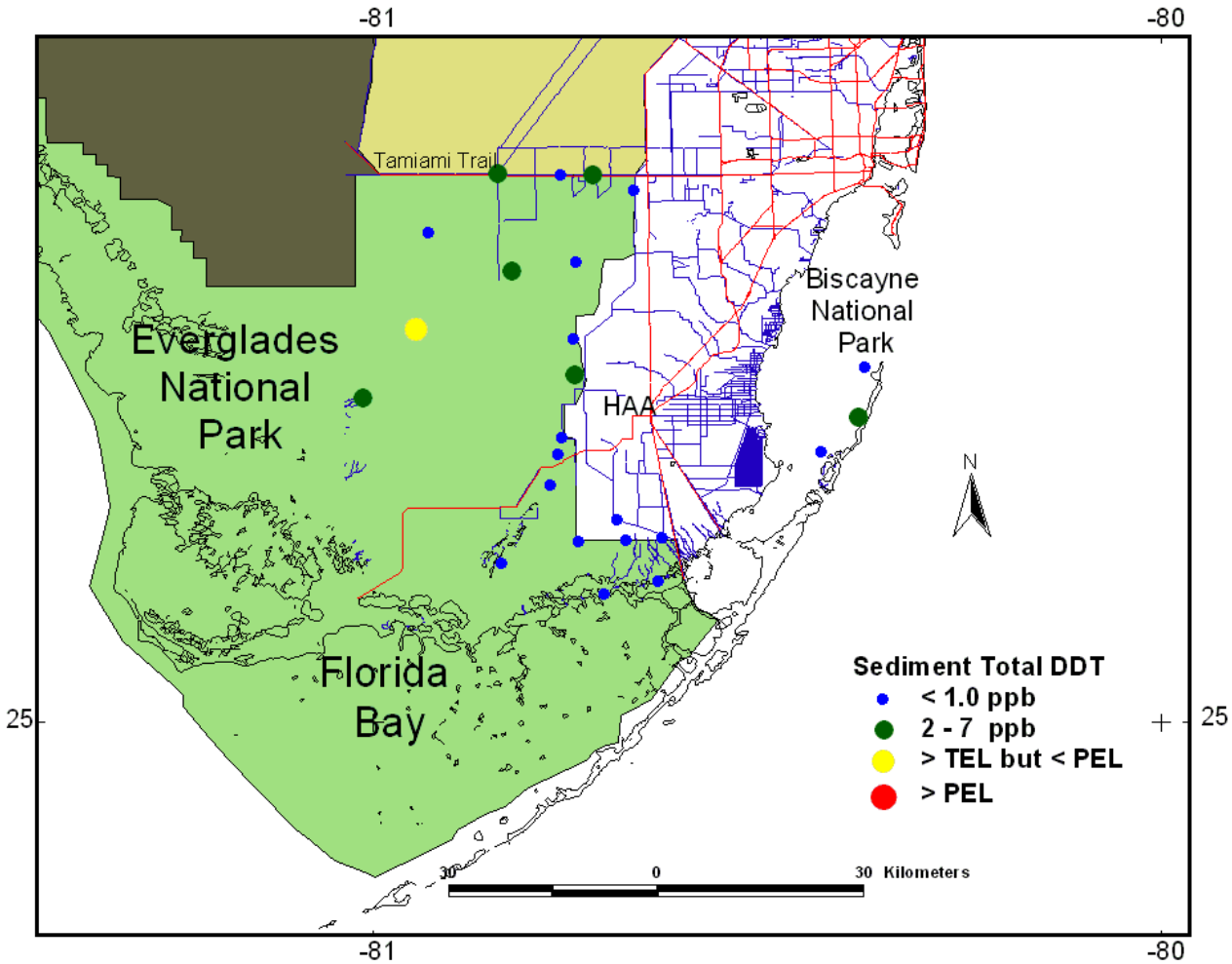


Figure 3.6.-.-Spatial distribution of Total DDT in sediment.

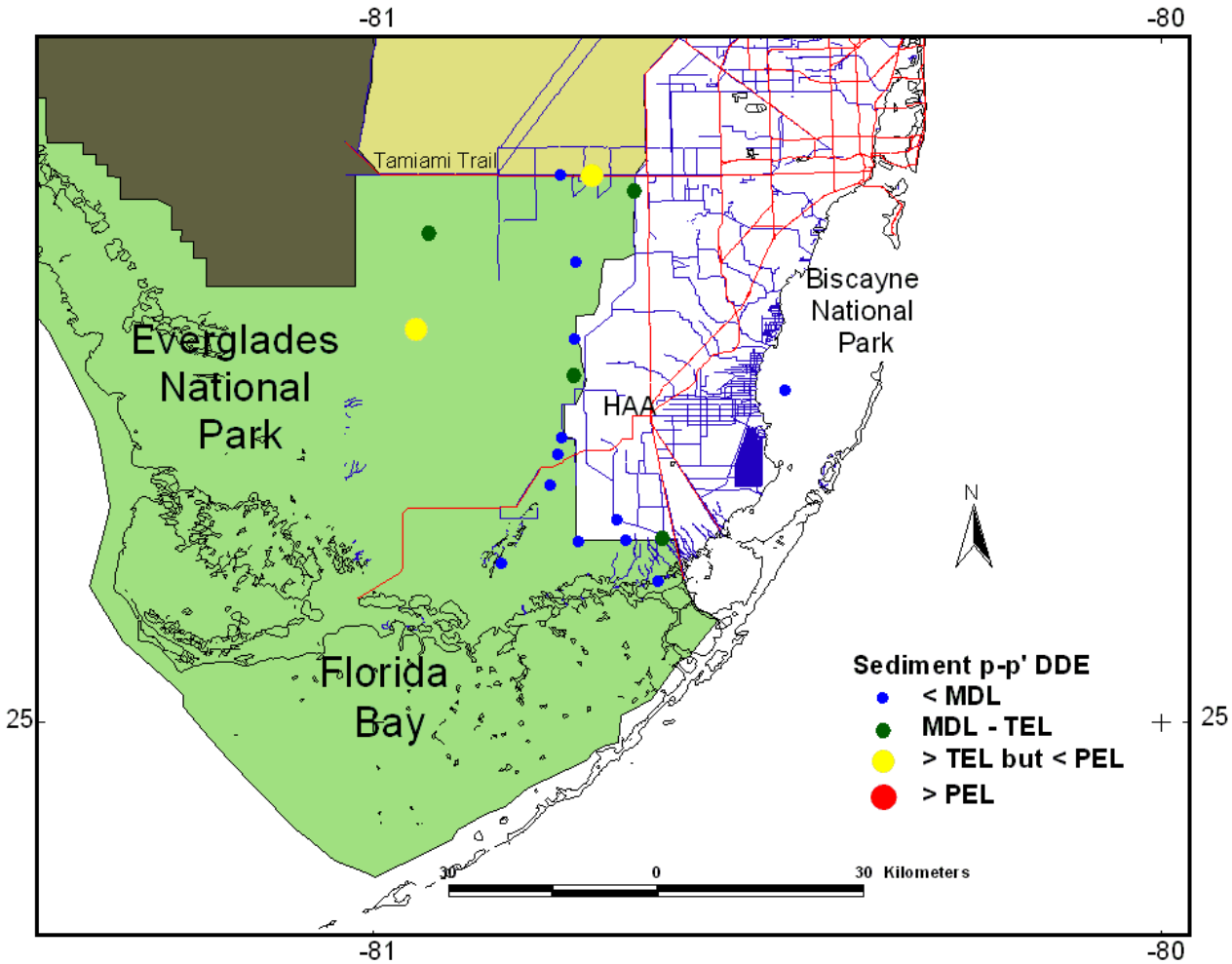


Figure 3.7.-.-Spatial distribution of p-p'DDE in sediment.

One compound of particular concern in south Florida because of its extensive use in the HAA is endosulfan. More than 70% of the endosulfan applied in the southeastern U.S. is applied to vegetable crops in south Florida (Scott et. al. 2002). Endosulfan has been classified as a toxicity class 1 highly toxic pesticide by the EPA and has a regulatory status of Restricted Use Pesticide (RUP). Technical endosulfan is comprised of two isomers α and β endosulfan that are usually applied in a 70/30% mixture (ATSDR 2002).

Endosulfan is moderately persistent in soil with estimated half-lives of 35 and 150 days for the α, and β isomers respectively, and both isomers are subject to photolysis, hydrolysis, oxidation, volatilization, biodegradation and sorption in the aquatic environment (EXTOXNET 1996). Endosulfan sulfate, which is also considered highly toxic, is the major product of metabolism for both isomers and is more persistent in the environment than its parents.

The analysis of sediments in this study revealed the occurrence of α-endosulfan, β-endosulfan, and endosulfan sulfate in 16, 22, and 35% of samples respectively at concentrations ranging from < MDL - 1.35 ng/g (dry wt.) for freshwater stations and from < MDL – 0.59 ng/g (dry wt.) for coastal stations. The spatial distribution of endosulfan sulfate in sediments is shown in figure 3.8. Ranked concentrations of endosulfan sulfate expressed in both ng/g dry weight and ng/g total OM is shown in figure 3.9 and 3.10 respectively.

Insufficient data were available for development of SQAGs for both α and β endosulfan or their primary metabolite endosulfan sulfate (MacDonald 1994). However, water quality criteria for α and β endosulfan have been developed by the U.S. EPA and its

applicability to this study will be discussed in more detail in the section concerning OCP contamination in fish tissue. Concentrations of α and β endosulfan, and endosulfan sulfate along the park lands were much lower than those previously reported by Miles and Pfeuffer (1997) of 16, 24, and 1200 μg/kg respectively, in the C-111 canal.

Regional Distribution of Organic Contaminants in Sediments

In order to facilitate comparison of observed concentrations of contaminants throughout the study area, sampling stations were divided into seven geographically distinct areas. For organic contaminants in sediments, the regions of interest are (1) the East Boundary, which is comprised of 7 stations along the eastern boundary of ENP which is adjacent to the Homestead Agricultural Area (HAA). (2) Taylor Slough which consists of 4 stations extending from near the southern entrance of ENP to near where Taylor Slough flows into Florida Bay. (3) Shark Slough, has 4 stations that transect the slough from just south of Tamiami Trail to the center of the park. (4) Tamiami, consisting of 4 stations along Tamiami Trail. (5) C-111, consists of 3 stations along (but not in) the C-111 canal which drains from the HAA. (6) BNP consists of the 9 stations sampled in the southern portion of Biscayne Bay. (7) Florida Bay which consists of 4 stations sampled in eastern Florida Bay.

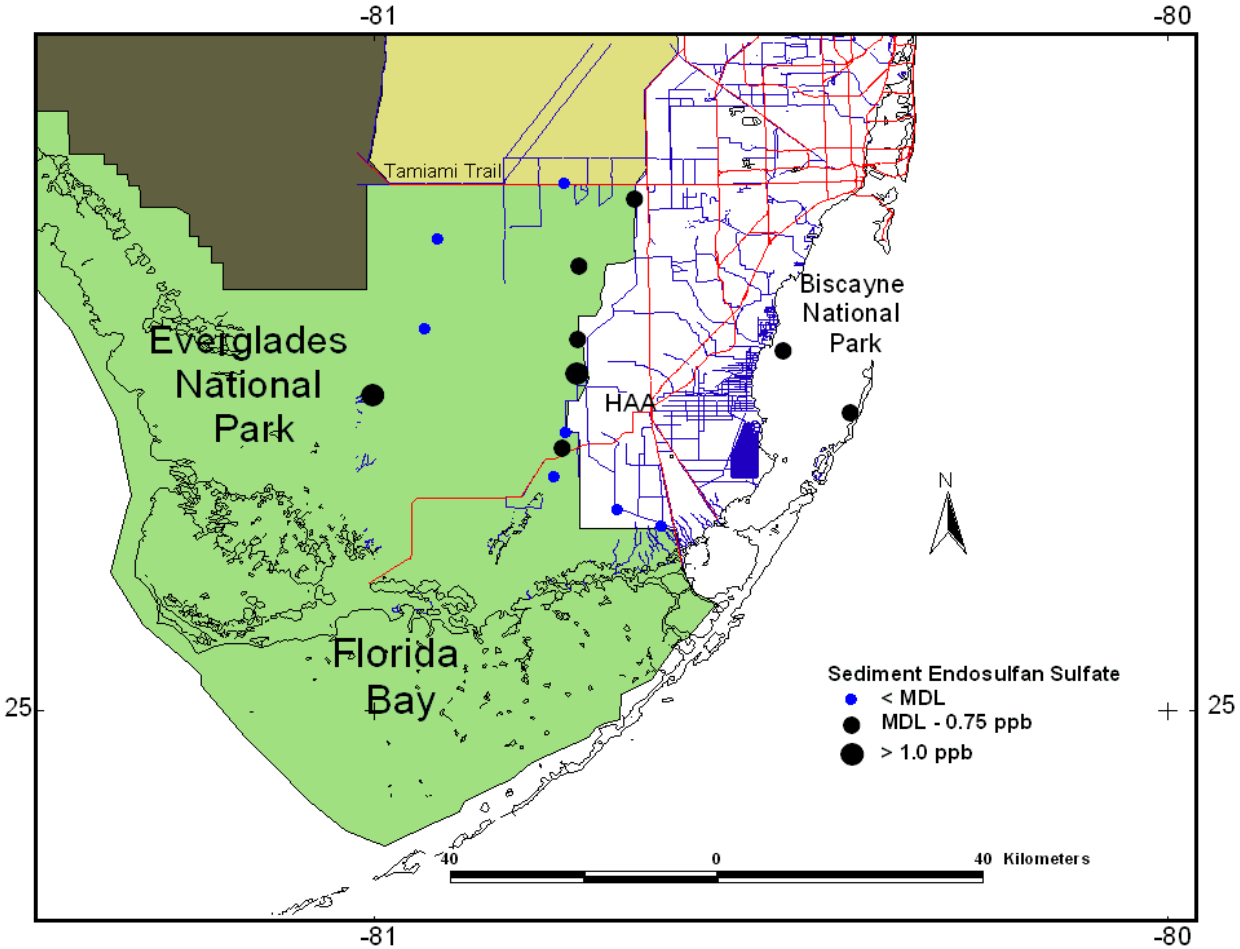


Figure 3.8.-Spatial distribution of Endosulfan sulfate in sediment.

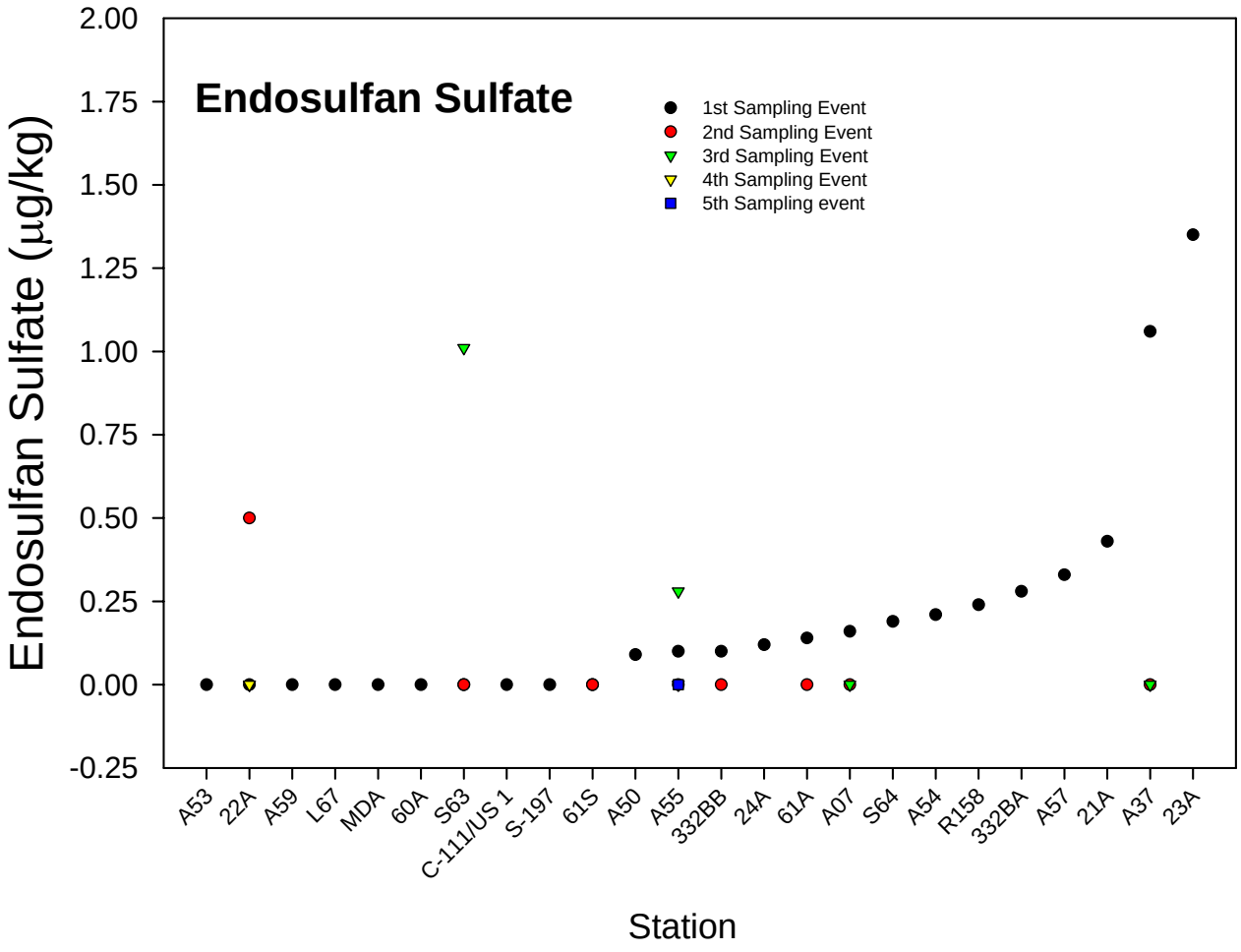


Figure 3.9.-Ranked concentrations of Endosulfan sulfate in ENP sediment.

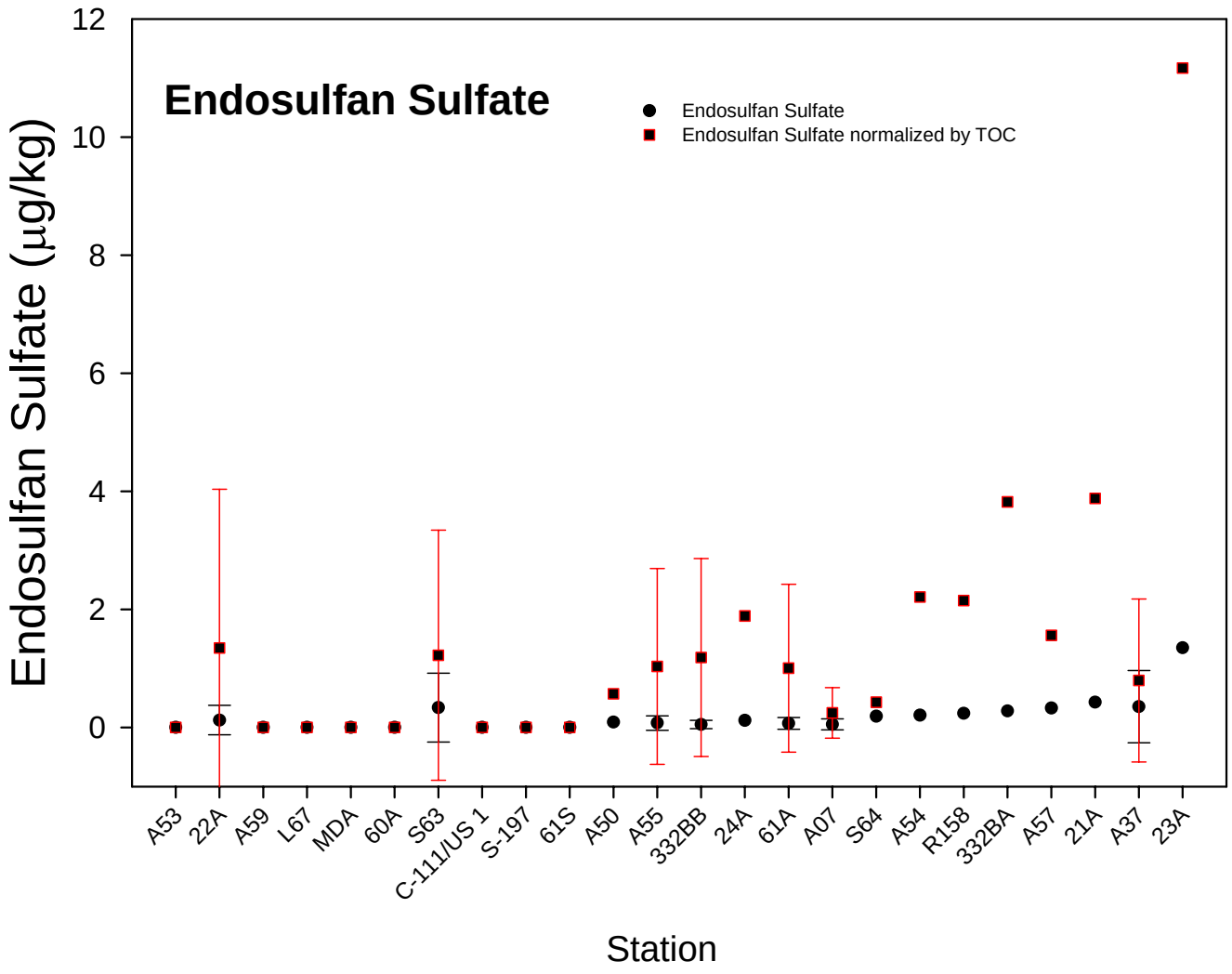


Figure 3.10.-Ranked concentrations of Endosulfan sulfate in ENP sediment.

Comparisons of the distribution of organic contaminants within the study area reveal some interesting results. As would be expected, the highest concentrations of OCPs were found along the Eastern Boundary stations nearest to the HAA. However, in the case of p-p'DDE, elevated concentrations were detected in two stations located in the Shark Slough area. This is illustrated in figures 3.4 to 3.5, which show that stations A07 and A37, which are both located in remote areas of ENP, have higher concentrations of these compounds than most other stations with in the park. It should be noted that both these stations have high TOC content and when concentrations are ranked normalized by TOC, the data show higher concentrations in the East Boundary stations than in the Shark Slough stations. Additional sediment samples were collected from A07 and A37 in October 2002 and March 2004, and the analysis of these samples revealed similar results indicating that this area of the park may be acting as a sink for organic contaminants. Higher than expected concentrations of p-p'DDE were also detected in one of the Tamiami stations, S63. Surprisingly little if any OCPs were detected in the C-111 area, which drains the HAA. This could result from the fact that sediment samples were collected from an area that until recently was separated from the canal by a levee formed during its excavation which prevented water to flow into or from ENP. This levee was removed as part of the hydrology restoration to allow more freshwater to enter the park (U.S.A.C.E. 1999). This area should be further monitored to evaluate the impact of this change on the levels of agriculture related contaminants. Box plot graphs of the distributions of total DDTs, p-p'DDE, and endosulfan sulfate are shown in figures 3.11 to 3.13.

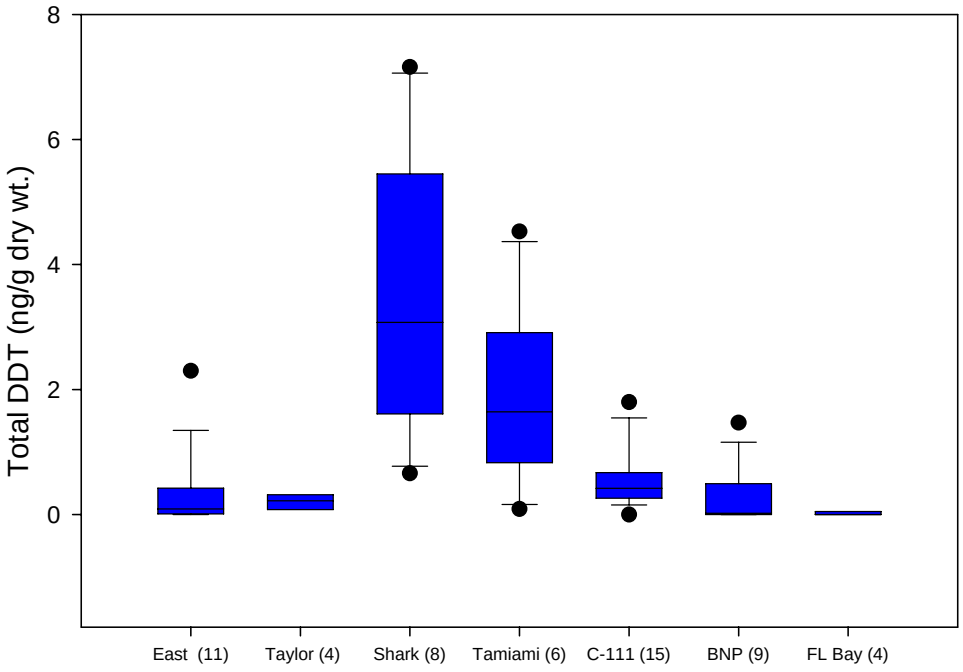


Figure 3.11.-Boxplot graph of total DDT distribution within study area.

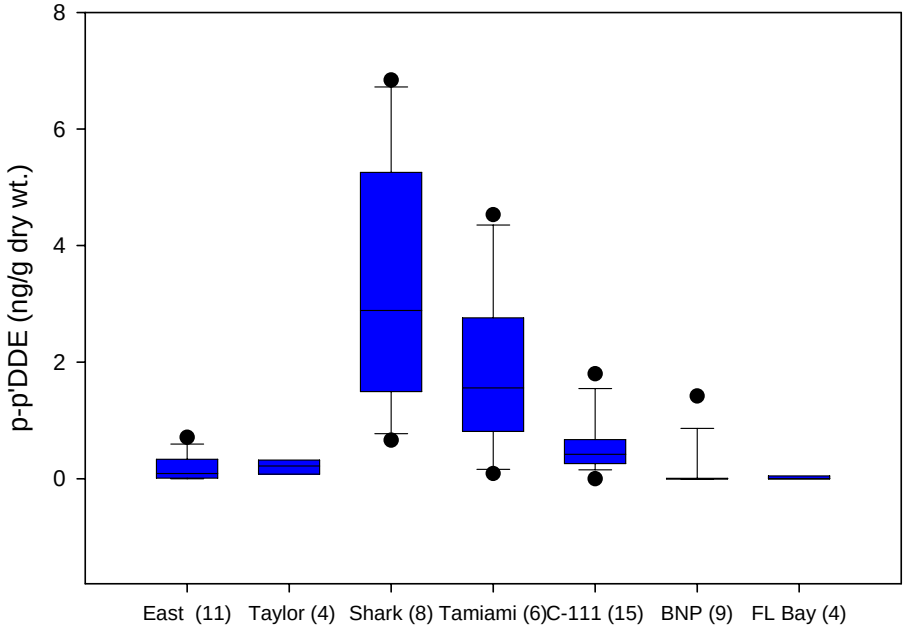


Figure 3.12.-Boxplot graph of p-p’DDE distribution within study area.

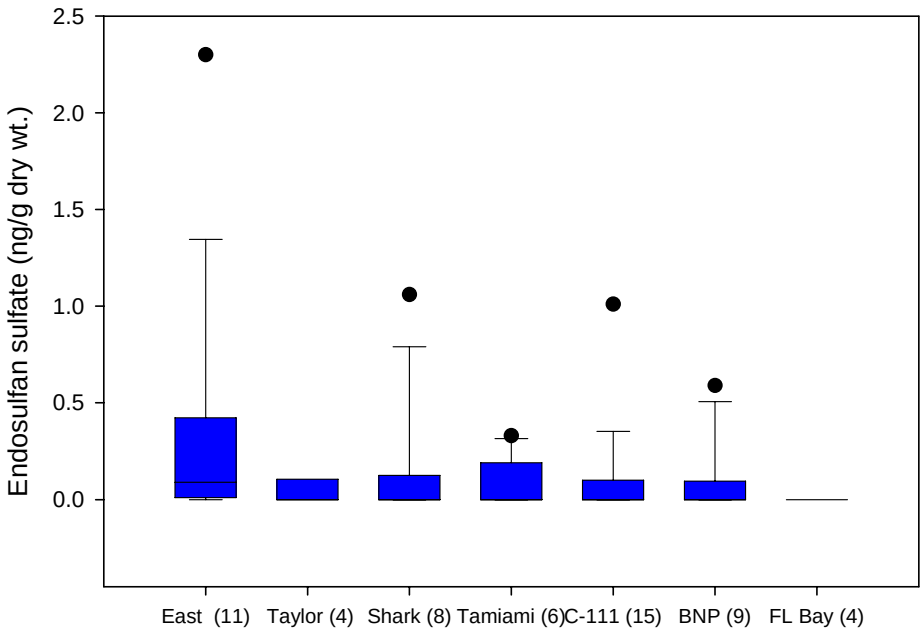


Figure 3.13.-Boxplot graph of Endosulfan sulfate distribution within study area.

Polychlorinated Biphenyls

PCB formulations, marketed as Aroclor mixtures, contain about 100-110 compounds with approximately 10-20% of them being major components. Thus, PCBs occur in environmental compartments as mixtures of congeners with distinct distribution patterns. Therefore, the determination of PCBs for this study is limited to those congeners that are representative of these mixtures and a list of these individual congeners was given in Table 4. Concentrations of total PCBs in this study are expressed as the sum of these congeners. In freshwater sediments, total PCB values range from < MDL – 7.10 ng/g (dry weight), with none of the stations within ENP exceeding TEL/TEC or PEL/PEC criteria, thus PCBs are not expected to have environmental

significance. In Biscayne National Park, concentrations of total PCBs range from < MDL – 42.02 ng/g (dry weight). One station in BNP, BBBP1, located in close proximity to Black Point Marina and the local landfill, exceeded the TEL but not the PEL criteria. The distribution of total PCBs in BNP sediments was similar to that reported by Long et al. (1999) with the highest concentrations detected near canal outflows and decreasing with distance from land. Concentrations of individual PCBs in Florida Bay did not exceed MDLs in any of the stations sampled. The spatial distribution of total PCBs for all sediment samples collected is given in figure 3.14. With the exception of the one station, BBBP1 in BNP that exceeded the total PCB TEL, concentrations of PCBs throughout the study area are low, and uniform in distribution and occurrence, as is shown in figure 3.15.

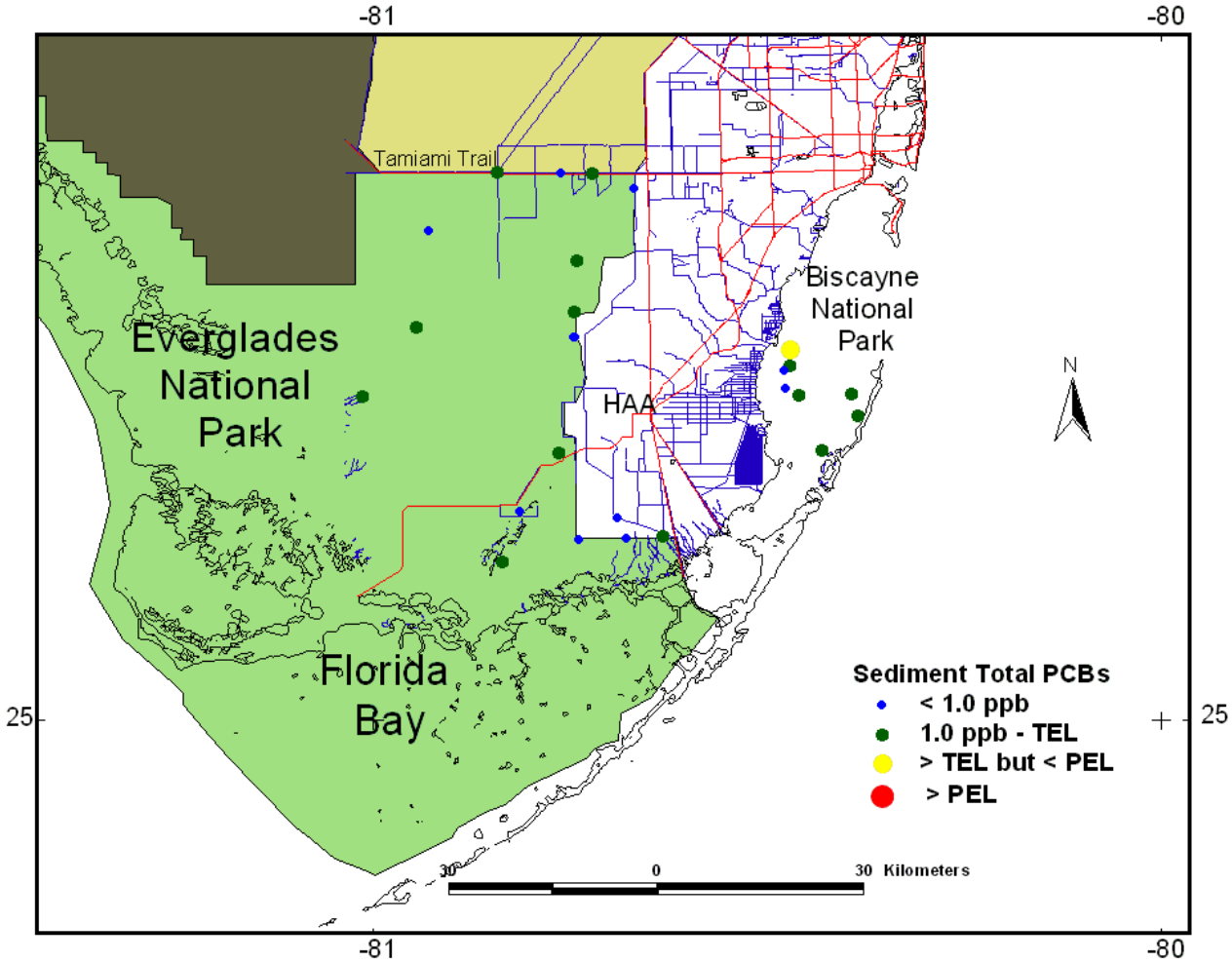


Figure 3.14.-Spatial distribution of Polychlorinated Biphenyls.

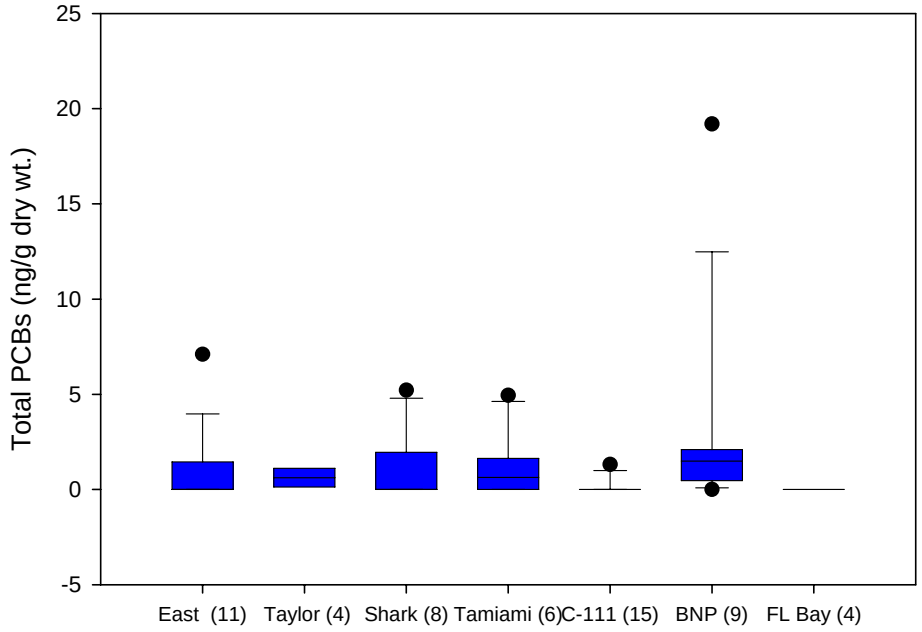


Figure 3.15.-Box plot graph of total PCB distribution within study area.

In comparison to other studies conducted in south Florida, the concentrations detected in sediments in this study (ND - 42.02, ng/g) are considerably lower than those reported in sediments by Wade et al. (1988) of (<0.01 - 189 ng/g) for NOAAs Status and Trends Program in the Gulf of Mexico. The most frequently occurring individual PCB congeners in ENP sediments being PCB 138/160, PCB 180, PCB 101/90, PCB 29, PCB 153/132, and PCB 170/190. However only few samples contained congener patterns that could be identified as Aroclors (e.i., BBBP1). Overall, PCB concentrations were quite low and no significant differences were observed between the different regions, although the highest concentrations for individual samples were observed at BNP and the East Boundary of ENP.

Polycyclic Aromatic Hydrocarbons

Total PAH concentrations detected for Everglades National Park, Biscayne National Park, and Florida Bay sediments fall below the TEL/TEC criteria and below the ranges reported by NOAA (1994) as significantly toxic for any toxicity tests (figure 3.16 and 3.17). The concentration ranges detected for total PAHs are 2.7 - 16,132 ng/g (median 64.4) for freshwater stations, and 1.48 – 912 ng/g (median 11.74) for coastal stations. One station located at S-197 was responsible for the highest concentration and clearly an outlier when the whole dataset is used. This station (16,132 ng/g) is located near the wood pilings at structure S-197 and the PAH distributions and concentrations could be related to the presence of creosote at the site. The spatial distribution of total PAHs for all sediment samples is given in figure 3.18, and a comparison of concentration distributions within the study area is given in figure 3.19. As these figures illustrate, the distribution of PAHs is relatively uniform throughout the study area with the exception of the stations adjacent to Tamiami Trail, which are slightly elevated, and two stations in the C-111 canal that exceed TEC criteria. One station in BNP in close proximity to a marina and the municipal landfill also showed elevated concentrations of PAHs. The composition of PAHs detected in sediment samples consist of both low molecular weight (LMW) PAHs and high molecular weight (HMW) PAHs

One method commonly used to evaluate the sources of PAH emissions is to determine the ratio of benzo[a]pyrene (BaP)/benzo[ghi]perylene (BghiP) (Lang et al. 2002). Values of BaP/BghiP from automobile emissions fall into the range between 0.30 – 0.44 where as BaP/BghiP values from sources such as coal combustion can be as high as 6.6. The median BaP/BghiP value for this study is 0.76. This value from indicates

that the predominant source of PAHs detected in this study is automobile emissions. The highest values (1.01 – 4.37) were found along the Tamiami Trail and the C-111 canal indicating that these stations are receiving PAH emissions from petrogenic sources.

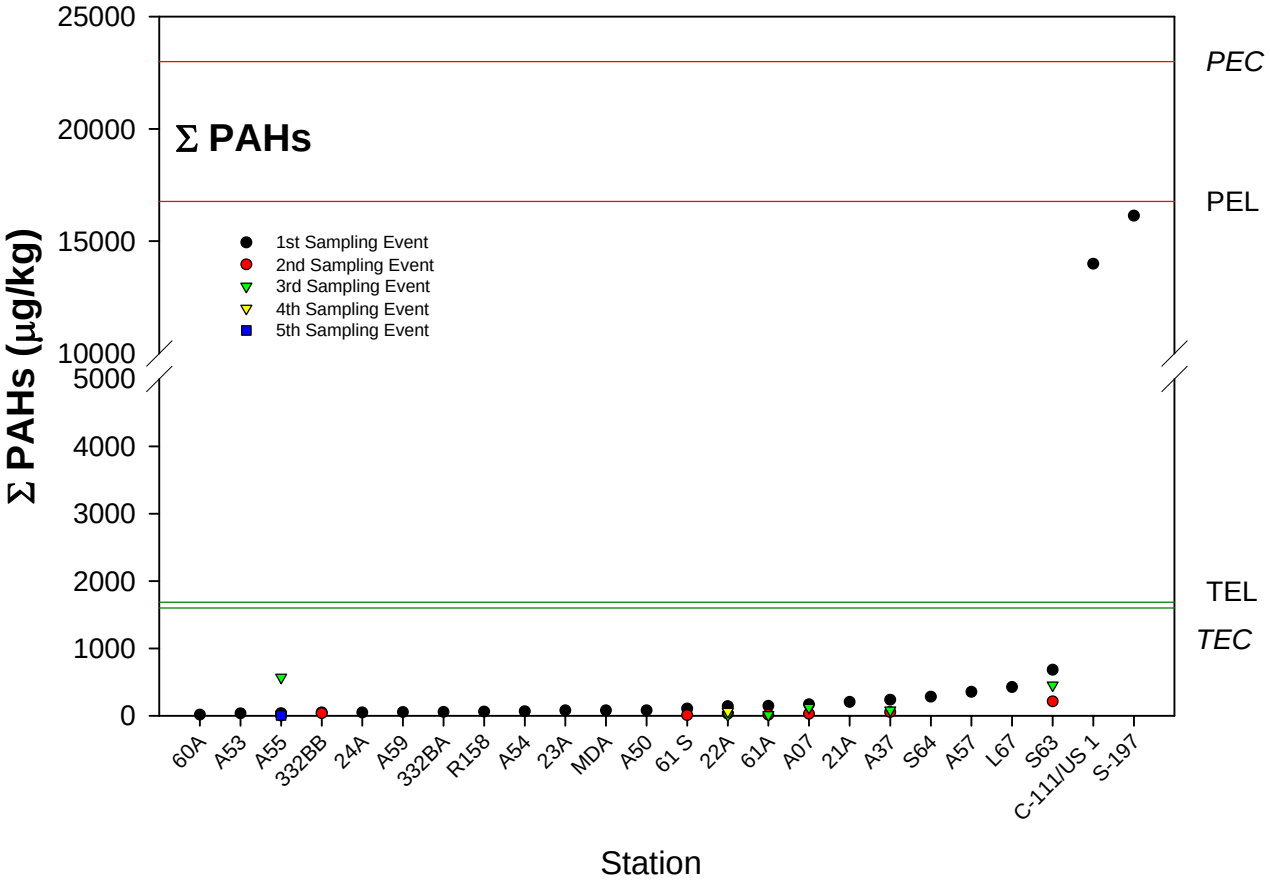


Figure 3.16.-Ranked concentration of Total PAHs in freshwater sediments.

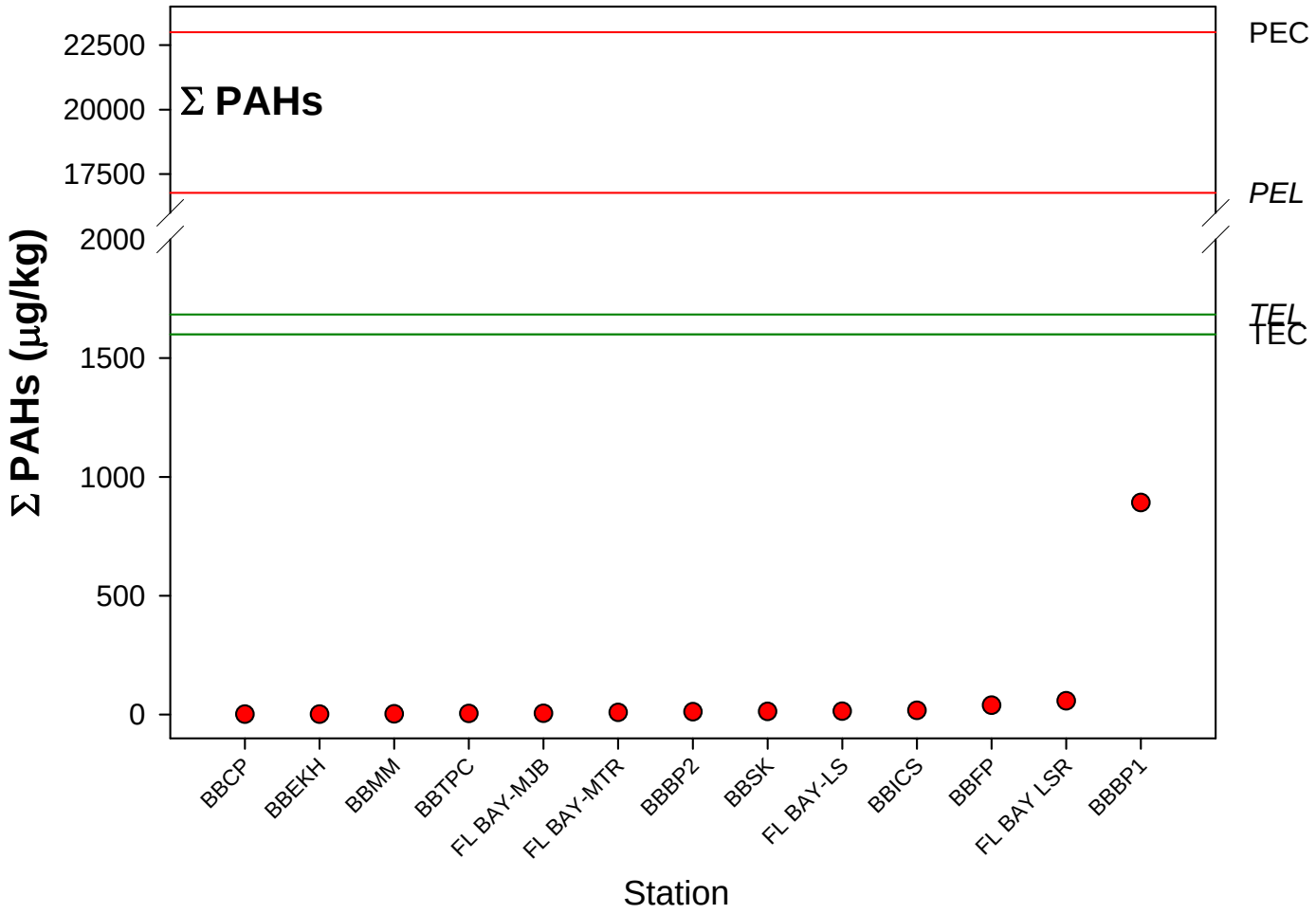


Figure 3.17.-Ranked concentration of Total PAHs in coastal sediments.

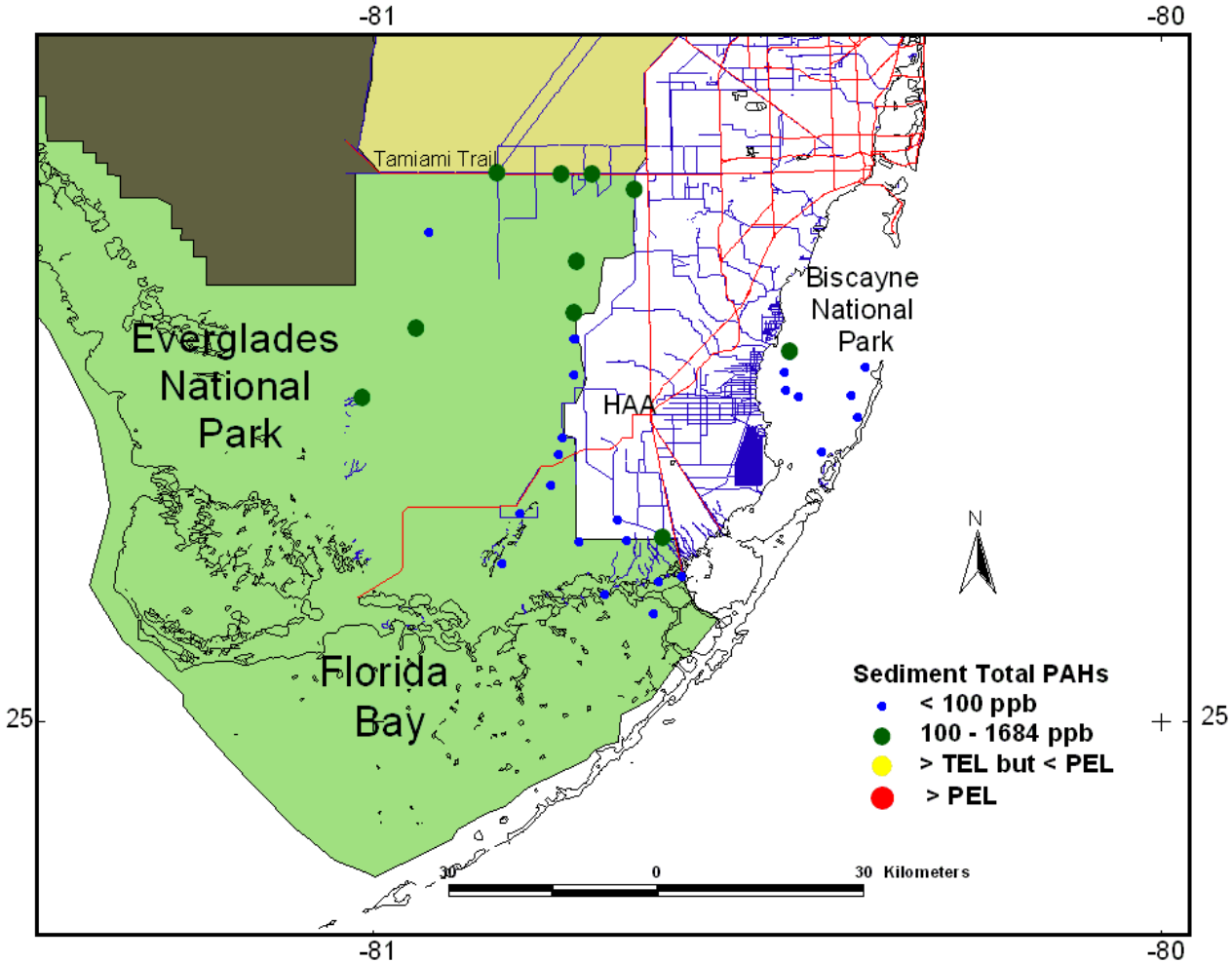


Figure 3.18.-Spatial distribution of total PAHs in sediment samples.

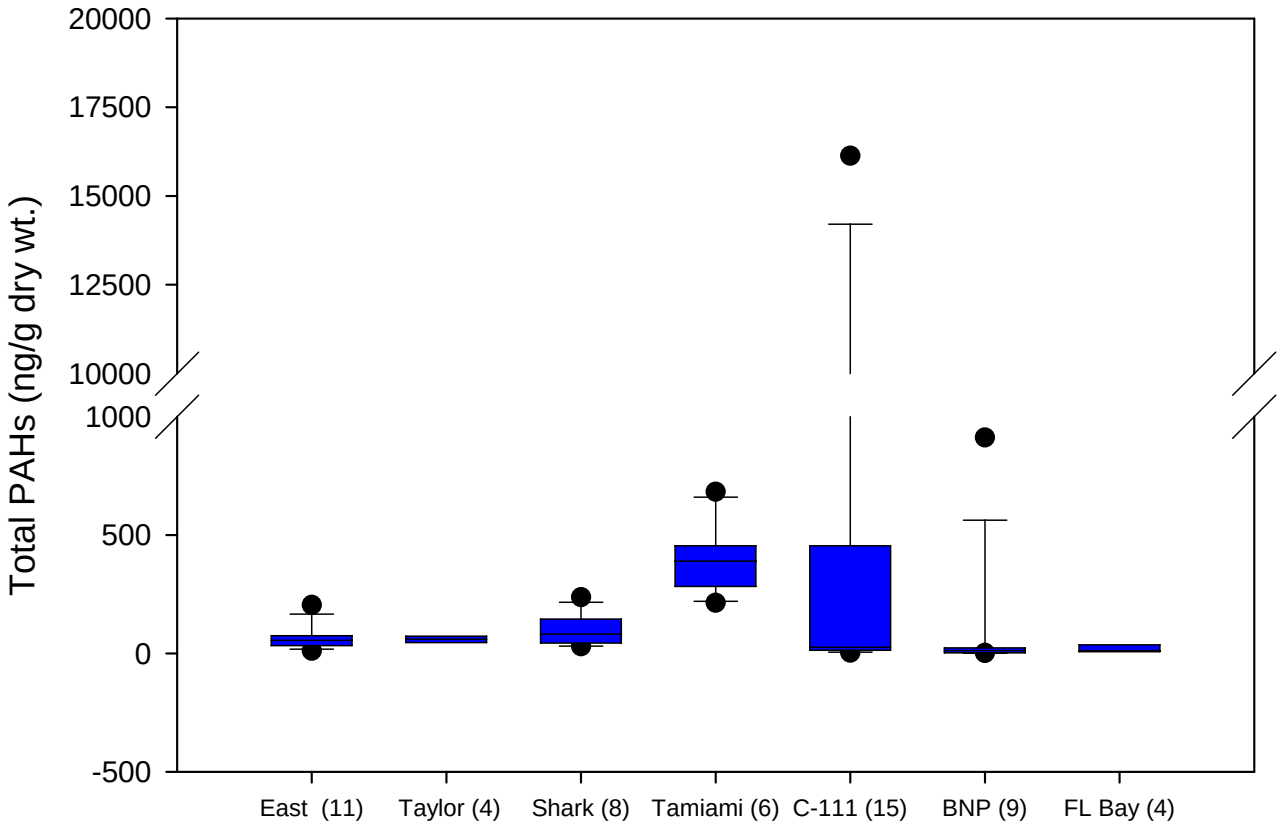


Figure 3.19.-Distribution of total PAHs in sediments within study area.

Trace Elements in Sediment

Eleven elements (Be, V, Cr, Co, Ni, Cu, Zn, As, Cd, Pb, and Al) were chosen for sediment analysis of freshwater and coastal sediments. Concentrations of the elements analyzed were ranked and plotted in reference to Sediment Quality Assessment Guidelines (SQAGs) for which definitive PEL/PEC and TEL/TEC criteria are available as promulgated by FDEP (MacDonald 1994, 2003). Of the elements determined only lead and chromium exceeded the PEC criteria in 4 and 8%, and exceeded the TEC in 16 and 24%of the freshwater stations respectively. While, arsenic, nickel, copper and zinc exceeded TEC criteria in 28, 8, 4, and 4% of freshwater samples respectively. Arsenic was the only element in exceedance of TEL criteria (38% of samples) in coastal stations. These concentrations occurred mostly in samples collected near the outfall of canals, which drain from the HAA, and at one of the stations near Black Point Marina and the municipal landfill.

The arsenic values obtained in this study for ENP (ND – 22.6 mg/kg), fall within the range reported as background for undisturbed Florida soils (0.01-38.2 mg/kg), however, the mean obtained in this study (6.9 mg/kg) is higher than that reported for disturbed Florida soils (1.43 ± 4.59 mg/kg) (Chen 2001). Lead concentrations detected in sediment samples in this study range from 0.3 – 251 mg/kg with an average of 19.4 mg/kg. These figures, however are skewed by the presence of one sample collected in

an area that appeared to be proliferated with lead bullet casings, therefore the median value for lead of 11.5 mg/kg is a better indicator of the lead concentrations detected in ENP sediments. This value falls within the lower end of the concentration range (3 – 40 mg/kg) detected in the Barron River Canal and Turner Rivers of Big Cypress National Preserve (Miller and Mcpherson, 1998). This value also falls well below the median values obtained from samples collected in residential, commercial, and public park areas in Miami and Gainesville, Florida (Chirenje et al. 2004). The range and mean values of chromium (0.40 - 194, 23.4 mg/kg) also appear to be skewed by a few samples with elevated concentration, the median value of 11.5 mg/kg however, falls at the lower end of the range (6 – 77 mg/kg) detected in Big Cypress by Miller and Mcpherson (1998). The ranges of copper and nickel concentrations detected in this study are in agreement with those reported in the Big Cypress study.

Figures 3.20 – 3.25 show plots of selected element concentrations in reference to TEL and PEL criteria for those elements that exceeded TELs in ENP and BNP. Of the elements analyzed, only arsenic concentrations fell within the range for significantly toxic sediments reported by NOAA for Tampa Bay based on amphipod and Microtox™ bioluminescence tests (NOAA, 1994). Figures 3.25 – 3.33 show the spatial distribution of trace metals in sediments from all stations sampled.

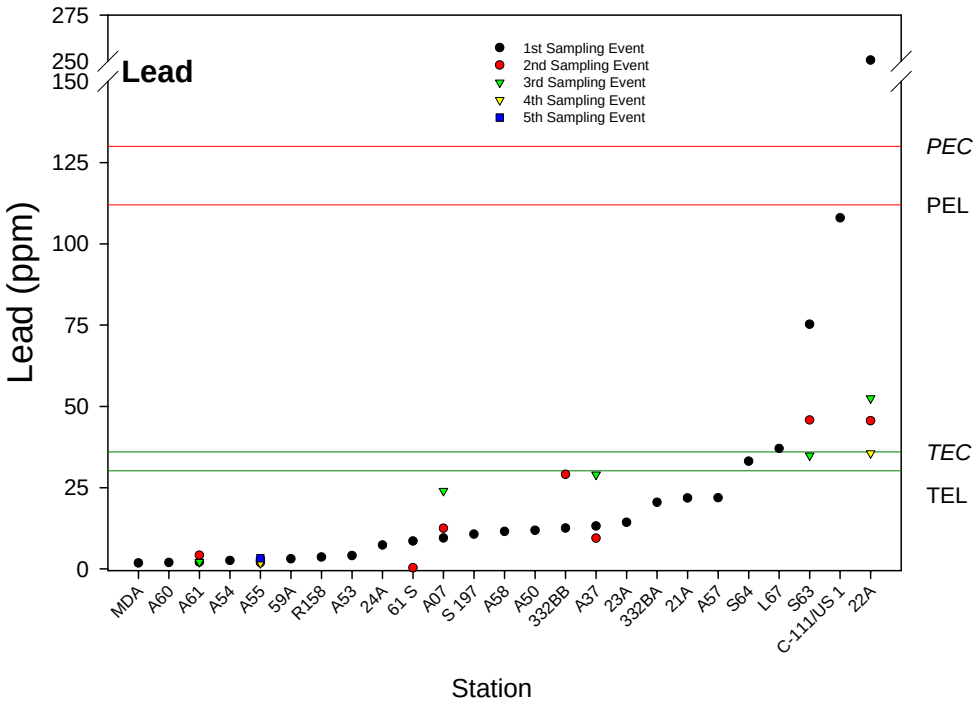


Figure 3.20.-Ranked concentrations of lead in ENP sediment.

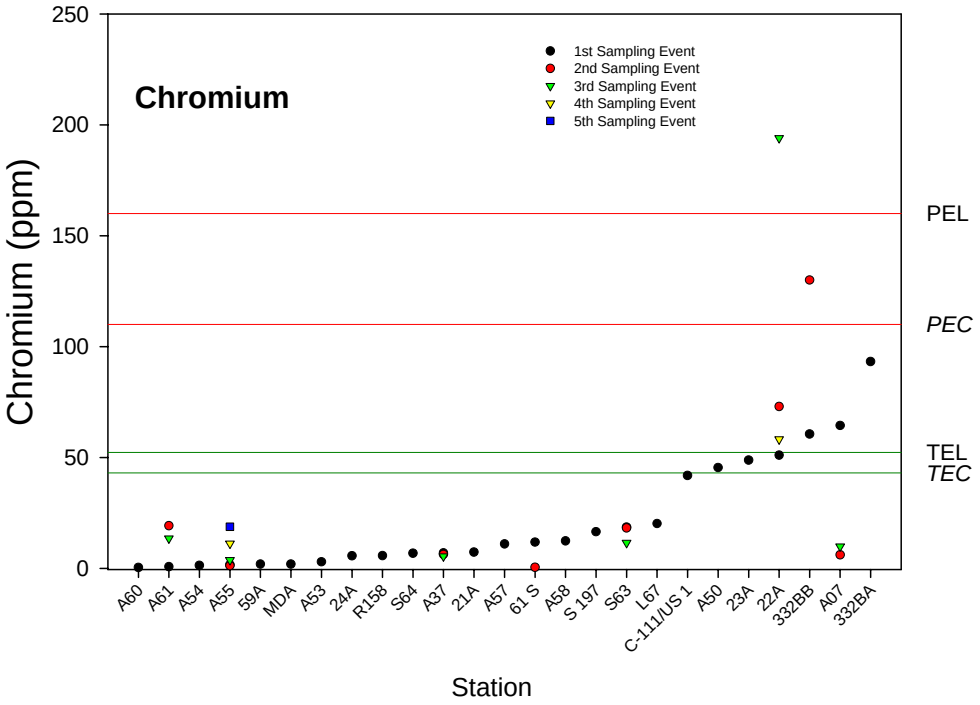


Figure 3.21.-Ranked concentrations of chromium in ENP sediments.

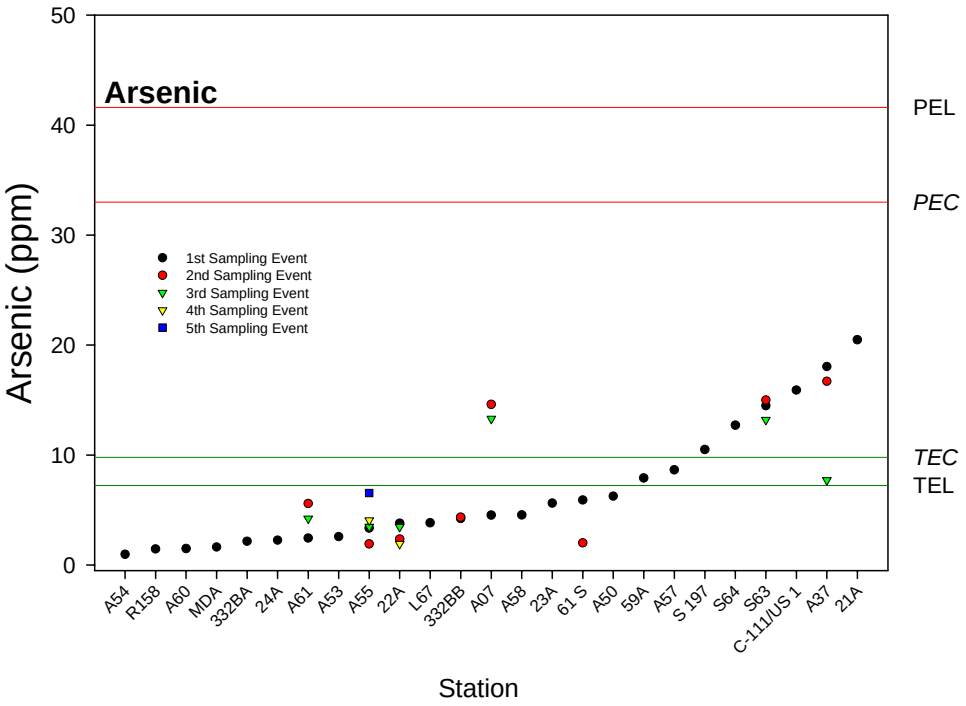


Figure 3.22.-Ranked concentrations of arsenic in ENP sediments.

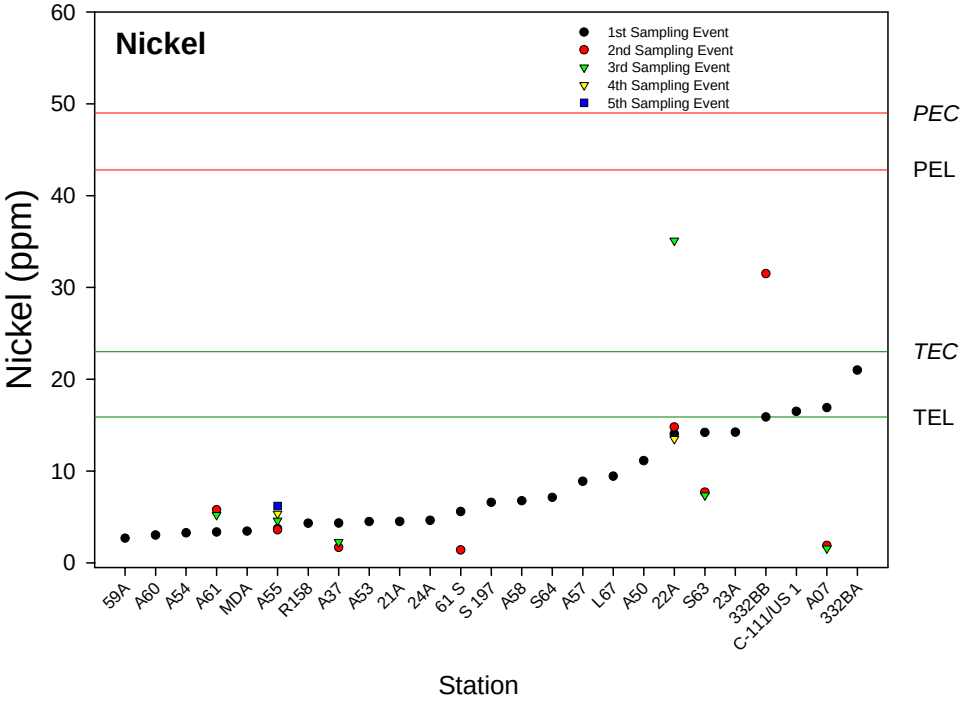


Figure 3.23.-Ranked concentrations of nickel in ENP sediments.

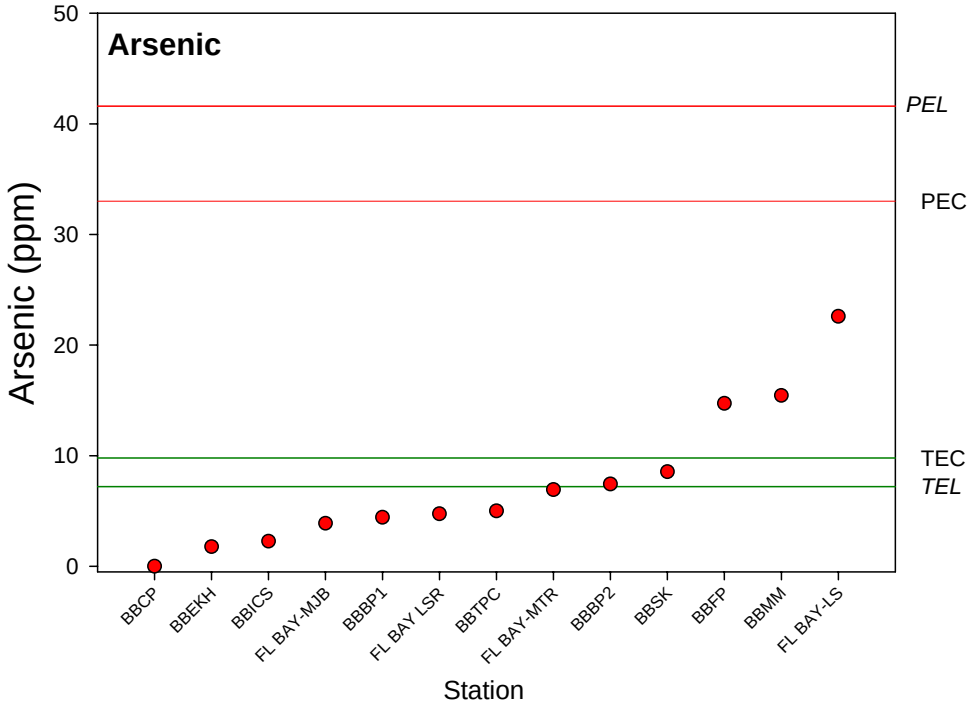


Figure 3.24.- Ranked concentrations of arsenic in coastal sediments.

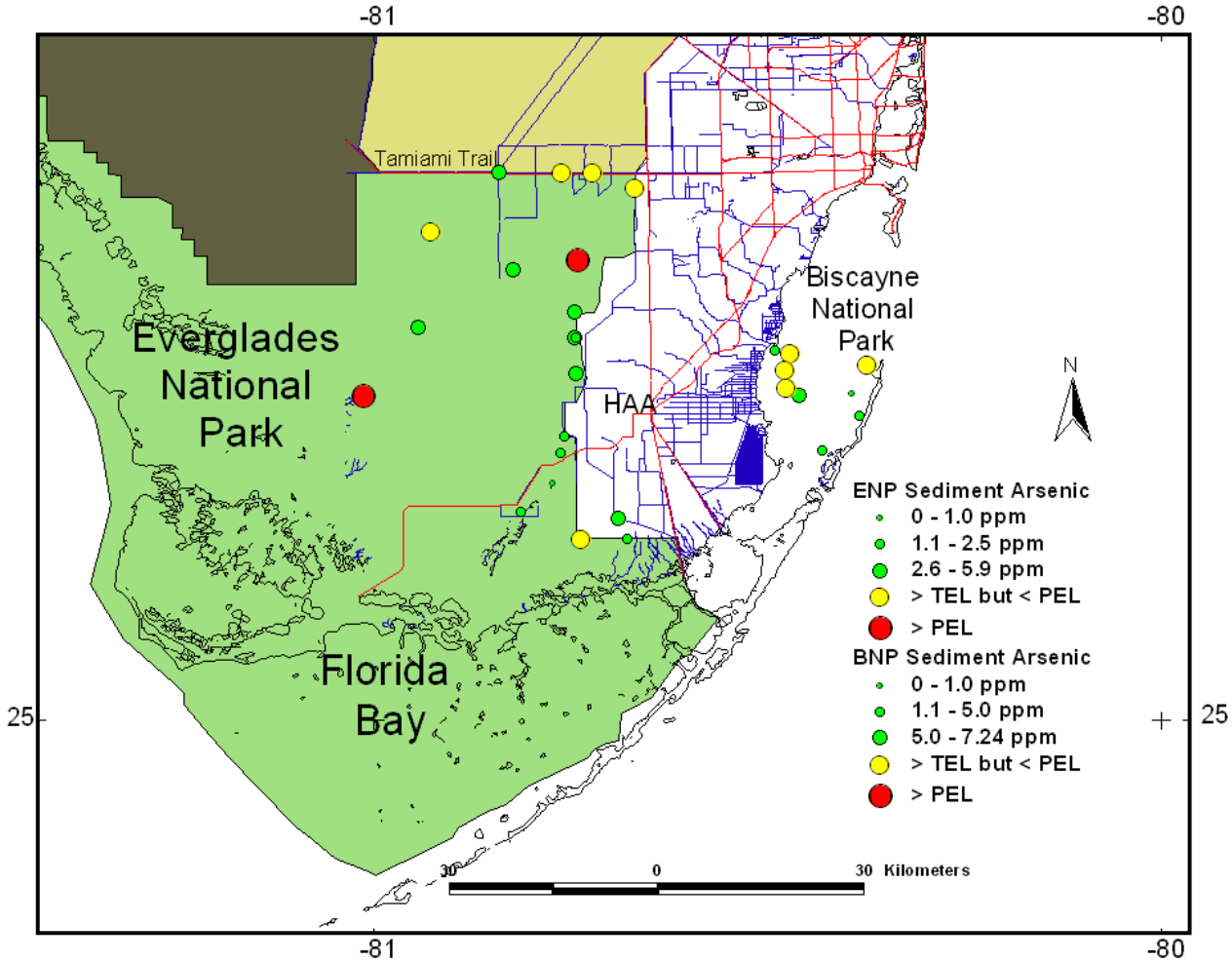


Figure 3.25.-Spatial distribution of arsenic in sediment samples.

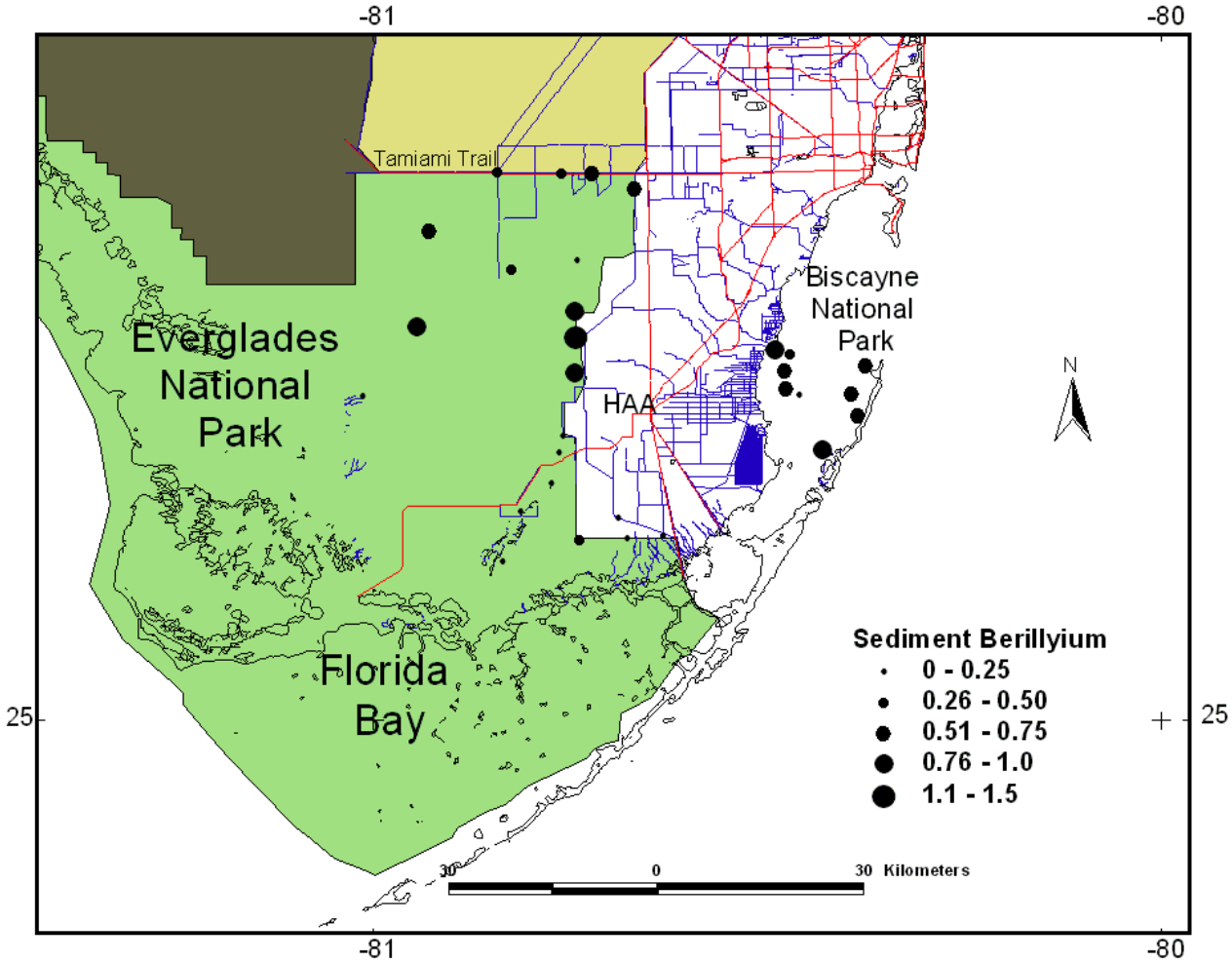


Figure 3.26.-Spatial distribution of beryllium in sediment samples.

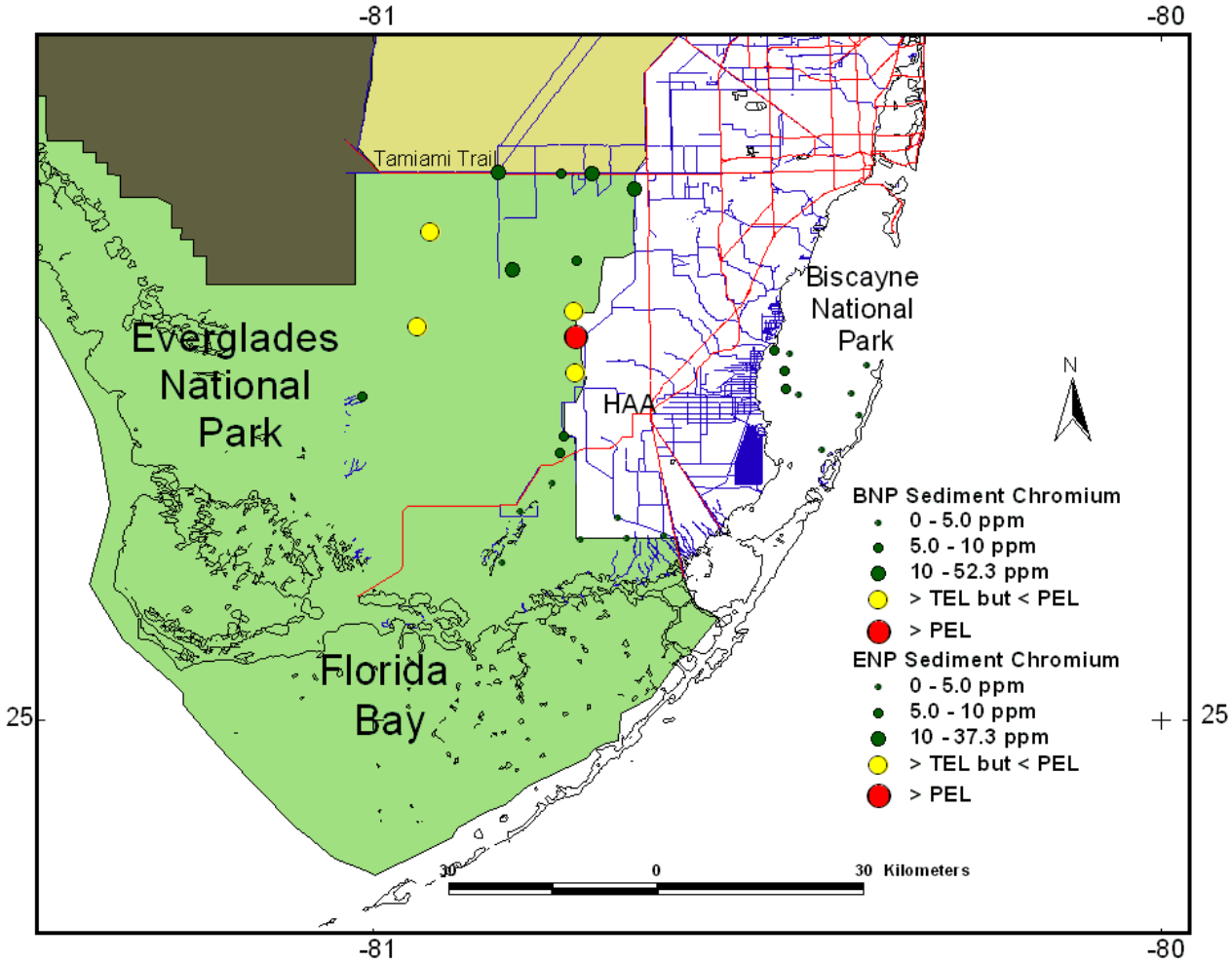


Figure 3.27.-Spatial distribution of chromium in sediment samples.

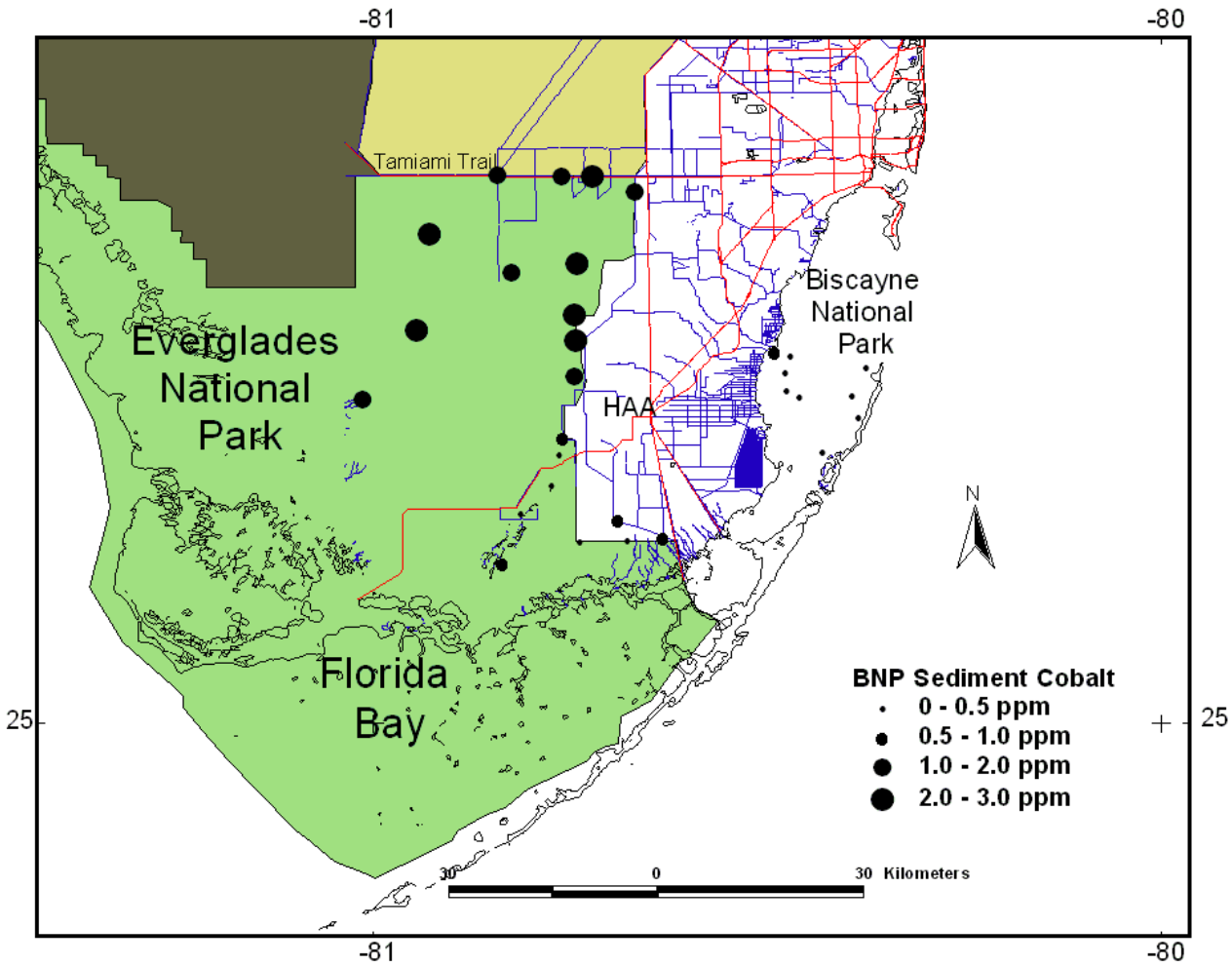


Figure 3.28.-Spatial distribution of cobalt in sediment samples.

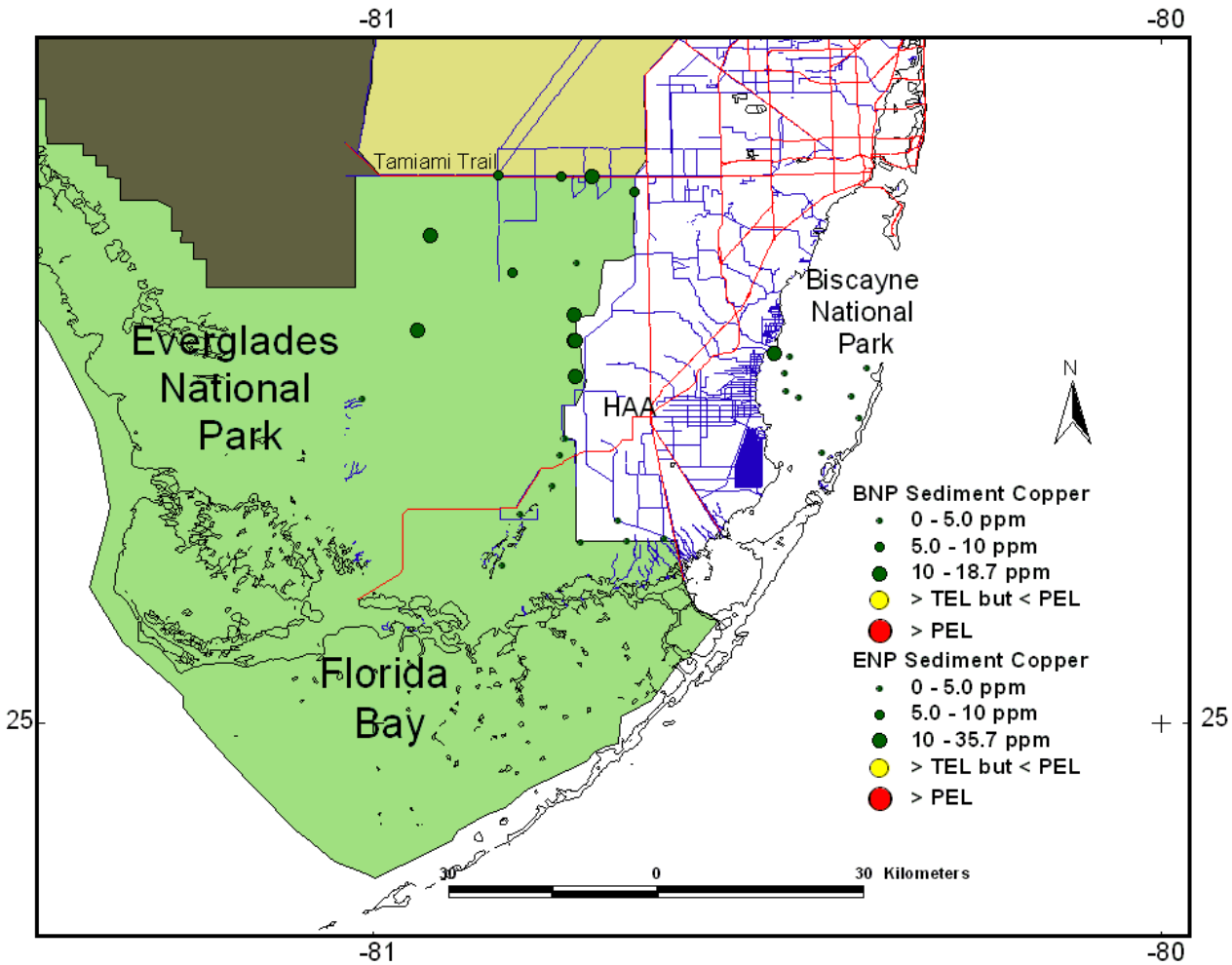


Figure 3.29.-Spatial distribution of copper in sediment samples.

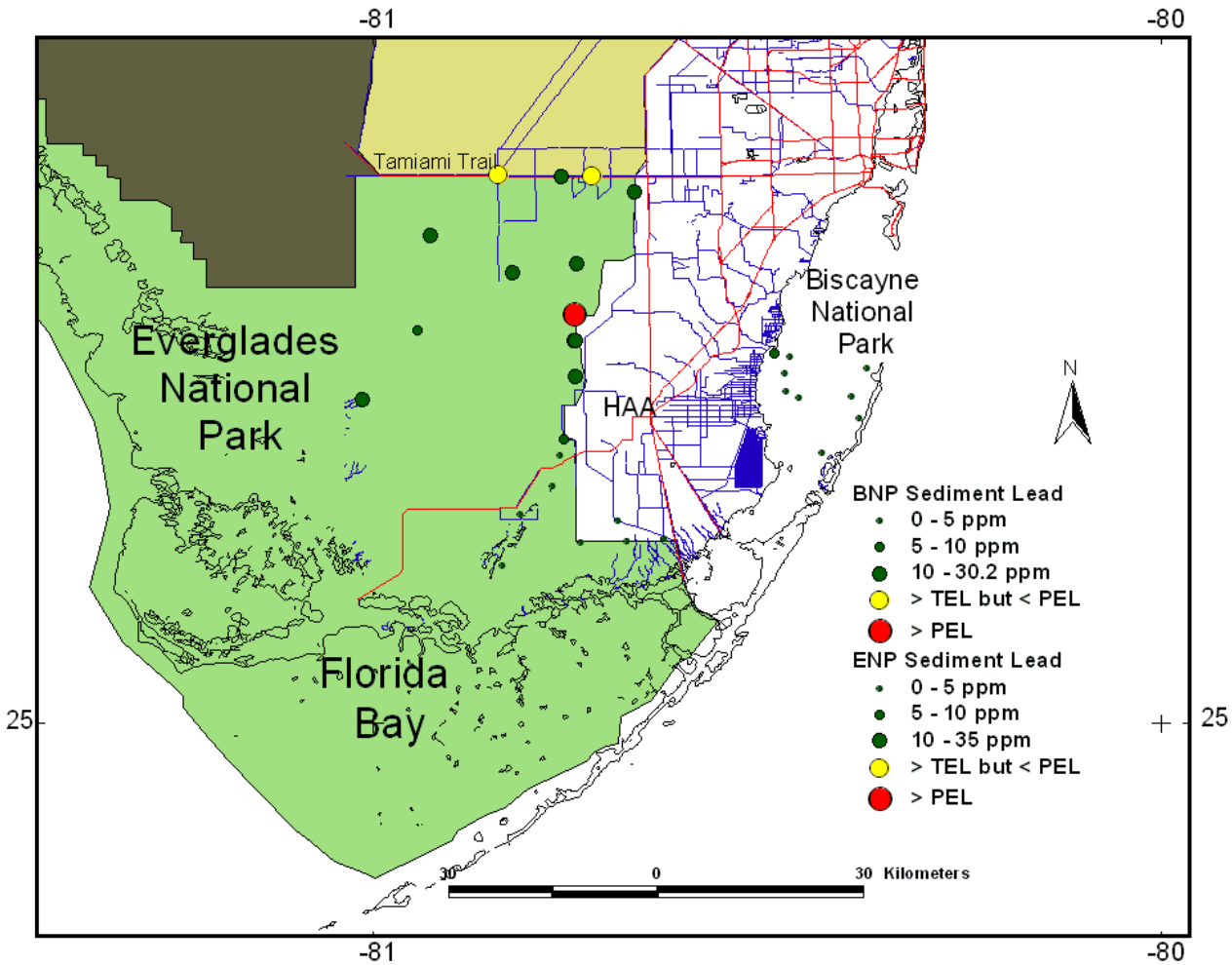


Figure 3.30.-Spatial distribution of lead in ENP sediments.

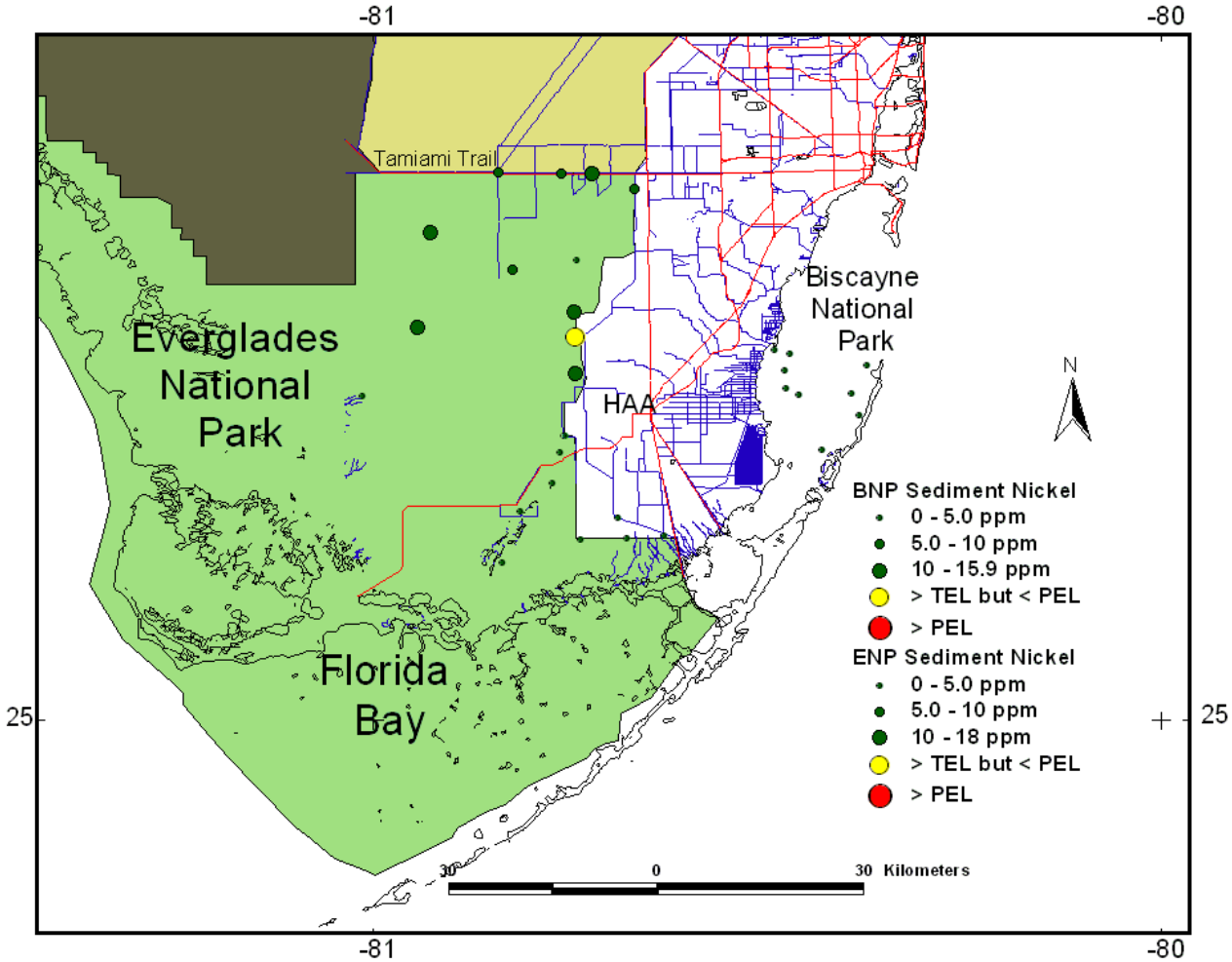


Figure 3.31.-Spatial distribution of nickel in sediment samples.

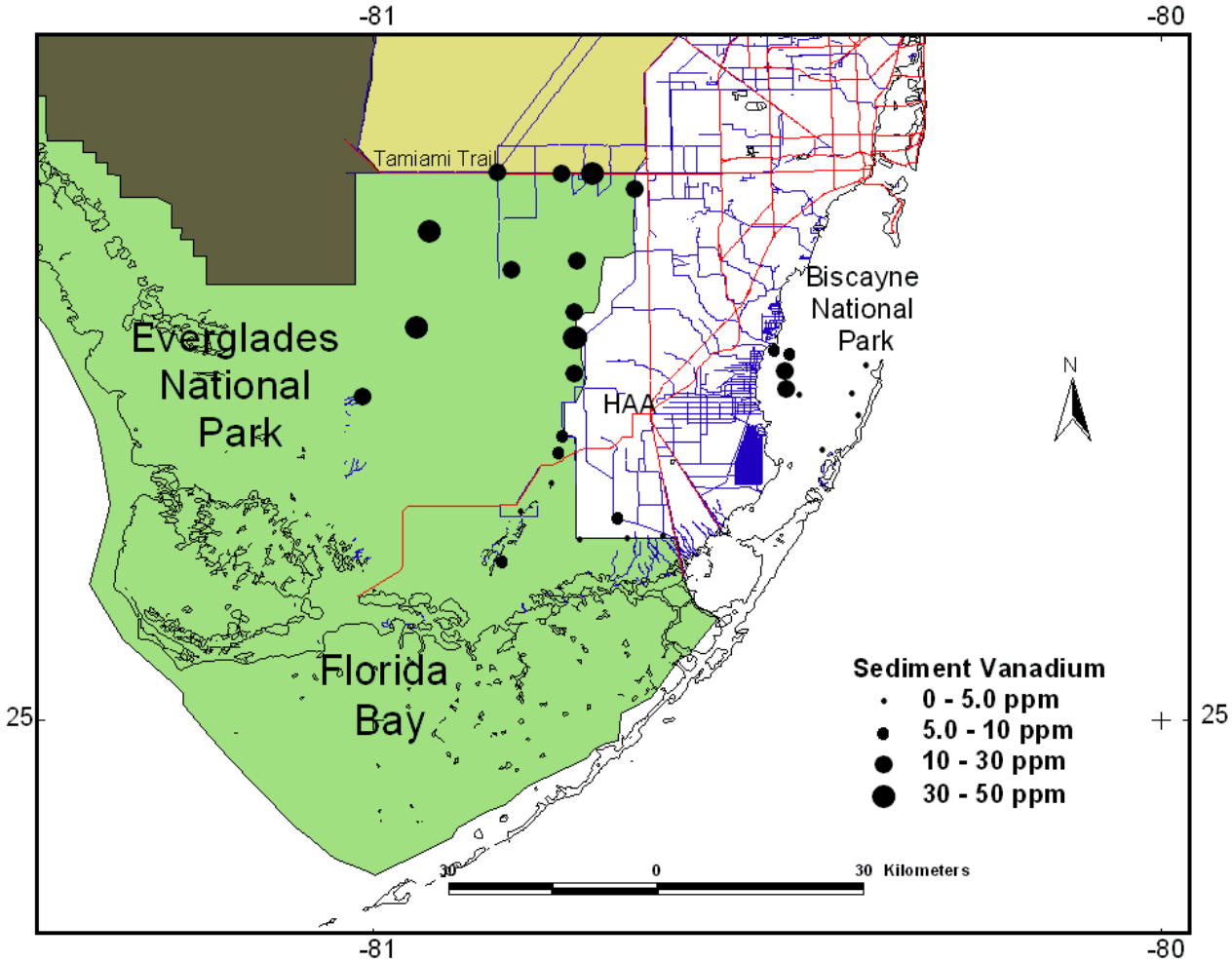


Figure 3.32.-Spatial distribution of vanadium in sediment samples.

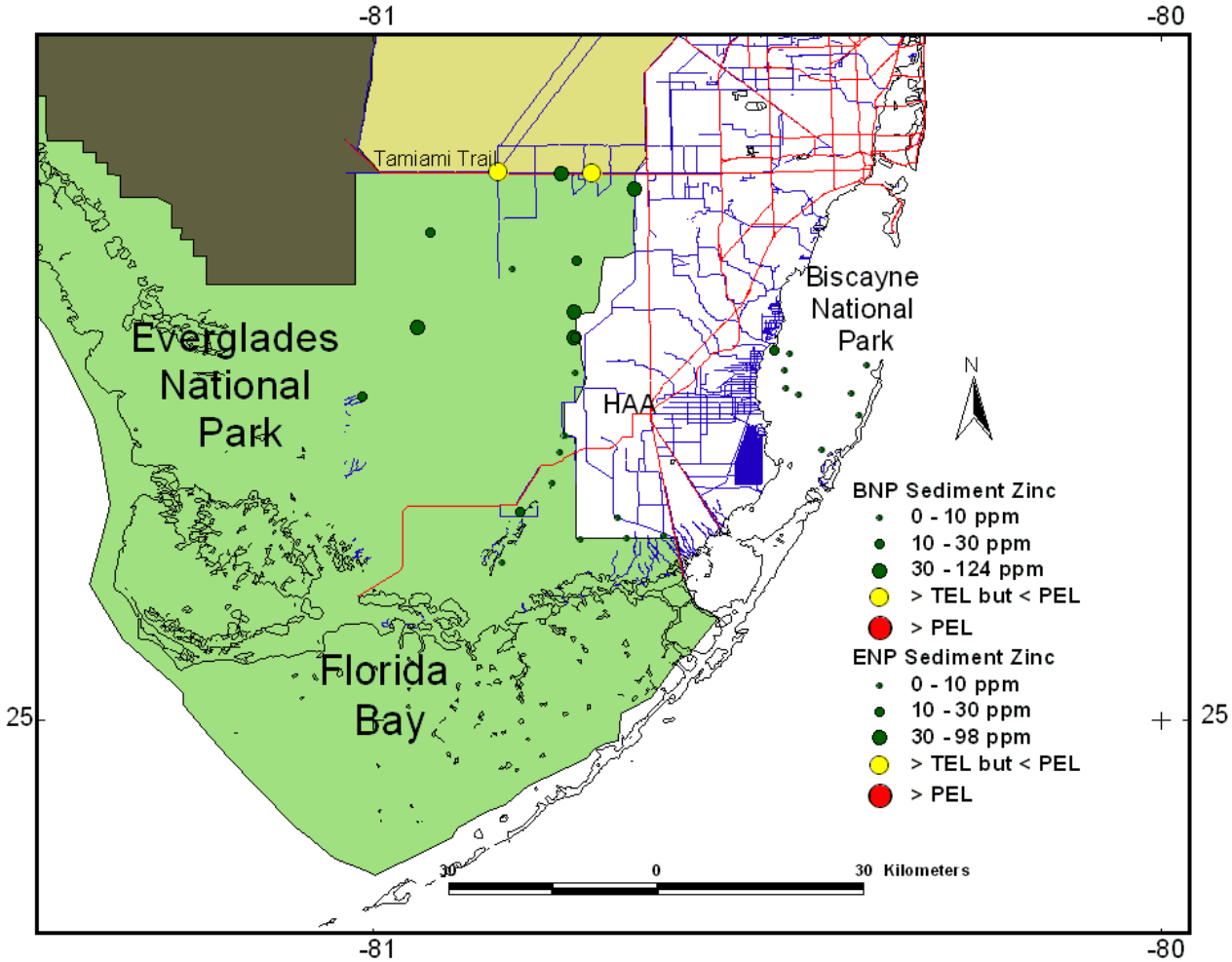


Figure 3.33.-Spatial distribution of zinc in sediment samples.

The distributions of metal concentrations in sediments vary widely within regions and are influenced by a variety of factors such as grain size, organic content and anthropogenic enrichment (Shropp and Windom, 1988). One method used to determine if metal concentrations in a given area are enriched above naturally occurring levels is to plot their concentrations against the concentration of a naturally occurring element that is not likely to be enriched by anthropogenic activity. As part of the Florida Coastal Management Program for FDEP, Shropp and Windom (1988) conducted a study for determining metal enrichment in sediments by comparing trace element concentrations against aluminum concentrations in clean sediments from estuarine areas throughout Florida. The results of this study produced correlations of trace element concentrations vs. aluminum concentrations for what are considered non-anthropogenically enriched sediments. These were plotted with a 95% confidence interval, above which, sediments may be considered enriched. Although these graphs do not provide exposure-based interpretation, as do the TEL/PEL plots, they indicate the likelihood that sediments are enriched for that element over its natural abundance.

The concentrations of trace elements in sediments of ENP and BNP were plotted against aluminum concentrations in reference to the 95% confidence level of the regression line determined by Shropp and Windom for non-anthropogenically enriched sediments. These results are plotted in figures 3.34 – 3.40. A comparison between the TEL/PEL plots and the element enrichment plots reveals that the stations, which exceeded TEL and PEL criteria, also fall above the 95% limit, which indicates anthropogenic enrichment. This method was applied to Biscayne Bay and Miami River sediments (Schropp et al. 1990) and the results revealed enrichment of cadmium, zinc, chromium, copper and lead

at stations at or near the mouth of the Miami River. Although this technique was applied in this study, the results should be interpreted cautiously. Van der Weijden (2002) illustrates this using a statistical perspective as well as realistic scenarios. Specifically he describes how this method for normalization excludes realistic estimates of sedimentary phases such as organic matter, which consequently, comprises a very large fraction of the samples analyzed in this study. Furthermore, the application of Shropp's correlations is better suited to areas that have a consistent source for aluminum such as clays, which are not present in the sediments analyzed in this study.

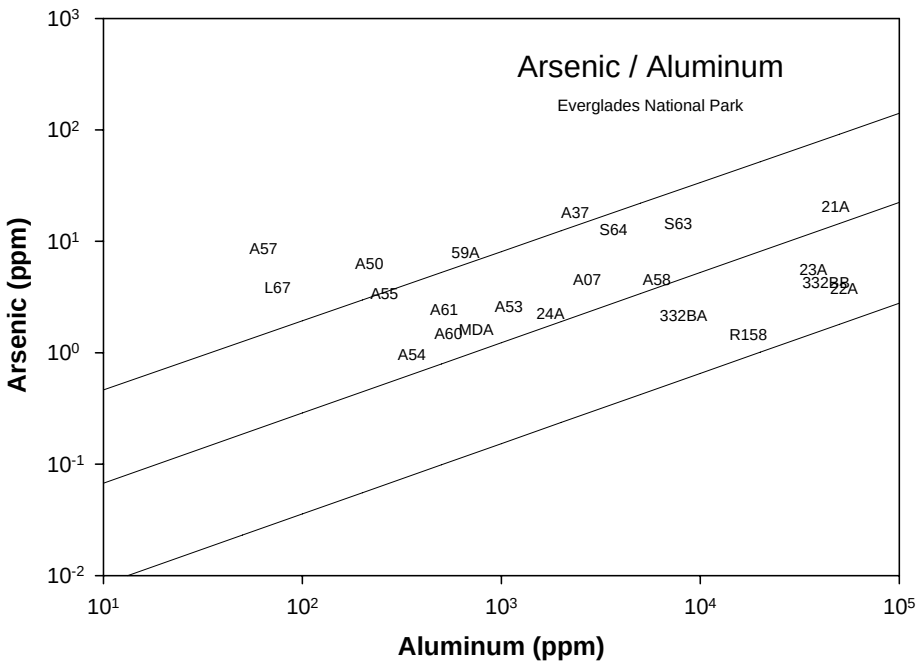


Figure 3.34.-Concentrations of arsenic vs. aluminum in ENP sediments.

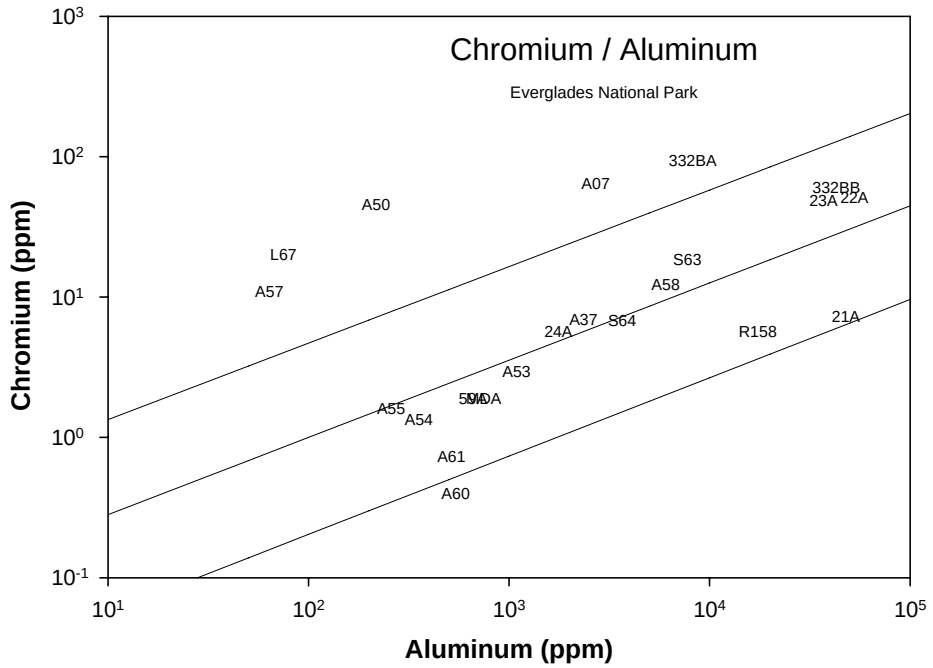


Figure 3.35.-Concentrations of chromium vs. aluminum in ENP sediments.

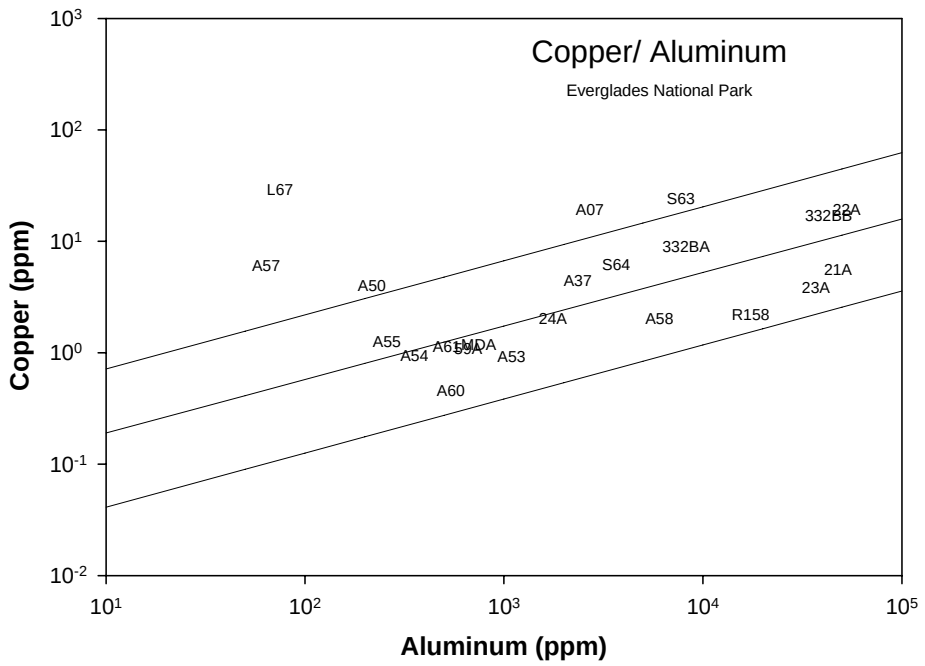


Figure 3.36.-Concentrations of copper vs. aluminum in ENP sediments.

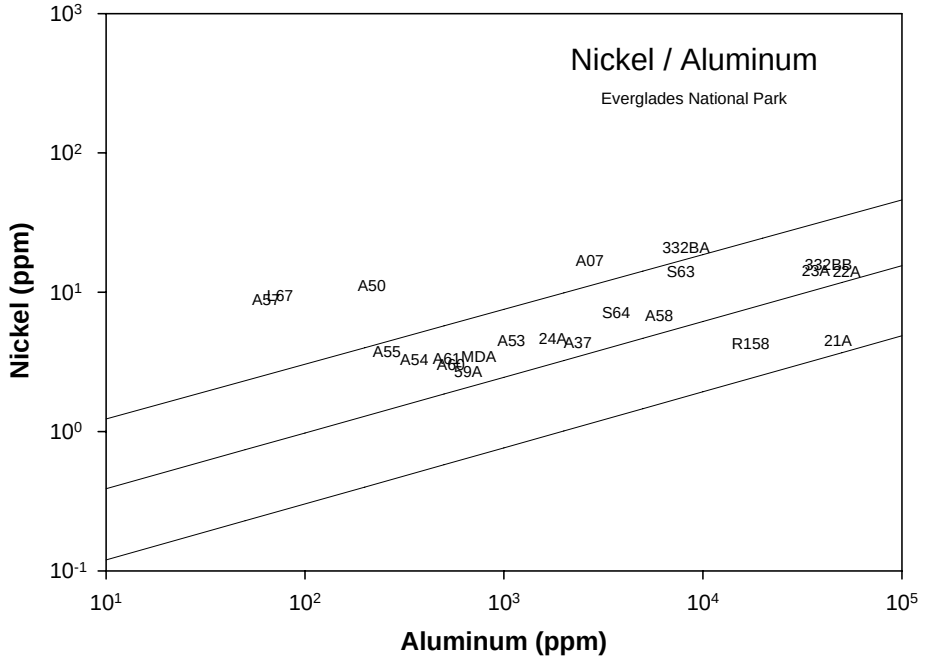


Figure 3.37.-Concentrations of nickel vs. aluminum in ENP sediments.

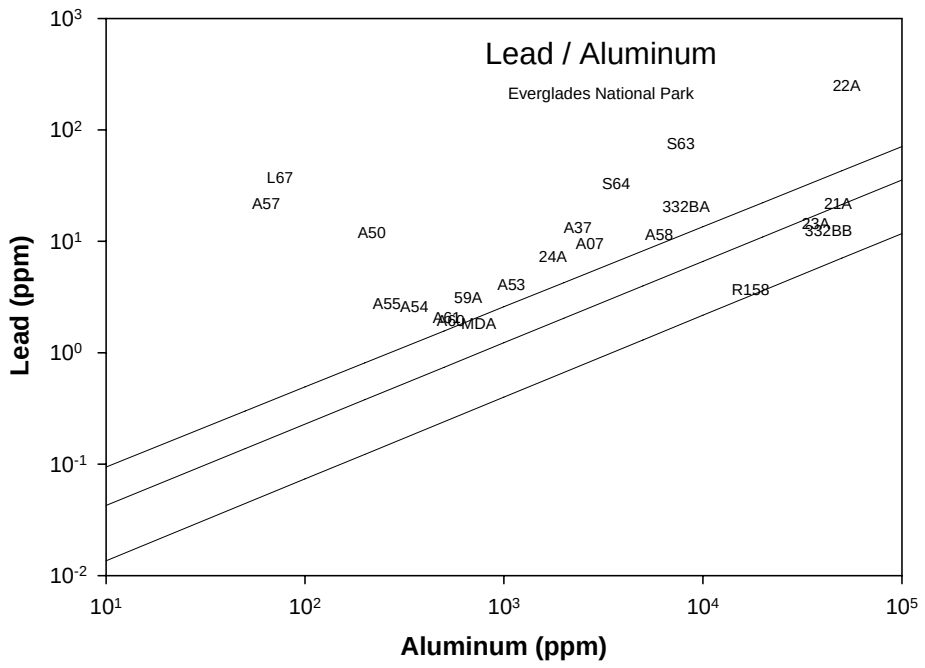


Figure 3.38.-Concentrations of lead vs. aluminum in ENP sediments.

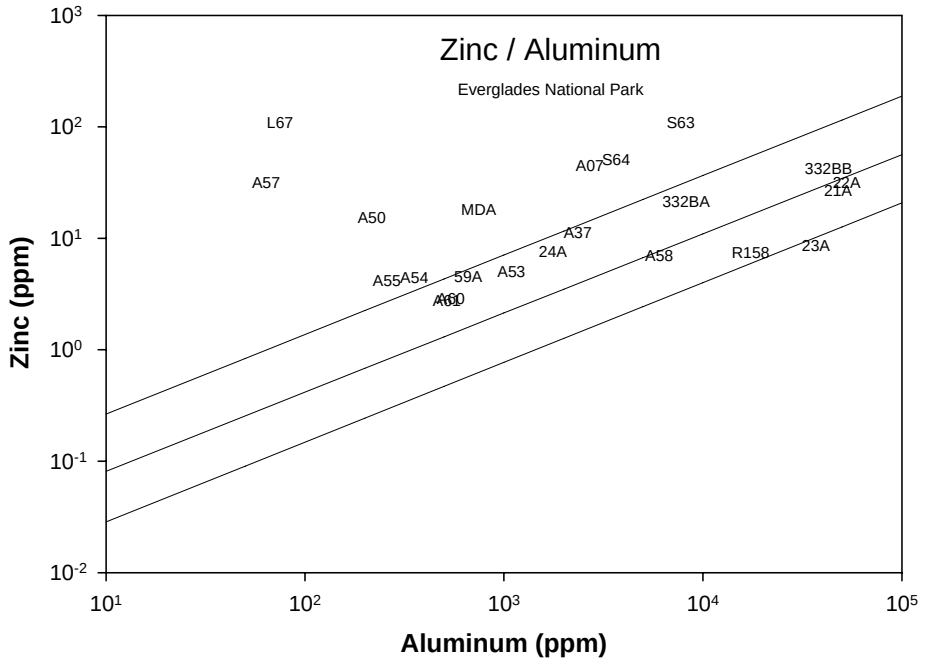


Figure 3.39.-Concentrations of zinc vs. aluminum in ENP sediments.

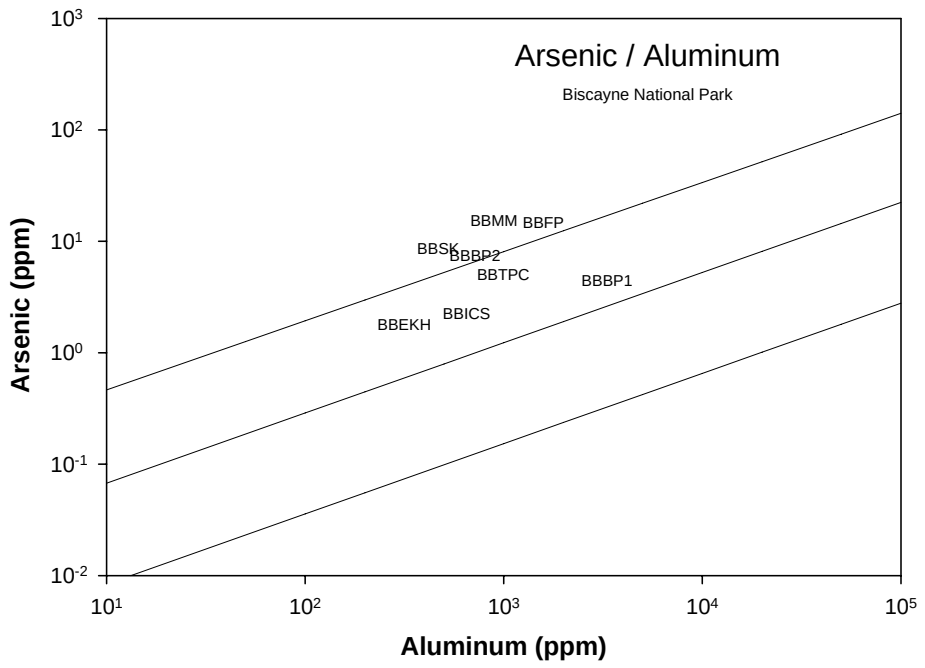


Figure 3.40.-Concentrations of arsenic vs. aluminum in BNP sediments.

Some trends are apparent in the distribution of trace elements among the different regions of the study area. Figures 3.41 – 3.49 show box plot graphs comparing the distribution of trace element concentrations with in the study area. These graphs indicate that the highest concentrations of beryllium, vanadium, and chromium are found in the Eastern Boundary and Shark Slough areas, while Cobalt and Nickel are highest in the Eastern Boundary, Shark Slough, and Tamiami areas. Copper, zinc, arsenic and lead all have higher concentrations in the Eastern Boundary and the Tamiami areas.

Although in many cases the variability in metal content for the different regions was not very large, it seems that the ENP East Boundary and Tamiami Trail regions

suffer the greatest trace metal impacts, although, as in the case of the organochlorine compounds, Shark Slough also seems to act as a sink for trace metals.

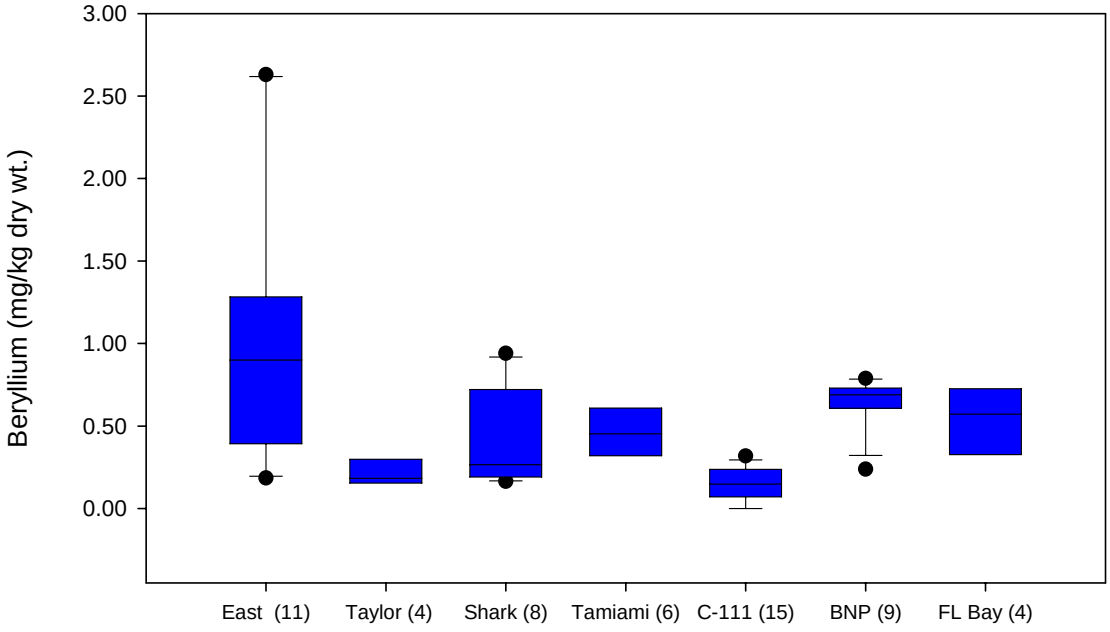


Figure 3.41.-Distribution of Beryllium in sediments within study area.

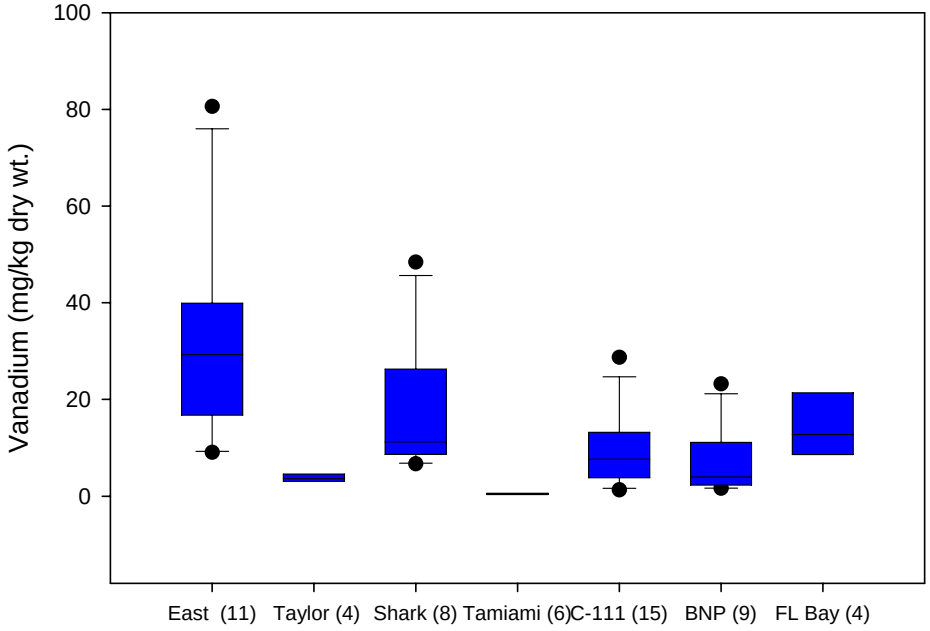


Figure 3.42.-Distribution of Vanadium in sediments within study area.

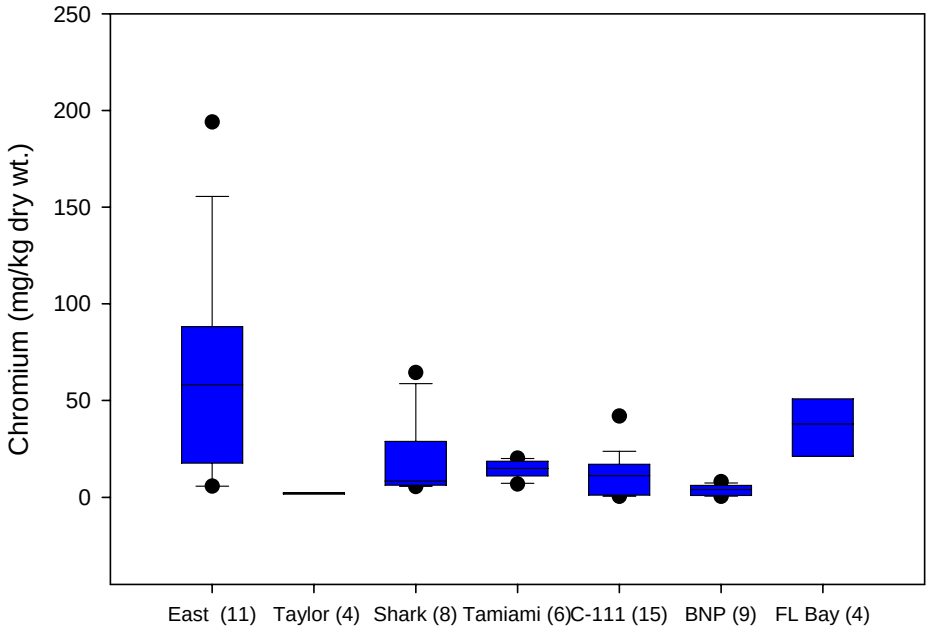


Figure 3.43.-Distribution of Chromium in sediments within study area.

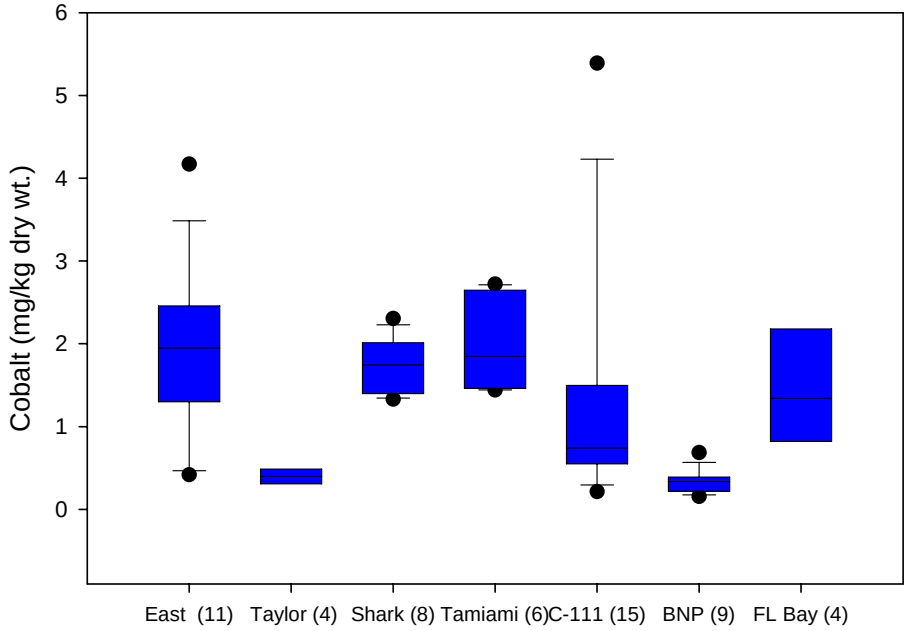


Figure 3.44.-Distribution of Cobalt in sediments within study area.

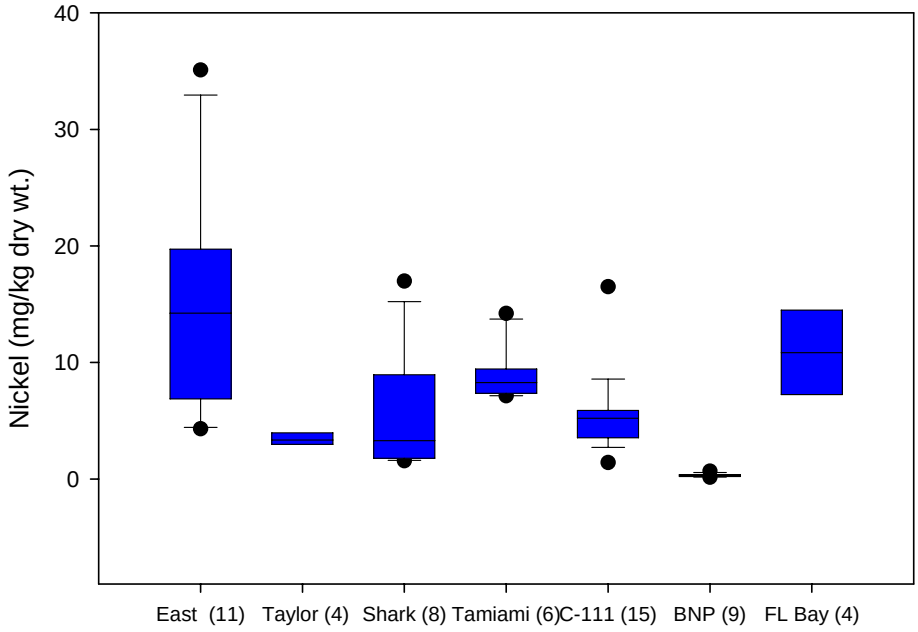


Figure 3.45.-Distribution of Nickel in sediments within study area.

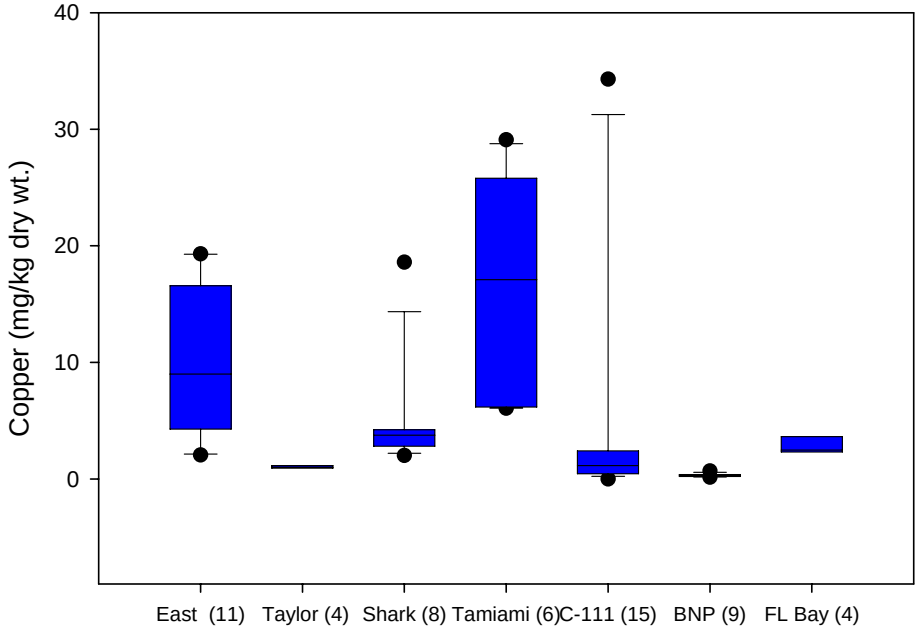


Figure 3.46.-Distribution of Copper in sediments within study area.

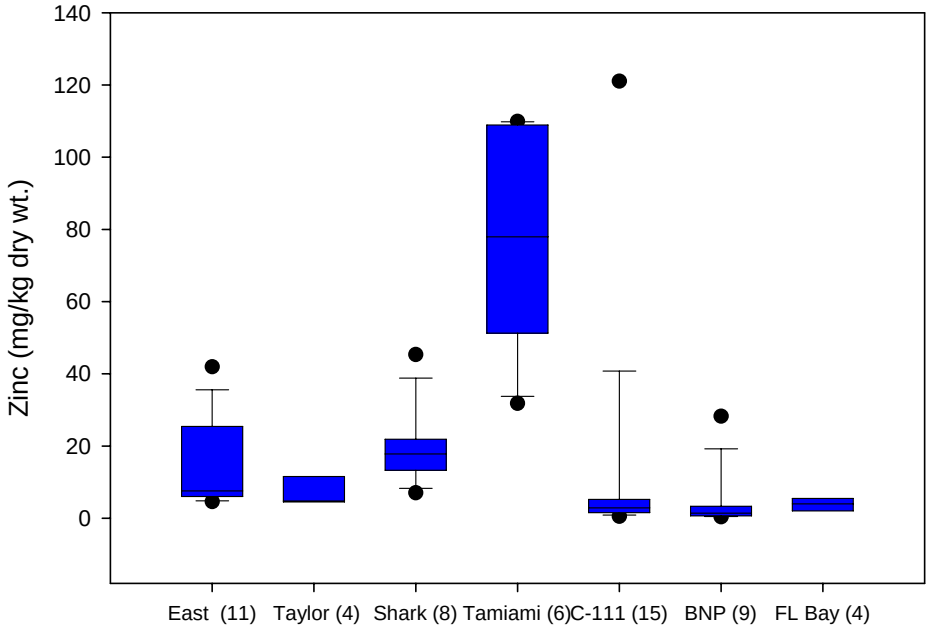


Figure 3.47.-Distribution of Zinc in sediments within study area.

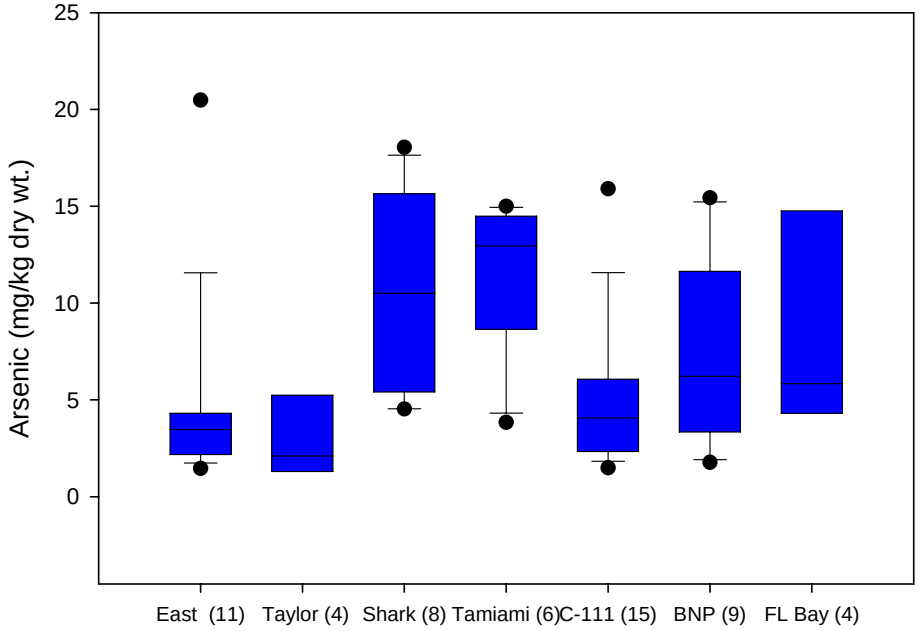


Figure 3.48.-Distribution of Arsenic in sediments within study area.

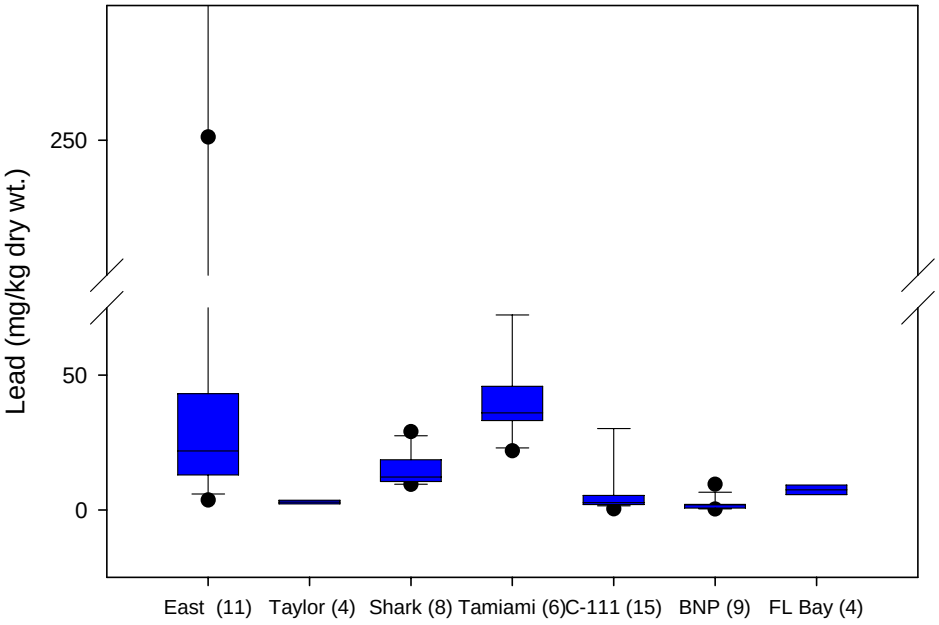


Figure 3.49.-Distribution of Lead in sediments within study area.

Organic Contaminants in Whole Fish Tissue Samples

Organochlorine Pesticides

A total of 63 fish samples from 14 stations in ENP and 6 stations in Florida Bay were analyzed for 25 organochlorine compounds and 18 PCBs. The most frequently detected contaminants in tissue samples were endosulfan sulfate, and p,p'-DDE occurring in 72 and 79 percent of samples respectively. Other less frequently detected pesticides (not confirmed by GC/MS) in fish tissues are chlorpyrifos, and dieldrin each occurring in 9 percent of samples. The spatial distributions of the most frequently detected pesticides are given in figures xx - yy. Here as well, a trend is apparent with the highest body burdens occurring at those stations closest to the HAA where the application of endosulfan and chlorpyrifos is still occurring (Shahane 1999). The concentrations and distribution of these pollutants in fish tissue is in accordance with the limited data available as reported by Scott et al., (2002), although endosulfan sulfate concentrations for a few samples in this study are considerably higher, the mean concentrations were similar.

The distribution of OCPs in fish tissue within the study area were more in line with the original hypothesis than the distribution found in sediments. Figures 3.50 – 3.54 show the distribution of concentrations of total DDTs, p-p'DDE, and endosulfan sulfate within the study area. These graphs clearly show that the highest concentrations of these pesticides are found in the Eastern Boundary stations, with elevated concentrations also detected in the C-111 stations.

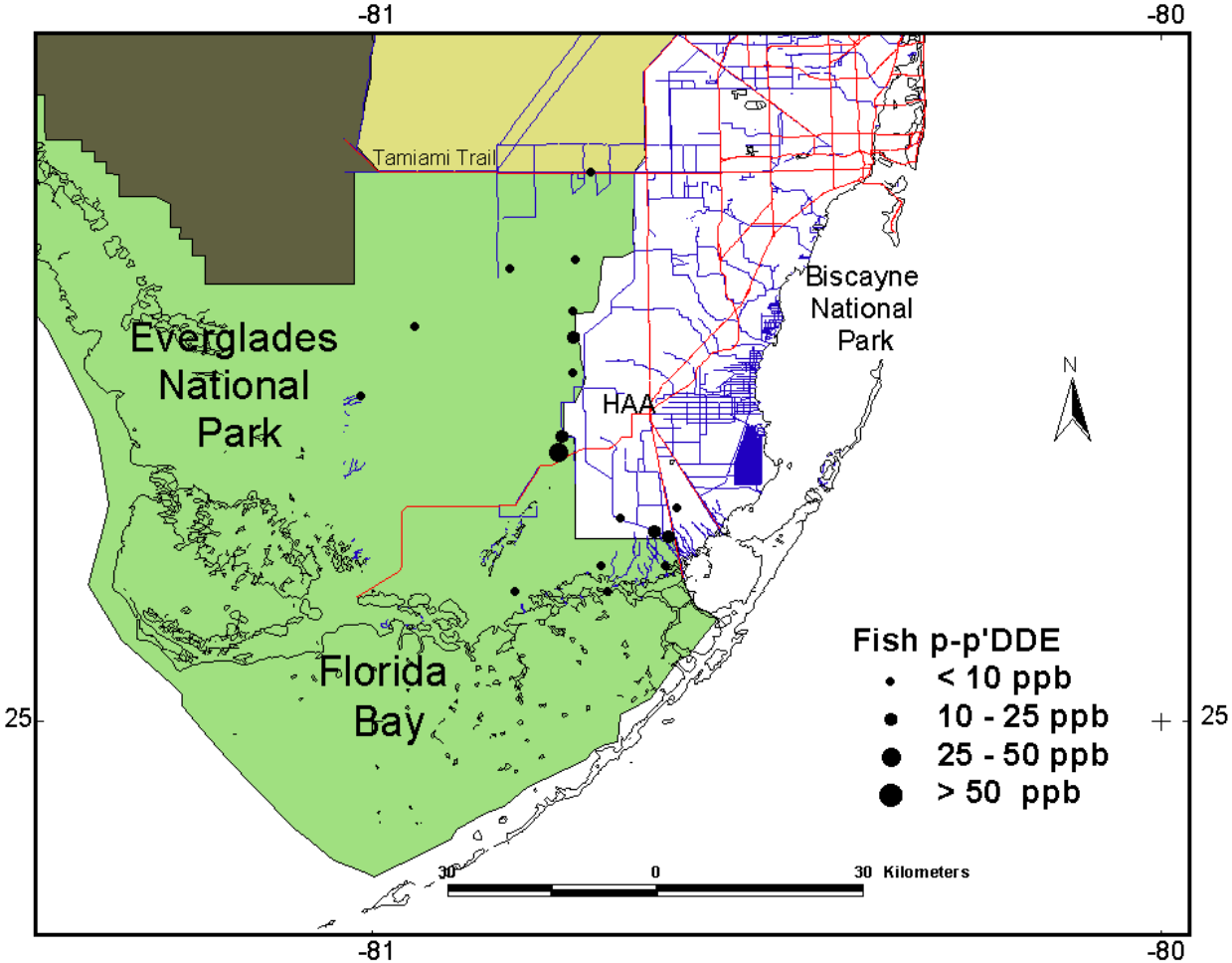


Figure 3.50.-Spatial distribution of p-p'DDE detected in fish tissue samples.

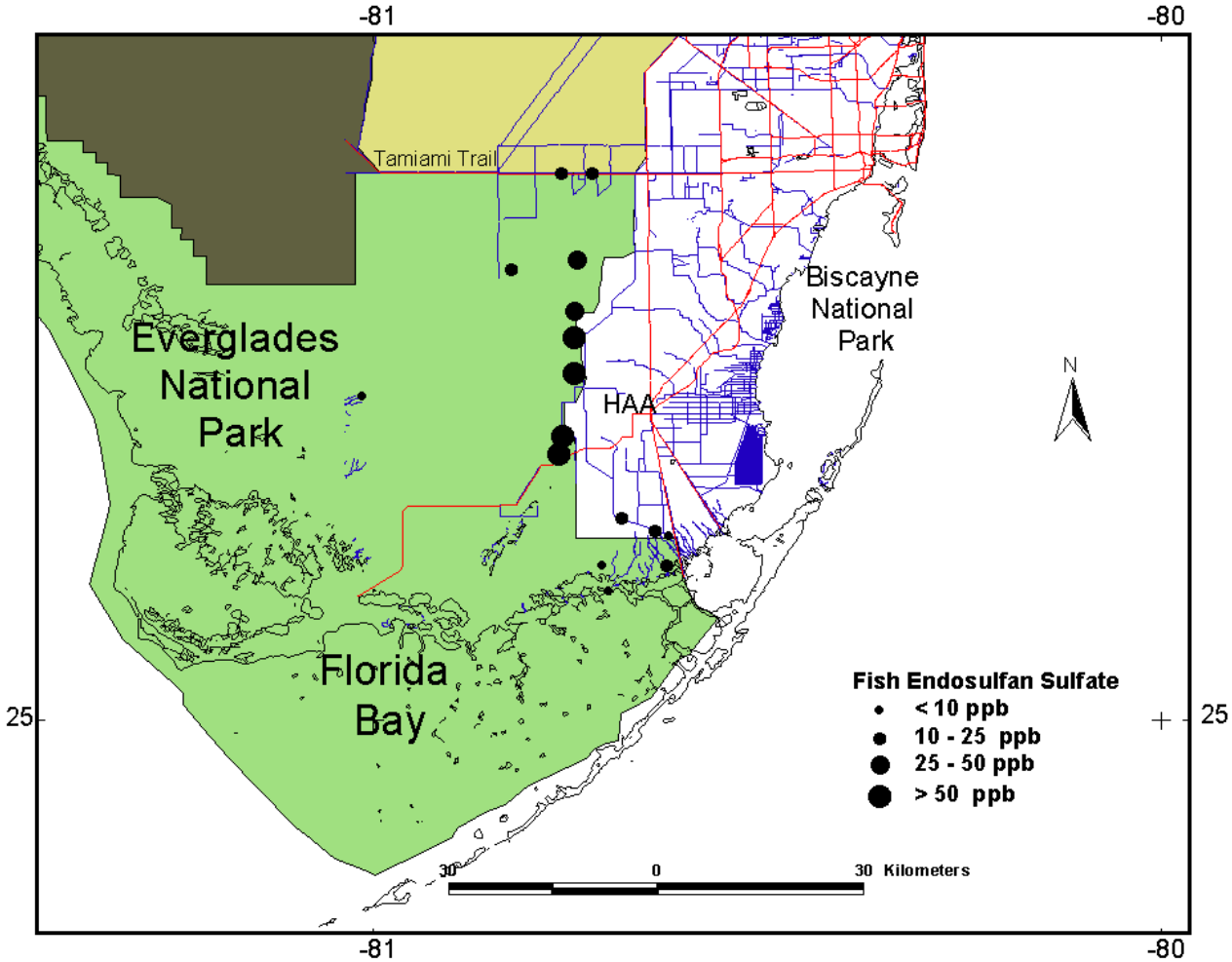


Figure 3.51.-Spatial distribution of Endosulfan sulfate detected in fish tissue samples.

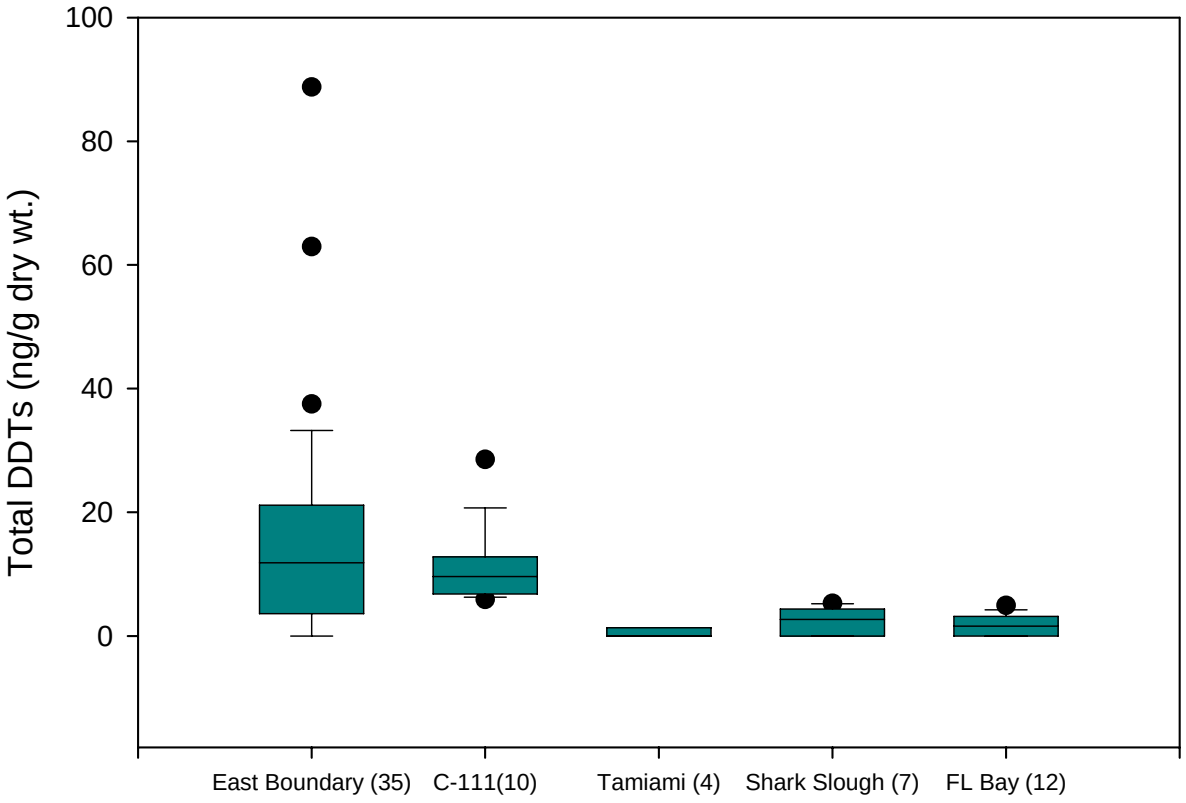


Figure 3.52.-Distribution of total DDT concentrations in fish within study area.

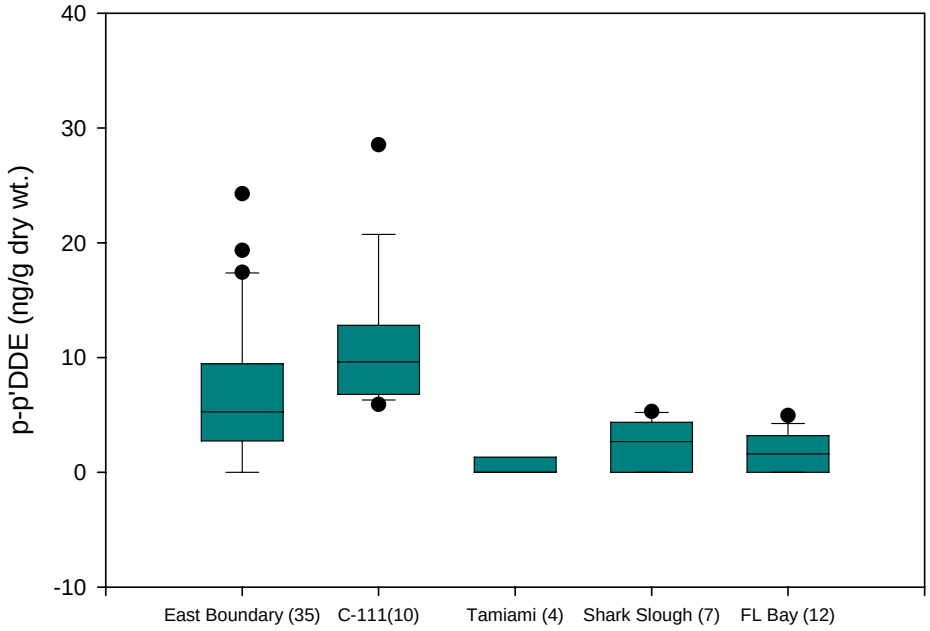


Figure 3.53.-Distribution of p-p'DDE concentrations in fish within study area.

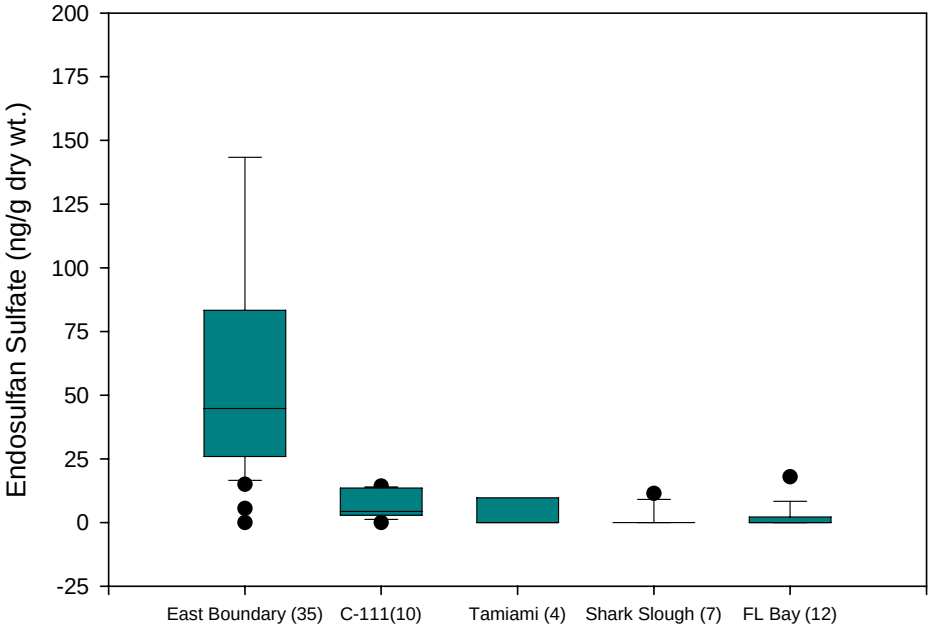


Figure 3.54.-Distribution of Endosulfan Sulfate concentrations in fish within study area.

It has been well documented that fish tissue concentrations (FTCs) can be used to estimate water concentrations using a bioconcentration factor (BCF) (Van der Oost 2003, Scott 2002, Verweij 2004). The water concentrations calculated in this fashion can then be indirectly applied to estimate if water quality criteria (WQC) have been exceeded.

$$WaterConcentration(mg/L) = \frac{FishTissueConentration(mg/Kg)}{BCF}$$

Using this formula and the established BCFs for α and β endosulfan, and endosulfan sulfate it is possible to roughly estimate the water concentrations in the areas where the fish were collected and determine if WQC were exceeded. The U.S. EPA has established Surface Water Quality Criteria for α and β endosulfan of 0.056 μg/L (56 ppt) for freshwater and 0.0087 μg/L (8.7 ppt) for marine waters, and has established BCF values for α and β endosulfan, and endosulfan sulfate of 600 (ATSDR 1991). Endosulfan sulfate, however, occurs more frequently (72% of samples) with a concentration range of up to 51.81 μg/Kg (wet weight) associated with water concentrations of up to 0.086 μg/L (86 ppt). Since no WQC have been established for endosulfan sulfate due to a lack of toxicity data on fish species (US EPA) the potential risks associated with these concentrations is difficult to assess. Nonetheless, as a comparative exercise, a spatial distribution map of estimated water concentrations of endosulfan sulfate based on tissue

residue concentrations is given in figure 3.55. It must be noted however, that the water quality criteria expressed in the figure are for α and β endosulfan, not endosulfan sulfate.

Analysis of fish samples collected from Florida Bay did not reveal the presence of α or β endosulfan. Endosulfan sulfate, on the other hand occurred in 54% of the samples with concentrations ranging from N.D. – 5.82 μg/Kg (wet weight) which correspond to estimated water concentrations of up to 0.0097 μg/L (9.7 ppt), with one station, Highway Creek barely exceeding the 8.7 ppt criteria for marine waters. NOAAs S&T Mussel Watch Program reports that three of the five highest concentrations for endosulfan in the country were detected in mussels from Florida Bay and Rookery Bay (Cantillo A.Y. et al. 1997)

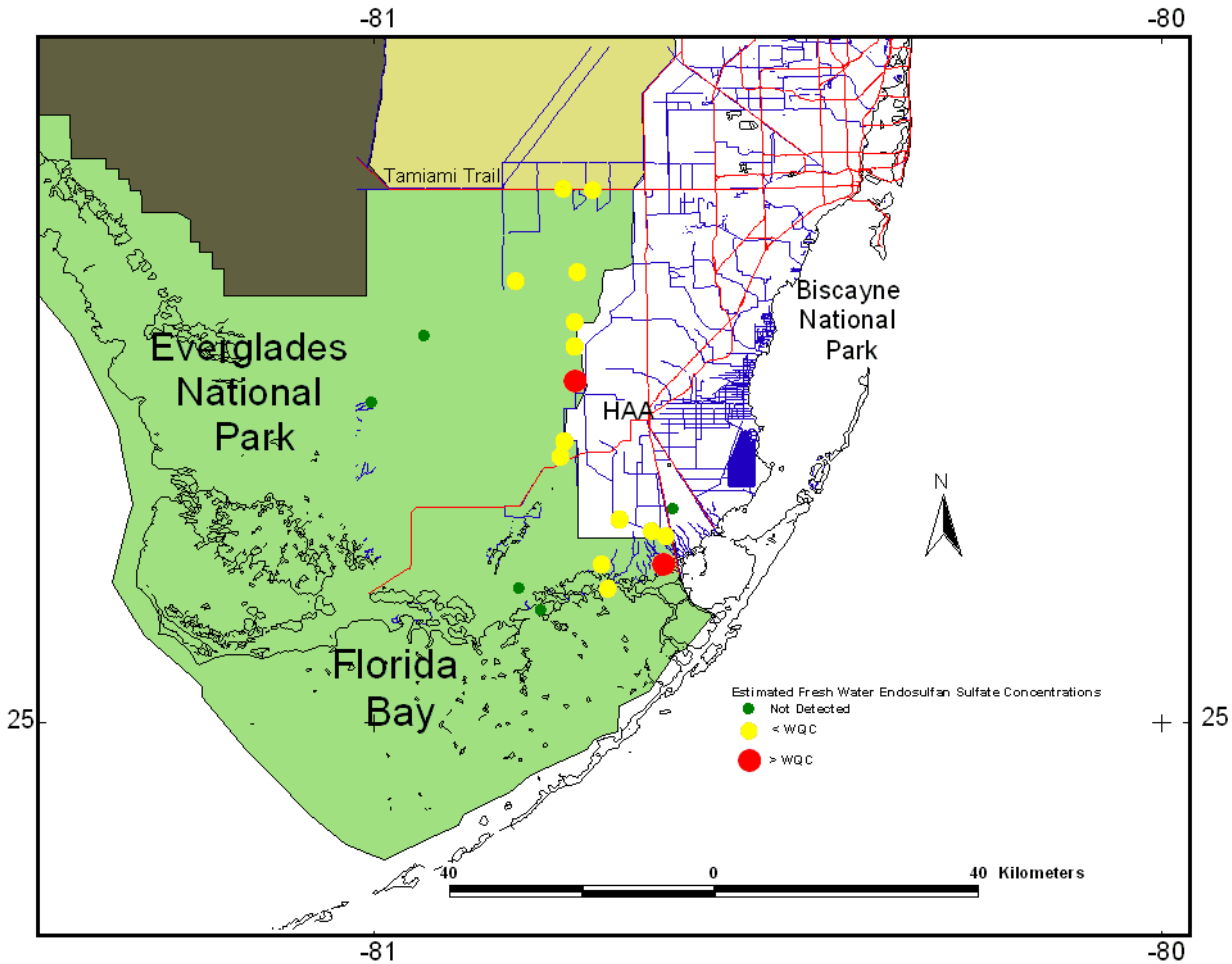


Figure 3.55.-Estimated Endosulfan sulfate water concentrations based on fish tissue concentrations.

Polychlorinated Biphenyls

The concentrations of PCBs were generally low and often at background levels. PCB distributions show less spatial variation than that of trace metals and pesticides indicating a more widespread distribution of these compounds (Figure 3.56 and 3.57). The highest PCB concentrations occur at those stations in the Eastern Boundary of Everglades National Park. Figure 3.57 shows the distribution of total PCB concentrations detected in this study. The concentrations of PCBs detected in fish (ND - 9.40 ng/g) are considerably lower than those reported for fish by Haag and McPherson (1997), (<50–140 μg/kg) in studies conducted in the 1970's and in the 1990's by the SFWMD and U.S.G.S. in various locations in South Florida.

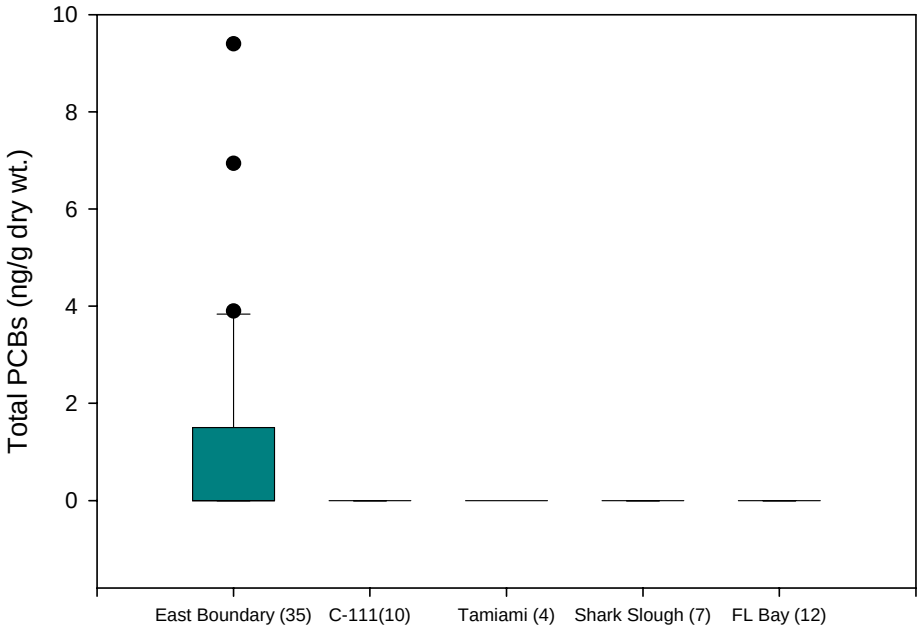


Figure 3.56.-Distribution of Total PCB concentrations in fish within study area.

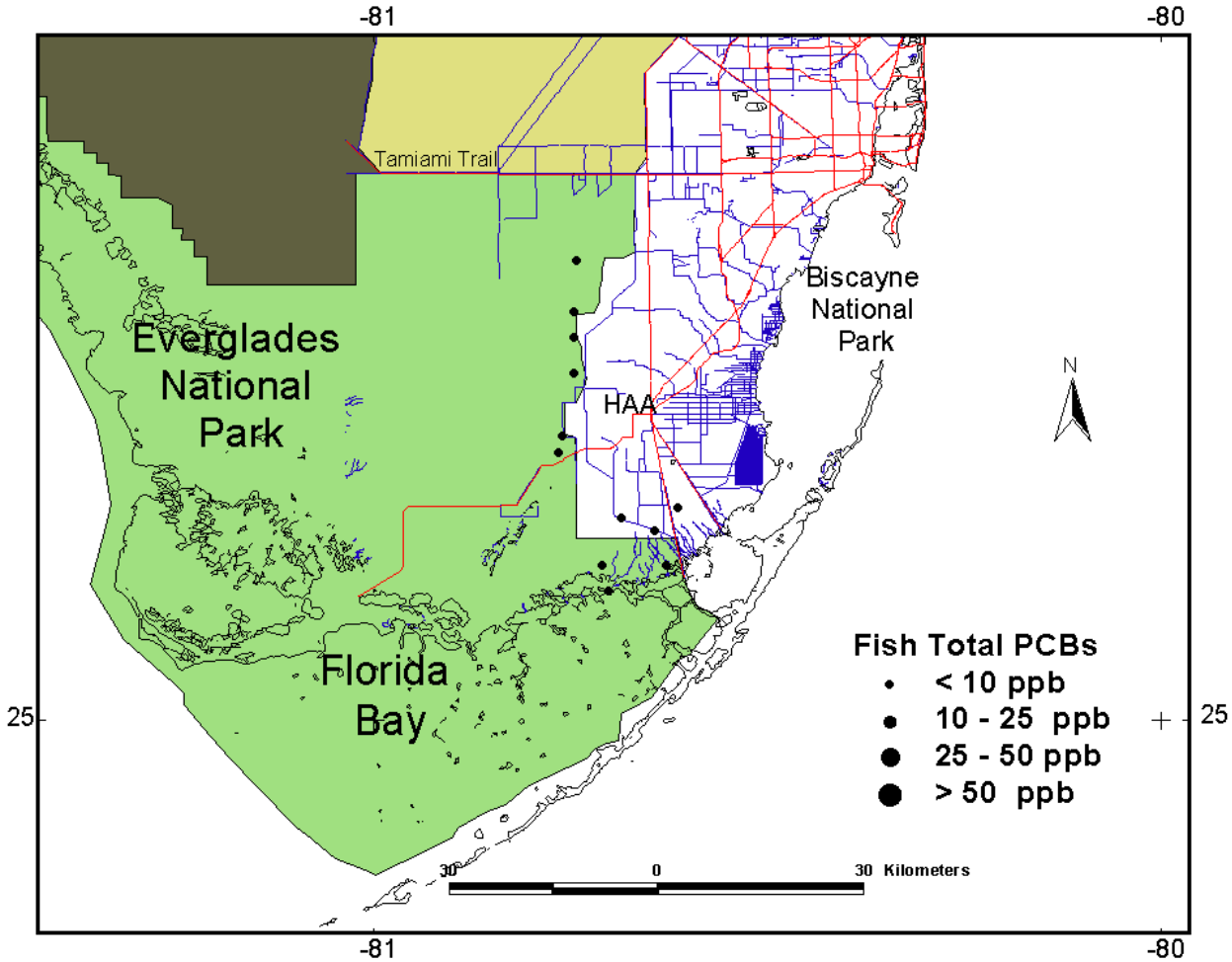


Figure 3.57.-Spatial distribution of total PCBs detected in fish tissue samples.

Polycyclic Aromatic Hydrocarbons

PAHs detected in fish include low molecular weight (LMW) PAHs such as naphthalene, biphenyl, 2-methylnapthalene, phenanthrene, and 1-methylnapthalene, high molecular weight (HMW) PAHs detected in fish samples include benzo[a]anthracene, flouranthene, and chrysene. Total PAH concentrations detected in fish tissues samples are relatively low (4.04 – 779 ng/g dry wt.) probably because fish tend to metabolize these compounds easily via phase I enzymes of the mixed function oxygenase system (Van der Oost, 2003). These concentrations detected do not indicate a significant hazard to the aquatic environment, and are at least an order of magnitude lower than those detected in edible fish tissue in samples collected from New York Bight and Long Island Sound (Kennish, 1997).

Figure 3.58 shows the spatial distribution of PAH concentrations detected in fish tissue samples, indicating a trend similar to that found in sediments with the highest concentrations being found at those stations closest to Tamiami Trail and the HAA again, probably resulting from street runoff. Figure 3.59 shows the distribution of total PAH concentrations in fish samples within the study area

Trace Elements in Whole Fish Tissue Samples

Eleven elements (Be, V, Cr, Co, Ni, Cu, Zn, As, Cd, Pb, and Ag) were chosen for analysis. Figures xx - yy show the spatial distribution of selected trace metals detected in fish samples collected throughout the park. A trend in the distribution of trace elements within the park is apparent for most trace elements (beryllium, vanadium, chromium, cobalt, nickel, copper, cadmium and lead), with the highest concentrations detected along

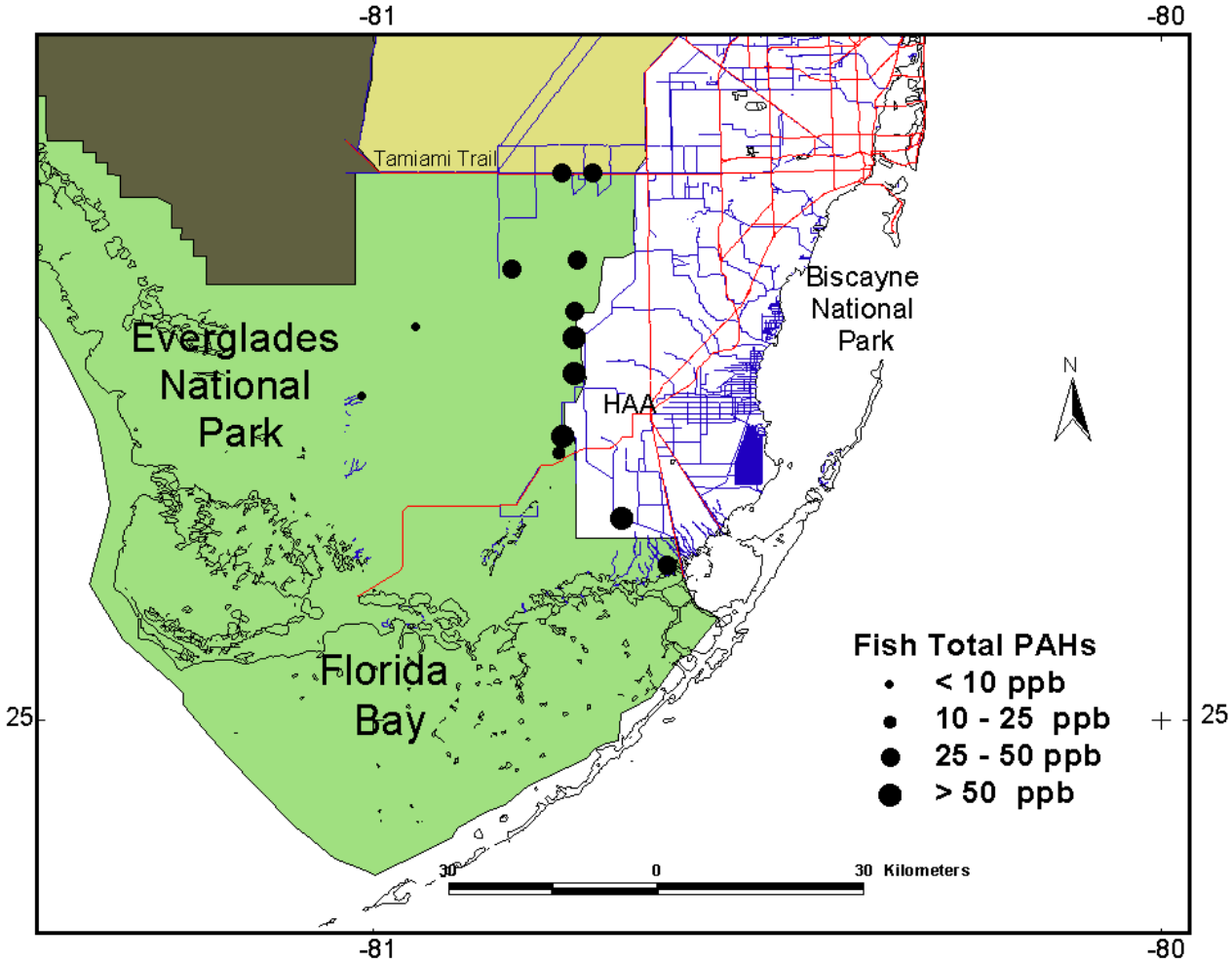


Figure 3.58.-Spatial distribution of total PAHs detected in fish tissue.

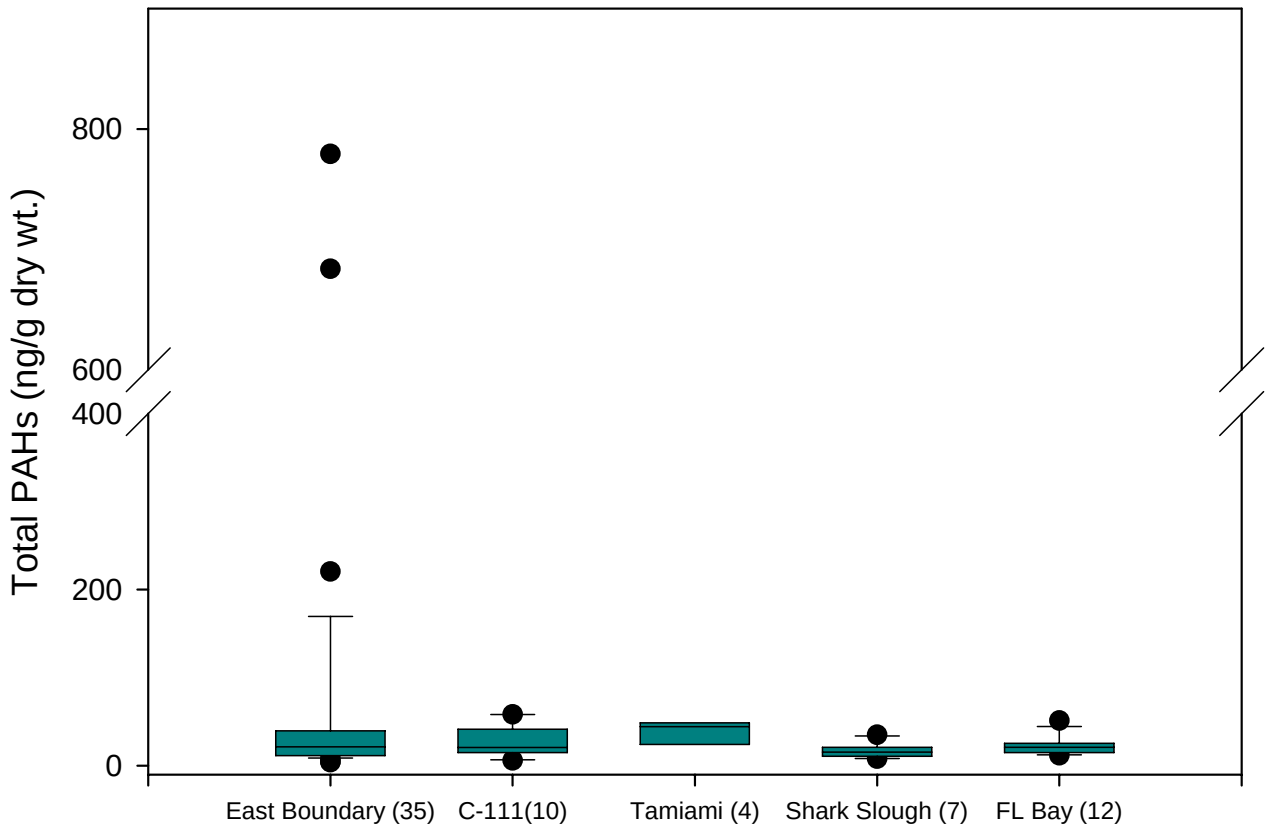


Figure 3.59.-Distribution of total PAHs in fish tissue within study area.

the eastern boundary of the park an area in close proximity to the HAA and the C-111 canal. . The highest concentrations of arsenic were detected at stations in Florida Bay, and the C-111 canal. The highest concentrations of silver were detected in fish samples from the C-111 canal and the east boundary of ENP. Zinc concentrations were in the range of 30.6 – 245 ppm, which is consistent with values reported for fish in uncontaminated areas (Barwick 2003, Papagiannis 2004), concentrations detected are relatively evenly distributed throughout the study area. Comparisons of the concentration distributions of trace elements in whole fish tissue are given in figures 3.60 – 3.80.

Lewis and coworkers (2002) analyzed fish in near coastal areas of the Gulf of Mexico for metals including arsenic, copper, and zinc. A comparison of the values they obtained reveals higher concentrations of arsenic (< 0.01 – 28.41 μg/g wet wt.), but lower values were reported for copper and zinc (0.07 - 0.34 and 2.86 – 10.57 μg/g wet wt.), than those detected in this study. Concentrations of zinc, arsenic, and cadmium detected in fish in this study were below the maximum concentrations detected in fish samples collected from the Mississippi River Basin as part of the USGS Biomonitoring of Environmental Status and Trends (BEST) Program. However, elements like lead and copper were found to be above their reported maxima for stations 22 and L-67 (Schmitt, 2002).

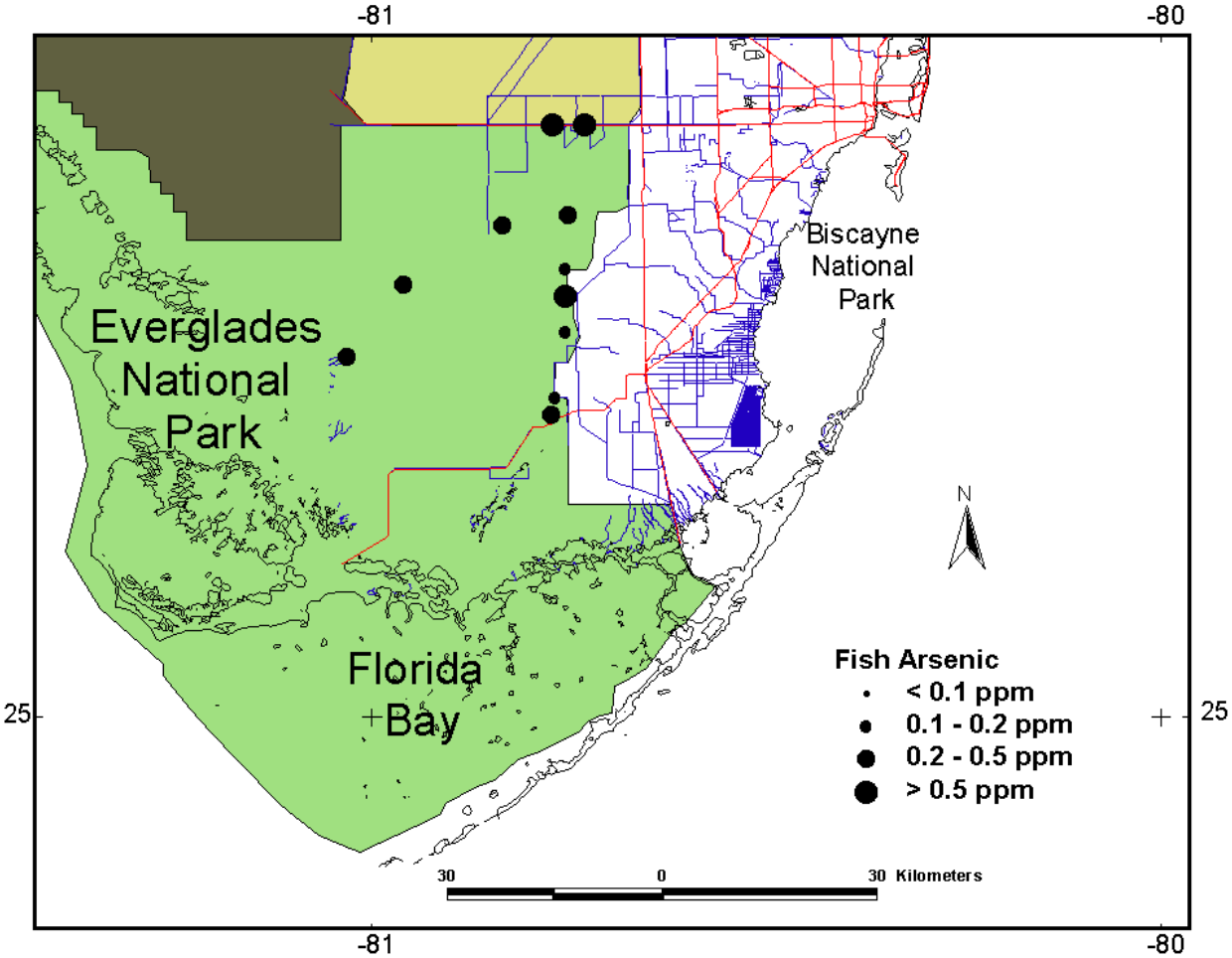


Figure 3.60.-Spatial distribution of arsenic in whole fish tissue.

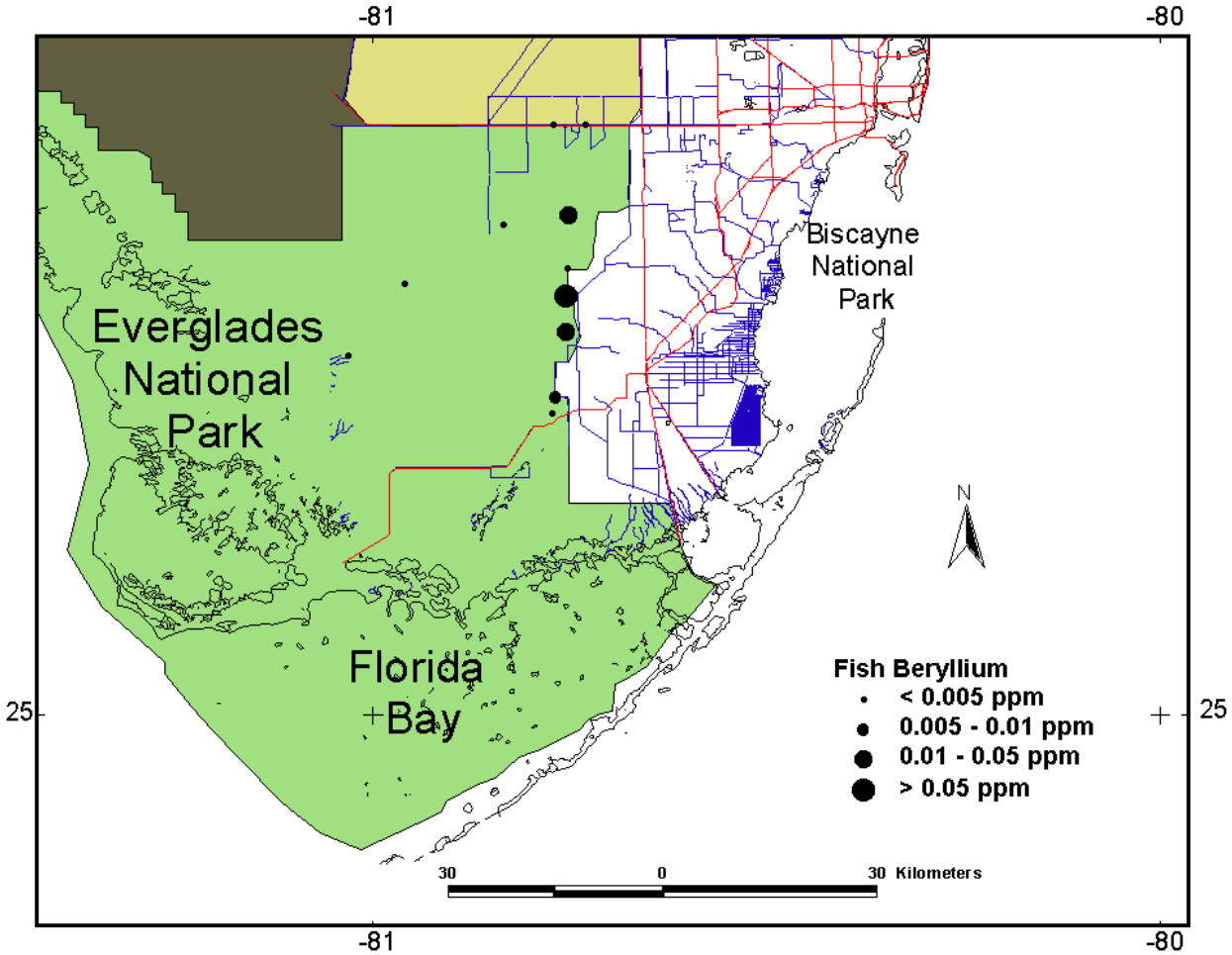


Figure 3.61.-Spatial distribution of beryllium in whole fish tissue.

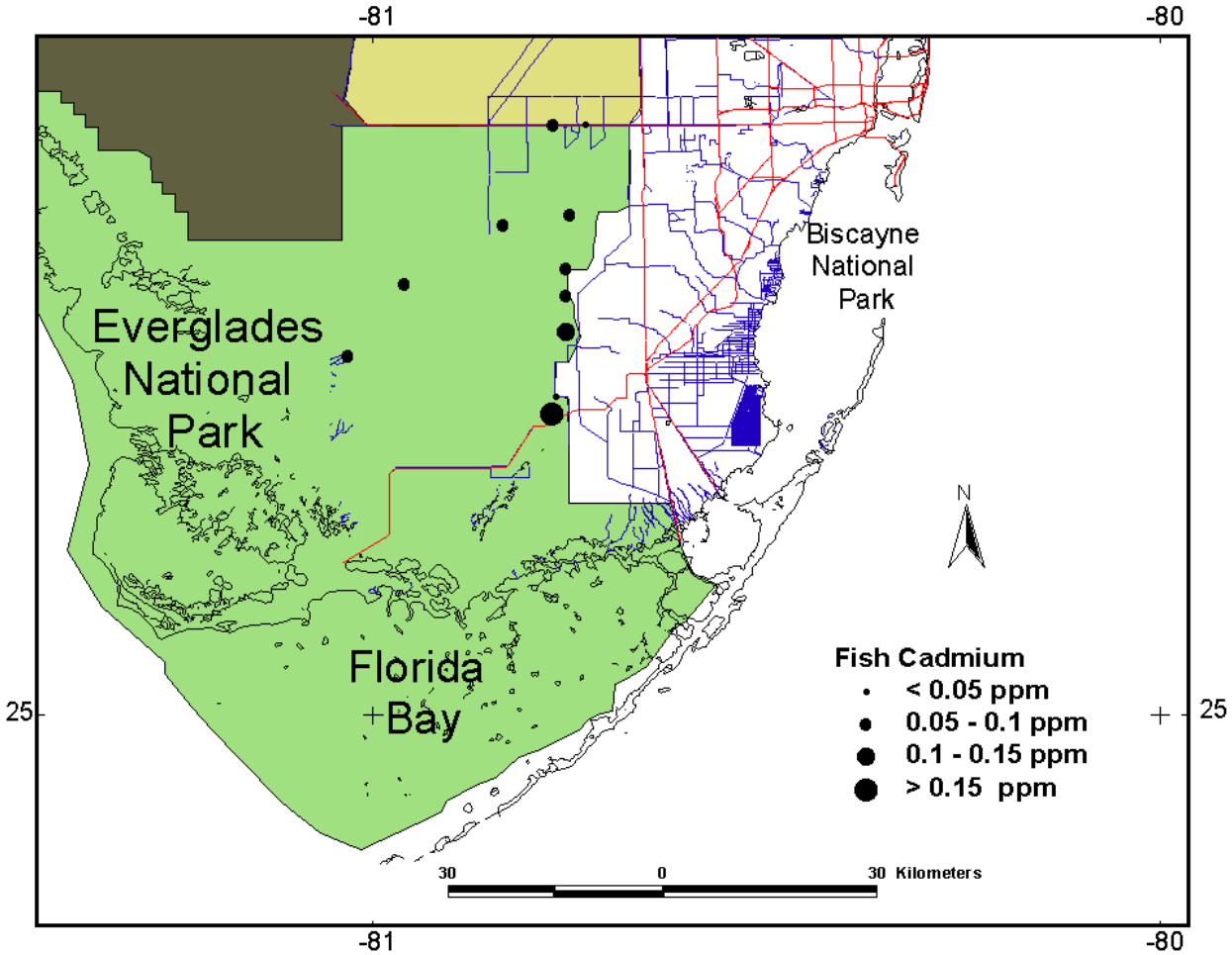


Figure 3.62.-Spatial distribution of cadmium in whole fish tissue.

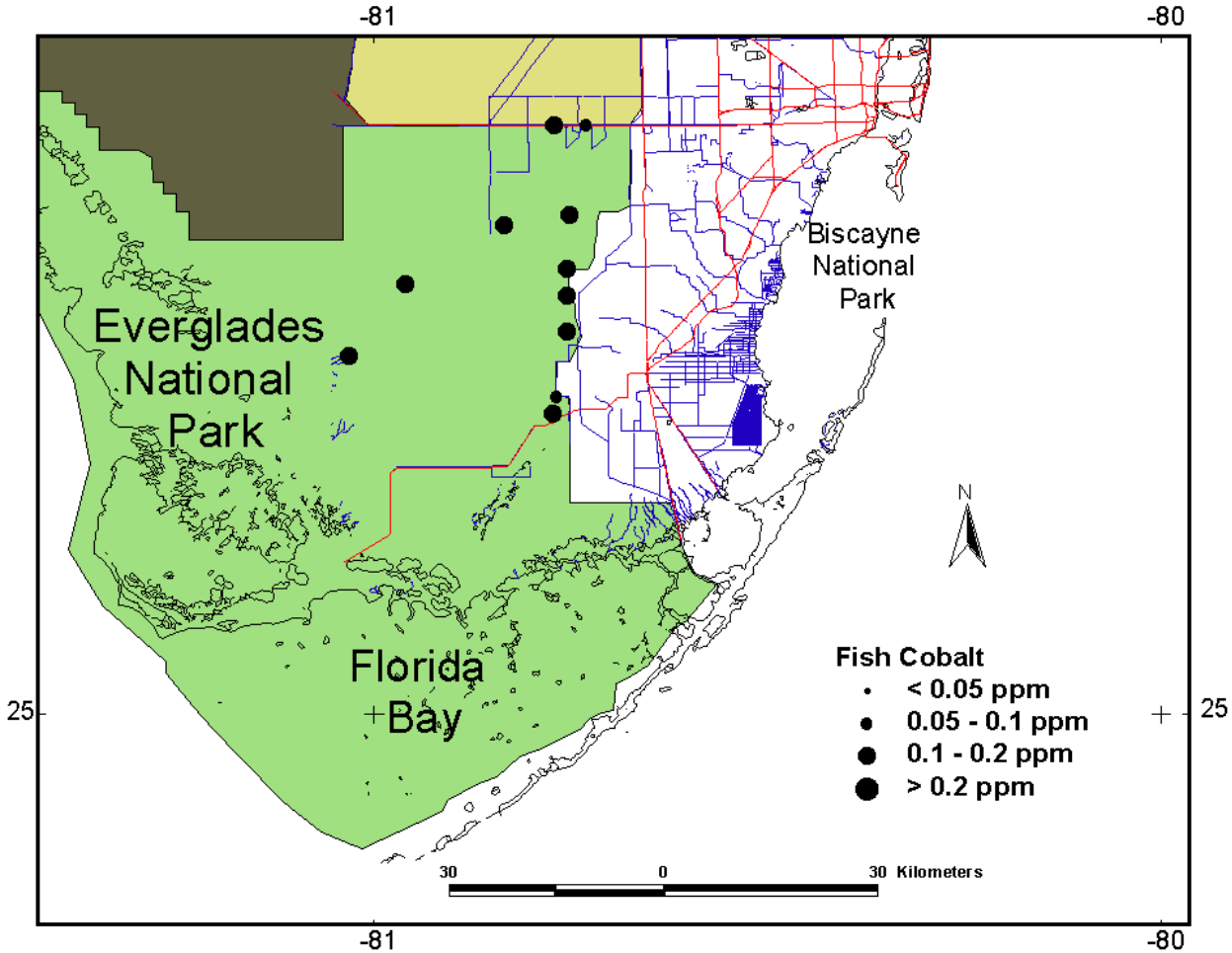


Figure 3.63.-Spatial distribution of cobalt in whole fish tissue.

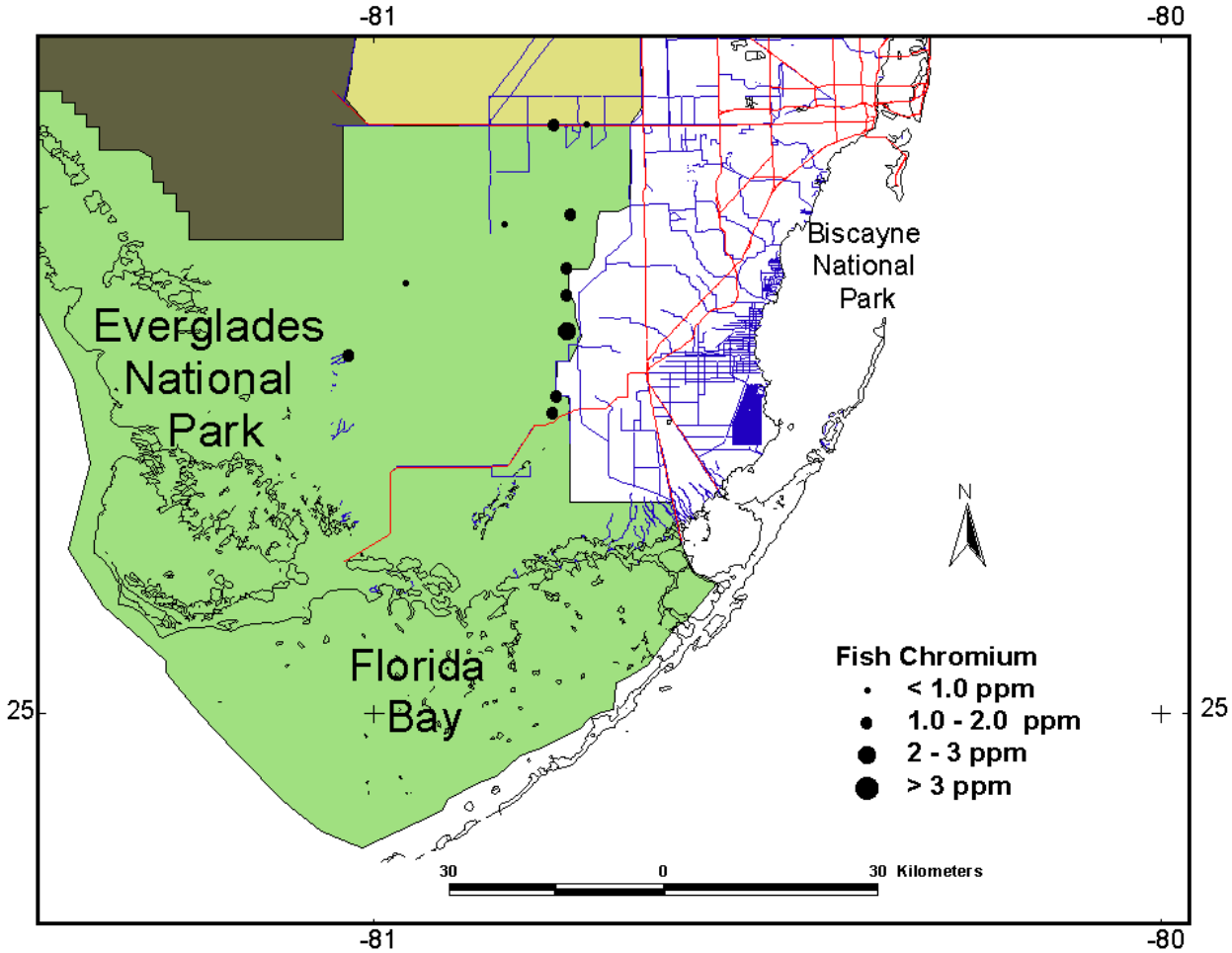


Figure 3.64.-Spatial distribution of chromium in whole fish tissue.

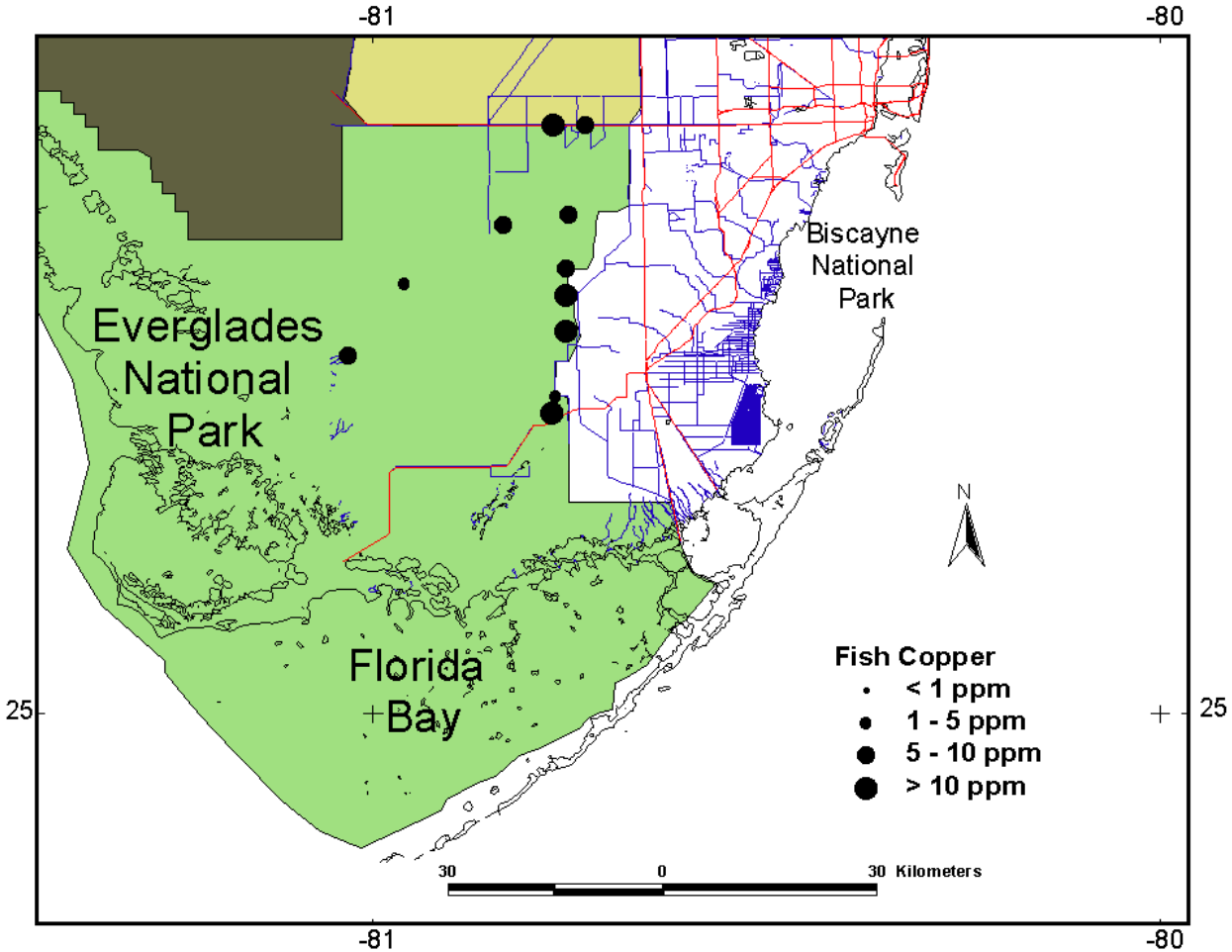


Figure 3.65.-Spatial distribution of copper in whole fish tissue.

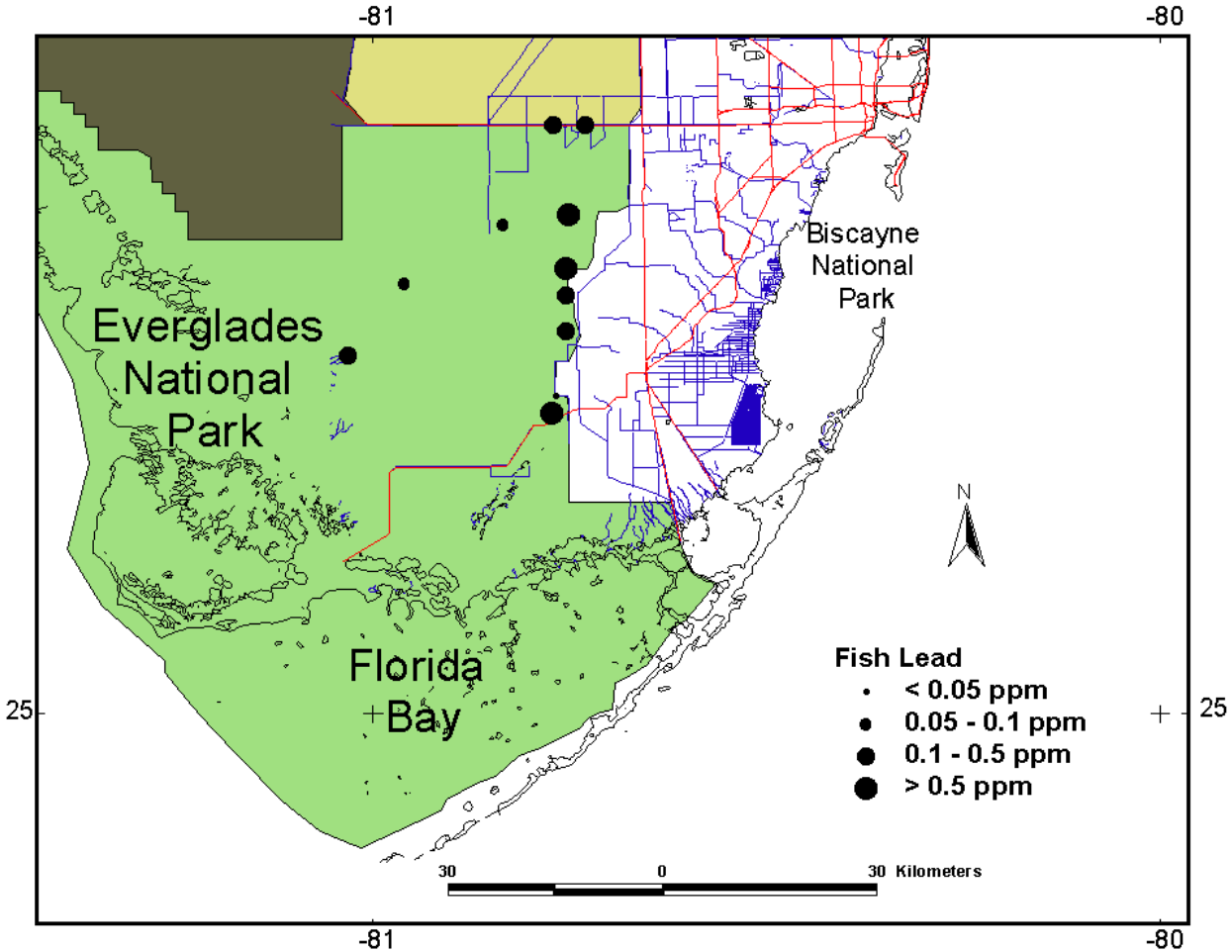


Figure 3.66.-Spatial distribution of lead in whole fish tissue.

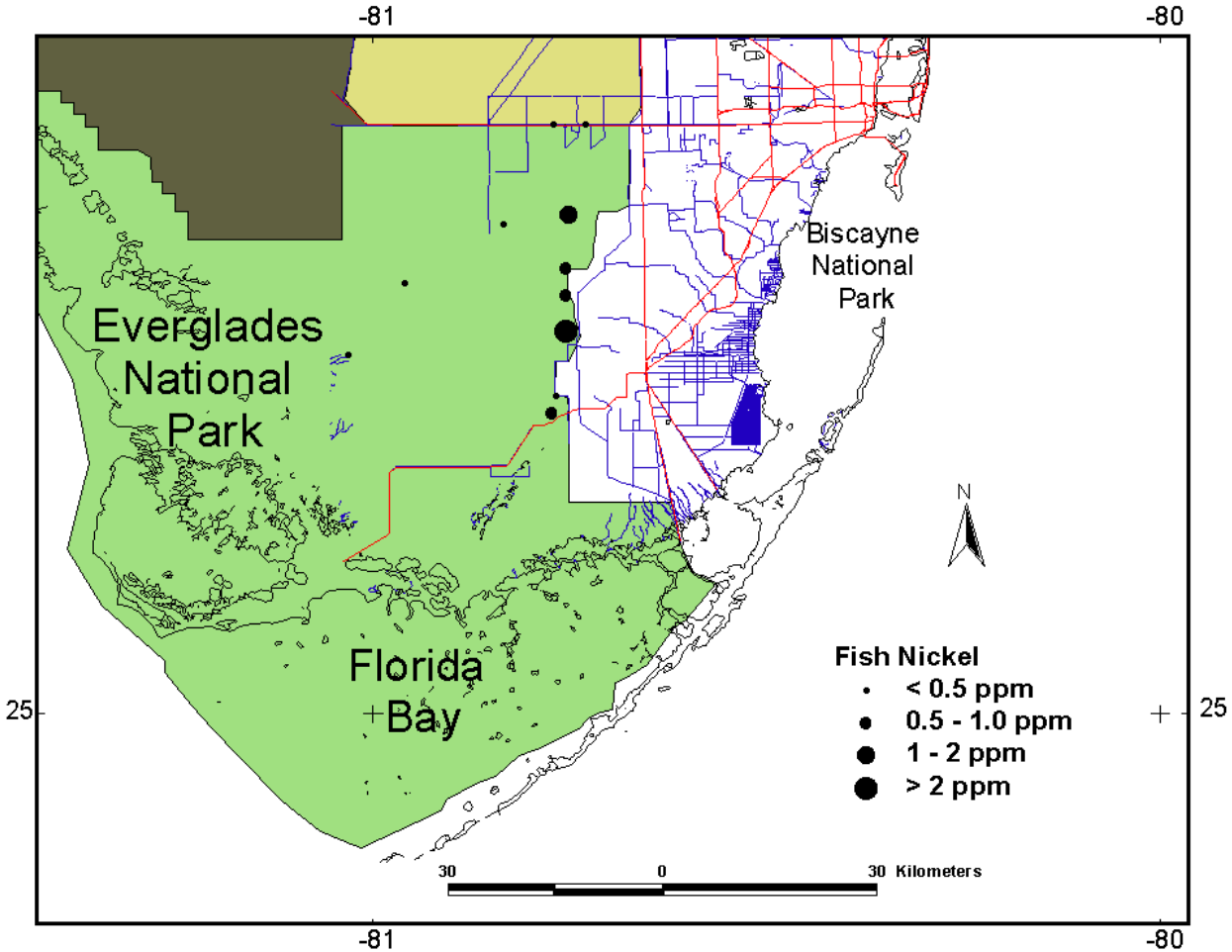


Figure 3.67.-Spatial distribution of nickel in whole fish tissue.

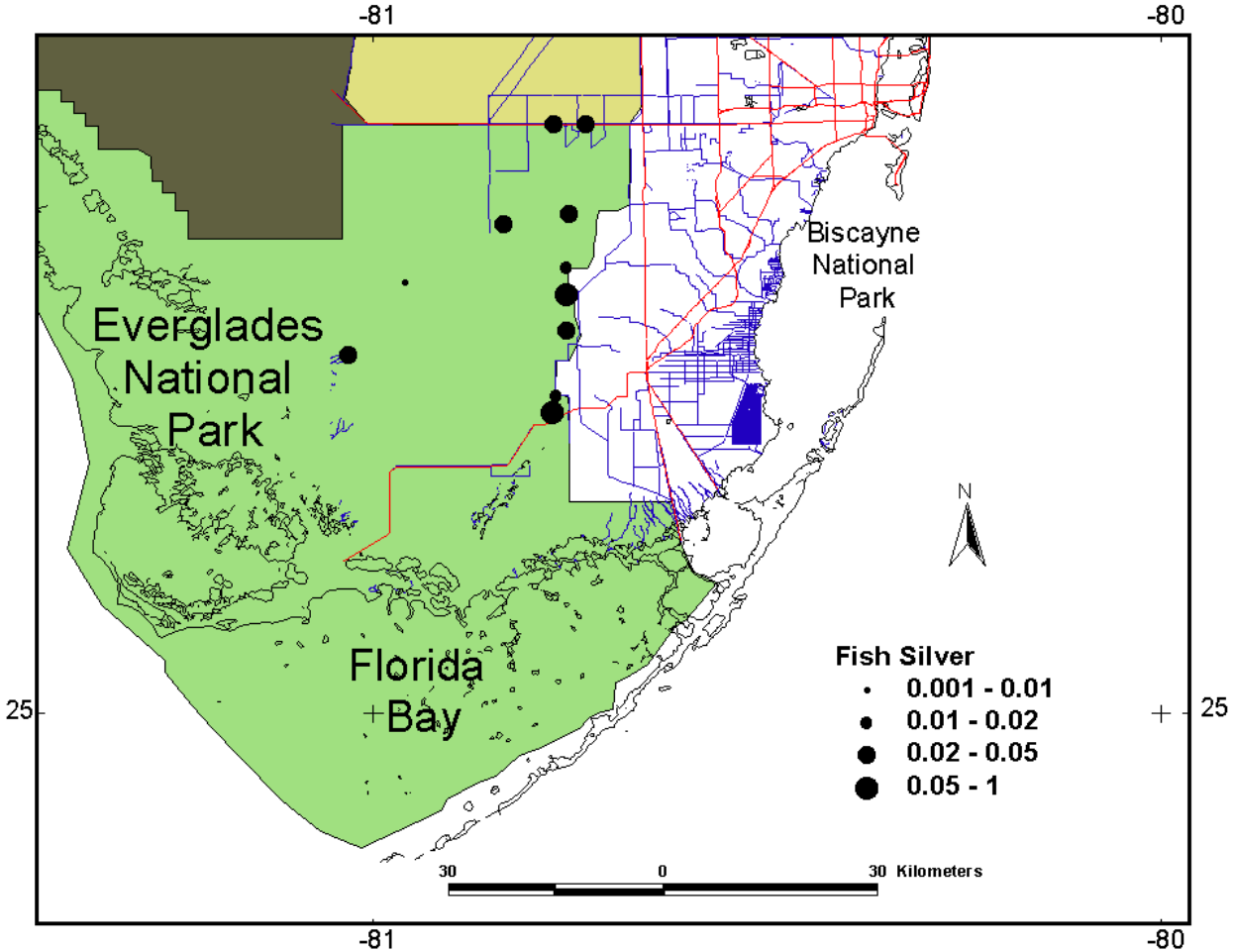


Figure 3.68.-Spatial distribution of silver in whole fish tissue.

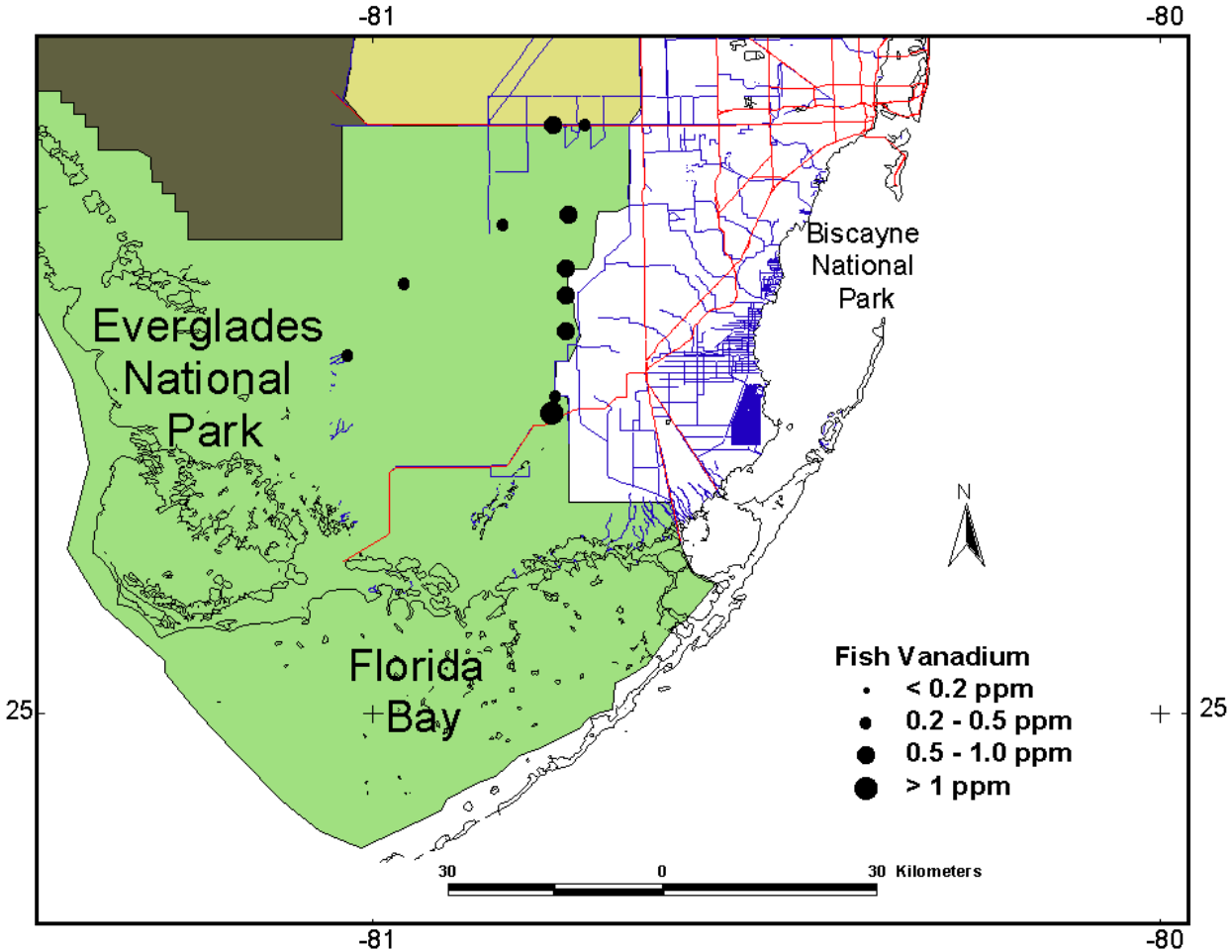


Figure 3.69.-Spatial distribution of vanadium in whole fish tissue.

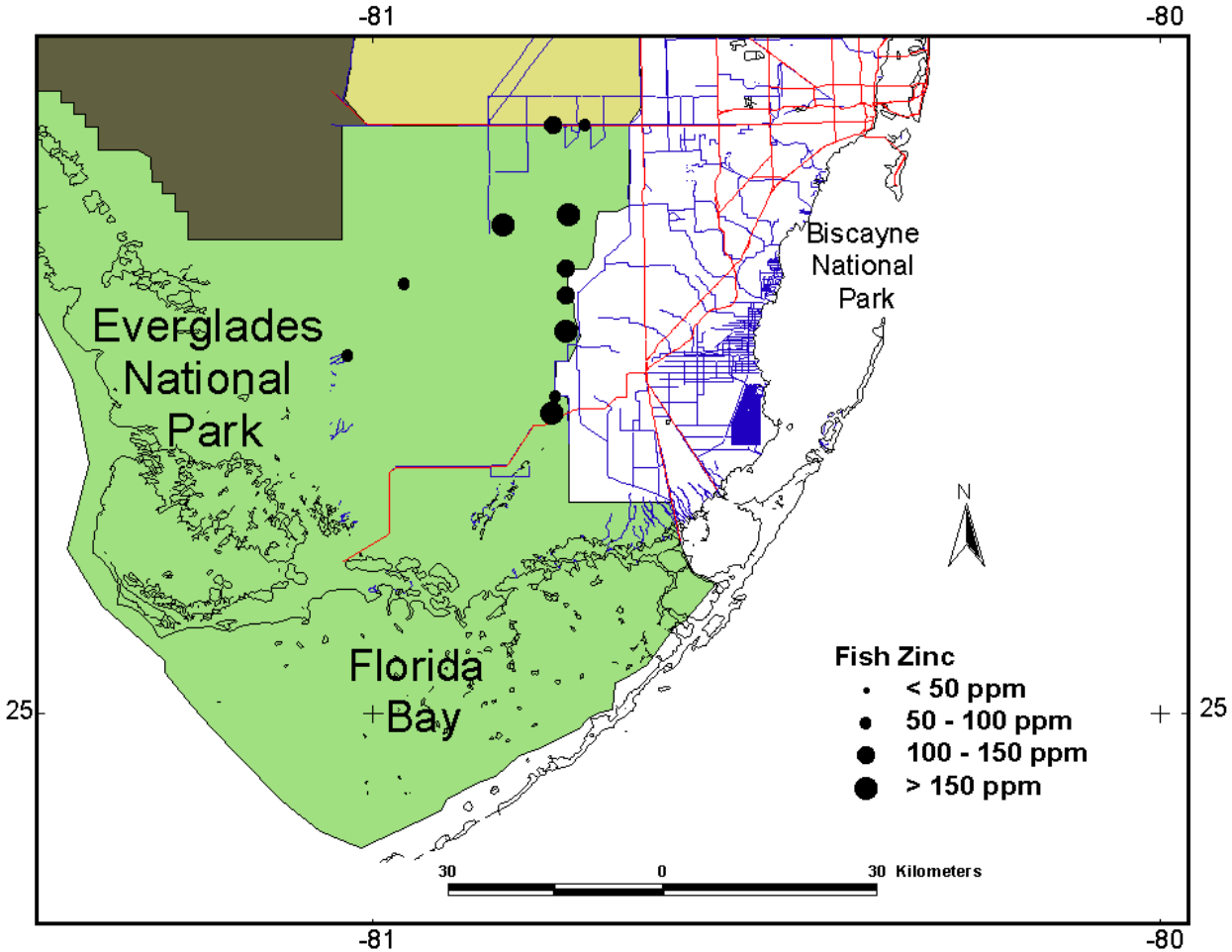


Figure 3.70.-Spatial distribution of zinc in whole fish tissue.

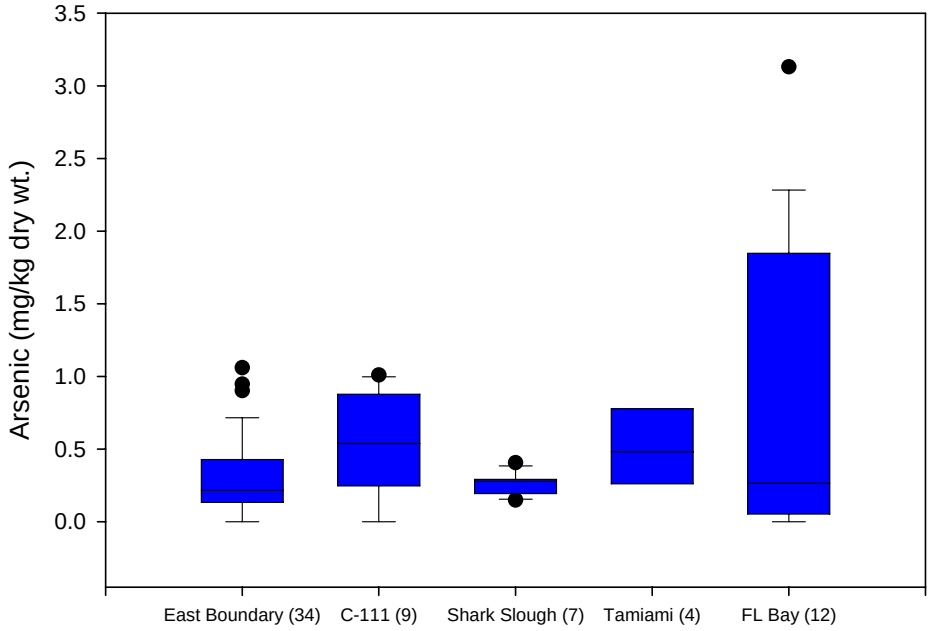


Figure 3.71.-Distribution of arsenic in fish within study area.

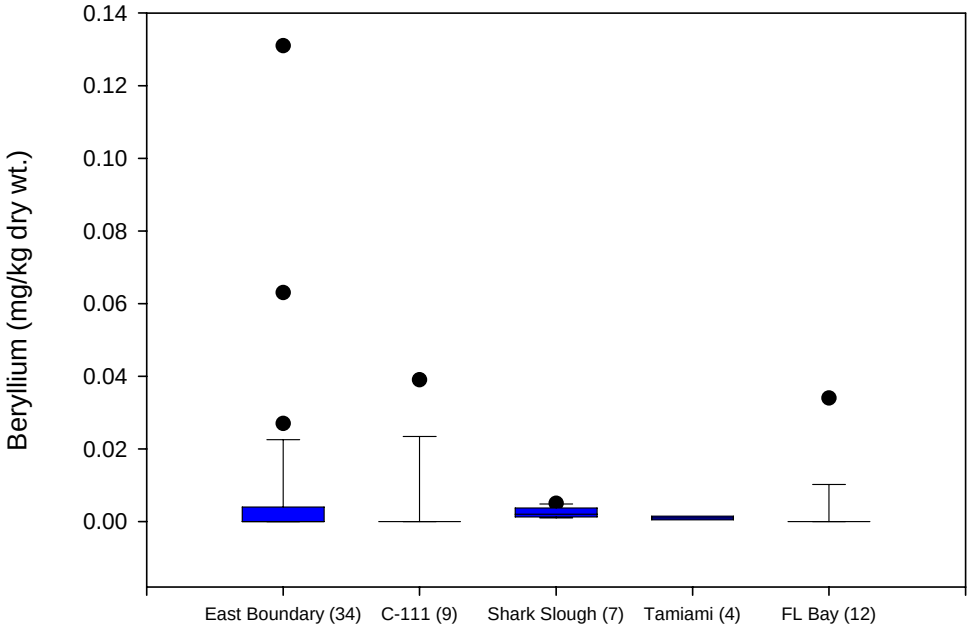


Figure 3.72.-Distribution of beryllium in fish within study area.

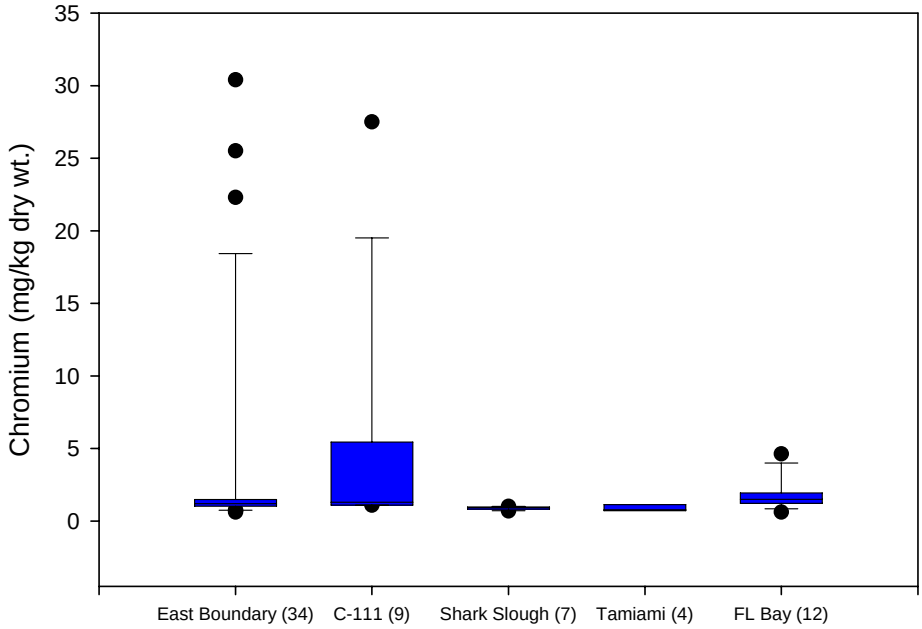


Figure 3.73.-Distribution of chromium in fish within study area.

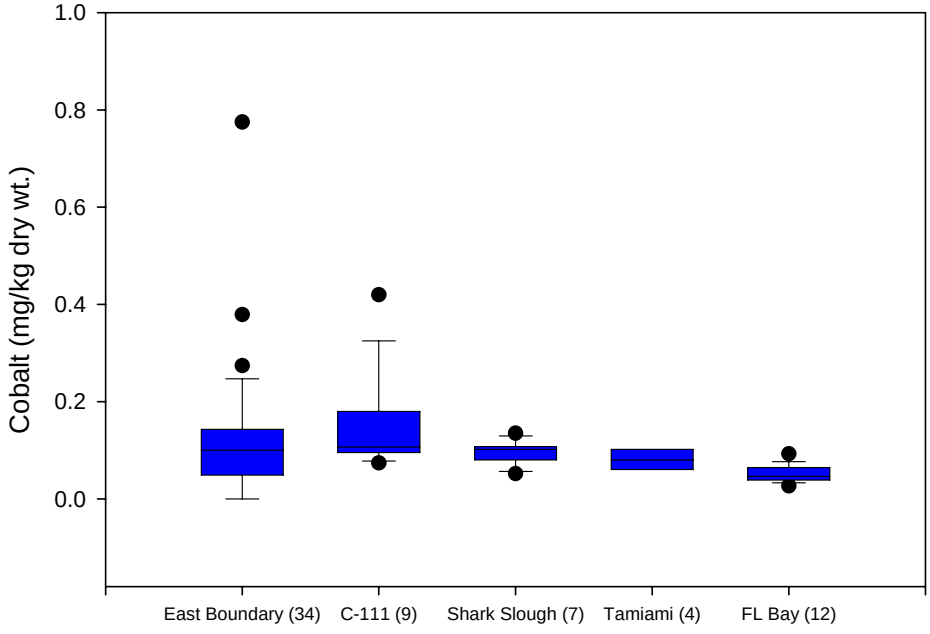


Figure 3.74.-Distribution of cobalt in fish within study area.

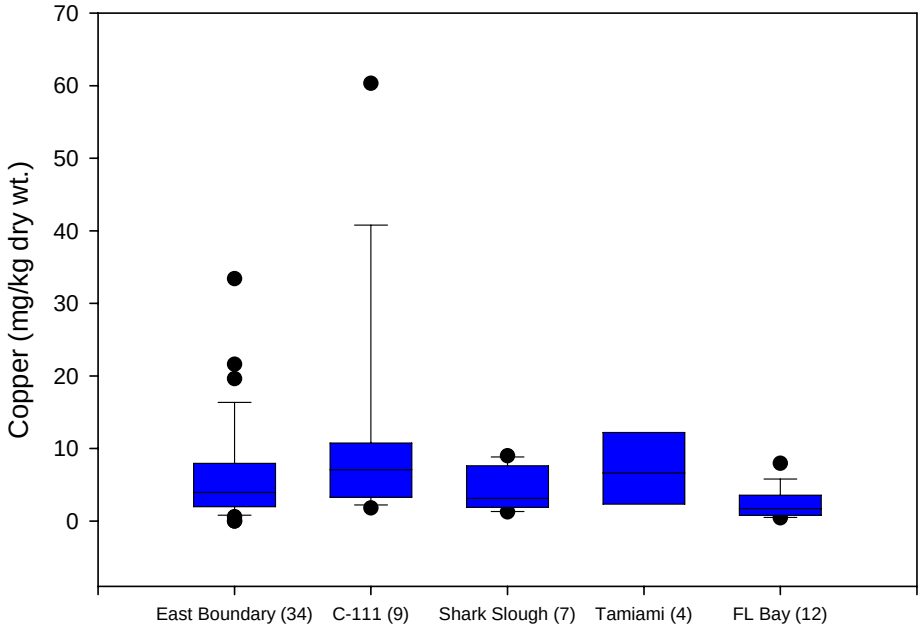


Figure 3.75.-Distribution of copper in fish within study area.

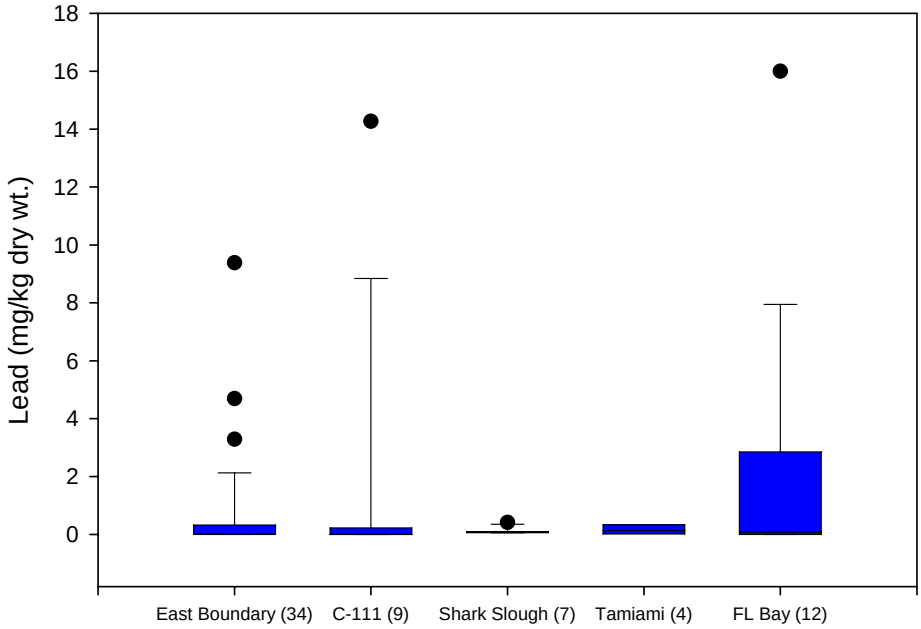


Figure 3.76.-Distribution of lead in fish within study area.

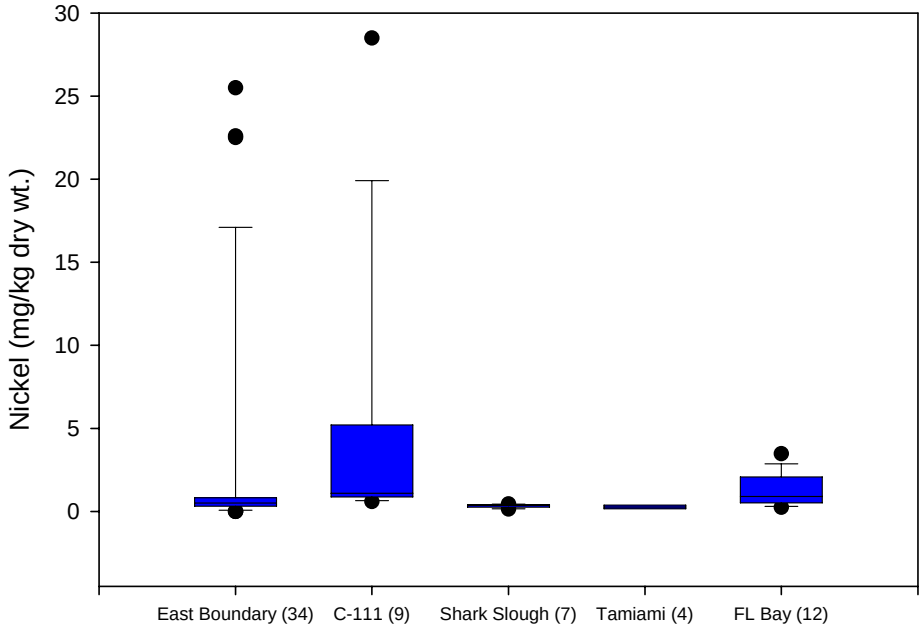


Figure 3.77.-Distribution of nickel in fish within study area.

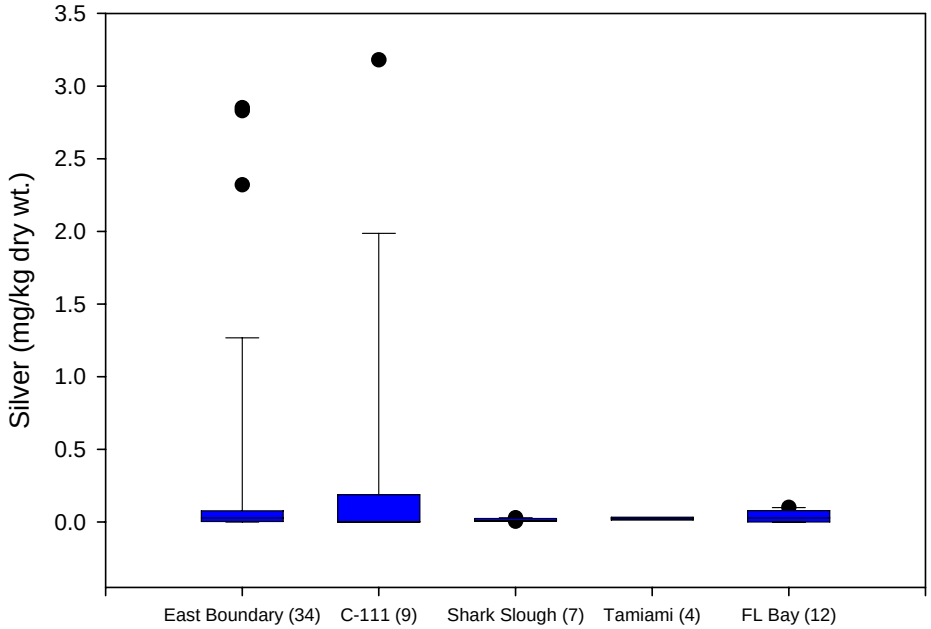


Figure 3.78.-Distribution of silver in fish within study area.

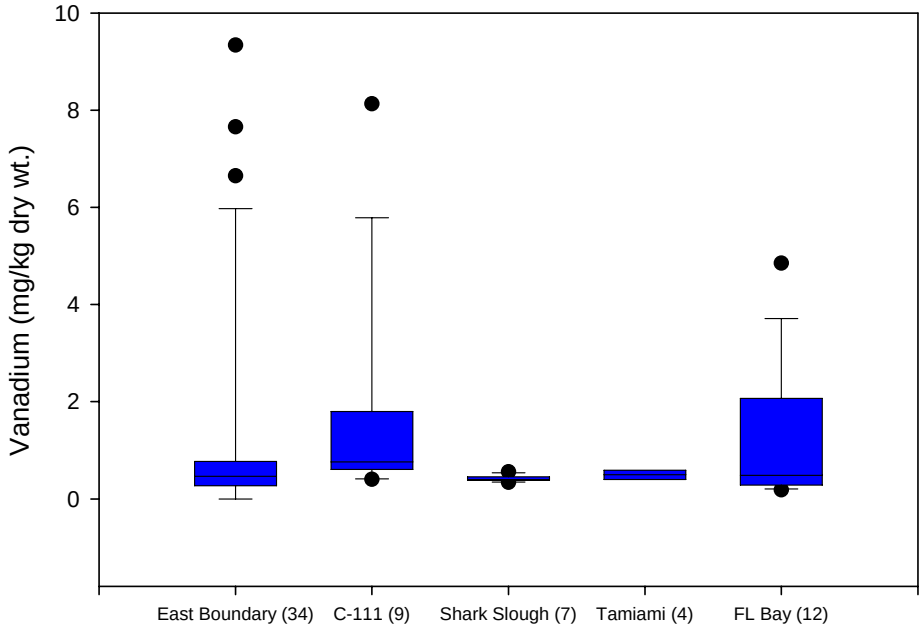


Figure 3.79.-Distribution of vanadium in fish within study area.

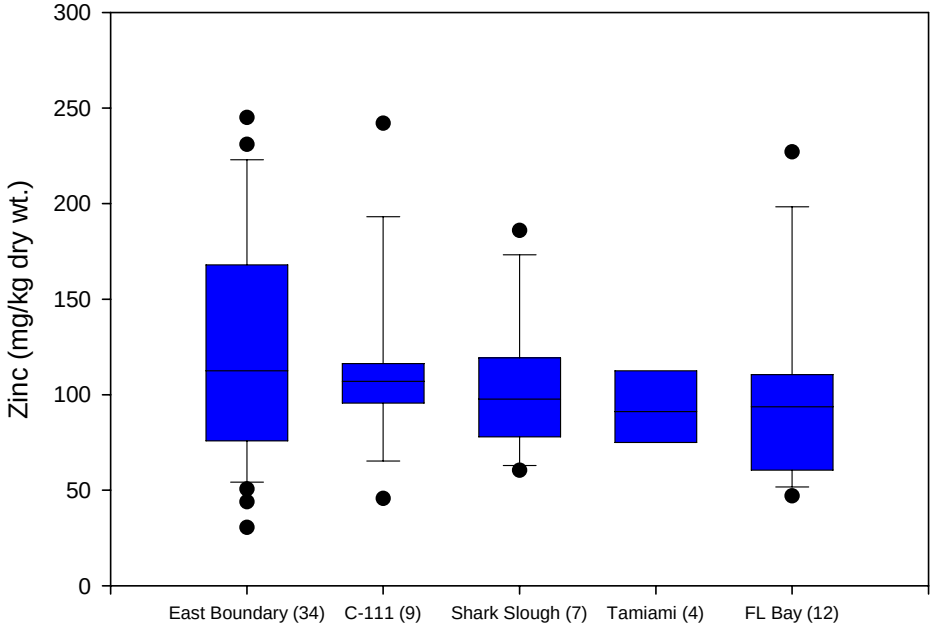


Figure 3.80.-Distribution of zinc in fish wthin study area.

Triazines Herbicides

The possibility to analyze both, triazine parent compounds and metabolites in a single run at very low concentration was explored by analyzing the same sampling sites surveyed for the occurrence of phenoxy acid herbicides. Nevertheless, none of the analytes of interest or the metabolites were found at concentrations above the method detection limit for some sampling sites as shown in table 3.5. These results were corroborated quantifying the same samples using a GC/MS instrument. The comparison was performed using a previously optimized with GC/MS method, which detection limits were similar to the obtained by LC/MS.

Both chromatographic methods, GC/MS and LC/MS, offered good analytical performance for the analysis of complex matrices, providing good precision, good accuracy and good detection limits. However, APCI LC-MS provides the added advantage of detecting also important metabolites like DIA and DEA, offering a good alternative for the screening and quantification of these analytes at very low concentrations in sediments and can also be applied to other environmental matrices such as water.

Table 3.5: Summary of results for Triazine herbicides in selected samples from ENP.

ID	DIA	DEA	Atratone	Prometon	Simetryn	Simazine	Atrazine	Ametryn	Prometryn	Terbutryn	Propazine	Terbutylazine
A-21	*	*	*	*	*	*	*	*	*	*	*	*
A-22	*	*	*	*	*	*	*	*	*	*	*	*
A-23	*	*	*	*	*	*	*	*	*	*	*	*
A-24	*	*	*	*	*	*	*	*	*	*	*	*
L-67-S	*	*	*	*	*	*	*	*	*	*	*	*
A-07	*	*	*	*	*	*	*	*	*	*	*	*
A-53	*	*	*	*	*	*	*	*	*	*	*	*
A-54	*	*	*	*	*	*	*	*	*	*	*	*
A-57	*	*	*	*	*	*	*	*	*	*	*	*
A-58	*	*	*	*	*	*	*	*	*	*	*	*
A-59	*	*	*	*	*	*	*	*	*	*	*	*
A-63	*	*	*	*	*	*	*	*	*	*	*	*

* below MDL

Phenoxy-acid herbicides

Sediments from Everglades and Biscayne Bay National Parks in Florida were also analyzed to assess the presence of these polar herbicides (see Figure 2.17 for details). The proposed method was applied to 30 different sampling sites. As was stated previously, the combination of ASE and SPE not only reduced the time of analysis but also proved to work efficiently even in samples with high content of organic matter. Due to the SPE advantages and the nature and characteristics of the sediment from the Everglades and Biscayne National Parks, solid phase extraction (SPE) is probably the best method available for simultaneously carrying fractionation and concentration of the studied organic contaminants.

Among the different compounds studied, only mecoprop was found above the method detection limit at sampling sites BBP2, 53 and 58 as shown in table 3.6. The ranges of concentration for this compound were from 12 ng/g (BBP2) to 89 ng/g (ENP-53). Figure 3.81 shows one of the chromatogram for a positive identification of mecroprop in sample ENP-53. This chromatogram shows the effectiveness of the proposed methodology for clean up and detection capabilities of the mass spectrometer even for complex matrices.

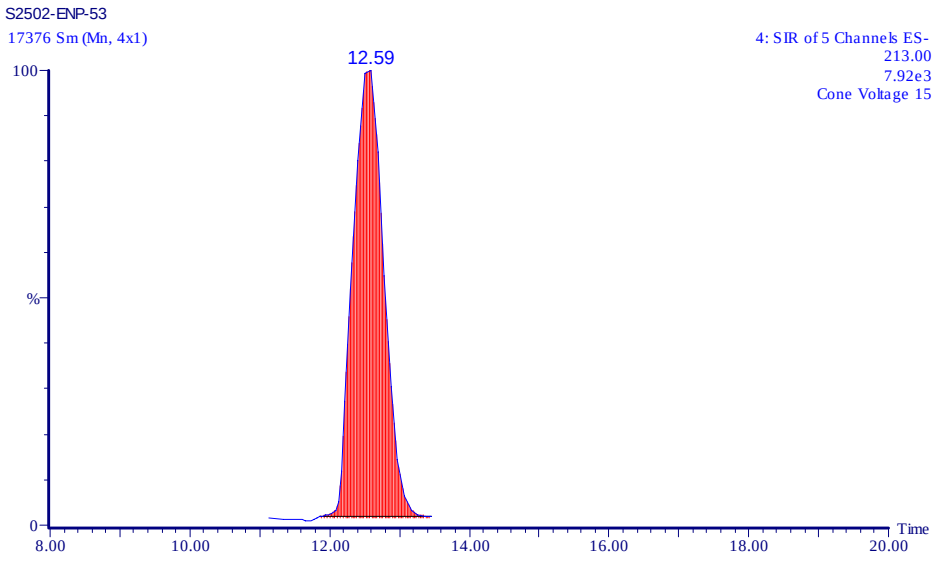


Figure 1:Extracted chromatogram for Mecoprop in sample ENP-53

ID	Picloram	Bentazon	Dicamba	MCPA	2,4-D	Mecoprop	Dichlorprop	2,4-DB	2,4,5-T	Silvex	Acifluorfen	Dinoseb
BBICS	*	*	*	*	*	*	*	*	*	*	*	*
BBMM	*	*	*	*	*	*	*	*	*	*	*	*
BBSK	*	*	*	*	*	*	*	*	*	*	*	*
BBP2	*	*	*	*	*	12.3	*	*	*	*	*	*
BBP1	*	*	*	*	*	*	*	*	*	*	*	*
BBCP	*	*	*	*	*	*	*	*	*	*	*	*
BBFP	*	*	*	*	*	*	*	*	*	*	*	*
BBEKH	*	*	*	*	*	*	*	*	*	*	*	*
BBTPC	*	*	*	*	*	*	*	*	*	*	*	*
332-BB	*	*	*	*	*	*	*	*	*	*	*	*
332-BAC	*	*	*	*	*	*	*	*	*	*	*	*
A-22	*	*	*	*	*	*	*	*	*	*	*	*
A-23	*	*	*	*	*	*	*	*	*	*	*	*
A-24	*	*	*	*	*	*	*	*	*	*	*	*
A-37	*	*	*	*	*	*	*	*	*	*	*	*
MDA	*	*	*	*	*	*	*	*	*	*	*	*
L-67-S	*	*	*	*	*	*	*	*	*	*	*	*
A-07	*	*	*	*	*	*	*	*	*	*	*	*
R-158	*	*	*	*	*	*	*	*	*	*	*	*
50-A	*	*	*	*	*	*	*	*	*	*	*	*
A-53	*	*	*	*	*	89.2	*	*	*	*	*	*
A-54	*	*	*	*	*	*	*	*	*	*	*	*
A-55	*	*	*	*	*	*	*	*	*	*	*	*
A-58	*	*	*	*	*	20.0	*	*	*	*	*	*
A-59	*	*	*	*	*	*	*	*	*	*	*	*
A-60	*	*	*	*	*	*	*	*	*	*	*	*
A-61	*	*	*	*	*	*	*	*	*	*	*	*
A-63	*	*	*	*	*	*	*	*	*	*	*	*
64-SD	*	*	*	*	*	*	*	*	*	*	*	*

* below MDL

Table 3.6 : Summary of samples analyzed for phenoxy acid herbicides within ENP and BBNP. Concentrations in (ng/g).

CONCLUSIONS

From the data obtained during the course of this study one key conclusion can be drawn: the concentrations of contaminants in both sediment and fish tissue surveyed in this study from Everglades National Park, Biscayne National Park, and Florida Bay, are low in comparison to impacted areas and similar to those found in pristine areas (Kennish 1997). However, it appears that anthropogenic activities have resulted in the enrichment of certain contaminants at various locations throughout the study area. Compounds of particular concern, based on the observed concentrations and environmental assessment guidelines, include: lead, chromium, arsenic, nickel, and DDT and its metabolites. Arsenic, lead, and chromium exceeded PEL criteria in 9, 5, and 5% of the ENP sediment samples and exceeded TEL criteria in 32, 14 and 27% of the samples respectively. Nickel exceeded the TEL criteria in 5% of the ENP sample stations. Arsenic exceeded TEL levels in 44% of the BNP sediment samples. Dieldrin, p-p'DDT, and p-p'DDD all exceeded TEL criteria in 5% of the samples analyzed while p-p'DDE exceeded the TEL in 14% of the sediment samples respectively. PCB and PAH concentrations were generally low, and only one station in BNP exceeded the TEL for total PCBs. Other contaminants such as triazine based herbicides and phenoxy acid herbicides were generally absent from the sediment/soils analyzed and not likely to present a potential for environmental impact in large scale. However, due to the diversity and widespread appliucations of these current use contaminants their long term monitoring should be considered a priority for future environmental assessments in the area.

Tissue data show clear indications that currently used pesticides such as endosulfan may pose a risk to sensitive biological endpoints and further studies are necessary to assess the effects of long-term chronic exposure particularly to higher trophic level organisms

where biomagnification could be important. Endosulfan, and its sulfate have been reported in multiple matrices (water, sediments and oysters) along the southern portions of Miami-Dade county and Florida Bay. Endosulfan sulfate was detected in 87% of the tissue samples and 64% of the sediment samples.

In the case of organochlorine pesticides which are still in use, specifically endosulfan and its metabolites, a trend is apparent with the highest concentrations of these compounds in close proximity to areas of intense agricultural production such as the Homestead Agricultural Area. Other organochlorine pesticides such as DDT, and its metabolites DDD and DDD, which are no longer in use, were also detected more frequently near agricultural areas, however the presence of these compounds were also detected in more remote areas suggesting that long range transport of these compounds is occurring throughout South Florida.

The distribution of Polychlorinated Biphenyls is relatively uniform throughout the areas sampled with the exception of one station sampled in Biscayne Bay, near a municipal landfill, which may be the source of the elevated levels of PCBs detected at that station. The observed concentrations for PCBs in both sediment and fish tissue throughout most of the stations sampled are low and are not expected to be of significant environmental concern based upon available sediment quality guidelines. Overall, it appears that PCB distribution in this area is probably due mostly to atmospheric deposition from long-range global dispersion.

Polycyclic Aromatic Hydrocarbon (PAH) concentrations detected throughout the study area are relatively low in comparison to other studies. The distribution of PAHs in sediments show more elevated concentrations at stations located in close proximity to

Tamiami Trail indicating street runoff as a potential source. An examination of the ratios of Benzo[a]pyrene/Benzo[ghi]perylene also indicate that automobile emissions are a predominant source of PAHs at most stations throughout the study area. The highest concentration of total PAHs detected in this study (912 ng/g) was detected at the BNP station (BBBP 1) located near a landfill and a marina, all other detections in BNP and Florida Bay were lower than those found in Everglades National Park.

Trace metal data indicate a potential for sediment enrichment above naturally occurring levels for elements including arsenic, chromium, copper, lead, nickel, and zinc at several of the stations sampled within ENP as well as arsenic in BNP. The trends in distribution show the highest concentrations of beryllium, vanadium, and chromium found near the east boundary of the park as well as in Shark Slough, while cobalt and nickel concentrations are highest at the Eastern boundary, Shark Slough and Tamiami Trail regions. Copper, zinc, arsenic and lead all showed elevated concentrations along the Eastern boundary, and Tamiami Trail. Trace metal distribution in fish tissue show similar trends to the sediment data with the exception of zinc, which had high concentrations at all stations. The reasons for the enrichment of this particular group of metals in ENP are not yet clear, but anthropogenic emissions from the urban areas of South Florida are the most likely source.

4. SEDIMENT TOXICITY TESTS

Toxicity tests

Toxicity tests with amphipods, *Hyalella azteca* and midges, *Chironomus tentans* were conducted for 10-day whole sediment exposures according to USEPA (2000) guidelines for sediments with freshwater invertebrates. Survival and growth (length and weight) were used as the endpoints for all tests. Tests were conducted using an automated overlying water-renewal system to maintain oxygen and low ammonia concentrations (Rand et al., 2003b). *H. azteca* and *C. tentans* were exposed in crystallizing dishes (80x100 mm; 500 ml) with 180 ml of sediment and 320 ml of water. Two-volume additions/day (640 ml) of overlying water were added to each exposure chamber at a delivery rate of 40 ml per replicate chamber using a 90-minute cycle (16 cycles/day x 40 ml volume/cycle). The water:sediment ratio and water replacement conformed to U.S.EPA sediment toxicity test guidelines. Eight replicate exposure chambers with 10 organisms per chamber were used for each sediment sample.

Single-species toxicity tests began with field-collected sediment samples after validation of the water-renewal system. An artificial sediment was formulated and used as reference control following procedures by Kemble et al. (1999) with α–cellulose as a source of carbon. Preparation of formulated sediments followed methods described by Walsh et al. (1991) and Harrahy and Clements (1997). Sand (Ottawa testing sand, US Silica, Ottawa, IL) was rinsed with RO water until water was clear, then rinsed with de-ionized water for 5 min, and air-dried. α–Cellulose was from Sigma Chemical (St. Louis, MO). A silt and clay mixture (ASP 400: Englehart, Edison NJ) was from Mozel (St. Louis, MO) and Dolomite (Spectrum Co.,Gardenia, CA) was used as a source of magnesium, calcium and bicarbonate buffers that naturally occur in soil and sediments.

Formulated sediment B (FSB) contained high sand (63%) and high TOC (7.4%). Formulated sediment was previously tested with *Hyalella azteca* and *Chironomus tentans* in 10-day toxicity tests using survival and growth as endpoints (Kemble et al., 1999, Rand et al., 2004).

Survival and growth (length and weight) were measured for each species after 10 days. Amphipod body length (±0.1 mm) was measured from the base of the first antennae to the tip of the third uropod along the curve of the dorsal surface using a Zeiss stereomicroscope and a stage micrometer. Head capsule widths of midge were measured to the nearest 0.01mm. Dry weight of test organisms was determined by combining all of the organisms from each replicate in a pre-dried aluminum weigh pan and drying them for 24 hours to a constant weight.

During the tests midges received a daily suspension of Tetrafin® and amphipods received a yeast-Cerophyl®-trout chow (YCT).

Test organisms

Mass cultures of *H. azteca* and *C. tentans* were maintained in the culture facilities at the SERC Ecotoxicology Laboratory according to U.S.EPA (2000) guidelines. Water from the City of North Miami Beach was air-stripped, carbon filtered, UV-sterilized, and supplied to the holding tanks by a recirculating system (hardness 75 mg/L as $CaCO_3$, alkalinity 55 mg/L as $CaCO_3$, pH 7.8). *H. azteca* and *C. tentans* starter cultures were obtained from I.E. Greer (Columbia Environmental Research Center, USGS, Columbia, MO).

To obtain mean 9 d old amphipods, the age of amphipods was determined on day -4 by placing a no. 45 sieve underneath a no. 35 sieve and passing the organisms through with a

gentle water current. Known age amphipods retained by the no. 45 sieve were placed in 1.5 L glass dishes with 1 L daily water-renewal until the initiation of the test. Neonates were fed YCT mixture diet twice daily while in the isolation chambers.

Third-instar larvae of *C. tentans* were obtained by isolating individual egg cases in 1.5 L glass dishes with 0.75 L of overlying water using silica sand as a substrate, ten days prior to exposure. Water was renewed daily. Newly hatched *C. tentans* were fed a Tetrafin® slurry.

Water quality

Temperature in exposure chambers was maintained (23 ±1.0° C) with a recirculating water bath controlled by a heat pump. Temperature and dissolved oxygen concentrations were measured daily. The pH, alkalinity, hardness, conductivity and total ammonia of water were measured on day 0 and day 9 in the 10-day test. In the 30-day test, pH was measured three times a week, conductivity was measured weekly, and alkalinity, hardness, conductivity and ammonia were measured weekly. Water quality characteristics were measured using standard procedures (APHA et al., 1992).

Fathead Minnow Embryo Larval Tests

Fathead minnow (*Pimphales promelas*) embryo larval sediment toxicity tests were conducted with C-111 site sediments (S-176, S-177, S-178, S-18C, S-197) according to McKim (1985). Exposure chambers and sediment to water ratios were similar to benthic invertebrate tests. Tests were initiated with embryos and continued for 28 days. Hatchability (%), hatching time (days), incubation time (days), fry length (mm) and weight (mg) were measured as endpoints. FSB served as the reference control.

Statistical analyses

SPSS for Windows was used to determine means and standard errors of biological endpoints and analysis of variance with post-hoc tests were used to determine significant differences in biological endpoints (SPSS, 1999).

Toxicity Test Results

Toxicity test results will be discussed by region (see Section 5.4).

East Boundary (EB) of Everglades National Park (ENP)

From the EB, field-collected sediments were obtained from sites 332 and 22 (Table 4.1). The daily mean temperature was 21 +/- 1° C and the mean dissolved oxygen concentrations were in the acceptable limits. The pH was 7.95-8.05 and total ammonia was 0.10- 0.11 mg/l. Table 4.1 presents the results of the 10-day tests with *Hyalella*. Survival was significantly (0.05) lower at 332 than FSB. Length was significantly (0.001) higher at 332 and 22 than FSB. Dry weight was not affected.

The results of a 10-day *Chironomus* test at site 22 are presented in Table 4.2. The daily mean temperature was 22 +/- 1.0^{o} C and the mean daily dissolved oxygen concentration was within acceptable limits. There were no significant differences in *Chironomus* survival and head capsule width, but dry weight was significantly (0.001) lower than controls.

Shark River Slough (SRS)

From SRS, field-collected sediments were obtained from SRS2 and SRS3. The daily mean temperature during tests was 21 +/- 1.0^{o} C and the mean daily dissolved oxygen concentrations were within acceptable limits. The pH was 7.96-7.98 and total ammonia was

0.14-0.15 mg/l. Table 4.3 presents the results of the 10-day tests with *Hyalella*. Survival was statistically lower (0.05) at SRS2 and SRS3. Length and dry weight were not affected.

C-111

C-111 toxicity testing consisted of field-collected sediment from S-176, S-177, S-178, S-18C, S-197 and sites 55 (i.e., 55, 55B) and 61 (61,61S). Sites 176 through 197 are sampling site names from the SFWMD monitoring program (see Section 5.2).

Toxicity tests at sites 55 and 61 were conducted at a different time than S-176, S-177, S-178, S-18C, and S-197 and therefore two different controls (FSB) were used (Table 4.4). The daily mean temperature was 22 +/- 1.0^{o} C and the mean daily dissolved oxygen concentration was within acceptable limits. The pH was between 7.92 and 8.25 and total ammonia concentration was 0.07 and 0.11 mg/l. Table 4.4 presents the results of the 10-day tests with *Hyalella*. Survival was not effected at S-176, S-177, S-178, S-18C, or S-197. Survival was significantly lower at 55B (0.01) and 61S (0.05) which are south of the SFWMD sites. Length of *Hyalella* was significantly lower at S-176 (0.01), S-177 (0.05), S-178 (0.01), S-18C (0.01), and S-197 (0.01). Length of *Hyalella* was significantly higher at sites 55 (0.05), 55B (0.001), 61 (0.001) and 61S (0.01). Dry weight was significantly lower at S-176 (0.01), S-177 (0.05), S-178 (0.01), S-18C (0.01) and S-197 (0.05) than controls. However, dry weight was significantly higher at sites 61 (0.01) and 61S (0.01). It should be noted that survival is a more sensitive indicator than length and weight for this species.

The results of the fathead minnow embryo-larval test (28 d) with sediments from S-176, S-177, S-178, S-18C and S-197 are shown in Tables 4.6 and 4.7. Embryo hatchability (%) was significantly lower (0.05) at S-176, S-178 and S-18C. Hatching time was higher in

all field-collected sediments, but only statistically significant at S-177 (0.05). Incubation time was generally higher at sites (except S-18C) than the control but only statistically significant at S-177 (0.01) and S-197 (0.05).

At the end of the test survival of young fry was lower in all field-collected sediments, but only statistically significant at S-176 (0.01). Length was higher in all field-collected sediments but only statistically significant at S-176 (0.05) and S-18C (0.05). Weight was also higher in all field-collected sediments but only statistically significant at S-176 (0.05).

Tamiami Trail

Toxicity tests were conducted with Hyalella (Table 4.8) and Chironomus (Table 4.9) and site 63 sediment. Survival (0.05) and weight (0.01) were significantly lower than controls in *Hyalella*. Survival of *Chironomus* was similar to controls but weight (0.01) was significantly lower than controls.

Table 4.1
Mean response (±sd) of Hyalella azteca in 10-day exposure to sediment at region Eastern Boundary

Sediment	Survival (%)	Length (mm)	Weight (mg)
FSB	97.50 (4.63)	2.31 (0.19)	0.08 (0.04)
332	82.50 (8.86)*	2.66 (0.14)***	0.10 (0.03)
22	91.25 (8.35)	2.56 (0.11)***	0.09 (0.01)

Table 4.2
Mean response (±sd) of Chironomus tentans in 10-day exposure to sediment at region Eastern Boundary

Sediment	Survival (%)	Head capsule width (mm)	Weight (mg)	Length (mm)
FSB	90 (14.14)	0.65 (0.01)	1.21 (0.183)	12.41 (1.14)
22	95 (5.77)	0.58 (0.08)	0.54 (0.15)***	10.60 (0.86)***

Table 4.3
Mean response (±sd) of Hyalella azteca in 10-day exposure to sediment at region Shark River Slough

Sediment	Survival (%)	Length (mm)	Weight (mg)
FSB	97.50 (4.63)	2.31 (0.19)	0.08 (0.04)
SRS2	70.00 (22.68)*	2.27 (0.11)	0.04 (0.01)
SRS3	73.75 (13.02)*	2.44 (0.10)	0.05 (0.01)

Table 4.4
Mean response (±sd) of Hyalella azteca in 10-day exposure to sediment at region C-111

Sediment	Survival (%)	Length (mm)	Weight (mg)
FSB	81.25 (11.26)	1.72 (0.24)	0.06 (0.03)
55	67.50 (21.21)	2.07 (0.28)*	0.08 (0.02)
61	76.25 (15.06)	2.59 (0.26)***	0.10 (0.02)**
55B	53.75 (22.64)**	2.27 (0.35)***	0.08 (0.03)
61S	62.50 (19.82)*	2.41 (0.29)***	0.08 (0.02)*
FSB	100.00 (0.00)	3.80 (0.23)	0.35 (0.07)
S176	97.50 (4.60)	2.94 (0.14)**	0.13 (0.01)**
S177	91.30 (6.40)	3.42 (0.16)*	0.22 (0.03)*
S178	93.75 (5.18)	3.28 (0.14)**	0.16 (0.02)**
S197	97.10 (7.60)	2.93 (0.17)**	0.15 (0.08)*
S18C	88.80 (15.50)	2.88 (0.10)**	0.16 (0.02)**

Table 4.5
Mean response (±sd) of Chironomus tentans in 10-day exposure to sediment at region C-111

Sediment	Survival (%)	Head capsule width (mm)	Weight (mg)	Length (mm)
FSB	99 (3.50)	0.68 (0.02)	1.85 (0.39)	13.26 (1.33)
S176	63 (16.70)**	0.37 (0.02)**	0.23 (0.09)**	6.73 (0.46)**
S177	85 (10.70)*	0.57 (0.08)*	0.78 (0.82)	9.78 (2.33)
S178	80 (12.00)*	0.47 (0.12)*	0.48 (0.26)**	8.02 (1.48)**
S18C	61 (16.40)**	0.36 (0.03)**	0.14 (0.05)**	5.71 (0.44)**
S197	61 (19.60)**	0.43 (0.06)**	0.27 (0.10)**	7.02 (0.75)**
FSB	90.00 (14.14)	0.65 (0.01)	1.21 (0.183)	12.41 (1.14)
55	97.50 (5.00)*	0.62 (0.01)*	0.63 (0.22)***	10.57 (0.99)

Table 4.6
Mean response (±sd) of Pimephales promelas in 28-day exposure to sediment at region C-111

Sediment	Survival (%)	Length (mm)	Weight (mg)
FSB	65 (10.00)	10.11 (0.54)	2.69 (0.25)
S176	24.44 (19.25)**	12.78 (1.47)*	6.44 (2.69)*
S177	56.67 (20.00)	10.96 (0.90)	3.72 (0.95)
S178	43.33 (27.49)	11.57 (1.52)	4.51 (2.25)
S18C	46.67 (23.09)	11.50 (1.21)*	4.41 (2.10)
S197	51.67 (28.48)	11.48 (1.34)	3.94 (2.06)

Table 4.7
Mean response (±sd) of Pimephales promelas in 28-day exposure to sediment at region C-111

Sediment	Hatchability (%)	Hatching time[1](d)	Incubation time[2] (d)
FSB	93.33 (7.70)	2.75 (0.96)	6.25 (0.50)
S176	57.78 (10.18)*	4.33 (1.16)	7.00 (1.00)
S177	90.00 (6.67)	5.75 (1.50)*	8.75 (0.96)**
S178	71.67 (21.34)*	4.50 (1.29)	8.00 (1.63)
S18C	75.00 (11.39)*	3.50 (1.29)	6.25 (0.96)
S197	86.67 (5.44)	4.00 (1.41)	7.50 (0.58)*

1. Hatching time is measured as the time elapsed between the first embryo hatching until the last embryo hatching
2. Incubation time is measured as the time elapsed from fertilization until completion of hatching

Table 4.8
Mean response (±sd) of Hyalella azteca in 10-day exposure to sediment at region Tamiami trail

Sediment	Survival (%)	Length (mm)	Weight (mg)
FSB	85.00 (12.91)	2.10 (0.12)	3.35 (4.41)
63	47.50 (22.17)*	1.83 (0.22)	1.71 (3.26)**

Table 4.9
Mean response (±sd) of Chironomus tentans in 10-day exposure to sediment at region Tamiami trail

Sediment	Survival (%)	Head capsule width (mm)	Weight (mg)	Length (mm)
FSB	90 (14.14)	0.65 (0.01)	1.21 (0.18)	12.41 (1.14)
63	82.50 (5.00)	0.65 (0.03)	0.80 (0.14)**	12.03 (1.19)

5. SCREENING LEVEL AQUATIC ECOLOGICAL ECOLOGICAL RISK ASSESSMENTS (SERAs)

The following section includes four SERAs. The first SERA (Section 5.1) is on historical data for pesticides (herbicides-atrazine, metolachlor, and insecticides- endosulfan, malathion and chlorpyrifos) monitored in surface water from the C-111 freshwater system, south Biscayne Bay and northeast Florida Bay by U.S.G.S., NOAA, and South Florida Water Management District from 1999-2000. The importance of the C-111 system as a potential source of pesticide contaminants into Everglades National Park is discussed. The U.S.EPA Ecological Risk Assessment (ERA) framework (USEPA, 1992, 1998) is also discussed in detail in the latter SERA. The next two SERAs are on historical data for pesticides (Section 5.2) and metals (Section 5.3) monitored in sediment from south Florida canals by South Florida Water Management District from1990-2002. The general ecological risk methods for pesticides and metals present in whole sediment are discussed in the second SERA (Section 5.2) on pesticides. The specific ecological risk approach that was used for metals in whole sediment is discussed in the third SERA.

The final SERA (Section 5.4) is on pesticides and metals in sediment from the present three-year monitoring program.

5.1 Pesticides from C-111 Basin, South Florida Water Management District Historical Data (1990-2002)

5.1.1 INTRODUCTION

The responsibilities of the Department of the Interior (DOI) in monitoring ecological impacts in Everglades restoration activities as well as their oversight of National Environmental Protection Act, Endangered Species Act, and Fish and Wildlife Coordination Act mandates led to the creation of a 1996 report entitled "A Comprehensive Plan for the Restoration of the Everglades" (NRC, 2003). This report called for ongoing restoration activities, the attainment of land necessary for the restoration process, enhancement of research activities to assist the restoration effort, and a system of cost sharing among local, state, and federal branches of government to achieve restoration goals (http://www.sfrestore.org/tf/otherres/comp.html). The Comprehensive Everglades Restoration Plan (CERP) (as part of the Water Resources Development Act), was passed by Congress in 2000. CERP outlines a restoration plan that will adjust the hydrology of South Florida ecosystems so that water that once flowed directly to sea will be diverted to areas where it can be utilized more efficiently to meet the needs of plants, animals, and humans. The goals of CERP and its approximately 200 performance measures are to: transform the current hydrology to a more natural state, sustain and protect existing habitats, improve degraded habitats or establish new ones to allow the propagation of plants and animals, and to permit human society to expand and function within the context of maintaining and protecting the ecosystems of South Florida.

Phosphorus and mercury contamination along with anthropogenic changes in hydrological patterns have been associated with compositional shifts of biota in South Florida ecosystems (Science Subgroup, 1996). Analysis of data collected from nearly two dozen Everglades sites over several years have shown positive and negative correlations between various macroinvertebrate species and hydroperiod and/or total phosphorus concentrations in soil (Trexler et al., 1998). Some of the more drastic ecosystem changes in South Florida are thought to have occurred due to historical drainage and water redistribution projects. For example, as a result of restricted freshwater input, a diminished hydroperiod and higher salinities may be causing shifts in fish community structure in Florida Bay mangrove ecosystems (Lorenz, 1999). One of the large and overlying focuses in the South Florida restoration activities that have been delineated by the Restoration Task Force is realigning the hydrology to provide the right amounts of water to sustain and improve the ecosystems. Reconstruction of the hydrologic system precedes the sustainability of ecological systems in many of the restoration plan's concepts and goals. The importance of considering the potential impacts of organic pesticides and contaminants in South Florida ecosystems has been emphasized in recommendations by the Science Subgroup (1996). Predictive and retrospective ecological risk assessment work in South Florida ecosystems was also advocated in a workshop entitled "Linking Ecotoxicity and Risk Management to Sustainable Restoration of South Florida Ecosystems" (LaPoint et al., 1998).

The objectives of the South Florida restoration process have emphasized water quantity issues while minimizing the consideration of current and future threats of water quality (Scott et al., 2002). Between 1997 and March 2002, two contaminant research-based studies out of a total of 155 studies were funded as part of the Critical Ecosystems Study

Initiative research program to support Everglades restoration (NRC, 2003). However, agriculture and urban areas represent major land usages in South Florida and the use of pesticides and other chemicals presents a potential risk to aquatic organisms. Biscayne Bay was ranked as one of the top three estuaries susceptible to hazards from pesticides in a National Oceanographic and Atmospheric Administration (NOAA) report that rated potential pesticide hazards around coastal ecosystems (Pait et al., 1992). From sub-lethal toxicity tests with amphipods, Long et al. (2002) found that conditions of sediment toxicity in Biscayne Bay had a larger spatial distribution than the national average for estuaries located in North America. The subtropical climate, long crop-growing season, application frequency, and multitude of uses (e.g., mosquito and termite control, golf courses) may render pesticides particularly hazardous in South Florida ecosystems.

The Everglades National Park (ENP) is separated from eastern agriculture and urban lands by the Canal 111 (Aerojet Canal or C-111) freshwater basin. Land use around the C-111 basin is largely made up of wetlands (48.5%) and agriculture (38%) with corn, squash, tomatoes, green beans, ornamentals, tropical fruits, carambola, avocado, papaya, lemon, lime, sapodilla and mango grown around the region (from http://www.sfwmd.gov/org/reg/esp/c111.html). Thus far analytical monitoring programs have detected the presence of organic pesticides in surface water (e.g., atrazine, chlorpyrifos, endosulfan, malathion, and metolachlor) of the lower C-111 freshwater canal basin and/or its confluent estuaries/saltwater systems (Figure 5.1.1). For example, the South Florida Water Management District (SFWMD) began monitoring pesticides in water and bottom sediment in South Florida canals in the mid-1980's (Pfeuffer, 1985, 1991).

From 27 sites, pesticides in surface waters of South Florida canals with the highest frequency of detection between 1991 and 1995 were atrazine, ametryn, bromacil, simazine, diuron, α-endosulfan, β-endosulfan, endosulfan sulfate, ethion, hexazinone and norflurazon (Miles and Pfeuffer, 1997). In sediment, DDE, DDD, ametryn, atrazine, dicofol, diquat, and endosulfan sulfate were found most often in sediment during the same time period (Miles and Pfeuffer, 1997). Several of the sampling sites were located in the Everglades Agricultural Area (EAA) and others in the Homestead Agricultural Areas (HAA) adjacent to the ENP. For example, detectable endosulfan residues (alpha and beta, and sulfate) in the C-111 (at S-178) were consistently present in surface water from 1991-1995 and occasionally exceeded Florida Department of Environmental Protection (FDEP) and United States Environmental Protection Agency (U.S.EPA) water quality criteria (WQC) (Miles and Pfeuffer, 1997). Consistent detections of endosulfan sulfate were made in S-178 sediment with less frequent detections of the isomers (Miles and Pfeuffer, 1997). Sediment at S-177 and S-18c also had measurable concentrations of α-endosulfan, β-endosulfan, and endosulfan sulfate. The U.S.EPA in 1995 monitored contaminants in surface and bottom water, sediment and biota in C-111 and creeks of Northeast Florida Bay (Goodman et al., 1999). Out of five sites sampled in C-111, a site with the highest measured salinity in surface water (21.1 psu) had residues of α-endosulfan and endosulfan sulfate detected in sediments. Three other sites in C-111 did not have detectable concentrations of endosulfan in sediment. α -Endosulfan was detected in sediments of Shell Creek, which flows between Long Sound and Florida Bay. Endosulfan sulfate was found in sediments of Trout Creek, which flows southward from Joe Bay to other areas in Northeastern Florida Bay. No endosulfan sediment concentrations were above Florida sediment quality guidelines (Goodman et al., 1999). Other organochlorine

contaminants such as cis-chlordane; trans-nonachlor; 2,4'-DDD; 2,4'-DDE; 4,4'-DDE; 2,4'-DDT; 4,4'-DDT; dicofol; dieldrin; endrin; heptachlor; and lindane occurred at low concentrations in sediments of canals and creeks and PCBs and PAHs were also at low concentrations but higher in C-111 than in creeks. At most sampling sites for water and sediment more than one pesticide was detected in each sample.

NOAA conducted a contaminant study of C-111 and Florida Bay from 1993-1998 (Scott et al., 2002). It indicated that the pesticides endosulfan (total), atrazine, chlorpyrifos and chlorothalonil were present in surface waters of canals adjacent to agricultural areas that drain into C-111 and in Northeast Florida Bay waters. Florida Bay waters occasionally exceeded U.S. EPA marine water quality criterion for endosulfan. Waters from canal sites contained detectable concentrations of endosulfan that exceeded U.S.EPA freshwater quality criterion. Detectable endosulfan (total) residues were also found in sediment fish tissue, and oysters. However, the insecticide chlorpyrifos was not detected in sediment or fish tissue. Toxicity tests with in-place sediments indicated potential adverse effects to copepods and clams in some canal sites and Joe Bay but the causative agent (s) was not determined. Data from NOAA's National Status and Trends Program (NSandT) Mussel Watch Project further indicated that the mean annual concentrations of endosulfan (II) residue in tissues (oysters) sampled from Joe Bay were within the top 15% of mean concentrations found in over 280 NSandT sites nationwide (Cantillo et al., 1999). In addition to pesticides, a site in Biscayne Bay closest to the mouth of the Miami River had the highest detected tissue concentrations of organic contaminants (i.e., PCBs, HCH) in oysters, Crassostrea virginica, over sites further away from the mouth of the river (Oliver et al., 2001).

To address the concerns about pesticides in the C-111 basin the National Park Service (Department of the Interior, DOI) requested that an aquatic probabilistic screening level ecological risk assessment (SERA) be conducted. This report is based on the report to the DOI and is the first phase of a study of potential ecological risks due to contaminant exposures in the lower C-111 basin. It focuses on the risk of adverse effects from pesticide exposure in surface water on aquatic organisms in a freshwater canal (C-111), and its confluent estuarine/saltwater systems (northeast Florida Bay-Joe Bay, Long Sound, Highway Creek; South Biscayne Bay). To-date this is the only site-specific SERA conducted as part of the Everglades restoration effort and it is being "exposure-driven" (Suter, 1993). Presently, there is little evidence that documented pesticide exposures in surface water are eliciting adverse biological effects in aquatic receptors in these systems or on their potential risk.

The SERA applied the ecological risk assessment framework under U.S.EPA guidelines (U.S.EPA, 1998) and it initially addresses the likelihood and ecological significance of the potential effects of surface water exposures to the herbicides atrazine and metolachlor and the insecticides malathion, chlorpyrifos and endosulfan obtained from monitoring programs from the United States Geological Survey (USGS), SFWMD, and NOAA. There have only been chemical-specific aquatic ecological risk assessments conducted thus far on atrazine (Solomon et al., 1996; Giddings et al., 2000a) and chlorpyrifos (Giesy et al., 1999).

5.1.2. STUDY AREA DESCRIPTION

This SERA is focused on risks within the C-111 basin in Miami-Dade County and estuarine sites that may be susceptible to discharges from the C-111 canal. The C-111 basin covers an area of nearly 100 square miles and borders the eastern side of the ENP (Figure 5.1.1). The L-31N borrow canal is a source of water delivery to the C-111 basin. C-111 is connected to C-111E south of Homestead and terminates in a lagoonal estuary (Manatee Bay in Barnes Sound) at S-197. Concern about pesticides in the C-111 basin originated from the drainage of agricultural areas, including Frog Pond, by the canals. Since the 1997 removal of dredged mounds impeding exchange between C-111 and the marsh systems that flow into Florida Bay, overflows from C-111 between S-18c and S-197 enter the southern marsh system of the ENP.

Though it once received water from precipitation, Shark Slough, and groundwater sources, Taylor Slough now receives a majority of its water from L-31W through canal structures S-175, S-332, and S-332D (Figure 5.5.1). Along with Shark Slough, Taylor Slough is one of the Everglades system's large flow-ways. The two sloughs border one another and are divided by the Rocky Glades and Long Pine Key. Peat in Taylor Slough contains calcitic mud and overlays the permeable Biscayne aquifer.

In conjunction with water that overflows marl prairies in the southern Everglades, water in Taylor Slough and C-111 enters creek systems to provide freshwater to northeastern Florida Bay's surface and groundwaters. Water movement from the C-111 and Taylor Slough systems dictate the salinity levels of Florida Bay mangrove swamps, in which wading birds, crocodiles, sportfish, and other species forage (Fourqurean and Robblee, 1999). Past discharges from C-111 through S-197 may have also been damaging to habitat in areas of

Biscayne Bay like Manatee Bay (a basin found in Barnes Sound). Freshwater input can have a strong impact on Manatee Bay given its shallow depth, long residence time of water, and weak tides. Thus, the freshwater that entered southern Biscayne Bay through C-111 persisted for a long duration as it vacillated between its estuaries and sounds (Chin Fatt and Wang, 1987). On the other hand, periods of low freshwater input can impart a hypersaline character to Manatee Bay and Barnes Sound. Saltwater moves toward shore during the dry season and the western portion of southern Biscayne Bay is especially susceptible to hypersaline conditions (Wang et al., 1978).

Florida Bay itself extends from the coast of southern Florida to the Florida Keys. Northeast Florida Bay includes the downstream freshwater marshes and estuarine systems that extend from the southern edge of Barnes Sound on the East to Madeira Bay on the West and include Little Madeira Bay, Joe Bay, Highway Creek and Long Sound.

Seagrass ecosystems have historically flourished in the Bay due to a mean depth of approximately 3 feet that allows light to reach the bottom (U.S.ACE and SFWMD, 1999). As a result of its shallow banks, constricted mixing in Florida Bay causes the water quality to exhibit a spatial patchiness (Boyer et al., 1997). Hydrodynamics in Florida Bay involve the transfer of freshwater from the northeast to the west and shelf water from the west to a central region where it may evaporate, leaving high salinity water, if it does not flow out of the Bay (Boyer et al., 1997). Mixing dynamics and depth in Florida Bay can cause water salinity to double that of full strength seawater (U.S.ACE and SFWMD, 1999). Though its current and historic contribution to salinity, pollutants, and water quality in Florida Bay are unknown, discharge from the Mississippi River at its flood stage was speculated to contribute unusually low salinity levels in the Summer of 1993 (Gilbert et al., 1996). The carbonate

mud sediments in the Bay are conducive to the sorption of inorganic phosphorus (U.S.ACE and SFWMD, 1999).

Indications of poor water quality in the Bay began in the mid-1980s with losses of turtle grass (*Thalassia testudinum*) and pink shrimp (*Penaeus duorarum*) (U.S.ACE and SFWMD, 1999). A survey of seagrasses at various stations in Florida Bay in 1984 and 1994 found that the overall distribution of turtle grass did not diminish between the time period but *Halodule wrightii* and *Syringodium filiforrme* shoot density and standing stock decreased by about 90% between surveys (Hall et al., 1999). Seagrasses such as *S. filiforme* and *H. wrightii* were observed to be strong determinants in the presence of spotted seatrout (*Cynoscion nebulosus*), gray snapper (*Lutjanus griseus*) and other fish species habitat in Florida Bay (Thayer et al., 1987). The decrease in seagrass habitat and increased, persistent algal blooms may have favored a shift in the composition of fish in Florida Bay to planktivorous species (Fourqurean and Robblee, 1999). In the mudbanks of Florida Bay, a shift from fish and invertebrate species associated with seagrass canopies to a predominance of benthic species may also be occurring (Matheson, Jr. et al., 1999).

Along with freshwater discharge from C-111, suspended solid, contaminant, and nutrient loads from upland agriculture and urban centers, as well as marshes, can eventually make their way to coastal regions of South Biscayne Bay and Northeast Florida Bay. A study on mercury transport to the lower Everglades and Florida Bay found that runoff contributed greater mercury concentrations to sites in Taylor Slough and Florida Bay than atmospheric transport, which was a dominant source in remote regions (Kang et al., 2000). In addition, Caccia et al. (2003) correlated metals in Florida Bay samples with riverine input from Taylor Slough and Shark River Slough. Sampling sites for water and sediment

monitoring programs in C-111, Florida Bay and Biscayne Bay are labeled in Figure 5.1.1. The Miami River may be an additional source of contaminants such as metals to Biscayne Bay (Schropp et al., 1990; Long et al., 2002).

To hasten urban development in the region and allow current residents greater access to flood control, the comprehensive Central and Southern Florida (CandSF) Flood Control Project carried out the channelization of C-111 in the 1960s. It was not until the 1980s that the role of C-111 as a contributor to environmental problems in the ENP was identified. A 1994 C-111 General Reevaluation Report and Environmental Impact Statement outlined a procedure to maintain water levels for areas of southern Miami-Dade County and enhance the timing and amount of freshwater deliveries to Taylor Slough, the eastern panhandle of the ENP, and Florida Bay (project description can be found at: http://www.saj.usace.army.mil/dp/MWDC111.htm).

5.1.3. OBJECTIVES

The objective of the SERA is to determine the potential likelihood of toxicological effects resulting from exposure to atrazine, metolachlor, endosulfan, malathion, and chlorpyrifos in the C-111 freshwater aquatic system and other adjacent confluent estuarine/saltwater coastal ecosystems that may be indirectly affected like south Biscayne Bay or “South Bay” (i.e., Manatee Bay, Barnes Sound) and Northeast Florida Bay (i.e., this includes downstream freshwater marshes and estuarine systems that extend from the southern edge of Barnes Sound on the East to Madeira Bay on the West and include Joe Bay, Highway Creek, Long Sound, Little Madeira Bay) based on presently available data. For simplification in the SERA all the latter saltwater ecosystems are collectively referred to as “estuarine sites” in figures and tables.

Presently available exposure data (concentrations of pesticides in water) and toxicological effects data in freshwater and saltwater environments were considered. Based on prior monitoring data (i.e., by USGS, NOAA, SFWMD) five pesticides (i.e., insecticides-endosulfan, chlorpyrifos, and malathion and the herbicides-atrazine and metolachlor) were considered for the single chemical SERA. Since each chemical is not used in isolation to control pests and may co-occur with the others; aquatic risk associated with the effects of joint exposures was also considered.

The SERA consisted of the first three phases (Figure 5.1.2) of the U.S.EPA ecological risk assessment framework (U.S.EPA, 1998): Problem Formulation, Risk Analysis and Risk Characterization. Problem Formulation defined the problem and the plan for analyzing and characterizing the risk. Data on stressor characteristics, ecosystems at risk, toxicological effects, and ecosystem(s) and receptor(s) characteristics

were synthesized for this phase. From these data, measurement and assessment endpoints (i.e., what we are trying to protect) and a conceptual model were developed to prepare the final product of Problem Formulation-the Analysis Plan (Risk Hypotheses were evaluated). The conceptual models used information on the ecosystems at risk, stressor characteristics, biological effects and relationships between endpoints to define exposure

and effects scenarios. The conceptual models for exposure and effects led to a set of questions.

The second phase of the SERA was Risk Analysis and it characterized and examined two major components of risk; exposure and effects. Risk Characterization was the final phase. This provided potential risk estimates to the ecological entities listed as assessment endpoints based on occurrence and magnitude of exposures and severity of adverse effects

resulting from such exposures. A tiered ecological risk assessment approach was suggested by the Aquatic Risk Assessment and Mitigation Dialogue Group (ARAMDGP) (SETAC, 1994) and endorsed by a panel commissioned by the U.S.EPA (ECOFRAM, 1999) that uses a stepwise approach progressing from the simple hazard quotient approach to more complex and more resource-intensive methods like probabilistic risk assessments (PRAs).

For risk characterization, the hazard quotient (HQ) approach was first used. The basic foundation of the HQ approach is the comparison of a sensitive species endpoint from a toxicity test (also called TRV: toxicity reference value or TBC: toxicological benchmark concentration) to a maximum measured environmental concentration (MEC) from monitoring data (Suter, 1993). Actual measured environmental concentrations (AMCs) were obtained from monitoring programs from state and federal agencies. A quotient greater than 1 can indicate the potential for risk. Within the jurisdiction of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), the HQ approach was utilized in the registration/reregistration process to predict acute/chronic toxicity to organisms and as a determinant for restricting, suspending, canceling, or registering pesticides (Urban and Cook, 1986). In the current assessment, the HQ approach relied upon screening benchmarks. Screening benchmarks are concentrations of chemicals that are believed to constitute thresholds for potential toxic effects of some receptor exposed to a chemical in some medium. U.S.EPA WQC are commonly used as screening benchmarks because exceedence of one of these values constitutes cause for concern. Measured concentrations of the pesticides in surface water were, therefore, compared to U.S EPA WQC that were available (i.e., endosulfan, chlorpyrifos, malathion, and atrazine). There is presently no WQC for metolachlor so low (protective) endpoints taken from toxicity tests were used. HQ

exceedences in Tier 1 were used to focus Problem Formulation and Risk Characterization on chemicals of potential ecological concern (COPECs). The latter risk characterization approaches are briefly discussed in Section 5.5 (Analysis Plan).

After the Tier 1 hazard assessment, a probabilistic assessment was conducted for the rest of the C-111 SERA in the Risk Analysis and Risk Characterization section. Sites and pesticides found to violate Tier 1 criteria were examined closest in the rest of the risk assessment. Aquatic invertebrates, plants, phytoplankton, and fish were included in the assessment, but reptiles, birds, and mammals were not. For risk characterization of single-chemicals, a probability distribution of AMCs in water was compared to a probability distribution of species response data (e.g., EC50s; i.e., the effective concentration for 50% of a sample population; LC50s, i.e., the lethal concentration for 50% of the sample population; and no observed effect concentrations (NOECs) from chronic studies) as determined from single-species laboratory toxicity tests (Suter, 1993; Solomon, 1996). The overlap of the distribution is a measure of risk for that chemical to aquatic life. For risk characterizations of multiple chemical exposures, joint action of two or more chemicals was considered based on mode of action (Traas et al., 2002; discussed in Analysis Plan Section 5.5). It was assumed that the insecticides chlorpyrifos and malathion have a similar mode of action on fish and invertebrates. When the insecticide endosulfan and the herbicides atrazine and metolachlor were considered in multiple exposures, each was assumed to have a different mode of action.

A decision-tree for the SERA is illustrated in Figure 5.1.3. The SERA was intended to evaluate the potential risk of the five pesticides in water not to determine the actual causes of any declines in populations of native invertebrates, fish, plants or amphibians that may be prevalent in the above ecosystems. Historical water development activities in the C-111

basin area may have altered habitats and impacted populations (see Section 2). Furthermore, other contaminants (e.g., mercury, lead, zinc) including nutrients in water and/or in sediment are not considered in the SERA and may likely also contribute to aquatic impacts in these freshwater/saltwater areas. The latter are addressed in data gaps (Section 10).

5.1.4. TIER 1 SCREENING ASSESSMENT

5.1.4.1. Introduction

As recommended by ECOFRAM (1999) for pesticide registration, the C-111 SERA followed a tiered process for evaluating potential risks from pesticide exposure to aquatic organisms. The Tier 1 Screening Assessment, which is described in this section, allowed us to negate the hypothesis that no hazard exists in the 1999 and 2000 pesticide monitoring data for the C-111 system. The results from Tier 1 were used to determine whether the assessment should or should not go to tier 2. Using a tiered risk assessment also allowed us to distinguish what scenarios may have higher risks than others as we moved to a higher, and more data intensive, tier.

For the Tier 1 assessment, actual concentrations of four of the five pesticides at different sampling sites were compared to each pesticide's respective WQC. Since metolachlor did not have an available WQC the classical HQ approach was used for this chemical in which an AMC was compared to the lowest acute toxicity test value from an actual toxicity test. Thus, by using conservative effect values for comparison to available monitoring data, this tier should be protective of risks to the ecosystems of concern (ECOFRAM, 1999). Potential risks found at this tier may be shown to be less than anticipated when more data are incorporated at higher tiers (ECOFRAM, 1999).

5.1.4.2. Comparison of Measured Concentrations of COPECs to WQC

Under Section 304(a)1 of the Clean Water Act, WQC is set by the U.S.EPA's Office of Water (OW), for a specific chemical compound. For fresh- and salt-water, two criteria are developed: a Criterion Continuous Concentration (CCC) and a Criterion Maximum Concentration (CMC). These values are supposed to be protective of aquatic life if they are not exceeded. The CCC is a four-day average concentration and the CMC denotes a one-hour average concentration (U.S.EPA, 1986). WQC regulations state that the CMC or the CCC should not be exceeded an average of more than once every three years to prevent water quality degradation and effects on its uses by aquatic life (U.S.EPA, 1986). The criteria can be more stringent in the case of endangered or threatened species or species with special significance such as keystone species or commercially important species. With the exception of atrazine, WQC for each pesticide was taken from U.S.EPA (2002a). For endosulfan, a priority pollutant, WQC from the EPA is available for α- and β-endosulfan from the 1980 WQC document. Endosulfan sulfate has no specified EPA WQC for ecological receptors. For freshwater, α-endosulfan has a CMC of 0.22 μg/L and a CCC of 0.056 μg/L. For saltwater, α-endosulfan has a CMC of 0.034 μg/L and a CCC of 0.0087 μg/L. For freshwater, β-endosulfan has a CMC of 0.22 μg/L and a CCC of 0.056 μg/L. For saltwater, β-endosulfan has a CMC of 0.034 μg/L and a CCC of 0.0087 μg/L. Since the WQC was generated from toxicity studies conducted with technical endosulfan each criterion is applicable to the summation of the α and β isomers (U.S.EPA, 2002a). For the C-111 SERA, endosulfan sulfate, the toxic degradate of endosulfan, was included in the summation under the assumption that it is as toxic as the parent compounds (IPCS, 1988), although no

criteria has been set for endosulfan sulfate. The rest of the pesticides found in C-111 and related estuarine sites are listed as non-priority pollutants. Malathion has a CCC of 0.1 μg/L for both freshwater and saltwater sites. There is no CMC for malathion. For freshwater, chlorpyrifos has a CMC of 0.083 μg/L and a CCC of 0.041 μg/L. For saltwater, chlorpyrifos has a CMC of 0.011 μg/L and a CCC of 0.0056 μg/L. WQC for atrazine is in draft form (U.S.EPA, 2003). For freshwater organisms, atrazine has a CMC of 1,511 μg/L. For saltwater organisms, atrazine has a CMC of 759.5 μg/L. The CCC of atrazine for freshwater is 10 μg/L. The CCC for atrazine in saltwater is 16.83 μg/L. There is no recommended WQC for the herbicide metolachlor.

From 291 samples taken in C-111 on separate days during 1999 and 2000, the highest detected concentration of atrazine in a freshwater site was found on June 7, 1999 at S-18C/Site E. This concentration was 0.337 μg/L and was below the recommended WQC for freshwater animals and plants. Out of 50 saltwater samples taken on separate days between 1999 and 2000, the highest detected concentration of atrazine found at an estuarine site was detected on September 26, 2000 at Joe Bay. This concentration, 0.104 μg/L, was also below the recommended WQC for saltwater organisms.

Out of 180 samples, the highest detected concentration for chlorpyrifos was found at S-177/Site B on March 10, 1999 at a concentration of 0.0234 μg/L. This was lower than the freshwater CCC for chlorpyrifos at 0.083 μg/L. Thus, no measured freshwater WQC violations occurred for chlorpyrifos during the study period, 1999 to 2000. The highest concentration for chlorpyrifos at an estuarine site was detected at Joe Bay on February 10, 1999 at a concentration of 0.00617 μg/L. This concentration was higher than the CCC for chlorpyrifos. The next highest concentration for chlorpyrifos in an estuarine site was

0.00369 μg/L detected at Highway Creek on February 10, 1999, the same day as the water quality violation that occurred in Joe Bay. This concentration did not exceed any WQC for chlorpyrifos. Thus, out of 50 samples taken for analysis in either Highway Creek or Joe Bay, 2% of the samples had water quality violations for chlorpyrifos. On February 15, 2000, a concentration of 0.0035 μg/L was measured in Card Sound (a state of Florida aquatic preserve and used as a reference site by NOAA due to its proximity to sites impacted by discharges of C-111). This value did not exceed WQC for chlorpyrifos.

Water quality violations for endosulfan were found in freshwater and estuarine sites. The majority of water quality violations in freshwater sites occurred at S-178/Site C. Ten samples taken on different days had concentrations that exceeded the CMC of endosulfan. Nine of these water quality violations occurred in February and one occurred in January, all at the peak of the dry season. Two of these values were detected by the SFWMD and eight were found by NOAA. An additional ten samples were found to exceed the CCC for endosulfan in freshwater sites. Seven of these samples were detected at S-178/Site C. Of these seven, all were detected in June. Two of the samples that exceeded the CCC were detected at S-177/Site B in February of 1999 and 2000 by NOAA and the SFWMD, respectively. One sample that violated the CCC for endosulfan was found at S-18C/Site E on February 16, 2000, a site directly downstream from S-178/Site C. Out of 266 samples taken for analysis of endosulfan in C-111 during 1999 and 2000, 7.5% were found to violate WQC. In estuarine sites, endosulfan water quality violations were found in all three sites sampled, including the reference site, Card Sound. No exceedences of the CMC for total endosulfan were found during the study period. However, in Joe Bay, five exceedences of the CCC for saltwater concentrations of endosulfan were found in February of 2000. In Highway Creek,

five exceedences of the CCC for saltwater concentrations of endosulfan were also found in February of 2000. Out of 50 samples taken at Highway Creek or Joe Bay, 20% were found to violate saltwater WQC for endosulfan. At a concentration of 0.0049 μg/L, one exceedence of the saltwater CCC for total endosulfan was found at Card Sound, an estuarine reference site chosen by NOAA away from the direct influence of C-111, on September 25, 2000.

In February and March of 1999, two samples from the USGS were found to equal the CCC for malathion. The first was 0.0716 μg/L and the second was 0.0837 μg/L. Both chlorpyrifos and malathion had their highest concentrations within freshwater sites found on March 10, 1999 at S-177/Site B. S-177/Site B was the only location where malathion was detected though it was analyzed at five other sites from 1999 to 2000. The USGS was also the only monitoring agency that detected malathion. The SFWMD analyzed for malathion but it was never found at any of their monitoring sites. Since NOAA did not analyze for malathion, possible concentrations in estuarine monitoring sites are unknown. Since malathion was detected in less than 10% of the water samples (found six out of 136 times), it was decided that its occurrence was too inconsistent and infrequent for it to be a COPEC. However, further work at the second tier of the risk assessment will examine malathion more closely at S-177/Site B since this was the only site that malathion was detected and measured concentrations there were found to equal WQC.

Since no WQC was available for metolachlor, standardized toxicity tests were used to find conservative effects measurements for aquatic taxa. Similar to a lower tier effects analysis procedure used in Giddings et al. (2000a), a database of core and supplementary studies, conducted under test guidelines and approved by the U.S. EPA for the registration and reregistration of pesticides, was used to find effects values for metolachlor (Montague,

2002). The following species toxicity endpoints were chosen to derive protective effects criteria for metolachlor (based on ECOFRAM, 1999 and Giddings et al., 2000a):

- *Daphnia magna* (represents freshwater invertebrates) acute toxicity data;
- *Oncorhynchus mykiss (*represents cold-water fish*)* acute toxicity data;
- *Lepomis macrochirus* and *Pimephales promelas* acute toxicity data (represent warmwater fish);
- a *Cyprinodon variegatus* acute toxicity data (represent saltwater fish);
- an *Americamysis bahia* acute toxicity data (represents saltwater invertebrates);
- a *Crassostrea virginica* acute toxicity data (represents saltwater molluscs);
- several freshwater and saltwater tests for acute effects on plant/algae species;
- toxicity endpoints from life cycle studies with daphnid and mysid species for chronic effects on freshwater and saltwater invertebrates;
- an *Oncorhynchus mykiss* early life stage test for chronic effects on fish;
- and chronic endpoints for plant/algae species.

After the above endpoints were compiled, the lowest (most sensitive) acute and chronic toxicity values for freshwater and saltwater plants and animals were selected. The lowest concentrations for each of these categories were then used as the denominator of a HQ with the maximum AMC for metolachlor in fresh or saltwater sites from 1999 and 2000 in the numerator. From ECOFRAM (1999), the following criteria were used for hazard levels. If the resulting value of the HQ (ratio of the maximum concentration for metolachlor and a conservative toxic effect value) for animal species was between 0.1 and 0.5, a lower hazard threshold would be exceeded. The higher hazard threshold for

animal species was 0.5. For algae or plant species, the hazard threshold for all levels of concern was 1.0.

Table 5.1.1 presents the acute and chronic toxicity values chosen for metolachlor for the Tier 1 HQ assessment. For metolachlor in freshwater with plants/algae, *S. capricornutum* was chosen with the lowest acute and chronic values. For freshwater, rainbow trout had the lowest acute value for animals and for saltwater, eastern oysters had the lowest acute value. For fresh-and salt-water chronic assessment, the rainbow trout value was used since we did not have a chronic saltwater test.

The results of the Tier 1 hazard assessment analysis for metolachlor are displayed in Table 5.1.2. All quotients were below any designated hazard threshold for aquatic animals and plants/algae from maximum measured concentrations in freshwater or saltwater sites.

5.1.4.3. Results of Tier 1

Measured concentrations of endosulfan and chlorpyrifos suggested possible hazards and malathion equaled its WQC in two samples but surface water detections were infrequent. Therefore, a second tier using probabilistic methods and criteria from field/mesocosm studies was conducted to assess the potential risks of chlorpyrifos and endosulfan on fish and arthropods. However, it was deemed necessary to do a general comparison of the magnitude and occurrences of all pesticides in freshwater sites. Also, a comparison of species sensitivity distribution (SSD) results for each compound for various taxa of freshwater and saltwater organisms in water exposures was conducted. Furthermore, to assess the potential joint toxicity of each of the compounds that did not have HQs or WQC exceeded, atrazine, and metolachlor were also assessed in higher tier work.

5.1.5. PROBLEM FORMULATION

5.1.5.1. Stressor Characteristics

5.1.5.1.1. Introduction

The following section describes the physical and chemical characteristics and environmental fate chemistry of the two chemicals of potential ecological concern (COPECs)- chlorpyrifos and endosulfan. This includes a summary of the various factors that influence the compound's degradation, persistence and transport in the aquatic environment. Additional information is presented on the fate of each of the two isomers of endosulfan and its toxic degradate, endosulfan sulfate.

The environmental effects section concludes with a summary of results of aquatic hazard studies from the U.S.EPA core and supplementary material for reregistration of the pesticides, as summarized in reregistration eligibility documents (REDs) published by U.S.EPA, along with the results of previous risk assessments that have been conducted.

For each pesticide undergoing reregistration, the U.S. EPA sets a level of concern (LOC) in their assessment (U.S.EPA, 2002b). LOCs are derived through the HQ approach using a single acute and chronic effect level from toxicity tests and a single expected environmental concentration (EEC) from models and/or field studies. The maximum acceptable quotient (e.g., 0.1, 0.5, 1) is the LOC. To predict hazard, a value is set for the quotient, e.g., 0.1 or 1, depending on the sensitivity of the effects endpoints or the importance of the assessment endpoint. For acute toxicity, the LOC set by the U.S.EPA from HQs cannot exceed 0.5 for non-endangered species or 0.05 for endangered species. For chronic toxicity, the LOC is set at 1.0 for HQs from both endangered and non-endangered species.

There is a large database including an ERA conducted for chlorpyrifos. This literature will be briefly summarized below. Some information for the chlorpyrifos physical/chemical properties and environmental behavior summary was first obtained from the National Library of Medicine's Hazardous Substance Database (available online at http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB) before consulting the primary citations. For additional information on the environmental fate and aquatic toxicity for this pesticide see Giesy et al. (1999) and Racke (1993). The environmental fate data for endosulfan have not been extensively reviewed therefore, this will be done below.

5.1.5.1.2. Chlorpyrifos

5.1.5.1.2.1. Introduction

As an organophosphate (OP) insecticide, chlorpyrifos, [*0,0*-diethyl *0*-(3,5,6-trichloro-2-pyridyl)-phosphorothioate], is used extensively in the United States (U.S.EPA, 2000). It is known commonly as Dursban and Lorsban. Of all OP compounds, chlorpyrifos has the highest national agricultural usage (Larson et al., 1997). In Florida, chlorpyrifos is used on corn, cotton, grapefruit, oranges, pecans, peaches, peanuts, sod, soybeans, sweet corn, and tobacco (FDOACS, 1999). Of these crops, sweet corn is cultivated intensively in the Everglades region with 24,400 reported acres and 42,000 lbs a.i. chlorpyrifos are applied annually on sweet corn throughout the state (FDOACS, 1999). Residential uses include structural treatment for termites. In 1995, applications of chlorpyrifos on crops and in industrial settings were almost equivalent (Nowell et al., 1999).

Florida has high chlorpyrifos usage along with California, Washington, Georgia, Arizona, Nebraska, Iowa, Illinois, and Wisconsin (U.S.EPA, 2000). In South Florida,

chlorpyrifos is applied on or near golf courses and residential areas (Scott et al., 2002) According to usage estimates compiled by Pait et al. (1992), over 5,500 pounds of chlorpyrifos may be applied per year around Biscayne Bay. Because an estimated 88 pesticides may be utilized in South Florida (Scheidt, 1989), an important factor to note is that pesticides like chlorpyrifos are in use year-round and can be applied in conjunction with each other. A survey of the STORET database found that chlorpyrifos has been detected in biota in Florida (Pait et al., 1992).

5.1.2.2. Chemical/Physical Properties and Environmental Behavior

Chlorpyrifos is an OP pesticide that belongs to the phosphorothionate class as a result of its P==S moiety (Chambers, 1992). Using a classification scheme developed by Ney, Jr. (1998), chlorpyrifos is not soluble and has a moderate volatility (water solubility and vapor pressure in Table 5.1.3). Once chlorpyrifos reaches a body of water, its half-life is depleted through biodegradation, volatilization, hydrolysis, and photolysis (Giesy et al., 1999). Chlorpyrifos primarily degrades to 3,5,6-trichloro-2-pyridinol (TCP) which can form carbon dioxide from the activity of microbes (Giesy et al., 1999).

From a study by Hughes et al. (1980) and from the basic characteristics listed in Table 5.1.3, chlorpyrifos is more likely to be bound to sediments than exist in the dissolved form. Chlorpyrifos can enter a water body through aerial drift and through soil runoff (U.S.EPA, 2000). Under some conditions, chlorpyrifos may enter a water body in the aqueous phase (U.S.EPA, 2000). The low soil-water partition coefficient for TCP indicates it is more likely to enter an aquatic system in the dissolved phase than chlorpyrifos and its mobility in soil was found to be higher in soil-column leaching experiments (U.S.EPA,

2000). Possibly as a result of desorption, Giddings et al. (1997) found half-lives for chlorpyrifos in aquatic microcosms to be initially greater when applied with a slurry (i.e., to represent soil runoff), than when applied directly to water. When contrasted with half-lives in the water column of the microcosms, Giddings et al. (1997) also observed that chlorpyrifos persisted longer in sediments. The usage of certain formulations of chlorpyrifos (i.e., wettable powders, emulsifiable concentrates) may further increase its aqueous half-life (U.S.EPA, 1987 as cited in Kamrin, 1997).

A high log K_{ow} is indicative of the potential for chlorpyrifos to accumulate in tissue. However, biotransformation of chlorpyrifos has been demonstrated in guppies (*Poecilia reticulata*), (Welling and de Vries, 1992) and in channel catfish (*Ictalurus punctatus*) (Barron et al., 1993). Oysters collected from a Texas salt marsh also had tissue concentrations seven times lower between measurements taken from the first and second day (Ludwig et al., 1968). TCP should not bioacccumulate in organisms based upon its low soil- partitioning ability (U.S.EPA, 2000). In the study on channel catfish by Barron et al. (1993), biotransformation of chlorpyrifos formed TCP and TCP glucuronide as the primary metabolites in blood and urine and bile, respectively.

Photolysis may affect chlorpyrifos in water. For example, the half-life of chlorpyrifos was 30 d in ambient light (pH 7, sterile water) contrasted with 74 d in dark controls (U.S.EPA, 2000). Also, for chlorpyrifos in seawater, the half-lives for dark and ambient sunlight exposed flasks were 7.1 and 4.6 days, respectively (Schimmel et al., 1983). Exposure of chlorpyrifos to sunlight can form TCP and diethylthiophosphate (Racke, 1992). TCP may photodegrade rapidly in soil (U.S.EPA, 2000).

Alkalinity increases can enhance the hydrolysis of chlorpyrifos (Kamrin, 1997; Meikle and Youngson, 1978; U.S.EPA, 2000). The hydrolysis half-lives of chlorpyrifos in sterile buffer solutions at pH 7 and 9 were 72 and 30 d, respectively (U.S.EPA, 2000). Aside from pH, copper ions (Liu et al., 2001; Meikle and Youngson, 1978) and/or salinity (Liu et al., 2001) in water samples may also be important catalysts for the hydrolytic degradation of chlorpyrifos. In sterilized waters collected in four adjoining rivers to the Chesapeake Bay, Liu et al. (2001) found hydrolysis half-lives in different sites to range from 24 to 126 d with a higher correlation to levels of salinity (r^2 = 0.93), and copper ions (r^2 = 0.95) than pH (r^2 = 0.09). TCP is the primary degradate from hydrolysis (Meikle and Youngson, 1978; Liu et al., 2001), and its longer persistence indicates that it may not be as susceptible (U.S.EPA, 2000).

Chlorpyrifos is susceptible to biodegradation in sediment/seawater systems (Schimmel et al., 1983) and in sandy loam and organic soil (Miles et al., 1979). Breakdown products for ^{14}C-ring-labeled chlorpyrifos in soil from recovered radioactivity were reported as TCP, an unextractable bound residue, and carbon dioxide (Getzin, 1981).

5.1.5.1.2.3. Effects of Chlorpyrifos on Aquatic Organisms

The RED document for chlorpyrifos states that enough information is available for a direct assessment of acute (survival) and chronic (reproductive) risks to freshwater and estuarine fish from exposures to dissolved concentrations of chlorpyrifos (U.S.EPA, 2000). However, not enough toxicity data were submitted to assess exposures to aquatic organisms from sediment-associated chlorpyrifos concentrations. Acute toxicity data were also

available for the assessment on formulated products and TCP, the major degradate of chlorpyrifos in the aquatic environment.

Based on available acute and chronic core and supplementary studies, the U.S.EPA Environmental Fate and Effects Division (EFED) found chlorpyrifos to be toxic to aquatic invertebrates and fish. A review by Pait et al. (1992) found that chlorpyrifos was not attributed to many fish kills in field monitoring reports but it was still ranked as a higher potential hazard and more likely to be found in coastal aquatic biota over other pesticides.

The acute and chronic HQs utilized by the U.S.EPA (2000) indicated that chlorpyrifos is a concern for freshwater and estuarine fish (see Section 5.1.1 for an explanation on the U.S. EPA's HQ methodology). All of the most sensitive toxicity values for freshwater and estuarine fish were below concentrations derived from typical usage scenarios in exposure modeling. In addition, four freshwater fish species had acute toxicity values surpassed by peak EECs for six major crop uses out of fourteen that were assessed. Acute risks for amphibian tadpoles were also of concern to EFED. For freshwater and estuarine aquatic invertebrates, HQs surpassed acute and chronic LOCs for all outdoor uses of chlorpyrifos. Acute toxicity values for three of four freshwater invertebrates were surpassed by peak EECs for eight out of fourteen major crop uses. Saltwater environments may be of concern since mysid species were more susceptible to chlorpyrifos than freshwater daphnids. However, in acute toxicity testing, mysids in general are typically the most susceptible species to pesticide exposure. Chlorpyrifos exposure concentrations monitored in some field studies surpassed some EECs from modeling data and the acute EC50 values for aquatic invertebrates.

A probabilistic ecological risk assessment for chlorpyrifos in North American aquatic ecosystems was conducted by Giesy et al. (1999). Risks from chlorpyrifos concentrations in surface waters to fish and invertebrates were evaluated while degradates of chlorpyrifos were not considered due to negligible toxicity and persistence. The chlorpyrifos ecological risk assessment followed a modified tiered process. Four tiers were used, the first three tiers used exposure values from fate models. Modeled concentrations from corn-growing usages of chlorpyrifos were the main source of HQ violations to fish and invertebrates in the first three tiers.

The final tier of the chlorpyrifos risk assessment utilized monitoring data from areas in the U.S. where chlorpyrifos usage was estimated to be highest (Giesy et al., 1999). These areas included the cornbelt in the Midwest, Lake Erie, California, and various other agricultural and urban watersheds. Exceedences of protective freshwater criteria in the highest tier were found in the Huron River, OH and in Lake Erie. Chronic risk criteria were exceeded in the Huron River, OH while protective freshwater criteria for arthropods were exceeded in some areas of Lake Erie. In the latter region, the 10th centile or the no observed adverse effect concentration (NOAEC) from field/mesocosm studies (0.1 μg/L) was exceeded in less than 10% of any of the Lake Erie areas for chlorpyrifos with sufficient monitoring data. In addition, freshwater fish acute toxicity 10th centiles from SSDs were not surpassed by any of the maximum detected concentrations in Lake Erie for any year assessed. Data for mainstem rivers in California were also below effect benchmarks with the exception of some small streams and drains for agriculture. In these cases, invertebrates may be affected but concentrations were below benchmarks for fish. Based on the available

data, the authors concluded that chlorpyrifos is not a significant source of risk for most areas in the U.S., although a few locations may pose higher risk potentials than others.

5.1.5.1.2.4. Interactive Effects of Chlorpyrifos

When applied together in static 96-h tests, the toxicity of atrazine and chlorpyrifos in water were greater than what would be predicted by an additive toxicity model to the midge, *Chironomus tentans* (Pape-Lindstrom and Lydy, 1997). Toxicity results with the two compounds together as a mixture were scaled into toxic units where the EC50 for a test from an individual toxicant was classified as one toxic unit. Nominal concentrations of the chemicals in a binary mixture could then be chosen so that each chemical would be equivalent to 0.5 toxic units. The toxic unit derived after exposing midges to a mixture of chlorpyrifos and atrazine was less than unity. The results, therefore, indicated that a toxic joint interaction may occur when the two compounds are present in the same sample. Further laboratory testing found a positive increase in the toxicity of chlorpyrifos (0.25 μg/L) to *C. tentans* when applied with varying atrazine concentrations (1, 10, 100, and 1,000 μg/L) (Jin-Clark et al., 2002). In the latter studies, the toxicity of atrazine was low, when applied alone. When 200 μg/L atrazine was applied with various effective concentrations of chlorpyrifos, effects on *C. tentans* were almost double the 25 and 50% effective concentrations of chlorpyrifos applied singularly and about one and a half times greater than the 90% effective concentration for chlorpyrifos alone (Jin-Clark et al., 2002). Greater than additive toxicity was also observed in survival of *C. tentans* when exposed to atrazine/malathion mixtures (Pape-Lindstrom and Lydy, 1997).

5.1.5.1.3. Endosulfan

5.1.5.1.3.1. Introduction

Endosulfan, commercially known as Thiodan®, is a sulfur-bearing chlorinated hydrocarbon of the cyclodiene subgroup. Technical endosulfan is a mixture of two sterioisomers (α and β endosulfan) at a ratio of 70:30. Endosulfan usage within the SFWMD is approximately 36 tons, annually (Miles and Pfeuffer, 1997). In the vicinity of the Biscayne Bay watershed, approximately 36,562 pounds of endosulfan are applied per year (Pait et al., 1992). Endosulfan can be utilized on tomatoes and squash in the Biscayne Bay region (Pait et al., 1992). A review of the EPA's Storet database found that endosulfan has been detected in surface water in Florida but was either undetected or at trace levels in sediment and biota (Pait et al., 1992).

Physical and chemical characteristics of technical endosulfan, each of the isomers, and endosulfan sulfate are summarized in Tables 5.1.4 to 5.1.7. From the classification scheme in Ney, Jr. (1998), endosulfan is not soluble in water and it has a moderate volatility. The K_{ow} for endosulfan indicates an affinity to accumulate in organisms (Ney, Jr., 1998).

5.1.5.1.3.2. Chemical/Physical Properties and Environmental Behavior

Environmental Fate and Transport of Endosulfan

Volatilization may be a source of removal for endosulfan from the aquatic environment. In addition, α-endosulfan has been found to be more volatile than β-endosulfan (Goebel et al., 1982). Calculated half-lives of α-endosulfan, and β-endosulfan were found to be much greater in PTFE sealed than unsealed vessels in a sterile aqueous

medium (Guerin and Kennedy, 1992). The differences in half-lives between the PTFE sealed and unsealed vessels were more pronounced for α-endosulfan than β-endosulfan. Approximately 25% of the α-isomer disappeared from vials left in the open air for 24 h while a majority of the β-isomer remained suggesting greater volatility for α-endosulfan over β-endosulfan (Peterson and Batley, 1993). A possible conversion of the β to the α isomer may also create noticeable differences in gas phase concentrations (Rice et al., 1997). Volatilization is also an important route for the removal of endosulfan from the soil environment. After 24 h of incubation, more than 10% of the applied endosulfan was found to volatilize from soil surfaces (Rüdel, 1997). In four soil types, higher concentrations of endosulfan sulfate were found in uncovered trays over covered trays possibly due to volatilization from the former treatment (Van Dyk and Van der Linde, 1976).

Sorption

K_{oc} values determined for α- and β-endosulfan indicate that both isomers are largely immobile in the soil environment (U.S.EPA, 2001). Endosulfan may have a preference for sediment (Peterson and Batley, 1993) or particulate-phases in the aquatic environment (Greve and Wit, 1971). After spraying a formulation of endosulfan on tomato and pepper plants, higher concentrations of β-endosulfan were found bound to soil for most treatments and in water samples from the vadose zone than α-endosulfan or endosulfan sulfate (Antonious and Byers, 1997).

Remobilisation of α-endosulfan from sediment was found to be greater than endosulfan sulfate and β-endosulfan (Peterson and Batley, 1993). Since treatments were shaken, some of the endosulfan in the supernatant may have been bound to colloids.

Calculated sediment-water partition coefficients for α-endosulfan were lower than β-endosulfan for six sediments with varying organic carbon. Log K_{oc} s calculated for α-endosulfan and β-endosulfan were 3.6 and 4.3 indicating a preference for sediment association in aqueous systems. In filtered lagoon water, a greater proportion of endosulfan sulfate was found bound to particulate matter than α-endosulfan, β-endosulfan, or endosulfan diol (hydrolysis metabolite), respectively. α-Endosulfan was not bound to colloidal matter and only a small proportion of β-endosulfan was measured while a higher quantity of endosulfan sulfate was found associated with colloids.

Photolytic Degradation

Endosulfan isomers may be resistant to photolytic degradation (Ali, 1978; Goebel et al., 1982; U.S.EPA, 2001) and endosulfan sulfate may be even more stable than the parent compound when exposed to sunlight (Callahan et al., 1979). No endosulfan sulfate was found after thin film ultraviolet irradiation of α- and β-endosulfan for seven days (Archer et al., 1972). Larger quantities of endosulfan diol and lesser quantities of endosulfan ether, endosulfan α-hydroxy ether, endosulfan lactone, and an unknown compound were formed after irradiating α- and β-endosulfan for a week with UV light (Archer et al., 1972).

Hydrolytic Degradation

Hydrolysis in alkaline conditions (pH > 7) is likely to be important in the removal of endosulfan from aqueous systems. Increasing pH values were found to be more important in the removal of endosulfan from aqueous systems than microbial activity or some other natural water characteristics (Peterson and Batley, 1993). Hydrolysis half-lives of α- and β-endosulfan can extend to more than a month at pHs < 7 and temperatures < 20°C (Callahan et

al., 1979) and treatments at pH 7 had a half-life of days for α- and β-endosulfan, while at pH 9, half-lives were reduced to hours (U.S.EPA, 2001). In controlled hydrolysis experiments, the α-endosulfan isomer degraded faster than the β-isomer in various river waters (Peterson and Batley, 1993). Endosulfan diol is the major decomposition product from alkaline hydrolysis (Goebel et al., 1982).

Further evidence on the importance of alkaline hydrolysis in the removal of endosulfan was given by Kaur et al. (1998) who found that endosulfan half-lives decreased with increasing pH (5.5 and 8.0) and temperature (20° and 30^oC) in distilled water treated with magnesium sulfate. In the previous experiments, half-life changes were more drastic with increasing pH (from 11.3 to 5.3-d and 11.8 to 5.0-d for α- and β-endosulfan, respectively) than temperature (from 11.3 to 9.8-d and 11.8 to 10.6-d for α- and β-endosulfan, respectively).

Biodegradation

Under different conditions, a variety of fungi and bacterial organisms have been found to degrade endosulfan (Martens, 1976; Guerin, 1999; Miles and Moy, 1979; Katayama and Matsumura, 1993; Kullman and Matsumura, 1996). In a static-culture flask screening method, negligible biodegradation was found for α-endosulfan, β-endosulfan, endosulfan sulfate, and other organochlorine compounds by Tabak et al. (1981). Evidence that endosulfan's carbon structure is resistant to biodegradation was given by the absence of $^{14}CO_2$ after a 10-day incubation period for bacteria and a six-week period for fungi (Martens, 1976).

However, the preceding studies assessed cultures of microorganisms and their capacities to degrade endosulfan in the laboratory. Biodegradation may be enhanced or

hindered by varying characteristics of water and soil. For instance, with two colonies of soil microbes from a contaminated industrial site, Awasthi et al. (1997) found that endosulfan degraded much faster with bacteria in culture medium alone than when the pesticide was bound to soil, possibly due to its strong adsorption and/or additional carbon sources.

Endosulfan sulfate may also be formed from biodegradation by various species of fungi (Kullman and Matsumara, 1976; Martens, 1976) and by bacteria (Martens, 1976). Based on results with 16 species of fungi and 15 species of bacteria with the capacity to degrade endosulfan, fungi may be more likely to form endosulfan sulfate as a primary decomposition product and bacteria may be more likely to form endosulfan diol (Martens, 1976).

In static laboratory microcosms, endosulfan diol was measured in the sediment before the aqueous phase suggesting a biological degradation pathway in this medium (Peterson and Batley, 1993). In the lower dosage treatments, higher concentrations of endosulfan sulfate were found. Formation of the diol was equivalent to the original doses indicating a concentration-dependent degradation. However, the highest concentration, 5000 μg/L, which also experienced a decline in pH, formed roughly the same amount of diol as the next lower concentration, 500 μg/L. No endosulfan diol was found in the sediment at the highest concentration indicating that the microbes degrading endosulfan may have been eradicated (Peterson and Batley, 1993).

When soil microorganisms were incubated with endosulfan sulfate and α- and β-endosulfan, interconversion of α- to β-endosulfan occurred with greater amounts of α-endosulfan formed from β-endosulfan (Miles and Moy, 1979). The primary degradate of α- and β-endosulfan was endosulfan diol in incubations in an aqueous medium. Endosulfan diol

was transformed to endosulfan α-hydroxyether. Separate incubations with the latter compound gave endosulfan lactone as a primary metabolic product, which had a rapid disappearance.

Bioconcentration

The potential for bioaccumulation seems high when examining the K_{ow} for endosulfan. However, depuration appears to play a large role in the bioaccumulation potential of endosulfan. Calculated bioconcentration factors (BCFs) for zebra fish were 2650 ± 441 in a 21-day study with around 62% of total endosulfan concentrations excreted after a 120 h depuration period (Toledo and Jonsson, 1992). Yellow tetra, *Hyphessobrycon bifasciatus*, had 21-d BCFs for endosulfan ranging from approximately 10,000 to 12,000 with calculated depuration half-lives for α-endosulfan, β-endosulfan, and α- and β-endosulfan of 2.01, 1.74, and 1.81 days, respectively (Jonsson and Toledo, 1993). A steady-state α–endosulfan BCF for the mussel, *Mytilus edulis*, of 600 was calculated with an elimination half-life of 33.8 h (Ernst, 1977). Roberts (1972) reported rapid depuration in another bioaccumulation study with *M. edulis*.

In bioaccumulation experiments with mussels, *M. edulis* and *Chlamys opercularis*, Roberts (1975) hypothesized a preferential accumulation of α-endosulfan due to β-endosulfan being detected at later periods during the experiment. However, Toledo and Jonsson (1992) found higher first-order elimination half-live calculations for β-endosulfan and endosulfan sulfate over α-endosulfan. In their bioaccumulation experiments, Toledo and Jonsson (1992) observed a preferential formation of endosulfan sulfate in zebrafish from the β-isomer than from the α-isomer. Novak and Ahmad (1989) found endosulfan sulfate at

greater liver and whole tissue concentrations in field-collected catfish, *Tandanus tandanus*, than the isomers.

Aqueous Disappearance Rates

From the few studies reviewed below, it appears that α-endosulfan may be more persistent in aqueous environments. In both water and a sterile growth medium, β-endosulfan was found to more chemically labile than α-endosulfan (Guerin and Kennedy, 1992). In filtered, sterile water and a sterile growth medium, β-endosulfan was found to degrade faster than α-endosulfan which, in turn, degraded more rapidly than endosulfan sulfate (Guerin and Kennedy, 1992).

Cotham, Jr. and Bidleman (1989) found half-lives in sterilized and unsterilized seawater from the North Inlet Estuary, South Carolina, and seawater/sediment microcosms to be higher for α-endosulfan than β-endosulfan. In unsterile seawater at pH 8.0, half-lives of 4.9 days for α-endosulfan, and 2.2 days for β-endosulfan were determined through first order degradation calculations. For sterile seawater (pH 8) the half-lives decreased to 3.1 days and 2.0 days for α- and β-endosulfan, respectively. For pH 8.2, the half-lives were slightly lower for all treatments. Half-lives of 22 days and 8.3 days for α- and β-endosulfan, respectively were determined in systems with sediment and seawater at a pH of 7.3 to 7.7. The lower pH in treatments with sediment may have explained endosulfan's longer half-life (Cotham, Jr., and Bidleman, 1989). Endosulfan diol was the only detected metabolite and endosulfan sulfate was not detected in the overlying water of seawater/sediment.

In another study using sterile and nonsterile water and seawater/sediment slurries, Walker et al. (1988) found that degradation rates for endosulfan in sterile systems were

greater than in nonsterile systems. However, the authors feel that the addition of formalin in sterile systems probably enhanced the disappearance of endosulfan giving inaccurate rate constants for degradation. In nonsterile estuarine water, degradation rates of endosulfan were higher than in nonsterile sediment/water slurries (Walker et al., 1988). In unsterilized Little Miami River water (Ohio), 10 μg/L α- and β-endosulfan in 20 L jars were completely degraded after four weeks (Eichelberger and Lichtenberg, 1971). After one week, 30% of the original endosulfan applied remained and 5% remained after two weeks.

Additional information on the disappearance of endosulfan in the aquatic environment is summarized in the field studies section.

Degradation in Soil

The degradation rates of the isomers of endosulfan in soil follow an opposite trend to their decomposition in water. Generally, β-endosulfan persists longer in the soil environment than α-endosulfan (Antonious and Byers, 1997; Stewart and Cairns, 1974: Ghadiri and Rose, 2001: U.S.EPA, 2001). Using a Lowell silty loam soil (5% OM), a study was conducted at the Kentucky State University Research Farm where Thiodan 3 EC was applied once at recommended rates (0.61 kg AI/ha) (Antonious and Byers, 1997). Over a three-month period, the β-isomer of endosulfan was found to have a higher persistence than the α-isomer and endosulfan sulfate was a significant degradation product in soil (Antonious and Byers, 1997). In Somerset sandy loam treatments, α-endosulfan was found to be less persistent than β-endosulfan with approximately half of each remaining at 60 and 800 days, respectively (Stewart and Cairns, 1974). However, a comparable quantity of endosulfan sulfate was detected with the disappearance of the isomers (Stewart and Cairns, 1974). Endosulfan sulfate also seemed persistent in the soil.

The presence of total endosulfan in soil may be largely dictated by the degree of soil hydration and temperature (Ghadiri and Rose, 2001). From four month experiments conducted with clay soils collected from cotton fields, β-endosulfan was more persistent than α-endosulfan in all treatments. In treatments with low water submergence and temperature, the half-life of β-endosulfan in soil was calculated to be over a year and 27 days for α-endosulfan (Ghadiri and Rose, 2001). In the temperature range of 20-30°C, maximum half-lives for all endosulfan compounds were calculated in submerged soil treatments (Ghadiri and Rose, 2001). Likewise, Awasthi et al. (2000) found that degradation of both isomers of endosulfan were lower in submerged soils than non-flooded soils. In drier soil treatments and treatments with moisture, endosulfan sulfate was the primary degradate from the parent compound, particularly the α-isomer, and temperature was positively correlated with its removal (Ghadiri and Rose, 2001). Endosulfan sulfate formation was hindered under submerged conditions. Within four weeks of its initial application, α-endosulfan concentrations in a treatment with high temperatures and moisture declined rapidly but were relatively persistent thereafter. Other treatments with varying water temperature and water content did not have this initial rapid removal of α-endosulfan and half-lives increased between drier soils and water-logged soils. Except under submerged conditions, a negative correlation for β-endosulfan was found between soil half-lives and water content/temperature with degradation more influenced by temperature than moisture (Ghadiri and Rose, 2001).

Similar to aqueous environments, the pH of soils may also be a factor contributing to endosulfan's degradation. In a soil with a pH of 6.3, the half-lives of α- and β-endosulfan were 27.4 and 27.5 days while in a soil with a pH of 7.5, they decreased to 14.1 and 15.1 days (Kaur et al., 1998). In soils inoculated with isolated *Bacillus* sp. from a contaminated

site, Awasthi et al. (2000) found degradation over a six week period was enhanced by nearly 50% at pHs of 7.5 and 8.5 and no enhancement was found at pH 3.0 and only slight enhancement at pH 5.0. After six weeks, significant degradation for uninoculated soils was found for pH values of 7.5 and 8.5. Degradation of endosulfan isomers in uninoculated soils was slower below this optimal pH range. Endosulfan diol was rapidly formed at higher soil pHs (10.0 and 12.0), whereas low amounts were found at the lower pH values. Formed endosulfan diol underwent some degradation at higher pHs for inoculated treatments.

Degradation products detected in soils included endosulfan diol, endosulfan lactone, endosulfan alcohol, endosulfan ether, and endosulfan sulfate (Awasthi et al., 2000; Martens, 1977; Rao and Murty, 1980; Stewart and Cairns, 1974; Van Dyk and Van der Linde, 1976). Though endosulfan diol was found, Awasthi et al. (2000) did not recover any endosulfan sulfate in soils with isolated *Bacillus* sp. from a contaminated site. However, in wet and dry soils, endosulfan sulfate was the primary degradate in all treatments with the exception of a dry treatment receiving a higher application where endosulfan alcohol and endosulfan ether were the primary degradates detected (Rao and Murty, 1980). After 50 days, endosulfan sulfate appeared in the latter treatment possibly from recovery of soil fungi capable of forming it (Rao and Murty, 1980).

In a variety of soils, degradation of endosulfan was evaluated for different conditions (Martens, 1977). Aerobic conditions were found to favor the formation of endosulfan sulfate at 30 to 60% of the original application after 15 weeks. Under the same conditions, one soil had detectable quantities of endosulfan diol and endosulfan lactone. Two soils had relatively higher concentrations of radiolabelled carbon dioxide gas evolved in the aerobic conditions. Less endosulfan sulfate (12 to 22% of the original application) was found in soils incubated

under anaerobic conditions. This signified that the experimental setup was not thorough enough to remove oxygen entirely. Besides having lower concentrations of endosulfan sulfate than soils in aerobic conditions, a study with flooded soil samples had some of the highest concentrations of endosulfan diol and endosulfan hydroxyether detected only in flooded conditions.

5.1.5.1.3.3. Effects of Endosulfan on Aquatic Organisms

For the endosulfan RED, the U.S. EPA conducted two primary risk assessments for effects on nontarget aquatic organisms (U.S.EPA, 2001). The first utilized hazard quotients (HQs) from standard toxicity tests. For freshwater fish, acute and chronic HQs were above levels of concern (LOCs) with ranges from 1.2 to 23 based on maximum applications for acute effects and from 0.5 to 29 for chronic effects based on typical applications. Acute HQs for freshwater aquatic invertebrates were above LOCs with ranges from 0.17 to 3.3 based on maximum applications. Freshwater aquatic invertebrate chronic HQs were also above LOCs with ranges from 1.1 to 61 based on typical applications. HQs for estuarine and marine fish and invertebrates were higher than HQs for freshwater species. Acute HQs for estuarine and marine fish ranged from 9.8 to 191 based on maximum applications. Chronic HQs for marine and estuarine fish ranged from 5 to 316 based on typical applications. For estuarine and marine invertebrates, acute, with maximum application rates, and chronic HQs, with typical application rates, were in the ranges of 2.2 to 42 and 1.6 to 85, respectively. Unlike chlorpyrifos and malathion, ranges for HQs in the assessment for endosulfan were higher for freshwater and saltwater species of fish than for freshwater and saltwater species of invertebrates from standard toxicity tests. From the distribution of acute freshwater fish HQs

and Monte Carlo simulations to predict exceedences from typical usages in crop scenarios, acute LOCs set by the U.S.EPA would be exceeded 99% of the time by acute HQs for seven out of eight crops modeled.

In the second phase of the endosulfan RED, the EFED conducted a probabilistic assessment of aquatic risk. Modeling data were developed with application rates for the compound with a 300-ft. spray drift buffer. Resulting joint probability curves predicted that for a scenario involving tomato sprayings in Florida, there is a 50% probability that at least 75% of aquatic species would experience mortality. For a spraying scenario involving apples, there was a 50% probability that at least 5% of aquatic species would experience mortality

According to the U.S.EPA, the cyclodiene class of pesticides which endosulfan belongs to had the third highest rate of reported incidents for organism kills out of any other pesticide class, accounting for nearly 5% of all incidents on the EPA's Ecological Incident Information System since 1971 (U.S.EPA, 2001). In particular, endosulfan has one of the highest numbers of reported aquatic incidents in the U.S. out of any other cyclodiene pesticide with 91 reports since 1971. Out of all of these incidents, 96% were attributed to effects on aquatic organisms with 82% related to fish kills while 7% were associated with aquatic macroinvertebrates (U.S.EPA, 2001). After 300 ft. spray-drift buffers were implemented, the frequency of reported incidents involving endosulfan were still reported (U.S.EPA, 2001). The highest percentages of reported incidents were from California, Louisiana, North Carolina, and South Carolina.

5.1.5.2. Ecosystems Potentially at Risk

To determine the areas in C-111, Northeast Florida Bay and South Biscayne Bay that were potentially at risk we considered: (1) where, when and what quantities the pesticides were found and (2) the stressor characteristics.

5.1.5.3. Assessment Endpoints

The U.S EPA (1998) provides three criteria for selection of assessment endpoints (i.e., "expressions of the actual environmental value that is to be protected" (U.S.EPA, 1998)). They are the importance of the endpoints to the ecology of the system, the sensitivity of the endpoints to actual or possible stressors, and the utility to risk management goals and decisions.

This leads to the following assessment endpoints:

1) Survival and production of algae, periphyton and seagrasses provide habitat, food and energy for consumers and control the diversity of consumers within the different ecosystems. Seagrass are important to many biological and geochemical processes in Florida Bay. They are a food source for organisms and a habitat/substrate for many species, including juvenile fish and crustaceans. Wading birds and forage fish consume species that reside in seagrass ecosystems of the Bay. They also adjust the water quality in the Bay by trapping sediments in their root systems, using nutrients, and filtering particles out of the water column with their leafy above-sediment biomass.

2) Survival and function of microbial decomposers essential to the recycling of nutrients in sediments and surface waters of the ecosystems.

3) Survival and production of macroinvertebrates (e.g., pink shrimp) which provide food in and on sediments. The multi-million dollar shrimp industry of the Tortugas relies on the health of pink shrimp populations in Florida Bay. Pink shrimp enter Florida Bay as postlarvae and spend part of their juvenile life-stage there before returning to the Tortugas to spawn. In addition, pink shrimp are an integral component of the food web in Florida Bay and are consumed by wading birds and game fish (citations for this paragraph in Browder et al., 2002).

4) Survival and production of invertebrate herbivores that exert functional control over the primary producers.

5) Survival and production of fish that exert functional control over the primary producers and primary consumers (herbivores). For many vertebrate species in the ENP, fish are an important food source (U.S.ACE, 2000). Biscayne Bay and Florida Bay sport-fishing is of economic importance to the region.

5.5.5.4. Conceptual Model

Exposure to a stressor is required for an effect to occur. Exposure can be through direct contact with a media (in this case, water) and involves either dermal contact with the contaminant or ingestion. Indirect exposures can also occur through consumption of an organism that has already accumulated the COPEC within its tissue. This type of exposure will not be assessed in this SERA. Risks from exposure to pesticides in the current SERA will be calculated from direct contact with the COPECs in surface water.

The major uses of the pesticides in the C-111 basin (e.g., Frog Pond) are for agriculture. Because pesticide input would occur mainly during spraying and surface runoff events (e.g., especially endosulfan and chlorpyrifos) and because most dissipate rapidly in surface water, pesticides would be expected to be present in intermittent pulses, rather than continuously. Defining the spatial and temporal exposure distribution of the five pesticides in the C-111 system and estuarine sites was a major objective of the SERA. A conceptual site exposure model was created to trace the path of COPECs from their sources to ecological receptors. It is a useful tool for evaluating assessment endpoints and measures of effect (U.S.EPA, 1994, 1997). The site conceptual exposure model is illustrated in Figure 5.1.4.

The SERA focused on plants, invertebrates and fish. Aquatic plants (e.g., algae, periphyton, seagrass) possess the target site for the herbicides (i.e., atrazine and metolachlor). There are limited toxicity data for the herbicides and seagrass. This is important since some seagrass meadows are found in shallow, nearshore habitat making them vulnerable to freshwater discharges and runoff. Invertebrate and fish groups are generally more sensitive to insecticides (e.g., chlorpyrifos, malathion and endosulfan) exposure which could may or may not cause direct effects or indirect effects on these populations. There are limited toxicity data on amphibians and microbial decomposers. The guild concept of Morrison et al. (1992) was adapted to create a conceptual model that considers the susceptibility of species to COPECs, due to sensitivity and exposure likelihood, and the value of the receptors. The site conceptual effects model is illustrated in Figure 5.1.5.

Measures of effect, also known as measurement endpoints, are used to quantify potential risks to assessment endpoints (U.S.EPA, 1998). Assessment endpoints may be directly measured or surrogate measurements may be used in place of them, if direct

measurements are unavailable, for a measure of effect. Along with measures of effect, measures of exposure and measures of ecosystem characteristics are used to evaluate the pathway from source to receptor, and to take into consideration characteristics of an ecosystem that may influence the interaction between an assessment endpoint and a stressor, respectively. These measures are discussed in the Analysis Plan (Section 5.5) and are used to focus the assessment on attributes important to estimating risk.

According to the U.S.EPA framework (U.S.EPA, 1998), the considerations for selecting or formulating measures of effect are ecological relevance, susceptibility to the effects associated with the stressors (COPECs) and policy goals and societal values. Given the latter considerations and based on the conceptual model of potential exposure and effects, the risk hypotheses including measures of effect and exposure were addressed:

1. The concentrations of insecticides in the C-111 system and related estuarine sites may be of sufficient magnitude to induce acute effects on fish or arthropods.
2. The concentrations of herbicides in the C-111 system and related estuarine sites may be of sufficient magnitude to induce effects on aquatic phytoplankton or plants.
3. The concentrations of pesticides in the C-111 system and related estuarine sites may be of sufficient magnitude to induce chronic effects on aquatic organisms.

The first risk hypothesis is related to assessment endpoint numbers 3, 4 and 5. The measurements of effect to test this hypothesis were from acute laboratory tests measuring LC/EC50s for survival. The second risk hypothesis is related to assessment endpoint 1. The measurements of effects to test this hypothesis were from laboratory toxicity studies measuring LC/EC50s for growth, reproduction, or survival. The third risk hypothesis is

related to assessment endpoint numbers 1, 3, 4, and 5. The measurements of effect to test this hypothesis were from chronic laboratory tests measuring NOECs for survival, growth, or reproduction. Field/mesocosm studies will be used as supporting information for the first and third hypotheses.

Assessment endpoint 2 was not addressed as fully as the others due to insufficient microbial toxicity information. All hypotheses were addressed in light of single and multiple chemical pesticide exposures in water.

If the two hypotheses are not negated, several factors can be further examined. These include what sites and time periods effects may occur, susceptible organisms or taxa of organisms, and what structural or functional roles the susceptible species play (e.g., an invertebrate that is an important food species to fish) (Giddings et al., 2001). The latter two items will not be addressed, while the first item will be, in this phase of the C-111 SERA. The fist item was addressed in the C-111 system, northeast Florida Bay and Biscayne Bay, by considering risk to aquatic receptors for fresh- and salt-water organisms as separate groups and analyzing sampling sites in these systems separately at peak dry (February) and wet (June) season months to determine where and when the potential risks were greatest. The latter two items can be assessed in the next phase using other models.

5.1.5.5. Analysis Plan

The following section describes the analysis plan for the ecological risk assessment of the five pesticides in the C-111 canal. The analysis plan consists of three components: An exposure analysis, an effects analysis, and a risk characterization. To evaluate the significance of ecological effects, the characteristics of the five pesticides detected with the highest consistency in C-111 and estuarine sites were reviewed and summarized to assess the

possible pathways for their fate and transport in C-111. This information was utilized to gain a picture of possible exposure pathways (see Figure 5.1.4).

The understanding of what segments of the aquatic community in the C-111 system and related estuarine sites that could be susceptible to each of these five pesticides was specified in our assessment endpoints and ecological effects information from single-species laboratory toxicity tests was compiled and reviewed for this purpose. Exposure values and effects data for all compounds were then aggregated to create a risk characterization for the C-111 system and estuarine sites that could account for the spatial heterogeneity in the system. Any uncertainties that arose from the analyses and available or missing data were articulated throughout the assessment or in the Uncertainties section. The C-111 risk assessment was a SERA but an attempt was made to include all pertinent exposure and effects data for the ecosystem at risk. This was done through collecting literature and database information on measured concentrations of pesticides in the system and their potential effects (see Sections 6.2 and 6.3). Two of the five compounds, atrazine and chlorpyrifos, have published aquatic risk assessments on usage in North America, which included reviews of many relevant studies (Solomon et al., 1996; Giesy et al., 1999).

5.1.5.5.1. Exposure Analysis

For exposure, data on the concentrations of the five pesticides in C-111, South Biscayne Bay and Florida Bay were obtained by using AMCs in surface water from monitoring studies from 1999-2000 (sampling sites in Figure 5.1.1). The monitoring sources included South Florida Water Management District (SFWMD), a state agency, the U.S. Geological Survey (USGS), and the National Oceanic and Atmospheric Administration

(NOAA). Out of all biocides analyzed in C-111 and estuarine sites, atrazine, chlorpyrifos, endosulfan, malathion, and metolachlor were detected by the various monitoring programs with the highest frequency. Tier 1 of the risk assessment (Section 4) was used to screen these chemicals with a conservative methodology to determine COPECs. All pesticides determined to be COPECs were further analyzed in Tier 2 of the risk analysis.

In Tier 2, the exposure analysis evaluated measured concentrations of atrazine, chlorpyrifos, endosulfan, malathion, and metolachlor in C-111 and estuarine sites. Data existed for some areas in Biscayne Bay and Florida Bay. After geocoding the various monitoring stations on a map (Figure 5.1.1) generated with ArcView Geographic Information System (GIS) software, sampling sites in C-111 were assessed separately. Since annual data were sporadic, in many cases, and sampling events sometimes spanned months, analytical measurements were used on an instantaneous basis for the assessment. For analytical concentrations that were reported on the same day, at the same site, and by the same monitoring agency, the highest concentration was taken to increase conservatism. Some of the monitoring data from NOAA consisted of 24 or 48 h composite surface water samples. If a composite sample spanned $\geq$ 24 h and fell on the same day as a discrete sample, concentrations reported from the composite were placed on the day that did not have a discrete or composite sample available. If each of the days a composite sample were taken fell on the day another sample was taken, analytical concentrations were chosen in the same manner as when two discrete samples fell on the same day. Monitoring data were then assessed on an annual basis (i.e., for two years, 1999, and 2000), with all sites aggregated, and also on a site-specific basis, with all years aggregated for each compound, whether detected in a freshwater site or brackish discharge site. Also data were aggregated for

months at sites where water quality violations were found. Concentration values were ranked to create cumulative distributions and nondetects were assigned a dummy value of zero for the lower ranks in a left-censored distribution (Giddings et al., 2000b). Plotting positions were calculated from the ranks as $(j*100)/(n+1)$ where j is the rank and n is the total number of observations.

In Tier 2, the 90th centile and median exposure concentration (exceedence of a value only 10 % of the time) was calculated as a benchmark for acute and chronic risks, respectively, and the corresponding concentrations were compared for each year and sampling site (Solomon et al., 1996). In some cases, an *e* value was found next to concentration values from USGS data on C-111. The *e* value usually signifies that a measured concentration was too low to be quantified or is below the normal reporting level. These values were only encountered on a few samples and the number following the *e* was used. Monitoring data used from the SFWMD at the time of the analysis did not include values below the method detection limit (MDL).

In Tier 1, ambient concentrations of pesticides at each site were compared to WQC and toxicity endpoints (LC/EC50s). This helped to focus the assessment on stressors, time periods and sites of high potential risks. HQ exceedences in Tier 1 were used to focus the risk characterization portion of the Tier 2 assessment. In Tier 2, benchmark values (90th centile estimates for exposure) were chosen for centile ranks and the corresponding concentrations were compared for each year and sampling site (Solomon et al., 1996). Any sample taken during a specific time frame and at a site has a 90% chance of being below the estimated 90th centile concentration if the values in the distribution are unbiased and accurately represent the concentrations found over that time period and location (Giddings et

al., 2000b). The 90th centile concentration estimates were determined using the nonparametric analyses below for the exposure data reported by the different agencies.

In most cases, the exposure data did not fit the log-logistic model used in the effects analysis well (see Section 5.5.2). In addition, most data sets were large. For these reasons, a nonparametric method was utilized to calculate the centile estimates of exposure.

The nonparametric method is as follows:

Let $X_1, \ldots, X_N$ be a random sample and $X_{(1)}, X_{(2)}, \ldots, X_{(N)}$ be order statistics.

Let $np = 0.9(n + 1)$. Then,

the 90th centile = $X_{(n1)} + (np - n_1)(X_{(n2)} - X_{(n1)})$

where n_1 is the integer part of np and $n_2 = n_1 + 1$. When np is greater than N, we let the 90th centile equal $X_{(N)}$.

If four values were reported above the MDL, a log-logistic distribution was created for monthly exposure scenarios (Hall, Jr., et al., 2000). α-Endosulfan, β-endosulfan, and endosulfan sulfate concentrations were summed to give a value for total endosulfan. The toxicity of endosulfan sulfate and the parent compound are similar (IPCS, 1988).

5.5.2. Effects Analysis

Published reports have used species sensitivity distributions (SSDs) derived from laboratory toxicity data to characterize effects and susceptibility of organisms at sites to chemical stressors (Hall, Jr. et al., 1998; Giddings et al., 2000b; Hall, Jr., et al., 2000). However, the majority of ecological assessments have relied on the deterministic usage of HQs. The HQ methodology typically divides an environmental concentration, usually worst case, by an effects measurement from a toxicity test (e.g., LC50, NOEC) (Solomon, 1996). We used the HQ approach for a Tier 1 screen (Section 4). The methodologies adopted for

the second tier of this risk assessment rely on SSDs for effects analysis and risk characterization (see Section 5.5). The SSD approach uses more toxicity information than the HQ approach and takes into consideration the likelihood of exceeding a certain proportion of toxicity values rather than only a single point estimate (Solomon et al., 1996). In the current SERA, the value of the SSD approach lies in its ability to distinguish areas that may have higher potential risks than others and to eliminate areas with low potential risk after using as much existing data as possible (Giesy et al., 1999). This can prioritize future research on the ecosystems and species that may be more susceptible to the direct and indirect effects of pesticides.

For effects, acute (LC/EC50) and chronic (NOEC) laboratory toxicity data for water exposures from atrazine, chlorpyrifos, endosulfan, malathion, and metolachlor were collected and analyzed. SSDs with LC/EC50s were created for aquatic plants/phytoplankton, arthropod invertebrates, and fish for each of the pesticides to characterize susceptibility at the different sites. For chronic curves, all organisms were combined and not separated into taxa because of the limited toxicity data. Acute endpoints were taken from databases of toxicity metrices maintained by the U.S.EPA, i.e., the AQUIRE database and the EPA One Liners Database (Montague, 2002). Additional data for atrazine effects, particularly on saltwater plants and algae, were taken from Giddings et al. (2000a). Due to a paucity of chronic information from AQUIRE for each compound, values were taken from published papers and various government monitoring reports (Crommentuijn et al., 1997; van de Plassche et al., 1994).

Only toxicity endpoints that could be clearly related to changes in population structure such as growth, reproduction, and survival were used and a species could only be

represented once in each distribution. Effects data were first screened for usage in SSDs. Endpoints with a > or < value preceding the toxicity estimate were not included in an SSD unless a > exceeded the water solubility. Species that were collected from polluted sites were not used. If a formulation was used and specified, then formulations containing less than 80% active ingredient were excluded (Crommentuijn et al., 1997). Endosulfan effects data were also screened for studies that used technical endosulfan. Studies with the individual isomers or with endosulfan sulfate were not included. A data point would have only been available for one additional species if this was done. Survival, growth, mortality, and reproductive endpoints were all included in the development of SSDs and other endpoints were excluded. In order to include enough species, toxicity tests that reported values derived from nominal concentrations were included. For fish, only species with reproducing populations in North America were included in SSDs using an internet database developed by Froese and Pauly (2002). Invertebrates (e.g., arthropods) were included whether they had populations established in the U.S. or not to capture a greater amount of sensitivities within their distributions for the probabilistic portion of the assessment. If organisms used in the test were not identified to the species level, their data were still included in the Tier 2 effects analysis. Toxicity tests with multiple species or that were conducted in the field were excluded from the SSDs.

For fish, amphibians, arthropods, and other invertebrates, acute test durations within the 24 to 96 h duration were included in the SSDs. Outside of this duration an 8 d acute teratogenic study with *Rana catesbaiana* and atrazine was included. In tests where several effect measurements were taken over an extended time period, only the final measurement was used as long as it fell within an acceptable time frame. LC/EC50s for plant and algae

species within the 144 to 168 h duration for exposure were used for any of the pesticides that had endpoints available within this duration. If LC/EC50 endpoints within this time frame were not available, acute toxicity tests from 24 h to 14 d were used for algae and multicellular plants, but only when 144 to 168 h measurements were missing for a single species. Eelgrass (*Zostera marina*) had several 21 d study LC50 studies that were included as a representative plant species for atrazine effects on seagrass.

Plant and algae data were lacking for some compounds (chlorpyrifos freshwater species, malathion fresh- and salt-water species, and endosulfan fresh- and salt-water species) so distributions could not be created. Also, saltwater data were missing for some pesticides and species taxa. In the case of metolachlor, only data from four saltwater species were available for assessment. In the case of estuarine fish and phytoplankton/plants, freshwater organisms with metolachlor acute toxicity endpoints were combined with saltwater organisms so risk levels could be established for these communities. The same was done with atrazine and saltwater and freshwater fish since only two saltwater species endpoints were available for atrazine and fish. A deficiency in toxicity data for amphibians was apparent for all the pesticides and only atrazine had a sufficient number of plotting points ($n \geq 4$) to create a SSD for this taxa. Malathion had two species of freshwater amphibians available for analysis and endosulfan had three.

After screening all aquatic species acute toxicity data for each compound, the geometric mean of all available endpoints from toxicity tests for each species was taken (Solomon et al., 2001). When data for a species with different responses (e.g., growth, biomass, survival, LC50, EC50, etc.) were available, these were integrated in the same manner. If life-stage information was available for a species, the most sensitive life stage,

based upon the geometric means for concentration, was chosen as an endpoint for effects analysis.

The available species geometric means were then partitioned into freshwater and saltwater species and further subdivided into fish, amphibians, phytoplankton and multicellular plants, arthropods, molluscs, and other invertebrates. To create proportions (percent ranks) for the species in the cumulative distributions, the species geometric mean data for each of the above partitions were ordered by concentration and plotting positions were calculated as $(j*100)/(n+1)$ where j is the rank and n is the total number of observations (Warren-Hicks et al., 2002). Tables 5.1.13 and 5.1.16 include data on the number of species plotted and the total number of species with acceptable endpoints for each distribution of acute effects.

Molluscs were generally not found to be sensitive or robust enough for a full assessment. The endpoint for adult molluscs is generally based upon shell growth. This is usually a tolerant endpoint so in cases where the value was above the water solubility of the compound, molluscs were excluded from plotting but used to calculate rank (n) in the assessment of all species. Likewise, all endpoints above the water solubility of the compound were not given a plotting position but used for the calculation of rank (n) (ECOFRAM, 1999). In plotting distributions for all organisms, this was done with acute effects data for multi-cellular plants and phytoplankton while dealing with insecticides due to their general tolerance (Solomon et al., 2001). For a distribution to be considered for analysis, at least four suitable species' endpoints had to be available (Aldenberg and Slob, 1993).

Log-transformed concentration endpoints were then plotted against the cumulative probabilities for each species and the 10th centiles for each distribution were gauged for analysis. Because they are generally conservative, 10th centile estimates from toxicity distributions were recommended for use as an upper concentration limit that is protective of aquatic ecosystems (SETAC, 1994).

All effects (toxicity) data used for SSDs were assumed to fit a log-logistic distribution and graphical output was produced through the software program S-Plus (1999). Though log-normal distributions have been utilized in many North American ecological risk assessments (Solomon et al., 1996; Hall, Jr., et al., 1998; Giesy et al., 1999; Giddings et al., 2000b; Hall, Jr., et al., 2000), "there are no theoretical grounds" for choosing a log-normal or log-logistic model (de Zwart, 2002). The preference for logistic probability density functions (PDFs) in this assessment was based on their mathematical tractability, particularly in the risk characterization for pesticide mixtures (Traas et al., 2002). In addition, the extended tails of the logistic distribution can give lower target effect concentrations imparting greater conservatism to the analysis (Aldenberg and Slob, 1993).

The linear regression form of the model used for calculating our results from the SSDs is as follows:

$$\text{logit}(p) = \log\left(\frac{p}{1-p}\right) = \alpha^* + \beta^* \log_{10}(x),$$

where x is the geometric mean of a species effect concentration (i.e., LC50, EC50) and p is the probability of an effect at a specific concentration. α and β are scale parameters derived from the sample mean of the log toxicity data and from the standard deviation of the log toxicity data multiplied by the 0.55 (or the square root of 3 divided by π), respectively. For compounds with the same toxic mode of action (TMoA), the β parameter, or the SSD's

slope, has been found to be similar for each distribution with a community of species tested, with a high enough *n* value, that share that mode of action (de Zwart, 2002). Parameter estimates generated from the above model are presented in Tables 5.1.13 and 5.1.16 and were based on parameters extracted from SSDs in Warren-Hicks et al. (2002). The root mean square error (MSE) in the table indicates the fit of the model's data, a smaller root MSE indicates a better fit in the logistic regression model generated from the equation above (Warren-Hicks et al., 2002). The parameters from each distribution were used to estimate the 10th centiles of the SSDs and for a multiple chemical assessment to consider the potential effects of contaminant mixture exposures on organisms in C-111 and estuarine sites.

5.1.5.5.3. Risk Characterization

Risk was assessed by comparing the overlap of the distributions of AMCs and toxicity values for sites and species of concern. The 90th centile of the AMCs for exposure was compared to the 10th centile of the SSDs for acute risk to arthropods and fish and risk to phytoplankton/aquatic plants (SETAC, 1994). The 50th centile of the AMCs was compared to the 10th centile of SSDs for chronic risks to aquatic organisms (Traas et al., 2002). When a centile concentration from the exposure data was applied to a SSD, a potentially affected fraction (PAF) of species number was derived for a single compound. Any exceedences above the 10th centile of a SSD were noted for acute and chronic risk. The PAF or fraction of species affected that is calculated from the SSD at a concentration (Klepper and Van de Meent, 1997) allows one to determine that "a certain fraction of species is expected to be (potentially) affected above its (acute or chronic) effect level at a given environmental concentration" (Traas et al., 2002). The PAF approach allow us to assess pesticides both

singly and as mixtures (i.e., the msPAF) and compare relative potential risks among different sites and time intervals within C-111 and related estuarine discharge sites (Traas et al., 2002).

For all individual substances, a PAF value was calculated in the equation for log-logistic toxicity data (from Traas et al., 2002):

$$\mathrm{PAF}_i(x) = \frac{1}{1 + e^{-(x-\alpha)/\beta}}$$

where α is the mean of log toxicity data and β is equal to $(\sigma \cdot \sqrt{3}) / \pi$ with σ the standard deviation and *x* the log of the exposure concentration. For assessing LC/EC50 effects data, *x* was determined to be the 90th centile of the exposure distribution for each compound. For the chronic effects assessment, *x* was the median concentration (fiftieth centile estimate) from the exposure data.

The last step in the single chemical PRA approach used was the generation of a joint probability curve (JPC) or exceedence profile for each exposure scenario assessed (Solomon et al., 2000). The JPC characterizes "the relationship between the magnitude of effect and the probability of occurrence for that effect" (ECOFRAM, 1999). With robust exposure and effects distributions, the JPC can be used to determine the proportion of toxicity values exceeded over the duration of the monitoring period. Constructing a JPC entails comparing a vertical axis for an exposure distribution, i.e., the cumulative probability of an observed or predicted concentration, to a vertical axis for an effects distribution, i.e., the probability of an effect level, for a regression (ECOFRAM, 1999). Concentration is the shared independent variable between the two aforementioned axes. JPCs were created with distributions of exposure concentrations at sites from 1999 and 2000 and used to perceive the amount of overlap between these measured concentrations and available effects data. Also, JPCs were

created with exposure concentrations from February (dry season) and June (wet season) at sites by comparing them to acute LC/EC50 data for fish and arthropod species.

The following estimated centile concentrations were extrapolated from an exposure distribution and compared to a distribution of acute effects to create a JPC: the 99th centile, the 95th centile, the 90th centile, the 75th centile, and the 50th centile concentration estimate. After the 90th centile exposure estimate is subtracted from 100, we can state that for 10% of the exposure concentrations, x% of the toxicity values would be surpassed (Solomon et al., 2000). The x% would be determined from where the 90th centile estimated concentration from the exposure distribution intersected the response axis of an effects distribution. The majority of the centiles chosen from the exposure distribution were at the upper tail of the distribution. This is consistent with measured concentrations in C-111, which generally only intersected the lower portion of the effects distribution. The centile concentrations for an exposure distribution were chosen utilizing a nonparametric method for the distributions with all available data from 1999 and 2000 at a site of concern. The centile concentrations for an exposure distribution from a particular month were chosen using a log-logistic regression of cumulative exposure values since the number of observations was too low for the nonparametric method.

A visual depiction of the creation of a JPC is presented in Figures 5.1.6 and 5.1.7. In Figure 5.1.6, both the exposure and effects data were fitted to log-logistic distributions. The solid black lines illustrate how the centiles of an exposure distribution (i.e., the 99th, 95th, 90th, 75th, and 50th) intersect an effects distribution to create a JPC. Figure 5.1.7 shows a JPC curve constructed by linear interpolation from Figure 5.1.6. From Figure 5.1.7, it can be stated

that 10% of the toxicity values potentially have a 1% probability of being exceeded by the exposure concentrations if no underlying assumptions from either distribution are violated. As the JPC approaches the axes, a lower potential risk is implied (Solomon et al., 2000).

JPCs were created to display comparative risks for the pesticides, sites, and scenarios that showed exceedences in the first tier of the assessment. These were generally scenarios that had a higher overlap in exposure and effects distributions. The distance the JPC curves were from the origin of the graph and the risk quotients derived from the centiles were utilized to rank spatial and temporal risk scenarios for C-111 and estuarine sites for each compound. Risks to various taxa of species (arthropods, fish, etc.) at various sites were also evaluated for individual pesticides. In addition, JPCs were created with exposure concentrations from February (dry season) and June (wet season) at sites by comparing them to acute LC/EC50 data for fish and arthropod species.

5.1.5.5.4. Multiple Substance Assessment

The potential risks from acute and chronic exposures to the joint action of pesticide mixtures were also compared among sampling sites and time periods. Methodologies used to estimate acute and chronic risks to organisms from being exposed to joint action of pesticides were adapted from the multiple substance potentially affected fraction (msPAF) assessment approach (Traas et al., 2002). This approach was modified for SSD applications from classical toxicological mixture theories (i.e., concentration and response addition). For risk characterization of multiple chemical exposures, individual PAF values were assimilated and used to calculate and predict the risk from exposure to a mixture of chemical stressors (i.e., the msPAF) (Traas et al., 2002).

Concentration addition (CA) is a concept utilized to describe the additive effects of mixtures of chemicals with the same TMoA (Plackett and Hewlett, 1952). A basic assumption in CA is that multiple chemicals have the same molecular site of action. For application into the CA portion of the multiple substance assessment, the concentration of concern for each pesticide in a site or time period was transformed to hazard units (HU) representing the relative potency of the actual measured environmental concentration to an SSD (Traas et al., 2002):

$$\mathrm{HU} = \frac{C_{\mathrm{ENV}}}{10^{\alpha}}$$

where α represents the mean of log toxicity data and C_{ENV} is an exposure concentration of concern. HU has no units and the transformation of exposure concentrations to HUs is similar to the scaling of toxic units in classical applications of CA theory (Traas et al., 2002). The sum of the HUs from a particular centile of the relevant exposure distribution was substituted into the equation below. For the msPAF values for CA, HUs were summed for all compounds with the same mode of action. The slopes of the SSDs, or β, were averaged for the compounds with the same TMoA and the values were substituted into the following equation (from Traas et al., 2002):

$$\mathrm{PAF}_{\mathrm{TMoA}} = \frac{1}{1 + e^{-\log(\Sigma \mathrm{HU}_{\mathrm{TMoA}})/\beta_{\mathrm{TMoA}}}}$$

CA was utilized on the two OP insecticides, chlorpyrifos and malathion. Chlorpyrifos and malathion are both OPs that act by inhibiting the enzyme acetylcholinesterase (AChE). Since plants and algae lack the receptor site necessary for the TMoA of chlorpyrifos and malathion, the rules of CA would not be applied to those classes of species for chlorpyrifos and malathion and response addition (RA) would be used.

However, chlorpyrifos was the only insecticide that had enough species available ($n \geq 4$) to create a SSD for plants and algae.

Because atrazine (inhibition of PS II) and metolachlor (inhibition of protein synthesis) are from two different chemical classes with different modes of action, their joint action was modeled using response addition (RA), which assumes dissimilar TMoAs in its application (Traas et al., 2002). Like CA, RA assumes no toxicological interaction (e.g., synergism) between compounds. Unlike CA, RA assumes dissimilarities in modes of action and target molecular sites between chemicals. Organisms are expected to have a similar overall response to contaminant exposure in RA (Faust et al., 2000).

RA theory includes the addition of a correlation coefficient, *r*, that accounts for the covariation of sensitivities of compounds in a mixture, or the sensitivities of organisms to different compounds in a mixture (Könemann, 1981). A range of +1 to –1 has been determined for *r* corresponding with complete negative and complete positive correlations at either end. For example, in a binary mixture, a shared sensitivity for an organism between both chemicals could be inferred at the positive end and an unshared sensitivity at the negative end, where an organism that is tolerant to one chemical is susceptible to another (Könemann, 1981). For SSD purposes, *r* refers to species sensitivities rather than individuals in a population (Traas et al., 2002). For practical purposes, *r* will be set at 0, thus assuming no correlation. This is justified since positive and negative correlations for *r* have not been proven to fully exist yet (Backhaus et al., 2000). Moreover, RA ($r = 0$) calculations have been reported to have accurate predicting power for the toxicity of complex mixtures to the marine bacterium, *Vibrio fischeri*, in recent experiments (Backhaus et al., 2000).

When using SSDs to estimate risks from multiple substance exposures, CA and RA models require different correlation approaches between pesticides (Traas et al., 2002). In CA, effects from two chemicals in a mixture are combined based on the toxic magnitude of each through HU scaling. While in RA, effects from two chemicals (A and B) are combined corresponding to the "probability of two nonexcluding processes" (Hewlett and Plackett, 1979 as cited in Traas et al., 2002):

$$P(A \cup B) = P(A) + P(B) - P(A \cap B)$$

The msPAF for RA was calculated using the nonaffected fraction (the derivation from the probability model above is found in Traas et al., 2002) with the following equation (from Traas et al., 2002):

$$\mathrm{PAF}_{\mathrm{RA}} = 1 - \prod_i (1 - \mathrm{PAF}_i)$$

for i = 1 to n pesticides, and $\mathrm{PAF}_{\mathrm{RA}}$ calculated for all compounds in RA with r = 0.

When two or more pesticides with the same TMoA were detected four or more times at a similar site between 1999 and 2000 or during the same year, the distribution for the two classes of compounds were aggregated based upon CA mathematical procedures (Traas et al., 2002). For each site and each year, CA was only applied to chlorpyrifos and malathion. When only one compound from each group was detected at a site, the single chemical PAF values were not integrated using CA with another pesticide. The individual PAF value could be applied to the RA calculations to integrate with other compounds in a mixture. The msPAF values obtained from CA for chlorpyrifos and malathion were then aggregated based

on RA with the PAF values for atrazine, metolachlor, and endosulfan to obtain msPAF values for each year or site.

Concentration and response addition were used to evaluate acute effects on fish, arthropods, and phytoplankton/plants exposed to the 90th centile exposure concentration from a site and/or a time period and to evaluate chronic effects on organisms from the median concentration from a site or year with all freshwater or saltwater sites combined. In addition, acute toxicity data were further examined using the joint toxicity models of Traas et al. (2002) by applying various exposure concentrations to create JPCs.

5.1.6. RISK ANALYSIS

5.1.6.1. Introduction

In the Risk Analysis portion, only statistics from measured concentrations and existing ecotoxicity data for the two COPECs determined in Tier 1 were discussed. Data on additional compounds are presented in tables and figures referenced throughout the section. For exposure, data on the concentrations of endosulfan and chlorpyrifos in C-111, South Biscayne Bay and Florida Bay were obtained by using AMCs from monitoring studies from 1999-2000 (Figure 5.1.1). The monitoring sources included the SFWMD, a state agency, the USGS, and NOAA. The sites utilized from the SFWMD monitoring program were sampled quarterly and located at S-176, the northernmost site in the region, S-177 and S-175 in the northwest, S-178 on C-111E and S-332 on L-31. Chlorpyrifos was not analyzed by SFWMD. USGS monitors surface water in South Florida as a part of the National Ambient Water-Quality Assessment Program (NAWQA). In C-111, the only site that was sampled by USGS

with consistency for pesticides was at S-177. Sampling by USGS at S-177 was approximately monthly. NOAA had the most comprehensive spatial sampling of the C-111 system with sampling three times per year to capture the wet, dry and transition periods. Sites in or adjacent to C-111 included E-1, E-2, W-1, W-2, and B. Samples by NOAA were also taken at A on L-31 and C on C-111E. Sites at Highway Creek and Joe Bay were at the Northeast part of Florida Bay. Card Sound was used as a reference site by NOAA.

For the assessment of acute risk, 90th centile estimates were chosen as the benchmark level for exposure (SETAC, 1994). Tables 5.1.9 and 5.1.11 present the 90th centile estimates for fresh and saltwater sites for the 1999 and 2000 period. Tables 5.1.10 and 5.1.12 present the 90th centile estimates for each year in all freshwater and saltwater sites. The reported 90th centile estimates were determined using the nonparametric analysis discussed in the Analysis Plan (Section 5.5) from the exposure data reported by the various monitoring agencies.

In the case of exposure concentrations that were separated into months (i.e., February and June) based on water quality violations (see Tier 1), distributions were assumed to be log-logistically distributed and various centile estimates for exposure concentrations (e.g., the 90th centile) were derived from this distribution. If four values were reported above the MDL, a log-logistic distribution was created for monthly exposure scenarios (Hall, Jr., et al., 2000).

α-Endosulfan, β-endosulfan, and endosulfan sulfate were summed to give a value for total endosulfan. Endosulfan sulfate and the parent compound have similar toxicity (IPCS, 1988). In the text, either of the isomers or the sulfate will be referred to as endosulfan. Each monitoring agency did not have data available for at least one of the target pesticides. The SFWMD did not have measured concentrations data for chlorpyrifos. NOAA did not analyze

for malathion. The USGS analyzed for all compounds except β-endosulfan and endosulfan sulfate. The USGS, however, did analyze for α-endosulfan in 1998 but not in years after so no endosulfan data were available from NAWQA for S-177/Site B. However, S-177/Site B was the only site that had pesticide monitoring data from 1999 to 2000, by all three agencies. S-175, S-176, and S-332 were only monitored for pesticides by the SFWMD. S-175 only had monitoring data for 1999 as a part of a special program to monitor water quality with changes in water movement and timing at the Site. Data were only available at S-175 from July to November of 1999, which did not capture pesticide concentrations at the height of the dry season. In addition, the SFWMD and NOAA monitored S-178/Site C and S-18C/Site E jointly. All of the remaining sampling sites were monitored exclusively by NOAA.

For the effects analysis used in this tier of the assessment, distributions of aqueous acute (e.g., LC50s, EC50s) and chronic (e.g., NOECs) toxicity endpoints for various taxa of species and species communities in freshwater and estuarine water were generated. These curves demonstrated the sensitivities for aquatic plants (phytoplankton), invertebrates and fish to the pesticides to characterize effects and susceptibility at the different sites. The analysis at this point of the SERA for C-111 clustered all static, renewal, and flow-through aquatic toxicity data that fit the established duration for acute and chronic analysis. Protocols for screening and handling data in the creation of SSDs are discussed in the Analysis Plan (Section 5.5). As mentioned in the analysis plan, only endpoints that could be clearly related to population structure such as growth, reproduction, and survival were used and a species could only be represented once in each distribution.

The linear regression form of the model used for calculating our results from the SSDs is as follows:

$$\text{logit}(p) = \log(\frac{p}{1-p}) = \alpha^* + \beta^* \log_{10}(x),$$

where x is the geometric mean of a species effect concentration(s) (i.e., LC50, EC50) and *p* is the probability of an effect at a specific concentration. α and β are scale parameters. Parameter estimates generated from the above model are presented in Tables 5.1.13 and 5.1.16.

5.1.6.2. Exposure Analysis

5.1.6.2.1. Data Analysis

The detection limits for pesticides in surface waters from each of the monitoring agencies are listed in Table 5.1.8. Detection limits for the USGS were taken from values listed in spreadsheets of raw data on measured concentrations. When a pesticide was not detected, a < value was placed next to the MDL in these spreadsheets. Atrazine was detected in every sample taken by the USGS so a MDL was not available for this pesticide.

Table 5.1.9 summarizes the various parameters assessed from the monitoring data for freshwater sites in C-111 (e.g., 90th centile estimates, median concentrations, maximum concentrations, etc.) All sample sites monitored for pesticides were divided into freshwater sites (S-175, S-176, S-332, Site A, S-177/Site B, S-178/Site C, S-18C/Site E, Site W1, Site W2, Site E1, and Site E2) and into estuarine sites (Joe Bay, Highway Creek, and Card Sound). At least four observations over the MDL were necessary to characterize a distribution. Tables 5.1.9 to 5.1.12 summarize the exposure data for each year (1999, and 2000) and for each site with all the years aggregated. The means and standard deviations were based only on the detected concentration data. No data points below the MDL were

included in the calculation of the mean and the standard deviation. The minimum, median, maximum and 90th centile estimate concentrations were based on the data and included undetected values.

5.1.6.2.2. Measured concentrations in freshwater sites

5.1.6.2.2.1. S-175

At S-175, atrazine was the only pesticide detected. Chlorpyrifos was not analyzed for at S-175 since the SFWMD was the only monitoring agency at this Site. Out of 26 samples, endosulfan was not detected at this site during its monitoring period which spanned from July to November of 1999.

5.1.6.2.2.2. S-176

The SFWMD was the only agency taking samples at S-176, and chlorpyrifos was not analyzed. Endosulfan was only found in one water sample at 0.004 µg/L out of 32 samples. This concentration of endosulfan was measured in the October/November sampling event of 1999. The median value for endosulfan at S-176 was a nondetect and the 90th centile could not be estimated at this site.

5.1.6.2.2.3. S-177/Site B

Although the lowest detection ratio for chlorpyrifos was found at S-177/Site B (39%), the two highest concentration values for chlorpyrifos were found at S-177/Site B at 0.0234 µg/L and 0.0232 µg/L. The maximum value for chlorpyrifos at S-177/Site B was nearly two times higher than the next highest maximum concentration for a site, which was measured at W2. However, the median value detected at S-177/Site B was nondetectable. This may

indicate the occurrences of pulsed exposures for organisms at S-177/Site B that are impacted by chlorpyrifos. The maximum value for chlorpyrifos was found in February of 1999. The two highest 90th centile estimates for chlorpyrifos were also found at S-177/Site B (0.00876 μg/L) and Site A (0.00608 μg/L).

At S-177/Site B, endosulfan concentrations peaked in the dry season of 1999 and 2000. The maximum concentration for total endosulfan at S-177/Site B was the second highest for any site at 0.0427 μg/L. Unlike chlorpyrifos, the median value for endosulfan at S-177/Site B was a measured concentration of 0.0013 μg/L. Though the USGS only monitored for α-endosulfan in 1998, S-177/Site B had an analytical database that was slightly more cohesive than many of the other sampling sites since all three agencies monitored there.

5.1.6.2.2.4. S-178/Site C

Though the site had the third highest detection frequency, chlorpyrifos concentrations were not relatively high at S-178/Site C. Site E1 and S-178/Site C had similar 90th centile estimates for chlorpyrifos with values of 0.00307 μg/L and 0.00337 μg/L, respectively. These sites are not located in the vicinity of one another in the C-111 system. Since the SFWMD never monitored for chlorpyrifos at this site, only NOAA data were available for the compound.

The highest concentration of endosulfan in C-111 was found at S-178/Site C at a concentration of 1.345 μg/L. This value was several orders of magnitude higher than the maximum detected concentrations at S-176 and S-332 which were around 0.004 μg/L. At S-178/Site C, higher concentrations of endosulfan were found in February of 2000 over the rest

of the months and years. S-178/Site C also had the highest median concentration for endosulfan and this value was an order of magnitude above the next highest at Site W2. Furthermore, S-178/Site C had the highest 90th centile estimate for endosulfan exposures, a value that was approximately an order of magnitude above the concentrations measured in sites in the south.

5.1.6.2.2.5. S-18C/Site E

At S-18C/Site E, the maximum concentration for chlorpyrifos in 1999 to 2000 was the seventh highest when comparing the maximum detected chlorpyrifos concentrations between sites. The median and maximum detected concentration along with the 90th centile estimate for chlorpyrifos were low at S-18C/Site E when compared to other sites.

S-18C/Site E had the third highest maximum detected concentration of endosulfan for a site and the fifth highest median detection. Endosulfan concentrations were higher in February of 1999 and February of 2000 at the site. Median concentrations for endosulfan were similar for S-177/Site B, Site E2, and S-18C/Site E. The estimated 90th centile for endosulfan was the third highest at S-18C/Site E.

5.1.6.2.2.6. S-332

At S-332, atrazine and endosulfan were the only compounds above the MDL for pesticide sampling data from 1999 to 2000. Although S-332 is a considerable distance downstream from S-176, measured concentrations of detected pesticides were similar between the two northernmost sampling sites in C-111.

Chlorpyrifos was not analyzed in S-332 between 1999 and 2000.

Like S-176, detections for endosulfan were low at S-332 with only two out of 32 samples having measurable concentrations. Endosulfan was detected in S-332 in the November sampling events for 1999 and 2000. Maximum concentrations for endosulfan were identical between the two sites, and these values were several orders of magnitude below the highest maximum concentration at S-178/Site C. The median value for endosulfan was a nondetect at S-332.

5.1.6.2.2.7. Site A

Though Site A is located directly south of S-332 and S-175, all pesticides analyzed at Site A had values that were above the MDL for most of the 1998 to 2000 sampling period. At Site A, distinct spikes in chlorpyrifos concentrations were observed in February of 1999 and 2000 along with endosulfan. The second highest 90th centile estimate for chlorpyrifos was also found at Site A (0.00608 μg/L). In comparison with other freshwater sites, however, the median concentration for endosulfan at Site A was much lower. Endosulfan and chlorpyrifos had similar 90th centile estimates at Site A.

5.1.6.2.2.8. Site E1

The highest concentrations of chlorpyrifos at E1were measured during the dry season of 1999. The maximum detected concentration was 0.00824 μg/L, which was the fourth highest when comparing the maximum concentrations found at other freshwater sites between 1999 and 2000. Site E1 also had the highest median detected concentration for chlorpyrifos at 0.00078 μg/L. E1 is located in the vicinity of some other Sites with higher median concentrations such as E2, and W2.

Endosulfan was found in 100% of the samples taken at Site E1. Endosulfan had its highest detected concentrations during February of 2000 with the maximum being 0.0215 μg/L. The median concentration of endosulfan at E1 was the third highest at 0.00186 μg/L. This value was similar to the median values at Site W1 and S-18C/Site E but much lower than the median concentration at S178/Site C. The 90th centile estimate for total endosulfan at E1 was 0.0165 μg/L, which was the fourth highest.

5.1.6.2.2.9. Site E2

The highest concentration of chlorpyrifos at E2 was 0.00911 μg/L which was measured during the dry season of 1999. The median concentration for chlorpyrifos at Site E2 was 0.00052 μg/L. The 90th centile estimate for chlorpyrifos was 0.00266 μg/L, the fifth highest.

At Site E2, endosulfan had peaks during the dry season of 2000 with a maximum concentration of 0.01382 μg/L. Similar to E1, at E2, endosulfan had its highest detected concentrations during February of 2000. The median concentration for endosulfan at E2 was 0.00108 μg/L. The 90th centile estimate for endosulfan at E2 was 0.0123 μg/L.

5.1.6.2.2.10. Site W1

The maximum detected concentration of chlorpyrifos at Site W1 was 0.00635 μg/L. This concentration was detected during the dry season of 1999. The 90th centile estimate for chlorpyrifos was the second lowest for any site at 0.00248 μg/L.

Site W1 had detectable levels of endosulfan found in 100% of the 29 samples taken on separate days between 1999 and 2000. The maximum detected concentration of total endosulfan at W1 was 0.0182 μg/L, when comparing the maximum detected endosulfan

concentrations at each site. At Site W1, endosulfan had clear peaks in the dry season of 1999 and 2000. The median concentration for endosulfan at W1 was 0.00185 μg/L which was similar to Site E1 but much lower than the median concentration at S-178/Site C. The 90th centile estimate at W1 was 0.0151 μg/L, which was the fifth highest for all freshwater sites.

5.1.6.2.2.11. Site W2

The highest percent detection for chlorpyrifos was at W2 where it was found in 85.7% of the samples taken over the 21 days it was analyzed for. In comparison with the maximum detected concentrations found at other sites, the second highest maximum concentration value of chlorpyrifos was also found at Site W2 at 0.0102 μg/L. This concentration was two times lower than the highest maximum concentration for a freshwater site, which was found at S-177/Site B. The median value of chlorpyrifos detected at Site W2 was the second highest median detected concentration for any freshwater site at 0.00063 μg/L. Like many sites, this value was much lower than the maximum detected concentration possibly indicating the occurrences of pulsed exposures of chlorpyrifos. Site W2, W1, E1, E2, and S-18C/Site E had similar 90th centile estimates for chlorpyrifos with values that ranged from 0.00212 μg/L to 0.00307 μg/L.

Endosulfan concentrations at Site W2 appeared similar over most of the years but distinct peaks were found during the dry season months in 1999 and 2000 and during the wet season in 2000. The maximum detected concentration for endosulfan was 0.01063 μg/L. This concentration was low relative to the maximum endosulfan concentrations detected at other freshwater sites. W2 had the second highest median concentration of endosulfan for any other site though this was an order of magnitude below the highest median concentration which was found at S-178/Site C.

5.1.6.2.2.12. Annual Distributions of Exposure for Freshwater Sites

Table 5.1.10 contains summary statistics for measured concentrations in all C-111 freshwater sites detected in either 1999 or 2000. For 1999 with all freshwater sites aggregated, chlorpyrifos had a distinct spike in concentrations during February and its highest concentration in March. A similar trend observed for 90th centile estimates for atrazine in freshwater sites was observed for chlorpyrifos where 1999 gave the higher 90th centile estimate for exposure.

Endosulfan had its highest measured concentrations, generally, at the end of the dry seasons for each year. In all freshwater sites for 1999, endosulfan was highest in February with high concentrations found in January and June. For the year 2000, endosulfan had its highest detected concentration in February. For the same year, higher levels of endosulfan were also found in June for the wet season. The 90th centile estimates for endosulfan in all freshwater sites increased annually.

5.1.6.2.2.13. Monthly Distributions of Exposure for Freshwater Sites

In sites that had water quality violations, chlorpyrifos and endosulfan measured concentrations detected in either February or June during 1999 and 2000 were examined more closely in the analysis of exposure. Measured concentrations of COPECs from sites, and compounds in February or June of 1999 and 2000 were assumed to fit a log- logistic distribution like the SSDs. Data from each year were combined to create the monthly distributions for sites. The nonparametric methodology used on annual and site data was not utilized on monthly data since data sets were generally small. February is the height of the

South Florida dry season. The two freshwater sites that had water quality violations in February were S-178/Site C, and S-177/Site B. February and June data in S-18C/Site E were used as a reflection of conditions downstream from S-178/Site C. At S-177/ Site B, the 90th centile estimate for chlorpyrifos was 0.0189 μg/L for measured concentrations in February. For total endosulfan at the same site, the 90th centile estimate was 0.0657 μg/L. At S-178/Site C, the 90th centile estimate for chlorpyrifos in February was 0.00569 μg/L. The 90th centile estimate for total endosulfan at the same site in February was 0.954 μg/L. At S-18C/Site E, measured concentrations in February were lower than the previous two sites. The 90th centile estimate for chlorpyrifos exposures in February at S-18C/Site E was 0.00435 μg/L. For total endosulfan in February at the same site, the 90th centile estimate was 0.0328 μg/L.

S-177/Site B and S-178/Site C also had water quality violations in June. S-18C/Site E was utilized as a source for comparisons with S-178/Site C for June measurements. June is the middle of the South Florida wet season. At S-177/Site B, the 90th centile for measured concentrations for chlorpyrifos was 0.00145 μg/L. The 90th centile estimate for measured concentrations of total endosulfan in June at S-177/Site B was 0.0019 μg/L. For chlorpyrifos in S-178/Site C, the 90th centile estimate for exposure was 0.00327 μg/L from June measurements. At S-178/Site C, the 90th centile estimate for measured concentrations of total endosulfan was 0.137 μg/L. S-18C/Site E had lower 90th centile estimates for chlorpyrifos than the previous two sites for June exposures. However, the 90th centile estimate for chlorpyrifos was very similar to S-177/Site B. For measured concentrations of chlorpyrifos at S-18C/Site E in June, the 90th centile estimate was 0.00143 μg/L. For measured concentrations of total endosulfan in June, the 90th centile estimate was 0.00285

μg/L at S-18C/Site E, which was higher than the June 90th centile estimate for S-177/Site B but lower than the same value at S-178/Site C.

5.1.6.2.3. Measured Concentrations in Estuarine Sites

Table 5.1.11 summarizes data on the various parameters (e.g., 90th centile estimates, median concentrations, maximum concentrations, etc.) assessed from the monitoring data for estuarine sites. Joe Bay, Highway Creek, and Card Sound had fewer detections and a smaller database for pesticide monitoring than the freshwater sites used for the annual assessments of pesticide concentrations. Both chlorpyrifos and endosulfan had detection frequencies over 50% between 1999 and 2000.

5.1.6.2.3.1. Card Sound

Card Sound was chosen as a reference site by NOAA to get background concentrations of pesticides away from the influence of C-111. At Card Sound, chlorpyrifos was the most frequently detected compound. The maximum concentration for chlorpyrifos at Card Sound was about half the maximum value found at Joe Bay. Card Sound had a higher median concentration for chlorpyrifos than Highway Creek but not than Joe Bay. The 90th centile estimates for chlorpyrifos at Card Sound was 0.00263 μg/L.

The maximum concentration of endosulfan at Card Sound was half the maximum concentration found at Highway Creek and Joe Bay. The highest concentrations of endosulfan were found in the October months of 1999 and 2000 at Card Sound. The only monitoring data in Card Sound were available for 1999 to 2000 and this was the limiting factor in choosing a time frame for exposure data for comparison and analysis. The median

concentrations detected for endosulfan was lower at Card Sound, 0.00042 μg/L than at Joe Bay and Highway Creek. Also, chlorpyrifos and total endosulfan had similar 90th centile estimates in Card Sound but not in any other estuarine site. Though endosulfan concentrations in both sites appeared similar, the 90th centile estimate for total endosulfan in Card Sound was the lowest for any estuarine site and approximately half of Highway Creek's, which was the next highest site. From 1999 to 2000, detections of endosulfan in Card Sound were generally lower than the other estuarine sites.

5.1.6.2.3.2. Highway Creek

Chlorpyrifos was detected on 21 out of 26 separate days at Highway Creek. The maximum concentration for chlorpyrifos at Highway Creek was 0.00369 μg/L, which was the second highest maximum value for an estuarine site. Chlorpyrifos concentrations appeared higher during the dry and wet season of 1999 in Highway Creek. The median concentration of chlorpyrifos at Highway Creek was 0.00095 μg/L. This was the lowest median value for all estuarine sites. The 90th centile estimates for chlorpyrifos were similar between Highway Creek and Joe Bay at 0.0031 μg/L and 0.0032 μg/L, respectively.

Endosulfan was found in 96% of the samples analyzed at Highway Creek. Endosulfan was the most frequently detected compound in Highway Creek. The maximum concentration for total endosulfan at Highway Creek was 0.00868 μg/L. In 2000, endosulfan had several peaks in concentration at the end of the dry season. The median concentration detected for endosulfan in Highway Creek (0.000868 μg/L) was slightly lower than Joe Bay's but higher than Card Sound's median concentration (0.00042 μg/L). Total endosulfan

in Highway Creek had a 90th centile estimate of 0.00656 μg/L that was double the estimated concentration for Card Sound.

5.1.6.2.3.3. Joe Bay

Chlorpyrifos also had high detections in Joe Bay (95.8%). Maximum concentrations for chlorpyrifos at Joe Bay were almost double the ones found at Card Sound and Highway Creek. In Joe Bay, chlorpyrifos had a high concentration during the end of the dry season for 1999 but appeared to have relatively similar concentrations between the rest of 1999 and 2000. The 90th centile estimate for chlorpyrifos in Joe Bay was higher than for any other estuarine site at 0.00319 μg/L.

Total endosulfan was found in approximately 95% of the samples at Joe Bay. Chlorpyrifos and total endosulfan were the most frequently detected compounds in Joe Bay. The maximum concentration of total endosulfan at Joe Bay was approximately twice as large as the maximum concentration found at Card Sound. In Joe Bay, endosulfan appeared highest during the dry season sampling event in 2000. The median concentration detected for endosulfan was higher at Joe Bay (0.00127 μg/L) than Highway Creek (0.00086 μg/L) or Card Sound (0.00042 μg/L). Between 1999 and 2000, the 90th centile estimate for total endosulfan in Joe Bay was higher than for any other estuarine site at 0.0101 μg/L.

5.1.6.2.3.4. Annual Distributions of Exposure for Estuarine Sites

Annual distributions were created for all estuarine monitoring data (Table 5.1.12). For these distributions, Highway Creek and Joe Bay data were combined for 1999 and 2000. Of the two years, the 90th centile estimate for chlorpyrifos in estuarine sites was found to be higher in 1999. In the year 2000, measured concentrations of chlorpyrifos in estuarine sites

appeared similar in the wet, dry, and transition seasons. Endosulfan concentrations appeared highest in the dry season at estuarine sites. Concentrations of endosulfan in surface water also seemed to be higher in the dry season of 2000 over the same time period in 1999. Similar to its freshwater sampling data, the 90th centile estimated for endosulfan increased with time so that 2000 had the highest value and 1999 had the lowest.

5.1.6.2.3.5. Monthly Distributions of Exposure for Estuarine Sites

Estuarine sites, compounds, and months in 1999 and 2000 that had water quality violations were examined more closely in the analysis of exposure. All exposure distributions were assumed to be log-logistically distributed like the SSDs. The nonparametric methodology was not utilized since data sets were generally too small. February is the height of the dry season. The two estuarine sites that had water quality violations in February were Joe Bay, and Highway Creek. February and June data in Card Sound were used as an estuarine reference site away from conditions that would allow the direct deposit of pesticides from C-111. At Highway Creek, the 90th centile estimate for chlorpyrifos was 0.00339 μg/L for measured concentrations in February. For total endosulfan at the same site, the 90th centile estimate was 0.0129 μg/L. At Joe Bay, the 90th centile estimate for chlorpyrifos in February was 0.00514 μg/L. The 90th centile estimate for total endosulfan at the same site in February was 0.0213 μg/L. The 90th centile estimate for chlorpyrifos exposures in February at Card Sound was 0.00432 μg/L. For total endosulfan in February at the same site, the 90th centile estimate was 0.00169 μg/L. Joe Bay had the highest 90th centile estimates for exposure for endosulfan while Card Sound had the lowest in February.

Joe Bay and Highway Creek also had water quality violations in June. Card Sound was utilized as a source for comparisons with Joe Bay and Highway Creek since it was selected by NOAA to be a reference site. At Highway Creek, the 90th centile for measured concentrations for chlorpyrifos was 0.0119 μg/L. The 90th centile estimate for measured concentrations of total endosulfan in June at Highway Creek was 0.00084 μg/L. For chlorpyrifos in Joe Bay, the 90th centile estimate for exposure was 0.00784 μg/L from June measurements. At Joe Bay, the 90th centile estimate for measured concentrations of total endosulfan was 0.00226 μg/L. Unlike the 90th centile estimates in February, Card Sound had a higher 90th centile estimate for chlorpyrifos than Joe Bay and a higher 90th centile estimate for total endosulfan than Highway Creek. For measured concentrations of chlorpyrifos at Card Sound in June, the 90th centile estimate was 0.00856 μg/L. For measured concentrations of total endosulfan in June, the 90th centile estimate was 0.00127 μg/L at Card Sound.

5.1.6.2.4. Exposure trends

Insecticides were generally found at their highest concentrations during the dry season. From 1999 to 2000, distinct spikes in total endosulfan concentrations were found in the dry seasons in estuarine and freshwater sites. An example of the increased concentrations of pesticides in the dry season is given in Figures 5.1.8 and 5.1.9. Figure 5.1.8 presents measured concentrations of atrazine, chlorpyrifos, endosulfan, malathion, and metolachlor in S-177/Site B from 1999 to 2000. After rescaling the concentration axis, figure 5.1.9 presents only measured concentrations of the insecticides in S-177/Site B from 1999 to 2000. Distinct spikes can be seen in the latter figure at the peak of the dry

season, in February of both years. For both graphs, all values below the MDL were plotted as a 0. In estuarine and freshwater sites, measured concentrations of α-endosulfan, β-endosulfan, and endosulfan sulfate were generally higher throughout the year 2000.

With endosulfan, S-178/Site C appeared to have consistently high concentrations. S-178/Site C had a high maximum and median detection concentration for endosulfan as well as one of the highest estimated 90th centiles. In freshwater sites, more than half of the pesticide samples taken at each site had concentrations above the detection limit for endosulfan, and chlorpyrifos. Six freshwater sites had chlorpyrifos detection frequencies close to one another with ranges from 67% to 76%. Most sites had maximum values for chlorpyrifos that were within approximately 50% of one another. However, analytical data for chlorpyrifos were not available for S-332, S-175, and S-176. S-177/Site B was the only site that had a nondetect for a median concentration for chlorpyrifos. From 1999 to 2000, sites in C-111 had 90th centile estimates for chlorpyrifos that were similar in the freshwater sites from S-18C/Site E downstream to Site E1. The range for all of these sites was from 0.0015 to 0.0032 μg/L.

For endosulfan, 90th centile estimates were similar for all freshwater sites along C-111 from S-177/Site B to sites downstream. Endosulfan was found in 100% of the samples it was analyzed for at Site W1, Site W2, and Site E-1, three of the southernmost sites along C-111. In estuarine sites, all pesticides were usually above the detection limits.

5.1.6.3. Effects Analysis

5.1.6.3.1. Acute Toxicity

Statistics for the acute toxicity distributions (SSDs) are presented in Table 5.1.13. The data were summarized similar to the methodology of Warren-Hicks et al. (2002). Community below indicates all species for fresh- or salt-water were grouped together in one SSD. Graphs of the SSDs for LC/EC50 toxicity data can be found in the Appendix .

5.1.6.3.1.1. Community

The most sensitive species group for chlorpyrifos was arthropods (Table 5.1.14). For chlorpyrifos, a total of 56 species were plotted in the logistic distribution for effects on freshwater organisms. One additional species was above the water solubility of chlorpyrifos and was not plotted but used in the calculation of ranks. The 10th centile for this distribution was estimated to be 0.20 μg/L. *Ceriodaphnia dubia* was the most sensitive freshwater organism to chlorpyrifos with a geometric mean EC50 of 0.057 μg/L. The least sensitive organism to chlorpyrifos in freshwater was the rotifer, *Brachionus calyciflorus*, with a geometric mean of 3713 μg/L from three acute toxicity tests.

For saltwater organisms and chlorpyrifos, a total of 26 species were plotted for effects. Two additional species had values above the water solubility of chlorpyrifos. The 10th centile of this distribution was estimated to be 0.11 μg/L. *Americamysis bahia* was the most sensitive species to chlorpyrifos with a geometric mean EC50 of 0.045 μg/L, while *Mytilus galloprovincialis*, the least sensitive, had an LC50 of 22500 μg/L.

Fish and arthropods were more sensitive in endosulfan toxicity tests than any other species taxa (Table 5.1.15). Fish, particularly, were more sensitive to endosulfan than any other

pesticide assessed. For total endosulfan, the number of species for the freshwater distribution totaled 59 and 12 freshwater species had acute endpoints above its water solubility. The 10th centile was estimated to be 0.37 μg/L. Two freshwater species were more sensitive to total endosulfan than others: the fish, *Carassius auratus*, and the freshwater crab, *Paratelphusa jacquemontii*, with LC50 values of 0.1 and 0.16 μg/L, respectively. The least sensitive freshwater organism was the gastropod, *Melanopsis dufouri*, with a geometric mean EC50 of 39892 μg/L from three toxicity tests.

For total endosulfan and saltwater organisms, the 10th centile was estimated to be 0.056 μg/L, for all saltwater organisms from the 27 species plotted. Saltwater organisms appeared more susceptible to endosulfan than freshwater but five species had acute values higher than the water solubility of the pesticide. The most sensitive organism to total endosulfan was *Penaeus duorarum*, with a 96-h LC50 of 0.04 μg/L. The saltwater rotifer, *Brachionus plicitalis*, was the least sensitive with an EC50 geometric mean of 6432 μg/L. A greater than value (>10000 μg/L) above the water solubility of endosulfan was noted for the cockle, *Cerastoderma edule*.

5.1.6.3.1.2. Fish

For all insecticides, the 10th centile estimates for fish were lower for saltwater SSDs than for freshwater SSDs. For chlorpyrifos, the 10th centile for freshwater fish was estimated to be 2.8 μg/L, from a total of 19 fish species that were plotted. The freshwater fish most sensitive to chlorpyrifos was *Cyprinus carpio*, with a 72-h LC50 of 1.3 μg/L. The freshwater eel, *Anguilla anguilla*, was the least sensitive organism, with a 96-h LC50 of 540 μg/L. For saltwater fish, the 10th centile for chlorpyrifos was estimated at 0.32 μg/L from a

total of 13 species of fish that were plotted in the distribution. *Morone saxatilis* was the most sensitive saltwater fish to chlorpyrifos with an LC50 of 0.58 μg/L. *Opsanus beta* was the least sensitive to chlorpyrifos with a geometric mean EC50 of 188 μg/L from two tests.

Total endosulfan had 21 different species of freshwater fish used for plotting points in the distribution that gave a 10th centile of 0.38 μg/L. The freshwater fish with the most sensitive endpoint to total endosulfan was *Carassius auratus*, with a 48-h LC50 of 0.1 μg/L. This was also the most sensitive organism out of all species with acute toxicity endpoints to endosulfan. The freshwater fish least sensitive to total endosulfan was the eel *Anguilla anguilla*, with a geometric mean LC50 of 34 μg/L from six toxicity tests. The 10th centile for saltwater fish exposed to endosulfan was 0.08 μg/L from a total of nine species. The most sensitive saltwater fish was the spot, *Leiostromus xanthurus*, with a 96-h LC50 of 0.09 μg/L. The inland silverside, *Menidia beryllina*,was the least sensitive of the nine species, with a 96-h LC50 of 1.5 μg/L.

5.1.6.3.1.3. Arthropods

The 10th centile estimates for arthropods for all compounds were generally lower than the 10th centile estimates for fish. The only exception to this was found in the SSDs for endosulfan and freshwater arthropods and fish. Also, 10th centile estimates were lower for saltwater SSDs and arthropods than freshwater SSDs. From the SSD derived for 37 different species, the 10th centile estimate for chlorpyrifos was 0.11 μg/L for freshwater arthropods. The water flea, *Ceriodaphnia dubia*, was the most sensitive in the ranking, with a geometric mean EC50 of 0.057 μg/L from four toxicity tests. The freshwater crab, *Oziotelphusa senex senex*., was the least sensitive freshwater arthropod, with a geometric mean EC50 of 322

μg/L from four toxicity tests. For saltwater arthropods, the 10th centile estimate was 0.026 μg/L from eight species plotted in the distribution. The saltwater species most sensitive to the chlorpyrifos was *Americamysis bahia*, with an acute geometric mean EC50 of 0.045 μg/L from three toxicity tests. The blue crab, *Callinectes sapidus*, was least sensitive with a 48-h LC50 of 5.2 μg/L.

For the distributions of arthropods exposed to total endosulfan, the 10th centile estimates were 0.45 μg/L and 0.038 μg/L for fresh and saltwater arthropods, respectively. Thirteen saltwater arthropods received plotting points while 24 freshwater arthropods were plotted. One saltwater arthropod was above the water solubility of endosulfan and was excluded from plotting but used for the calculation of rank and one freshwater arthropod had an acute value above the water solubility of endosulfan. The freshwater arthropod most sensitive to endosulfan toxicity was the freshwater crab, *Paratelphusa jacquemontii*, with a 96-h LC50 of 0.159 μg/L. However, another freshwater crab, *Oziotelphusa senex senex*, was least sensitive, with a geometric mean EC50 of 7060 μg/L from five toxicity tests. Of the 14 saltwater arthropods tested, the most sensitive to total endosulfan was *Penaeus duorarum*, with a 96-h LC50 of 0.04 μg/L. The fiddler crab, *Uca pugilator* was the least sensitive saltwater arthropod with a 48-h LC50 of 789.5 μg/L.

5.1.6.3.1.4. Phytoplankton/Macrophytes

Chlorpyrifos had four saltwater phytoplankton and macrophyte species toxicity tests that were acceptable for distributional analysis. Chlorpyrifos was the only insecticide assessed with enough phytoplankton/macrophytes species for a distributional analysis. The 10th centile for chlorpyrifos was estimated to be 82 μg/L in this category. Since this was the

highest 10th centile for chlorpyrifos in any category, saltwater macrophytes and phytoplankton are not sensitive to chlorpyrifos. Among those tested, the organism that appeared to be the most sensitive was *Isochrysis galbana*. It displayed a geometric mean of 139 μg/L, while the least sensitive saltwater organism, *Skeletonema costatum*, had a value of 390 μg/L.

5.1.6.3.1.5. Molluscs

Molluscs generally had the highest values in tests with the pesticides. Two species acute values were used for saltwater molluscs exposed to chlorpyrifos. They were 435 μg/L for *Crassostrea virginica* and 22500 μg/L for *Mytilus galloprovincialis*.

While six species had endpoints available for freshwater acute tests with endosulfan, none of the species' acute EC/LC50s were above the water solubility of endosulfan. The most sensitive mollusc species in the distribution for total endosulfan was *Lymnaea natalensis*, with a 48-h LC50 of 4370 μg/L, and the least sensitive species was *Indoplanorbis exustus* with a 48-h LC50 of 21000 μg/L. For saltwater molluscs, acute values ranged from a 55 μg/L (EC50 for the development of embryos of *Crassostrea virginica*) to >10000 μg/L (48-h LC50 for adult *Cerastoderma edule*.)

5.1.6.3.1.6. Amphibians

Endosulfan had a total of three freshwater species available for assessment. Of the organisms tested, the most sensitive to endosulfan was *Rana tigrina*, with a 96-h LC50 of 1.8 μg/L, while the least sensitive to endosulfan was *Bufo bufo japonicus*, with a 48-h LC50 of 9000 μg/L.

5.1.6.3.1.7. Microbial Decomposers

After collecting microbes that colonized substrates in an estuary located in South Carolina, DeLorenzo et al. (1999) examined the effects of pesticides on these microbial populations in a laboratory. The estuary that the collections of species came from was one without a history of contamination problems. Each mixed-species microcosm was spiked with 1 or 10 μg/L of either chlorpyrifos or endosulfan and allowed to incubate for 72 h. Results from the chlorpyrifos-dosing portion of the experiment found that the number of heterotrophic ciliates were significantly reduced, the abundance of flagellates were significantly reduced, bacterial abundance increased, and some primary production water quality indicators decreased (i.e., dissolved oxygen concentrations, chlorophyll *a*, phototrophic biovolume). Major changes were found primarily in the 10 μg/L treatment of chlorpyrifos. The authors stated that this is a concentration not typically measured in the environment (DeLorenzo et al., 1999). For the endosulfan treatments, bacterial abundance was significantly decreased at both concentrations, carbon assimilation rate measurements increased, phototrophic biovolume decreased 24 h into the experiment, and several algae taxa disappeared at the 10 μg/L endosulfan level. The phototrophic portion of the bacteria changes in abundances seemed to reflect gross losses of bacteria. Phototrophic variables like dissolved oxygen, chlorophyll *a*, and carbon assimilation; heterotrophic ciliates; and flagellates showed no significant trends from endosulfan exposure.

5.1.6.3.2. Chronic Toxicity

The 10th centile estimates and data for graphs of log-logistically distributed NOECs are presented in Table 5.1.16. The 10th centile estimates for chronic effects in increasing order

were: chlorpyrifos (0.0180 μg/L), and endosulfan (0.1227 μg/L). Each compound's 10th centile for log-logistically distributed chronic effects distributions were smaller than any of their corresponding acute 10th centiles. Chlorpyrifos had a 10th centile estimate for chronic effects nearly an order of magnitude below the estimated value for endosulfan.

5.1.6.3.3 Field/Mesocosm Studies

5.1.6.3.3.1 Chlorpyrifos Field Studies

In their risk assessment for North American aquatic ecosystems and chlorpyrifos, Giesy et al. (1999) summarized available aquatic field/mesocosm studies to derive threshold values for individual species taxa. From the available data, estimated threshold concentrations of 0.1, and 0.2 μg/L were extracted as values where effects on invertebrates were not likely to be observed and where effects may occur but recovery within two to eight weeks was likely. For survival and growth of fish, reductions were observed at concentrations over 0.5 μg/L. For conservatism, 0.1 μg/L was chosen as the protective benchmark (NOAEC) of ecological structure and function from exposures to chlorpyrifos (Giesy et al., 1999). This value was supported by field studies in outdoor mesocosms/ditches conducted by van den Brink et al. (1996) and van Wijngaarden et al. (1996). They found a field NOEC of 0.1 μg/L over an extended period (>1 yr) that looked at recovery of populations along with decreases in population abundances and a short-term study that found a 48 h EC50 of 0.1 to 2.8 μg/L for populations of free-roaming species in outdoor experimental ditches. I concur with their results.

5.1.6.3.3.2 Endosulfan Field Studies

An Australian study looked at the effects of endosulfan on pond microcosms (Barry and Logan, 1998). Sediment was taken from dried pond areas and hydrated in laboratory aquaria, allowing dormant eggs and resting stages of organisms in the sediment to recolonize. Exposures to technical endosulfan lasted 71 days. Concentrations of endosulfan applied were 1, 10, and 50 μg/L and doses were applied once after six weeks of acclimation (day 0) and on the third week after that. A water column half-life of 24 h was calculated and 6 to 12% of the applied endosulfan was in sediment as either α-endosulfan, β-endosulfan, or endosulfan sulfate by the end of the test. In the high concentration tanks, two species of ostracods, *Cypretta* sp. and *Eucypris* sp., were eliminated. Reduced populations were also noted for the two species in the medium dosage tanks but effects on ostracods in the low dosage tanks were not significant. In the high and medium concentration treatments, oligochaates were also reduced. Chydoridae species, *Alona cambouei* and *Chydorus sphaerricus*, were not significantly affected in any of the treatments. Calonoid copepods, *Calomoecia* sp., did not survive in the 10 and 50 μg/L treatments. *Ceriodaphnia* sp. populations were only significantly lower in the high treatments. A larger quantity of Tardigrades was observed in medium and high dosage treatments. In the 1 and 10 μg/L range, decreases in ostracod and ceriodaphnid populations preceded increases in *Simocephalu*s, tardigardes, phytoplankton, and filamentous algae. Correlation analyses found that ostracods may have been limiting filamentous algae. In the same treatments, decreases in nutrient concentrations may have resulted from the increases in primary producers as an indirect effect of endosulfan exposures. *Simocephalus* sp. also increased with populations of filamentous algae in the 10 and 50 μg/L treatments. This increase was

possibly due to the appearance and role of certain algae as a food source for *Simocephalus* sp.

Drift samples in Canadian freshwater bodies (adjacent to Albany Corner, Prince Edward Island) from several endosulfan (Thiodan 50 WP; applied at 500 g a.i./ha) aerial spraying events were collected for toxicity and chemical analysis (Ernst et al., 1991). Over three spraying events, concentrations of endosulfan in water were 500 to 900 μg/L at 10 m and 3 to 5 μg/L at 200 m away from the crop fields for α- and β-endosulfan. In static 24 h on-site exposures with field-collected organisms, mortality to the threespine stickleback (*Gasterosteus aculeatus*) was higher than for invertebrates. At the maximum distance assessed, 200m from the edge of the crop field, 90% mortality was observed for threespine stickleback in the bioassays with collected water samples. Mortality of water boatmen (*Sigara alternata*) and caddisfly larvae (*Limnephilus* spp.) was significant but not as dramatic. Mortality (50%) in water boatmen occurred in water samples taken 50 m away from the crop field and caddisfly larvae had emergence inhibition (50%) from samples taken 10 m away from the target field in two spray events (measured α- and β-endosulfan concentrations ranged from 119 to 6 μg/L) and 30 m in one other (measured α- and β-endosulfan concentrations ranged from 128 to 70 μg/L). Other invertebrate species such as bivalve molluscs (*Pisidium* spp.), bloodworms (*Chironomiidae* spp.), and water fleas (*Daphnia magna*; not field-collected) experienced little to no acute effects. A NOEC could not be determined from this study.

A study was initiated on the effects of sediment-associated endosulfan applied to artificial stream mesocosms containing macroinvertebrates from a stream in New South Wales, Australia (Hose et al., 2002). Control streams received clean sediment and nominal

spiked concentrations were 2, 0.2, 0.02, and 0.002 mg endosulfan/kg sediment. Artificial stream outlets were blocked and sediment was allowed to settle for 12 h. After the initial 12 h exposures followed by a 96 h monitoring period, effects on benthic macroinvertebrate community structure were negligible at peak pore water concentrations of 6.14 μg/L. However, a significant sublethal response was noted in the high-dose treatments. Benthic invertebrates Tanypodinae, Notonectidae, and especially the burrowing mayfly, *Jappa kutera*, drifted from contaminated substrates in elevated numbers, possibly as a response mechanism to pollutant levels. The authors reported that the NOEC for drift measurements for this species was 1.07 μg/L endosulfan. The opposite trend occurred for one species as drift of abundances of *Triplectides* sp. were reduced at a pore water concentration of 1.07 μg/L endosulfan from the highest dosed treatment at 36 hrs. The results from this study show the importance in field-testing to determine effects in population structure that may not be related to lethality when assessing contamination (Hose et al., 2002). A NOEC of 6.14 μg/L from porewater concentration effects on benthos was chosen from this study.

A similar experiment evaluated the consequences from exposing macroinvertebrates to surface water concentrations of endosulfan for 12 h and 48 h (Hose et al., 2003). Nominal (measured) concentrations of 0.01 (0.07 ± 0.01) 0.05 (0.22 ± 0.04), 0.5 (1.35 ± 0.02), 5 (8.69 ± 3.46), and 50 (48.87 ± 10.54) μg/L were used for the 12 h exposures and 1 (1.00 ± 0.08), 5 (6.87 ± 0.65), and 25 (30.70 ± 0.35) μg/L were used for the 48 h exposures. For the 12 h exposures, a single application was made and water flow was impeded. For the 48 h exposures, applications were made every six hours over the entire duration of the experiment with water flow impeded until each dosing occurred. The initial dosing for the 12 h exposure was followed by 108 h of monitoring and the initial dosing for the 48 h exposure was

followed by 144 h of monitoring for macroinvertebrates. In addition, a single sample in a section of the stream with a mud substrate was taken in the 48 h exposure 120 h after dosing. Significant effects for treatments were obtained using Monte Carlo permutation tests at each sampling date and additional multivariate statistics were used to determine a community NOEC. Fifty or sixty different taxa were observed in each study with insects dominating the invertebrate component before treatment. Based upon measured concentrations in the treatments, the NOEC for the 12 h treatment was 8.69 μg/L. The NOEC for the 48 h treatment was 1.00 μg/L. A decrease in mayfly, *Jappa kutera*, counts was a large reason for the significance registered. In the 6.87 and 30.70 μg/L treatments of the 48 h study, algal blooms and reductions in tadpole populations were evident. A NOEC for invertebrate community structure of 1.00 μg/L was chosen from this study. This was the lowest NOEC and it is the value that will be applied in the risk characterization.

In a Georgia farm pond study, Thiodan 3EC™ (35% a.i.) was applied at the maximum application rate (1 lb a.i./a) three times with 14 days between each application in two treated ponds (Fischer, 1994). Since a drought occurred in the summer of 1988, simulated rainfall was applied to the fields through irrigation to induce runoff. The only clear case of treatment-related mortalities for fish was found at shallow surface runoff locations where dead fish fry and small fish were found within 48 h of the events. Effects could not be attributed to endosulfan for phytoplankton, zooplankton, benthos, and fish populations. A pond that received higher doses of endosulfan also had a case of decreased chironomid collections over an application interval. However, a comparable decline was found in the reference pond over a different time period and emergence was not affected. In addition, measured endosulfan concentrations in another pond were higher in sediment

without decreases in chironomid density. The decrease in chironomid density found in the former pond was possibly correlated with a thunderstorm that brought in soil runoff. Chaoborids were not affected but oligochaetes appeared to be affected in a treated pond. Spike rush (*Eleocharis* sp.) was reduced in one pond receiving applications but this was probably the result of drying that was noted in an area of the pond. The average maximum measured concentrations in each of the ponds were 1.3 μg/L and 0.58 μg/L. In sediment, avereage maximum concentrations were 49 μg/kg and 99 μg/kg. Average maximum concentrations in runoff water for each of the ponds were 203 μg/L and 75 μg/L and in drift cards placed above the water surface, 218 $\mu g/m^2$ and 99.3 $\mu g/m^2$.

A field study in the Okavango Delta in Botswana, Africa was undertaken to determine whether low-dose applications of endosulfan to control the tsetse fly, *Glossina morsitans* Westw., were causing acute toxicity to fish populations (Fox and Matthiessen, 1982). Twelve replicates of fish species, *Aplocheilichthys johnstonii*, in tanks that were placed in a pool of water at a depth of 20 cm were used to assess effects from spray drift to nontarget organisms. Four replicates only contained swamp water, four had vegetation added, and four were covered controls. In addition, four cages were used with silt and vegetation that were also placed in the pool. Transect surveys were used to assess habitat effects. Endosulfan (35% EC at 6 to 12 g/ha) was applied aerially every 14 to 20 days for a total of six applications in the habitat effect study. In the caged fish species study, endosulfan was applied once aerially at 9.5 g/ha. In the transect studies, dead fish were found only in shallow habitats 12 to 36 h after applications. Estimated mortalities were about 1% of the fish community following each spraying. Based on laboratory toxicity data, the authors felt that observed mortality of *Barbus* sp., the most susceptible in laboratory toxicity

tests and found in large abundances in the field, were smaller than expected from measured concentrations of endosulfan in surface water. After all six applications, population losses were 24% and 60% for *Hepsetus* and *Serranochromis* sp. for one site. This was the worst case of mortality found in a sample and a rarity in the study. The spatially irregular pattern in measured fish kills was possibly due to endosulfan's uneven deposition around the marsh. Within 9 h of an aerial application at 9.5 g/ha, concentrations of endosulfan (α, β, and sulfate) in surface waters from various habitats in the region ranged from 0.2 to 4.2 μg/L with a mean of 1.2 μg/L. Measurable concentrations of endosulfan dissipated in shallower waters with high vegetation by 5 days. In lagoon and swamp areas that had less vegetation, concentrations persisted from 10 to 20 days. Likewise, in outdoor experiments with cages, endosulfan applied by air left higher concentrations of residues in the water of tanks or cages with only water vs. cages with silt or vegetation. For the tanks with swamp water only, 34% of the fish died while in the tanks with water and vegetation, 36% died. For control tanks and cages with vegetation and silt added, no mortalities were observed.

Pond mesocosm studies were carried out in Australia with caged silver perch (NRA, 1998). A nominal concentration of 25 μg/L endosulfan was applied into treatments with cages of previously acclimated fish placed in the mesocosms at 24 h intervals. In three of the ponds, none of the fish initially placed in the pond survived in the first six hours after the application. After 48 h, mortality slowed but was still observed for newly placed fish species up to 96 h after spraying. Losses of fish after 96 h occurred in another pond that had less suspended material in the water and more vegetation. Mortality rates in this pond declined at 288 h and stopped at 384 h. Initial measured concentrations of endosulfan in the ponds were 18 μg/L and these declined to 1 μg/L after 48 h. Filtered water samples had lower

concentrations of endosulfan hinting at sorption on to suspended solids. Loss of endosulfan in water was fastest in ponds with higher densities of plants and algae. Reported results were not definitive.

In the Namoi River, Australia, higher concentrations of endosulfan were found in areas with lower invertebrate abundances from measurements taken in two growing seasons (1995 to 1996 and 1997 to 1998) (Leonard et al., 2000). In both seasons of the survey, decreases in abundances of caddisfly larvae and mayfly nymphs at downstream sites were found with higher concentrations of endosulfan over reference sites. Partial recoveries of caddisfly and mayfly populations were noted before each corresponding growing season. Passive samplers were utilized to collect endosulfan and measure concentrations at sites so effect levels could not be correlated with surface water concentrations for purposes of this risk assessment. In the study, measured concentrations in passive samplers were used to rank high and low sites of exposure. For each month and site assessed, mean concentrations of total endosulfan ranged from 1 to 911 μg/L at affected sites between 1995 and 1998. In some areas downstream from agricultural regions, measured endosulfan concentrations were 10 to 25 times greater during the growing season. After spraying stopped for each sampling event, more than 80% of the detected endosulfan in passive samplers was endosulfan sulfate. Since total endosulfan concentrations were associated with rainfall, runoff was determined to be the main source of entry in the river. Multivariate analyses found that endosulfan concentrations were a significant correlate (25%) with variability in the densities of macroinvertebrates. Other factors at exposed sites that may have contributed to invertebrate population instability included turbidity, the appearance of other pesticides, and hydrodynamics. From principal components analysis, river discharge rates were found to

have a positive correlation with macroinvertebrate community densities in two reference sites of the first growing season evaluated.

In four week studies using static laboratory microcosms with field collected sediments and water, no significant effects on invertebrate communities were observed at concentrations of endosulfan below 500 μg/L (Peterson and Batley, 1993). At 500 and 5000 μg/L, ostracods, nematodes, and worm populations in sediment decreased while significant changes for ostracods in the water column and cladocerans in sediment were not detected. At 5 μg/L, chlorophyll *a* increased indicating endosulfan was a possible food source at this concentration for zooplankton. Endosulfan diol was found in sediment at all treatments except the highest treatment indicating that the organisms contributing to this degradatory mechanism may have been eliminated. The pH and DO were lowered in the highest treatment concentration.

From the endosulfan field studies, a NOEC of 1 μg/L was chosen for invertebrate species and for fish species. The NOEC for fish species may be lower since most existing studies did not correlate effects on fish species with measured surface water concentrations clearly. In addition, Ernst et al. (1991) found greater mortality for fish than invertebrates in their study.

5.1.7. RISK CHARACTERIZATION

In contrast with the worst-case scenario HQ approach, this tier of the assessment used a refined analysis of both exposure and effects. The effects data were characterized as distributions of acute or chronic values for species. The linear regression model used to derive effect levels and exposure levels and risk distribution curves was based on the following equation:

$$\text{logit}(p) = \log(\frac{p}{1-p}) = \alpha + \beta \log_{10}(x)$$

where x is the geometric mean of an effect concentration for a species tested for the distribution of effects, and p is the probability of an effect or value occurring. The derivation of 90th centile estimates for exposure was discussed in the Tier 2 exposure analysis (Section 6.2).

The model, however, used by Traas et al. (2002) for the PAF and msPAF assessment was as follows:

$$\log it(p) = \log(\frac{p}{1-p}) = \frac{\log_{10}(x) - \alpha^*}{\beta^*}$$

where $\alpha^* = -\alpha/\beta$ and $\beta^* = 1/\beta$. Thus, α and β were taken from the previous model and converted into the one utilized by Traas et al. (2002) for calculations of potentially affected fractions of species at the ninety percent exposure level for SSDs with acute endpoints and at the median concentration (fiftieth centile) for SSDs with chronic endpoints.

For the individual compounds, PAF and msPAF values were determined from the 90th centile exposure estimates applied to the acute effects distributions (Tables 5.1.17 to 5.1.20) and the median exposure concentrations (Tables 5.1.21 to 5.1.23) applied to distributions for chronic effects. JPCs were also constructed for sites, years, and months for related compounds that showed a high qualitative overlap in distributions for effects and exposures.

5.1.7.1. Acute PAF/msPAF Assessment

5.1.7.1.1. Acute Single Substance Assessment (PAF)

For the most part, PAF values for species distributions and compounds detected at sites in C-111 and its areas of discharge were low. Tables 5.1.19 and 5.1.20 summarize the

estimated PAF and msPAF (%) for species exposed to the 90th centile exposure concentration for concentrations combined for freshwater and estuarine sites in 1999 and 2000, respectively. For each site between 1999 and 2000, none of the PAF values for individual compounds exceeded 10% of any species taxa affected. Several PAF values that were found to be higher than others were noted. In 1999, the PAF derived from the estimated 90th centile exposure concentration for endosulfan at estuarine sites indicated that 3.6% of the acute toxicity values for arthropods could have been exceeded (Table 5.1.17). The estimated 90th centile exposure concentration for endosulfan in 2000 was found to potentially exceed approximately 5.9 % of the acute toxicity values for arthropod species in estuarine sites (Table 5.1.18). For freshwater arthropods, approximately 3.0 % of their toxicity values were estimated to be lower than the 90th centile for measured concentrations of endosulfan at all freshwater sites in the year 2000 (Table 5.1.18). As mentioned previously, the estimated 10th centile effect concentration for endosulfan and saltwater arthropods was lower than the same value for freshwater arthropods.

In S-178/Site C, risks appeared higher for endosulfan over other freshwater sites for 1999 to 2000 (Table 5.1.19). In this sampling site, PAF values for fish and arthropods from measured concentrations of endosulfan were 5.2% and 6.7%, respectively. PAF values for all other pesticides and species were lower at other freshwater sites. Endosulfan was not detected with enough frequency in S-175, S-176 or S-332 to create a distribution of exposure.

With the exception of S-178/Site C, endosulfan had higher arthropod PAF values at estuarine sites, i.e., Joe Bay, Highway Creek, and Card Sound, than freshwater sites from the 90th centile estimates derived from distributions of measured concentrations in 1999 to 2000 (Table 5.1.20). Total endosulfan reached a PAF level of 5.9% and 5.0% for acute effects on

arthropods at Joe Bay and Highway Creek, respectively. At all three sampling stations (Joe Bay, Highway Creek, and Card Sound), chlorpyrifos gave a PAF value of approximately 2.1% to 2.4% for acute effects on arthropod communities.

5.1.7.1.2. Acute Multisubstance Assessment (msPAF)

In 1999, freshwater msPAF values were all below 3% for acute toxicity (Table 5.1.17). For estuarine arthropods, however, in 1999, the msPAF was 6.1% due to the potential acute effects from the joint concentrations of the 90th centile exposure concentration of chlorpyrifos and endosulfan (Table 5.1.17). Likewise, in 2000, the estimated msPAF from the joint acute effects of atrazine, chlorpyrifos, and endosulfan was 7.9% for the estimated 90th centile exposure concentration for all estuarine sites (i.e., Highway Creek and Joe Bay; Table 5.1.18). In freshwater sites, the msPAF for fish species never exceeded 2% in annual distributions.

For freshwater sites, higher acute msPAF values for arthropods due to joint toxicity were found at S-177/Site B (6.2%) and at S-178/Site C (7.5%) (Table 5.1.19). With few measured insecticide concentrations in surface water, sampling sites S-175, S-176 and S-332 had low msPAF values (~0%) for arthropods. Most msPAF values for fish were below 1% in freshwater sites. However, at S-178/Site C, the msPAF value for acute risks to fish was estimated to be 5.3% (Table 5.1.19). The two freshwater sites (S-178/Site C and S-177/Site B) with consistently higher percentages of affected species are located adjacent to one another in the northern portion of the C-111 region, an area with high agricultural land usage (Figure 5.1.1).

In saltwater sites, the msPAF estimates for acute risks were higher than most freshwater sites for arthropods (5.7 to 8.2% range) (Table 5.1.20). The msPAF value at Joe Bay exceeded the msPAF values for arthropods at all freshwater sites. Endosulfan appeared to be contributing most of the toxicity in these sites. Fish msPAF values at the three saltwater sites were < 2%.

5.1.7.2. Chronic PAF/msPAF Assessment

5.1.7.2.1. Chronic Single Substance Assessment (PAF)

For chronic effects, the PAF value was determined by comparing the median exposure concentration to the logistic distributions of log-NOEC data using the models specified above. The chronic effects distributions were only for all species and were not divided into taxonomic groups. For freshwater sites in each year, chronic risks were low with individual PAF values ranging from 0.1 to 2.1% (Table 5.1.21). The highest PAF value was found for endosulfan in 2000 at 2.1%. In 1999, the median concentration for endosulfan was a nondetect. For each year, the only other compound that displayed potential chronic risks for freshwater exposures was chlorpyrifos at 0.9%. In estuarine sites, chronic PAF values were also low (Table 5.1.21). However, chlorpyrifos had higher PAFs for 1999 and 2000 at 1.2% and 1.5%, respectively. Endosulfan PAF values for chronic risks were also low for 1999 to 2000 with a range from 1.0 to 1.2%. Based upon the PAF values, chronic risks from herbicides were generally low.

For each freshwater station, individual PAF values for chronic effects from compounds detected in C-111 were all below 10% (Table 5.1.22). Endosulfan, however, had a PAF value of 6.4% at S-178/Site C from the median exposure value for all sampling data between 1999 and 2000. At Site A, the median detected concentration of chlorpyrifos

between 1999 and 2000 gave a PAF of 3.1%. Site A is in the vicinity of S-175, S-176, and S-332 (see Figure 5.1.1). With the exception of endosulfan at S-178/Site C and chlorpyrifos at Site A, PAF values for chronic effects at freshwater sites were below 2%. PAF values for chronic effects from endosulfan exceeded 1% at Site E1 (1.4%), Site W2 (1.9%), S-18C/Site E (1.2%), and Site W1 (1.4%). Each of these stations are located in the south and S-178/Site C is in the north on a tributary (C-111E) that discharges into C-111. At S-177/Site B, also located in the north, the PAF for endosulfan and chronic exposures was 1.2%.

Individual PAF values for chronic effects in estuarine stations were also low (Table 5.1.23). Chlorpyrifos consistently had the highest PAF values for each station. At Card Sound, a reference site away from the direct influence of C-111, the PAF value for chlorpyrifos was 1.5% while endosulfan's value was 0.7%. This PAF value for chlorpyrifos was identical to Joe Bay's. Highway Creek and Joe Bay had similar PAF values for endosulfan at 1.1% and 1.0%, respectively. Chronic effects from atrazine at estuarine stations never exceeded 0.0% and the median concentrations for metolachlor were all nondetectable.

5.1.7.2.2. Chronic Multisubstance Assessment (msPAF)

The results from the msPAF risk assessment for chronic effects on organisms from multiple chemical stressors are also presented in Tables 5.1.21 to 5.1.23. With the exception of the year 2000, chronic risks from multiple chemical exposures were generally low. In 2000, msPAF values reached 3.0% (RA) in all freshwater sites (Table 5.1.21). Similarly, in 2000, the msPAF was 2.7% for estuarine sites from potential exposures to all compounds in 2000. This was similar to 1999, where the msPAF was calculated to be 2.3%

For 1999 to 2000, potential chronic effects from multiple substance exposures for freshwater sites were highest at S-178/Site C and Site A with msPAF values of approximately 7% and 4.5%, respectively (Table 5.1.22). Site E1 had a chronic msPAF of 2.5% and Site W2 reached 2.8%. Chronic msPAF values for estuarine sites from the median exposure level for 1999 to 2000 were below 5% (Table 5.1.23). The highest value was for Joe Bay at 2.7% and the lowest msPAF values were found at Card Sound and Highway Creek at 2.1% for each.

5.1.7.3. Risk Distribution Functions for Chlorpyrifos and Endosulfan at Sites of Concern

Figures 5.1.10 to 5.1.13 present JPCs comparing measured concentrations of chlorpyrifos and endosulfan in all freshwater and estuarine sites between 1999 and 2000 with ecotoxicity endpoints for arthropods as the effects metrices used for the assessment. From Figure 5.1.10, there is a slight increase in potential risk to freshwater arthropods from chlorpyrifos in 1999 over 2000 below the 0.1 exceedence probability. As is apparent from Figure 5.1.11, an increase in risk from endosulfan in freshwater sites is observable in the 2000 monitoring data when compared with the data from 1999. For saltwater arthropods, a slight increase in risk is also observed in Figure 5.1.12 for estuarine site concentrations of chlorpyrifos in 1999 over 2000. For endosulfan in estuarine sites, potential risk to saltwater arthropods increased in 2000 when compared to 1999 (Figure 5.1.13). Thus, the trends illustrated in Figures 5.1.10 to 5.1.13 for both compounds were similar between 1999 and 2000 with potential risk for chlorpyrifos being slightly higher in 1999 and potential risk for endosulfan being slightly higher in 2000 in both estuarine and freshwater sites. JPCs for each site are presented in Figures 5.1.14 to 5.1.19 for endosulfan and chlorpyrifos over 1999

and 2000. Figures 5.1.14 to 5.1.19 illustrate distributions for acute effects on arthropods for endosulfan and chlorpyrifos and the potential overlap of concurrent nonparametric exposure distributions for the years 1999 to 2000. JPCs were derived by applying the various centiles of exposure for endosulfan and chlorpyrifos, determined by the nonparametric method specified in Risk Analysis, to log-logistically derived effects distributions for fish and arthropods following the PAF and msPAF determination methodology of Traas et al. (2002). Sites and pesticides chosen for the creation of JPCs were based on water quality and HQ exceedences observed in Tier 1.

The sites selected for JPC assessment were the estuarine sites Joe Bay and Highway Creek along with the freshwater sites S-178/Site C and S-177/Site B. A JPC was also created for Card Sound for comparison purposes with Joe Bay and Highway Creek. NOAA chose Card Sound as a reference saltwater site since C-111 discharges would not directly affect the occurrence of pesticides there. In addition, a JPC was created for S-18C/Site E since it represents downstream conditions from S-178/Site C, a site located directly adjacent to agriculture in a location with lower water flow (Miles and Pfeuffer, 1997). The two compounds chosen for JPC creation were chlorpyrifos and endosulfan. These were selected on the same basis as the sites. However, malathion was included on the multiple substance JPC distributions for fish and arthropods in S-177/Site B since a potential contribution to toxicity was observed in the acute msPAF assessment from the preceding sections. With the exception of S-178/Site C, JPCs for fish are presented using the joint action of endosulfan and chlorpyrifos. This was due to the low PAF values at each concentration assessed for the single chemical distributions. For S-178/Site C, almost all of the visible potential risk to fish

is due to endosulfan, so JPCs are presented for fish due to the potential risk of endosulfan only.

Figures 5.1.14 to 5.1.16 present the JPCs for S-177/Site B, S-178/Site C, and S-18C/Site E, respectively. Potential risks of endosulfan to fish and arthropods were highest at S-178/Site C except for arthropods exposed to chlorpyrifos where potential risks were higher at S-177/Site B. From the multiple substance distribution for arthropods at S-178/Site C, endosulfan was contributing the largest portion of the potential risk. Endosulfan also was contributing a higher potential for risk than chlorpyrifos in the multiple substance arthropod distribution for S-18C/Site E, which is directly downstream from S-178/Site C. However, potential risks were lowest at S-18C/Site E in comparison with S-178/Site C and S-177/Site B. For fish, S-178/Site C and S-177/Site B also have higher potential risks from measured concentrations than S-18C/Site E. There appeared to be a particularly higher potential for risk for fish in the JPC for S-178/Site C over S-177/Site B. Chlorpyrifos was contributing negligible potential risks for fish at S-178/Site C and was not included with endosulfan for a multiple substance joint toxicity plot. At S-177/Site B, however, chlorpyrifos, endosulfan, and malathion created a higher potential for risk when various centiles of exposure were introduced into the msPAF model created by Traas et al. (2002).

For the estuarine sites, potential risks appeared to be only slightly higher at Joe Bay for arthropods than at Card Sound and Highway Creek (Figures 5.1.17, 5.1.18 and 5.1.19). For example, potential exceedences of 5% of the species sensitivity data for arthropods between 1999 and 2000 were estimated to be surpassed by concentrations of chlorpyrifos and endosulfan 9% of the time at Joe Bay and 8% of the time at Highway Creek. Potential risks for estuarine fish were low at all estuarine sites.

Figures 5.1.20 to 5.1.31 present JPCs calculated for monthly exposure data. Out of all of the months, only February and June had water quality violations and sufficient data to create exposure distributions ($n \geq 4$) for 1999 and 2000 (n cutoff value used in Hall, Jr., et al., 2000). Unlike the previously described graphs where exposure data from all months were combined, monthly exposure data were assumed to be log-logistically distributed and were assimilated, screened, and ranked in accordance with previous work (e.g.,ECOFRAM, 1999). The non-parametric method was not used in the monthly distributions due to the low number of data points available. The same sites used to create distributions with all 1999 and 2000 exposure data aggregated were also used for the monthly risk characterization from Tier 1 infractions. S-18c/Site E had no water quality violations but was useful for the risk characterization portion as a downstream comparison to S-178/Site C. Card Sound was an estuarine reference site chosen by NOAA as a location away from the direct influence of water from C-111. Chlorpyrifos and endosulfan were analyzed separately for February and June at each of the sites and jointly under the assumption of additive toxicity. Risks to fish were assessed using only the msPAF approach while risks to arthropods were assessed using single and multiple substance analyses (Figures 5.1.20 to 5.1.31). Fish JPCs were reported for single compounds and not for the joint toxicity of both if one compound was contributing a majority of the risk as in the case with endosulfan at S-178/Site C.

At S-177/Site B, clear discrepancies in JPCs can be noted for February and June (Figures 5.1.20 and 5.1.21). For arthropods, potential risk is low in June while an increase is observed in February. Potential risks from chlorpyrifos and endosulfan at S-177/Site B were higher for endosulfan than chlorpyrifos in February. At S-178/Site C, potential risks from endosulfan outweigh those for chlorpyrifos to arthropods in both February and June (Figure

5.1.22 and 5.1.23). In June, there was an estimated 10% probability that 5% of the arthropod acute toxicity data were potentially exceeded by endosulfan concentrations in S-178/Site C. In February, there was an estimated 10% exceedence probability for 15% of arthropod acute toxicity values by endosulfan concentrations in S-178/Site C. At S-18c/Site E, the potential risks are greater in February than June (Figures 5.1.24 and 5.1.25). Potential risks to arthropods from measured concentrations of chlorpyrifos and endosulfan appeared negligible in both months but even lower in June.

Although Card Sound was selected as a reference site for comparisons to estuarine sites affected by C-111 discharges, potential risks from pesticides in surface waters at Card Sound existed (Figures 5.1.26 to 5.1.27). Risks extrapolated from JPCs, however, were usually lower at Card Sound than Highway Creek (Figures 5.1.28 and 5.1.29) or Joe Bay (Figures 5.1.30 and 5.1.31). Potential risks from chlorpyrifos at Card Sound and Highway Creek sites were higher in June than February, particularly from exposure to concentrations estimated at the upper centiles of the exposure distributions. Potential risks for endosulfan in Joe Bay and Highway Creek, however, were higher in February than in June. Chlorpyrifos risks were higher in June than endosulfan at Card Sound and Highway Creek. However, endosulfan potential risks were about twice as high for arthropods in February than for chlorpyrifos at Highway Creek and Joe Bay. For June and February exposure data, potential risks to fish from chlorpyrifos and endosulfan exposures were generally lower than for arthropods in most scenarios (Figures 5.1.20 to 5.1.31). However, at S-178/Site C, potential risk to fish species were particularly high in February where there was an estimated 10% probability of exceeding 24% of the toxicity values for fish species (Figures 5.1.22 and 5.1.23). In June, there was an estimated 10% probability of exceeding 3% of the toxicity

values for fish species at S-178/Site C. Endosulfan exposure was contributing almost all of the potential risk to fish species in February and June at S-178/Site C. Endosulfan was also creating a greater potential risk at S-178/Site C for arthropods during both February and June than for the other freshwater sites.

At S-177/Site B, risks to fish and arthropods from exposure to joint action of chlorpyrifos and endosulfan were higher in February than June (Figures 5.1.20 and 5.1.21). At S-177/Site B in February, there was an estimated 5% exceedence probability for 10% of the acute toxicity values for arthropods (Figure 5.1.20). In June, there was an estimated 5% exceedence probability for 1% of the acute toxicity data for arthropod species (Figure 5.1.21). This same trend was observed at S-18c/Site E at a lower scale (Figures 5.1.24 and 5.1.25). For both of these sites, potential risks from joint action to arthropods were greater than for fish.

Of all the estuarine sites, potential risks of chlorpyrifos and endosulfan joint exposures were highest during February at Joe Bay (Figures 5.1.26 to 5.1.31). Potential risks of joint actions of chlorpyrifos/endosulfan to arthropods were higher at all estuarine sites for February and June than to fish. Higher potential risks to arthropods were found in June over February at Card Sound and Highway Creek but in February over June for Joe Bay. In February, endosulfan appeared to be contributing greater potential risks at Joe Bay and Highway Creek while in June, chlorpyrifos appeared to be contributing greater potential risks to arthropods from exposure to joint actions at the same sites. Chlorpyrifos appeared to have a slightly greater potential for risk during both months at Card Sound.

The 1 μg/L NOEC for the effects of endosulfan on aquatic invertebrates (Hose et al., 2003) and fish from field studies was exceeded once at S-178/Site C on February 16, 2000.

This was the highest measured concentration of endosulfan. The next highest measured concentration of endosulfan was found a day later at the same site. This value (0.2555 μg/L) did not exceed the NOEC. The highest measured concentration of chlorpyrifos was found at S-177/Site B at 0.0234 μg/L. This value did not exceed the field NOEC of 0.1 μg/L for aquatic invertebrates or fish.

5.1.8. RESULTS/COMPARISONS OF COPEC CONCENTRATIONS TO EFFECTS DATA FOR NATIVE SPECIES

Analysis of the predicted adverse ecological effects related to the assessment endpoints indicates the following:

Assessment Endpoint

1. ***Primary Producers***

   No significant risk was directly calculated from measured concentrations of herbicides and existing toxicity data.

2. ***Microbial Decomposers***

   A study was available that assessed the effects of chlorpyrifos and endosulfan on a naturally collected microbial food web in a South Carolina estuary (DeLorenzo et al., 1999; see Effects Analysis.) Based on this study, effects from measured concentrations of chlorpyrifos and endosulfan in C-111 and estuarine sites between 1999 and 2000 should not inhibit microbial decomposers. However, based on the results of the study by Delorenzo et al. (1999), bacterial abundance may decrease at the highest measured

concentration of endosulfan (1.345 μg/L) found in February of 2000 at S-178/Site C. After deploying substrates in surface waters for 4 d, DeLorenzo et al. (2001) were not able to discern clear trends in effects on bacterial community abundance with pesticide concentrations in some of the freshwater and estuarine sites monitored by NOAA for pesticides. Possibly from nutrient input, S-178/Site C, the site closest to agriculture, appeared to have higher chlorophyll *a* concentrations, and protist taxa richness. S-178/Site C also generally had greater bacterial densities than sites further downstream. An overall decline in bacterial densities was found from 1999 to the conclusion of their study in 2000 (DeLorenzo et al., 2001). More work is needed to fully address this issue.

3. ***Invertebrate Herbivores (non-mollusc)***

Generally, may be at low risk (directly) from single and multiple chemical exposures in freshwater and saltwater. Pink shrimp may be at low risk from saltwater insecticide exposures in Florida Bay. The highest concentration for chlorpyrifos was found at Joe Bay on February 10, 1999 at 0.00617 μg/L Maximum concentrations at Highway Creek and Card Sound were 0.00369 and 0.0035 μg/L (found on February 10, 1999 and February 14, 2000, respectively.) The only acute toxicity LC50 available for pink shrimp and chlorpyrifos was a 48 h concentration of 2.4 μg/L. This value is above the maximum concentration of chlorpyrifos found at an estuarine site. The maximum concentration of endosulfan found at an estuarine site was also found at Joe Bay in February. This concentration was 0.0109 μg/L. A 96-h

LC50 for pink shrimp and endosulfan was available for assessment from a flow through toxicity study at 0.04 μg/L. The maximum concentration detected in Joe Bay was 27% of the acute toxicity value for endosulfan. Four other measured concentrations of endosulfan in surface water taken from February 14 to 18 of 2000 at Joe Bay were within 23 to 26% of the acute toxicity value for endosulfan and pink shrimp. All other concentrations of total endosulfan measured at Joe Bay are below 10% of the acute toxicity value for pink shrimp. At Highway Creek, the highest concentration of total endosulfan was also found on February 13, 2000 at 0.008675 μg/L. This concentration was 22% of the LC50 value for endosulfan with pink shrimp. From February 14 to 18, 2000, four measured concentrations of total endosulfan at Highway Creek were from 14 to 17% of the acute toxicity value for pink shrimp. Additional samples taken at Highway Creek were below 10% of the acute toxicity value for pink shrimp. At Card Sound, one endosulfan sample (0.00487 μg/L) taken on September 25, 2000 was 12% of the acute toxicity value for pink shrimp. All other measured endosulfan concentrations were below 10% of the acute toxicity value for pink shrimp including samples taken in February of 2000 at Card Sound.

4. ***Fish***

Fish may be at low risk (indirectly) from low food resources impacted by insecticides at estuarine/freshwater sites. The maximum concentration of chlorpyrifos in a freshwater site was found at S-177/Site B (0.0234 μg/L). This value would not exceed the lowest acute concentration for a fish species

found in Taylor Slough (Trexler et al., 2000; SFWMD, 1992) since the lowest geometric mean from acute toxicity data was 4.2 μg/L for bluegill. From AQUIRE, the lowest reported acute toxicity value for bluegill exposed to chlorpyrifos was 1.7 μg/L from a 96-h LC50 measurement.

In February at S-178/Site C, fish may be at high risk (directly) from pulsed exposures to endosulfan. The maximum concentration of endosulfan measured in C-111 (1.345 μg/L) is close to the 96-h LC50 for channel catfish (1.5 μg/L), a fish species in the Everglades (SFWMD, 1992). This concentration also exceeds a reported 96-h LC50 for bluegill (1.2 μg/L), a native species of Taylor Slough (Trexler et al., 2000), and several 96-h LC50s from an interlaboratory study for sheepshead minnow, an estuarine species found in both Taylor Slough (Trexler et al., 2000) and Florida Bay (Lorenz, 1999). The highest endosulfan concentration found in an estuarine site was 0.01 μg/L at Joe Bay. This value was below all toxicity values for saltwater fish, whether they were Florida Bay species or not. Several native and non-native fish species known to reside in ecosystems around either freshwater or saltwater sampling sites that did not have LC50s exceeded by measured concentrations of endosulfan included western mosquitofish (geometric mean EC50 of 10.5 μg/L), pinfish (saltwater fish with an LC50 of 0.3 μg/L), walking catfish (geometric mean EC50 of 9.2 μg/L), inland silverside (saltwater fish with an LC50 of 1.5 μg/L), and *Tilapia* sp (geometric mean EC50 range of 2.6 to 5.9 μg/L for various species). Though the geometric mean LC50s for each *Tilapia* species were lower, one LC50 for *Tilapia*

mossambica was 0.6 μg/L which was exceeded by the maximum concentration measured by NOAA at S-178/Site C (1.345 μg/L).

Although not an assessment endpoint, potential risks to amphibians (i.e., frogs) could not be fully assessed from the joint toxicity of measured concentrations of pesticides since the toxicity databases are limited. The microbial population assessment was based on a laboratory mesocosm study (Delorenzo et al., 1999) and field data collected while NOAA was monitoring pesticide concentrations (Delorenzo et al., 2001). The data from the two studies gave some evidence but was not conclusive enough to allow us to assess this endpoint as fully as others.

5.1.9. CONCLUSION

The first phase of a screening level ecological risk assessment (SERA) was completed to evaluate the potential risks of organic pesticides found in water in the lower Canal 111 (C-111) Basin and adjacent tidal zones in South Florida. This study was the first PRA conducted specifically for a South Florida ecosystem. Previously collected data were assimilated and used to predict potential effects on nontarget aquatic species. The goal was to develop a perspective on chemical stressors present in an area undergoing large-scale hydrologic restoration, as recommended by interagency evaluation of contaminant issues in Everglades restoration. It is the first phase in development of a retrospective ecological risk assessment, and it focuses on an area where a critical Everglades restoration project is underway (C-111 Project). Results are intended to be used by the appropriate state and federal jurisdictions for interpretation, evaluation, and application of appropriate remedial actions for protection of fishery and wildlife resources and are expected to identify areas with

data gaps and information needs, that if met, will provide risk information detailed enough to support water quality management planning and increase the probability of success of Everglades restoration.

This SERA was conducted under general U.S. EPA guidelines and focused only on potential affects of water exposure to the herbicides atrazine and metolachlor and to the insecticides chlorpyrifos, endosulfan, and malathion. It did not take into account the potential additional effects of exposure of organisms to other contaminants present, such as heavy metals, or other types of exposure, such as through sediment or bioaccumulation from consuming food items that have also been exposed.

A two tiered approach was presented to quantify potential risks of pesticides in surface waters of the C-111 canal system and related estuarine sites. In the first tier, screening benchmarks were used to determine which areas and species may be at risk. The second tier incorporated greater amounts of data and realism to obtain a probabilistic measure of risk using a SSD approach. The methods used were dependent on the quantity and quality of data available. Thus, uncertainties arising from the ecological realism of test endpoints and species selection along with the uncertainties arising from spatial and temporal sampling regimes could not be controlled in this phase of the risk assessment for C-111 (see Section 11).

Several conclusions were reached from results of the initial evaluations of risk of acute effects from pesticide exposure. The first conclusion is that the highest risk was associated with endosulfan effects on estuarine arthropods, followed by endosulfan on freshwater arthropods. Out of all of the freshwater sites, regions near S-178 and S-177 had the highest acute PAF values to arthropods from the 90th centile exposure concentration estimate of

endosulfan (see Table 5.1.19). The second conclusion is that the highest risk of acute effects from joint toxicity of chemicals considered was to estuarine arthropods. For fish, the highest acute PAF value for endosulfan at an estuarine site was 1.0% at Joe Bay. For arthropods, the highest acute PAF value for endosulfan at an estuarine site from exposure to the 90th centile concentration estimate was 5.9% also at Joe Bay. The third conclusion is that the highest risk of acute effects in fresh water are associated at sites near water control structure S-178 and canal C-111E, a branch of canal C-111. An acute PAF of 6.7% was found for freshwater arthropods and of 5.2% for freshwater fish at this site. Also, in the JPC for the potential risk of measured concentrations in 1999 and 2000, it is apparent that the majority of potential risks to arthropods were due to endosulfan concentrations at S-178 and not chlorpyrifos (see Figure 5.1.15 and Table 5.1.19). From the JPCs and PAF tables, higher potential risks for fish were also generally confined to S-178 at C-111E, out of all of the sites assessed. The fourth conclusion is that the highest risk of acute effects for salt water organisms is in Joe Bay, which receives water discharges from C-111. PAF and msPAF values at Joe Bay for acute and chronic exposure equaled or exceeded those found at Highway Creek and Card Sound. The fifth conclusion is that results from initial evaluations of risk of chronic effects from pesticide exposure show that the highest risk is associated with endosulfan in fresh water. Similar to the acute PAF assessment, the highest potential chronic effects in 1999 and 2000 were found at S-178/Site C for endosulfan. The chronic assessment only evaluated distributions of all species to gain a picture of community-level risk so taxa-specific PAF values were not available. Probability-based statistical models of joint pesticide action (PRA) showed risk increased from single to multiple exposures.

Although pesticides are mentioned in the document as a potential threat in the C-111 basin, the U.S. Army Corps of Engineers stated that canal water in the C-111 Basin is "made up of good quality seepage water from ENP and seepage from the urban/agricultural area east of the Park. The overall water quality of this mixture in the L-31N canal usually meets or exceeds the applicable criteria. However, actual constituent levels currently existing prior to construction of the May 1994 (Final Integrated General Reevaluation Report) plan will need to be determined." (U.S.ACE, 2000 Sec 4.4.2). In some areas in the C-111 basin south of L-31 N, pesticide concentrations exceeded protective criteria used in the current assessment. Results indicated that potential risk may exist for certain segments of the biota in sites in the C-111 basin south of L-31N. The removal of the spoil mounds along a 5-mile stretch of C-111 to facilitate water flow into ENP and away from S-197 may be detrimental to organisms in that area of the ENP if pesticides enter at concentrations found at S-178/Site C. However, the latter site is located in a canal surrounded by agriculture with low water levels and little water flow making it conducive for higher concentrations (Miles and Pfeuffer, 1997). In addition, potential risk levels at S-18c/Site E, directly downstream from S-178/Site C had much lower levels of potential risk possibly due to dilution of pesticide concentrations. Two sites south of C-111 in freshwater regions of the ENP, Site E2 and W2, had measured concentrations of pesticides that did not exceed any criteria from Tier 1 and had acute and chronic PAF values that were typically less than 3%. A 10% criteria was set for aquatic organisms in the present assessment but this level of protection was based more on prior recommendations than on any ecological significance.

Though uncertainties and data gaps exist regarding the implications of the results and the data that went into the assessment (see Sections 10 and 11), potential risks to community

structure of arthropods and fish from the second tier risk characterization were below the numerical criteria set at the beginning of the assessment. For each of the taxa-related SSDs that were constructed (i.e., for fish, arthropods, and plants and algae), the probability of exceeding the 10th centile of acute toxicity SSDs was 0% up to the 99th centile exposure concentration for all sites and pesticides when monitoring data was compiled for 1999 and 2000 except endosulfan and S-178/Site C. Concern, however, can still exist particularly if there are species with sensitivity to biocidal stressors below the 10th centile concentration estimate for a distribution. Since criteria were not focused on native species within the potentially affected ecosystems, native organisms vital to the structure and functioning of the ecosystems that were not accounted for may have had a high susceptibility to the pesticides at the magnitude and duration they were detected in during the corresponding time frame used in the risk assessment.

When considering the PAF and msPAF values obtained in the assessment, significance of the numbers must also be considered in light of the potentially affected organisms' reproductive abilities. Arthropods generally had higher PAF values than ones obtained for fish and plants and algae. A K-strategist would be expected to have slower reproduction, lower number of offspring, slower development, a longer generation time, and lower dispersal ability than r-selected species. Zooplankton populations may have rapid growth rates and reproductive cycles with populations of many species doubling in days under proper conditions and copepod and cladoceran species were observed to recover within weeks from various field/mesocosm studies with exposures to pyrethroid compounds (Giddings et al., 2001).

To corroborate the results from this assessment, biological and chemical monitoring data in water and sediment and laboratory toxicity testing with native species would be useful. To evaluate potential effects from pollution on resident species, past surveys have found that important trends could be noted in weight of evidence approaches with chemical and biological monitoring when used in conjunction with purposefully designed sampling protocols (Camargo, 1994; Van Dolah et al., 1999; An et al., 2002). Specialized community indices for Taylor Slough, Florida Bay, and Biscayne Bay based on such multi-metric indices as the index of biological integrity (Karr, 1991) could be used in field surveys of fish and invertebrates as a way to preliminarily determine trends and patterns in species composition due to anthropogenic stressors. These indices should be grounded in "sound ecological principles" and chosen based on the sensitivity of native populations or ecosystem performance measures to the stressors of concern (Barbour et al., 1995). Such indices can be calibrated to reference sites away from the influence of C-111 in Taylor Slough and in Florida or Biscayne Bay. However, there may be some uncertainty about what areas are available, particularly in Biscayne or Florida Bay. Card Sound, the reference site chosen by NOAA away from the influence of C-111 in Northern Biscayne Bay, had measured concentrations of pollutants that potentially impacted estuarine arthropod communities (see Section 7). The development of data sets of measured pesticide concentrations in areas with similar habitat type and hydrodynamics in Taylor Slough to sites in C-111 such as near S-177 and S-178 should be identified and established as a way of determining reference sites. These approaches have remarkable precedence in statewide water quality monitoring programs with most states having established multi-metric biomonitoring programs (Davis et al., 1996). The FDEP has developed multi-metric biocriteria for streams in delineated

ecoregions of Florida and is in the process of developing biocriteria for marine and wetland habitats that can be very useful for these undertakings. (See http://www.dep.state.fl.us/water/bioassess/currproj.htm for updates and more information.)

5.1.10. DATA GAPS

Examples of information gaps that can contribute to an over- or under-estimation of exposure or effects, but are not limited to:

Table 5.1.24. Data gaps

Gap	**Importance/ Specific Impact**
Lack of knowledge of pesticide fate and transport in Taylor Slough/Florida Bay/Biscayne Bay	More data are needed on sources and sinks of biocides in and adjacent to these systems to fully assess the risk of contact with ecological receptors and to develop a more detailed conceptual model.
Metal exposures in surface water	Single metals may be potentially toxic alone and/or in joint action with other chemicals to aquatic organisms.
Contaminant exposures in sediment	Chemicals in sediment may be potentially toxic to aquatic organisms. Sediment exposure may be the most significant long-

	term route.
Risk to wildlife including birds and amphibians	Wildlife may be directly or indirectly at risk. Effects of biocides on South Florida indicator species (e.g., wading birds) not included in the present SERA should be assessed
Chemical monitoring in water and sediment	Analytical monitoring should be compiled with consistent, systematic sampling, especially in saltwater (and sediment). Present limited concentration-exposure data may under- or over-estimate exposures.
Ecotoxicity testing with relevant species native to freshwater and saltwater and with multiple chemical exposures	Toxicity testing presently available from literature with surrogates may be under- or over-estimates of toxicity. Tests do not consider relevant Florida native species.

Ecosystem modeling (e.g., AQUATOX) needed	A model should be applied that relates effects, toxicity, and risk to ecological endpoints relevant to C-111 and estuarine sites and that considers additional endpoints besides direct lethality, and growth or reproduction inhibition (e.g., predator-prey effects, trophic transfer, etc.).
Field-based studies	The establishment of routine field-monitoring assessments of organisms can allow us to generate data that will infer a greater degree of causality about impacts on nontarget biota from current pesticide applications.
Validity of the msPAF model	Whether the msPAF model is protective enough to be used to generate surrogate endpoints for the effects of pesticides on communities of organisms in the field and whether interactive effects from multiple stressors in South Florida may be occurring,

	i.e., synergism and/or antagonism, warrants testing in field/mesocosm scenarios.

5.1.11. UNCERTAINTIES

From the risk characterization of the C-111 SERA, a weight of evidence approach was used to establish the generalized results reported in Section 8. Uncertainty in an ecological risk assessment can arise from natural variation (stochasticity within the system), missing data, faulty assumptions in the models used, and/or mistakes (U.S.EPA, 1992; Suter, 1993). With care, all general uncertainties can be reduced with the exception of stochasticity which is a property of the system being assessed and can not be controlled. It still may be identified and discussed (Suter, 1993).

5.1.11.1. Uncertainties in Exposure Analysis

The characterization of exposure in the C-111 system had limits in both spatial and temporal dimensions. Although the C-111 canal consists of over a 100 square mile basin and several ecologically distinct discharge sites, only a dozen total sites were sampled for pesticides in areas related to C-111. Sampling frequencies appeared to be unbiased by all monitoring agencies in regards to pesticide applications. In addition, all agencies had predetermined sampling intervals taken on an annual basis. For the most part, temporal sampling designs were congruous with an exposure analysis that allowed unbiased statistical analysis of frequency distributions. One of the largest sources of uncertainty in the analysis of exposure arose from analytical data for pesticides that were detected frequently or at high concentrations by some monitoring programs but were not analyzed in other monitoring

programs. The SFWMD maintains an ongoing pesticide monitoring program at several structures located at upstream sites in C-111 and related tributaries. Sampling occurs quarterly throughout the year, allowing a snapshot of surface water events at each site in corresponding seasons. Chlorpyrifos, however, was not analyzed for by the SFWMD.

Most of the spatial data for various sites in C-111 came from a project commissioned by the SFWMD but carried out by personnel at NOAA. Sampling was initiated to measure changes in wet, dry, and transition seasons. However, only several dates were sampled for each season. Also, the majority of the sites downstream in C-111 (W-1, W-2, E-1, E-2, Joe Bay, and Highway Creek) did not have sampling data available in 1998 until August of that year and Card Sound was added on at the height of the dry season in 1999. Thus, exposure analysis and risk characterization for freshwater and estuarine sites before 1998 is largely incomplete and uncertain. On the other hand, the USGS sampled S-177 on a monthly basis throughout the two years considered in this assessment. Though endosulfan was a pesticide of importance in all tiers of the C-111 risk assessment, only α-endosulfan was analyzed by the USGS in surface waters for 1998 and none of the isomers or degradates of endosulfan were measured by the USGS at S-177 in following years. In addition, NOAA did not analyze for malathion in any of its sampling sites.

5.1.11.2. Uncertainties in Effects Analysis

When extrapolating from laboratory single-species toxicity testing to the field, the resulting uncertainties can increase imprecision and inaccuracy in results. Like mammalian toxicology, ecotoxicological testing has been primarily focused on individual species (ECOFRAM, 1999). Pesticide registration testing under FIFRA requires single-species

testing on a subset of aquatic species to predict effects on all biota. Ecotoxicology however is concerned with effects on populations, communities, and ecosystems and not on single species unless the species of concern is threatened, endangered or pivotal ("Keystone Species") in an ecosystem. Relying on a limited database of single-species toxicity tests to predict effects on higher levels of organization also may lead to problems when the majority of standard test species may not be native to the area undergoing an ecological risk assessment. It was evident from the SERA that more ecotoxicity testing has to be completed for native species in the C-111 basin and for Northeast Florida Bay and Biscayne Bay. However, an attempt was made in the current SERA to use as large a database of acute and chronic toxicity endpoints for COPECs as possible while realizing that the *n* value for species endpoints fitted to SSDs could not be the true *N* value, and thus the true distribution, for the sensitivities of all species in the sites assessed (Suter, 1993).

Another source of effects uncertainty is the exposure duration found in the laboratory vs. the field. Most standard acute tests have durations that range from 24 to 96 h. In the field, pesticide exposures are often pulsed and vary with application frequency (ECOFRAM, 1999). Dissipation of pesticide residues in the water column commonly take hours to days but applications can be repeated within a growing season (ECOFRAM, 1999). In South Florida, pesticides can be applied frequently (up to ten or more times) with a year-round growing season. Furthermore, the resistance and/or sensitivity of organisms may increase from frequent pulsed exposures, especially for invertebrates with short life cycles (ECOFRAM, 1999). Having knowledge of the effects from pulsed exposures to chemicals on organisms would give risk assessors a greater ability to evaluate whether and over what time period organisms may recover between exposure events, whether latent effects may

occur, and the development of resistance to future exposures (Naddy et al., 2000). Pulsed exposures are not considered in the ecotoxicity testing of pesticides by chemical manufacturers because there are no protocols for these types of exposure tests and they are not required under FIFRA ecotoxicity testing guidelines.

Extrapolating from laboratory toxicity data to population level effects in the field is also difficult if population dynamics and reproduction of site-specific organisms are considered. The influence of pesticide exposures in C-111 and estuarine sites on birth, death, and recruitment rates for organisms would be impossible to predict based on single-species toxicity tests alone. For instance, invertebrate populations exposed to pesticide concentrations equaling their LC50 may be able to maintain their population abundance due to reductions in resource competition and increased compensatory reproduction rates (ECOFRAM, 1999). Even more difficult to model are community level effects. Sublethal exposures to pesticides may cause mechanisms of intoxications that decrease an organism's ability to escape from prey. Changes could occur in trophic levels, and trophic interactions (e.g., predator-prey). At each emergent level, compensatory mechanisms may exist for organisms to mitigate against effects from stressors (ECOFRAM, 1999). There is currently not enough information available for any model to take this into consideration (ECOFRAM, 1999).

Though the toxicity of α-endosulfan, β-endosulfan, and endosulfan sulfate have been designated as being similar (IPCS, 1988), some available toxicity data may indicate otherwise. From 96-h LC50 results reported for Indian carp, *Cirrhinus mrigala*, and Indian catfish, *Channa punctata*, the toxicity of α- and β-endosulfan alone were about twice as toxic and seven times less toxic (Swarup et al., 1981); and 30 times more toxic and 0.7 times less

toxic (Devi et al., 1981) than LC50 results for technical endosulfan for each respective fish. Summing the measured concentrations of both isomers of endosulfan and its primary degradate allowed a comparison to a voluminous effects database that would have been unavailable had each related compound been assessed alone. In fact, satisfactory toxicity endpoints were inadequate for a distributional assessment of acute and chronic effects for either α-endosulfan, β-endosulfan, or endosulfan sulfate. Degradates of other compounds, such as malaoxon, that had little toxicity data available or were not analyzed for may have increased mixture toxicity to organisms in C-111.

5.1.11.3. Uncertainties in Mixture Assessment

Concentration- and response-addition may not always account for the effects from mixture toxicity. The application of laboratory toxicity tests to these models has validated the use of these theories, in many situations, for predicting the effects from mixtures (Altenburger et al., 2000; Arrenhius et al., 2004; Backhaus et al., 2000; De Wolf et al., 1988; Deneer et al., 1988; Faust et al., 2000). Yet, the development of methods for a probabilistic assessment of joint effects from mixtures (i.e., is multiple chemical stressors) is not fully developed (Giesy et al., 1999; De March, 1987; Suter et al., 2002). The effects of a mixture of atrazine and chlorpyrifos, and atrazine and malathion in water on laboratory- reared *C. tentans* found effects greater than additivity in both instances (Pape-Lindstrom and Lydy, 1997). Chlorpyrifos and malathion are both OP compounds. This indicates an interactive joint toxicity for binary combinations of these pesticides contrasted with the noninteractive joint toxicity models of CA and RA. However, atrazine concentrations in the tests were much higher than typical environmental concentrations and synergistic interactions from chemical stressors are still the exception, particularly in chemical mixtures exceeding binary

and ternary combinations where their occurrences are less common in the literature (Pape-Lindstrom and Lydy, 1997). Further bioassay work with chlorpyrifos and atrazine also found synergistic effects on *C. tentans* and pointed to possible mechanisms (Jin-Clark et al., 2004). For the exposed midges, inhibition of AChE was found to increase with atrazine concentrations in treatments with unchanging chlorpyrifos concentrations though atrazine alone was an ineffective inhibitor of AChE (Jin-Clark et al., 2002). Concentrations of atrazine and chlorpyrifos in the latter study were also generally lower than what was found in C-111. Though they may not always be representative, CA and RA are still the excepted models for predicting the toxicity of mixtures. However, more work needs to be done to develop mixture models for atrazine and OPs and the hazard/risk from other contaminant mixtures that can not be accurately described by existing joint toxicity models (Pape-Lindstrom and Lydy, 1997).

5.1.12. RECOMMENDATIONS

This type of probabilistic ecological risk approach should be conducted elsewhere in Florida for contaminants including metals, pesticides, nutrients, etc. This PRA approach not only provides useful risk information on ecological receptors for risk management decisions but it also provides a way to define the critical data needs to fill gaps in our understanding of the impact of contaminants on aquatic organisms and wildlife. This is extremely relevant where water management activities (e.g., changes in water quality, salinity, etc.) have potentially plated a key role with other anthropogenic activities (e.g., agriculture and pesticide use, development) in changing animal populations. The data needs we have established for C-111 and related estuarine sites (N.E. Florida Bay, South Biscayne Bay) are consistent with those supported by the Science Subgroup report (1996), the peer review

workshop in 1998 (LaPoint et al., 1998), and the US General Accounting Office report (U.S.GAO, 2003).

The need for robust contaminant information is critical since it serves as a baseline for and affects our understanding of CERP and the efficacy of water management projects. Baseline contaminant data become extremely important in this state because of the frequency of usage of pesticides, intensive development and population growth. Water management should prevent the possibility of moving contaminated water and soil to relatively undisturbed and uncontaminated areas so that we do not increase risks to ecological receptors where they did not exist before.

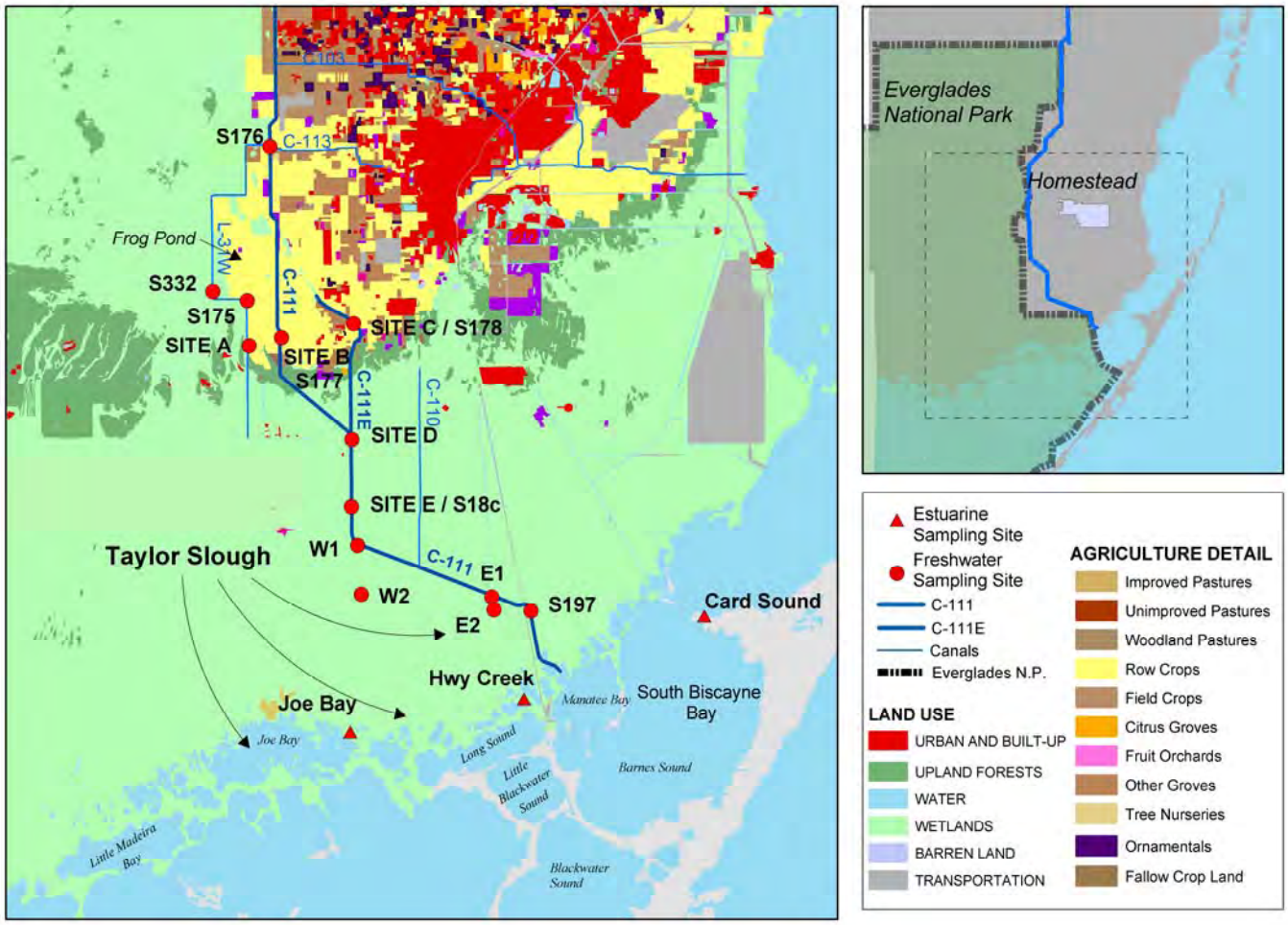


Figure 5.1.1. Land use and drainage canals in the C-111 flood control basin in southeast Florida.

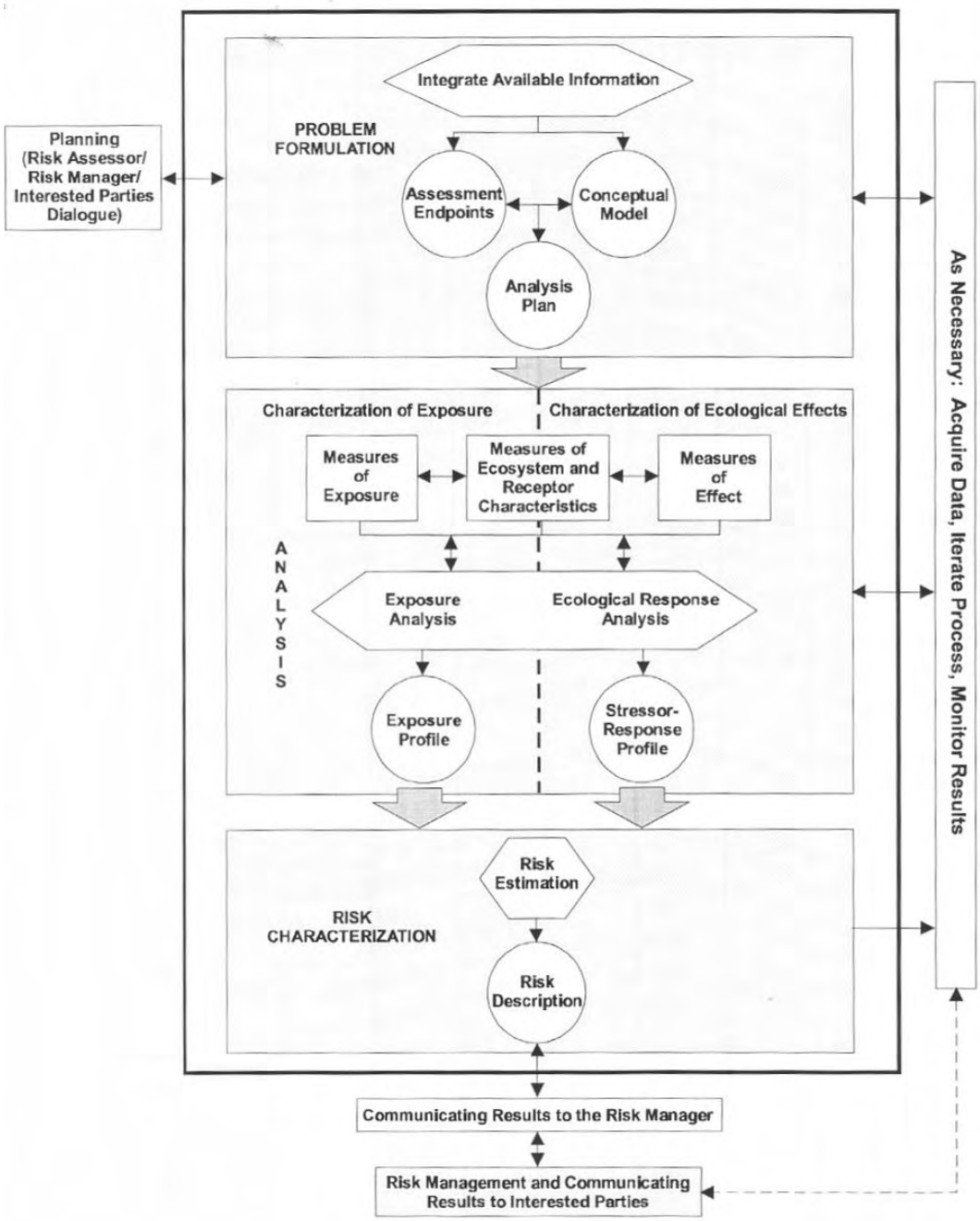


Figure 5.1.2. U.S. EPA framework for ecological risk assessment (from U.S.EPA, 1998).

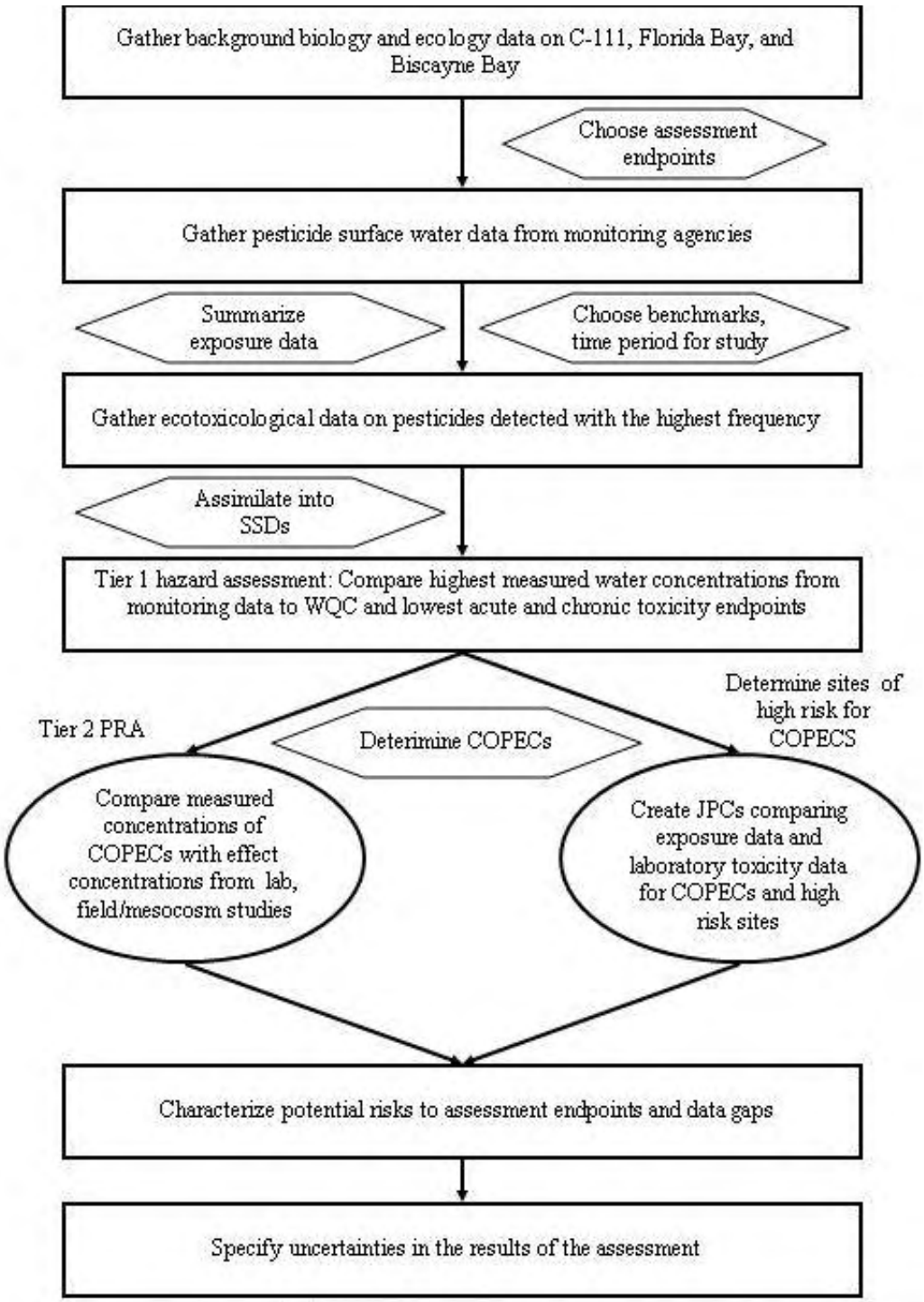


Figure 5.1.3. Decision tree for C-111 SERA. SSDs=species sensitivity distributions, COPECs= chemicals of potential ecological concern, JPCs=joint probability curves, PRA=probabilistic risk assessment, WQC=water quality criteria.

Table 5.1.1. Tier 1 effects data for metolachlor

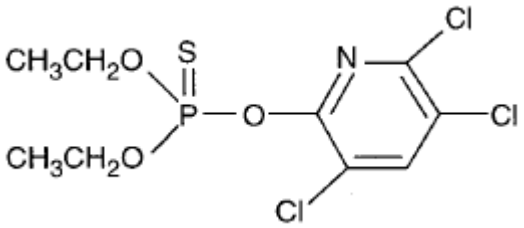
	Species	Common name	Endpoint	Concentration (µg/L)	Reference
Acute Toxicity	*Lemna Gibba*	Duckweed	14-d EC50	48	(Montague, 2002)
	Selenastrum capricornutum	Green algae	5-d EC50	10	(Montague, 2002)
	Skeletonema costatum	Diatom (saltwater)	5-d EC50	61	(Montague, 2002)
	Navicula pelliculosa	Diatom (freshwater)	5-d EC50	380	(Montague, 2002)
	Anabaena flos-aquae	Blue-green algae	5-d EC50	1200	(Montague, 2002)
	Oncorhynchus mykiss	Rainbow trout	96-h LC50	3900	(Montague, 2002)
	Cyprinodon variegatus	Sheepshead minnow	96-h LC50	7900	(Montague, 2002)
	Pimephales promelas	Fathead minnow	96-h LC50	8000	(Montague, 2002)
	Lepomis macrochirus	Bluegill sunfish	96-h LC50	10000	(Montague, 2002)
	Daphnia magna	Water flea	48-h EC50	23500	(Montague, 2002)
	Mysidopsis bahia	Mysid shrimp	96-h LC50	4900	(Montague, 2002)
	Crassostrea virginica	Eastern oyster	96-h EC50	1600	(Montague, 2002)
Chronic Toxicity	*Lemna Gibba*	Duckweed	14-d EC50	48	(Montague, 2002)
	Daphnia magna	Water flea	21-d NOEC	600	(Crommentuijn et al., 1997)
	Selenastrum capricornutum	Green algae	5-d NOEC	31	(Crommentuijn et al., 1997)
	Oncorhynchus mykiss	Rainbow trout	28-d NOEC	100	(Crommentuijn et al., 1997)

Table 5.1.2. Hazard quotients for Tier 1 Assessment of metolachlor measured concentrations in freshwater (FW) and saltwater (SW) sites

Acute FW	Peak concentration (µg/L)	Acute hazard quotient Animal	Acute hazard quotient Plant/Algae
Metolachlor	0.062	0.00	0.01
Acute SW	**Peak concentration (µg/L)**	**Acute hazard quotient Animal**	**Acute hazard quotient Plant/Algae**
Metolachlor	0.00722	0.00	0.00
Chronic FW	**Peak concentration (µg/L)**	**Chronic hazard quotient Animal**	**Chronic hazard quotient Plant/Algae**
Metolachlor	0.062	0.00	0.00
Chronic SW	**Peak concentration (µg/L)**	**Chronic hazard quotient Animal**	**Chronic hazard quotient Plant/Algae**
Metolachlor	0.00722	0.00	0.00

Table 5.1.3. Physical and chemical characteristics of chlorpyrifos

Structure**:

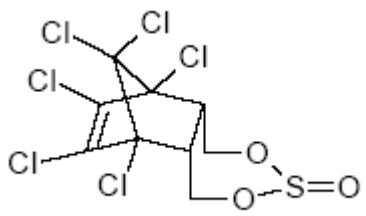


Property	Value*
CAS number	2921-88-2
Chemical name	*O*,*O*-Diethyl*O*-(3.5,6-trichloro-2-pyridyl)-phosphorothioate
Molecular weight	350.6 g/mole
Molecular formula	$C_9H_{11}NO_3PSCl_3$
Melting point	41-44^oC
Water solubility	1.39 mg/L @ 25^oC
Vapor pressure	2.0 x 10^{-5} mm Hg @ 25^oC
Henry's law constant	6.64 x 10^{-3} atm-L mol^{-1}
Log K_{ow}	4.7-5.3

*from Giesy et al., 1999
**from ATSDR, 1997

Table 5.1.4. Physical and chemical characteristics of technical endosulfan

Structure*:

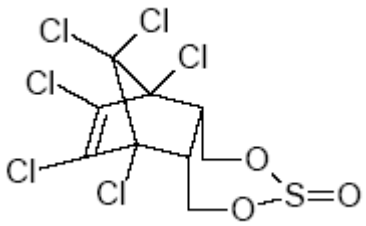


Property	Value*
CAS number	115-29-7
Chemical name	6,7,8,9,10,10-hexachloro-1,5,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo(e)-dioxathiepin-3-oxide
Molecular weight	406.95 g/mol
Molecular formula	$C_9H_6Cl_6O_3S$
Melting point	70-100^oC
Water solubility	60-100 μg/L @ 25^oC
Vapor pressure	$1x10^{-5}$ mmHg @ 25^oC
Henry's law constant	$1x10^{-5}$ atm m^3 mol^{-1} @ 24.8^oC
Log K_{ow}	3.55 and 3.62

*from ATSDR, 2000

Table 5.1.5. Physical and chemical characteristics of α-endosulfan

Structure*:

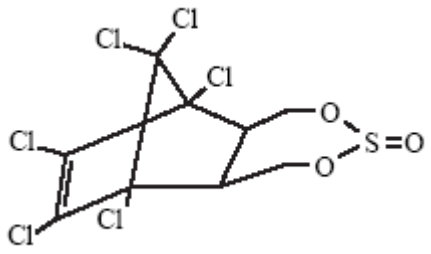


Property	Value*
CAS number	959-98-8
Chemical name	6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide (3α, 5a β, 6α, 9a α, 9β)-
Molecular weight	406.93 g/mol
Molecular formula	$C_9H_6Cl_6O_3S$
Melting point	108–110 ^oC
Water solubility	0.53 mg/L @ 25^oC
Vapor pressure	1 x 10^{-5} mm Hg @ 25^oC
Henry's law constant	1.01 x 10^{-4} atm m^3 mol^{-1} @ 25^oC
Log K_{ow}	3.83

*from ATSDR, 2000

Table 5.1.6. Physical and chemical characteristics of β-endosulfan

Structure*:

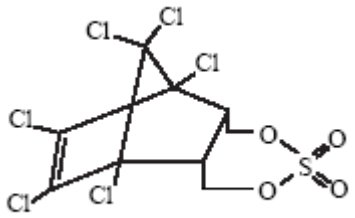


Property	Value*
CAS number	33213-65-9
Chemical name	6,7,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodiozathiepin-3-oxide, (3α, 5aα, 6β, 9β, 9aα)-
Molecular weight	406.9 g/mol
Molecular formula	$C_9H_6Cl_6O_3S$
Melting point	207–212 ^oC
Water solubility	0.33 mg/L @ 22^oC
Vapor pressure	1 x 10^{-5} mm Hg @ 25^oC
Henry's law constant	1.91 x 10^{-5} atm m^3 mol^{-1} @ 25^oC
Log K_{ow}	3.52

*from ATSDR, 2000

Table 5.1.7. Physical and chemical characteristics of endosulfan sulfate

Structure*:



Property	Value*
CAS number	1031-07-8
Chemical name	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-,6,9-methano-2,4,3-benzodiozathiepin-3,3-dioxide
Molecular weight	422.9 g/mol
Molecular formula	$C_9H_6Cl_6O_4S$
Melting point	198-201^oC
Water solubility	0.22 mg/L @ 22^oC
Vapor pressure	$1x10^{-5}$ mmHg @ 25^oC
Henry's law constant	$2.61x10^{-5}$ atm m^3 mol^{-1} @ 25^oC
Log K_{ow}	3.66

*from ATSDR, 2000

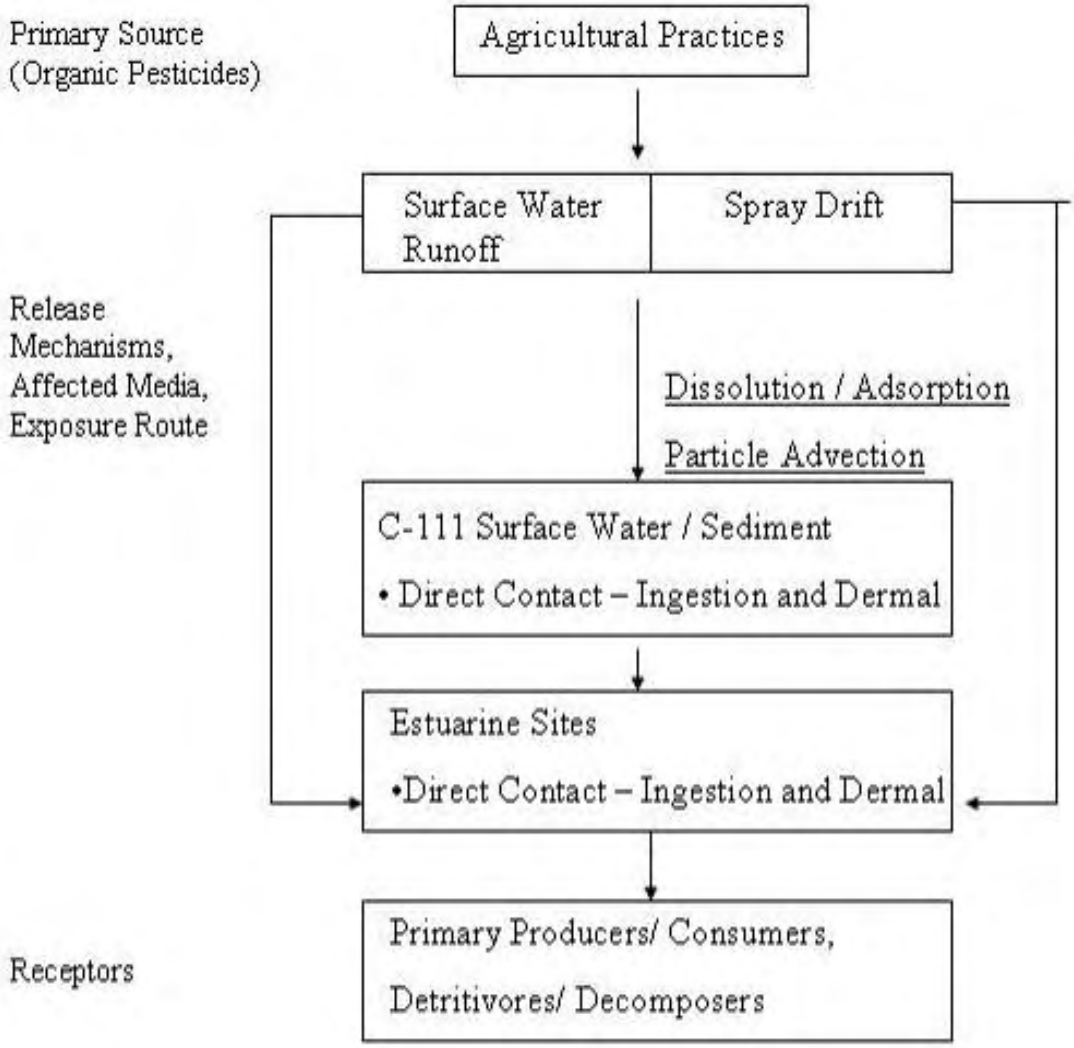


Figure 5.1.4. Conceptual exposure model.

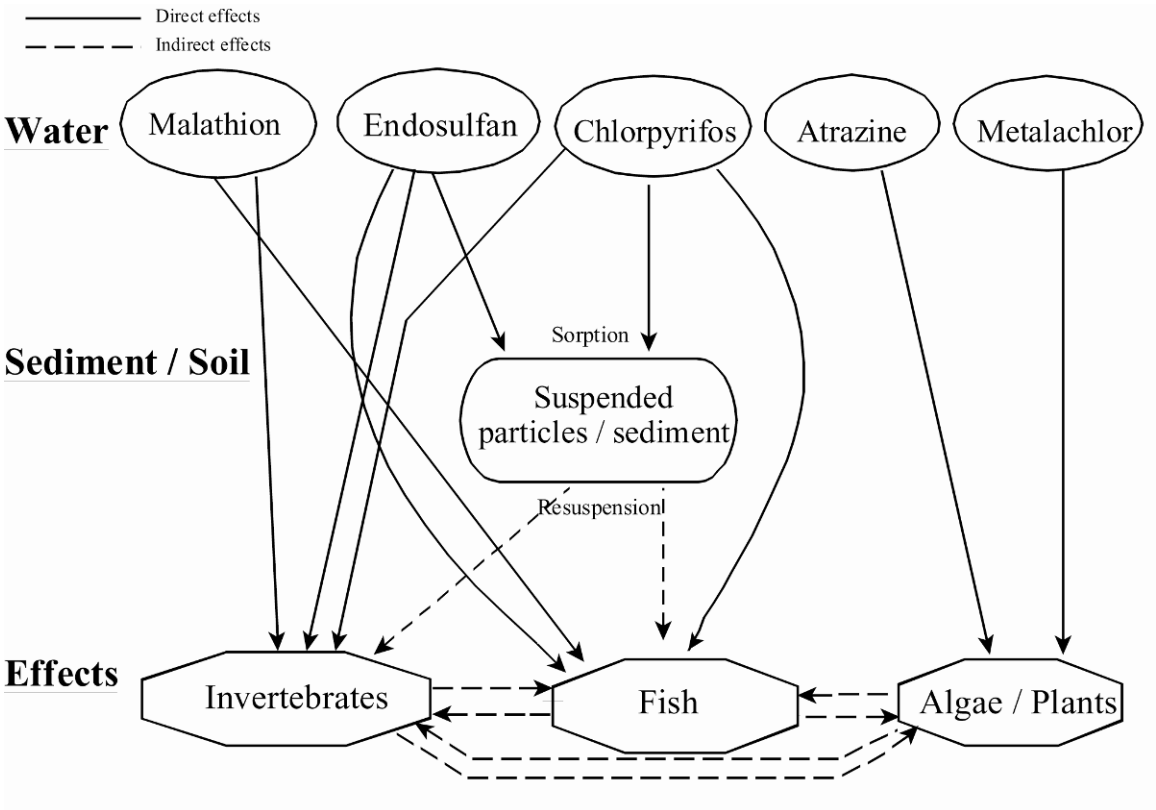


Figure 5.1.5. Conceptual effects model.

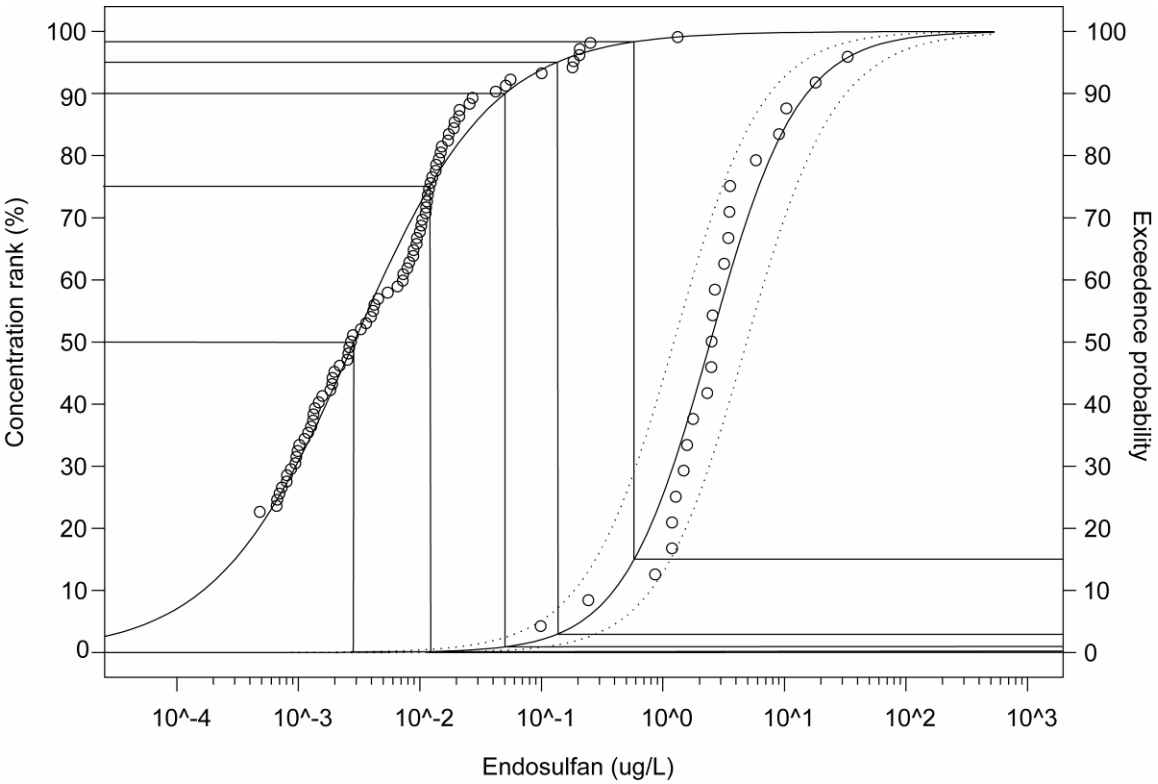


Figure 5.1.6. Illustration of the overlap of a distribution of measured concentrations and a distribution of toxicity values for creating a joint probability curve (JPC). Various centile concentrations are estimated from the exposure distribution and their intersection with the response factors from an effects distribution are the essential components in JPC creation.

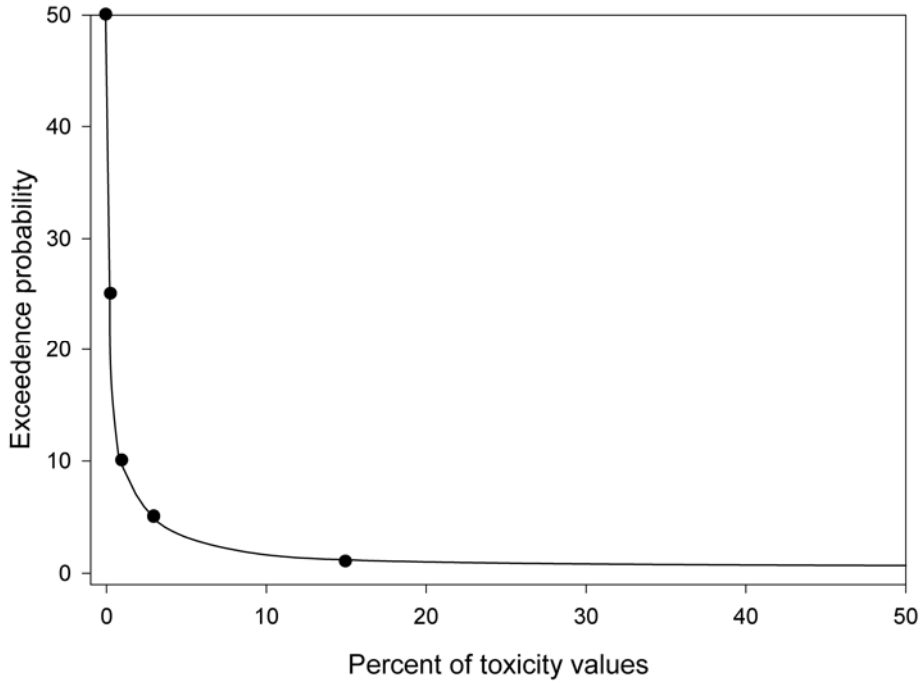


Figure 5.1.7. An example JPC created from the overlap of the distribution of environmental concentrations and toxicity values from Figure 6. See Analysis Plan text for interpretation.

Table 5.1.8. Detection limits (μg/L) for pesticides in surface waters

Pesticide	NOAA	SFWMD	USGS
Atrazine	0.00216	0.0094-0.24	NL
Chlorpyrifos	0.00004	NA	0.004-0.005
α-Endosulfan	0.00023	0.0019-0.0097	NA
β-Endosulfan	0.00007	0.0019-0.0097	NA
Endosulfan sulfate	0.00003	0.0019-0.0097	NA
Malathion	NA	0.028-0.15	0.005-0.027
Metolachlor	0.00670	0.047-0.24	0.001-0.013

NA=not analyzed, NL=not listed

Table 5.1.9. Summary of monitoring data for freshwater sites in C-111 (1999 and 2000) (ND = not detected)

S-175	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	1.8E-02	3.6E-02	6.5E-02	3.7E-02	1.1E-02	26	2	24	92.3	5.01E-02
Metolachlor	ND	ND	ND			26	26	0	0.0	
Chlorpyrifos						0				
Malathion	ND	ND	ND			26	26	0	0.0	
Endosulfan	ND	ND	ND			26	26	0	0.0	

S-176	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	1.0E-02	4.1E-02	1.4E-01	4.7E-02	2.9E-02	32	2	30	93.8	7.77E-02
Metolachlor	ND	ND	ND			32	32	0	0.0	
Chlorpyrifos						0				
Malathion	ND	ND	ND			32	32	0	0.0	
Endosulfan	4.0E-03	ND	4.0E-03	4.0E-03		32	31	1	3.1	

S-177/Site B	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	7.5E-03	2.1E-02	2.9E-01	4.4E-02	6.0E-02	43	1	42	97.7	1.54E-01
Metolachlor	4.2E-03	6.3E-03	6.2E-02	1.4E-02	1.3E-02	43	14	29	67.4	2.02E-02
Chlorpyrifos	2.1E-04	ND	2.3E-02	6.7E-03	7.7E-03	36	22	14	38.9	8.76E-03
Malathion	3.2E-03	ND	8.4E-02	3.3E-02	3.6E-02	32	26	6	18.8	2.03E-02
Endosulfan	5.9E-04	1.3E-03	4.3E-02	1.0E-02	1.4E-02	19	6	13	68.4	3.01E-02

S-178/Site C	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	7.6E-03	2.5E-02	8.5E-02	2.8E-02	1.5E-02	30	0	30	100.0	4.28E-02
Metolachlor	4.9E-03	ND	1.9E-02	1.2E-02	4.9E-03	30	18	12	40.0	1.66E-02
Chlorpyrifos	1.2E-04	3.1E-04	3.7E-03	1.0E-03	1.2E-03	23	6	17	73.9	3.37E-03
Malathion						7	7	0	0.0	
Endosulfan	4.5E-03	4.7E-02	1.3E+00	1.4E-01	2.6E-01	30	4	26	86.7	2.10E-01

Table 5.1.9 (continued)

S-18C/Site E	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	1.0E-02	2.3E-02	3.4E-01	6.1E-02	9.3E-02	32	0	32	100.0	2.83E-01
Metolachlor	4.8E-03	ND	2.1E-02	9.7E-03	4.7E-03	32	21	11	34.4	1.01E-02
Chlorpyrifos	2.7E-04	4.7E-04	4.0E-03	1.1E-03	1.0E-03	25	7	18	72.0	2.53E-03
Malathion						7	7	0	0.0	
Endosulfan	3.0E-04	1.3E-03	2.8E-02	5.7E-03	7.5E-03	32	5	27	84.4	1.95E-02

S-332	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	1.4E-02	3.3E-02	7.5E-02	3.6E-02	1.6E-02	32	2	30	93.8	6.22E-02
Metolachlor	ND	ND	ND			32	32	0	0.0	
Chlorpyrifos						0				
Malathion	ND	ND	ND			32	32	0	0.0	
Endosulfan	3.5E-03	ND	4.0E-03	3.8E-03	3.5E-04	32	30	2	6.3	

Site A	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	9.0E-03	2.6E-02	1.6E-01	5.3E-02	5.0E-02	12	0	12	100.0	1.51E-01
Metolachlor	6.7E-03	3.4E-03	3.1E-02	2.1E-02	8.7E-03	12	6	6	50.0	2.96E-02
Chlorpyrifos	2.0E-04	5.5E-04	6.8E-03	1.9E-03	2.4E-03	12	4	8	66.7	6.08E-03
Malathion						0				
Endosulfan	8.4E-05	8.4E-04	8.9E-03	2.4E-03	2.7E-03	12	2	10	83.3	7.61E-03

Site E1	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	5.3E-03	1.2E-02	2.4E-02	1.4E-02	5.3E-03	21	3	18	85.7	2.12E-02
Metolachlor	6.8E-03	ND	8.8E-03	7.4E-03	7.3E-04	21	15	6	28.6	7.39E-03
Chlorpyrifos	1.9E-04	7.8E-04	8.2E-03	1.6E-03	2.0E-03	21	5	16	76.2	3.07E-03
Malathion						0				
Endosulfan	2.6E-04	1.9E-03	2.1E-02	5.1E-03	6.1E-03	21	0	21	100.0	1.65E-02

Table 5.1.9 (continued)

Site E2	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	8.3E-03	1.1E-02	2.1E-02	1.3E-02	4.3E-03	18	4	14	77.8	2.01E-02
Metolachlor	6.2E-03	ND	8.3E-03	6.9E-03	9.4E-04	18	14	4	22.2	6.94E-03
Chlorpyrifos	2.8E-04	5.2E-04	9.1E-03	1.5E-03	2.4E-03	18	6	12	66.7	2.66E-03
Malathion						0				
Endosulfan	6.5E-04	1.1E-03	1.4E-02	4.3E-03	4.9E-03	18	2	16	88.9	1.23E-02

Site W1	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	4.1E-03	1.5E-02	3.1E-01	4.2E-02	7.8E-02	24	0	24	100.0	1.68E-01
Metolachlor	5.9E-03	ND	9.5E-03	8.3E-03	1.2E-03	24	17	7	29.2	9.11E-03
Chlorpyrifos	2.5E-04	4.1E-04	6.4E-03	1.2E-03	1.5E-03	24	7	17	70.8	2.48E-03
Malathion						0				
Endosulfan	4.9E-04	1.9E-03	1.8E-02	5.2E-03	5.6E-03	24	0	24	100.0	1.51E-02

Site W2	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	3.2E-03	1.2E-02	4.5E-02	1.4E-02	1.2E-02	21	0	21	100.0	3.90E-02
Metolachlor	7.3E-03	ND	8.3E-03	7.9E-03	4.4E-04	21	17	4	19.0	8.10E-03
Chlorpyrifos	2.3E-04	6.3E-04	1.0E-02	1.4E-03	2.3E-03	21	3	18	85.7	2.12E-03
Malathion						0				
Endosulfan	8.5E-04	3.4E-03	1.1E-02	4.4E-03	3.0E-03	21	0	21	100.0	1.02E-02

Table 5.1.10. Summary of annual (1999 or 2000) monitoring data for measured concentrations in C-111 freshwater sites

FW-1999	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	3.2E-03	2.7E-02	3.4E-01	4.6E-02	5.8E-02	185	14	171	92.4	7.38E-02
Metolachlor	4.2E-03	ND	6.2E-02	1.4E-02	1.0E-02	185	133	52	28.1	1.41E-02
Chlorpyrifos	1.2E-04	ND	2.3E-02	3.6E-03	5.2E-03	89	46	43	48.3	6.31E-03
Malathion	3.2E-03	ND	8.4E-02	3.4E-02	4.0E-02	109	104	5	4.6	
Endosulfan	8.4E-05	ND	2.0E-01	1.5E-02	3.9E-02	173	96	77	44.5	6.17E-03

FW-2000	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	3.3E-03	1.3E-02	2.0E-01	2.4E-02	2.9E-02	106	0	106	100.0	6.25E-02
Metolachlor	4.3E-03	ND	1.7E-02	8.4E-03	3.2E-03	106	79	27	25.5	8.40E-03
Chlorpyrifos	1.9E-04	5.8E-04	1.1E-02	1.0E-03	1.4E-03	91	14	77	84.6	1.47E-03
Malathion	2.6E-02	ND	2.6E-02	2.6E-02		27	26	1	3.7	
Endosulfan	4.9E-04	4.2E-03	1.3E+00	3.8E-02	1.5E-01	93	9	84	90.3	4.80E-02

Table 5.1.11. Summary of monitoring data for estuarine sites (1999 and 2000)

Card Sound	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	2.1E-03	2.3E-03	7.9E-02	1.1E-02	2.4E-02	17	7	10	58.8	2.00E-02
Metolachlor	ND	ND	ND			17	17	0	0.0	
Chlorpyrifos	8.0E-05	1.2E-03	3.5E-03	1.4E-03	9.5E-04	17	3	14	82.4	2.63E-03
Malathion						0				
Endosulfan	3.7E-04	4.2E-04	4.9E-03	1.4E-03	1.4E-03	17	7	10	58.8	3.26E-03

Hwy Creek	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	1.7E-03	8.5E-03	3.3E-02	1.2E-02	8.1E-03	26	6	20	76.9	2.40E-02
Metolachlor	5.7E-03	ND	5.7E-03	5.7E-03		26	25	1	3.8	
Chlorpyrifos	2.5E-04	9.5E-04	3.7E-03	1.6E-03	1.0E-03	26	5	21	80.8	3.10E-03
Malathion						0				
Endosulfan	1.7E-04	8.6E-04	8.7E-03	2.1E-03	2.5E-03	26	1	25	96.2	6.56E-03

Joe Bay	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	2.7E-03	7.5E-03	1.0E-01	1.4E-02	2.2E-02	24	2	22	91.7	2.80E-02
Metolachlor	5.8E-03	ND	7.2E-03	6.5E-03	9.9E-04	24	22	2	8.3	2.91E-03
Chlorpyrifos	2.5E-04	1.3E-03	6.2E-03	1.7E-03	1.4E-03	24	1	23	95.8	3.19E-03
Malathion						0				
Endosulfan	2.1E-04	1.3E-03	1.1E-02	3.2E-03	3.7E-03	24	1	23	95.8	1.01E-02

Table 5.1.12. Summary of annual (1999 or 2000) monitoring data for measured concentrations in estuarine sites

SW-1999	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	1.7E-03	1.0E-02	3.3E-02	1.4E-02	9.7E-03	24	3	21	87.5	2.84E-02
Metolachlor	ND	ND	ND			24	24	0	0.0	
Chlorpyrifos	2.5E-04	9.4E-04	6.2E-03	1.9E-03	1.5E-03	24	5	19	79.2	3.61E-03
Malathion						0				
Endosulfan	1.8E-04	9.3E-04	3.8E-03	1.3E-03	1.1E-03	24	1	23	95.8	2.99E-03

SW-2000	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)	Mean (µg/L)	SD	# of times analyzed	# of non-detects	# of detects	% detects	90th centile (µg/L)
Atrazine	2.7E-03	7.7E-03	1.0E-01	1.2E-02	2.1E-02	26	5	21	80.8	1.19E-02
Metolachlor	5.7E-03	ND	7.2E-03	6.2E-03	8.5E-04	26	23	3	11.5	5.72E-03
Chlorpyrifos	2.5E-04	1.2E-03	3.4E-03	1.4E-03	9.1E-04	26	1	25	96.2	2.77E-03
Malathion						0				
Endosulfan	1.7E-04	1.3E-03	1.1E-02	3.9E-03	3.9E-03	26	1	25	96.2	1.00E-02

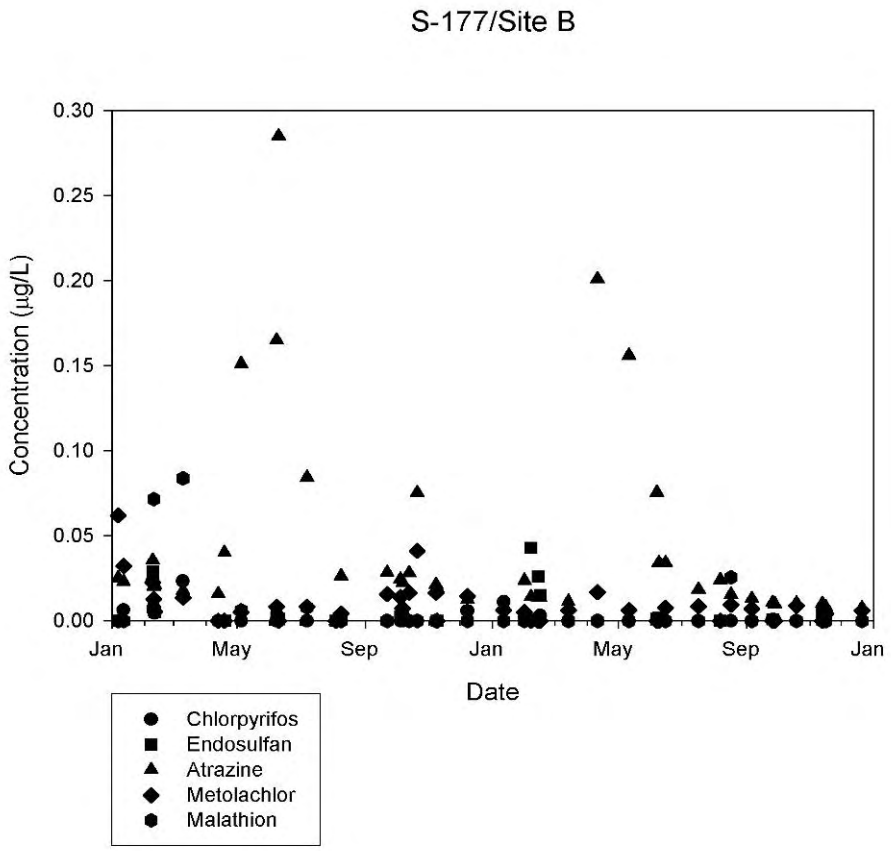


Figure 5.1.8. Measured pesticide concentrations in water at S-177/Site B from 1999 to 2000.

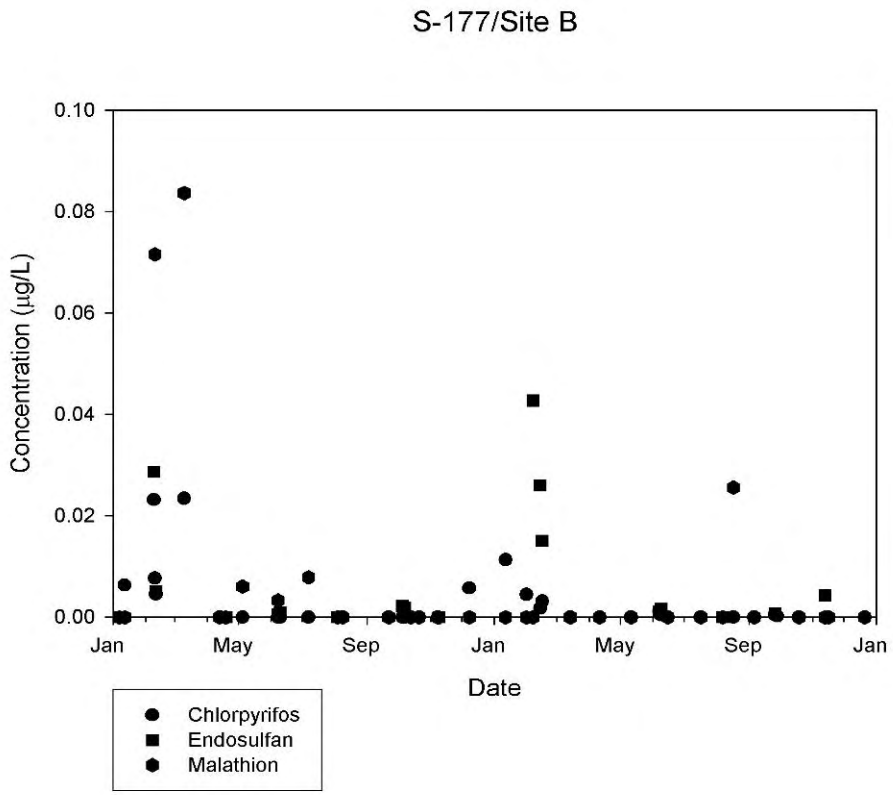


Figure 5.1.9. Measured insecticides in water at S-177/Site B from 1999 to 2000.

Table 5.1.13. Statistics for acute toxicity species sensitivity distributions

Compound	Medium	Taxa	Tenth Centile (µg/L)	Number of species below solubility	Total number of species	α	β	α SE	β SE	Root MSE
Atrazine	Freshwater	All species	30	72	82	-4.1248	1.3041	0.1126	0.0371	0.3225
Atrazine	Freshwater	Fish	1700	13	17	-8.3427	1.9096	1.2927	0.3164	0.5653
Atrazine	Freshwater	Arthropods	480	13	13	-8.7336	2.4403	0.8052	0.2224	0.4404
Atrazine	Freshwater	Plants/Algae	18	40	40	-5.2216	2.4069	0.1893	0.0836	0.3454
Atrazine	Freshwater	Amphibians	4.0	4	5	-2.6212	0.7068	0.4350	0.1299	0.3031
Chlorpyrifos	Freshwater	All species	0.20	56	57	-1.1971	1.4409	0.0403	0.0303	0.2446
Chlorpyrifos	Freshwater	Fish	2.8	19	19	-3.0119	1.8412	0.1732	0.0954	0.3278
Chlorpyrifos	Freshwater	Arthropods	0.11	37	37	-0.5750	1.6838	0.0466	0.0468	0.2663
Endosulfan	Freshwater	All species	0.37	47	59	-1.6543	1.2551	0.0794	0.0625	0.4056
Endosulfan	Freshwater	Fish	0.38	21	21	-1.0765	2.6839	0.1001	0.1479	0.3695
Endosulfan	Freshwater	Arthropods	0.45	24	25	-1.7420	1.3272	0.0781	0.0486	0.2508
Malathion	Freshwater	All species	4.1	100	102	-2.8849	1.1182	0.0548	0.0190	0.2701
Malathion	Freshwater	Fish	36	35	35	-5.0919	1.8597	0.2723	0.0953	0.4622
Malathion	Freshwater	Arthropods	0.52	43	43	-1.8817	1.1240	0.0967	0.0444	0.4060
Metolachlor	Freshwater	All species	43	20	20	-4.6918	1.5282	0.1982	0.0616	0.2656
Metolachlor	Freshwater	Fish	3200	6	6	-27.9893	7.3593	4.4333	1.1647	0.4338
Metolachlor	Freshwater	Plants/Algae	11	12	12	-3.7132	1.4547	0.3293	0.1214	0.3859
Atrazine	Saltwater	All species	19	25	28	-4.0277	1.4289	0.2532	0.0926	0.4037
Atrazine	Saltwater	Fish	1800	15	19	-9.2099	2.1517	1.1683	0.2883	0.5246
Atrazine	Saltwater	Arthropods	130	9	11	-5.3998	1.5212	0.4351	0.1308	0.2671
Atrazine	Saltwater	Plants/Algae	19	14	14	-6.2237	3.1289	0.4305	0.2113	0.3489
Chlorpyrifos	Saltwater	All species	0.11	26	28	-1.0903	1.1760	0.0863	0.0644	0.3685
Chlorpyrifos	Saltwater	Fish	0.32	13	13	-1.3026	1.8125	0.2459	0.2442	0.6211
Chlorpyrifos	Saltwater	Arthropods	0.026	8	8	0.4629	1.6770	0.1461	0.1874	0.3863
Chlorpyrifos	Saltwater	Plants/Algae	82	4	4	-12.5184	5.3930	2.7303	1.1727	0.4245
Endosulfan	Saltwater	All species	0.056	27	32	-1.0082	0.9526	0.0844	0.0612	0.3976
Endosulfan	Saltwater	Fish	0.077	9	9	0.8471	2.7368	0.1917	0.3507	0.4741
Endosulfan	Saltwater	Arthropods	0.038	13	14	-0.7865	0.9921	0.0906	0.0660	0.2951
Malathion	Saltwater	All species	2.1	29	29	-2.5958	1.2448	0.1200	0.0496	0.3281
Malathion	Saltwater	Fish	17	13	13	-5.0552	2.3349	0.3792	0.1691	0.3556
Malathion	Saltwater	Arthropods	0.76	12	12	-2.0024	1.6157	0.1699	0.1137	0.3285
Metolachlor	Saltwater	All species	17	4	4	-3.6113	1.1443	0.9988	0.3060	0.5109
Metolachlor	Saltwater	Fish	3500	7	7	-29.4459	7.7014	4.8825	1.2760	0.5037
Metolachlor	Saltwater	Plants/Algae	10	13	13	-3.7134	1.4893	0.3364	0.1268	0.4137

Table 5.1.14. Geometric means of acute toxicity values (LC/EC50 in µg/L) for representative aquatic species used in the creation of chlorpyrifos species sensitivity distributions (n= number of LC/EC50s used to calculate the geometric mean) (table structured akin to Giddings et al., 2000b)

Scientific Name	Common Name	Media Type	EC_{50} or LC_{50} (geometric mean, µg/L)	*N*	Species Category
Americamysis bahia	Opossum shrimp	SW	0.045	3	Arthropod
Ceriodaphnia dubia	Water flea	FW	0.057	4	Arthropod
Hyalella azteca	Scud	FW	0.082	3	Arthropod
Rhepoxynius abronius	Amphipod	SW	0.099	3	Arthropod
Gammarus lacustris	Scud	FW	0.11	1	Arthropod
Daphnia pulex	Water flea	FW	0.12	1	Arthropod
Paratya australiensis	Shrimp	FW	0.16	9	Arthropod
Chironomus thummi	Midge	FW	0.17	2	Arthropod
Gammarus pseudolimnaeus	Scud	FW	0.18	1	Arthropod
Ampelisca abdita	Amphipod	SW	0.25	2	Arthropod
Penaeus aztecus	Brown shrimp	SW	0.25	2	Arthropod
Gammarus fasciatus	Scud	FW	0.32	1	Arthropod
Ephemerella	Mayfly	FW	0.33	1	Arthropod
Daphnia magna	Water flea	FW	0.37	9	Arthropod
Palaemonetes pugio	Daggerblade grass shrimp	SW	0.37	1	Arthropod
Pteronarcella badia	Stonefly	FW	0.38	1	Arthropod
Claassenia sabulosa	Stonefly	FW	0.57	1	Arthropod
Morone saxatilis	Striped bass	SW	0.58	1	Fish
Leptoceridae	Longhorn caddisfly family	FW	0.77	1	Arthropod
Peltodytes	Beetle	FW	0.8	1	Arthropod
Copepoda	Copepod subclass	FW	0.94	1	Arthropod
Chironomus tentans	Midge	FW	0.97	3	Arthropod
Chaoborus americanus	Midge	FW	1.3	1	Arthropod
Cyprinus carpio	Common, mirror, colored, carp	FW	1.3	1	Fish
Menidia peninsulae	Tidewater silverside	SW	1.3	25	Fish
Neoplea striola	Pygmy backswimmer	FW	1.4	2	Arthropod
Menidia menidia	Atlantic silverside	SW	1.6	6	Fish
Leuresthes tenuis	California grunion	SW	1.8	24	Fish
Fundulus grandis	Gulf Killifish	SW	1.8	1	Fish
Procambarus acutus acutus	White river crayfish	FW	2	1	Arthropod
Laccophilus fasciatus	Beetle	FW	2.1	1	Arthropod
Penaeus duorarum	Pink shrimp	SW	2.4	1	Arthropod
Asellus aquaticus	Aquatic sowbug	FW	2.7	1	Arthropod
Esox lucius	Northern pike	FW	3.3	1	Fish
Fundulus similis	Longnose killifish	SW	3.6	2	Fish
Lepomis macrochirus	Bluegill	FW	4.2	9	Fish
Laccophilus decipiens	Beetle	FW	4.6	1	Arthropod
Fundulus heteroclitus	Mummichog	SW	4.7	1	Fish
Pungitius pungitius	Ninespine stickleback	FW	4.7	1	Fish
Penaeus vannamei	Whiteleg shrimp	SW	4.8	1	Arthropod
Atherinops affinis	Topsmelt	SW	5.0	2	Fish
Callinectes sapidus	Blue crab	SW	5.2	1	Arthropod
Chaoborus punctipennis	Phantom midge	FW	5.4	1	Arthropod
Mugil cephalus	Striped mullet	SW	5.4	1	Fish
Orconectes immunis	Crayfish	FW	6	1	Arthropod
Thermonectus basillaris	Predaceous beetle	FW	6	1	Arthropod
Menidia beryllina	Inland silverside	SW	6.5	2	Fish
Leiostomus xanthurus	Spot	SW	7	1	Fish
Tropisternus lateralis	Beetle	FW	8	1	Arthropod
Berosus styliferus	Beetle	FW	9	1	Arthropod
Leuciscus Idus	Ide	FW	10	1	Fish
Pteronarcys californicus	Stonefly	FW	10	1	Arthropod
Oncorhynchus clarki	Cutthroat trout	FW	14	4	Fish
Belostoma	Giant water bug	FW	15	1	Arthropod
Hydrophilus triangularis	Beetle	FW	20	1	Arthropod
Procambarus clarkii	Red swamp crayfish	FW	21	1	Arthropod
Oncorhynchus mykiss	Rainbow trout,donaldson trout	FW	26	9	Fish

Table 5.1.14 (continued)

Scientific Name	Common Name	Media Type	EC_{50} or LC_{50} (geometric mean, µg/L)	*N*	Species Category
Tilapia mossambica	Mozambique tilapia	FW	26	1	Fish
Simulium vittatum	Blackfly	FW	27	1	Arthropod
Heptageniidae	Mayfly family	FW	29	1	Arthropod
Lepomis cyanellus	Green sunfish	FW	29	2	Fish
Notonecta undulata	Backswimmer	FW	35	1	Arthropod
Notemigonus crysoleucas	Golden shiner	FW	40	2	Fish
Hygrotus	Beetle	FW	40	1	Arthropod
Tinca tinca	Tench	FW	45	1	Fish
Hydrophilus	Black beetle	FW	100	1	Arthropod
Cyprinodon variegatus	Sheepshead minnow	SW	140	1	Fish
Isochrysis galbana	Haptophyte	SW	140	2	Algae/Plant
Salvelinus namaycush	Lake trout, siscowet	FW	150	6	Fish
Thalassiosira pseudonana	Diatom	SW	150	1	Algae/Plant
Tilapia nilotica	Nile tilapia	FW	150	1	Fish
Pimephales promelas	Fathead minnow	FW	160	3	Fish
Opsanus beta	Gulf toadfish	SW	190	2	Fish
Poecilia reticulata	Guppy	FW	220	1	Fish
Bellerochea polymorpha	Diatom	SW	240	1	Algae/Plant
Gambusia affinis	Western mosquitofish	FW	320	13	Fish
Oziotelphusa senex senex	Crab	FW	320	4	Arthropod
Skeletonema costatum	Diatom	SW	390	8	Algae/Plant
Tilapia aurea	Tilapia	FW	420	1	Fish
Crassostrea virginica	American or virginia oyster	SW	440	5	Mollusc
Ictalurus punctatus	Channel catfish	FW	520	4	Fish
Anguilla anguilla	Common eel	FW	540	1	Fish
Brachionus plicatilis	Rotifer	SW	2600	4	Other invert
Brachionus calyciflorus	Rotifer	FW	3700	3	Other invert
Mytilus galloprovincialis	Mediterranean mussel	SW	23000	1	Mollusc

Table 5.1.15. Geometric means of acute toxicity values (LC/EC50 in μg/L) for representative aquatic species used in the creation of endosulfan species sensitivity distributions (n= number of LC/EC50s used to calculate the geometric mean) (table structured akin to Giddings et al., 2000b)

Scientific Name	Common Name	Media Type	EC50 or LC50 (geometric mean, μg/L)	*N*	Species Category
Penaeus duorarum	Northern pink shrimp	SW	0.04	1	Arthropod
Leiostomus xanthurus	Spot	SW	0.09	1	Fish
Carassius auratus	Goldfish	FW	0.1	1	Fish
Morone saxatilis	Striped bass	SW	0.1	1	Fish
Acartia tonsa	Calanoid copepod	SW	0.14	6	Arthropod
Paratelphusa jacquemontii	Crab	FW	0.16	1	Arthropod
Crangon septemspinosa	Bay shrimp, Sand shrimp	SW	0.2	1	Arthropod
Penaeus aztecus	Brown shrimp	SW	0.24	1	Arthropod
Morone saxatilis	Striped bass	FW	0.30	5	Fish
Daphnia longispina	Water flea	FW	0.3	1	Arthropod
Lagodon rhomboides	Pinfish	SW	0.3	1	Fish
Mugil cephalus	Striped mullet	SW	0.35	2	Fish
Atalophlebia australis	Mayfly	FW	0.6	2	Arthropod
Mugil curema	White mullet	SW	0.6	1	Fish
Cheumatopsyche	Caddisfly	FW	0.70	6	Arthropod
Palaemonetes pugio	Daggerblade grass shrimp	SW	0.82	3	Arthropod
Oncorhynchus mykiss	Rainbow trout,donaldson trout	FW	0.87	44	Fish
Jappa kutera	Mayfly nymph	FW	0.98	2	Arthropod
Americamysis bahia	Opossum shrimp	SW	0.98	21	Arthropod
Cymatogaster aggregata	Shiner perch	SW	1.1	2	Fish
Misgurnus anguillicaudatus	Oriental weatherfish	FW	1.2	1	Fish
Pimephales promelas	Fathead minnow	FW	1.3	31	Fish
Atherinops affinis	Topsmelt	SW	1.3	1	Fish
Cyprinodon variegatus	Sheepshead minnow	SW	1.4	18	Fish
Ictalurus punctatus	Channel catfish	FW	1.5	1	Fish
Menidia beryllina	Inland silverside	SW	1.5	1	Fish
Danio rerio	Zebra danio	FW	1.6	1	Fish
Rana tigrina	Tiger frog, indian bullfrog	FW	1.8	1	Amphibian
Salmo trutta	Brown trout	FW	1.8	1	Fish
Pteronarcys californicus	Stonefly	FW	2.3	1	Arthropod
Bidyanus bidyanus	Silver perch	FW	2.3	2	Fish
Cyprinus carpio	Common, mirror, colored, carp	FW	2.5	4	Fish
Tilapia aurea	Tilapia	FW	2.6	8	Fish
Salvelinus fontinalis	Brook trout	FW	2.6	1	Fish
Tilapia mossambica	Mozambique tilapia	FW	2.7	3	Fish
Catostomus commersoni	White sucker	FW	3.2	2	Fish
Macrognathus aculeatus	Spiny eel	FW	3.5	1	Fish
Lepomis macrochirus	Bluegill	FW	3.6	9	Fish
Macrobrachium rosenbergii	Giant river prawn	FW	4.9	2	Arthropod
Gammarus lacustris	Scud	FW	5.8	1	Arthropod
Tilapia	Tilapia	FW	5.9	1	Fish
Gammarus fasciatus	Scud	FW	6	1	Arthropod
Palaemon macrodactylus	Korean or Oriental shrimp	SW	7.6	2	Arthropod
Caridina weberi	Pugnose caridina	FW	7.8	4	Arthropod
Clarias batrachus	Walking catfish	FW	9.2	2	Fish
Asellus aquaticus	Aquatic sowbug	FW	10	1	Arthropod
Crangon crangon	Common shrimp, sand shrimp	SW	10	1	Arthropod
Eretes sticticus	Beetle	FW	10	1	Arthropod
Gambusia affinis	Western mosquitofish	FW	11	3	Fish
Cancer magister	Dungeness or edible crab	SW	15	1	Arthropod
Enallagma	Damselfly	FW	18	1	Arthropod
Poecilia reticulata	Guppy	FW	18	2	Fish
Callinectes sapidus	Blue crab	SW	19	1	Arthropod
Procambarus clarkii	Red swamp crayfish	FW	24	1	Arthropod
Anguilla anguilla	Common eel	FW	34	6	Fish
Spicodiaptomus chilospinus	Calanoid copepod	FW	40	1	Arthropod
Chironomus plumosus	Midge	FW	53	1	Arthropod
Crassostrea gigas	Pacific oyster	SW	55	1	Mollusc
Crassostrea virginica	American or virginia oyster	SW	81	8	Mollusc

Table 5.1.15 (continued)

Scientific Name	Common Name	Media Type	EC50 or LC50 (geometric mean, μg/L)	*N*	Species Category
Ischnura	Damselfly	FW	88	2	Arthropod
Bufo melanostictus	Common indian toad	FW	120	1	Amphibian
Daphnia carinata	Water flea	FW	180	1	Arthropod
Eucalanus	Calanoid copepod	SW	180	1	Arthropod
Scylla serrata	Crab	SW	180	1	Arthropod
Nereis arenaceodentata	Polychaete worm	SW	200	4	Other invertebrate
Mytilus edulis	Common bay mussel,blue mussel	SW	210	1	Mollusc
Moinodaphnia macleayi	Water flea	FW	220	1	Arthropod
Daphnia magna	Water flea	FW	250	23	Arthropod
Lucifer	Decapod	SW	290	1	Arthropod
Daphnia pulex	Water flea	FW	300	1	Arthropod
Potamonautes	Crab	FW	360	1	Arthropod
Sagitta	Chaetognaths	SW	420	1	Other invertebrate
Ceriodaphnia dubia	Water flea	FW	490	1	Arthropod
Cambarus	Crayfish	FW	500	1	Arthropod
Hydra viridissima	Hydra	FW	670	1	Other invertebrate
Uca pugilator	Fiddler crab	SW	790	1	Arthropod
Hydra vulgaris	Hydra	FW	810	1	Other invertebrate
Dendraster excentricus	Sand dollar	SW	820	1	Other invertebrate
Dinophilus gyrociliatus	Archiannelid	SW	1000	2	Other invertebrate
Lymnaea natalensis	Pond snail	FW	4400	1	Mollusc
Brachionus calyciflorus	Rotifer	FW	5200	1	Other invertebrate
Tubifex tubifex	Tubificid worm	FW	6000	1	Other invertebrate
Brachionus plicatilis	Rotifer	SW	6400	3	Other invertebrate
Physella acuta	european physa, bladder snail	FW	6400	1	Mollusc
Oziotelphusa senex senex	Crab	FW	7100	5	Arthropod
Semisulcospira libertina	Marsh snail	FW	7400	1	Mollusc
Cipangopaludina malleata	Mud snail	FW	8500	1	Mollusc
Bufo bufo japonicus	Toad	FW	9000	1	Amphibian
Indoplanorbis exustus	Snail	FW	21000	1	Mollusc
Melanopsis dufouri	Gastropod	FW	40000	3	Mollusc
Cerastoderma edule	Cockle	SW	>10000	1	Mollusc

Table 5.1.16. Statistics for chronic toxicity species sensitivity distributions

Compound	α	β	α-SE	β-SE	Root MSE	10th centile (μg/L)	Number of Species
Atrazine	-3.8119	1.8814	0.0929	0.0425	0.0341	7.2	28
Chlorpyrifos	0.7828	1.7088	0.1169	0.1285	0.1224	0.0180	12
Endosulfan	-1.1943	1.1221	0.1819	0.1167	0.1765	0.1227	10
Malathion	-0.8085	0.8546	0.1075	0.0570	0.1296	0.0237	15
Metolachlor	-2.6403	1.1569	0.3225	0.1288	0.1227	2.4	7

Table 5.1.17. Acute potentially affected fraction (PAF) (%) of species and multiple substance potentially affected fraction (msPAF) (%) of species exposed to the ninetieth centiles for annual pesticide concentrations (µg/L) for combined freshwater and estuarine site data from 1999

1999					
		Phytoplankton/ plants	Fish	Arthropods	90th centile (µg/L)
FW	Atrazine	0.0	0.0	0.0	7.38E-02
	Metolachlor	0.2	0.0		1.41E-02
	Chlorpyrifos		0.1	1.4	6.31E-03
	Malathion				
	Endosulfan		0.1	0.9	6.17E-03
	msPAF(CA)				
	msPAF(RA)	0.2	0.2	2.3	
SW	Atrazine	0.0	0.0	0.0	2.84E-02
	Metolachlor				
	Chlorpyrifos	0.0	0.3	2.6	3.61E-03
	Malathion				
	Endosulfan		0.2	3.6	2.99E-03
	msPAF(CA)				
	msPAF(RA)	0.0	0.6	6.1	

Table 5.1.18. Acute potentially affected fraction (PAF) (%) of species and multiple substance potentially affected fraction (msPAF) (%) of species exposed to the ninetieth centiles for annual pesticide concentrations (µg/L) for combined freshwater and estuarine site data from 2000

2000					
		Phytoplankton/ plants	Fish	Arthropods	90th centile (µg/L)
FW	Atrazine	0.0	0.0	0.0	6.25E-02
	Metolachlor	0.1	0.0		8.40E-03
	Chlorpyrifos		0.0	0.5	1.47E-03
	Malathion				
	Endosulfan		1.0	3.0	4.80E-02
	msPAF(CA)				
	msPAF(RA)	0.1	1.0	3.4	
SW	Atrazine	0.0	0.0	0.0	1.19E-02
	Metolachlor	0.1	0.0		5.72E-03
	Chlorpyrifos	0.0	0.3	2.1	2.77E-03
	Malathion				
	Endosulfan		1.0	5.9	1.00E-02
	msPAF(CA)				
	msPAF(RA)	0.1	1.2	7.9	

Table 5.1.19. Acute potentially affected fraction (PAF) (%) of species and multiple substance potentially affected fraction (msPAF) (%) of species exposed to the ninetieth centiles for site-specific pesticide concentrations (µg/L) in the C-111 system for years combined (1999 to 2000)

S-175

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (µg/L)
Atrazine	0.0	0.0	0.0	5.01E-02
Metolachlor				
Chlorpyrifos				
Malathion				
Endosulfan				
msPAF(CA)				
msPAF(RA)	0.0	0.0	0.0	

S-176

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (µg/L)
Atrazine	0.0	0.0	0.0	7.70E-02
Metolachlor				
Chlorpyrifos				
Malathion				
Endosulfan				
msPAF(CA)				
msPAF(RA)	0.0	0.0	0.0	

S-177/Site B

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (µg/L)
Atrazine	0.1	0.0	0.0	1.54E-01
Metolachlor	0.2	0.0		2.02E-02
Chlorpyrifos		0.1	1.7	8.76E-03
Malathion		0.0	2.2	2.03E-02
Endosulfan		0.6	2.3	3.01E-02
msPAF(CA)		0.1	4.0	
msPAF(RA)	0.3	0.7	6.2	

S-178/Site C

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (µg/L)
Atrazine	0.0	0.0	0.0	4.28E-02
Metolachlor	0.2	0.0		1.66E-02
Chlorpyrifos		0.1	0.9	3.37E-03
Malathion				
Endosulfan		5.2	6.7	2.10E-01
msPAF(CA)				
msPAF(RA)	0.2	5.3	7.5	

S-18C/Site E

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (µg/L)
Atrazine	0.1	0.0	0.0	2.83E-01
Metolachlor	0.1	0.0		1.01E-02
Chlorpyrifos		0.0	0.7	2.53E-03
Malathion				
Endosulfan		0.3	1.8	1.95E-02
msPAF(CA)				
msPAF(RA)	0.3	0.4	2.5	

Table 5.1.19 (continued)

S-332

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (µg/L)
Atrazine	0.0	0.0	0.0	6.22E-02
Metolachlor				
Chlorpyrifos				
Malathion				
Endosulfan				
msPAF(CA)				
msPAF(RA)	0.0	0.0	0.0	

Site A

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (µg/L)
Atrazine	0.1	0.0	0.0	1.51E-01
Metolachlor	0.1	0.0		2.96E-03
Chlorpyrifos		0.1	1.3	6.08E-03
Malathion				
Endosulfan		0.1	1.0	7.61E-03
msPAF(CA)				
msPAF(RA)	0.1	0.2	2.4	

Site E1

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (µg/L)
Atrazine	0.0	0.0	0.0	2.12E-02
Metolachlor	0.1	0.0		7.39E-03
Chlorpyrifos		0.0	0.8	3.07E-03
Malathion				
Endosulfan		0.3	1.6	1.65E-02
msPAF(CA)				
msPAF(RA)	0.1	0.3	2.4	

Site E2

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (µg/L)
Atrazine	0.0	0.0	0.0	2.01E-02
Metolachlor	0.1	0.0		6.94E-03
Chlorpyrifos		0.0	0.7	2.66E-03
Malathion				
Endosulfan		0.2	1.4	1.23E-02
msPAF(CA)				
msPAF(RA)	0.1	0.2	2.1	

Site W1

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (µg/L)
Atrazine	0.1	0.0	0.0	1.68E-01
Metolachlor	0.1	0.0		9.11E-03
Chlorpyrifos		0.0	0.7	2.48E-03
Malathion				
Endosulfan		0.3	1.5	1.51E-02
msPAF(CA)				
msPAF(RA)	0.2	0.3	2.2	

Site W2

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (µg/L)
Atrazine	0.0	0.0	0.0	3.90E-02
Metolachlor	0.1	0.0		8.10E-03
Chlorpyrifos		0.0	0.6	2.12E-03
Malathion				
Endosulfan		0.2	1.2	1.02E-02
msPAF(CA)				
msPAF(RA)	0.1	0.2	1.8	

Table 5.1.20.Acute potentially affected fraction (PAF) (%) of species and multiple substance potentially affected fraction (msPAF) (%) of species exposed to the ninetieth centiles for site-specific pesticide concentrations (μg/L) in estuarine sites for years combined (1999 to 2000)

Card Sound

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (μg/L)
Atrazine	0.0	0.0	0.0	2.00E-02
Metolachlor				
Chlorpyrifos	0.0	0.3	2.1	2.63E-03
Malathion				
Endosulfan		0.3	3.7	3.26E-03
msPAF(CA)				
msPAF(RA)	0.0	0.5	5.7	

Highway Creek

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (μg/L)
Atrazine	0.0	0.0	0.0	2.40E-02
Metolachlor				
Chlorpyrifos	0.0	0.3	2.3	3.10E-03
Malathion				
Endosulfan		0.6	5.0	6.56E-03
msPAF(CA)				
msPAF(RA)	0.0	0.9	7.2	

Joe Bay

Compound	Phytoplankton/ Plants	Fish	Arthropods	90th centile (μg/L)
Atrazine	0.0	0.0	0.0	2.80E-02
Metolachlor	0.1	0.0		2.91E-03
Chlorpyrifos	0.0	0.3	2.4	3.19E-03
Malathion				
Endosulfan		1.0	5.9	1.01E-02
msPAF(CA)				
msPAF(RA)	0.1	1.3	8.2	

Table 5.1.21. Chronic potentially affected fraction (PAF) (%) and multiple substance potentially affected fraction (msPAF) (%) of species exposed to annual median pesticide concentrations (μg/L)

		1999		2000	
		PAF (%)	Median (μg/L)	PAF (%)	Median (μg/L)
FW	Atrazine	0.1	2.70E-02	0.1	1.27E-02
	Metolachlor				
	Chlorpyrifos			0.9	5.80E-04
	Malathion				
	Endosulfan			2.1	4.15E-03
	msPAF(CA)				
	msPAF(RA)	0.1		3.0	
SW	Atrazine	0.1	1.03E-02	0.0	7.66E-03
	Metolachlor				
	Chlorpyrifos	1.2	9.40E-04	1.5	1.24E-03
	Malathion				
	Endosulfan	1.0	9.30E-04	1.2	1.33E-03
	msPAF(CA)				
	msPAF(RA)	2.3		2.7	

Table 5.1.22. Chronic PAF (%) and msPAF (%) results for species exposed to median pesticide concentrations (µg/L) in freshwater sites (1999 to 2000)

S-175	PAF (%)	Median (µg/L)
Atrazine	0.1	3.60E-02
Metolachlor		
Chlorpyrifos		
Malathion		
Endosulfan		
msPAF(CA)		
msPAF(RA)	0.1	

S-176	PAF (%)	Median (µg/L)
Atrazine	0.2	4.10E-02
Metolachlor		
Chlorpyrifos		
Malathion		
Endosulfan		
msPAF(CA)		
msPAF(RA)	0.2	

S-177/ Site B	PAF (%)	Median (µg/L)
Atrazine	0.1	2.11E-02
Metolachlor	0.6	6.29E-03
Chlorpyrifos		
Malathion		
Endosulfan	1.2	1.30E-03
msPAF(CA)		
msPAF(RA)	1.8	

S-178/Site C	PAF (%)	Median (µg/L)
Atrazine	0.1	2.45E-02
Metolachlor		
Chlorpyrifos	0.5	3.10E-04
Malathion		
Endosulfan	6.4	4.72E-02
msPAF(CA)		
msPAF(RA)	7.0	

S-18C/Site E	PAF (%)	Median (µg/L)
Atrazine	0.0	2.29E-02
Metolachlor		
Chlorpyrifos	0.7	4.70E-04
Malathion		
Endosulfan	1.2	1.33E-03
msPAF(CA)		
msPAF(RA)	2.0	

S-332	PAF (%)	Median (µg/L)
Atrazine	0.1	3.30E-02
Metolachlor		
Chlorpyrifos		
Malathion		
Endosulfan		
msPAF(CA)		
msPAF(RA)	0.1	

Site A	PAF (%)	Median (µg/L)
Atrazine	0.1	2.59E-02
Metolachlor	0.4	3.37E-03
Chlorpyrifos	3.1	5.50E-04
Malathion		
Endosulfan	1.0	8.40E-04
msPAF(CA)		
msPAF(RA)	4.5	

Site E1	PAF (%)	Median (µg/L)
Atrazine	0.1	1.16E-02
Metolachlor		
Chlorpyrifos	1.1	7.80E-04
Malathion		
Endosulfan	1.4	1.86E-03
msPAF(CA)		
msPAF(RA)	2.5	

Site E2	PAF (%)	Median (µg/L)
Atrazine	0.1	1.10E-02
Metolachlor		
Chlorpyrifos	0.8	5.20E-04
Malathion		
Endosulfan	1.1	1.08E-03
msPAF(CA)		
msPAF(RA)	1.9	

Site W1	PAF (%)	Median (µg/L)
Atrazine	0.1	1.50E-02
Metolachlor		
Chlorpyrifos	0.7	4.10E-04
Malathion		
Endosulfan	1.4	1.85E-03
msPAF(CA)		
msPAF(RA)	2.1	

Site W2	PAF (%)	Median (µg/L)
Atrazine	0.1	1.18E-02
Metolachlor		
Chlorpyrifos	0.9	6.30E-04
Malathion		
Endosulfan	1.9	3.44E-03
msPAF(CA)		
msPAF(RA)	2.8	

Table 5.1.23. Chronic PAF (%) and msPAF (%) results for species exposed to median pesticide concentrations (µg/L) in estuarine sites (1999 to 2000)

Card Sound	PAF (%)	Median (µg/L)
Atrazine	0.0	2.30E-03
Metolachlor		
Chlorpyrifos	1.5	1.19E-03
Malathion		
Endosulfan	0.7	4.20E-04
msPAF(CA)		
msPAF(RA)	2.1	

Highway Creek	PAF (%)	Median (µg/L)
Atrazine	0.0	8.51E-03
Metolachlor		
Chlorpyrifos	1.2	9.50E-04
Malathion		
Endosulfan	1.0	8.60E-04
msPAF(CA)		
msPAF(RA)	2.1	

Joe Bay	PAF (%)	Median (µg/L)
Atrazine	0.0	7.46E-03
Metolachlor		
Chlorpyrifos	1.5	1.27E-03
Malathion		
Endosulfan	1.1	1.27E-03
msPAF(CA)		
msPAF(RA)	2.7	

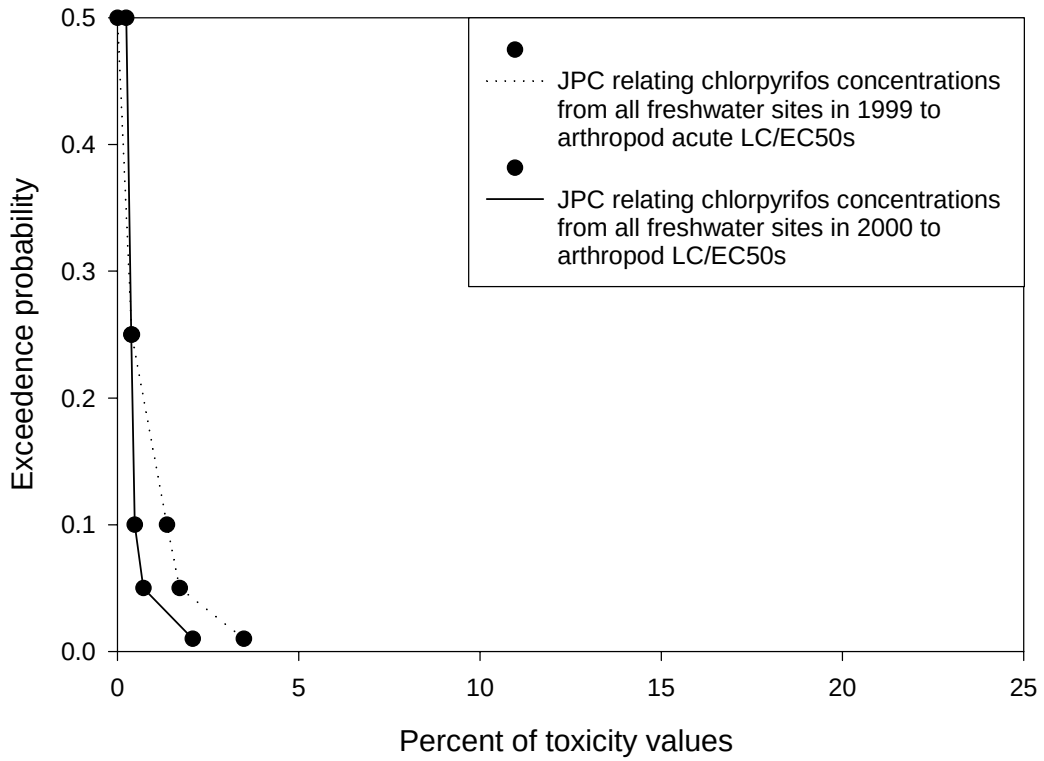


Figure 5.1.10. Joint Probability Curves relating chlorpyrifos concentrations in freshwater sites to arthropod acute toxicity data (LC/EC50s).

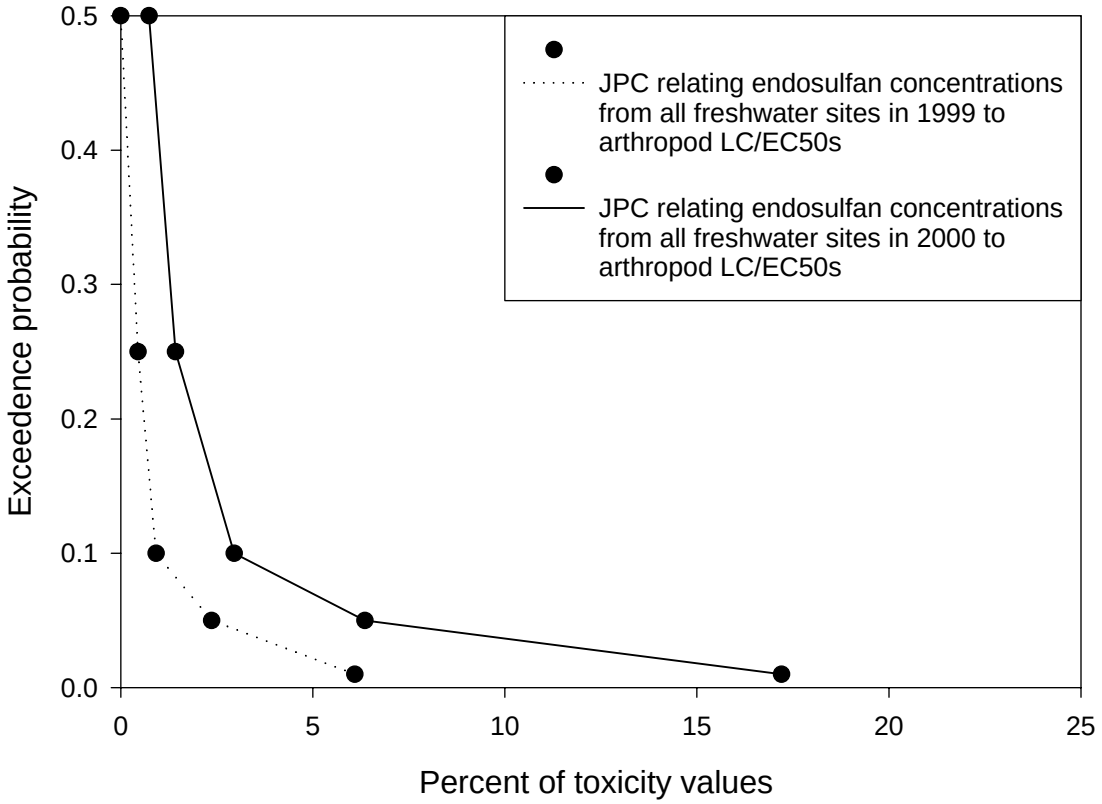


Figure 5.1.11. Joint Probability Curves relating endosulfan concentrations in freshwater sites to arthropod acute toxicity data (LC/EC50s).

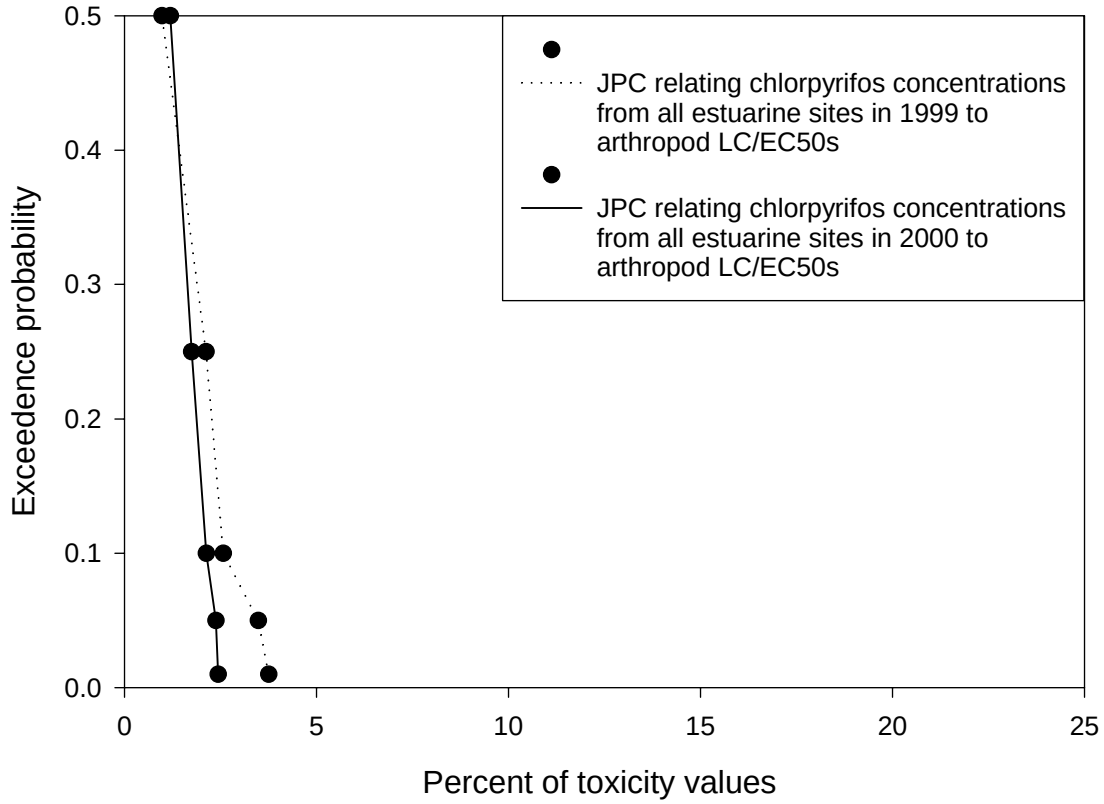


Figure 5.1.12. Joint Probability Curves relating chlorpyrifos concentrations in estuarine sites to arthropod acute toxicity data (LC/EC50s).

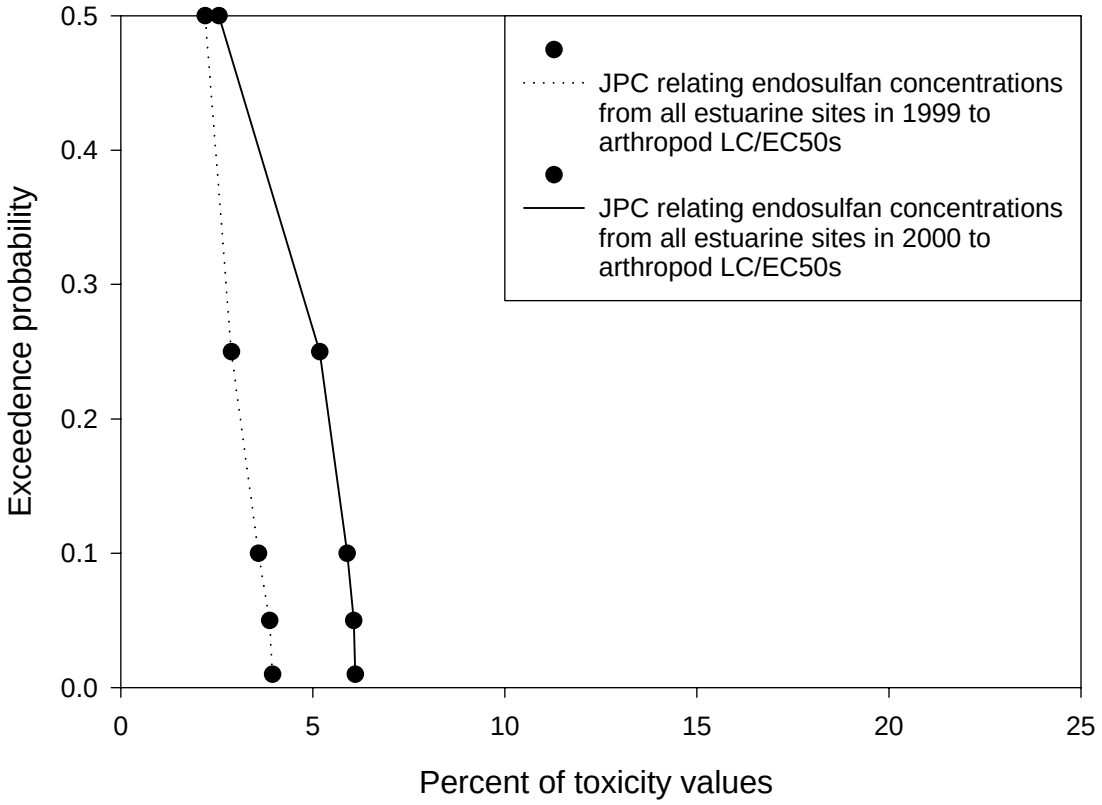


Figure 5.1.13. Joint Probability Curves relating endosulfan concentrations in estuarine sites to arthropod acute toxicity data (LC/EC50s).

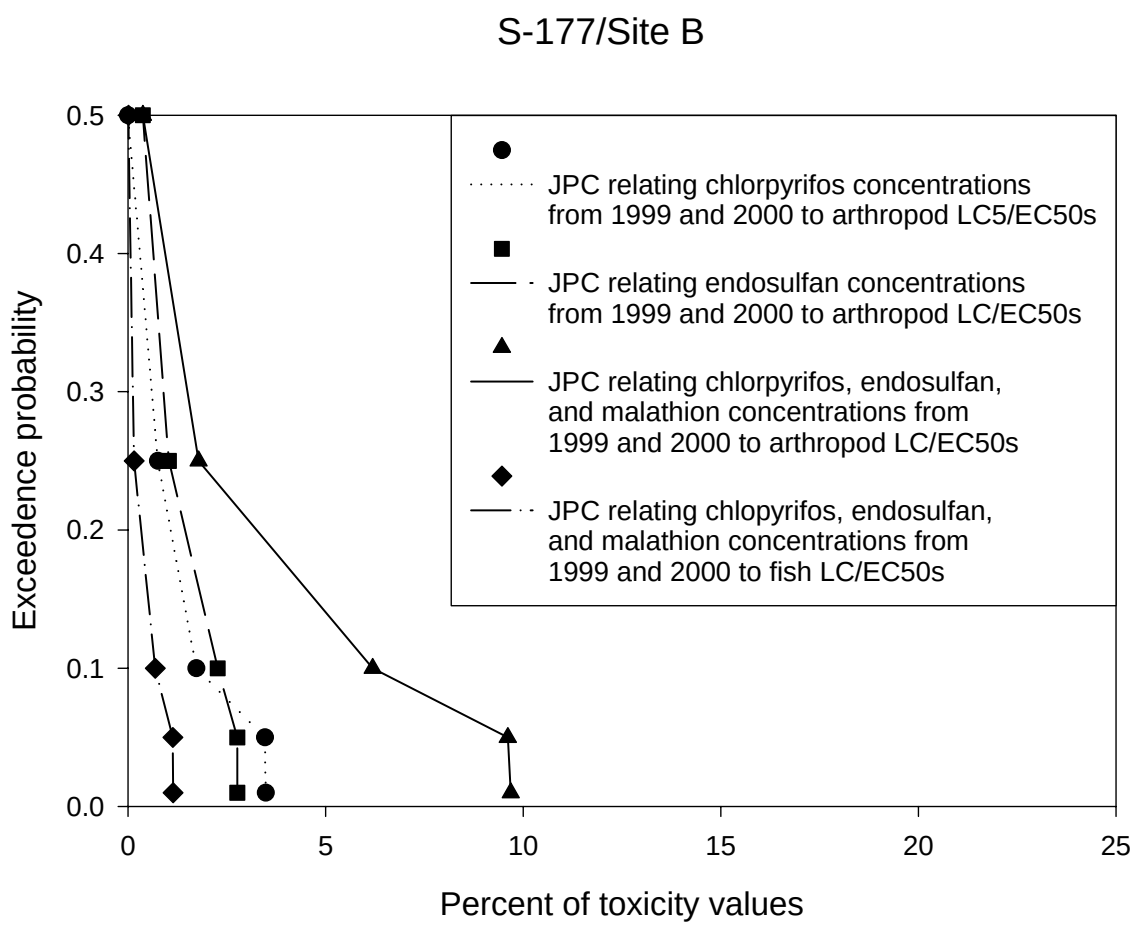


Figure 5.1.14. Joint Probability Curves relating malathion, endosulfan and chlorpyrifos concentrations in S-177/Site B to arthropod and fish acute toxicity data (LC/EC50s).

S-178/Site C

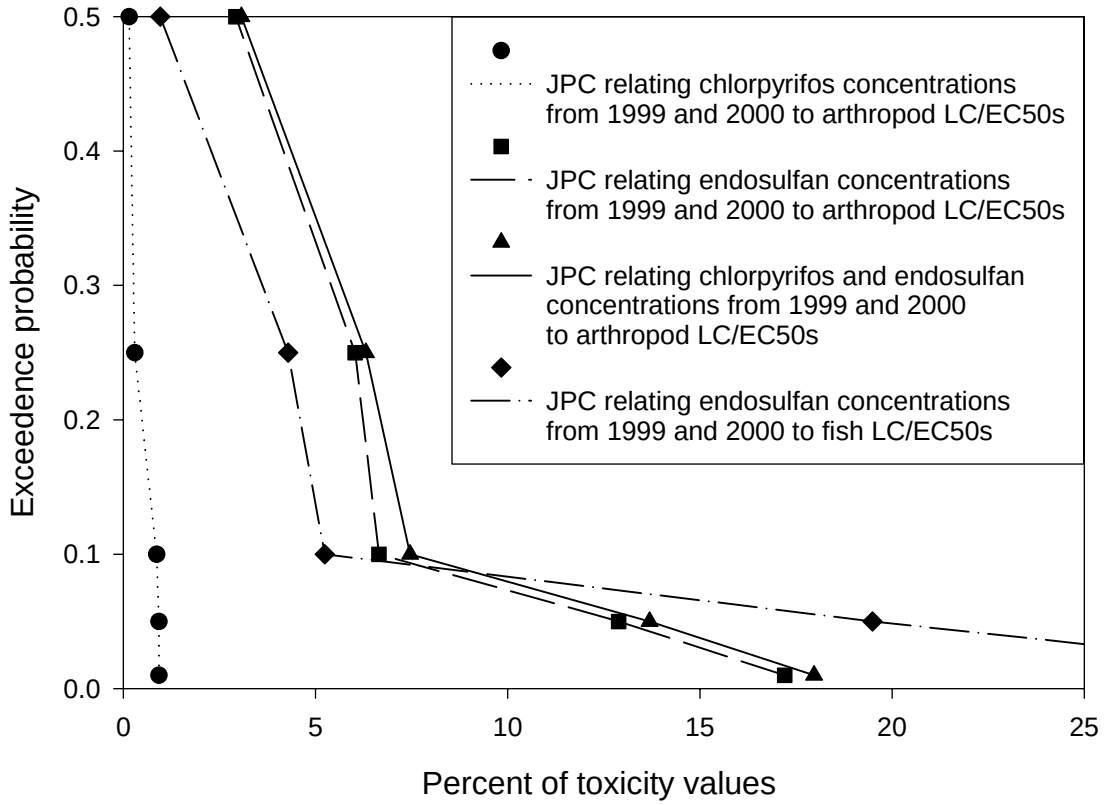


Figure 5.1.15. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-178/SiteC to arthropod and fish acute toxicity data (LC/EC50s).

S-18c/Site E

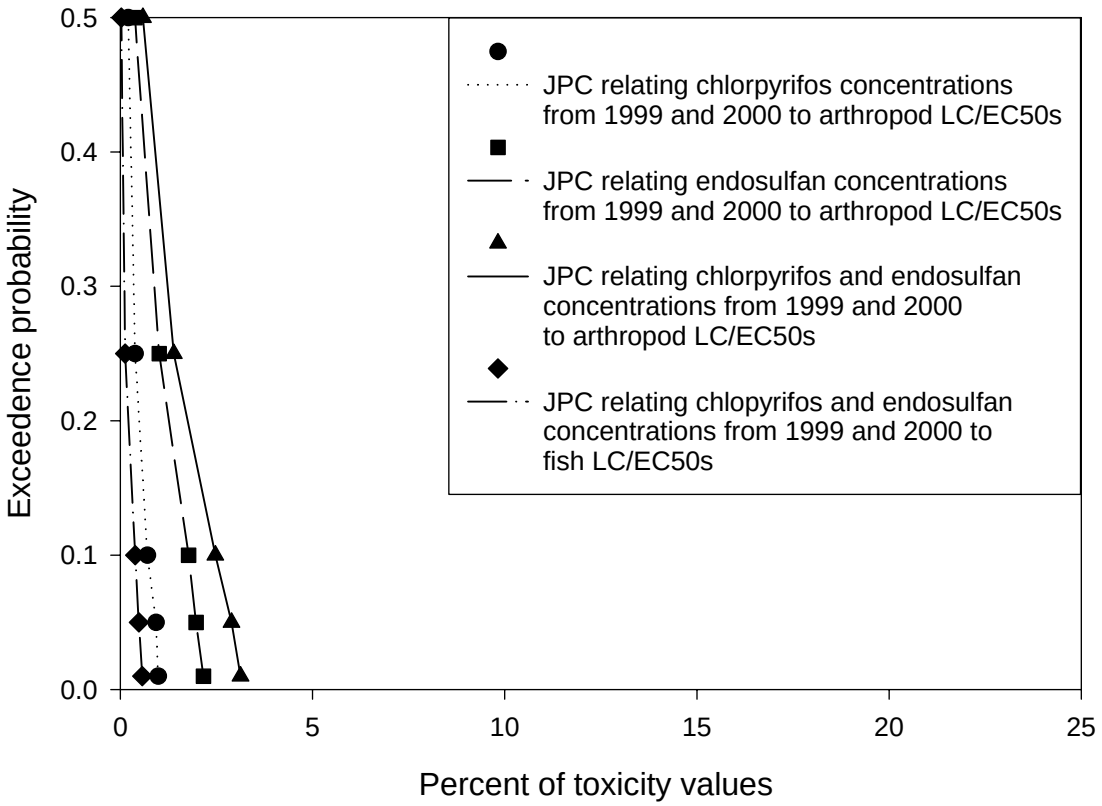


Figure 5.1.16. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-18C/Site E to arthropod and fish acute toxicity data (LC/EC50s).

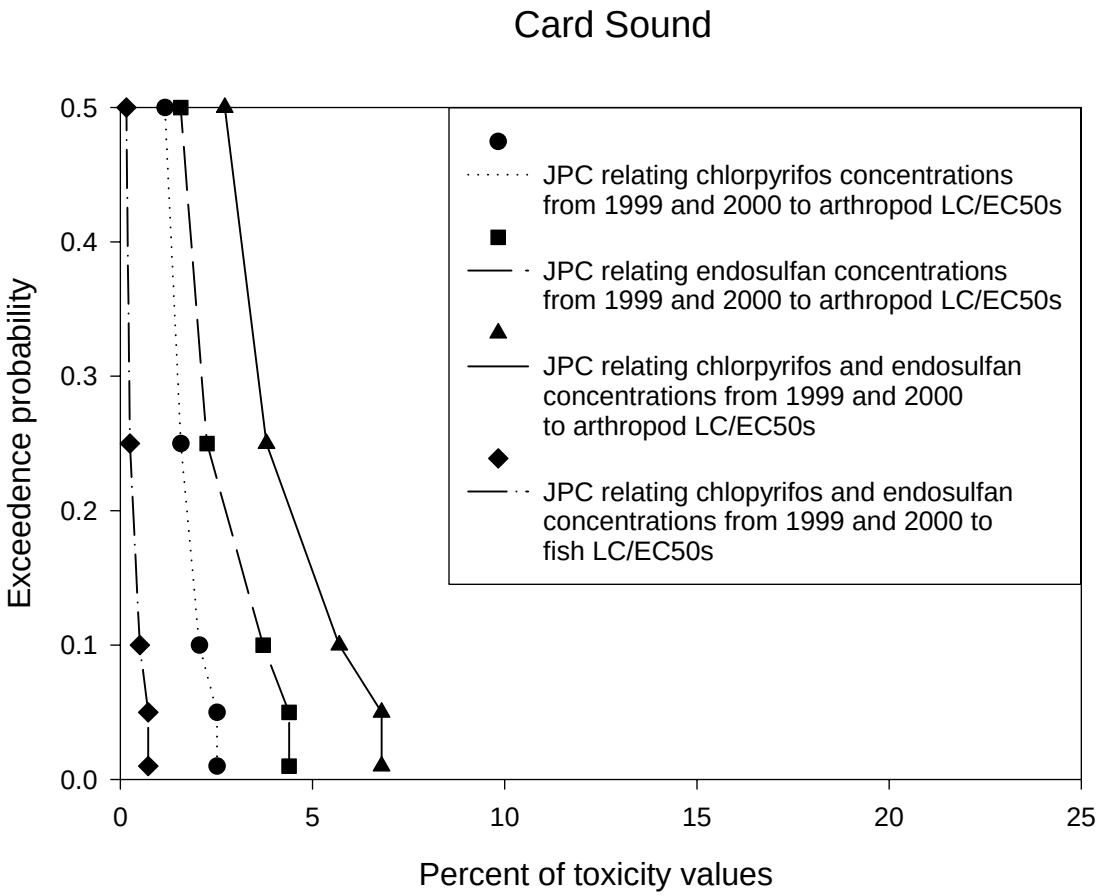


Figure 5.1.17. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Card Sound to arthropod and fish acute toxicity data (LC/EC50s).

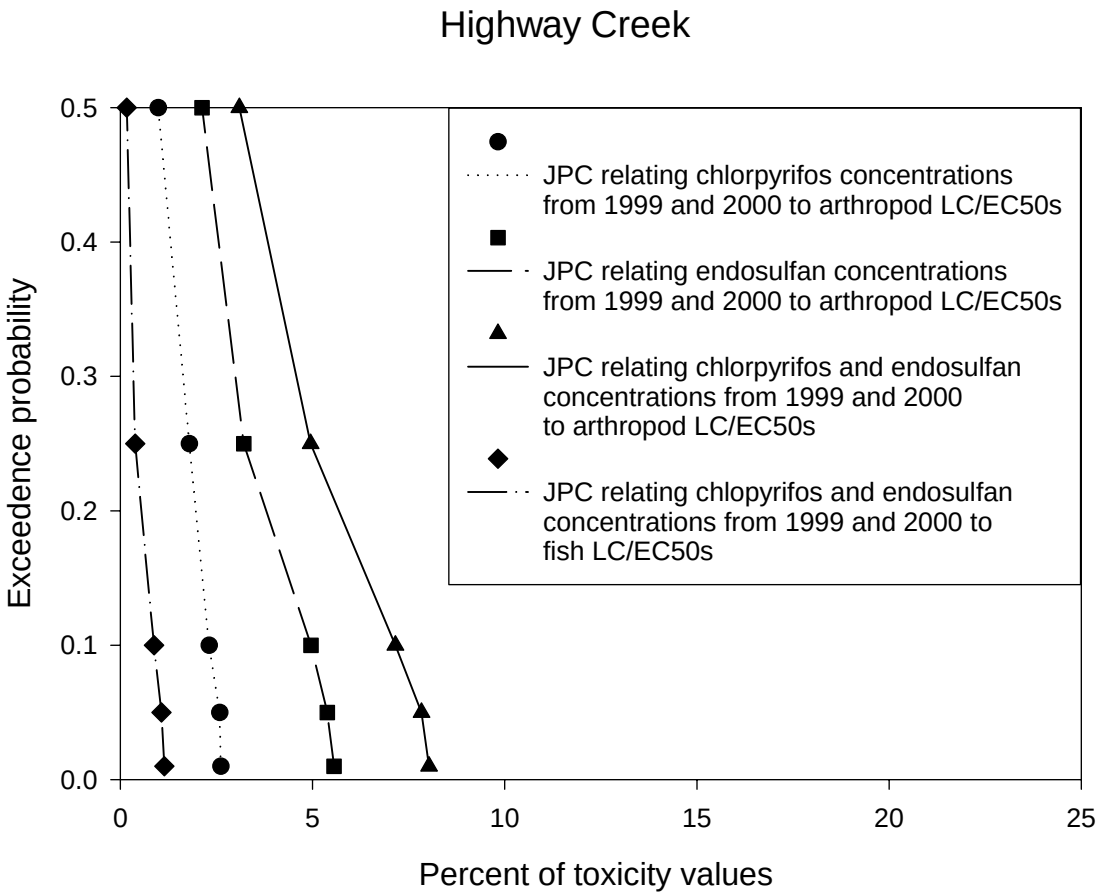


Figure 5.1.18. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Highway Creek to arthropod and fish acute toxicity data (LC/EC50s).

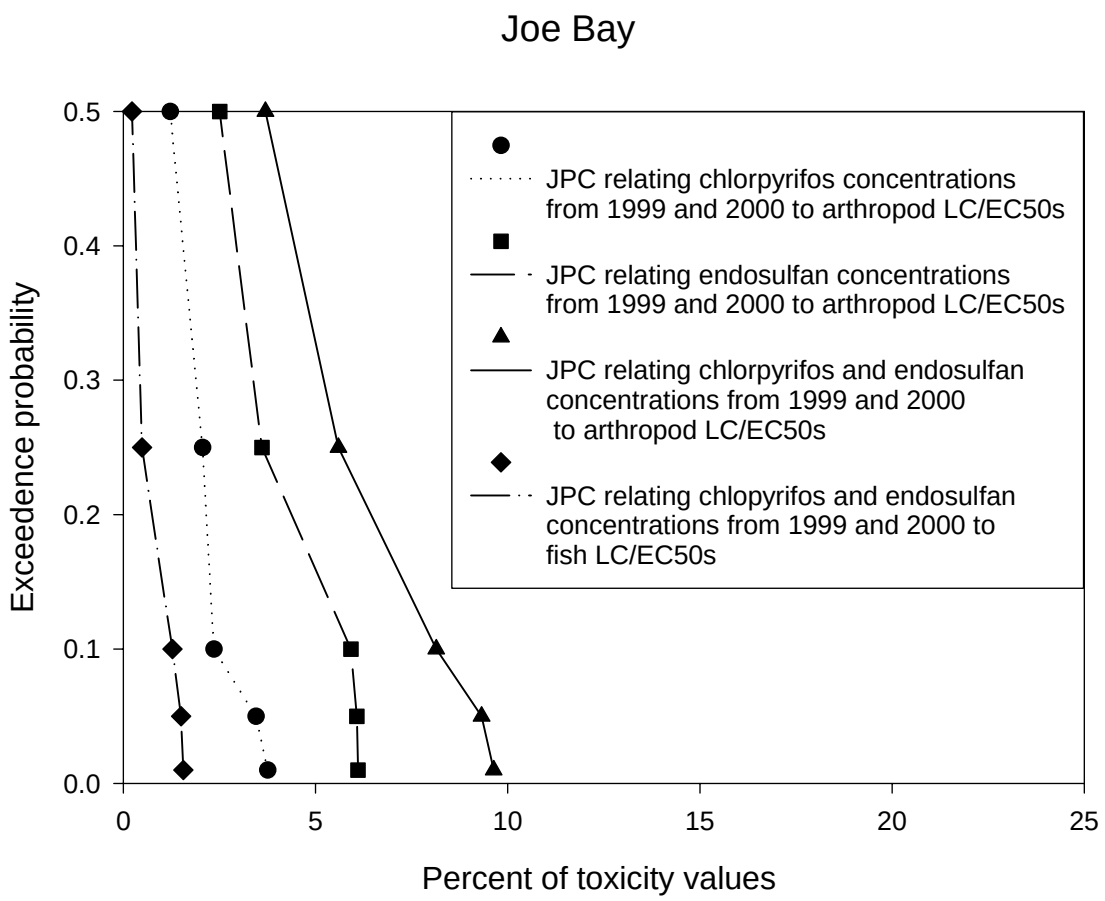


Figure 5.1.19. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Joe Bay to arthropod and fish acute toxicity data (LC/EC50s).

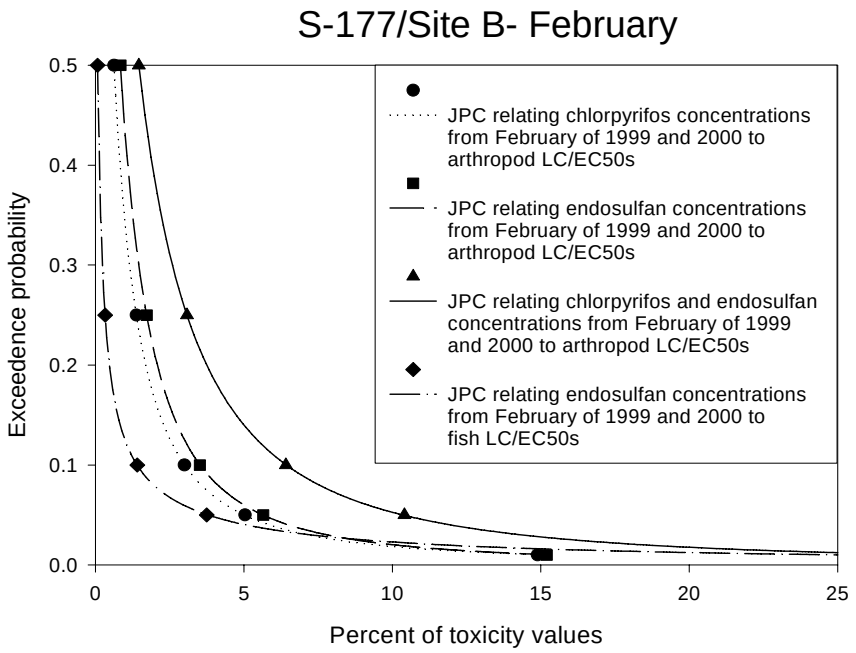


Figure 5.1.20. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-177/Site B in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

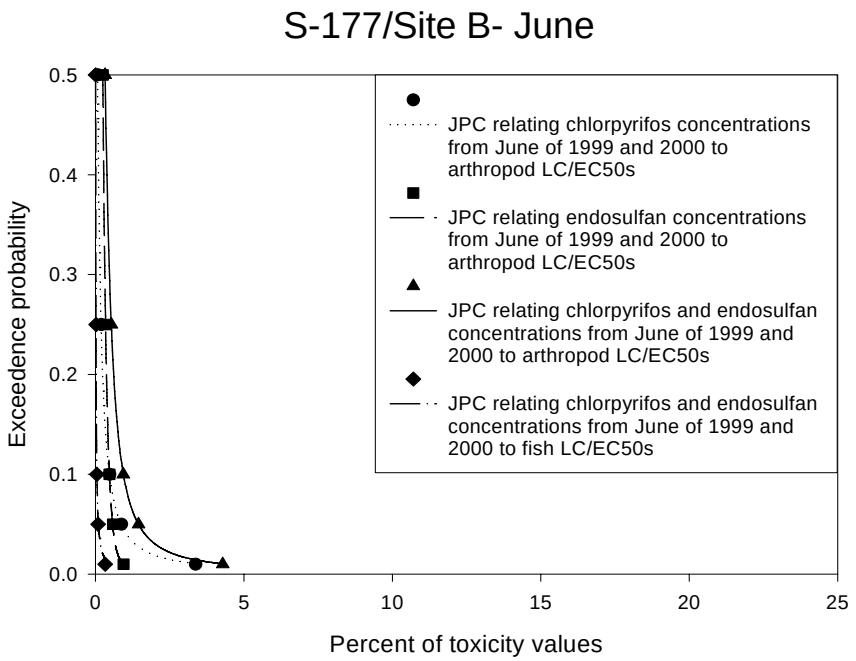


Figure 5.1.21. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-177/Site B in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

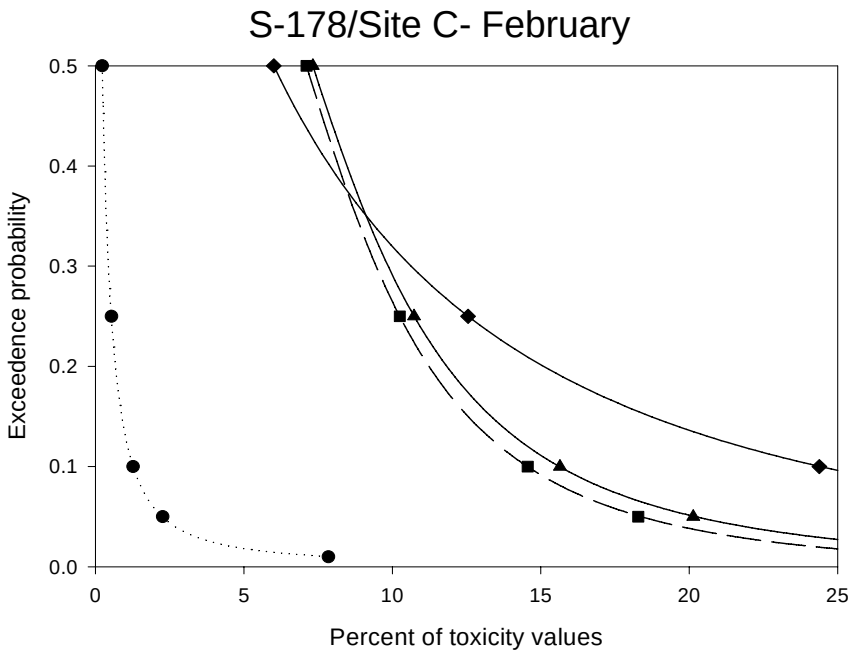


Figure 5.1.22. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-178/Site C in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

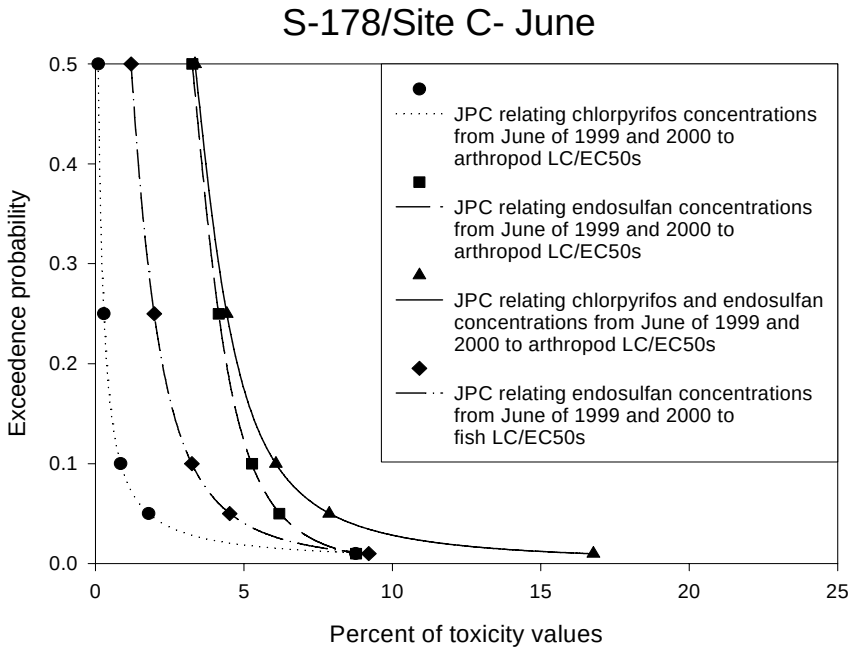


Figure 5.1.23. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-178/Site C in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

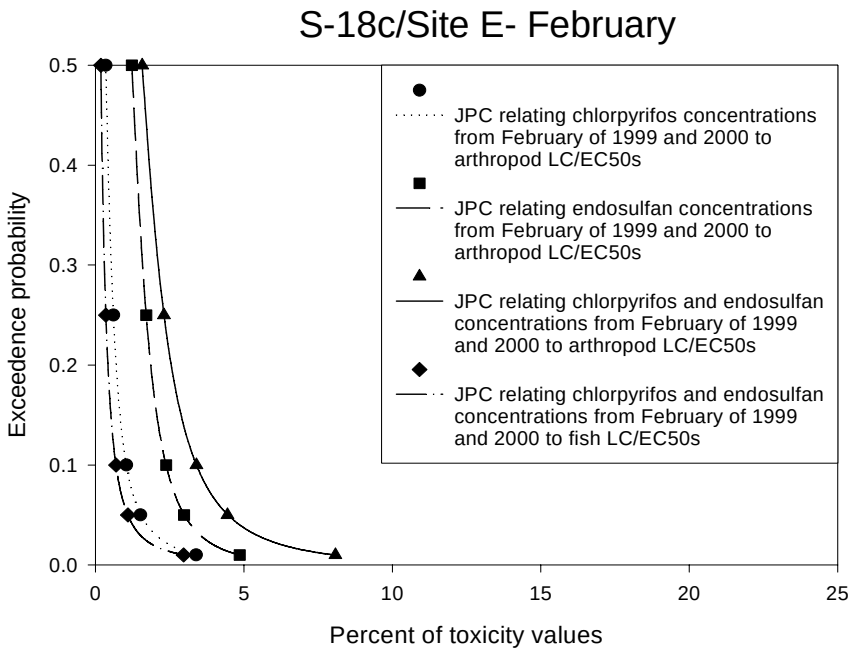


Figure 5.1.24. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-18c/Site E in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

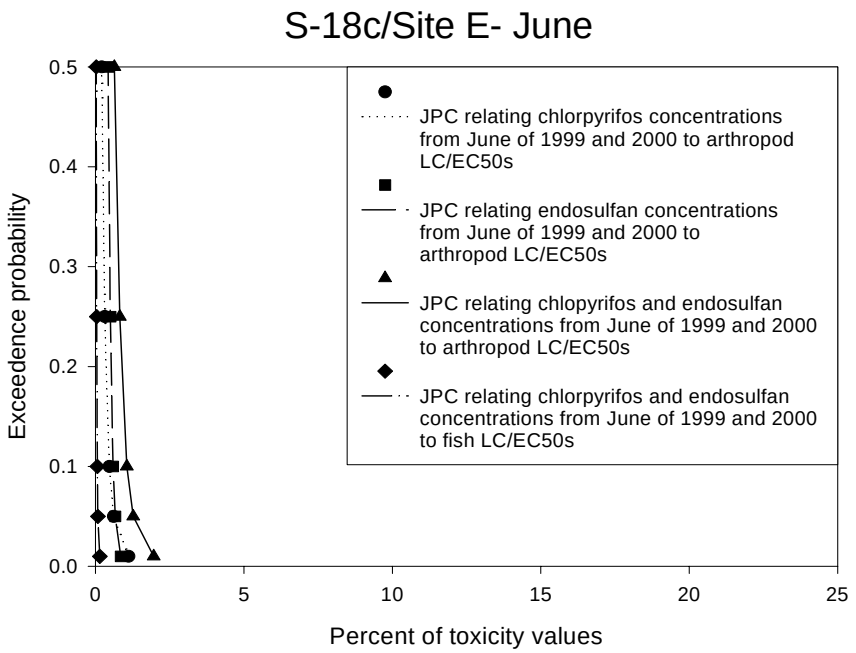


Figure 5.1.25. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-18c/Site E in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

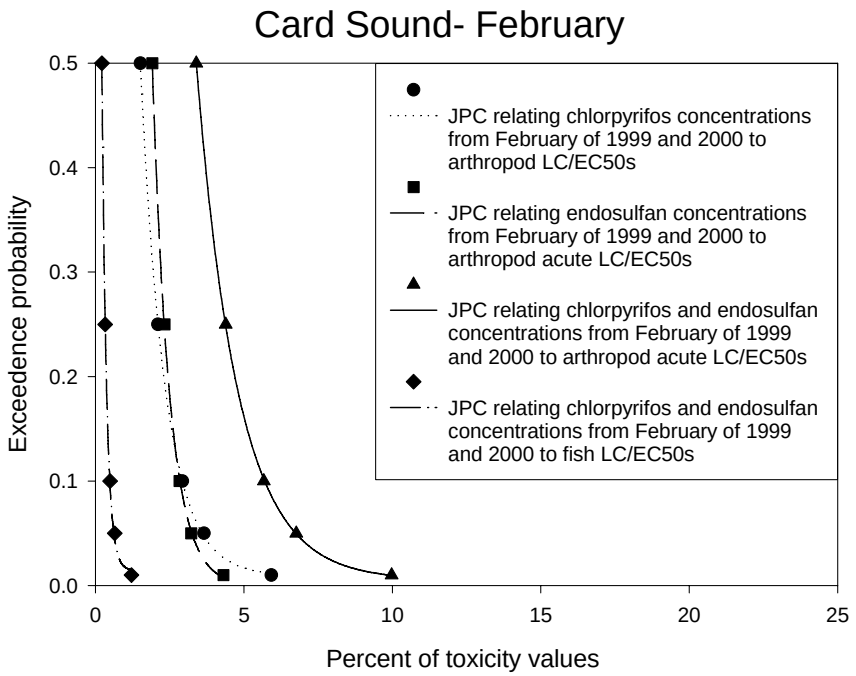


Figure 5.1.26. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Card Sound in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

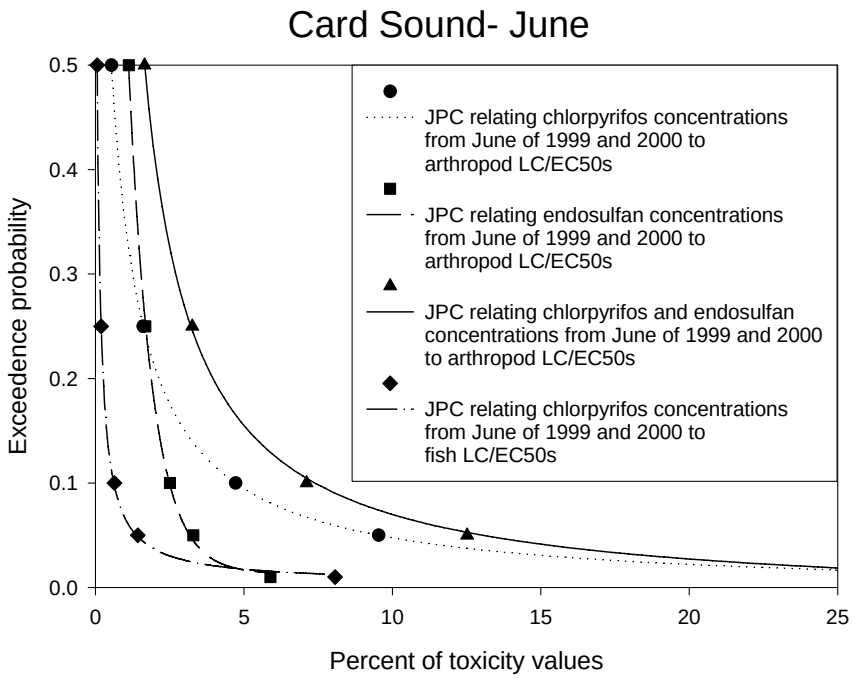


Figure 5.1.27. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Card Sound in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

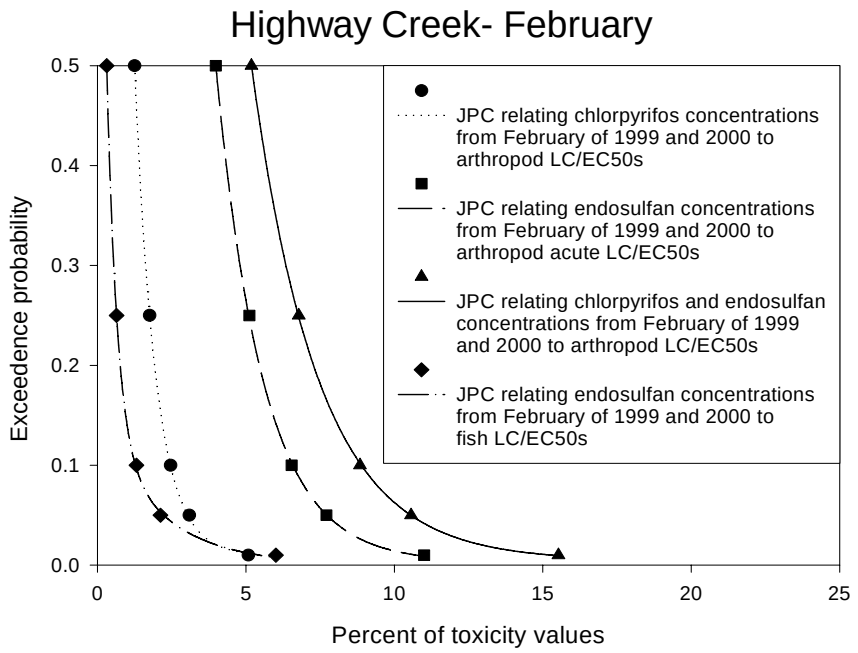


Figure 5.1.28. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Highway Creek in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

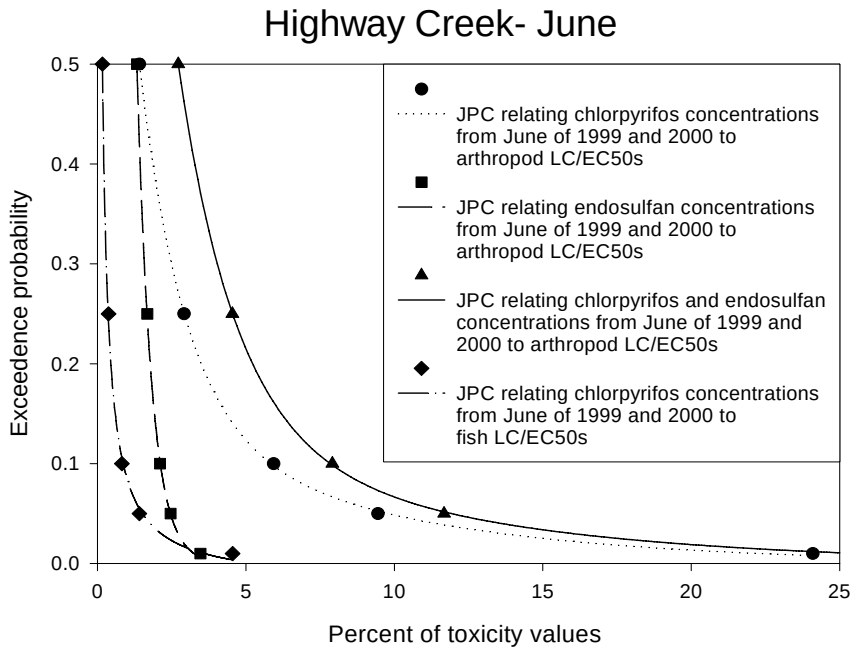


Figure 5.1.29. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Highway Creek in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

Joe Bay- February

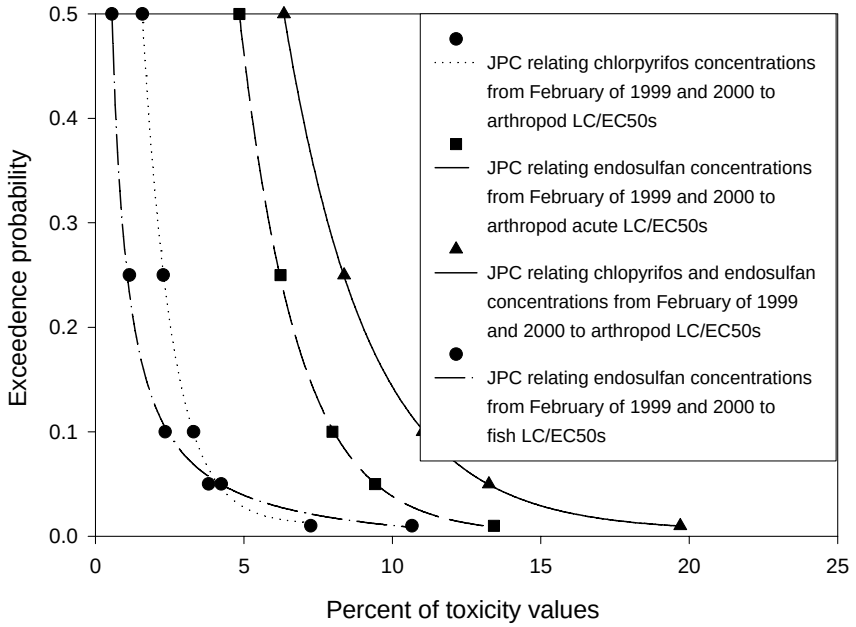


Figure 5.1.30. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Joe Bay in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

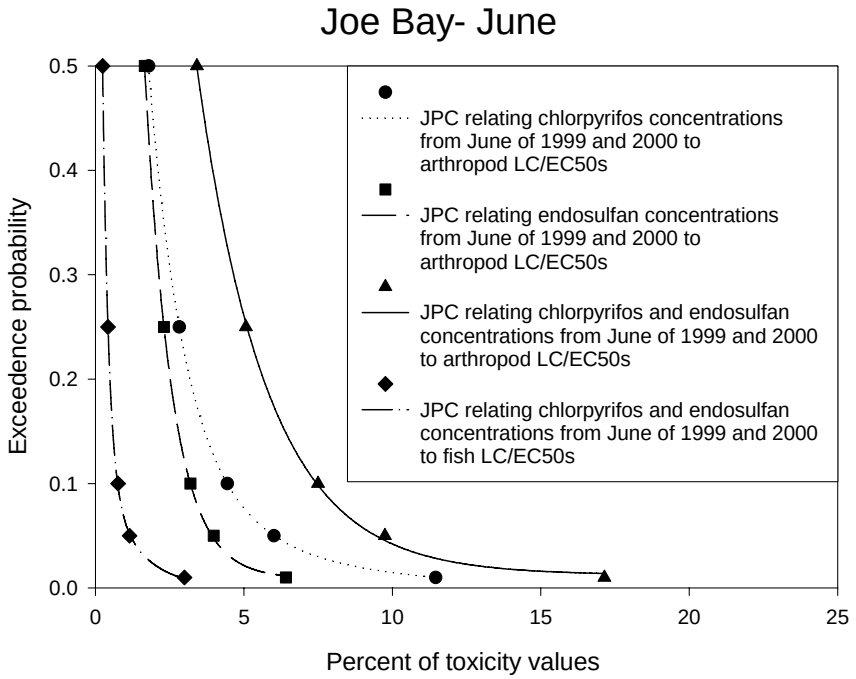


Figure 5.1.31. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Joe Bay in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

5.2. Pesticides from South Florida Canals-South Florida Water Management District Historical Data (1990-2002)

5.2.0. ABSTRACT

A two-tier ecological risk assessment was conducted for pesticides monitored in sediment at 52 sampling sites in south Florida freshwater canals from 1990-2002. For tier 1, we identified the chemicals of potential ecological concern (COPECs) as DDT, DDD, DDE, chlordane and endosulfan based on their exceedence of sediment quality standards at 28 sites. For 18 sites with data on the fraction of organic carbon in sediments, whole sediment concentrations of COPECs were converted to pore water concentrations based on equilibrium partitioning**.** In tier 2, a probabilistic risk assessment compared distributions of pore water exposure concentrations of COPECs with effects distributions of freshwater arthropod response data from laboratory toxicity tests. Arthropod effects distributions included benthic and non-benthic arthropod species for chlordane (n = 9), DDD (n = 12), DDE (n = 5), DDT (n = 48), and endosulfan (n = 26). The overlap of predicted pore water concentrations and arthropod effects distributions was used as a measure of risk. DDE was the most frequently detected COPEC in sediment at the 18 sites. Chlordane was present at only one site. The mean 90th centile concentration for pore water exposure was highest for endosulfan and lowest for DDT. The estimated acute 10th centile concentration for effects was highest for chlordane and lowest for DDD. The probability of pore water exposures of COPECs exceeding the estimated 10th centile concentrations for species sensitivity distributions of arthropod acute toxicity data was between 0 and 1 %. The estimated NOEC 10th centile concentration from

arthropod chronic toxicity distributions was exceeded by the estimated DDE 90th centile concentration for pore water distributions at three sites. Endosulfan had the highest potential chronic risk at S-178 in the C-111 canal system, based on the probability of pore water exposure concentrations exceeding the arthropod estimated chronic NOEC 10th centile at 41 %. The COPEC with the next highest probability of exceeding the chronic NOEC 10th centile was DDD at 17.7 % and 19.8 % in the Everglades Agricultural Area (at S-2 and S-6). DDT had minimal potential chronic risk based on NOEC data. Uncertainties in exposure and effects analysis and risk characterization are discussed.

5.2.1. INTRODUCTION

Sediment contamination is typically associated with the presence of persistent metals, and classes of organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organophosphate/organochlorine pesticides, chlorinated benzenes, polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) (Burton, 1992; U.S.EPA, 1997). Concentrations of one or more of these substances in sediment furthermore may pose a risk to infaunal, epibenthic or water column organisms as a result of direct exposure (i.e., to bed sediment and/or pore water), ingestion, or resuspension back into the water column. Considerable resources have been expended in the U.S. for determining sediment quality in freshwater, estuarine, and coastal areas through federal, state, and local monitoring programs (e.g., U.S. Geological Survey's (USGS) Pesticide Monitoring Network (PMN), National Oceanic and Atmospheric Administration's (NOAA) National Status and Trends Program (NS&T) for marine quality). Monitoring

programs are surveys across a wide range of spatial and temporal scales that evaluate the occurrence, geographic distribution and trends of detections for specific contaminants or contaminant classes in bed sediment. However, monitoring studies typically do not review the analytical data on contaminants to understand the potential risks associated with sediment exposures. The goal of this study was to integrate sediment monitoring data and toxicity response data to develop an assessment of ecological risk of sediment contaminants in south Florida canals.

Currently, the South Florida Water Management District (SFWMD) is responsible for managing water resources in a 1400-mile system of canals in south Florida, authorized by Congress over 50 years ago as the Central and South Florida Project (C & SF) (Perry, 2004; Rand and Gardinali, 2004). Designed for an anticipated population of two million in 2000, the system now serves over six million people in a rapidly expanding urban economy. As a flood control system that diverted most of the regional rainfall into coastal estuaries, the C & SF project was a success that permitted extensive urban development along the coast and agricultural expansion inland. However, wetland loss, altered regional hydrology, and deteriorating water quality also resulted in significant degradation of the south Florida and Everglades ecosystem. The issue of environmental impacts and water management has been addressed in a series of remedial actions since the 1960's and most recently with the Comprehensive Everglades Restoration Plan (CERP) that seeks to address both hydrology and water quality issues (Perry, 2004).

Since 1984, the SFWMD has maintained a pesticide-monitoring network for water and sediment that includes 52 sampling sites from Lake Okeechobee through the Everglades Agricultural Area (EAA) and down to Everglades National Park (ENP) (Miles and Pfeuffer,

1997). To assess violations of sediment quality criteria in south Florida canals under the jurisdiction of SFWMD, concentrations of pesticides in sediment are compared to numerical standards (Pfeuffer and Rand, 2004). When a pesticide standard (or criteria) is not available, the highest sediment concentration for the pesticide is compared to its lowest acute toxicity value. When the pesticide concentration either exceeds the standard (or criteria) or the lowest acute toxicity value it is considered a violation. The latter two methods use a comparison of point estimates or what is typically referred to as the hazard quotient (HQ) approach (Urban and Cook, 1986). The HQ can serve as an initial screening tool in the ecological risk assessment (ERA) process (ECOFRAM, 1999). It provides a risk manager with the ability to make a qualitative decision (yes or no) with regard to hazard. It does not, however, consider either the range of species that inhabit an aquatic ecosystem (and their sensitivities) or the range of exposure concentrations that are typically encountered in the aquatic environment. Regulatory decisions require quantitative information for risk decisions that define the likelihood or probability of adverse biological effects occurring to different phylogenetic groups from different environmental exposure scenarios.

In the last ten years, the scientific community has applied probabilistic risk assessment (PRA) methodology to the ERA process by comparing distributions of all available species toxicity response data (or species sensitivity distributions, SSDs) with actual environment exposure concentrations (AEC) or modeled concentrations (Hall, Jr. and Gardinali, 2004; SETAC, 1994; Solomon, 1996; Solomon et al., 2000). This approach assumes that the extent of overlap between exposure and toxicity distribution curves is proportional to the magnitude of potential risk for a contaminant or the probability that a certain percentage of species may be adversely affected. By using the range of environmental exposures and all available

species toxicity effect data, a range of species sensitivities are being considered and the potential probability that a certain percentage of the environmental exposures (e.g., in sediment, water) that exceed species acute (e.g., LC50s) and/or chronic no observable effect concentrations (i.e., NOECs) can be estimated using joint probability curves (JPCs) (ECOFRAM, 1999; Solomon et al., 2000). The PRA approach has been used in surface water with single chemicals such as atrazine (Solomon et al., 1996), Irgarol (Hall, Jr. et al., 1999; Hall, Jr. and Gardinali, 2004), chlorpyrifos (Giesy et al., 1999; Hall, Jr. and Anderson, 2003), diazinon (Giddings et al., 2000), copper and cadmium (Hall, Jr. et al., 1998), and tributyltin (Hall, Jr. et al., 2000).

The objective of this study is to conduct a probabilistic ERA to quantify the likelihood that adverse effects will occur from sediment exposures to pesticides in south Florida canals using a two–tier approach with JPCs to characterize risk. The study uses an approach that provides a screening tool to define chemicals of potential ecological concern (COPEC) in sediment assuming that organisms are directly exposed to pesticides from pore water concentrations. A COPEC is a chemical that is suspect of producing ecological harm based on initial screening of it's actual environmental concentrations (AECs) in a medium compared to screening benchmarks such as toxicological effect concentrations or quality criteria/standards (Suter et al., 2000).

5.2.2. MATERIALS AND METHODS

The sediment ecological risk assessment (ERA) consisted of the first three phases of the United States Environmental Protection Agency (U.S. EPA) ERA framework (U.S.EPA, 1998): Problem Formulation, Analysis, and Risk Characterization. In problem formulation,

we summarized COPEC characteristics (i.e., fate and transport) and assessment (i.e., what is at risk and in need of protection) and measurement endpoints (i.e., what will reveal effects on assessment endpoint). For the analysis, we characterized two major risk components; exposure and effects. Risk characterization, the final phase, provided estimates of risk probability to the ecological entity listed as an assessment endpoint.

A two-tiered ERA approach was suggested by the Aquatic Risk Assessment and Mitigation Dialogue Group (ARAMDG) (SETAC, 1994) and endorsed by the U.S. EPA (ECOFRAM, 1999) that first uses a hazard quotient (HQ) to screen for COPECs followed by probabilistic risk assessment (PRA). This two-tier ERA approach was used to prioritize hazardous pesticide COPECs in sediment of the South Florida Water Management District (SFWMD) database. SFWMD has monitored concentrations (μg/Kg) of over 70 pesticides (and degradation products) in sediment semi-annually from 1984 to the present (R. Pfeuffer, SFWMD; personal communication) at 52 sampling sites in south Florida canals (Figure5.2.1). Trace metals were also analyzed but less frequently. The potential risks of trace metals are discussed in the next SERA (Section 5.3). All chemical analyses were conducted by the Florida Department of Environmental Protection (FDEP) Central Laboratory (Tallahassee, FL) using U.S.EPA methods and quality assurance procedures. Contaminants detected included organochlorine pesticides, organonitrogen-phosphorous pesticides, organophosphate insecticides, carbamate insecticides, phenoxy acid herbicides, urea herbicides, quarternary amine herbicides, ethylene thiourea (ETU), benomyl, and glyphosphate.

In Problem Formulation for tier 1, concentrations of the pesticides at each of the 52 sites from 1990-2002 were compared to the FDEP sediment quality criteria (SQC). When no

Florida SQC was available for a pesticide, we compared pesticide concentrations to the lowest sediment quality screening benchmark (e.g., U.S. EPA, NOAA SQuiRTs, etc.) which were available from the Oak Ridge National laboratory (http://risk.lsd..ornl.gov/). SQC for pesticides are listed in the Appendix. However, for each of the endosulfan isomers (α-, β-endosulfan) measured concentrations were compared to their respective sediment criteria. For endosulfan sulfate (a major oxidation degradate of endosulfan) measured concentrations were compared to total endosulfan concentration since it is a more conservative estimate. When a screening benchmark was exceeded (≥0.5) by a pesticide concentration three or more times at a site, the contaminant was considered a COPEC. This was done to eliminate COPECs that were detected infrequently. When numerous pesticides were present at a site a Hazard Index (HI) was calculated for the site when it contained at least one COPEC (see Section 1 for HI methodology).

The hypothesis considered in the SERA is: pesticide COPECs may cause effects at the species and community levels for aquatic organisms in South Florida canals and these effects may adversely affect community structure and function. The ecological risk of each COPEC was evaluated separately.

There are four sources of uncertainty in an ERA: stochasticity (natural variation), lack of information (i.e., data gaps), human and analytical error and flawed model assumptions (Suter, 1993). The nature and degree of uncertainties in the findings was considered in light of our exposure and effects analysis and risk characterization. Methods for risk analysis and risk characterization of the PRA are discussed below.

5.2.3. Risk Analysis

Exposure.

After determining which pesticides were potential COPECs, the actual measured whole sediment concentration for each pesticide at each site from the SFWMD database was converted to predicted pore water (i.e., interstitial water) concentrations (PPW_c) for the exposure distribution (Figure 5.2.2) based on equilibrium partitioning (EqP) methodology (DiToro et al., 1991). This approach assumes that sediment-pore water exposure is the source of toxicity in sediment to organisms. Pore water exposures are extrapolated from bulk sediment concentration measurements through the use of empirically-derived K_{oc} (equilibrium partition coefficient for sediment organic carbon) values. The mass fraction of organic carbon (f_{oc}) for sediments at the sampling sites was greater than 0.2% (Table 5.2.1a) and therefore organic carbon was considered the major phase for sorption. To convert from measured whole sediment concentrations (μg/Kg) to pore water concentrations the mean of all K_{oc} values (L/Kg) available from the U.S. Dept. of Agriculture Pesticide Properties Database (http://www.arsusda.gov/acsl/ppdb.html) was first converted to K_p values (partition coefficient, L/Kg) by multiplying by the mass fraction of organic carbon (f_{oc}) in site sediments according to:

$$K_p = K_{oc} * f_{oc}$$

The fraction of organic carbon (f_{oc}) content was taken from the SFWMD database for a sediment. The mean f_{oc} was used for sampling sites with multiple f_{oc} values. Sites with no organic carbon data were excluded from the PRA.

The predicted porewater concentration (PPW_c) was then calculated for each COPEC using the EqP method and derived using the following equation:

PPW_c (μg/L) = MC_{sed}/K_p MC_{sed} is the measured concentration of COPEC

Pore water concentrations were then fit to lognormal exposure distributions when there were four or more values above the detection limit (Solomon et al., 2000). Concentrations were ranked from smallest to highest and assigned a centile ranking (j) at each site using the equation j*100/(n+1), where j is the rank assigned to a particular concentration and n is the total number of sample observations (including non-detects) at each site (Hall, Jr. and Gardinali, 2004). Centile rankings were converted to probits and plotted against the corresponding $\log_{10}$ values of the PPW_c. Linear regression was performed using the algorithms found in PRAT-1 software (Solomon et al., 2000). Samples below the detection limit were given dummy values of 0, and although not included in the regression analysis, they were assigned a rank and assumed to be distributed at the lower end of the distribution (Hall, Jr. et al., 1999; Solomon et al., 1996). α-Endosulfan, β-endosulfan and endosulfan sulfate concentrations were summed to obtain an endosulfan (total) pore water exposure distribution at each site.

The 90th centile exposure concentration was calculated from the lognormal concentration distribution for each COPEC at all sites. The 90th centile is an "exposure benchmark" used in PRA (Solomon et al., 1996). It assumes that any sample taken has a 90 % chance of being below the estimated 90th centile concentration if the values in the exposure distribution are unbiased and accurately represent the concentrations found over that time period and location (Giddings et al., 2000).

Effects.

Toxicity data (see Appendix) for the PRA includes a distribution of the range of species responses (or SSDs) to each COPEC. Most of the COPECs are insecticides that possess a

receptor mediated-mode of toxicity. This indicates that COPECs will be highly toxic to arthropods because they possess the specific receptor site for insecticidal action and are phylogenetically similar to the target insects for these insecticides. Toxicity data for snails, flat worms, and bivalves were, therefore, excluded from the distributions. All available toxicity data for freshwater arthropods were thus used in the preparation of SSDs. The SSD for endosulfan included toxicity data for exposure to technical grade material.

Acute toxicity data (i.e., LC50, EC50) for freshwater arthropods were first obtained from the AQUIRE database (http://www.epa.gov/ecotox/). Regulatory reviews such water quality criteria and registration documents were also used. Toxicity data on snails, flatworms and bivalves were excluded. Since the majority of COPECs were organochlorine insecticides that show environmental persistence, we determined that predicting the likelihood of potential risks associated with chronic exposures would be the most applicable scenario. No Observable Effect Concentrations (NOECs) were therefore also used to prepare SSDs (SETAC, 1994). Since chronic NOECs were not available for several COPECs, we used an acute-to-chronic ratio (ACR) of 20 as an application factor with the LC50 for each COPEC to obtain a chronic NOEC value. An ACR of 20 is typically used by the State of Florida to estimate chronic NOECs when chronic data are not available (Florida Administrative Code 62-302).

The distribution of NOECs for arthropods to each COPEC was evaluated using the approach described in SETAC (1994). Toxicity values were ranked by concentration, and for each species toxicity value the centile ranking was calculated by multiplying individual ranks by 100/ (n+1), where n is the total number of species. A single species with toxicity endpoints (i.e., LC50s) only appeared once in a distribution. If multiple toxicity endpoints

were available for a single species, the geometric mean of the endpoints was used to represent the toxicity for that species (ECOFRAM, 1999). These centiles were plotted against log-transformed concentration and linear regression was conducted to define each distribution. The 10th centile of the SSD for each COPEC from acute data (LC50, EC50) and chronic NOEC data are the "toxicity benchmarks" that were used since they are widely accepted and used to characterize risk (Solomon et al., 1996).

5.2.4. Risk Characterization-Tier 2

Potential risk to freshwater arthropods from chronic exposure to COPECs in porewater was determined by comparing pore water exposure distributions by sampling site with the 10th centiles from the acute LC50 and chronic NOEC data distributions for each COPEC. The percent exceedence of the 10th centile for each COPEC was used as a risk estimate (Solomon et al., 1996).

The last step in the PRA used joint probability curves (JPCs; or exceedence profiles) for each exposure at a site to rank potential risk of COPECs and sites. JPCs were constructed using PRAT-1 software (Solomon et al., 2000). They characterize the relationship between magnitude of effect and probability of occurrence for that effect (ECOFRAM, 1999).

An example of the derivation of a JPC is illustrated in Figure 5.2.3. The PPW_c and NOEC distributions are characterized by regression lines (Figure 5.2.3a) and are used to generate a joint probability function of the exceedence data (Fig. 5.2.3b). A point on the curve (Figure 5.2.3b) thus represents the likelihood that a sample from the set of pore water exposures would contain a higher COPEC concentration than the corresponding centile of species toxicity values. For example, from point A in Figure 5.2.3b the probability of pore

water concentrations exceeding the NOEC for 2% of the arthropod species values is 50%. From point D in Figure 5.2.3b the probability of pore water concentrations exceeding the NOEC for 25% of the arthropod species values is 5%.

We also used the exposure data for sites with COPECs to determine the probability of exceedence of TEC and PEC standards (Hall et al., 2003). PECs and TECs are discussed in Section 1.2. The PEC and TEC were determined through a consensus-based approach and were adopted as effects-based sediment quality assessment guidelines (SQAG) developed by the Florida Department of Environmental Protection for inland waters (MacDonald et al., 2000a, 2003).

5.2.5. RESULTS AND DISCUSSION

5.2.5.1. Problem Formulation

Tier 1. Tier 1 indicates that the organochlorine insecticides chlordane, DDD, DDE, DDT and endosulfan are COPECs since Florida sediment quality criteria were exceeded at 28 sampling sites throughout the canals within the South Florida Water Management District (Table 5.2.2). Figure 5.2.1 shows the sampling locations of the sediment quality violations for the COPECs. Compounds had multiple violations at sites from 1990 to 2002. For example, DDT and its metabolites, DDD and DDE had the most sediment quality violations**.** Chlordane, another organochlorine insecticide, had multiple violations at S-2 (near Lake Okeechobee). Endosulfan had multiple violations at S-177 and S-178 in the C-111 system. α-Endosulfan and β-endosulfan were COPECs at S-177 and S-178. Endosulfan sulfate was only a COPEC at S-178. The 28 sites with COPECs represent approximately 54 % of the total sampling sites monitored by the SFWMD for pesticides. DDT, DDE, DDD, and

chlordane were also determined to be the most frequently detected organochlorine insecticides in sediment and aquatic biota monitoring programs in freshwater systems in the 1990's (Nowell et al., 1999).

The hazard index for all sites is summarized in Figure 5.2.4 and Table 5.2.3. S-177, S-178, S-2, S-3, S-4, S-5A, S-6, S-7 S-8, and S-9 had the highest HI's of the 52 sampling sites. S-6 had the highest HI followed by S-5A and are primarily affected by sugarcane agriculture.

S-177 and S-178 are on the C-111 system and show HIs of 7.1 and 14.7, respectively. The main pesticides at S-177 responsible for the high HI were DDD, DDE, DDT and endosulfan. The main pesticides at S-178 responsible for the high HI were DDE and endosulfan. Both sites are affected by the Frog Pond Ag area. S-176 and S-18C which are also on the C-111 had low HI's.

5.2.5.2. COPEC Characteristics in the Environment.

Since Tier 1 indicated that DDT, DDE, DDD, chlordane and endosulfan were COPECs a brief summary of their environmental characteristics is discussed below.

DDT was widely used in the U.S. on a variety of crops and to control insect-borne diseases (U.S.EPA, 1980a). U.S.EPA cancelled all crop uses of DDT in 1972. DDT has a low water solubility (low ppb), is fairly volatile (high Henry's law constant), has a high log K_{ow} (~6), and strongly sorbs to soil (high log K_{oc} ~ 6). It thus biodegrades slowly in the environment with a soil half-life estimated at approximately 15 years (Agricultural Research Service, 1997). The metabolites of DDT, DDD and DDE are also environmentally persistent, less volatile but they also have low water solubilities (low ppb), sorb to soil/sediment (log K_{oc}>3.0), bioaccumulate (log K_{ow} >6.0, and high bioconcentration factors), and possess long

sediment/soil half-lives (Agricultural Research Service, 1997; U.S.EPA, 1980a, 1992). The major fate processes in aquatic systems for DDT, DDD, and DDE are bioaccumulation, and sorption to sediment.

Chlordane is a mixture of over 140 constituents and is derived from cyclopentadiene and hexachlorocyclopentadiene (U.S.EPA, 1980b). It was widely used as an insecticide on corn, grapes, strawberries, and other crops including home and garden use and as a termiticide. Certain uses were cancelled and being gradually phased out in 1978 until 1988 when no commercial sale, distribution, or use was permitted (U.S.EPA, 1990, 1992). Chlordane is moderately volatile (moderately high Henry's law constant), has a low water solubility (low ppb), sorbs moderately to sediment/soil (log K_{oc}>4.0), and tends to bioaccumulate (log K_{ow}>6.0 , and bioconcentration factor). Chlordane components vary in their persistence.

Endosulfan is used as an insecticide and acaricide on a variety of crops, including citrus, small fruits, forage crops, grains and vegetables (U.S.EPA, 2001). Technical endosulfan is a mixture of two isomers: endosulfan I (α-endosulfan) and endosulfan II (β-endosulfan) (NRCC, 1975). Endosulfan has low water solubility, sorbs strongly to soil, and bioaccumulates to some extent (U.S.EPA, 2001). Endosulfan sulfate, the principle oxidation breakdown product in soil and sediment is more persistent than the parent. The estimated half–lives for endosulfan sulfate range from months to years.

All five COPECs display a propensity for sediment in aquatic systems with potential for residual activity based on their persistence. This supports the importance of comparing distributions of chronic NOECs to pore water concentrations.

5.2.5.3. Assessment and Measurement Endpoints.

Survival of freshwater arthropods in laboratory toxicity tests is the measurement endpoint that will be used to define impact on arthropods. The specific assessment endpoint is the protection of at least 90% of the species 90% of the time from COPEC exposures. Chronic sediment exposures and risk resulting from such exposures to arthropods is the primary consideration because of the environmental persistence of all the COPECs in sediment and their slow desorption to the water column. The amount of the particulate form of the COPEC suspended into the water column due to diffusive events (e.g., bioturbation, waves) cannot be entirely considered insignificant but given the long aging process and that bioturbation and wave action is minimal in freshwater canal systems we assume desorption into the water column will be minimal. It should be noted that the particulate forms present potential exposures for water column organisms by ingestion of particle sorbed contaminants. Furthermore, when both particle-sorbed organics and metals are suspended into the water column there is an increase of dissolved and colloidal contaminant concentrations in water (O'Conner and Connolly, 1980; DiToro, 1985).

The assessment endpoint is in keeping with the management goals set forth by the Science Subgroup (1996) of the south Florida ecosystem restoration. Not presently included within the assessment endpoint are any specific endangered or threatened species.

5.2.5.4. Risk Analysis

Exposure.

The average organic carbon content (mg/kg) at sediment sampling sites with COPECs is presented in Table 5.2.1a. PRAs were conducted at 18 out of 28 sites with COPECs. For ten sites (G-211, ACME1DS, S-5A, S-79, S-331, S-31, S-190, G94D, FECSR78, S-142) data on

organic carbon concentrations were not available to determine pore water concentrations and therefore PRAs were not conducted at these sites although DDE exceeded sediment quality standards at these sites**.** At S-5A, DDD, DDE, and DDT exceeded sediment quality standards.

Partition coefficients used to determine predicted pore water concentrations for COPECs are listed in Table 5.2.1b**.** Table 5.2.4a presents the statistics for the lognormal distributions of the predicted porewater concentrations for the COPECs at the 18 sampling sites. All sites are in or adjacent to agriculture lands (Figure 5.2.1). The DDE 90th centiles ranged from 0.2 ng/L at water control structure and lock S-80, located on canal C-44, to 9.1 ng/L at pumping station S-2, near Lake Okeechobee. Canal C-44 connects Lake Okeechobee to the St. Lucie River in St. Lucie County and is used for water level management of Lake Okeechobee and drainage and irrigation of surrounding citrus communities. Station S-2 is a large pumping station that is used to drain over 466 sq. km of agricultural land south and east of the structure into Lake Okeechobee. Agriculture in the drainage area, part of the Everglades Agricultural Area (EAA) is primarily sugar cane, but also includes turfgrass and winter vegetable farming**.** DDE was also the most frequently detected COPEC at the 12 sites. The DDD 90th centiles ranged from 0.4 ng/L at pumping station S-8 to 17.3 ng/L at pumping station S-6. S-8 pumps water that drains 538 sq. km. of agricultural land north of the structure, mostly sugarcane, discharging into the Miami Canal and Water Conservation area (WCA) 3a. S-6 pumps water from Lake Okeechobee and the EAA northwest of the pumping station into WCA 2A. The S-6 drainage is over 377 sq. km., also primarily sugarcane production. Under certain operational conditions, water is first passed through a storm water treatment area (STA-2) to control phosphorus concentration before it is discharged into the

WCA for storage (Chimney et al., 2000). The DDT 90th centiles ranged from 0.3 ng/L at S-177 to 1.1 ng/L at pump S-2. The chlordane 90th centile at pumping station S-2 in the EAA was 2.4 ng/L. The endosulfan 90th centiles ranged from 17.9 ng/L at water control structure S-177 to 116.8 ng/L at water control structure S-178 on the C-111 canal system (i.e., C-111E) near Homestead. S-177 and S-178 are surrounded by agricultural production. The C-111 basin and Taylor Slough are located in the southeastern portion of Florida and form the eastern hydrologic boundaries for freshwater delivered to ENP and northeast Florida Bay. Authorized in 1962 as part of the Central and South Florida (C & SF) Project to provide flood control to agricultural lands in south Dade County, the C-111 system drains over 310 sq. km. of productive winter vegetable agriculture, orchards, and horticulture. In 1968, the system was authorized to provide water to ENP, which was damaged from the hydrologic isolation of the C & SF project. In the C-111 drainage, endosulfan was also one of the most frequently detected pesticides based on surface water monitoring from 1993-1997 by NOAA (Scott et al., 2002). The highest concentration of endosulfan reached 477 ng/L and 10% of the samples from canal sites exceeded the U.S.EPA chronic freshwater water quality criterion (56 ng/L). The highest percentage (40%) of water quality violations, based on U.S.EPA criteria was detected in samples from S-178. NOAA in 1999-2000 also found endosulfan concentrations were highest (mean dry season concentration ~300 ng/L) in the C-111E (Fulton et al., 2004).

The mean 90th centile concentration for pore water exposures at the sites was highest for endosulfan and lowest for DDT.

Table 5.2.4b presents the statistics for the lognormal distributions of the bulk sediment concentrations for the COPECs at the 18 sampling sites. The DDE 90th centiles ranged from

8.43 μg/kg at HOLYSD3 to 289.9 μg/kg at pumping station S-6. The DDD 90th centiles ranged from 1.29 μg/kg at pumping station S-8 to 203.87 μg/kg at pumping station S-6. The DDT 90th centiles ranged from 2.81 μg/kg at S-177 to 19.34 μg/kg at S-6. The endosulfan 90th centiles ranged from 10.05 μg/kg at S-177 to 116.63 μg/kg at S-178. Chlordane was detected once at S-2 at 12.58 μg/kg.

The mean 90th centile concentration for bulk sediment exposures at the sites was highest for DDE (S-6) and lowest for DDD (S-8).

Effects.

Species effects data for COPECs are summarized in Table 5.2.5. Native and nonnative species of freshwater arthropods used in toxicity tests for each COPEC are listed in the Appendix. For chlordane (n = 9 species), acute toxicity data ranged from 290 ng/L for *Chironomus tentans* to 500,500 ng/L for the aquatic sowbug, *Idotea balthica*. For DDD (n = 12 species), acute toxicity data ranged from 9.5 ng/L for *Hyalella azteca* to 19,000 ng/L for the stonefly, *Pteronarcys californicus*. For DDE (n = 5 species), acute toxicity data ranged from 50 ng/L for the water flea, *Bosmina longirostris,* to 500 ng/L for the copepod, *Diacyclops thomasi*. For DDT (n = 48 species), acute toxicity data for DDT ranged from 3.5 ng/L for *H. azteca* to 50,000 ng/L for the mayfly, *Hexagenia bilineata*. For endosulfan (n =26 species), acute toxicity data for endosulfan ranged from 7.95 ng/L for the freshwater crab, *Paratelphusa jacquemontii*, to 7,060,000 ng/L for the crab, *Oziotelphusa senex senex*. Acute 10th centile values were 7061, 155, 377, 586 and 545 ng/L, for chlordane, DDD, DDE, DDT and endosulfan, respectively. The SSDs of NOEC data for each COPEC are presented in Figure 5.2.5. The NOEC freshwater arthropod 10th centile values were 330, 6.3, 19, 27 and 25 ng/L, for chlordane, DDD, DDE, DDT and endosulfan, respectively.

5.2.5.5. Risk Characterization

The probability of pore water exposures of all COPECs exceeding the arthropod acute 10th centile values was between 0 and 1 %. The probability of predicted pore water exposures exceeding the arthropod chronic NOEC 10th centile values for each COPEC at each site is presented in Table 5.2.6. The site with the highest potential chronic risk from a single COPEC was at S-178 in the C-111 system, based on the probability of pore water exposures exceeding the NOEC 10th centile value at 41 % for endosulfan. The only other PRA conducted in the C-111 system also found that the highest potential risk was in S-178 and was associated with the acute effects of endosulfan to arthropods (Rand and Carriger, 2004). The organochlorine insecticide with the next highest probability of exceeding the NOEC 10th centile was DDD at 17.7 % in S-2 and 19.8 % in S-6. Although DDE was a COPEC at all 18 sites where PRAs were conducted the probability of exceeding the arthropod chronic NOEC 10th centile value was between 0 and 3.6%. Based on the pore water exposure concentrations of DDT and the NOEC distribution, it appears that DDT has minimal potential chronic risk at the three sites that it was a COPEC.

Sediment from S-177, S-178, S-2, S-3, S-6 and S-7 contained two or more COPECs that had a probability of more than 1% of exceeding chronic NOEC 10th centile values. JPCs for these sites are illustrated in Figures 5.2.6 to 5.2.11. Each point on each curve represents the percentage of time exposure concentrations will exceed a percentage of species NOEC values. Sites S-177 and S-178 serve as a potential source of endosulfan, DDD and DDE to Everglades National Park. S-2 and S-3 serve as a potential source of DDD and DDE to Lake

Okeechobee. S-6 and S-7 serve as a potential source of DDD and DDE to storm water treatment areas and water conservation areas. DDT had minimal potential risk at all sites.

The probability of COPEC bulk sediment concentrations exceeding the FDEP SQAG TEC and PEC by site is presented in Table 5.2.7. The probability of DDE exceeding the sediment TEC is 19.27 % at S-8 to 99.97 % at LOX10. The probability of DDE exceeding the PEC was <0.01 % at S-18C to 49.8 % at S-178. The probability of DDD exceeding the sediment TEC is 0.44 % at S-8 to 62.54 % at S-6. The probability of DDD exceeding the PEC was <0.01 % at S-8 to 33.4 % at S-6. There are no standards for endosulfan in sediment. As expected the highest probability of COPECs (DDD, DDE) producing adverse effects (or exceeding PECs) and risk to the benthic communities are in the Everglades Agricultural Area (EAA) where sites S-2 and S-6 are found and in the C-111 system where S-177 and S-178 are found. Sugar cane agriculture dominates in the EAA and vegetable crops dominate around the C-111 system.

5.2.5.6. Uncertainties

Exposure.

Exposure data for this assessment were obtained from the South Florida Water Management District monitoring program for 1990-2002 from 52 sampling sites in freshwater canals. This is the most comprehensive sediment contaminant database in south Florida. Although chemical analyses of all contaminants was from one laboratory the total number of sampling sites in the monitoring program is limited considering the 1400-mile system of canals in south Florida. The sampling frequency is also limited since sites were sampled only two times per year. Therefore, the database is inadequate to determine real differences in

contaminant exposure between the wet and dry seasons. This is extremely relevant for endosulfan, which is still registered for use in agriculture and may enter aquatic systems especially during surface runoff events. This is not as relevant for DDT, DDD, DDE and chlordane that have been removed from permitted use. However, rain events may resuspend organic contaminants from sediment back into the water column for exposure to fish and invertebrates and transport to other parts of the water management system, National Park lands, estuaries, and bays in south Florida.

Pore water concentrations for exposure distributions were estimated from the whole sediment concentrations of COPECs based on the equilibrium partition coefficient (EqP) which assumes that for nonionic organic chemicals the chemical sorbed to sediment organic carbon and pore water are in equilibrium and that concentrations are related by K_{oc} (DiToro et al., 1991). Sediment -pore water exposure should thus be similar to water-only exposure because at equilibrium chemical activity is the same in each system. The latter are obvious inherent uncertainties in the model. Sorption potential for nonionic organics is primarily controlled by the mass fraction of organic carbon in the sediment. The site sediments contained f_{oc}> 0.2 % (by weight). Therefore, organic carbon should be the major phase for chemisorption. This assumption is supported by the fact that when f_{oc}< 0.2 % the factors controlling secondary order effects on partitioning (e.g., particle size) become more significant (DiToro et al., 1991).

Effects.

There were few acute and chronic sediment toxicity studies for COPECs. We therefore assumed that toxicity to pore water would be similar to water only exposures and used acute

toxicity data from water only tests to prepare SSDs. There is uncertainty in this assumption; however, several investigations have found that toxicity estimates from water only acute tests were similar to exposures from measured porewater concentrations in bulk sediment tests with *Hyalella azteca* (Hoke et al., 1994; Lotufo et al., 2001).

As a result of the limited number of species used in toxicity tests for the COPECs there is uncertainty of extrapolating these data to responses of native species from south Florida ecosystems. However, many of the freshwater arthropod species used in toxicity tests with COPECs are native to south Florida ecosystems (see Appendix). Hose and Van den Brink (2004) also found that SSDs for endosulfan and native and nonnative arthropod species in Australia were similar.

Extrapolating from acute to chronic effects using a general application factor (or acute to chronic ratio; ACR) of 20 may have introduced uncertainty as well. For example, in the water quality criteria document for DDT (U.S.EPA, 1980a), the U.S.EPA used a final ACR of 65 based on fathead minnow data. However, based on acute (LC50s from 0.5-4.7 μg/L) and chronic (0.05 μg/L) data for the freshwater cladoceran, *Daphnia magna* the ACR range is 10-94. In the water quality criteria document for chlordane (U.S.EPA, 1980b), the U.S.EPA estimated a final ACR value of 14, based on fish (e.g., bluegill ACR=37) and arthropods (e.g., daphnids ACR=3.6). In the water quality criteria document for endosulfan (U.S.EPA, 1980c), the U.S.EPA estimated a final acute to chronic ratio of 3.9 based on fish (e.g., fathead minnow ACR=3.0) and invertebrates (e.g., daphnid ACR range = 4.4 to 39). However, in the U.S.EPA re-registration document for endosulfan, the ACR for *Daphnia magna* was 83 (U.S.EPA, 2001). All acute and chronic data used to estimate a single ACR for a COPEC by the U.S.EPA came from tests conducted in the same laboratory. However,

there were no chronic data for DDD and DDE to estimate any ACRs. Therefore, using 20 as a general ACR to predict NOECs for organochlorine COPECs also is an uncertainty.

It should also be noted that when toxicity is manifested in growth, reproduction or other sublethal endpoints an acute toxicity test (e.g., LC50) might not be appropriate for extrapolation to chronic effects since acute endpoints are most often based on survival. In the development of ACRs by the U.S.EPA in criteria documents, chronic effects were associated with changes in both survival and growth although typically the most sensitive endpoint in chronic tests is survival (Woltering, 1984). However, use of classical effect endpoints may not be indicative of adverse effects for hydrophobic organochlorine chemicals that are accumulated from water, sediment as well as the diet.

Risk Characterization.

One source of uncertainty that was not considered is the potential effects from COPECs through joint or interactive effects with other contaminants (e.g., heavy metals, transient concentrations of other compounds during the growing season) and with one another. Monitoring studies have shown that canals contain numerous contaminants in sediment and water (Miles and Pfeuffer, 1997; Pfeuffer and Rand, 2004). Our characterization of ecological risk is limited to the locale of sites from which sediments were analyzed. However, there are regional implications, because of the likelihood of sediment transport to other parts of the water management system, including water conservation storage areas (WCA's), productive coastal estuaries, and Everglades and Biscayne National Parks.

COPECs were found at 28 sites (54 % of SFWMD sampling sites) but probabilistic risk assessments were only conducted at 18 sites since organic carbon concentration data were

not available for ten sediment sites to use equilibrium partitioning methodology to determine pore water exposure concentrations. Therefore, there is uncertainty as to the extent of risk for COPECs at these 10 sites.

5.2.6. CONCLUSIONS

Based on a tier 1 assessment of over 70 pesticides and degradates in sediment at 52 sampling sites from south Florida freshwater canals only DDT, DDD, DDE, chlordane and endosulfan exceeded sediment quality criteria and were therefore classified as COPECs. Risk associated with acute exposures of freshwater arthropods to COPECs was estimated to be low. In addition, probabilistic risk assessment showed that the potential risk to freshwater arthropods from chronic exposures to DDT, DDE and chlordane was estimated to be low based on NOEC 10th centiles. The highest potential chronic risk to arthropods was associated with exposures to endosulfan, followed by DDD. Endosulfan and DDD are COPECs that should be a high priority for future sediment monitoring programs in south Florida canals. The latter gains in importance in lieu of the fact that most of the arthropod species used in the probability response distributions to develop risk estimates were native to South Florida and therefore may be at risk.

Based on the presence and persistence of these COPECs and the potential water quality changes related to water management activities of the CERP, it would be helpful to investigate joint actions of organochlorine contaminants and other non-chemical stressors. Studying joint action is especially relevant for organochlorines, since they are ubiquitous in the U.S. and may be chronic stressors that compromise existing benthic communities in both fresh- and salt-water systems.

Table 5.2.1a
Mean organic carbon content (standard deviation) in sediment at sites with COPECs.

Site	Organic carbon (mg/kg)	*N*
S-176*	6,454 (4202)	4
S-177	7,870 (8777)	4
S-178	13,967 (11600)	4
S-18c	7,655 (7151)	4
S-2	12,650 (4730)	3
S-3	9,892 (12273)	3
S-4	15,367 (12023)	3
S-6	51,040 (60492)	5
S-7	10,859 (7083)	3
S-8	12,522 (8119)	3
S-80	64,500 (7778)	2
S-99	22,000 (11314)	2
CA2-15**	446,750 (19,050)	4
CA3-15	485,750 (17,056)	4
HOLYSD3	334,667 (173,820)	6
LOX10	478,500 (27,197)	4
LOX8	502,500 (4,203)	4
WCA2F1	435,500 (30,730)	4

*Sites S-176 thru S-99 include data thru 2002
** Sites CA2-15 thru WCA2F1 include data thru 2003

Table 5.2.1b
Partition coefficients for sediment/porewater (pesticides)

Metal	Log K_{oc}
Chlordane	5.6
DDD	5.4
DDE	5.9
DDT	6.0
Endosulfan	4.9

Table 5.2.2
Results of Tier 1 Assessment: Use of Screening Benchmarks to Determine COPECs in Sediment

Chemical	COPEC	Comments
2,4,5-T	No	Detected infrequently and did not exceed SQC[1].
2,4,5-TP	No	Detected only twice past 1990 in sediment and did not exceed SQC.
2,4-D	No	Only one detection and SQC violation past 1990. The method detection limit (MDL) was greater than the criteria.
Acifluorfen	No	Not detected in sediment.
Alachlor	No	Not detected in sediment.
Aldicarb	No	Not detected in sediment.
Aldrin	No	Not detected in sediment past 1990.
Ametryn	No	No SQC data available. Detected at multiple sites.
Atrazine	YES	Detected multiple times in sediment. Found to be a COPEC at S5A and S8.
Azinphos methyl	No	Detected only once in sediment at S5A. No SQC available.
Benomyl	No	Not detected in sediment.
BHC Alpha	No	Not detected in sediment beyond 1990.
BHC Beta	No	Multiple SQC violations were found but never twice at the same site.
BHC Delta	No	Not detected beyond 1990 in sediment.
BHC Gamma	No	Only one SQC violation beyond 1990.
Bromacil	No	Detected at multiple sites, but never more than once. No SQC was available.

Carbaryl	No	Only detected once beyond 1990 and no SQC available.
Carbofuran	No	Detected in sediment once after 1990. No SQC available.
Carbophenothion	No	Not detected in sediment.
Chlordane	Yes	Detected in sediment at multiple sites, multiple times. Found to be a COPEC at S-2, S6, and S5A.
Chlorothalonil	No	Not detected in sediment.
Chlorpyrifos	No	Not detected in sediment beyond 1990.
Chlorpyrifos ethyl	No	Not detected in sediment.
Chlorpyrifos methyl	No	Not detected in sediment
Cypermethrin	No	Not detected in sediment.
p,p'-DDD	Yes	Found to violate SQC at multiple sites on multiple dates. Canal sites are primarily around Lake Okeechobee, and the Everglades.
p,p'-DDE	Yes	Found to violate SQC at multiple sites on multiple dates throughout South Florida.
p,p'-DDT	Yes	Found to violate SQC at S-177, S-2, S-5A, and S-6.
Demeton	No	Not detected in sediment.
Diazinon	No	Not detected in sediment beyond 1990. MDL was generally greater than the criteria.
Dicofol	No	Detected at multiple sites but no SQC available.
Dieldrin	No	Four SQC violations but all at separate sites.
Diquat	No	Detected in sediment at multiple sites but no SQC available.
Disulfoton	No	Not detected in sediment.

Diuron	No	Detected at multiple sites but no SQC available.
Endosulfan	Yes	Found to violate SQC multiple times at S-177 and S-178. Several sites had single violations.
Endrin	No	Not detected in sediment beyond 1990. The MDL was greater than the criteria.
Endrin aldehyde	No	Not detected in sediment beyond 1990.
Ethion	No	Detected in sediment multiple times, primarily at S-80 and S-99 but no SQC available.
Ethoprop	No	Not detected in sediment.
Fenamiphos	No	Not detected in sediment.
Fonofos	No	Not detected in sediment.
Heptachlor	No	Only one SQC violation beyond 1990 at US41-25.
Heptachlor epoxide	No	No SQC violations nor detections beyond 1990.
Hexazinone	No	Not detected in sediment.
Linuron	No	Detected once at S-12c. No SQC available.
Malathion	No	Not detected in sediment beyond 1990. The MDL was greater than the criteria.
Methamidophos	No	Not detected in sediment past 1990. No SQC available.
Methomyl	No	Detected twice in sediment at sites southwest of Lake Okeechobee. No SQC available.
Methoxychlor	No	Not detected in sediment.
Metolachlor	No	Not detected in sediment.
Metribuzin	No	Detected twice in sediment at S-176 and S-177 in February of 1992. No SQC available.

Mevinphos	No	Not detected in sediment.
Mirex	No	Not detected in sediment.
Monocrotophos	No	Not detected in sediment.
Naled	No	Detected in sediments at S-176, S-78 on C-43 and L3BRS in February of 1992. No SQC available.
Norflurazon	No	Detected in sediment three times at S-80 and once at S-99. No SQC available.
Oxamyl	No	Not detected in sediment.
Paraquat	No	Not detected in sediment beyond 1990. No SQC available.
Parathion	No	Not detected in sediment.
Parathion ethyl	No	Not detected in sediment.
Parathion methyl	No	Not detected in sediment.
Permethrin	No	Not detected in sediment.
Phorate	No	Single violations found in February of 1992 at S-31, S-8, S-9, and S-12c. The MDL was greater than the criteria.
Prometryn	No	Detected only once at S-6. No SQC available.
Simazine	No	Not detected in sediment. No SQC available.
Toxaphene	No	One SQC violation at S-6 in 1998. The MDL was greater than the criteria.
Trifluralin	No	Inconsistently detected at multiple sites. No SQC available.

[1]SQC; Sediment Quality Criteria

Table 5.2.3

Summary of mean pesticide hazard indices at sites (n=52) in the South Florida Water Management District monitoring program (1990-2002).

DistrictSite	Mean	N	Std. Deviation	Median	Minimum	Maximum	Range
ACME1DS	.85	9	1.28	.00	.00	3.50	3.50
CA2-15	2.98	8	1.28	.00	.00	3.50	3.50
CA3-15	3.67	8	4.77	1.28	.00	14.06	14.06
CA3-3	.00	8	3.40	4.54	.00	9.38	9.38
CR33.5T	.00	7	.00	.00	.00	.00	.00
FECSR78	.93	26	.00	.00	.00	.00	.00
G123	.19	10	4.32	.00	.00	22.09	22.09
G211	.86	6	.59	.00	.00	1.86	1.86
G94D	.99	10	1.07	.63	.00	2.63	2.63
GORDYRD	.00	1	1.37	.38	.00	3.55	3.55
HOLYSD1	3.70	18	.	.00	.00	.00	.00
HOLYSD2	1.96	17	15.71	.00	.00	66.67	66.67
HOLYSD3	.56	17	8.08	.00	.00	33.33	33.33
HOLYSD4	.00	17	1.07	.00	.00	2.84	2.84
L3BRS	.14	25	.00	.00	.00	.00	.00
L40-1	.00	1	.30	.00	.00	.96	.96
LO308C	.00	1	.	.00	.00	.00	.00
LOX10	4.38	8	.	.00	.00	.00	.00
LOX8	4.75	8	3.78	5.79	.00	8.44	8.44
S12C	.16	23	5.54	3.44	.00	14.21	14.21
S140	.00	11	.46	.00	.00	1.94	1.94
S142	1.91	10	.00	.00	.00	.00	.00
S176	.63	25	2.77	.47	.00	7.13	7.13
S177	7.40	25	1.34	.00	.00	5.63	5.63
S178	15.22	26	7.74	4.38	.00	23.21	23.21
S18C	.22	28	12.82	17.63	.00	41.33	41.33
S190	.23	26	.48	.00	.00	1.69	1.69
S191	.12	26	.41	.00	.00	1.38	1.38
S2	15.57	24	.37	.00	.00	1.47	1.47
S235	.25	24	17.55	8.32	.00	56.28	56.28
S3	6.12	25	1.15	.00	.00	5.63	5.63
S31	2.78	26	7.64	3.72	.00	33.10	33.10
S331	.43	10	2.52	3.38	.00	7.01	7.01
S332	1.46	25	.44	.44	.00	1.22	1.22
S355A	.10	3	.17	.00	.00	.30	.30
S355B	.37	3	.64	.00	.00	1.10	1.10
S38B	.66	10	1.42	.00	.00	4.38	4.38
S4	8.21	25	12.87	5.19	.00	58.48	58.48
S5A	34.08	26	47.40	14.40	.00	197.29	197.29
S6	45.23	21	74.42	13.49	.00	260.43	260.43
S65E	.02	26	.12	.00	.00	.63	.63
S7	12.57	23	34.60	.94	.00	160.00	160.00
S78	.14	24	.36	.00	.00	1.28	1.28

S79	2.23	25	3.18	.34	.00	11.44	11.44
S8	6.91	25	15.72	.00	.00	61.17	61.17
S80	1.17	24	1.49	.74	.00	6.03	6.03
S9	.02	24	.08	.00	.00	.38	.38
S99	.92	26	2.10	.00	.00	10.14	10.14
STA2C1SD	.00	1	.	.00	.00	.00	.00
US41-25	.16	23	.66	.00	.00	3.17	3.17
WCA2F1	6.39	8	5.02	6.10	.00	17.19	17.19
WHTCYPRK	.00	1	.	.00	.00	.00	.00

Table 5.2.4a
Statistics for lognormal distributions of predicted pore water concentrations for COPECs including 90th centile concentration (ng/l)

Site	COPEC	Number of times analyzed	Number of Detections	Slope	Intercept	r^2	*p*-value	90th centile ng/l
CA2-15	DDE	8	4	1.31	11.44	0.86	7.29E-02	0.1
CA3-15	DDE	8	5	3.47	19.84	0.86	2.32E-02	0.1
HOLYSD3	DDE	17	4	3.17	20.70	0.86	7.41E-02	0.0
LOX10	DDE	8	5	4.71	25.66	0.76	5.23E-02	0.1
LOX8	DDE	8	4	3.32	19.73	0.76	1.31E-01	0.1
S-176	DDE	25	10	1.21	9.79	0.8	4.41E-04	1.3
S-177	DDD	25	9	1.40	9.78	0.95	1.15E-05	3.2
	DDE	25	20	1.63	9.63	0.95	2.29E-13	8.8
	DDT	25	5	3.36	17.92	0.93	8.19E-03	0.3
	Endosulfan	25	8	0.81	7.69	0.92	1.38E-04	17.9
S-178	DDE	25	18	2.47	11.44	0.82	2.01E-07	8.2
	Endosulfan	26	13	1.58	7.75	0.87	3.59E-06	116.8
S-18c	DDE	27	4	4.16	20.77	1	6.78E-05	0.3
S-2	Chlordane	22	3	0.71	8.14	0.96	1.35E-01	2.4
	DDD	22	16	1.58	9.41	0.96	3.77E-11	10.6
	DDE	23	21	1.78	9.91	0.97	6.88E-16	9.1
	DDT	23	5	0.63	8.17	0.84	2.94E-02	1.1
S-3	DDD	24	14	1.36	9.20	0.96	7.43E-10	7.1
	DDE	23	19	1.72	10.10	0.97	8.22E-15	6.1
S-4	DDD	23	9	2.46	12.85	0.9	8.06E-05	2.1
	DDE	22	15	2.30	11.98	0.89	1.46E-07	3.3
S-6	DDD	21	15	0.99	8.02	0.97	2.75E-11	17.3
	DDE	19	13	1.11	8.71	0.93	1.45E-07	6.4
	DDT	20	7	0.98	9.60	0.95	1.49E-04	0.4
S-7	DDD	23	8	1.11	8.95	0.97	1.02E-05	3.9
	DDE	22	10	0.86	8.33	0.98	1.76E-08	4.1
S-8	DDD	24	4	2.30	14.00	0.92	4.12E-02	0.4
	DDE	23	9	1.24	10.26	0.95	9.41E-06	0.6
S-80	DDE	24	11	1.92	13.40	0.65	2.68E-03	0.2
S-99	DDE	24	9	1.05	9.65	0.95	7.77E-06	0.6
WCA2F1	DDE	8	7	2.80	17.13	0.91	9.26E-04	0.1

Table 5.2.4b
Statistics for lognormal distributions of bulk sediment concentration data for COPECs including 90th centile concentration (ug/kg dry weight)

Site	COPEC	Number of times analyzed	Number of Detections	Slope	Intercept	r^2	*p*-value	90th centile ug/kg
CA2-15	DDE	8	4	1.31	4.10	0.86	7.29E-02	46.0
CA3-15	DDE	8	5	3.47	1.11	0.86	2.32E-02	31.1
HOLYSD3	DDE	17	4	3.17	3.34	0.86	7.41E-02	8.4
LOX10	DDE	8	5	4.71	-0.84	0.76	5.23E-02	32.5
LOX8	DDE	8	4	3.32	0.95	0.76	1.31E-01	40.1
S176	DDE	25	10	1.21	5.24	0.80	4.41E-04	7.3
S177	DDD	25	9	1.40	5.22	0.95	1.15E-05	5.8
	DDE	25	20	1.63	3.37	0.95	4.09E-13	61.5
	DDT	25	5	3.36	4.95	0.93	8.19E-03	2.5
	ENDOSULFAN	25	8	0.81	5.47	0.92	1.38E-04	10.1
S178	DDE	25	18	2.47	1.32	0.82	2.01E-07	101.7
	ENDOSULFAN	26	13	1.58	3.03	0.87	3.59E-06	116.6
S18C	DDE	27	4	4.16	4.81	1.00	6.78E-05	2.3
S2	CHLORDANE	22	3	0.71	5.50	0.96	1.35E-01	12.6
	DDD	22	16	1.58	3.92	0.96	3.77E-11	31.0
	DDE	23	21	1.78	2.70	0.97	6.88E-16	102.0
	DDT	23	5	0.63	5.59	0.84	2.94E-02	12.5
S3	DDD	24	14	1.36	4.64	0.96	7.43E-10	16.3
	DDE	23	19	1.72	3.31	0.97	8.22E-15	53.0
S4	DDD	23	9	2.46	4.12	0.90	8.06E-05	7.6
	DDE	22	15	2.30	2.48	0.89	1.46E-07	45.2
S6	DDD	21	15	0.99	4.00	0.97	2.75E-11	203.9
	DDE	19	13	1.11	3.55	0.93	1.45E-07	289.9
	DDT	20	7	0.98	5.02	0.95	1.49E-04	19.3
S7	DDD	23	8	1.11	5.18	0.97	1.02E-05	9.8
	DDE	22	10	0.86	4.91	0.98	1.76E-08	39.6
S8	DDD	24	4	2.30	6.03	0.92	4.12E-02	1.3
	DDE	23	9	1.24	5.24	0.95	9.41E-06	6.9
S80	DDE	24	11	1.92	4.29	0.65	2.68E-03	11.0
S99	DDE	24	9	1.05	5.16	0.95	7.77E-06	11.7
WCA2F1	DDE	8	7	2.80	1.51	0.91	9.26E-04	50.7

Table 5.2.5

Statistics for pesticide SSDs of COPECs including 10th centile concentrations (ng/L)

COPEC	Number of different species	Slope	Intercept	r^2	*p*-value	NOEC 10th centile
Chlordane	9	1.636	4.511	0.97	9.83×10^{-6}	330
DDD	12	0.846	5.579	0.97	4.45×10^{-9}	6.3
DDE	5	1.675	6.606	0.88	1.83×10^{-2}	19
DDT	48	0.979	5.259	0.96	9.52×10^{-33}	27
Endosulfan	26	0.804	5.006	0.98	1.11×10^{-22}	25

Table 5.2.6
Probability of exceedence of the arthropod NOEC 10th centiles for pore water concentrations at SFWMD sediment sites

Site	COPEC	Probability of exceedence of 10th centile (%)
CA2-15	DDE	0.0
CA3-15	DDE	0.0
HOLYSD3	DDE	0.0
LOX10	DDE	0.0
LOX8	DDE	0.0
S-176	DDE	0.4
S-177	DDD	4.5
	DDE	3.5
	DDT	0.0
	Endosulfan	8.2
S-178	DDE	1.5
	Endosulfan	41.4
S-18c	DDE	0.0
S-2	Chlordane	0.3
	DDD	17.7
	DDE	3.3
	DDT	1.5
S-3	DDD	11.3
	DDE	1.7
S-4	DDD	0.7
	DDE	0.1
S-6	DDD	19.8
	DDE	3.6
	DDT	0.1
S-7	DDD	6.5
	DDE	3.2
S-8	DDD	0.0
	DDE	0.1
S-80	DDE	0.0
S-99	DDE	0.2
WCA2F1	DDE	0.0

Table 5.2.7

Probability of exceeding the Florida sediment quality assessment guidelines (SQAG) for bulk sediment concentrations

Site	COPEC	probability of exceeding TEC as %	probability of exceeding PEC as %
CA2-15	DDE	59.28	14.51
CA3-15	DDE	98.40	10.10
HOLYSD3	DDE	52.12	0.11
LOX10	DDE	99.97	11.76
LOX8	DDE	99.10	18.11
S176	DDE	19.81	2.05
S177	DDD	11.87	1.25
	DDE	79.01	21.26
	DDT	2.04	<.01
	ENDOSULFAN	NA	NA
S178	DDE	99.26	49.80
	ENDOSULFAN	NA	NA
S18C	DDE	2.76	<.01
S2	CHLORDANE	19.52	8.19
	DDD	49.44	11.28
	DDE	91.86	35.92
	DDT	16.31	4.21
S3	DDD	28.30	5.45
	DDE	79.28	18.92
S4	DDD	20.71	0.37
	DDE	91.31	18.25
S6	DDD	62.54	33.40
	DDE	81.22	41.83
	DDT	26.37	3.72
S7	DDD	17.21	3.72
	DDE	36.53	11.70
S8	DDD	0.44	<.01
	DDE	19.27	1.83
S80	DDE	39.92	1.60
S99	DDE	24.42	4.23
WCA2F1	DDE	98.10	24.71

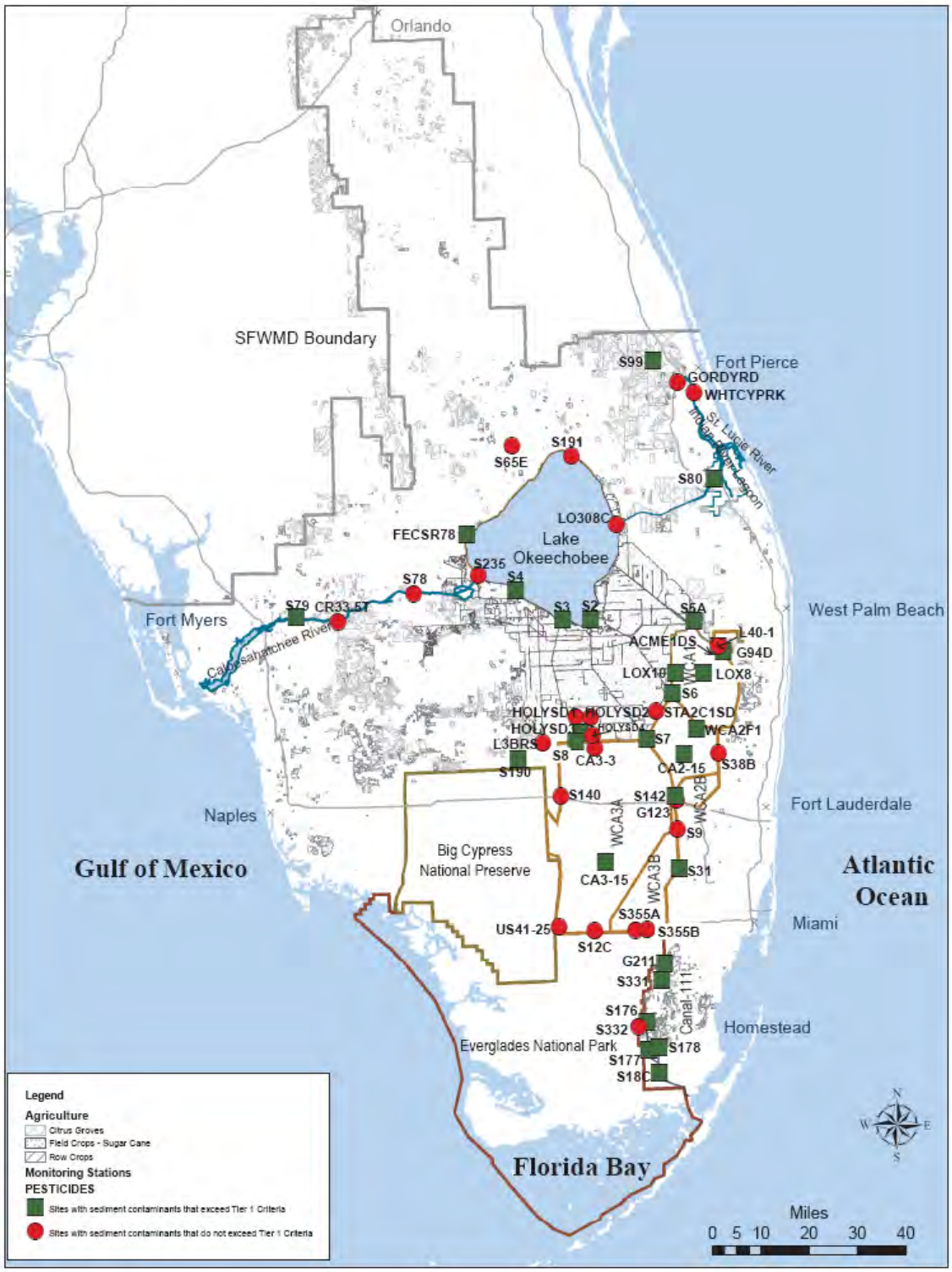


Figure 5.2.1
South Florida Water Management District sediment pesticide monitoring stations

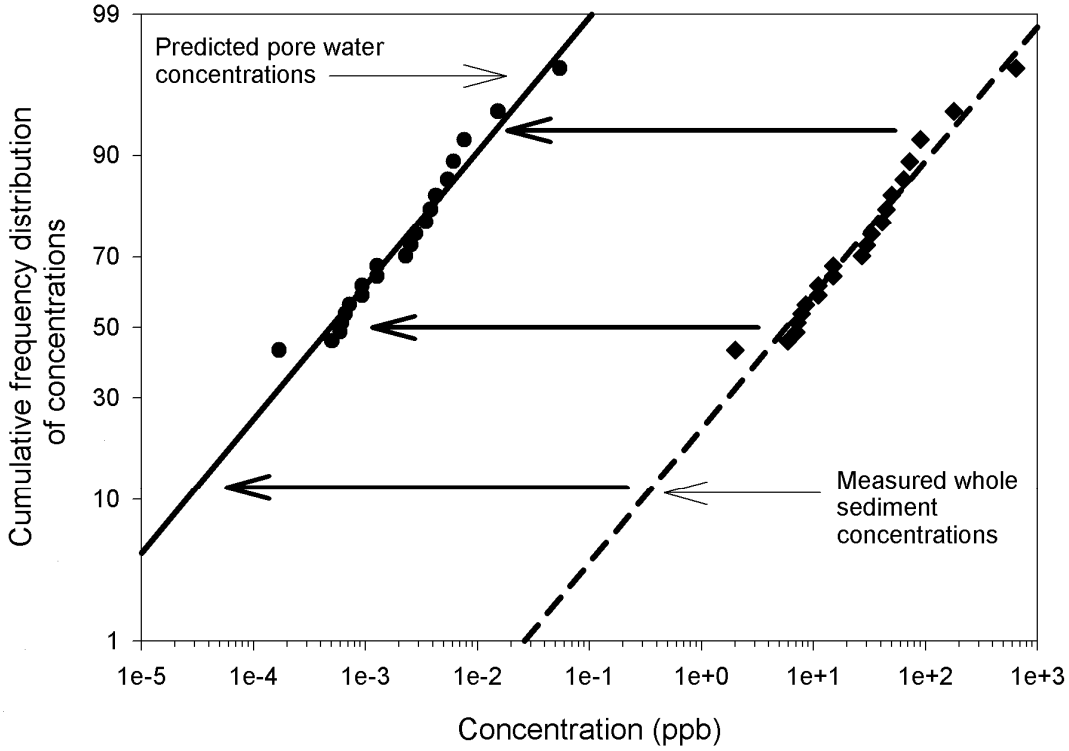


Figure 5.2.2

Actual measured whole sediment concentrations (μg/kg) converted into pore water concentrations (μg/L). See text for methodology.

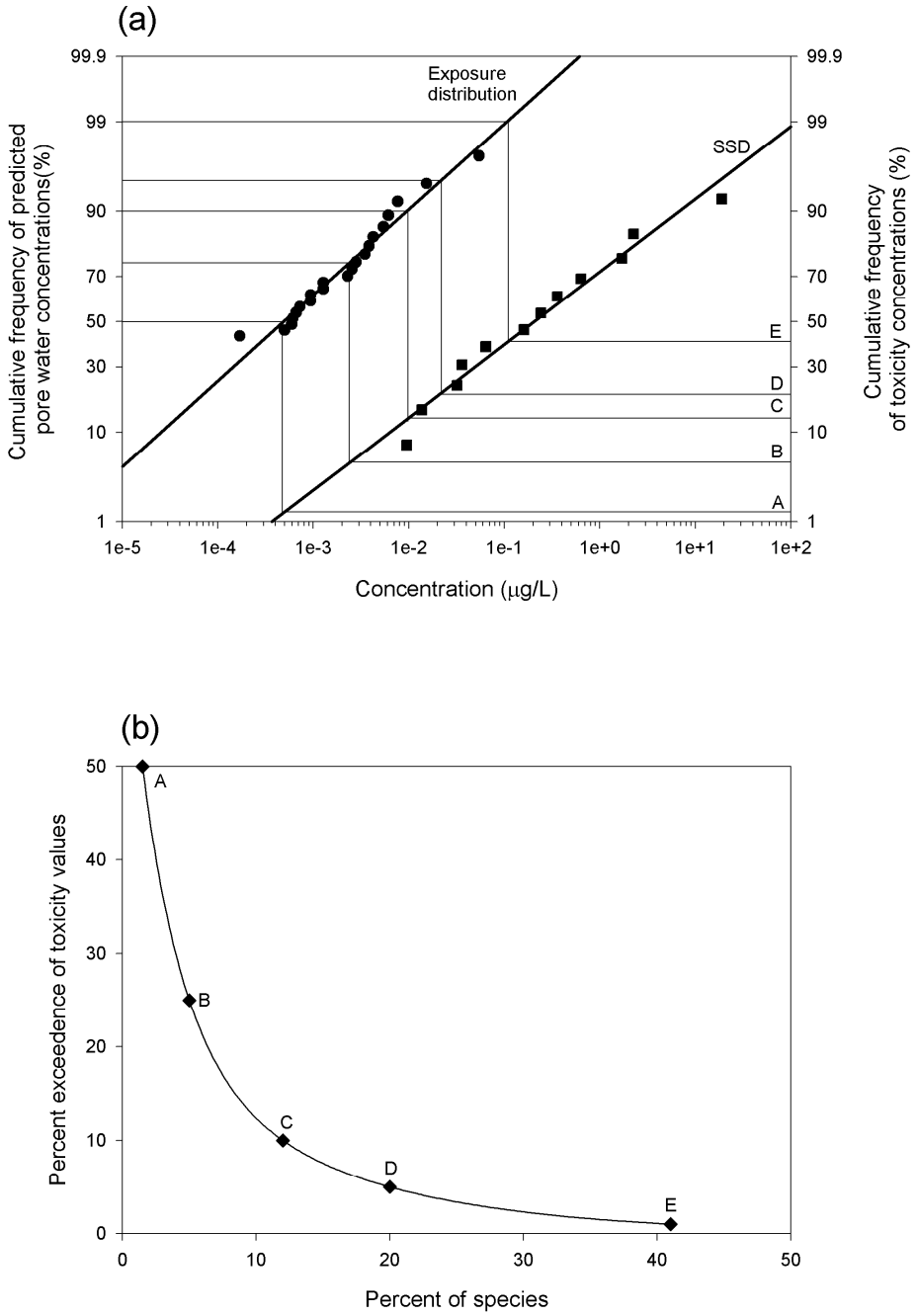


Figure 5.2.3

Derivation of Joint Probability Curve (JPC). (a) Lognormal distribution of toxicity values (or right) or SSD and predicted pore water concentrations (on left). The intersection at various points on each distribution is used to plot a JPC. (b) A JPC created from the lognormal distribution in 3a. (adapted from Solomon et al., 2000).

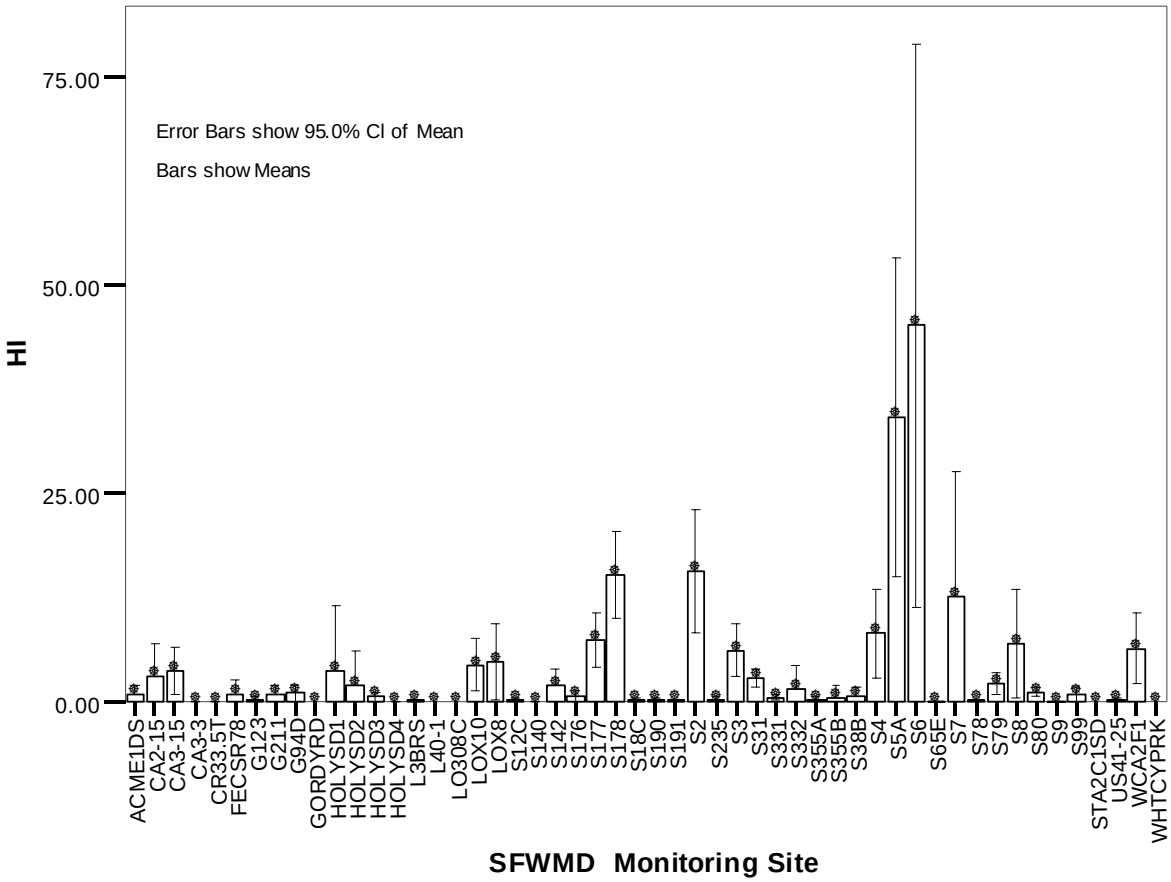


Figure 5.2.4

Summary of mean pesticide hazard indices at sites (n=52) in the South Florida Water Management District monitoring program (1990-2002).

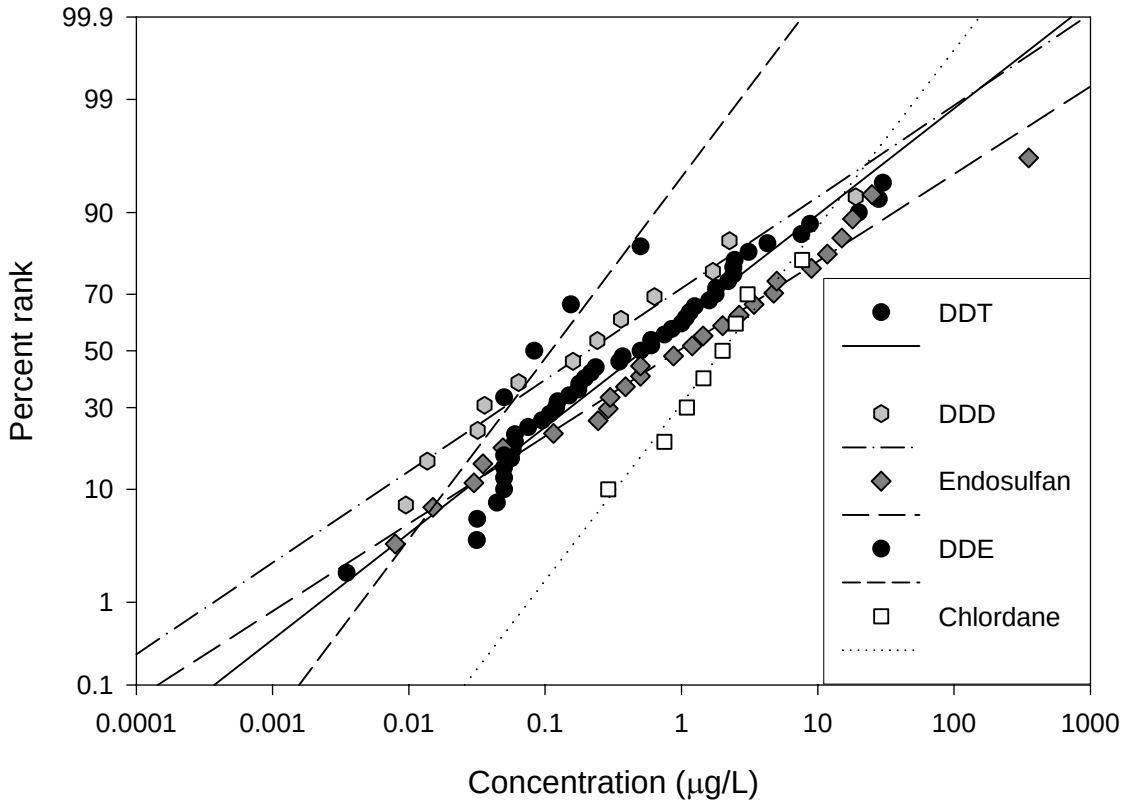


Figure 5.2.5

Distribution of NOEC values for freshwater arthropods and COPECs.

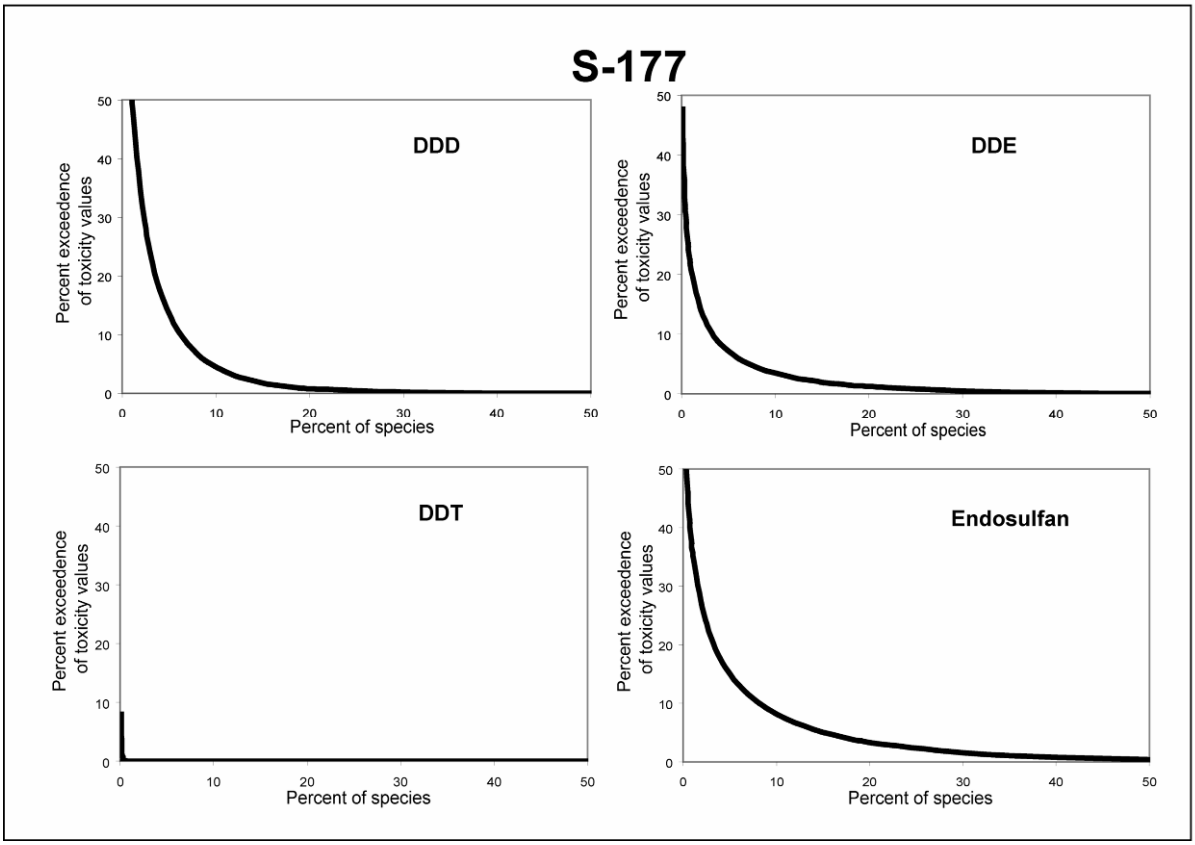


Figure 5.2.6

JPCs for predicted pore water concentrations of DDD, DDE, DDT, and Endosulfan for freshwater arthropods at S-177.

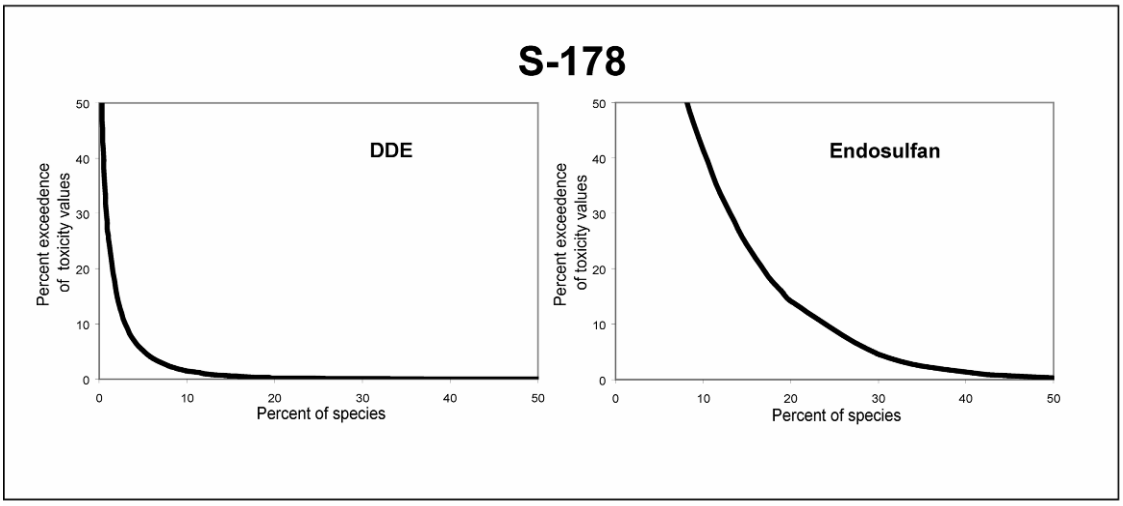


Figure 5.2.7

JPCs for predicted pore water concentrations of DDE and endosulfan for freshwater arthropods at S-178.

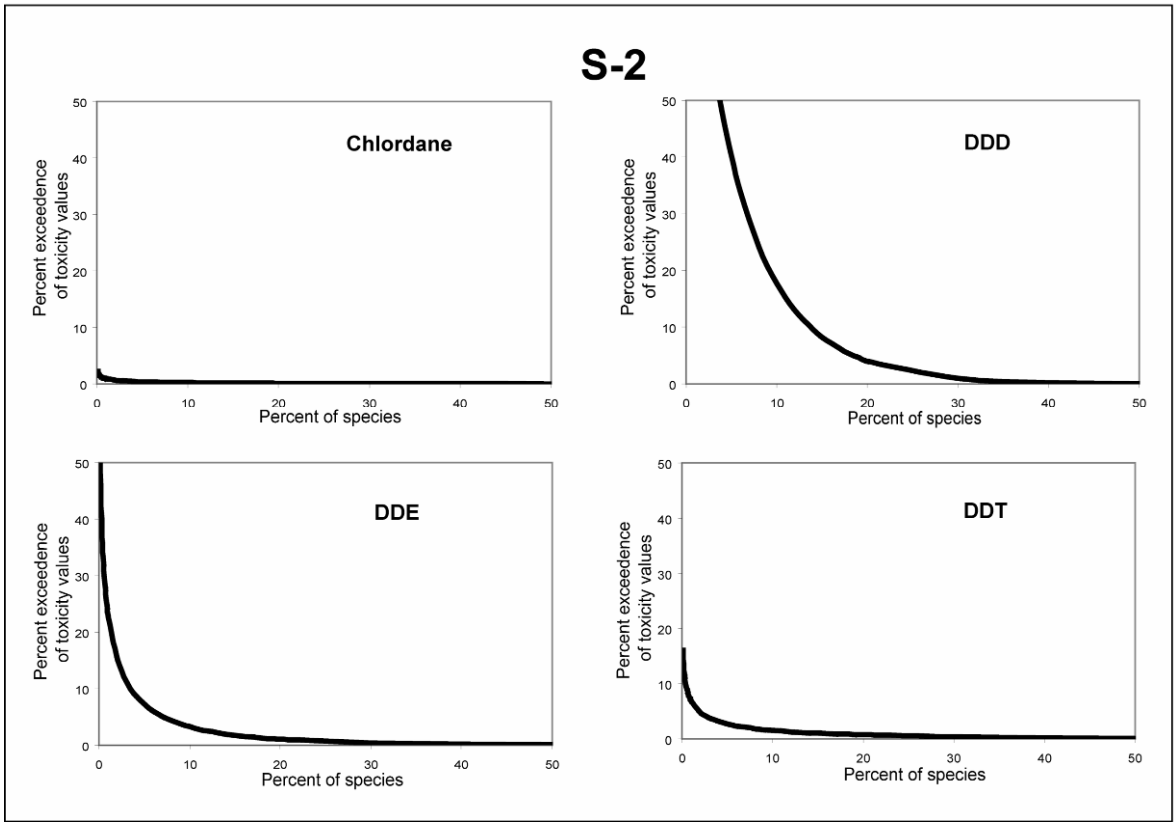


Figure 5.2.8

JPCs for predicted pore water concentrations of chlordane, DDD, DDE, and DDT for freshwater arthropods at S-2.

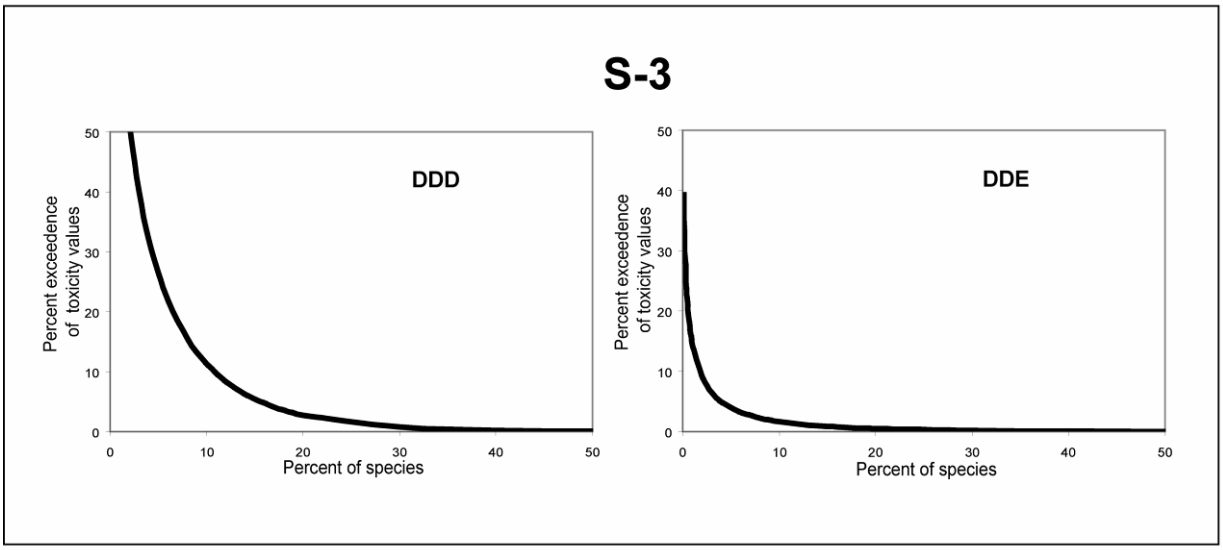


Figure 5.2.9

JPCs for predicted pore water concentrations of DDD and DDE for freshwater arthropods at S-3.

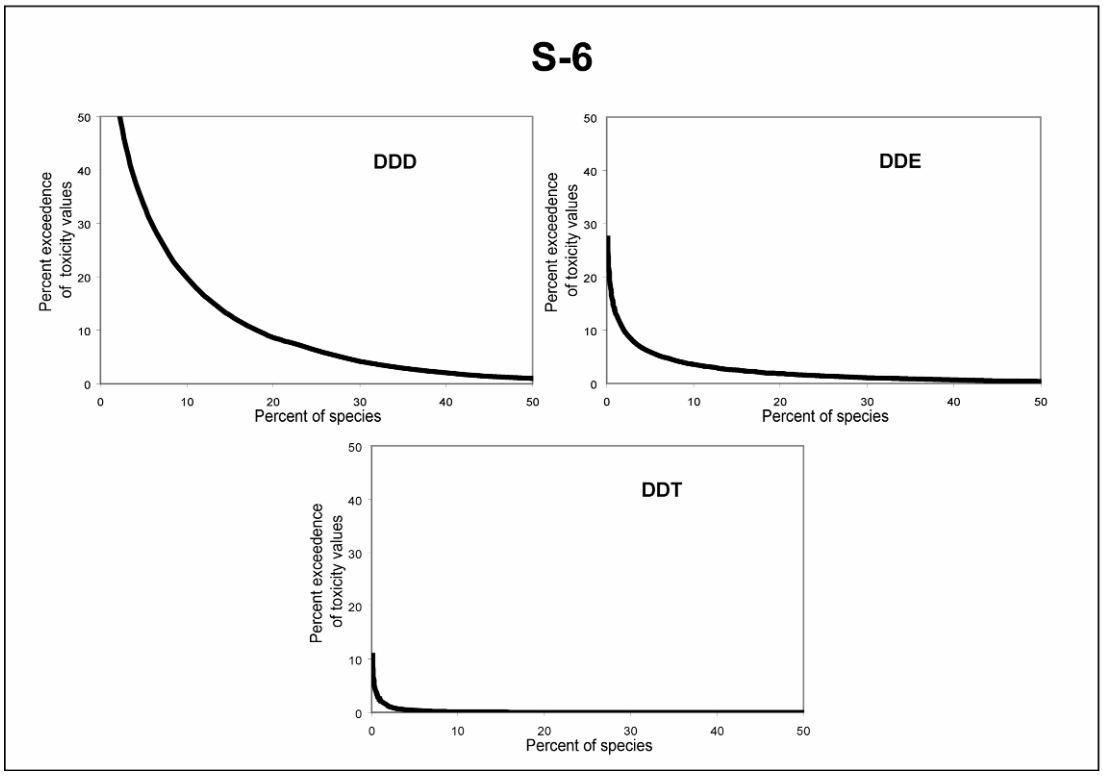


Figure 5.2.10

JPCs for predicted pore water concentrations of DDD, DDE, and DDT for freshwater arthropods at S-6.

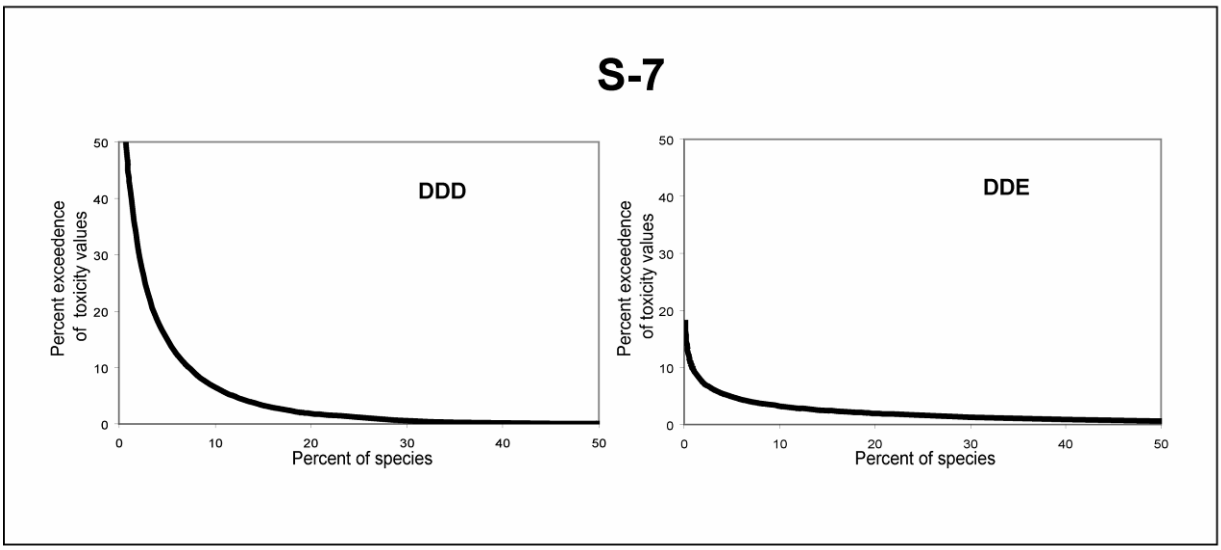


Figure 5.2.11

JPCs for predicted pore water concentrations of DDD and DDE for freshwater arthropods at S-7.

5.3 Metals from South Florida Canals-South Florida Water Management District Historical Data (1990-2002)

5.3.0. ABSTRACT

A two-tier ecological risk assessment was conducted for metals monitored in sediment at 32 sampling sites in South Florida freshwater canals from 1990-2002. For tier 1, we identified the chemicals of potential ecological concern (COPECs) as arsenic, antimony, cadmium, chromium, copper, lead, nickel and zinc based on their exceedence of sediment quality standards at 10 sites. For all sites with data on the sediment-pore water partition coefficients, whole sediment concentrations of COPECs were converted to pore water concentrations based on equilibrium partitioning**.** We also compared concentrations of acid-volatile sulfide (AVS) to the total molar sum of the cationic metals (Cd, Cu, Ni, Pb, Zn) that were extracted (∑TEM) to predict toxicity based on the AVS approach and excess metal. In tier 2, a probabilistic risk assessment compared distributions of pore water exposure concentrations of COPECs with effects distributions of freshwater response data from laboratory toxicity tests. The overlap of predicted pore water concentrations and biological effects distributions was used as a measure of risk. In tier 2, we also determined the probability of metal exposure data for various sites to exceed Florida Department of Protection TECs and PECs for sediment quality. Arsenic (25%) in the Holey Land tracts and chromium (25%) in the C-111 system were the most frequently detected COPECs in sediment. Antimony (6%), zinc (6%) and lead (5%) were the least frequently detected COPECs in sediment. The mean hazard

index for metals was highest at S-178 since chromium, copper, nickel and zinc were all COPECs. Based on extractable metal concentrations exceeding $AVS_{10th\ perecentile}$ at S-178 in the C-111 system, metal toxicity was predicted. The mean 90th centile concentration for pore water exposure was highest for arsenic and lowest for cadmium and chromium. Bulk sediment concentrations were highest for zinc (at S-178) and lead (S-176). The estimated acute 10th centile concentration for effects was highest for chromium (III) and fish and lowest for chromium (VI) and arthropods. The probability of pore water exposures of COPECs exceeding the estimated 10th centile concentrations for species sensitivity distributions of acute toxicity data was between 0 and 100 (copper at S-178) %. The estimated NOEC10^{th} centile concentration was exceeded by the estimated 90th centile concentration for pore water distributions at six sites. Copper had the highest potential chronic risk at S-178 and S-177 in the C-111 canal system, based on the probability of pore water exposure concentrations exceeding the estimated chronic NOEC 10th centile at 100 % and 93.32 %, respectively. The COPEC with the next highest probability of exceeding the chronic NOEC 10th centile was lead at 18.48 % in S-176. Zinc and nickel had lower potential chronic risk at S-178. Uncertainties in exposure and effects analysis and risk characterization are discussed.

5.3.1. INTRODUCTION

The objective of this study is to conduct a metal probabilistic ERA to quantify the likelihood that adverse effects will occur from sediment exposures to metals in south Florida canals based on South Florida Water Management District (SFWMD) historical metal monitoring data from 1990-2002 using a two–tier approach with JPCs to characterize risk. As discussed in Section 1.0 natural background concentrations of certain metals do exist in sediment but

the significance of these concentrations is not well understood. Furthermore, some metals are essential to organisms (e.g., chromium III, copper, iron, selenium, zinc) and some metals have no known beneficial effects (e.g., aluminum, antimony, cadmium, lead). An “added risk approach” was not attempted because it is presently considered unreliable (USEPA, 2004). Therefore, the potential risk of “total metal concentrations” to aquatic organisms was considered.

The study uses an approach similar to Sections 5.1 and 5.2 on pesticides with the screening of metals to define contaminants (metals) of potential ecological concern (COPEC) in sediment of canals at 32 sites assuming that organisms are directly exposed to metals from pore water concentrations. In tier 1, we used a hazard quotient approach by comparing metal bulk (whole) sediment concentrations to Florida Department of Protection Sediment Quality Assessment Guidelines for Inland Waters (MacDonald et al., 2003) to determine those metals that exceeded criteria and were thus COPECs. For metal COPECs with sediment-pore water partition coefficients we then estimated pore-water exposure concentrations. We also used the simultaneously extracted metals/acid-volatile sulfide (SEM/AVS) method for predicting the lack of toxicity of the metals Cd, Cu, Ni, Pb, and Zn found at sites (DiToro et al., 1990, 1991) since these metals form insoluble metal sulfides by reacting with iron sulfide (FeS) in sediments and are thus unavailable. DiToro et al. found that no toxicity exists if the AVS of sediment exceeds the molar sum of the metals that are simultaneously extracted. For sediments with SEMs in excess of the AVS toxicity may or may not occur. This can be observed in the studies by Berry et al. (1996) and Hansen et al. (1996). When the SEM to AVS ratio is greater than one, 57% of the sediments were toxic and 43% were not. Even when the ratio is greater than one implying all binding capacity is filled there appears to be

other components of the sediment that are binding metals and reducing its availability and toxicity. We therefore accounted for partitioning to sediment particulate carbon as well as the effect of AVS to predict the occurrence of toxicity (DiToro et al. in press). In tier 2, we compared probability pore water exposure distributions with species response (toxicity) distributions (LC50s, chronic NOECs). The overlap of the distributions is a measure of potential risk to aquatic organisms. The distribution of metal bulk sediment exposure data for various sites was also used to determine the probability of exceeding Florida DEP sediment TECs and PECs for COPECs.

5.3.2. MATERIALS AND METHODS

As in the first two ecological risk assessments the sediment ecological risk assessment (ERA) consisted of the first three phases of the United States Environmental Protection Agency (U.S. EPA) ERA framework (U.S.EPA, 1998): Problem Formulation, Analysis, and Risk Characterization. For additional guidance on the risk of metals to aquatic organisms we also used the recent draft document "Framework for Inorganic Metals Risk Assessment" (USEPA, 2004). In problem formulation, we summarized metal COPEC characteristics (i.e., fate and transport) and assessment (i.e., what is at risk and in need of protection) and measurement endpoints (i.e., what will reveal effects on assessment endpoint). For the analysis, we characterized two major risk components; exposure and effects. Risk characterization, the final phase, provided estimates of risk probability to the ecological entity listed as an assessment endpoint.

A two-tiered ERA approach was suggested by the Aquatic Risk Assessment and Mitigation Dialogue Group (ARAMDG) (SETAC, 1994) and endorsed by the U.S. EPA

(ECOFRAM, 1999) that first uses a hazard quotient (HQ) to screen for COPECs followed by probabilistic risk assessment (PRA). This two-tier ERA approach was used to prioritize hazardous metal COPECs in sediment of the South Florida Water Management District (SFWMD) database. SFWMD has monitored concentrations (mg/Kg) of over 10 metals in sediment from 1990 to the present (R. Pfeuffer, SFWMD; personal communication) at 32 sampling sites in south Florida canals (Figure 5.3.1). All analyses were conducted by the Florida Department of Environmental Protection (FDEP) Central Laboratory (Tallahassee, FL) using U.S.EPA methods and quality assurance procedures. Metals detected included arsenic, antimony, aluminum, beryllium, cadmium, chromium, copper, lead, nickel, zinc, etc. We did not assess the impact of selenium (no Florida DEP sediment criteria), iron (no Florida DEP sediment criteria), magnesium (no Florida DEP sediment criteria) and thallium (no Florida DEP sediment criteria). Mercury was not considered because we did not include it in our three-year monitoring program. Mercury would require a separate ecological risk assessment.

In Problem Formulation for tier 1, concentrations of the metals at each of the 32 sites from 1990-2002 were compared to the FDEP sediment quality criteria (SQC). When a screening benchmark was exceeded ($\geq$0.5) by a metal concentration three or more times at a site, the contaminant was considered a COPEC. SQC for metals are listed in the Appendix. When numerous metals were present at a site a Hazard Index (HI) was also calculated for the site (see Section 1 for HI methodology). In tier 1, to predict toxicity, concentrations of AVS in sediments at sites were compared to the sum of the TEMs ($\sum TEM = TEM_{Cd} + TEM_{Cu} + TEM_{Ni} + TEM_{Pb} + TEM_{Zn}$) at sites. Since we did not have the simultaneously extracted metal (or SEM) we used total extractable metal (or TEM) as an approximation of SEM. The TEM

analysis uses a concentrated acid while the SEM analysis uses a dilute acid. TEM is thus an overestimate of SEM. To take into consideration metal partitioning to organic carbon when the TEM exceeded the AVS estimate the excess metal concentration was normalized to the organic carbon (f_{oc}) at the site. Values for organic carbon came from the pesticide PRA (Section 5.2). We determined the median and 10th percentiles for AVS (µmol/g) from the database (see Appendix) of all SFWMD sites. When the concentration of AVS in sediment exceeded those of TEM it was assumed that no adverse biological effects would occur. We used the latter approach with the median AVS ($TEM\text{-}AVS_{median}$) and 10th percentile AVS ($TEM\text{-}AVS_{10th\ percentile}$) values. The onset of acute and chronic toxicity was considered at $SEM_{x.oc}$ ~100 µmol/gOC (USEPA, 2000; DiToro et al., 2002). No acute toxicity occurs when $SEM_{x.oc}$<100µmol/gOC. The AVS/TEM approach with organic carbon normalization was used to determine the presence of potential metal toxicity in the sediment SERA.

The hypothesis considered in the SERA is: metal COPECs may cause effects at the species and community levels for aquatic organisms in South Florida canals and these effects may adversely affect community structure and function. The ecological risk of each COPEC was evaluated separately.

The nature and degree of uncertainties in the findings was considered in light of our exposure and effects analysis and risk characterization. Methods for risk analysis and risk characterization of the PRA are discussed below.

5.3.3. Risk Analysis

Exposure.

After determining which metals were potential COPECs, the actual measured whole sediment concentration for each metal at each site from the SFWMD database was converted to predicted pore water (i.e., interstitial water) concentrations (PPW_c) for the exposure distribution based on equilibrium partitioning (EqP) methodology (DiToro et al., 1991) (see Figure 5.2.3 Section 5.2). This approach assumes that sediment-pore water exposure is the source of toxicity in sediment to organisms. To convert from measured bulk (whole) sediment metal concentrations (mg/kg) for each COPEC to predicted pore water concentrations (PPW_c), metal K_p (L/kg) values (partition coefficient between pore water and sediment solids) were used in the following equation:

PPW_c (μg/L) = MC_{sed}/K_p MC_{sed} is the measured concentration of COPEC

Metal partition coefficients (Table 5.3.1) were obtained from USEPA (1999). Values were estimated by regression or from the model MINTEQA2.

Pore water concentrations were then fit to lognormal exposure distributions when there were four or more values above the detection limit (Solomon et al., 2000). A log normal distribution of the exposure data (i.e., monitoring data) was assumed as documented in the literature (Solomon et al., 1996; Hall et al., 1999). Concentrations were ranked from smallest to highest and assigned a centile ranking (j) at each site using the equation j*100/(n+1), where j is the rank assigned to a particular concentration and n is the total number of sample observations (including non-detects) at each site (Hall, Jr. and Gardinali, 2004). Centile rankings were converted to probits and plotted against the corresponding $\log_{10}$ values of the PPW_c. Linear regression was performed using the algorithms found in PRAT-1 software

(Solomon et al., 2000). Samples below the detection limit were given dummy values of 0, and although not included in the regression analysis, they were assigned a rank and assumed to be distributed at the lower end of the distribution (Hall, Jr. et al., 1999; Solomon et al., 1996). The latter approach for pore water exposure distributions was also followed for bulk sediment concentrations of metals.

The 90th centile pore water exposure concentration was calculated from the lognormal concentration distribution for each COPEC at all sites. The 90th centile is an "exposure benchmark" used in PRAs (Solomon et al., 1996). It assumes that any sample taken has a 90 % chance of being below the estimated 90th centile concentration if the values in the exposure distribution are unbiased and accurately represent the concentrations found over that time period and location (Giddings et al., 2000). The 90th centile bulk sediment exposure concentration was also calculated from the lognormal concentration distribution for each COPEC at all sites.

Exposure distributions were not prepared for either metal COPECs that had toxicity data bases that were insufficient to prepare species sensitivity distributions or for sites that were located distant from the Parks and therefore would not impact these resources.

Effects.

Toxicity data (see Appendix) for the PRA includes a distribution of the range of species responses (or SSDs) to each COPEC. All available toxicity data for freshwater organisms (fish, invertebrates, etc.) were used in the preparation of SSDs.

Acute (i.e., LC50, EC50) toxicity data for freshwater organisms were first obtained from the AQUIRE database (http://www.epa.gov/ecotox/). Regulatory reviews such as water

quality criteria documents were also used. We also determined that predicting the likelihood of potential risks associated with chronic exposures would also be an applicable scenario. No Observable Effect Concentrations (NOECs) from chronic tests were therefore also used to prepare SSDs and obtained from the above sources.

The SSD distribution of acute toxicity data and chronic NOECs for organisms to each COPEC was evaluated using the approach described in SETAC (1994). However, for freshwater toxicity studies with metals, hardness (concentrations of calcium and magnesium) is one water quality parameter that significantly influences toxicity (Hamelink et al., 1994). As water hardness increases the toxicity of trace metals to aquatic biota generally decreases due to its effects on the ability of an organism to osmoregulate or to its influence on altering metal bioavailability. The U.S.EPA addresses the influence of hardness on toxicity of metals in development of freshwater quality criteria (U.S.EPA, 2002). For metal toxicity data (i.e., cadmium, copper, chromium III, lead, nickel, zinc) used in this risk assessment, hardness was considered in the ranking of sensitivities of freshwater species. Therefore, to compare freshwater toxicity data among species, all acute data were adjusted to a consistent hardness of 200 mg/L $CaCO_3$. This value was selected because it is the mean hardness for the entire South Florida Water Management District database. If hardness data were not available with a freshwater toxicity test value for a species, then the toxicity data were not used in the analysis. The following equation (Hicks et al., 2002) was used to adjust the freshwater acute toxicity data:

$$\text{Adjusted LC50} = [200/\text{hardness}]^{\text{slope}} * \text{LC50}$$

where hardness is that associated with the original toxicity test, 200 (mg/L $CaCO_3$) is the adjusted hardness, and slope is the pooled slope taken from the water quality criteria document (U.S.EPA, 2002). Note that the adjusted toxicity values are based on total metals sine we will be comparing these toxicity distributions to distributions of pore water concentrations which are also based on total measured metal in sediment. Chronic toxicity data were not normalized to consistent hardness because the data base was too small. Normalizing for hardness would have decreased the chronic toxicity data base even further because hardness calculations were not made in several chronic tests and therefore these tests would have been eliminated making the chronic data base even smaller. However, Crommentuijn et al. (1997) point out that the relationship between hardness and chronic toxicity of metals appears to be much less consistent than between hardness and acute toxicity and that the influence can be relatively small, especially in the range of hardness between 50 and 200 mg/L (as $CaCO_3$).

Toxicity values (i.e., LC50s, NOECs) were ranked by concentration, and for each species toxicity value the centile ranking was calculated by multiplying individual ranks by 100/ (n+1), where n is the total number of species. These centiles were plotted against log-transformed concentration and linear regression was conducted to define each distribution. The 10th centile of the SSD for each COPEC from acute data (LC50, EC50) and chronic NOEC data are the "toxicity benchmarks" that were used since they are widely accepted and used to characterize risk (Solomon et al., 1996). Acute toxicity values were only used if they came from tests with measured concentrations. A single species with toxicity endpoints (i.e., LC50s) only appeared once in a distribution. NOEC values were only used from toxicity tests greater than 96 hours in duration with endpoints that included survival, growth, development,

and reproduction. If multiple acute toxicity endpoints were available for a single species, the geometric mean of the endpoints was used to represent the toxicity for that species (ECOFRAM, 1999).

5.3.4. Risk Characterization-Tier 2

Potential risk to freshwater organisms from exposures to COPECs in porewater was determined by comparing pore water exposure distributions by sampling site with the 10th centiles from the acute LC50 and chronic NOEC data distributions for each COPEC. The percent exceedence of the 10th centile for each COPEC was used as a risk estimate (Solomon et al., 1996).

The last step in the PRA used joint probability curves (JPCs; or exceedence profiles) for each exposure at a site to rank potential risk of COPECs and sites. JPCs were constructed using PRAT-1 software (Solomon et al., 2000).

We also used the exposure data for sites with metal COPECs to determine the probability of exceedence of FDEP sediment quality TEC and PEC standards (Hall et al., 2003). PECs and TECs are discussed in Section 1.2.

5.3.5. RESULTS AND DISCUSSION

5.3.5.1.Problem Formulation

Tier 1.

Tier 1 indicates that the metals arsenic, antimony, cadmium, chromium, copper, lead, nickel and zinc are COPECs since Florida sediment quality criteria were exceeded at 10 sampling sites throughout the canals within the South Florida Water Management District (Table 5.3.2). Figure 5.3.1 shows the sampling locations of the sediment quality violations for the

COPECs. Metals had multiple sediment quality violations at sites from 1990 to 2002. Arsenic (25%) in the Holey Land tracts and chromium (25%) in the C-111 system were the most frequently detected metal COPECs. The least frequently detected metal COPECs were: cadmium (12%), nickel (11%), copper (10%), antimony (6%), zinc (6%) and lead (5%). Antimony, chromium, copper, lead, nickel and zinc had sediment quality violations on some part the C-111 system (S-176, S-177, S-178, S-18C) which may be important as a source of water for ENP. Cadmium was only a COPEC in the Holey Land tracts (SD2, 3, 4). The 10 sites with COPECs represent approximately 31 % of the total sediment sampling sites monitored by the SFWMD for metals.

The hazard index for all sites is summarized in Figure 5.3.2 and Table 5.3.3. S-176, S-177, S-178, and S-18C on the C-111 system had some of the highest HI's of the 32 sampling sites. S-178 had the highest HI of all C-111 sites and is primarily affected by the Frog Pond Agriculture area. S-177 and S-178 also had high HIs for pesticides (see Section 5.2). The main metals at S-178 responsible for the high HI were zinc, followed by copper, chromium and nickel. The main metals at S-177 responsible for the high HI were chromium, copper and antimony. At S-176 lead, chromium and antimony were responsible for the HI. At S-18C chromium, nickel arsenic and zinc were responsible for the HI.

For all SFWMD AVS data the $AVS_{10th\ percentile}$ was 1.71μmol/g and the AV S_{median} was 7.15. Using the TEM-AVS_{median} approach to predict toxicity there was no excess metal for any site but using the TEM-$AVS_{10th\ percentile}$ approach there was excess metal at S-178 (Table 5.3.4). When the excess (TEM-$AVS_{10th\ percentile}$) was normalized for organic carbon it was >100μmol/gOC (Table 5.3.5). The latter result suggests the potential for metal toxicity (i.e., acute and/or chronic) at S-178 (DiToro et al., in Press).

Although antimony is a COPEC there is insufficient toxicity data to prepare species sensitivity distributions. In addition, we did not consider cadmium any further because it was predominately found in the Holey Land tract which is in north Broward County far north of the National Parks.

COPEC Characteristics in the Environment.

Since Tier 1 indicated that arsenic, chromium, copper, lead, nickel, and zinc were COPECs a brief summary of their environmental characteristics is discussed below.

Chromium. The environmental distribution and effects of chromium (Cr) have been discussed in reviews (Ecological Analysts, 1981; Eisler, 1985). Chromium is principally used in the U.S. in metallurgy and chemical industries. Weathering processes and anthropogenic activities are responsible for amounts mobilized in the environment.

Atmospheric emissions contribute 4 to 6 times more Cr to aquatic systems than do liquid wastes. For aquatic environments the major sources are electroplating and metal finishing industries and publicly owned treatment plants (POTWs); minor sources are chemical plants, tanneries textile manufacturing and urban/residential runoff. Coal combustion and cooling towers (as corrosive inhibitor) from the electric power industry also serves as a minor source of Cr (especially +6 form, see below). Chromium in phosphates used as fertilizers may be an important source in soil and water. Elemental chromium is stable but is not usually found pure in nature. chromium can exist in oxidation states from -2 to +6 but is most frequently found in the environment in the trivalent (+3) and hexavalent (+6) oxidation states. The other forms (+2, +4, +5) are unstable and are rapidly converted to +3 which is oxidized to +6.

Chromium +3 functions (maintains glucose, lipid, protein metabolism) as an essential element in mammalian species. Hexavalent chromium is more toxic than the +3 form. Chromium toxicity in aquatic systems is affected by hardness, temperature, pH, and water salinity. Under oxic conditions hexavalent chromium dominates in aquatic systems. Hexavalent Cr can exist in three forms depending on pH and are very water soluble. It oxidizes organic matter and yields oxidized organic matter and Cr +3. Trivalent Cr forms stable complexes with negatively charged inorganic and organic compounds and is unlikely to be found uncomplexed in aqueous solutions. Hexavalent Cr is more toxic to freshwater biota in soft and acid waters. The organisms most sensitive to Cr+6 based on LC50s were freshwater crustaceans and rotifers. Growth of algae and the common duckweed, and the survival and fecundity of *Daphnia magna* were effected at 10 ppb (Eisler, 1986). In sediments, Cr exists in the two oxidation states. Cr +6 is highly oxidized and unstable in reducing environments (DeLaune et al., 1998). Cr+6 is very soluble and highly toxic while Cr+3 has low solubility at environmentally relevant pH (DeLaune et al., 1998; Barnhart, 1997) and it has low toxicity (Wang et al. 1997; Thompson et al., 2002).

Chromium is not typically included among the soluble extractable metals (SEM) because in contact with AVS it does not form an insoluble sulfide but it rather produces oxidation of the sulfide with reduction of chromium. However, it has been hypothesized through scientific investigation that in anoxic sediment where AVS is present Cr will be present as Cr+3 since the Cr+6 is not stable in reducing environments such as anoxic sediments (Berry et al., 2004). These investigators showed that pore water contain little Cr when measurable amounts of AVS are present in sediment and any sediment toxicity that is found cannot be correlated with it.

Copper. Copper is an essential micronutrient (in hemoglobin formation, carbohydrate metabolism, catecholamine synthesis) for plants and animals at low concentrations and is naturally occurring in surface waters. For example, background concentrations have ranged from 0.03-0.23 ug/l in surface saltwater and from 0.2-30 ug/L in surface fresh waters. However, copper concentrations in water receiving anthropogenic input (from mine tailings) can vary up to100 ug/L.

The major global copper sources include mining and smelting, industrial emissions (combustion of fossil fuels) and effluents, municipal wastes and sewage sludge. Copper has been widely used to control unwanted species of freshwater algae and macrophytes. In fact, copper sulfate is approved by USEPA as an algicide in water to raise fish for human consumption. Copper compounds are used to control freshwater snails that are vectors of human disease. Copper is also the active ingredient in many antifouling paints. It should be noted that out of all of the uses of copper only a small percentage is used to manufacture chemicals but mainly copper sulfate (65% for agriculture-as fungicides, algicides, insecticides, repellents, nutritional supplements; 28% is used in wood preservatives, electroplating, and azo dyes; 7% is used in water treatment to control algae).

Copper exists in four valence states: Cu^{0}, Cu^{t1}, Cu^{t2}, and Cu^{t3}. Cupric ions account for about 1% of total dissolved copper in saltwater and less than 1% in freshwater (Boyle, 1979). The free ionic copper (Cu^{2t}) is the most readily bioavailable and toxic chemical species and availability is modified by biological and abiotic factors (alkalinity, pH, organic matter, temperature). The free ion concentration is sensitive to complexation in the presence of natural organic chelators.

The USEPA since 1980 has published five guidance documents concerning ambient aquatic water quality life criteria for copper (USEPA, 1980, 1985, 1986, 1996, 2003).

Up until the 2003 document, previous water quality criteria for metals was based on "total metals" and water hardness as the rate limiting water quality component. Recently, the USEPA made the decision to allow criteria development on the basis of "dissolved metal" because it is thought to be the bioavailable fraction. The USEPA used the Biotic Ligand Model (BLM) in the 2003 document to develop acute copper water quality criteria since it "accounts for the important water chemistry factors that affect toxicity". Toxicity is related to the metal bound at an active site and binding is related to dissolved metal concentrations and complexing ligands in water. The WER is important in establishing site-specific variations to water quality criteria of metals but the BLM can be applied across spatial and temporal scales. The BLM will predict the dissolved concentrations of copper required to cause acute mortality. BLM incorporates metal speciation reactions and organic interactions and will thus allow prediction of metal effect levels to a variety of organisms over a wide range of water quality conditions.

In south Florida copper has a long history of use in agriculture (e.g., citrus groves) as a fungicide and it is found in fertilizers. In the early 1900's copper containing fertilizers accounted for as much as 34 kg Cu/ha annually and fungicidal sprays contributed an additional 10kg Cu/ha annually. Surface soils for mature citrus groves contained as much as 540kg Cu/ha.

Lead. Lead is used primarily in the manufacture of storage batteries, pigments, alloys and ammunition. It is ubiquitous in the environment. It is neither essential nor beneficial to living

organisms. Lead (Pb) occurs in four valence states: Pb^0, Pb^+, Pb^{2+}, Pb^{4+}. All forms are environmentally relevant except the monovalent from. In nature it mainly occurs as Pb^{2+}, and it is oxidized to Pb^{4+}under strong oxidizing conditions. Lead is most soluble and bioavailable under conditions of low pH, low organic content, low concentrations of suspended sediments and low concentrations of salts. Lead in natural waters is precipitated to the sediment as carbonates or hydroxides. In sediments, lead is mobilized and released when pH is decreased or ionic composition changes. Lead in sediment may be transformed to tetraalkyllead compounds. Methylation of lead occurs in sediments at increased temperatures, reduced pH and microbial activity. Lead concentrations in non-biological materials were higher in sediments, soils and pore waters than in the atmosphere and other hydrological compartments.

Nickel. Nickel is ubiquitous in the environment. It is an essential micronutrient for normal of many species including microorganisms. Activities that contribute to nickel loadings in the environment include mining, smelting, refining, alloy processing, scrap metal reprocessing, fossil fuel combustion, and waste incineration. More than 90% of the world's nickel is obtained from pentlandite, a nickel-sulfitic mineral. The rest of the nickel is obtained from nickel minerals such as laterite, a nickel oxide ore. Natural sources of airborne nickel include soil dust, sea salt, forest fires, and vegetation exudates. They account for 16% of atmospheric nickel burden. Human sources account for 84% of all atmospheric nickel. Chemical/physical degradation of rocks/soil, atmospheric deposition and discharges of industrial and municipal wastewater release nickel into surface waters. It is also poorly removed from wastewater. Disposal of sewage sludge or application of sludge as a fertilizer

is a primary human source. Atmospheric emissions and emissions from electric power plants are secondary sources.

Nickel normally occurs in the 0 and +2 oxidation states although other states exist. In natural water Ni^{2+} is the dominant chemical species in the form of $(Ni(H_20)_6)^{2+}$. In alkaline soils, the major components of the soil solution are Ni^{2+} and $Ni(OH)^{+}$, in acidic soils, the main solution species are Ni^{2+}, $NiSO_4$ and $NiHPO_4$. Nickel enters surface waters through three natural sources: as particulate matter in rainwater, through dissolution of primary bedrock materials and from soil phases. In aquatic systems nickel occurs as soluble salts adsorbed or associated with clay particles, organic matter, and other substances. The divalent ion is the dominant species in natural water at pH 5-9 occurring as $(Ni(H_20)_6)^{2+}$. Fate of nickel in fresh- and salt-water is affected by pH, pE, ionic strength, type and concentration of ligands and the availability of solid phases for adsorption.

There is little evidence for biomagnification of nickel in the food chain. Although algae and macrophytes have elevated concentrations of nickel animals appear to regulate content in their tissues. Nickel concentrations do not increase with ascending trophic levels of the food chain and predatory organisms do not have higher concentrations.

Nickel is an essential micronutrient for maintaining health of species of invertebrates and plants. It reduces the photosynthesis and growth of algae. Effects of excess have been noted on echinoderms, fishes, amphibians, mollusks and crustaceans. Ionic nickel is lethal to sensitive species of aquatic organisms at 11-113 μg/L. Deaths occur in rainbow trout embryos at 11-90 μg/L, daphnids at13 μg/L, embryos of channel catfish at more than 38 μg/L and embryos of largemouth bass at113 μg/L. However, most adverse effects to aquatic

organisms occur in the mg/L range. Nickel is most lethal to freshwater crustaceans and fish at pH 8.3 and least at pH 6.3.

Zinc. Zinc is 25th in order of abundance of metals. It is found in coal, oils, lubricants, tire, and fossil fuels. Zinc is used in ht production of iron corrosive alloys and brass and in galvanizing steel and iron products. Zinc undergoes oxidation at the surface. Galvanized products are widely used in construction materials, automobile parts and household appliance. Zinc oxide is use to form pigments in rubber processing and to coat photocopy paper. Zinc sulfate is used in fungicides and in zinc deficient soils. It is used with copper and arsenic lead wettable powders and it can minimize the toxic effects these metals. Major source of anthropogenic zinc to the environment include electroplating, smelting, and ore processors, drainage from active and inactive mining operations, domestic and industrial sewage, combustion of fossil fuels and solid wastes, road runoff, corrosion of zinc alloys and galvanized surfaces, and erosion of agricultural soils.

Zinc in the aquatic environment is eventually partitioned into sediment. Zinc released is enhanced under conditions of high dissolved oxygen, low salinity, and low pH. Dissolved zinc consists of the toxic aquo ion Zn $(H_2O)_6^{2+}$ and other complex species. Aquo ions and other zinc toxic species have their greatest effect on aquatic organisms under conditions of low pH, low alkalinity, low dissolved oxygen and elevated temperature. The primary target site in fish is the gill epithelial.

Zinc can occur as a sulfide, oxide, or carbamate. In water it is divalent and it coordinates with six water molecules to form the aquo ion. Zinc ligands are soluble in neutral and acidic solutions. In freshwater, zinc is most soluble at low pH and low alkalinity. It exists

predominately as the aquo ion at pH>4 and <7. The aquo ion is suspected as being the most toxic species however aquo ion concentrations decrease under conditions of high alkalinity, at pH 7.5 and increasing salinity. Under conditions of high alkalinity and pH 6.5, the most abundant species are $ZnHCO_3^+$, Zn^{2+} and $ZnCO_3$, at low alkalinity and at elevated pH 8.0, the descending order of abundance was Zn^{2+}, $ZnCO_3$, zinc humic acid, $ZnOH^+$, and $ZnHCO_3$. Water hardness is the principal modifier of acute toxicity. Increased alkalinity or water hardness decreases toxicity to freshwater organisms. When zinc is dissolved this effect is associated with decreased concentration of aquo ions and is heightened by increased pH. Suspended zinc carbonate may be toxic and suspended zinc hydroxide is relatively non-toxic. Zinc carbonate composes <1% of dissolved zinc at low pH and low alkalinity but it predominates at high pH and high alkalinity. Organozinc are not stable but under reducing conditions may liberate Zn^{2+}.

In seawater, zinc can exist in dissolved state, as a precipitate or adsorbed to particles. Soluble zinc in seawater exists as free hydrated ions, in inorganic complexes or as organic complexes. At pH 8.1 the dominant species of soluble zinc are zinc hydroxide followed by the free ion. at pH 7 the percentage of dissolved zinc present as the free ion increases to 50%.When dissolved organic materials are present most of the zinc is present as organozinc complexes. In estuaries at high salinities the aquo ion predominates but at low salinities zinc phosphate predominates.

Most of the zinc in the aquatic environment is sorbed onto hydrous iron and manganese oxides, clay minerals and organics and eventually partitions into the sediment. In sediments it is present as precitated zinc hydroxide, ferric and maganic oxyhydroxide precipitates, insoluble complexes and insoluble sulfides.

Zinc interacts with numerous chemicals (cadmium -antagonistic, copper-more than additive, lead-more than additive) and with nickel the effects are additive. Zinc produces adverse effects on growth, survival, and reproduction of aquatic organisms at nominal concentrations between 10 and 25 Zn μg/L. Crustaceans appear to the most group.

Arsenic. Arsenic is a naturally metalloid as sulfides which ranks 20th in abundance in the earth's crust (Cullen and Reimer, 1989). Weathering and anthropogenic inputs due to smelting operations and fossil fuel combustion are responsible for emission of arsenic into the atmosphere where it is redistributed to terrestrial and aquatic environment by rain and dry fallout. The major uses of arsenic are in the production of herbicides, insecticides, dessicants, wood preservatives and growth stimulants for plants and animals. Some evidence suggests that arsenic is an essential micronutrient in animals (Uthus, 1992). Arsenic has four valence states in water and sediment: -3, 0, +3 and +5. Arsenic is rarely found in it's free state. As^{-3} is found in highly reducing environments. The dominant form of arsenic in oxygenated water is arsenate (As V). Arsenate dominates in oxidized sediments and is associated with iron oxyhydroxides. In reducing sediments, arsenate is reduced to arsenite and is associated primarily with sulfide minerals. The trivalent species are generally considered to be more toxic, more soluble and more mobile than As^{+5} species. In water arsenic occurs in both inorganic and organic forms and in dissolved and gaseous states. The form of arsenic in water depends on Eh, pH, organic content, suspended solids, dissolved oxygen and other variables. Arsenic primarily exists in water as a dissolved ionic species. Common forms of arsenic in water are arsenate, arsenite, methanearsonic acid (MMA), and dimethylarsinic acid (DMA). The formation of inorganic pentavalent arsenic, the most common species in water,

is favored by under high dissolved oxygen, basic pH, high Eh and reduced content of organic material. Also contributing to higher levels are the natural levels of phosphate species. Arsenates are readily adsorbed by colloidal humic material, low ph low phosphate and low mineral content. Arsenic is removed from seawater by iron hydroxide. In sediments arsenate is reduced to arsenite and methylated to MMA and DMA. Arsenates are more strongly sorbed to sediments than other arsenic forms.

Assessment and Measurement Endpoints.

The long term viability of aquatic communities in south Florida canals is the assessment endpoint. The specific assessment endpoint is the protection of at least 90% of the species 90% of the time (10th percentile from species sensitivity distributions) from COPEC exposures. Aside from acute sediment exposures, chronic sediment exposures and risk resulting from such exposures to organisms is a primary consideration because of the environmental persistence of all the metal COPECs in sediment and their slow desorption to the water column. The amount of the particulate form of the COPEC suspended into the water column due to diffusive events (e.g., bioturbation, waves) cannot be entirely considered insignificant but given the long aging process and that bioturbation and wave action is minimal in freshwater canal systems we assume desorption into the water column will be minimal. It should be noted that the particulate forms present potential exposures for water column organisms by ingestion of particle sorbed contaminants. Furthermore, when both particle-sorbed organics and metals are suspended into the water column there is an increase of dissolved and colloidal contaminant concentrations in water (O'Conner and Connolly, 1980; DiToro, 1985). Measurement endpoints include all metal toxicity data

(survival, growth, and reproduction) generated from laboratory toxicity studies. The latter will be used to define acute and chronic impact on aquatic communities.

The assessment endpoint is in keeping with the management goals set forth by the Science Subgroup (1996) of the south Florida ecosystem restoration. Not presently included within the assessment endpoint are any specific endangered or threatened species.

5.3.5.2. Risk Analysis

Exposure.

The partition coefficients (K_p) of metal COPECs are presented in Table 5.3.1. PRAs were conducted at 10 out of the 32 sites with COPECs. Table 5.3.6a presents the statistics for the lognormal distributions of metal bulk sediment concentrations for the COPECs at the 10 sampling sites. The highest 90th percentile for bulk sediment was for zinc at S-178 followed by lead at S-176, both on the C-111 system. The highest 90th percentiles for copper, chromium and nickel were also at S-178. The lowest 90th percentiles were for cadmium in the Holey Land tract. Arsenic was detected in the Holey Land tracts SD1, 2, and 3 and antimony was detected infrequently. Table 5.3.6b presents the statistics for the lognormal distributions of the predicted porewater concentrations for the COPECs at the 10 sampling sites. The highest 90th percentiles were for arsenic in the Holey Land tract. The lowest 90th percentiles were for chromium in the C-111 system (S-176, S-177, S-178 S-18C) and cadmium in the Holey Land tract (SD 2, 3, and 4).

Effects.

Species acute effects data for COPECs are summarized in Table 5.3.7**.** Native and nonnative species of freshwater organisms used in toxicity tests for each COPEC are listed in the Appendix. Acute toxicity 10th percentile values were lowest for copper and chromium VI in arthropods. It should be noted that based on the presence of measurable AVS at sediment sites, it is assumed that hexavalent Cr will not be present because of the reducing environment and most of the Cr will be in the trivalent form and that pore water will have insignificant concentrations of Cr so that any toxicity at sites will not be related to Cr exposure (Berry et al., 2004). Typically, fish had the highest 10th percentiles (least sensitive) for all metal COPECs. In general, the lowest 10th percentiles for metals were for arthropods.

The SSDs of NOEC data for each COPEC are presented in Table 5.3.8. There were not enough chronic tests for arsenic and chromium to determine a NOEC 10th percentile concentrations. The lowest NOEC 10th percentile was for copper (all) at 0.68 µg/L. This was a "community-based" NOEC because it included "all" the available chronic toxicity data for "all" species.

5.3.5.3. Risk Characterization

The probability of pore water exposures of all COPECs exceeding the arthropod acute 10th centile values are presented in Table 5.3.9**.** Risk estimates were only determined for arthropods because they represented the most sensitive group to metals (Table 5.3.7). Copper at S-178 and S-177 had the highest acute risk estimates followed by zinc at S-178. Arsenic risk estimates were highest in the Holey Land tract. The probability of predicted pore water exposures exceeding the chronic NOEC 10th centile values for each COPEC at each site is

presented in Table 5.3.10**.** The sites with the highest potential chronic risk from a single COPEC was in the C-111 system, based on the probability of pore water exposures exceeding the NOEC 10th centile value at 100 % for copper at S-178 and at 93% at S-177. The metal with the next highest probability of exceeding the NOEC 10th centile was lead at 18.5 % at S-176. Zinc and nickel were also present at S-178 with low chronic risk. There was insufficient toxicity data to assess chronic risk for arsenic.

JPCs for sites with potential acute risk to aquatic organisms are illustrated in Figures 5.3.3 to 5.3.12. Each point on each curve represents the percentage of time exposure concentrations will exceed a percentage of species acute values. Sites S-177 and S-178 serve as a potential source of copper and zinc to Everglades National Park. S-18C serves as a potential source of arsenic to the Park. JPCs for sites with potential chronic risk to aquatic organisms are illustrated in Figures 5.3.13 to 17.

The probability of COPEC metal bulk sediment concentrations exceeding the FDEP SQAG TEC and PEC by site is presented in Table 5.3.11. The probability of copper exceeding the sediment TEC is 99.96 % at S-178 to 6.81 % at S-177. The probability of copper exceeding the PEC was 0.07 % at S-177 to <0.01 % at S-178. The probability of chromium exceeding the sediment TEC is 39.11 % at S-178 to 0.08 % at S-176. The probability of chromium exceeding the PEC was <0.01 % at S-176, S-177, S-18C to 0.03 % at S-178.

5.3.5.4. Uncertainties

Exposure.

Exposure data for this assessment were obtained from the South Florida Water Management District monitoring program for 1990-2002 from 32 sampling sites in freshwater canals. This

is the most comprehensive sediment contaminant database in south Florida. Although chemical analyses of all contaminants was from one laboratory the total number of sampling sites in the monitoring program is limited considering the 1400-mile system of canals in south Florida. The sampling frequency is also limited since sites were sampled only 1-2 times per year and not consistently. Therefore, the database is inadequate to determine real differences in contaminant exposure between the wet and dry seasons.

Chromium is a COPEC based on measuring total Cr. However, in sediments it exits in two oxidations states: Cr(III) and Cr(VI). Cr(III) has low solubility at environmentally relevant pHs and it possesses low toxicity. Cr(VI) is unstable in reducing environments like anoxic sediments and it is toxic. Cr speciation was not measured. We assumed that since AVS is formed only in anoxic sediments those sediments with measurable AVS concentrations will not contain toxic concentrations of Cr(VI) (Berry et al., 2004). Therefore, most of the chromium will be present as the non-toxic Cr(III).

For the SEM/AVS comparison we used TEM instead of SEM since it was not measured in the present monitoring program. TEM represents an overestimate of SEM. For AVS we determined the $AVS_{10th\ percentile}$ and the AVS_{median} from the SFWMD AVS database. Excess metal only occurred using $AVS_{10th\ percentile.}$ Using the 10th percentile is a conservative approach. We then normalized the excess values to consider partitioning to sediment organic carbon when in fact other phases may also be important for metal sorption.

Pore water concentrations for exposure distributions were estimated from the whole (bulk) sediment concentrations of COPECs based on the use of metal partition coefficients from the USEPA (USEPA, 1999).

Effects.

There were few acute and chronic sediment toxicity studies for COPECs. We therefore assumed that toxicity to pore water would be similar to water only exposures and used acute toxicity data from water only tests to prepare SSDs. There is uncertainty in this assumption; however, several investigations have found that toxicity estimates from water only acute tests were similar to exposures from measured porewater concentrations in bulk sediment tests with *Hyalella azteca* (Hoke et al., 1994; Lotufo et al., 2001).

There was insufficient acute and chronic water toxicity tests for antimony to characterize SSDs. Chronic water tests were not available for arsenic and chromium (III, VI). Therefore chronic NOECs were not available for chronic risk characterizations of these metals. There were chronic water toxicity tests for lead, nickel and zinc but they were limited in number. Therefore, all chronic NOECs from tests for the latter metals were combined into one SSD for each metal and separate SSDs for fish, invertebrates, etc. could not be determined because the n values were too small.

As a result of the limited number of species used in acute and chronic toxicity tests for the COPECs there is uncertainty of extrapolating these data to responses of native species from south Florida ecosystems. However, many of the freshwater species used in toxicity tests with COPECs are native to south Florida ecosystems (see Appendix).

Risk Characterization.

One source of uncertainty that was not considered is the potential effects from COPECs through joint or interactive effects with other contaminants and with one another. Monitoring studies have shown that canals contain numerous metal and organic contaminants

in sediment and water (Miles and Pfeuffer, 1997; Pfeuffer and Rand, 2004). Our characterization of ecological risk is limited to the locale of sites from which sediments were analyzed. However, there are regional implications, because of the likelihood of sediment transport to other parts of the water management system, including water conservation storage areas (WCA's), productive coastal estuaries, and Everglades and Biscayne National Parks.

There were insufficient chronic toxicity data for arsenic and chromium (III and VI) and chronic NOECs were not estimated. Therefore, there is uncertainty as to the extent of chronic risk for arsenic at five sites (Holey Land tracts SD1, 2, and 3 and S-18C, WCA2F1) and chromium at four sites (S-176, S-177, S-178, S-18C). The C-111 sites are potential sources of contaminants for ENP. Also chronic risk to individual species groups could not be determined for lead, nickel and zinc because of the small chronic toxicity databases for these metals. We did not characterize risk to cadmium although it was a COPEC because it was only detected in the Holey Land tracts SD2, SD3 and SD4 which should not be a source of contaminants for Everglades or Biscayne National Parks. Antimony was a COPEC but both the acute and chronic toxicity databases were limited so that risk characterizations could not be conducted.

5.3.6. CONCLUSIONS

Based on a tier 1 assessment of over 10 metals in sediment at 32 sampling sites from south Florida freshwater canals only arsenic, antimony, cadmium, chromium, copper, lead, nickel and zinc exceeded sediment quality criteria and were therefore classified as COPECs. Risk associated with acute exposures of freshwater arthropods to copper and zinc was estimated to

be high only in the C-111 system. In addition, the potential risk to freshwater organisms from chronic exposures to copper followed by lead was estimated to be high based on NOEC 10th centiles. Copper, zinc and lead are COPECs that should be a high priority for future sediment monitoring programs in south Florida canals (C-111) impacting Everglades National Park.

Table 5.3.1
Partition coefficients for sediment/porewater (metals)

Metal	Log K_d
Antimony	3.7
Arsenic	2.4
Cadmium	3.3
Chromium	4.9
Copper	3.5
Lead	4.6
Nickel	3.9
Zinc	4.1

Table 5.3.2

Results of Tier 1 Assessment: Use of Screening Benchmarks to Determine Metal COPECs in Sediment

Chemical	COPEC	Comments
Arsenic	Yes	Exceeded SQC[1] 59 times. COPEC at sites: HOLYSD1, HOLYSD2, HOLYSD3, S18C, and WCA2F1.
Antimony	Yes[2]	Exceeded SQC 14 times. COPEC at sites: S176, S177, S18C and S332.
Aluminum	No	Exceeded SQC once at CA3-3 and HOLYSD2.
Berrylium	No	No SQC available for compound
Cadmium	Yes[3]	Exceeded SQC 16 times COPEC at sites: HOLYSD2, HOLYSD3 and HOLYSD4.
Chromium	Yes	Exceeded SQC 32 times. COPEC at sites: S176, S177, S178 and S18C.
Copper	Yes	Detected in sediment 144 times. Exceeded SQC 19 times. COPEC at sites: S177, & S178.
Lead	Yes	Exceeded SQC 35 times. COPEC at site S176.
Nickel	Yes	Exceeded SQC 14 times. COPEC at sites: S178 and S18C.
Selenium	No	No SQC for compound. Most frequently detected in Holeyland.
Zinc	Yes	Exceeded SQC 17 times. COPEC at site S178.

1. SQC; Sediment Quality Criteria (HQ $\geq$ 0.5)
2. Cannot conduct PRA for this compound because of insufficient toxicity data for SSD
3. Will not conduct PRA on this compound because COPEC sites do not impact ENP

Table 5.3.3

Summary of mean metal hazard indices at sites (n=32) in the South Florida Water Management District monitoring program (1990-2002).

Site	Mean	N	Std. Deviation	Median	Minimum	Maximum	Range
ACME1DS	1.57	1	.	1.57	1.57	1.57	.00
CA2-15	.85	6	.66	.94	.01	1.80	1.79
CA3-15	2.75	6	1.96	2.83	.40	4.70	4.30
CA3-3	2.13	6	.72	2.15	1.07	2.97	1.90
G94D	.20	1	.	.20	.20	.20	.00
GORDYRD	.18	1	.	.18	.18	.18	.00
HOLYSD1	1.78	19	1.11	1.53	.31	4.42	4.11
HOLYSD2	2.13	18	1.84	1.49	.26	6.92	6.66
HOLYSD3	1.15	17	.73	1.03	.41	3.24	2.83
HOLYSD4	1.26	18	.89	1.04	.17	3.64	3.47
LO308C	2.73	1	.	2.73	2.73	2.73	.00
LOX10	1.49	6	.83	1.57	.31	2.64	2.33
LOX8	1.23	6	.97	.79	.36	2.60	2.24
S176	2.32	16	1.41	2.07	.65	5.39	4.74
S177	2.40	15	2.31	1.60	.51	9.33	8.82
S178	4.86	16	1.83	5.04	1.78	7.10	5.31
S18C	2.13	18	1.78	1.51	.58	8.00	7.42
S2	1.15	1	.	1.15	1.15	1.15	.00
S235	.09	1	.	.09	.09	.09	.00
S3	.60	1	.	.60	.60	.60	.00
S332	1.82	15	1.36	1.23	.52	4.43	3.92
S355A	.99	2	.13	.99	.90	1.08	.19
S355B	.94	2	.69	.94	.45	1.43	.98
S4	3.17	1	.	3.17	3.17	3.17	.00
S6	.92	1	.	.92	.92	.92	.00
S78	.19	1	.	.19	.19	.19	.00
S79	4.13	1	.	4.13	4.13	4.13	.00
S80	2.38	1	.	2.38	2.38	2.38	.00
S99	.40	2	.40	.40	.12	.69	.56
STA2C1SD	.66	1	.	.66	.66	.66	.00
WCA2F1	1.37	6	.60	1.45	.36	2.10	1.74
WHTCYPRK	.08	1	.	.08	.08	.08	.00

Table 5.3.4

SFWMD excess total extractable metal (TEM) using the median and 10th centile AVS (umol/kg)

Site	Collection Date	TEM umol/kg	Excess Metal by Median AVS umol/kg	Excess Metal by 10th Centile AVS umol/kg
ACME1DS	15-Dec-1998	302.33	-6848.32	-1406.94
CA215	8-Jul-1998	0	-7150.66	-1709.27
CA215	29-Jun-2001	289.86	-6860.8	-1419.41
CA2-15	28-May-1997	31.85	-7118.8	-1677.42
CA2-15	25-May-1999	66.36	-7084.3	-1642.91
CA2-15	25-Jun-2002	388.04	-6762.62	-1321.24
CA2-15	30-Apr-1996	527.26	-6623.4	-1182.01
CA315	29-Jun-2001	1055.48	-6095.17	-653.788
CA3-15	25-May-1999	22.59	-7128.07	-1686.68
CA3-15	28-May-1997	65.15	-7085.5	-1644.12
CA3-15	30-Apr-1996	1103.43	-6047.23	-605.843
CA3-15	25-Jun-2002	1165.45	-5985.21	-543.824
CA3-15	8-Jul-1998	1443.01	-5707.64	-266.259
CA33	29-Jun-2001	502.31	-6648.35	-1206.96
CA3-3	28-May-1997	255.33	-6895.33	-1453.94
CA3-3	25-May-1999	319.37	-6831.29	-1389.9
CA3-3	8-Jul-1998	331.82	-6818.83	-1377.45
CA3-3	30-Apr-1996	423.14	-6727.51	-1286.13
CA3-3	25-Jun-2002	548.06	-6602.59	-1161.21
G94D	15-Dec-1998	141.10	-7009.55	-1568.17
GORDYRD	13-Jul-2000	88.13	-7062.53	-1621.15
HOLYSD1	28-Aug-1995	0	-7150.66	-1709.27
HOLYSD1	14-Jul-1992	20.27	-7130.38	-1689
HOLYSD1	22-Feb-1993	26.32	-7124.34	-1682.95
HOLYSD1	26-May-1999	89.56	-7061.1	-1619.71
HOLYSD1	29-Sep-1998	104.35	-7046.31	-1604.92
HOLYSD1	9-May-1995	157.37	-6993.29	-1551.9
HOLYSD1	21-Mar-1994	177.08	-6973.57	-1532.19
HOLYSD1	3-Mar-1992	194.53	-6956.13	-1514.74
HOLYSD1	8-Apr-1996	239.41	-6911.24	-1469.86
HOLYSD1	29-Sep-1998	280.20	-6870.45	-1429.07
HOLYSD1	27-Oct-1993	331.00	-6819.65	-1378.27
HOLYSD1	24-Jun-2002	333.41	-6817.24	-1375.86
HOLYSD1	28-Jun-2001	345.94	-6804.72	-1363.33
HOLYSD1	15-Sep-1994	353.87	-6796.79	-1355.4
HOLYSD1	12-Sep-1990	417.22	-6733.43	-1292.05
HOLYSD1	15-Apr-1997	538.85	-6611.8	-1170.42
HOLYSD1	9-Sep-1996	604.07	-6546.58	-1105.2
HOLYSD1	18-Jan-1990	614.25	-6536.4	-1095.02

HOLYSD1	28-Jan-1991	627.81	-6522.84	-1081.46
HOLYSD2	14-Jul-1992	25.10	-7125.56	-1684.17
HOLYSD2	3-Mar-1992	33.30	-7117.35	-1675.97
HOLYSD2	8-Apr-1996	41.51	-7109.15	-1667.76
HOLYSD2	26-May-1999	158.84	-6991.81	-1550.43
HOLYSD2	9-May-1995	202.82	-6947.83	-1506.45
HOLYSD2	28-Jan-1991	203.50	-6947.16	-1505.77
HOLYSD2	22-Feb-1993	220.11	-6930.55	-1489.16
HOLYSD2	15-Sep-1994	232.08	-6918.58	-1477.19
HOLYSD2	28-Aug-1995	237.43	-6913.22	-1471.84
HOLYSD2	9-Sep-1996	243.95	-6906.71	-1465.32
HOLYSD2	21-Mar-1994	371.54	-6779.11	-1337.73
HOLYSD2	30-Jul-2002	386.96	-6763.69	-1322.31
HOLYSD2	27-Oct-1993	474.15	-6676.5	-1235.12
HOLYSD2	28-Jun-2001	482.81	-6667.84	-1226.46
HOLYSD2	29-Sep-1998	591.84	-6558.82	-1117.43
HOLYSD2	15-Apr-1997	747.54	-6403.12	-961.736
HOLYSD2	18-Jan-1990	759.25	-6391.41	-950.023
HOLYSD2	12-Sep-1990	1199.80	-5950.86	-509.472
HOLYSD3	22-Feb-1993	49.34	-7101.31	-1659.93
HOLYSD3	14-Jul-1992	55.02	-7095.64	-1654.25
HOLYSD3	21-Mar-1994	58.88	-7091.77	-1650.39
HOLYSD3	15-Apr-1997	71.91	-7078.74	-1637.36
HOLYSD3	3-Mar-1992	77.70	-7072.95	-1631.57
HOLYSD3	8-Apr-1996	82.05	-7068.61	-1627.22
HOLYSD3	28-Jan-1991	97.07	-7053.58	-1612.2
HOLYSD3	26-May-1999	133.06	-7017.6	-1576.21
HOLYSD3	28-Aug-1995	215.28	-6935.37	-1493.99
HOLYSD3	28-Jun-2001	274.24	-6876.41	-1435.03
HOLYSD3	9-Sep-1996	331.03	-6819.63	-1378.24
HOLYSD3	24-Jun-2002	395.68	-6754.97	-1313.59
HOLYSD3	12-Sep-1990	482.71	-6667.95	-1226.56
HOLYSD3	18-Jan-1990	530.80	-6619.85	-1178.47
HOLYSD3	15-Sep-1994	554.60	-6596.06	-1154.67
HOLYSD3	27-Oct-1993	663.60	-6487.06	-1045.67
HOLYSD3	9-May-1995	1127.35	-6023.3	-581.92
HOLYSD4	15-Apr-1997	29.54	-7121.12	-1679.73
HOLYSD4	14-Jul-1992	56.47	-7094.19	-1652.8
HOLYSD4	22-Feb-1993	86.49	-7064.16	-1622.78
HOLYSD4	26-May-1999	137.58	-7013.07	-1571.69
HOLYSD4	28-Jun-2001	201.06	-6949.59	-1508.21
HOLYSD4	9-May-1995	202.39	-6948.26	-1506.88
HOLYSD4	28-Jan-1991	242.00	-6908.65	-1467.27
HOLYSD4	9-Sep-1996	277.03	-6873.63	-1432.24
HOLYSD4	3-Mar-1992	289.11	-6861.55	-1420.16
HOLYSD4	29-Sep-1998	294.32	-6856.33	-1414.95
HOLYSD4	21-Mar-1994	305.90	-6844.75	-1403.37
HOLYSD4	24-Jun-2002	328.82	-6821.84	-1380.45

HOLYSD4	8-Apr-1996	378.30	-6772.36	-1330.97
HOLYSD4	15-Sep-1994	390.01	-6760.64	-1319.26
HOLYSD4	18-Jan-1990	483.76	-6666.9	-1225.51
HOLYSD4	12-Sep-1990	491.54	-6659.11	-1217.73
HOLYSD4	28-Aug-1995	959.92	-6190.74	-749.351
HOLYSD4	27-Oct-1993	1069.04	-6081.61	-640.229
LO308C	11-Jul-2000	532.21	-6618.44	-1177.06
LOX10	29-May-1997	48.26	-7102.39	-1661.01
LOX10	8-Jul-1998	184.65	-6966	-1524.62
LOX10	25-May-1999	217.15	-6933.5	-1492.12
LOX10	30-Apr-1996	545.85	-6604.8	-1163.42
LOX10	24-Jun-2002	616.01	-6534.64	-1093.26
LOX10	29-Jun-2001	746.30	-6404.35	-962.968
LOX8	8-Jul-1998	48.26	-7102.39	-1661.01
LOX8	25-May-1999	127.28	-7023.38	-1581.99
LOX8	29-May-1997	162.64	-6988.01	-1546.63
LOX8	30-Apr-1996	386.79	-6763.87	-1322.48
LOX8	29-Jun-2001	695.80	-6454.85	-1013.47
LOX8	25-Jun-2002	811.57	-6339.09	-897.705
S176	15-Jun-1998	70.90	-7079.76	-1638.37
S176	12-Nov-2002	110.62	-7040.03	-1598.65
S176	8-Dec-1998	207.20	-6943.45	-1502.06
S176	1-May-2000	279.10	-6871.55	-1430.17
S176	3-Mar-1997	343.69	-6806.96	-1365.58
S176	14-May-2001	509.60	-6641.06	-1199.67
S176	19-Apr-1999	520.20	-6630.46	-1189.08
S176	25-Jan-1996	539.04	-6611.61	-1170.23
S176	16-Dec-2001	560.96	-6589.69	-1148.31
S176	25-Jul-1996	692.67	-6457.99	-1016.6
S176	2-Jun-2002	713.91	-6436.75	-995.364
S176	30-Mar-1995	858.78	-6291.88	-850.495
S176	13-Nov-2000	860.72	-6289.93	-848.549
S176	9-Nov-1999	1275.71	-5874.95	-433.563
S176	10-Aug-1995	1330.44	-5820.21	-378.83
S176	25-Aug-1997	1484.55	-5666.1	-224.718
S177	3-Mar-1997	141.80	-7008.85	-1567.47
S177	8-Dec-1998	161.35	-6989.3	-1547.92
S177	16-Dec-2001	205.64	-6945.02	-1503.63
S177	14-May-2001	328.32	-6822.34	-1380.95
S177	25-Aug-1997	332.20	-6818.45	-1377.07
S177	15-Jun-1998	361.30	-6789.35	-1347.97
S177	19-Apr-1999	374.06	-6776.6	-1335.21
S177	30-Mar-1995	412.64	-6738.01	-1296.63
S177	2-Jun-2002	432.76	-6717.9	-1276.51
S177	9-Nov-1999	459.59	-6691.07	-1249.68
S177	1-May-2000	680.00	-6470.65	-1029.27
S177	10-Aug-1995	687.16	-6463.5	-1022.11
S177	25-Jan-1996	863.50	-6287.16	-845.772

S177	25-Jul-1996	892.66	-6257.99	-816.608
S177	13-Nov-2000	1699.36	-5451.3	-9.91516
S178	12-Nov-2002	249.06	-6901.59	-1460.21
S178	16-Dec-2001	927.54	-6223.11	-781.728
S178	8-Dec-1998	1166.39	-5984.27	-542.882
S178	19-Apr-1999	1230.83	-5919.83	-478.443
S178	2-Jun-2002	1771.09	-5379.57	61.81588
S178	25-Aug-1997	1823.13	-5327.53	113.8559
S178	1-May-2000	2324.12	-4826.54	614.8489
S178	13-Nov-2000	2345.96	-4804.69	636.6932
S178	14-May-2001	2557.26	-4593.4	847.986
S178	25-Jan-1996	2717.85	-4432.81	1008.575
S178	10-Aug-1995	3619.35	-3531.31	1910.078
S178	25-Jul-1996	3858.89	-3291.77	2149.617
S178	3-Mar-1997	4102.57	-3048.09	2393.297
S178	30-Mar-1995	4143.71	-3006.95	2434.436
S178	9-Nov-1999	4169.08	-2981.58	2459.808
S178	15-Jun-1998	4418.50	-2732.15	2709.23
S18C	10-Aug-1995	14.48	-7136.18	-1694.79
S18C	19-Apr-1999	32.37	-7118.28	-1676.9
S18C	12-Nov-2002	35.52	-7115.14	-1673.75
S18C	14-May-2001	48.77	-7101.89	-1660.51
S18C	15-Jun-1998	63.22	-7087.44	-1646.06
S18C	3-Mar-1997	150.31	-7000.35	-1558.97
S18C	1-May-2000	198.24	-6952.42	-1511.03
S18C	25-Jan-1996	282.76	-6867.9	-1426.51
S18C	16-Dec-2001	287.35	-6863.3	-1421.92
S18C	30-Mar-1995	301.58	-6849.08	-1407.69
S18C	8-Dec-1998	422.48	-6728.18	-1286.79
S18C	8-Dec-1998	446.13	-6704.53	-1263.14
S18C	9-Nov-1999	499.82	-6650.83	-1209.45
S18C	25-Aug-1997	559.18	-6591.47	-1150.09
S18C	30-Mar-1995	566.83	-6583.83	-1142.44
S18C	2-Jun-2002	601.77	-6548.89	-1107.5
S18C	13-Nov-2000	677.93	-6472.73	-1031.34
S18C	25-Jul-1996	1009.75	-6140.9	-699.52
S2	15-Dec-1998	540.16	-6610.5	-1169.11
S235	15-Dec-1998	81.87	-7068.79	-1627.4
S3	15-Dec-1998	541.67	-6608.99	-1167.6
S332	25-Jan-1996	15.13	-7135.53	-1694.14
S332	8-Dec-1998	152.04	-6998.62	-1557.23
S332	1-May-2000	235.05	-6915.61	-1474.22
S332	16-Dec-2001	259.48	-6891.17	-1449.79
S332	15-Jun-1998	306.92	-6843.73	-1402.35
S332	14-May-2001	321.83	-6828.82	-1387.44
S332	30-Mar-1995	330.04	-6820.62	-1379.24
S332	19-Apr-1999	350.20	-6800.45	-1359.07
S332	9-Nov-1999	355.95	-6794.7	-1353.32

S332	2-Jun-2002	543.92	-6606.73	-1165.35
S332	25-Aug-1997	586.27	-6564.39	-1123
S332	13-Nov-2000	591.78	-6558.88	-1117.49
S332	10-Aug-1995	761.90	-6388.76	-947.372
S332	25-Jul-1996	1082.54	-6068.12	-626.733
S332	3-Mar-1997	2489.90	-4660.76	780.625
S355A	12-Nov-2002	25.33	-7125.33	-1683.95
S355A	16-Dec-2001	278.82	-6871.83	-1430.45
S355B	12-Nov-2002	23.20	-7127.46	-1686.07
S355B	16-Dec-2001	338.97	-6811.68	-1370.3
S4	15-Dec-1998	1090.91	-6059.75	-618.365
S6	18-Jul-2000	218.91	-6931.75	-1490.36
S78	14-Dec-1998	81.197	-7069.46	-1628.07
S79	14-Dec-1998	1499.95	-5650.71	-209.324
S80	18-Jul-2000	895.45	-6255.2	-813.817
S99	21-May-2001	0	-7150.66	-1709.27
S99	13-Jul-2000	289.16	-6861.5	-1420.11
STA2C1SD	11-Jul-2000	76.06	-7074.59	-1633.21
WCA2F1	28-May-1997	58.88	-7091.77	-1650.39
WCA2F1	25-Jun-2002	228.59	-6922.06	-1480.68
WCA2F1	25-May-1999	236.27	-6914.38	-1473
WCA2F1	8-Jul-1998	237.10	-6913.55	-1472.17
WCA2F1	29-Jun-2001	356.90	-6793.75	-1352.37
WCA2F1	30-Apr-1996	691.31	-6459.34	-1017.96
WHTCYPRK	18-Jul-2000	37.77	-7112.89	-1671.5

Table 5.3.5

SFWMD organic carbon normalized TEM_{oc} (umol/g_{oc})

Site	Collection Date	TEM umol/kg	Excess Metal by Median AVS umol/kg	Excess Metal by 10th Centile AVS umol/kg	Site Mean f_{oc} kg_{oc}/kg_{sed}	Excess AVS by 10th Centile TEM_{oc} umol/g_{oc}
S178	2-Jun-2002	1771.09	-5379.57	61.82	0.014	4.43
S178	25-Aug-1997	1823.13	-5327.53	113.86	0.014	8.15
S178	1-May-2000	2324.12	-4826.54	614.85	0.014	44.02
S178	13-Nov-2000	2345.96	-4804.69	636.69	0.014	45.59
S178	14-May-2001	2557.26	-4593.40	847.99	0.014	60.71
S178	25-Jan-1996	2717.85	-4432.81	1008.57	0.014	72.21
S178	10-Aug-1995	3619.35	-3531.31	1910.08	0.014	136.76
S178	25-Jul-1996	3858.89	-3291.77	2149.62	0.014	153.91
S178	3-Mar-1997	4102.57	-3048.09	2393.30	0.014	171.35
S178	30-Mar-1995	4143.71	-3006.95	2434.44	0.014	174.30
S178	9-Nov-1999	4169.08	-2981.58	2459.81	0.014	176.12
S178	15-Jun-1998	4418.50	-2732.15	2709.23	0.014	193.97
S332	3-Mar-1997	2489.90	-4660.76	780.63	0.010	78.06

Table 5.3.6a
Statistics for lognormal distributions of bulk sediment concentration data for COPECs including 90th centile concentration (mg/kg dry weight)

Site	COPEC	Number of times analyzed	Number of Detections	Slope	Intercept	r^2	*p*-value	90th centile mg/kg
HOLYSD1	Arsenic	19	17	2.91	2.41	0.97	4.26E-13	21.46
HOLYSD2	Arsenic	18	14	2.36	3.30	0.95	3.44E-09	18.31
HOLYSD2	Cadmium	18	10	1.05	6.17	0.98	7.42E-08	1.28
HOLYSD3	Arsenic	17	8	3.46	3.36	0.97	9.40E-06	6.98
	Cadmium	17	7	1.14	6.48	0.95	2.08E-04	0.66
HOLYSD4	Cadmium	18	11	1.20	6.08	0.96	1.29E-07	1.46
S176	Antimony	16	4	0.28	5.99	0.51	2.86E-01	11.32
	Chromium	15	15	8.47	-5.67	0.94	3.94E-09	25.74
	Lead	11	11	1.85	2.55	0.79	2.37E-04	105.17
S177	Antimony	15	4	0.33	5.91	0.59	2.32E-01	13.96
	Chromium	15	13	3.99	0.57	0.92	2.52E-07	26.92
	Copper	12	11	2.55	2.66	0.95	4.25E-07	26.50
S178	Chromium	15	15	7.67	-7.26	0.98	3.33E-12	58.13
	Copper	12	12	11.23	-15.24	0.94	2.40E-07	82.42
	Nickel	15	11	2.54	2.83	0.97	4.28E-08	22.73
	Zinc	14	14	4.05	-3.27	0.94	1.68E-08	227.62
S18C	Antimony	18	4	0.36	5.97	0.71	1.59E-01	7.72
	Arsenic	16	14	2.74	3.16	0.96	7.88E-10	13.71
	Chromium	16	15	5.19	-1.17	0.97	4.98E-11	27.36
	Nickel	17	14	2.34	3.52	0.99	2.16E-12	15.17
S332	Antimony	15	3	5.00	1.40	0.79	3.04E-01	9.47
WCA2F1	Arsenic	5	4	4.21	1.19	0.85	7.96E-02	16.18

Table 5.3.6b
Statistics for lognormal distributions of predicted pore water concentrations for COPECs including 90th centile concentration (ug/l)

Site	COPEC	Number of times analyzed	Number of Detections	Slope	Intercept	r^2	*p*-value	90th centile ug/l
HOLYSD1	Arsenic	19	17	2.91	0.67	0.97	4.26E-13	85.45
HOLYSD2	Arsenic	18	14	2.36	1.88	0.95	3.44E-09	72.89
	Cadmium	18	10	1.05	6.48	0.98	7.42E-08	0.64
HOLYSD3	Arsenic	17	8	3.46	1.29	0.97	9.40E-06	27.77
	Cadmium	17	7	1.14	6.83	0.95	2.08E-04	0.33
HOLYSD4	Cadmium	18	11	1.20	6.44	0.96	1.29E-07	0.73
S176	Antimony	16	4	0.28	6.16	0.51	2.86E-01	2.84
	Chromium	15	15	8.47	10.43	0.94	3.94E-09	0.32
	Lead	11	11	1.85	5.50	0.79	2.37E-04	2.64
S177	Antimony	15	4	0.33	6.10	0.59	2.32E-01	3.51
	Chromium	15	13	3.99	8.16	0.92	2.52E-07	0.34
	Copper	12	11	2.55	3.93	0.95	4.25E-07	8.38
S178	Chromium	15	15	7.67	7.32	0.98	3.33E-12	0.73
	Copper	12	12	11.23	-9.62	0.94	2.40E-07	26.06
	Nickel	15	11	2.54	5.12	0.97	4.28E-08	2.86
	Zinc	14	14	4.05	1.19	0.94	1.68E-08	18.08
S18C	Antimony	18	4	0.36	6.18	0.71	1.59E-01	1.94
	Arsenic	16	14	2.74	1.52	0.96	7.88E-10	54.57
	Chromium	16	15	5.19	8.68	0.97	4.98E-11	0.34
	Nickel	17	14	2.34	5.63	0.99	2.16E-12	1.91
S332	Antimony	15	3	5.00	4.40	0.79	3.04E-01	2.38
WCA2F1	Arsenic	5	4	4.21	-1.34	0.85	7.96E-02	64.40

Table 5.3.7
Statistics for SSDs of metal COPECs including acute 10th centile concentrations (ug/L)

COPEC	Number of species	Slope	Intercept	r^2	*p*-value	Acute 10th centile ug/l
Arsenic All	20	1.33	-0.3	0.89	6.75E-10	1069.11
Arsenic Fish	10	1.49	-1.16	0.87	8.60E-05	1903.59
Arsenic Arthropods	6	0.83	2.03	0.78	1.97E-02	107.92
Arsenic Non-vertebrates	9	1.07	0.97	0.9	8.21E-05	377.54
Chromium VI All	41	0.62	2.63	0.87	9.09E-19	58.66
Chromium VI Fish	20	0.99	0.55	0.66	1.39E-05	1654.84
Chromium VI Arthropods	17	0.47	3.53	0.86	6.89E-08	2.47
Chromium III All	23	0.80	1.66	0.74	1.7E-07	359.73
Chromium III Fish	11	4.69	-16.53	0.93	1.46E-06	20735.45
Chromium III Arthropods	8	0.57	2.88	0.86	8.47E-04	30.02
Copper All	38	1.03	2.46	0.76	1.02E-12	16.50
Copper Fish	22	0.97	2.52	0.63	9.80E-06	17.14
Copper Arthropods	8	0.63	3.50	0.71	8.90E-03	2.20
Lead All	11	.61	2.45	.93	6.10 E-06	115.51
Lead Fish	5	.76	1.94	.85	2.66E-02	223.2
Lead Arthropods	5	.38	3.36	.86	7.52E-02	8.73
Nickel All	14	1.17	0.50	0.94	8.74E-09	574.66
Nickel Fish	7	1.33	-0.80	0.86	2.82E-03	2543.23
Nickel Invertebrates	5	1.79	-0.87	0.92	9.96E-03	363.90
Zinc All	24	1	1.57	0.93	1.26E-14	136.72
Zinc Fish	12	1.03	1.39	0.90	3.07E-06	184.22
Zinc Arthropods	5	0.77	3.00	0.83	3.25E-02	8.54

Table 5.3.8

Statistics for metal SSD's of COPECs including NOEC 10th centile concentrations (ug/l)

Compound	N	Slope	Intercept	R2	p value	10th centile ug/l
Arsenic	NA	NA	NA	NA	NA	NA
Chromium III or IV	NA	NA	NA	NA	NA	NA
Lead All	4	0.68	3.57	0.93	34E-03	1.63
Nickel All	4	0.74	3.26	0.76	126.0E-03	4.19
Copper All	15	0.99	3.89	0.88	9.0 E-07	0.68
Copper Fish	5	0.54	4.41	0.92	10.0E-03	0.05
Copper Arthropods	4	2.26	2.53	0.98	9.0E-03	3.34
Zinc All	7	1.19	2.21	0.96	1.3E-04	18.4

Table 5.3.9
Probability of exceedence of the arthropod acute 10th centiles for pore water concentrations at SFWMD sediment sites

Site	COPEC	Probability of exceedence of acute LC50 10th centile (%)
HOLYSD1	Arsenic	5.75
HOLYSD2	Arsenic	4.61
HOLYSD3	Arsenic	0.04
S-176	Chromium	0.00
	Lead	1.25
S-177	Chromium	0.00
	Copper	57.72
S-178	Chromium	0.00
	Copper	100.00
	Nickel	0.00
	Zinc	51.53
S-18c	Arsenic	1.81
	Chromium	0.00
	Nickel	0.00
WCA2F1	Arsenic	1.3

Table 5.3.10
Probability of exceedence of the chronic NOEC 10th centiles for pore water concentrations at SFWMD sediment sites

Site	COPEC	Probability of exceedence of chronic NOEC 10th centile (%)
HOLYSD1	Arsenic	NA
HOLYSD2	Arsenic	NA
HOLYSD3	Arsenic	NA
S-176	Chromium	NA
	Lead	18.48
S-177	Chromium	NA
	Copper	93.32
S-178	Chromium	NA
	Copper	100.00
	Nickel	4.43
	Zinc	9.53
S-18c	Arsenic	NA
	Chromium	NA
	Nickel	1.88
WCA2F1	Arsenic	NA

Table 5.3.11

Probability of exceeding the Florida sediment quality assessment guidelines (SQAG) for bulk sediment concentrations

Site	COPEC	Probability of exceedence of TEC as %	Probability of Exceedence of PEC as %
HOLYSD1	Arsenic	38.51	3.40
HOLYSD2	Arsenic	26.09	2.97
HOLYSD2	Cadmium	12.1	2.86
HOLYSD3	Arsenic	3.66	0.01
	Cadmium	6.88	1.13
HOLYSD4	Cadmium	13.93	2.73
S176	Antimony	NA	13.10*
	Chromium	0.08	<.01
	Lead	33.64	7.33
S177	Antimony	NA	14.39*
	Chromium	1.81	<.01
	Copper	6.81	0.07
S178	Chromium	39.11	0.03
	Copper	99.96	<.01
	Nickel	9.77	1.66
	Zinc	43.83	0.59
S18C	Antimony	NA	12.81*
	Arsenic	18.90	1.00
	Chromium	1.08	<.01
	Nickel	4.42	0.67
S332	Antimony	NA	88.73*
WCA2F1	Arsenic	35.78	0.49

* NOAA fresh water upper effects threshold (UET)
There was no Florida DEP criteria for antimony

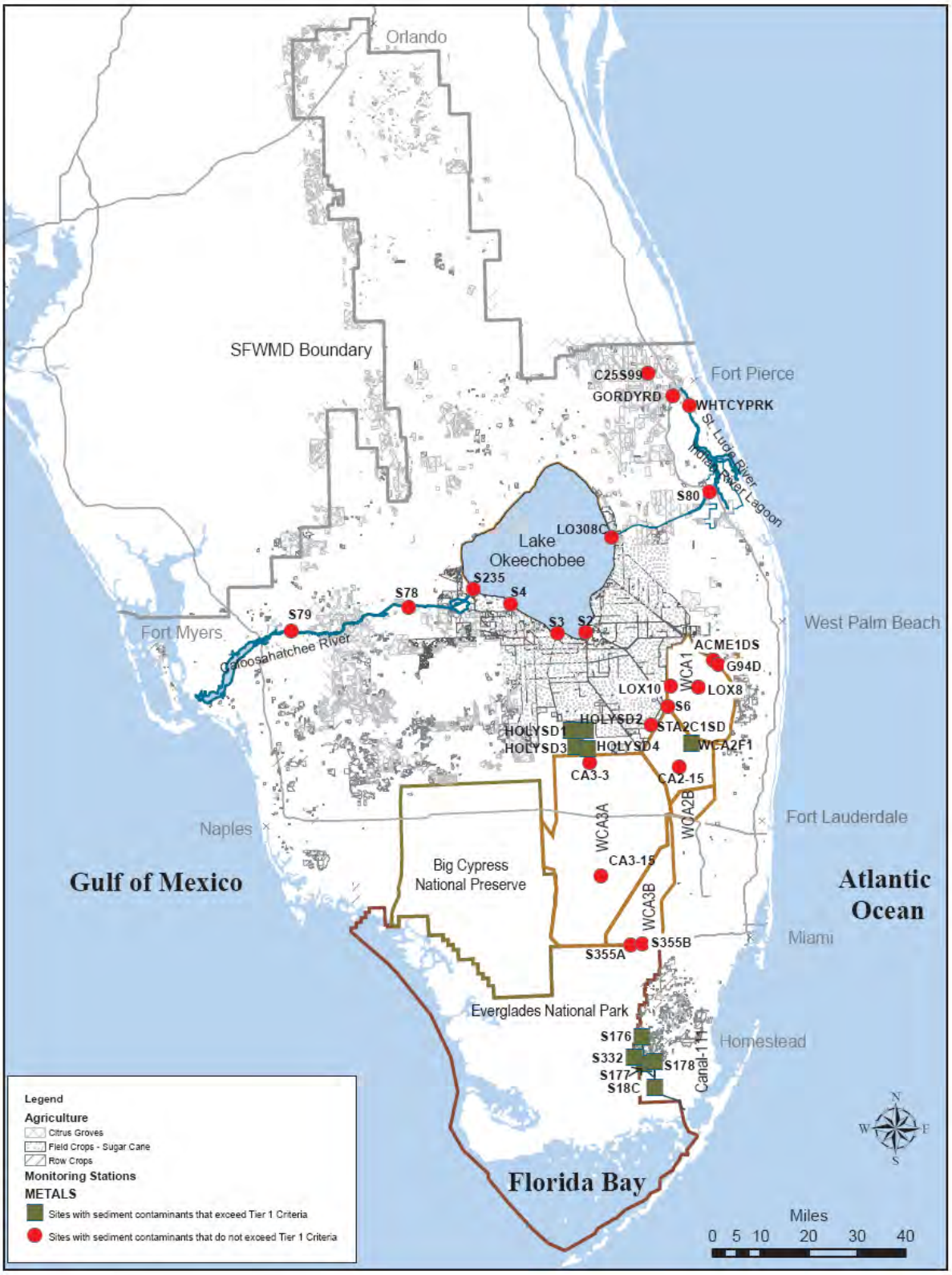


Figure 5.3.1
South Florida Water Management District sediment metal monitoring stations

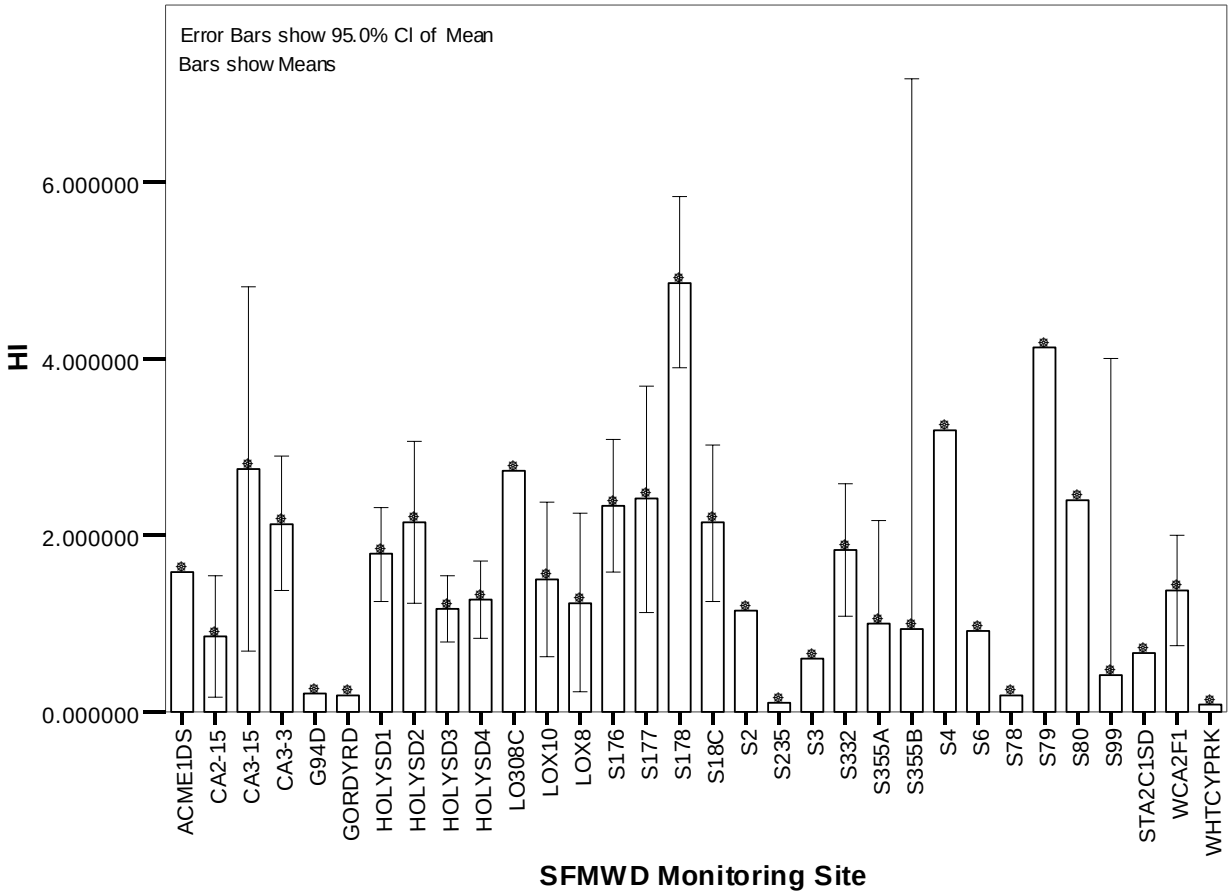


Figure 5.3.2

Summary of mean metal hazard indices at sites (n=32) in the South Florida Water Management District monitoring program (1990-2002).

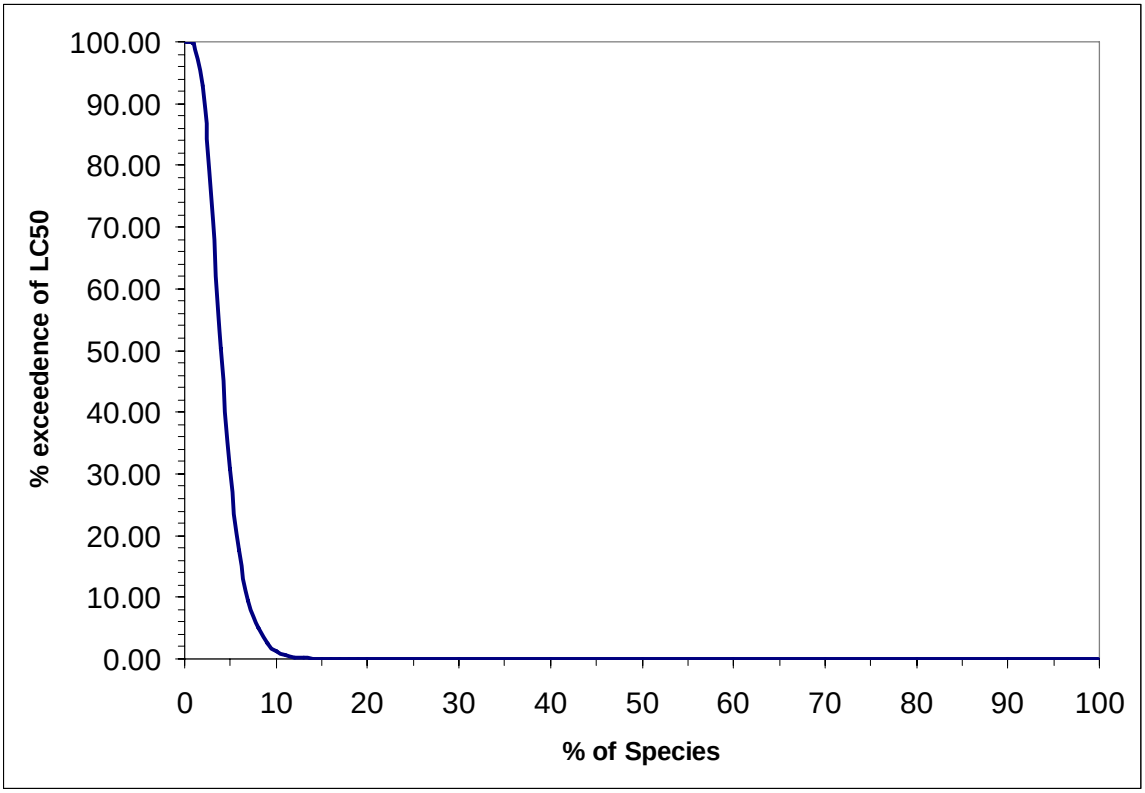


Figure 5.3.3
JPC for predicted pore water concentrations of lead for freshwater arthropods at S176

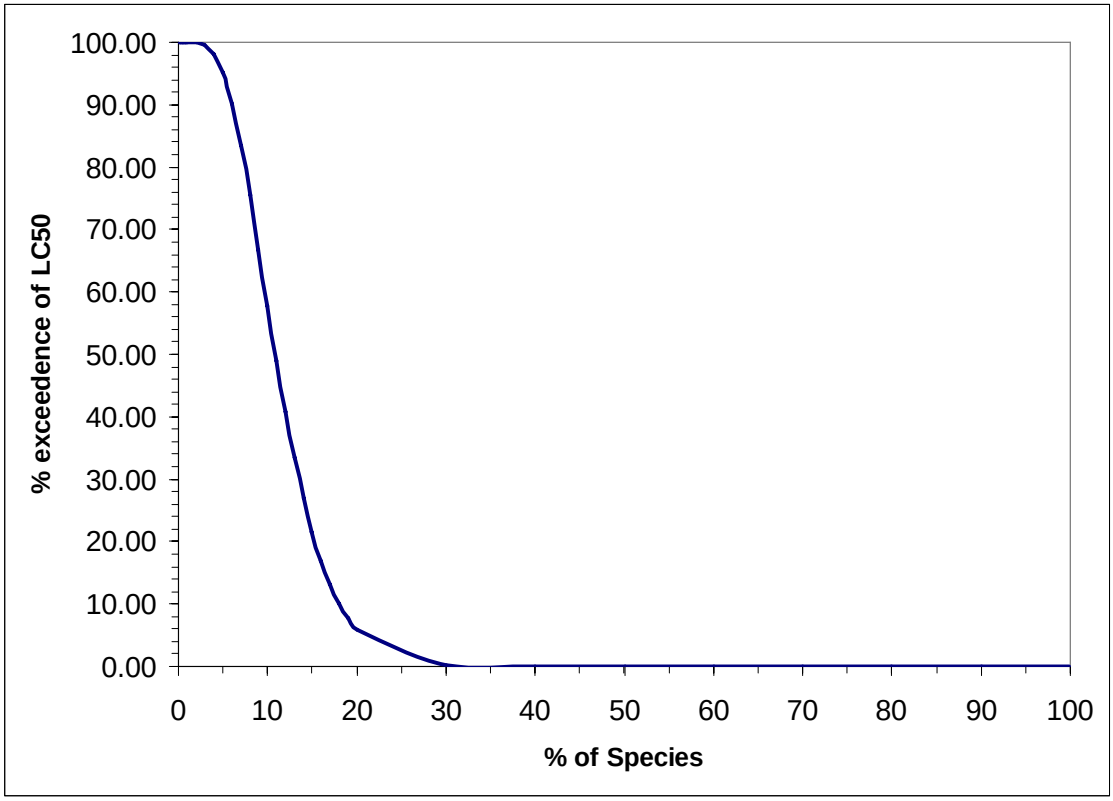


Figure 5.3.4
JPC for predicted pore water concentrations of copper for freshwater arthropods at S177

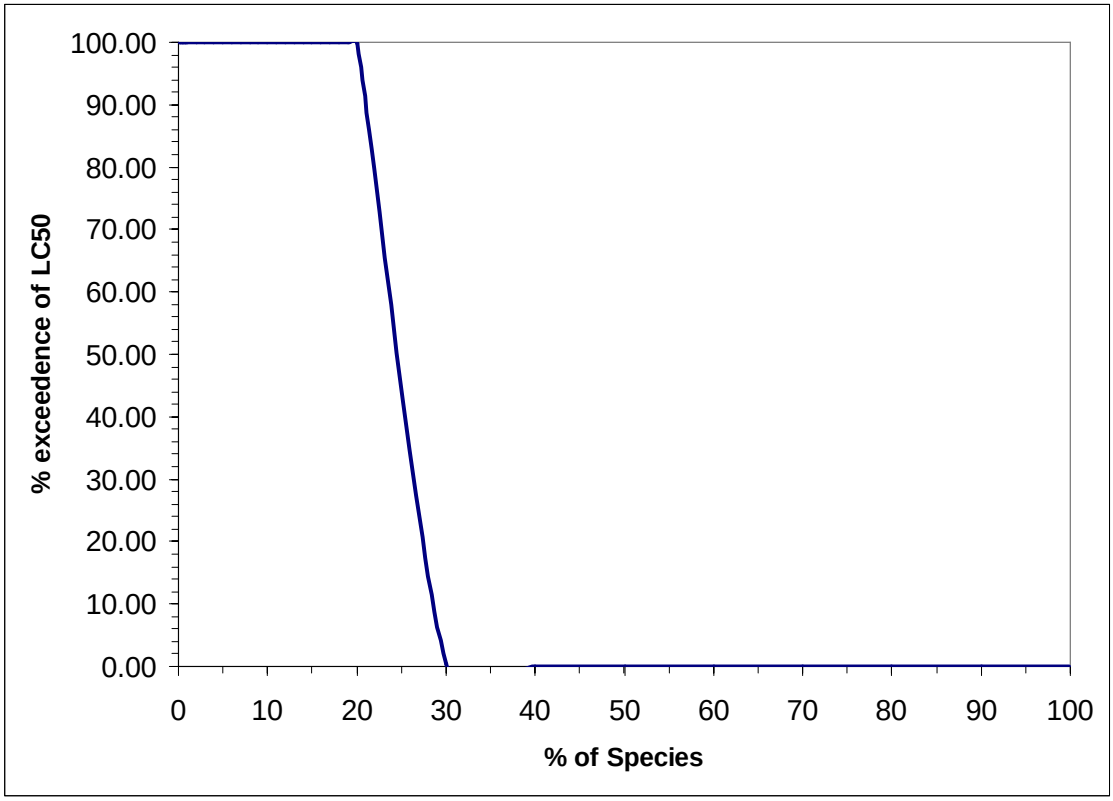


Figure 5.3.5
JPC for predicted pore water concentrations of copper for freshwater arthropods at S178

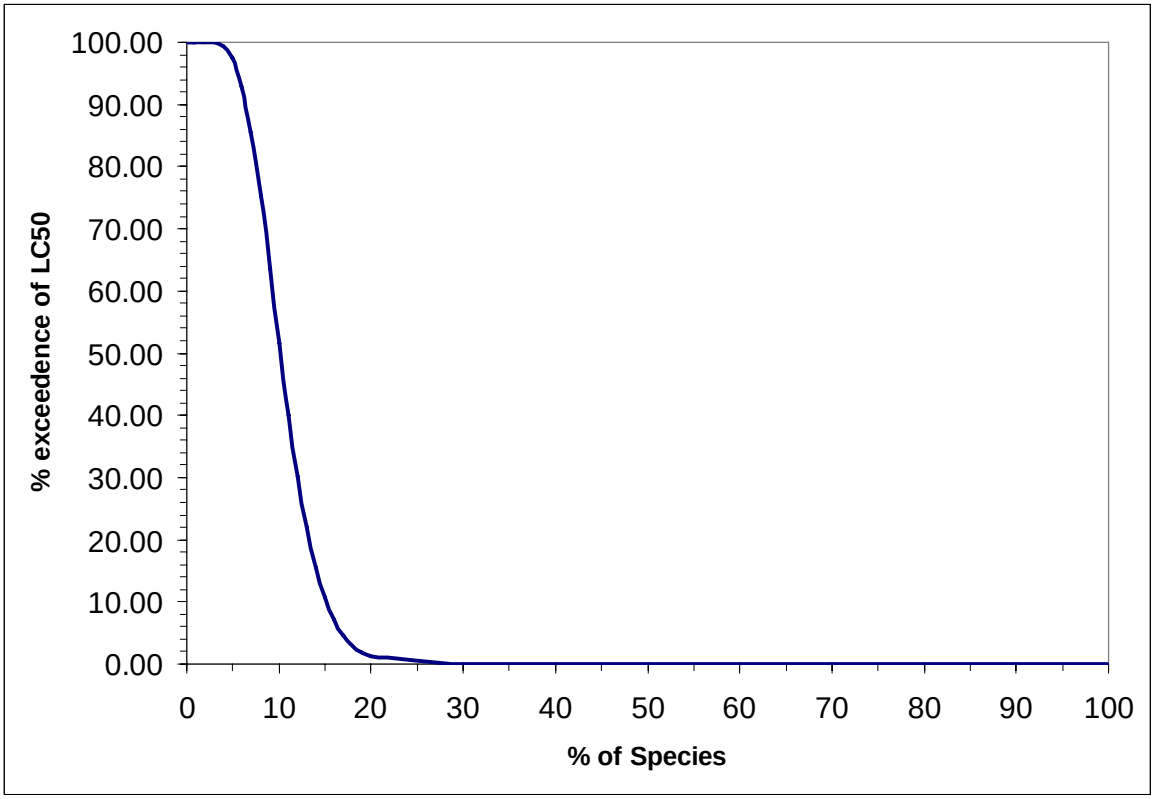


Figure 5.3.6
JPC for predicted pore water concentrations of zinc for freshwater arthropods at S178

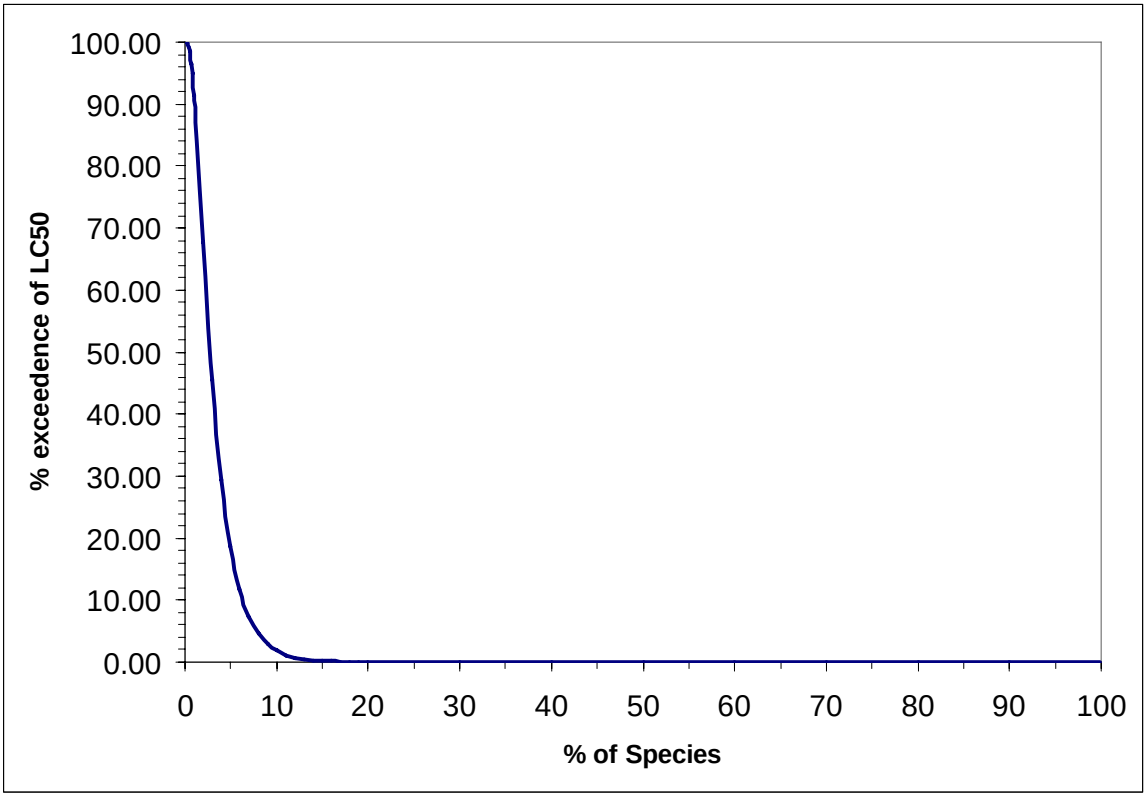


Figure 5.3.7
JPC for predicted pore water concentrations of arsenic for freshwater arthropods at S18C

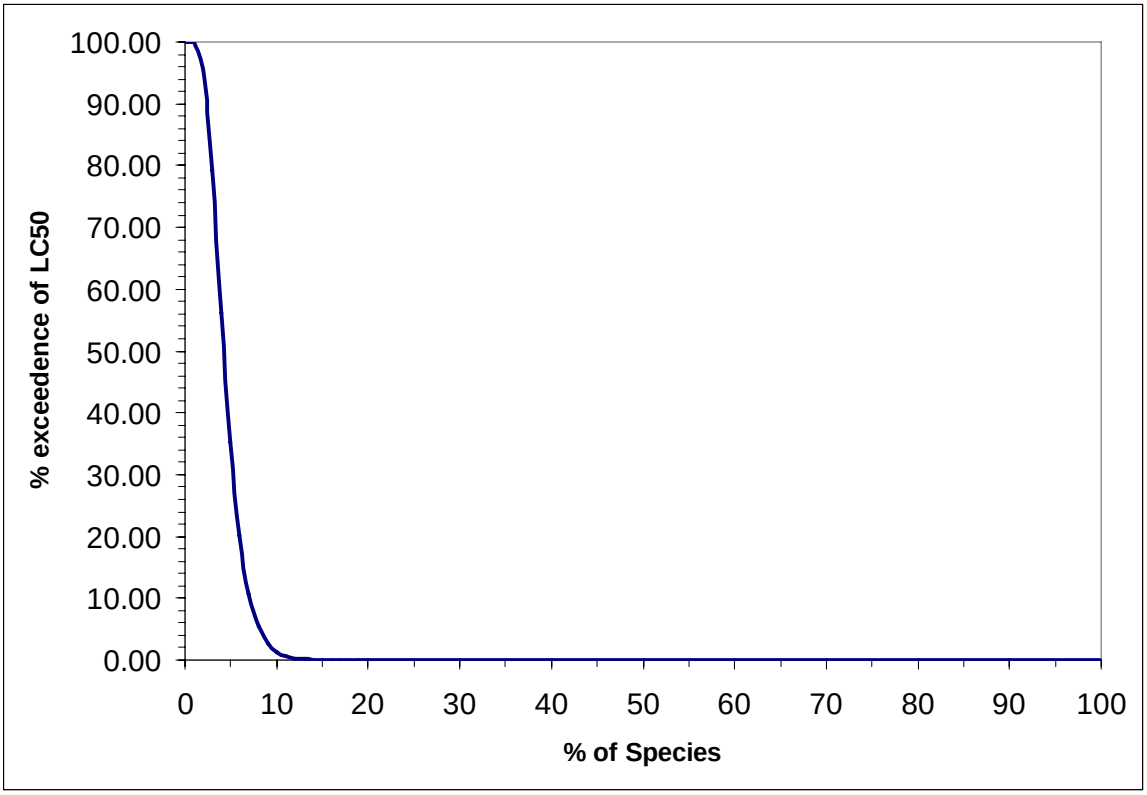


Figure 5.3.8
JPC for predicted pore water concentrations of arsenic for freshwater arthropods at WCA2F1

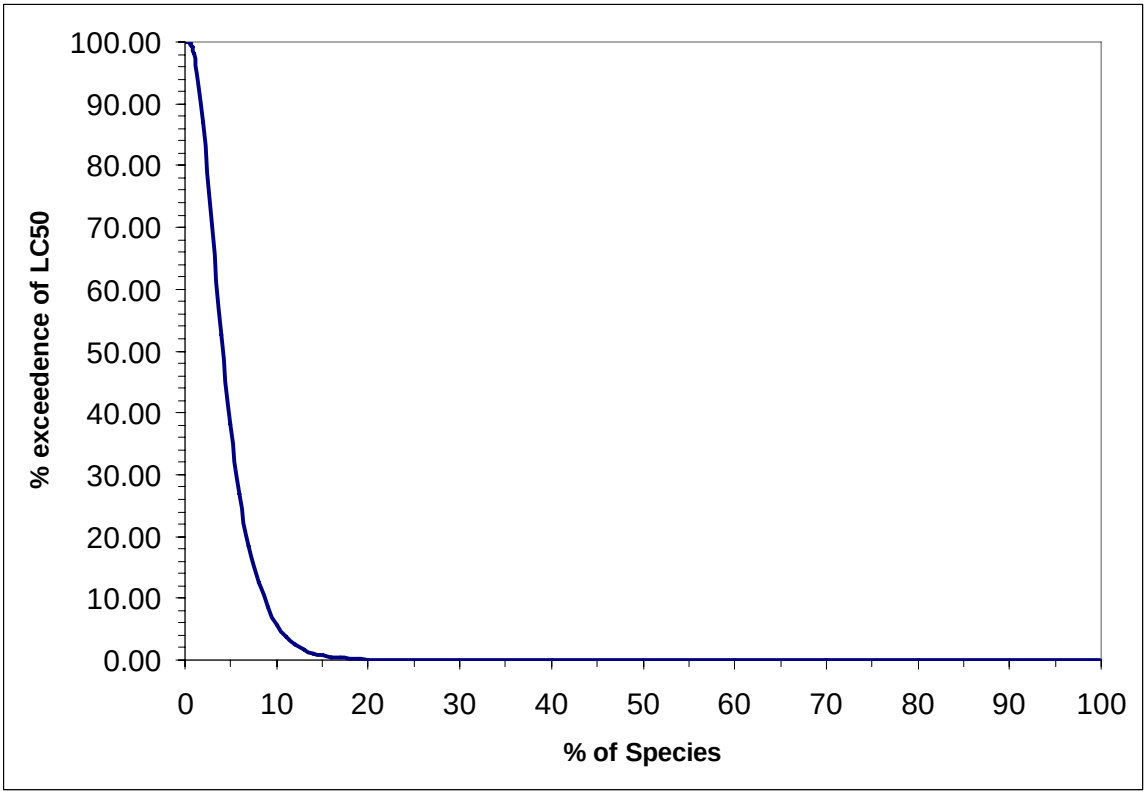


Figure 5.3.9
JPC for predicted pore water concentrations of arsenic for freshwater arthropods at HOLYSD1

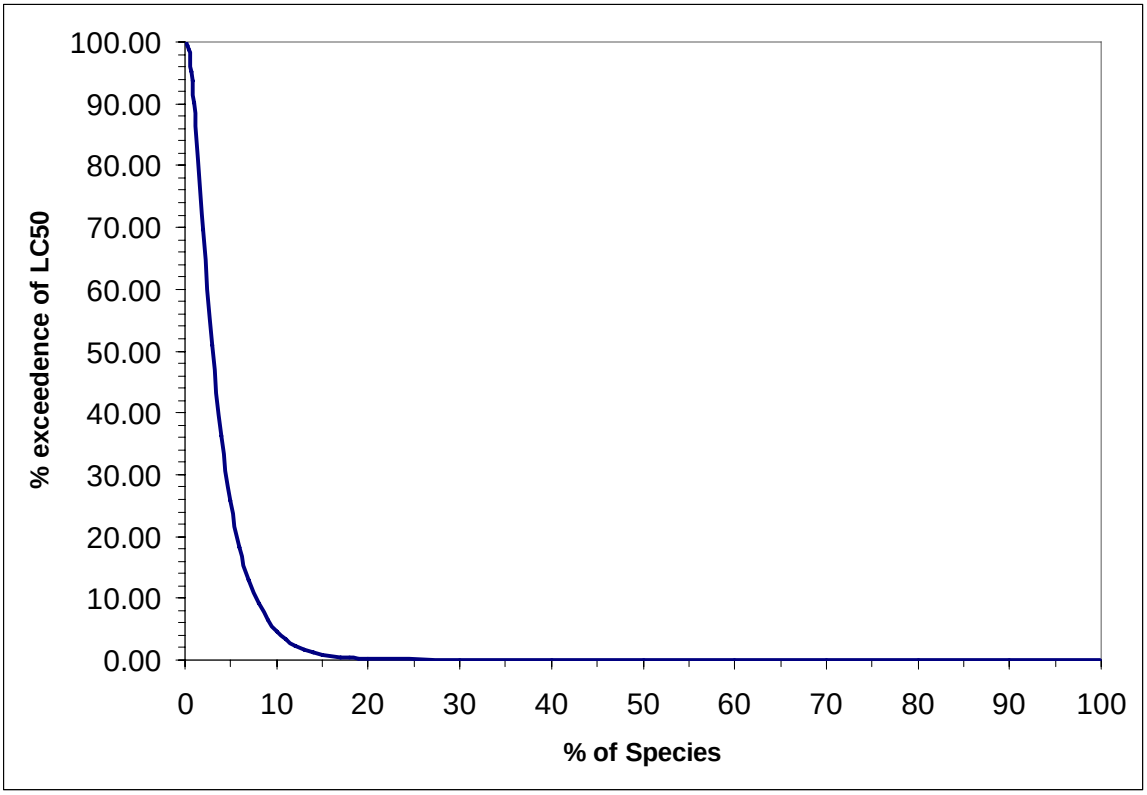


Figure 5.3.10
JPC for predicted pore water concentrations of arsenic for freshwater arthropods at HOLYSD2

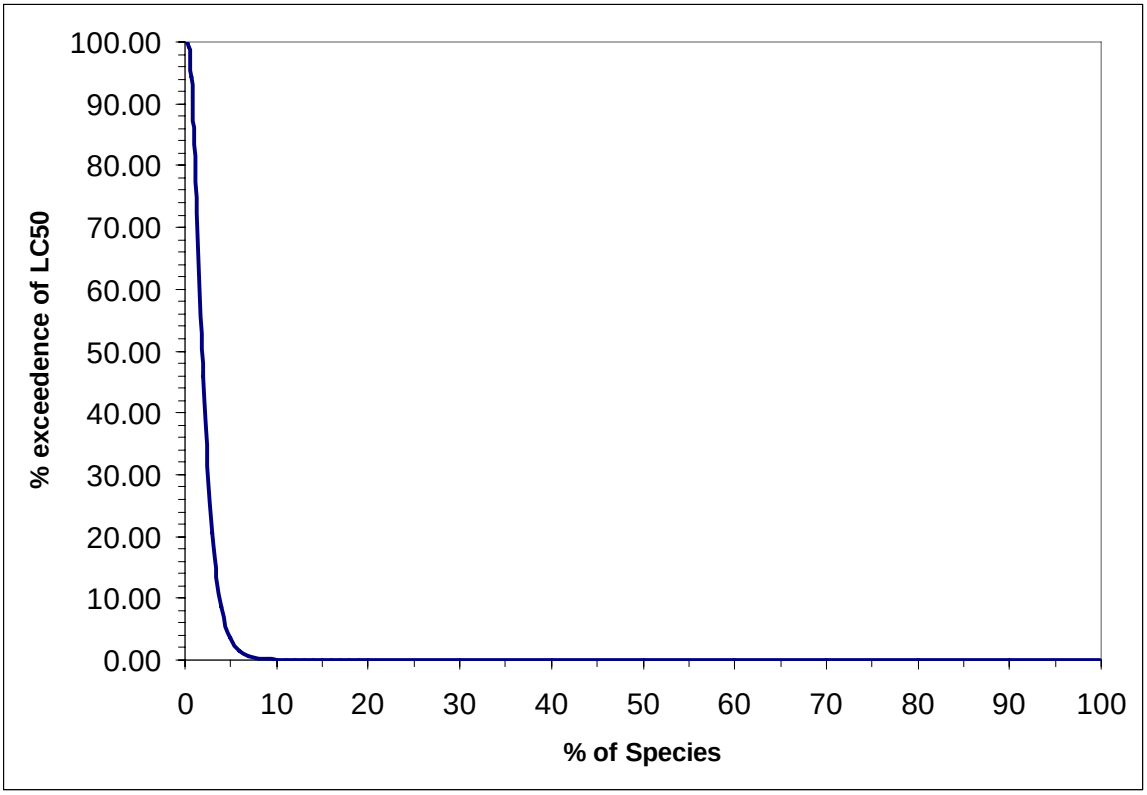


Figure 5.3.11
JPC for predicted pore water concentrations of arsenic for freshwater arthropods at HOLYSD3

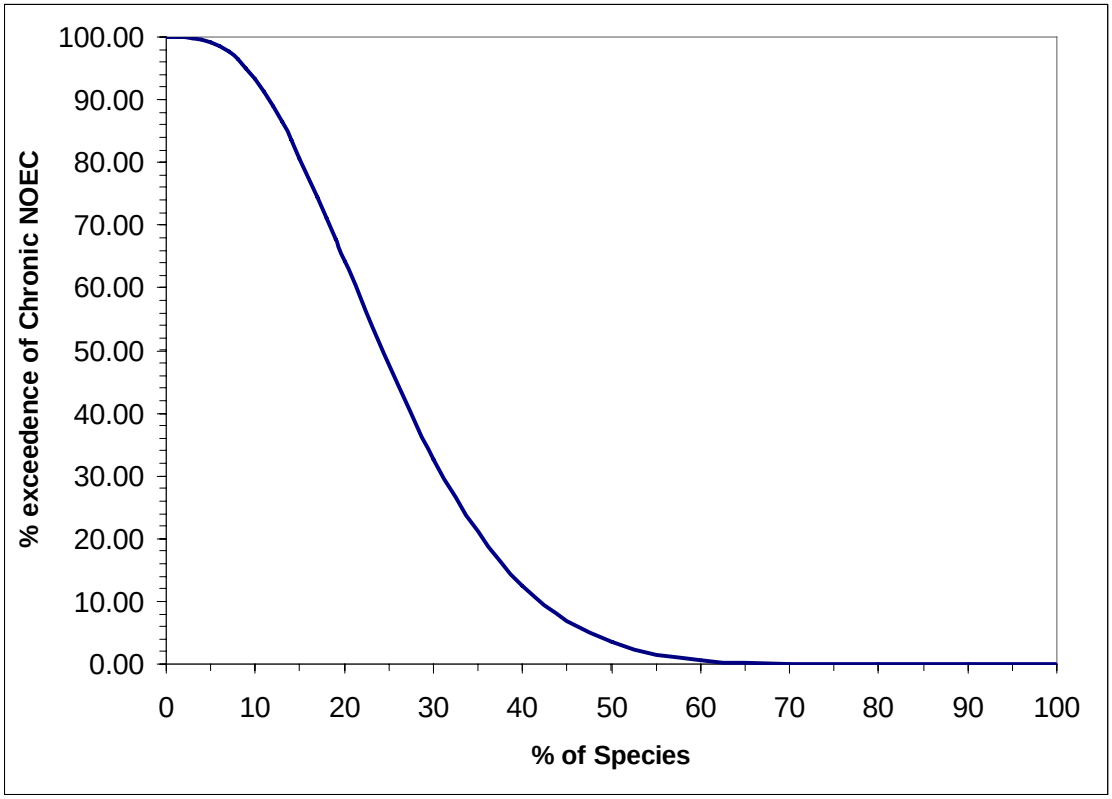


Figure 5.3.12
JPC for predicted pore water concentrations of copper for aquatic community NOECs at S177

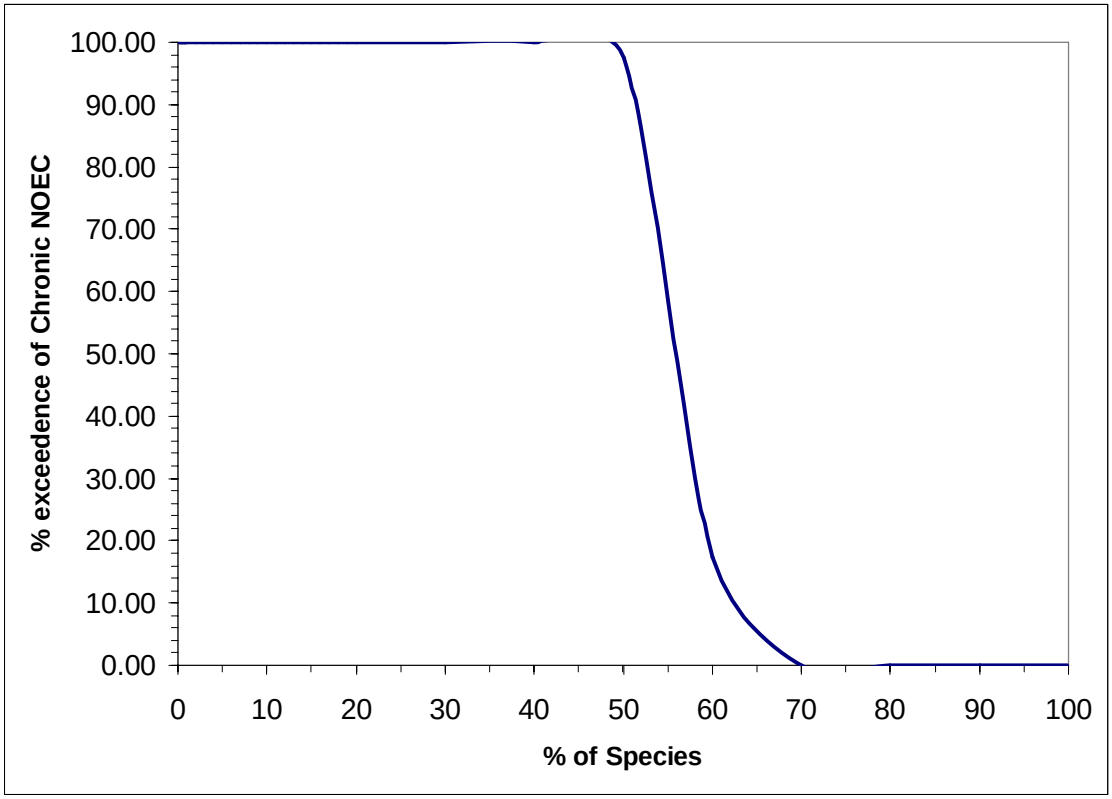


Figure 5.3.13
JPC for predicted pore water concentrations of copper for aquatic community NOECs at S178

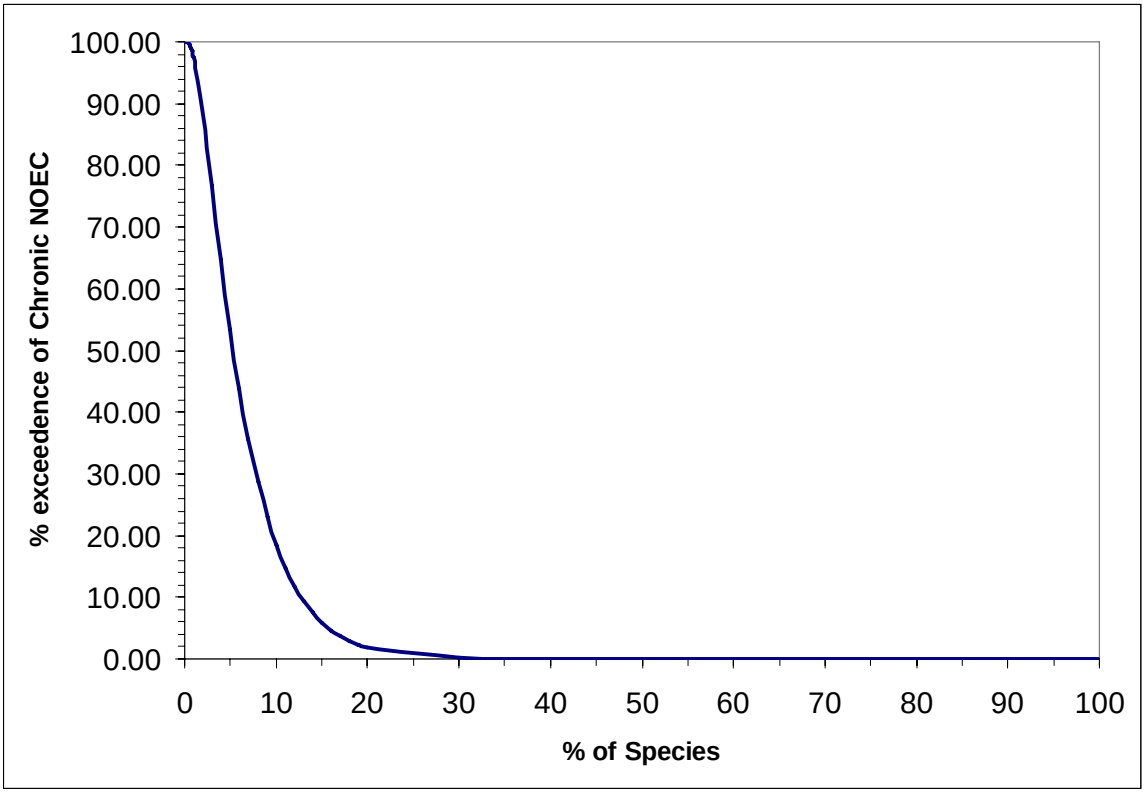


Figure 5.3.14
JPC for predicted pore water concentrations of lead for aquatic community NOECs at S176

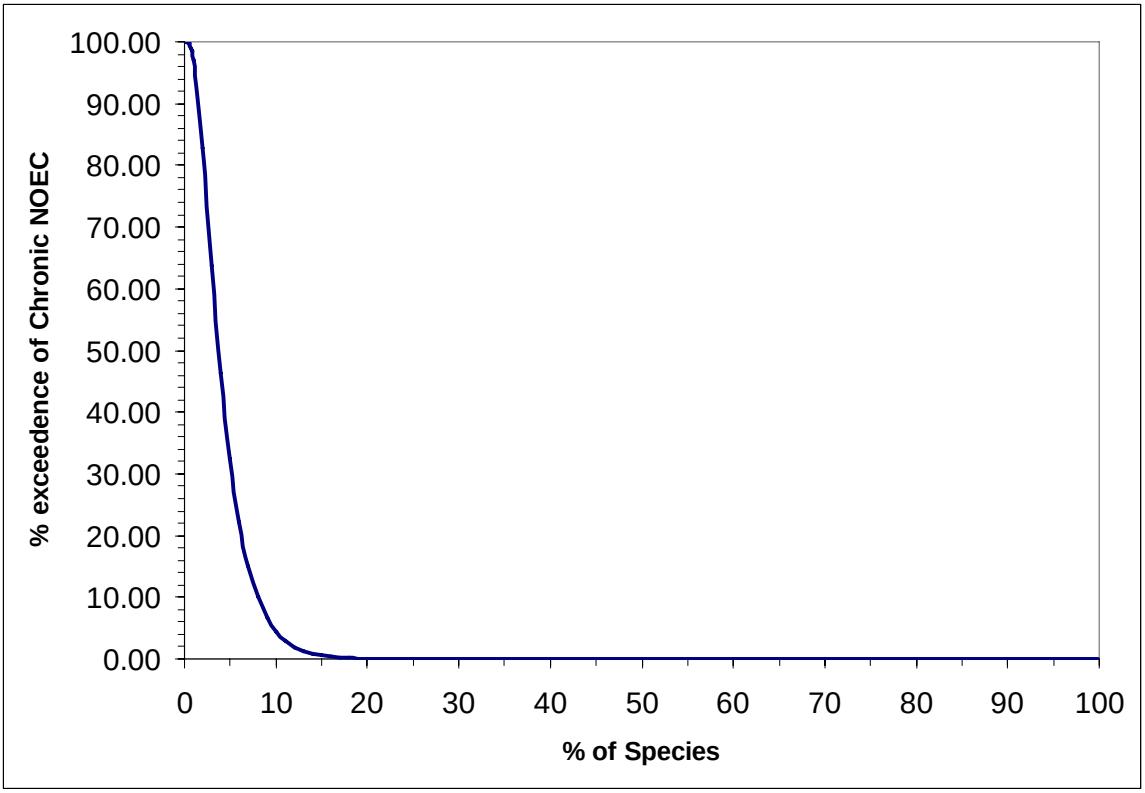


Figure 5.3.15
JPC for predicted pore water concentrations of nickel for aquatic community NOECs at S178

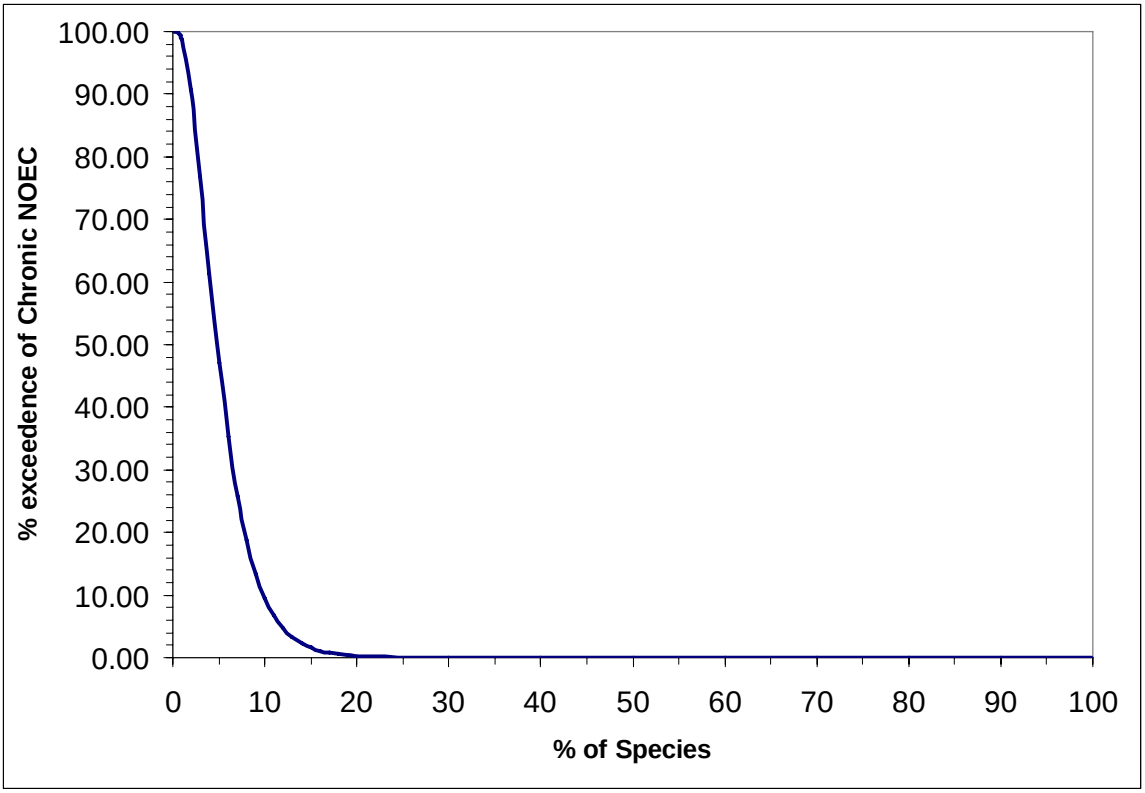


Figure 5.3.16
JPC for predicted pore water concentrations of zinc for aquatic community NOECs at S178

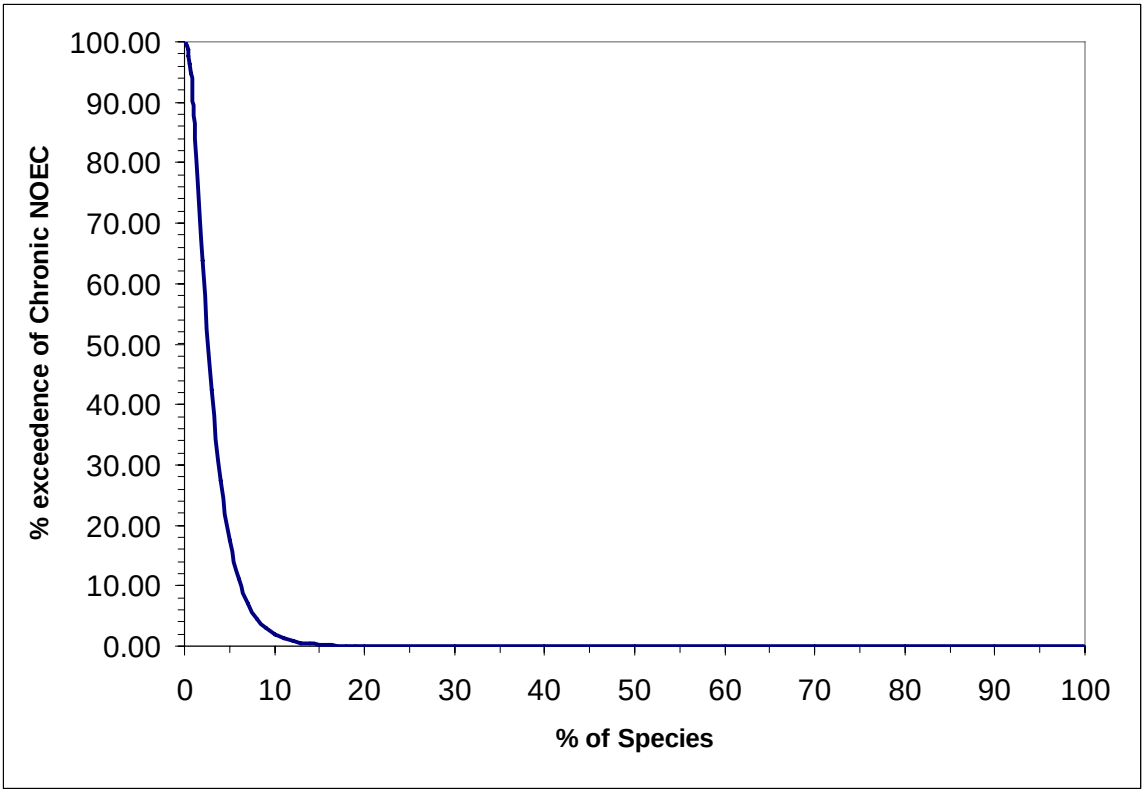


Figure 5.3.17
JPC for predicted pore water concentrations of nickel for aquatic community NOECs at S18C

5.4 Pesticides and Metals from a Three-Year Monitoring Study for Everglades and Biscayne National Parks (2001-2004).

5.4.0. ABSTRACT

The objective of this screening level aquatic ecological risk assessment (SERA) was to determine ecological risk of organic and inorganic contaminants (metals) analyzed in sediment (2001-2004) collected from 35 sampling sites (stations) in Everglades and Biscayne National Parks using a probabilistic approach. The sites were divided into seven regions for the SERA. For tier 1, we identified the chemicals of potential ecological concern (COPECs) as arsenic, chromium, copper, lead, nickel and zinc based on their exceedence of sediment quality standards. DDE was the most frequently detected pesticide COPEC in sediment. Arsenic was the only COPEC present in all seven regions. Shark River Slough (SRS) followed by Tamiami Trail (TT) had the highest pesticide hazard indices (HIs) of the seven regions. Florida Bay (FB) had the lowest pesticide HI. The Eastern Boundary (EB) of ENP and TT had the highest HIs for metals. The main metals at the EB were arsenic, followed by chromium, copper, nickel, and lead. The main metals at TT were arsenic, followed by copper, zinc, lead and nickel. FB had a higher metal HI than Biscayne Bay. The highest acute risk was associated with copper in TT and EB. Arsenic acute risk potential was low except for FB. The highest chronic risk potential was associated with copper in TT, followed by copper in the EB.

5.4.1. INTRODUCTION

Based on a two-tier ecological risk framework under the USEPA guidelines and use of the probabilistic approach and other best available technology for ecological risk assessment methods accepted by the scientific community we completed three SERAs (Section 5.1, 5.2, 5.3) on historical analytical data for contaminants from sediment and water to develop background information for south Florida to determine:

- distribution (spatial and temporal) of contaminants and COPECs
- potential acute and chronic risks of COPECs to ecological receptors at various locations and to rank risk (high to low) for these locations
- potential target organisms

The above information provides the data needed to determine potential sources of contaminants to the Parks and it also serves as a baseline for comparison with our three-year monitoring program (2001-2004). South Florida is defined here as the land mass under the jurisdiction of the South Florida Water Management District (SFWMD) (Rand and Gardinali, 2004). Results from the two sediment SERAs on south Florida canals indicate:

- DDT, DDD, DDE, chlordane and endosulfan were chemicals of potential ecological concern (COPECs) in sediment of south Florida Canals based on their exceedence of sediment quality standards
- DDE was the most frequently detected COPEC in sediments and chlordane was the least frequently detected COPEC in sediments in south Florida canals

- predicted pore water exposure was highest for endosulfan and lowest for DDT
- probability of pore water exposures exceeding 10th percentiles for species sensitivity distributions was <1% for all COPECs
- endosulfan had the highest chronic risk to freshwater arthropods in the C-111 canal system (at S-178) based on the probability of pore water exposure concentrations exceeding arthropod estimated chronic NOEC 10th percentile at 41%. Endosulfan had potential chronic risk (8.1%) to arthropods at S-177 (on C-111) as well. S-177 and S-178 are potential sources of COPECs to ENP. DDD had the next highest potential chronic risk at S-2 (southeast part of Lake Okeechobee) and at S-6 (on L-15 near WCA1 and 2).
- DDT presents no acute or chronic risks to freshwater arthropods.
- arsenic, antimony, cadmium, chromium, copper, lead, nickel and zinc were COPECs in sediment of south Florida Canals based on their exceedence of sediment quality standards
- arsenic (25%) found in the Holey Land tracts and chromium (25%) found in the C-111 system were the most frequently detected metal COPECs and antimony (6%), zinc (6%) and lead (5%) were the least frequently detected COPECs
- mean hazard index for metals was highest at S-178 in the C-111 system based on the presence of chromium, copper, nickel and zinc
- bulk sediment exposures were highest for zinc (at S-178) and lead (at S-176) in the C-111 system
- the probability of pore water exposures exceeding the acute10^{th} percentile for SSDs was highest for copper at S-178 and S-177

- the probability of pore water exposures exceeding the chronic NOEC 10th percentile for SSDs was highest for copper at S-178 and S-177

Results of the surface water SERA in the C-111 system indicate:

- Initial screening results of measured concentrations indicated possible hazards from surface water exposure concentrations of endosulfan and chlorpyrifos. Malathion equaled its WQC in two samples and surface water detections were infrequent. Surface water concentrations of atrazine and metolachlor did not exceed screening benchmark values. Therefore, a second tier using probabilistic methods and criteria from field/mesocosm studies was conducted to assess the potential risks of chlorpyrifos and endosulfan on fish and arthropods.
- The highest 90th centile concentration estimate for endosulfan was found at S-178/Site C. Concentrations of endosulfan at S-178/Site C were generally higher in samples taken at the height of the dry season (February) than the wet season (June). Concentrations of endosulfan decreased downstream of S-178/Site C.
- The two highest concentrations of chlorpyrifos were found at S-177/Site B, which also had the highest 90th centile concentration estimate for chlorpyrifos.
- When measured concentrations from all freshwater sites were aggregated together, the 90th centile concentration estimate for endosulfan was higher in 2000 than in 1999.
- The 90th centile concentration estimate for chlorpyrifos and endosulfan were higher at Joe Bay than other estuarine sites.

- For chlorpyrifos and endosulfan effects, the 10th centile effect concentration estimates were generally lower for saltwater species than for freshwater species.
- The 10th centile effect concentration estimates for chlorpyrifos in freshwater and saltwater were lower for arthopods than fish. The 10th centile effect concentration estimate for endosulfan was lower for freshwater fish than freshwater arthropods but higher for saltwater fish than saltwater arthropods.
- From a review of field and mesocosm studies for both endosulfan and chlorpyrifos, threshold effect concentrations of 0.1μg/L and 1.0μg/L, for each respective compound, were chosen.
- Based on joint probability curves that compared the overlap of distributions of measured concentrations and acute effect values, potential risk was higher for arthropods in freshwater or estuarine sites exposed to chlorpyrifos in 1999 over 2000. Potential risk was greater for arthropods exposed to endosulfan in freshwater and estuarine sites for 2000 versus 1999.
- Joint probability curves for all data from 1999 and 2000 at various sites found the highest potential risk for freshwater arthropods to be from measured endosulfan concentrations at S-178/Site C. Likewise, the highest potential risk for freshwater fish was found at S-178/Site C from measured endosulfan concentrations. Potential risks to freshwater fish and arthropods decreased at a site (S-18c/Site E) directly downstream from S-178/Site C, possibly from dilution.
- For the estuarine sites, potential risks appeared to be only slightly higher at Joe Bay for arthropods than at Card Sound and Highway Creek. Potential risks at all estuarine

sites were higher for endosulfan and arthropods than chlorpyrifos and arthropods. The potential risks to estuarine fish were lower than for estuarine arthropods.

- Potential risks at all freshwater sites were higher for measured concentrations in February (dry season) than June (wet season). Potential risks for measured concentrations in estuarine sites were variable.
- In all scenarios, potential risk increased from single chemical exposures to multiple chemical exposures.
- The 1 μg/L NOEC for the effects of endosulfan on aquatic invertebrates and fish from field studies was exceeded once at S-178/Site C on February 16, 2000. The highest measured concentration of chlorpyrifos at S-177/Site B did not exceed a NOEC of 0.1 μg/L from field and mesocosm studies.

The following SERA focuses on analytical data generated for sediment collected from sites (stations) within Everglades National Park (ENP) and Biscayne National Park (BNP). ` Sediments were collected from 22 sites in ENP, 9 sites in BNP and 4 sites in northeast Florida Bay (see Figure 2.1 in Section 2). The 35 sites are divided into seven regions. The sampling strategy and the specific site (station) locations are discussed in Section 2. The analytical chemical results of all sediment monitoring stations and fish tissue analyses are presented in Section 3. The specific organochlorine pesticides (n=25), polychlorinated biphenyls (PCBs, n=18), polycyclic aromatic hydrocarbons (PAHs, n=27) and metals (n=11) that were analyzed are enumerated in Section 3. The objectives for the SERA are similar to the first three SERAs: determine COPECs in Tier 1 using sediment quality guidelines and

then conduct a probabilistic ERA on COPECs in Tier 2 to quantify the likelihood that adverse effects will occur from sediment exposures to organic and inorganic (metals) contaminants in ENP and BNP using JPCs to characterize risk. Whole (bulk) sediment concentrations of COPECs in regions were used to estimate pore water concentrations. Pore water exposure distributions for regions were then compared to species response distributions for COPECs. The extent of overlap was used to estimate potential acute and chronic risks.

5.4.2. MATERIALS AND METHODS

The procedures used in this risk assessment were described in detail in the first three assessments (Sections 5.1, 5.2, 5.3). Three distinct phases of the U.S.EPA ERA framework were followed: Problem Formulation, Analysis and Risk Characterization. In problem formulation we defined the organic and metal COPEC (stressors) characteristics, assessment and measurement endpoints, ecosystems at risk, types of ecological effects data used and sources and a conceptual model for the SERA. Stressor characteristics include a summary of the physical and chemical characteristics of organic and metal COPECs. The sources, solubility, toxic forms, bioavailability and bioconcentration potential are discussed. When COPECs were similar to the other risk assessments contained in this report we refer the reader back to those assessments for more information on the characteristics of the stressors. The analysis phase consists of a technical evaluation of the existing data on potential adverse ecological effects (from laboratory toxicity tests) and exposure (environmental monitoring) of the COPECs. Risk characterization involves estimation of the probability of adverse effects on aquatic populations in ENP and BNP.

The aquatic ecosystems addressed in this assessment are organisms within ENP and BNP. The assessment endpoints for this risk assessment are the protection of the long-term viability of aquatic communities (e.g., invertebrates, fish). The specific assessment endpoint is the protection of 90% of the species 90% of the time (using the 10th percentile from the species sensitivity distributions) from acute and chronic COPEC exposures. Ecological effects acute and chronic data were obtained from the same sources used in the first three SERAs (e.g., AQUIRE, etc.). Pesticides and metals effects data were screened using the same approach and procedures as in the first three SERAs. A summary of the number of toxicity tests used for each COPEC species sensitivity distributions is documented in the tables. The Appendix includes a list of the types of native and nonnative species used in toxicity tests for all COPECs.

For the SERA, the 22 sites in ENP were divided into five regions: East Boundary (EB: stations 332Ba, 332Bb, 21, 22, 23, 24 and R158), Shark River Slough (SRS: stations 07, 37, 50, 58), Tamiami Trail (TT: stations 63, 64, 57, L67), Taylor Slough (TS: stations 53, 54, MDA, 59), C-111 (C-111: stations 55, 60, 61). Biscayne Bay (BB: stations BBTPC, BBICS, BBEKH, BBCP, BBSK, BBBP2, BBBP1, BBFP, BBMM) and Florida Bay (FLB: stations FBMTR, FBMJB, FBLS, FBLSR) were considered separate regions for the SERA, to compose a total of seven regions. The interpretation of fish tissue residues are discussed at the end of the SERA.

For each region the two-tier approach was used to first screen for metal and pesticide COPECs. Sediment concentrations were compared to FDEP sediment quality criteria (SQC). In tier 1, when a screening benchmark was exceeded ($\geq$ 0.5) by a metal or pesticide concentration three or more times in a region, the metal and/or pesticide was considered a

COPEC. SQCs for metals and pesticides are listed in the Appendix for Section 5.2 and 5.3. When numerous metals and/or pesticides were present in a region, regardless if they were COPECs, a Hazard Index was calculated for metals and/or pesticides for that region. To predict toxicity for metals AVS concentrations were compared to the sum of total extractable metals (TEM) in the regions. To obtain AVS values we used the 10th centile of AVS from all sites south of Lake Okeechobee from the South Florida Water Management District database (R. J. Pfeuffer, personal communication). When TEM exceeded the AVS estimate the excess metal was normalized to the organic carbon concentration at the region to predict the potential for acute and chronic aquatic toxicity (DiToro et al., in Press). The fraction of organic carbon (f_{oc}) content for each sediment site is listed in Table 5.4.1.

The hypothesis considered in the three-year monitoring SERA is: COPECs may cause effects at the species and community levels for aquatic organisms in ENP and BNP and these effects may adversely affect community structure and function. The ecological risk of each COPEC was evaluated separately.

5.4.2.1. Risk Analysis

Exposure.

The actual measured whole (bulk) sediment concentrations of pesticide and metal COPECs were converted to predicted pore water concentrations (PPW_c) for preparation of exposure distributions (see Sections 5.2 and 5.3). Metal partition coefficients (K_p) were obtained from USEPA (1999) to derive pore water concentrations. To convert from measured whole sediment concentrations (μg/Kg) to pore water concentrations for pesticides the mean of all K_{oc} values (L/Kg) available from the U.S. Dept. of Agriculture Pesticide Properties Database

(http://www.arsusda.gov/acsl/ppdb.html) was first converted to K_p values (partition coefficient, L/Kg) by multiplying by the mass fraction of organic carbon (f_{oc}) in site sediments according to:

$$K_p = K_{oc} * f_{oc}$$

Organic carbon concentrations are listed in Table 5.4.1. Distributions of pore water exposure concentrations were determined similarly to Section 5.2 and 5.3. The 90th percentile pore water exposure concentration and 90th percentile bulk sediment exposure concentrations for COPECs were also calculated from lognormal concentration distributions for each COPEC at all seven regions (i.e., BB, C-111, EB, FB, SRS, TS, TT) when a COPEC was present.

Effects.

Toxicity data used to prepare SSDs for the metal and pesticide COPECs are listed in the Appendix. A comprehensive review and synthesis of the literature related to the COPECs aquatic toxicity (e.g., LC50s, NOECs) was conducted using literature searches (e.g., AQUIRE, etc.). SSDs were prepared for acute and chronic toxicity data for each COPEC (SETAC, 1994). Acute freshwater toxicity data for metals (i.e., copper, cadmium, chromium, lead, nickel, zinc) were standardized to a hardness of 200 mg/L $CaCO_3$ based on procedures from Section 5.3. When freshwater acute toxicity test data did not have water hardness data it was not used in the SSD. Toxicity distributions were prepared similarly to Sections 5.2 and 5.3. The primary toxicity benchmark used for this SERA was the10th centile of the SSD from acute and chronic exposures. The assumption when using this benchmark is that protecting a large percentage of the species will preserve ecosystem

structure and function. This level of protection is not acceptable when the unprotected 10% are threatened/endangered, keystone or of commercial or of recreational significance.

5.4.2.2. Risk Characterization-Tier 2

Potential risk to freshwater organisms from acute and chronic exposures to COPECs in porewater was determined by comparing pore water exposure distributions by region with the 10th centiles from the acute LC50 and chronic NOEC data distributions for each COPEC. The percent exceedence of the 10th centile for each COPEC was used as a risk estimate (Solomon et al., 1996). The last step in the PRA used joint probability curves (JPCs; or exceedence profiles) for each exposure at a region to rank potential risk of COPECs and regions. JPCs were constructed using PRAT-1 software (Solomon et al., 2000). We also used the exposure data for sites with metal and pesticide COPECs to determine the probability of exceedence of FDEP sediment quality TEC and PEC standards (Hall et al., 2003). PECs and TECs are discussed in Section 1.2.

5.4.3. RESULTS AND DISCUSSION

5.4.3.1. Problem Formulation

Tier 1.

Tier 1 indicates that the pesticide DDE is a COPEC since Florida sediment quality criteria were exceeded in two regions (Table 5.4.2). The metals arsenic, chromium, copper, lead, nickel and zinc were also COPECs in multiple regions (Table 5.4.3). Tables 5.4.2 and 5.4.3 show the regions with the sediment quality violations. DDE was the most frequently detected pesticide in sediment. All metal COPECs were frequently (43-48 times) detected in sediment

and cadmium was the least frequently detected metal. Arsenic was the only COPEC present in all seven regions and it also had the highest number of SQC exceedences. Lead had the next highest number of SQC exceedences. Lead was a COPEC in four regions (C-111, East boundary, Shark River Slough and Tamiaimi Trail) and was only found as a metal COPEC in the C-111 (S-176) in the SFWMD database. Cadmium was not a COPEC in this study but it was a COPEC in the SFWMD database in the Holey Land tracts (SD2, 3 and 4).

The pesticide hazard indices (HIs) for all seven regions are summarized in Figure 5.4.1 and Table 5.4.4. Shark River Slough followed by Tamiami Trail had the highest pesticide HIs of the seven regions. Florida Bay had the lowest pesticide HI. The main pesticide responsible for the high HIs was DDE. The metal HIs for all seven regions are summarized in Figure 5.4.2 and Table 5.4.5**.** East Boundary and Tamiami Trail had the highest HIs for metals. The main metals at EB responsible for the high HI were arsenic, followed by chromium, copper, nickel and lead. The main metals at TT responsible for the high HI were arsenic, followed by copper, zinc, lead and nickel. Florida Bay's HI was greater than the Biscayne Bay HI. In both saltwater systems arsenic was predominately responsible for the high HIs.

For all SFWMD AVS data the $AVS_{10th\ percentile}$ was 2.20μmol/g and the AVS_{median} was 7.15μmol/g. Note to calculate these AVS data we used all sites south of Lake Okeechobee from the SFWMD database (see Appendix). Using the TEM-AVS_{median} approach to predict toxicity there was no excess metal for any site within a region but using the TEM-$AVS_{10th\ percentile}$ approach there was excess metal at sites C111/US1, 22, 63 and L67 (Table 5.4.6). When the excess (TEM-$AVS_{10th\ percentile}$) was normalized for organic carbon it was <100μmol/gOC (Table 5.4.7). The latter result suggests that there is no potential for metal toxicity (i.e., acute and/or chronic) at the sites with excess metals (DiToro et al., in Press).

COPEC Characteristics in the Environment.

The characteristics of DDE are discussed in Section 5.2 and the characteristics of the metals are discussed in Section 5.3.

Assessment and Measurement Endpoints.

The long-term viability of aquatic communities (e.g., fish, invertebrates, etc.) within ENP and BNP are addressed in this SERA. The specific assessment endpoint is the protection of 90% of the species 90% of the time (using the 10th percentile from the species sensitivity distributions) from acute and chronic COPEC exposures. Chronic sediment exposures and risks from such exposures is of utmost importance here because of the environmental persistence of all the COPECs. The measurement endpoints include all the pesticide and metal toxicity data (survival, growth, reproduction) generated from freshwater and saltwater laboratory toxicity studies. These data will be used to define acute/chronic risks to aquatic communities.

5.4.3.2. Risk Analysis

Exposure.

The only pesticide COPEC was DDE. The partition coefficients for DDE were 5.45 and 5.42, respectively for SRS and TT. Table 5.4.8 presents the statistics for the lognormal distributions of the bulk sediment concentrations for DDE at SRS and TT. The DDE 90th centiles ranged from 9.93 µg/Kg in the Shark River Slough to 13.35 µg/Kg in Tamiami Trail. However, the DDE 90th centiles ranged from 8.43 µg/kg in HOLYSD3 to 289.9 µg/kg at pumping station S-6 data from the South Florida Water Management District database.

Higher DDE concentrations at the SFWMD sites may reflect the prior historical use of DDT in agriculture south of Lake Okeechobee. Table 5.4.9 presents the statistics for the lognormal distributions of the predicted pore water concentrations for DDE in SRS and TT. DDE 90th centiles ranged from 0.035 ng/L in SRS to 0.050 ng/L in TT. DDE 90th centiles were over one hundred fold higher at S-2, S-3 and S-4 (the lowest at 3.3ng/L) near Lake Okeechobee and S-6 (near WCA1 and WCA2) and S-7 (near WCA2 and WCA3). The SFWMD S-177 and S-178 sites in C-111 were two of the highest predicted pore water concentrations for DDE 90th centiles at 8.8 and 8.2 ng/L, respectively. In the 3-year monitoring study little organochlorine pesticides were detected at C-111 sampling sites which were south of the District sites. Table 5.4.10 presents the statistics for the lognormal distributions of the bulk sediment concentrations for the metal COPECs in the seven regions. The highest 90th percentile for bulk sediment was for chromium (317.73 mg/Kg) in the East Boundary followed by zinc (160.8 mg/Kg) at Tamiami Trail. In the SFWMD database the highest 90th percentile (58.13 mg/kg) was for chromium and it was also at S-178. However, our C-111 and Shark River Slough findings had high chromium 90th percentiles of 53.00 mg/Kg and 66.17 mg/Kg, respectively which are consistent with S-178. In the SFWMD database zinc was only a COPEC in the C-111 with the highest 90th percentile at S-178 (227.62 mg/Kg). Arsenic 90th percentiles ranged from 11.44 mg/Kg (East Boundary) to 33.33 mg/Kg (Florida Bay). In the SFWMD database arsenic 90th percentiles were similar and ranged from 6.98 mg/Kg (Holey Land SD3) to 21.46 mg/Kg (Holey Land SD1). Copper was found as a COPEC in five regions (BB, C-111, EB, SRS, TT) at a 90th percentile range of 11.64 mg/Kg (BB) to 41.98 mg/Kg (TT). In the SFWMD database copper was only a COPEC in the C-111 (S-177 and S-178) with 90th percentiles of 26.50 (S-177) and 82.42

(S-178) mg/Kg. Nickel was a COPEC in five regions with a 90th percentile range of 10.06 mg/Kg (C-111) to 41.56 mg/Kg (EB). In the SFWMD database nickel was only a COPEC in the C-111 at S-178 (90th percentile-22.73 mg/Kg) and S-18C (90th percentile-15.17 mg/Kg).

Table 5.4.11 presents the statistics for the lognormal distributions of the predicted porewater concentrations for the metal COPECs. The highest 90th percentiles were for arsenic with a range of 45.53 μg/L in the East Boundary to132.68 μg/L in Florida Bay. In comparison the SFWMD database indicated that the Holey Land Tracts (SD1 and 2) had the highest arsenic 90th percentiles (72.89 to 85.45 μg/L) followed by WCA2F1 (64.4 μg/L) and S-18C (54.57 μg/L) in the C-111. Except for zinc in TT (12.77 μg/L) most of of the 90th percentiles were below 10 μg/L for all other metal COPECs.

Effects.

The statistics for the acute and chronic (NOEC) 10th percentiles for DDE and metal COPECs are summarized in Section 5.2 and 5.3, respectively.

5.4.3.3. Risk Characterization

The probability of pore water exposures of DDE in Shark River Slough and Tamiami Trail exceeding arthropod acute and chronic 10th percentiles was zero. The probability of pore water exposures of all metal COPECs exceeding the arthropod acute 10th percentile values are presented in Table 5.4.12. Risk estimates were only determined for arthropods because they represent the most sensitive group to metals. The probability of copper concentrations in Tamiami Trail and the East Boundary sediment samples exceeding the arthropod acute 10th percentiles was 75 and 54 %, respectively. These were the highest acute risk estimates of all metal COPECs for all seven regions. In the SFWMD database the highest acute risk

estimates were also for copper in the C-111 at S-177 (58%) and S-178 (100%). Acute risk estimates for copper were lower (21%) in the present study in the C-111 region but it was the metal COPEC with the highest acute risk out of six metal COPECs present in the C-111 region. The probability of arsenic concentrations in Florida Bay sediment samples exceeding the arthropod acute 10th percentiles was 13 %. This was the only metal COPEC in Florida Bay producing any potential acute risk while in Biscayne Bay both arsenic (6.6%) and copper (12.7%) were of potential acute concern. Aside from Tamiami Trail having the highest acute risk estimate for copper it also had the high potential acute risk from zinc (25%). The probability of nickel, lead and chromium had the lowest acute risk estimates at between 0 and <1 %. Arsenic in Taylor Slough was the only metal COPEC displaying low potential for acute risk.

The probability of predicted pore water exposures of all metal COPECs exceeding the arthropod chronic NOEC 10th percentile values are presented in Table 5.4.13. The highest potential chronic risk for a single metal COPEC was for copper based on the probability of pore water exposures exceeding the NOEC 10th percentiles in Tamiami Trail (98%) and in the East Boundary (90%). This was followed by Shark River Slough (72%), C-111 (39%) and Biscayne Bay (21%). The next metal COPEC that presented chronic risk potential was lead since the probability of pore water exposures exceeding the NOEC 10th was 23% in the East Boundary and 17% in Tamiami Trail. Lead in the East Boundary (23%) and in Tamiami Trail (17%) followed by nickel in the East Boundary (15%) also displayed high potential chronic risks. There was insufficient data to assess chronic risk for arsenic.

JPCs for sites with potential acute risk to aquatic organisms are illustrated in Figures 5.4.3 to 5.4.22. JPCs for sites with potential chronic risk to aquatic organisms are illustrated in Figures 5.4.23 to 5.4.38.

The probability of DDE bulk sediment concentrations exceeding the FDEP SQAG TEC and PEC by site is presented in Table 5.4.14. The probability for DDE exceeding the TEC at Shark River Slough and Tamiami Trail was high (30-42%) but less than 5% of exceeding the PEC. The probability of metal bulk sediment concentrations exceeding the FDEP SQAG TEC and PEC by site is presented in Table 5.4.15. The highest probability of any metal COPEC exceeding the sediment TEC was for lead in TT at 54.76 % followed by arsenic in TT at 52.7 %. The probability of zinc exceeding the sediment TEC in TT was also high at 20.32 %. Arsenic had high probabilities of exceeding the TEC in Shark River Slough (47.47%), and in the two saltwater regions (Florida Bay at 50.42%, Biscayne Bay at 36.12%). In the East Boundary chromium (48%), lead (38%) and nickel (26%) had a high probability of exceeding the TEC. The highest probability of any metal COPEC exceeding the sediment PEC was for chromium in East Boundary at 26.53 % followed by lead in the East Boundary at 10.61 %. All other metal COPEC probabilities of exceeding the PEC were less than 8%, including arsenic. Copper also did not appear to be a concern using the FDEP SQAG TEC/PEC probability approach.

5.4.3.4. Uncertainties

Exposure.

The exposure data used for this SERA were obtained from 22 sampling stations in Everglades National Park (ENP), 9 stations in Biscayne National Park (BNP) and 4 stations in Florida Bay (FB) from 2001 to 2004. The spatial scale of these data was limited considering the size of ENP, BNP and FB. The temporal scale (sampling frequency) of the available exposure data was also limited. In most cases only a limited number of measurements were made for metals and pesticides. Neither rain event nor wet and dry season sampling was considered. Uncertainty also existed because the exposure data were not collected from a random sampling design which is consistent with unbiased statistical analysis.

Analytical and sampling techniques were consistent because one laboratory was involved reducing uncertainty.

We used predicted pore water exposure distributions for DDE that were calculated by estimating K_p values from site-specific organic carbon and K_{oc} data from U.S.DA. We also used predicted pore water exposure distributions for metal COPECs that were calculated by using K_p values obtained from the U.S.EPA. These are two sources of uncertainty in the exposure assessment. However, as we explained in Section 1.3 (page 21-22) there is a limited toxicity database for species exposed to single contaminants in sediment so that it would be difficult to prepare acute and chronic species sensitivity distributions (SSDs) to compare to whole (bulk) sediment exposure distributions. However, according to the literature sediment toxicity exposures to organisms are typically as a result of pore water exposures which should be similar to toxic effect concentrations in water-only exposures. Therefore, we used predicted pore water exposure distributions for COPECs to compare to toxicity distributions to estimate risk.

Effects.

More acute and chronic data on the toxicity of single pesticide and metal COPECs in sediment are needed to prepare SSDs for comparison with whole sediment exposures. In addition, copper in the acute probabilistic assessment has the highest potential risk to arthropods. It would have been applicable and highly relevant to also prepare SSDs for copper and plants since it affects photosynthesis. However, the copper toxicity database was particularly limited for plants (phytoplankton and macrophytes). We assumed that the non-toxic chromium III was the major form of chromium present in sediment because of a reducing environment as a result of the presence of AVS (see Section 5.3). This is a source of uncertainty and it would be more accurate to have measured the concentrations of each of the chromium valence states (III, VI). In general, the chronic effects database was limited for all COPECs but little to no chronic effects toxicity data was available for arsenic and chromium III.

Using the modified AVS/SEM (or AVS/TEM) approach we predicted a lack of toxic effects by the divalent metals when normalized to organic carbon. However, this approach used TEM which is a "worst case scenario". SEM would have predicted even lower concentrations of "excess metals" and should have been determined in our study.

Risk Characterization.

Since six regions contain more than one COPEC "joint toxicity" may exist. The co-occurrence of several contaminants present at the same time makes it difficult to assess the risk of single COPECs in isolation.

5.4.4. CONCLUSIONS

Based on a Tier 1 assessment of pesticides and metals in sediment at 35 stations from ENP, BNP, and Florida Bay only DDE was a pesticide COPEC since Florida sediment quality criteria were exceeded in two regions.. The metals arsenic, chromium, copper, lead, nickel and zinc were also COPECs in multiple regions. DDE was the most frequently detected pesticide in sediment. All metal COPECs were frequently detected in sediment and cadmium was the least frequently detected metal. Arsenic was the only COPEC present in all seven regions and it also had the highest number of SQC exceedences. Lead had the next highest number of SQC exceedences. Shark River Slough followed by Tamiami Trail had the highest pesticide HIs of the seven regions. Florida Bay had the lowest pesticide HI. East Boundary and Tamiami Trail had the highest HIs for metals. The main metals at EB responsible for the high HI were arsenic, followed by chromium, copper, nickel and lead. The main metals at TT responsible for the high HI were arsenic, followed by copper, zinc, lead and nickel. Florida Bay's HI was greater than the Biscayne Bay HI. In both saltwater systems arsenic was predominately responsible for the high HIs. The highest acute risk was associated with copper in TT and EB. Arsenic acute risk was low except for FB. The highest chronic risk potential was associated with copper in TT followed by copper in EB.

Table 5.4.1
Mean organic carbon content (standard deviation) in sediment

Region	Organic carbon (mg/kg)	*N*
C-111	84,541 (29,004)	18
EB	92,462 (27,066)	11
SRS	319,994 (151,965)	9
TS	106,669 (19,172)	4
TT	297,676 (124,008)	6

Table 5.4.2

Results of Tier 1 Assessment: Use of Screening Benchmarks to Determine COPECs in Sediment

Chemical	COPEC	Comments
Total Chlordanes (I + II)	NO	Detected in sediment 12 times. Never exceeded SQC.
Total PCBs	NO	Detected in sediment 26 times. Exceeded SQC once. COPEC in region BB[3].
Tetrachlorobenzene 1,2,4,5	NO	Never detected in sediment.
Tetrachlorobenzene 1,2,3,4	NO	Never detected in sediment
Pentachlorobenzene	NO	Detected in sediment 4 times. Never exceeded SQC.
Hexachlorobenzene	NO	Detected in sediment 21 times. Never exceeded SQC.
Alpha HCH	NO	Detected in sediment 8 times. Never exceeded SQC.
Beta HCH	NO	Detected in sediment 2 times. Never exceeded SQC.
Gamma HCH	NO	Detected in sediment 3 times. Exceeded SQC once in region BB. COPEC in region BB[2].
Delta HCH	NO	Detected in sediment 3 times. Never exceeded SQC.
Heptachlor	NO	Never detected in sediment.
Heptachlor Epoxide/OCS	NO	Detected once in sediment. Did not Exceed SQC.
Aldrin	NO	Detected in sediment 13 times. Exceeded SQC 11 times. COPEC in regions; EB, TS[2], TT[2], SRS[2],
Dieldrin	NO	Detected in sediment 5 times. Exceeded SQC once in region C-111. COPEC in Region C-111[2].
Endrin	NO	Detected in sediment 10 times. Never exceeded SQC.
Chlorpyrifos	NO	Detected in sediment 3 times. No SQC available.
Mirex	NO	Never detected in sediment.
Endosulfan Sulfate	NO	Detected in sediment 19 times. Never exceeded SQC.
Endosulfan II	NO	Detected in sediment 12 times. Exceeded SQC once in region SRS[2].
2,4' DDE/ENDOSULFAN I	Cannot Determine	Compounds co-elute.
4,4' DDE	YES	Detected in sediment 34 times. Exceeded SQC 9 times. COPEC in regions; SRS, BB[2], TT.
2,4' DDD	NO	Detected in sediment 2 times. No SQC available
4,4' DDD	NO	Detected in sediment 4 times. Exceeded SQC once. COPEC in region BB[2].
2,4' DDT	NO	Never Detected in sediment
4,4' DDT	NO	Detected in sediment 3 times. Never exceeded SQC.

1. SQC; Sediment Quality Criteria (HQ $\geq$ 0.5)
2. Too few regional detections to create exposure distribution
3. Cannot predict pore water concentrations because of variability in partitioning of PCB compounds

Table 5.4.3

Results of Tier 1 Assessment: Use of Screening Benchmarks to Determine COPECs in Sediment

Chemical	COPEC	Comments
Arsenic	Yes	Exceeded SQC[1] 29 times. COPEC in regions: BB, C-111, TS, FLB, SRS, TT, & EB.
Aluminum	No	Exceeded SQC 4 times in region EB
Berrylium	No	No SQC available for compound
Cadmium	No	Never exceeded SQC.
Chromium	Yes	Exceeded SQC 14 times. COPEC in regions: EB, SRS, FLB, & C-111.
Cobalt	No	Never exceeded SQC.
Copper	Yes	Exceeded SQC 10 times. COPEC in regions: EB, TT, SRS, & C-111
Lead	Yes	Exceeded SQC 16 times. COPEC in regions: EB, TT, SRS, C-111.
Nickel	Yes	Exceeded SQC 14 times. COPEC in regions: EB, TT, SRS, FLB, & C-111.
Vanadium	No	No SQC available for compound.
Zinc	Yes	Exceeded SQC 5 times. COPEC in regions: TT & C-111.

1. Sediment Quality Criteria (SQC)

Table 5.4.4

Summary of mean pesticide hazard indices at sites (n=7) in the 3-year monitoring program.

Region	Mean	N	Std. Deviation	Minimum	Maximum	Range	Median
BB	.32	9	.34	.00	.89	.89	.08
C-111	.29	13	.53	.00	2.01	2.01	.15
EB	.23	11	.28	.00	.76	.76	.06
FLB	.01	4	.03	.00	.05	.05	.00
SRS	1.27	8	.82	.25	2.17	1.92	1.20
TS	.28	4	.08	.20	.39	.19	.26
TT	.80	6	.53	.29	1.74	1.45	.57
Total	.46	55	.59	.00	2.17	2.17	.23

Table 5.4.5

Summary of mean metal hazard indices at sites (n=7) in the 3-year monitoring program.

Region	Mean	N	Std. Deviation	Median	Minimum	Maximum	Range
BB	1.76	9	1.02	1.82	.38	3.08	2.70
C-111	1.90	13	2.39	1.18	.34	9.30	8.96
EB	5.68	11	3.58	4.82	1.10	11.55	10.45
FLB	3.78	4	2.14	3.14	2.10	6.76	4.66
SRS	2.99	8	.83	2.73	2.12	4.70	2.58
TS	.80	4	.30	.76	.48	1.20	.72
TT	4.77	6	1.54	4.39	3.02	7.24	4.22
Total	3.16	55	2.66	2.54	.34	11.55	11.21

Table 5.4.6

Excess total extractable metal (TEM) using the median and 10th centile AVS (umol/kg)

Site	Collection date	region	TEM umol/kg	Excess Metal by Median AVS umol/kg	Excess Metal by 10th centile AVS umol/kg
BBBP1	14-Nov-2001	BB	755.57	-6395.09	-1443.30
BBBP2	14-Nov-2001	BB	90.57	-7060.09	-2108.30
BBCP	14-Nov-2001	BB	21.22	-7129.44	-2177.64
BBEKH	14-Nov-2001	BB	32.69	-7117.96	-2166.17
BBFP	14-Nov-2001	BB	89.93	-7060.72	-2108.93
BBICS	14-Nov-2001	BB	33.23	-7117.43	-2165.63
BBMM	14-Nov-2001	BB	70.10	-7080.56	-2128.76
BBSK	14-Nov-2001	BB	108.38	-7042.27	-2090.48
BBTPC	14-Nov-2001	BB	157.73	-6992.92	-2041.13
55	30-Jul-2003	C-111	125.15	-7025.51	-2073.72
55	10-Dec-2003	C-111	130.80	-7019.85	-2068.06
55	21-Jun-2002	C-111	137.12	-7013.53	-2061.74
55	16-Dec-2002	C-111	158.13	-6992.52	-2040.73
55	16-Sep-2001	C-111	160.26	-6990.39	-2038.60
60	16-Sep-2001	C-111	112.45	-7038.21	-2086.42
61	10-Dec-2003	C-111	113.71	-7036.94	-2085.15
61	16-Sep-2001	C-111	127.90	-7022.75	-2070.96
61	30-Jul-2003	C-111	162.78	-6987.87	-2036.08
61S	10-Dec-2003	C-111	55.74	-7094.91	-2143.12
61S	30-Jul-2003	C-111	350.92	-6799.73	-1847.94
C111/US1	16-Sep-2003	C-111	2647.89	-4502.76	449.03
S197	16-Sep-2003	C-111	961.68	-6188.98	-1237.18
21	9-Aug-2001	ENP EB	681.20	-6469.45	-1517.66
22	24-Mar-2004	ENP EB	615.20	-6535.46	-1583.66
22	21-Jun-2002	ENP EB	847.05	-6303.60	-1351.81
22	13-Dec-2002	ENP EB	1166.13	-5984.53	-1032.74
22	9-Aug-2001	ENP EB	2230.42	-4920.24	31.56
23	9-Aug-2001	ENP EB	504.53	-6646.13	-1694.33
24	9-Aug-2001	ENP EB	262.97	-6887.68	-1935.89
332BA	9-Aug-2001	ENP EB	921.13	-6229.52	-1277.73
332BB	24-Mar-2004	ENP EB	925.52	-6225.14	-1273.34
332BB	16-Aug-2001	ENP EB	1240.63	-5910.03	-958.23
R158	9-Aug-2001	ENP EB	239.32	-6911.34	-1959.54
LS	22-May-2002	FLB	364.37	-6786.28	-1834.49
LSR	22-May-2002	FLB	297.11	-6853.55	-1901.76
MJB	22-May-2002	FLB	358.73	-6791.92	-1840.13
MTR	22-May-2002	FLB	282.35	-6868.30	-1916.51
7	1-Oct-2002	SRS	413.70	-6736.95	-1785.16
7	16-Aug-2001	SRS	1321.03	-5829.63	-877.83
37	1-Aug-2001	SRS	380.28	-6770.38	-1818.59
37	1-Oct-2002	SRS	393.47	-6757.18	-1805.39

50	22-Aug-2001	SRS	543.82	-6606.83	-1655.04
58	26-Feb-2001	SRS	312.75	-6837.90	-1886.11
SRS2	15-Mar-2004	SRS	445.45	-6705.20	-1753.41
SRS3	15-Mar-2004	SRS	525.89	-6624.76	-1672.97
57	22-Aug-2001	Tam	838.69	-6311.96	-1360.17
63	13-Dec-2002	Tam	1589.09	-5561.56	-609.77
63	21-Jun-2002	Tam	1880.28	-5270.37	-318.58
63	22-Aug-2001	Tam	2651.98	-4498.68	453.11
64	22-Aug-2001	Tam	1162.80	-5987.86	-1036.06
L67	22-Aug-2001	Tam	2478.17	-4672.49	279.31
53	30-Aug-2001	TS	187.95	-6962.71	-2010.91
54	30-Aug-2001	TS	151.86	-6998.79	-2047.00
59	16-Sep-2001	TS	147.70	-7002.95	-2051.16
MDA	30-Aug-2001	TS	363.18	-6787.48	-1835.68

Table 5.4.7

Organic carbon normalized TEM_{oc} (umol/g_{oc})

Site	Collection date	region	TEM umol/kg	Excess Metal by median AVS umol/kg	Excess Metal by 10th Centile AVS umol/kg	Site Specific foc kg_{oc}/kg_{dw}	Excess AVS by 10th Centile TEM_{oc} umol/g_{oc}
C111/US1	16-Sep-2003	C-111	2647.89	-4502.76	449.03	0.074	6.07
22	9-Aug-2001	EB	2230.42	-4920.24	31.56	0.091	0.35
63	22-Aug-2001	Tam	2651.98	-4498.68	453.11	0.13	3.49
L67	22-Aug-2001	Tam	2478.17	-4672.49	279.31	0.094	2.97

Table 5.4.8
Statistics for Lognormal Distributions of Bulk Sediment Concentration Data for COPECs Including 90th Centile Concentration (ug/kg dry weight)

Region	COPEC	Number of times analyzed	Number of Detections	Slope	Intercept	r^2	*p*-value	90th centile ug/kg
SRS	4,4 DDE	8	8	2.18	4.11	0.96	1.66E-05	9.93
TT	4,4 DDE	6	6	1.20	4.93	0.86	7.71E-03	13.35

Table 5.4.9
Statistics for Lognormal Distributions of Predicted Pore Water Concentrations for COPECs Including 90th Centile Concentration (ng/l)

Region	COPEC	Number of times analyzed	Number of Detections	Slope	Intercept	r^2	*p*-value	90th centile ng/l
SRS	4,4 DDE	8	8	2.18	15.99	0.96	1.66E-05	0.035
TT	4,4 DDE	6	6	1.20	11.43	0.86	7.71E-03	0.050

Table 5.4.10
Statistics for Lognormal Distributions of Bulk Sediment Concentration Data for COPECs Including 90th Centile Concentration (mg/kg dry weight)

Region	COPEC	Number of times analyzed	Number of Detections	Slope	Intercept	r^2	*p*-value	90th centile mg/kg
BB	Arsenic	9	8	2.01	3.62	0.96	2.75E-05	20.94
BB	Copper	9	4	0.64	5.60	0.82	92.54E-03	11.64
C-111	Arsenic	13	13	2.74	3.30	0.96	2.41E-09	12.28
C-111	Chromium	13	13	1.20	4.21	0.91	5.00E-07	53.00
C-111	Copper	13	12	1.03	4.93	0.84	3.07E-05	20.26
C-111	Lead	13	13	1.32	4.29	0.79	4.79E-05	31.88
C-111	Nickel	13	13	3.74	2.53	0.90	1.00E-06	10.06
C-111	Zinc	13	13	1.29	4.33	0.91	4.11E-07	32.41
EB	Arsenic	11	11	2.48	3.66	0.84	6.69E-05	11.44
EB	Chromium	11	11	1.42	2.73	0.86	3.96E-05	317.73
EB	Copper	11	11	2.27	2.98	0.94	1.07E-06	28.43
EB	Lead	11	11	1.69	2.68	0.94	6.48E-07	136.12
EB	Nickel	11	11	2.48	2.26	0.90	1.02E-05	41.56
FLB	Arsenic	4	4	1.95	3.31	0.86	7.01E-02	33.33
FLB	Chromium	4	4	2.69	0.95	0.92	3.90E-02	96.18
FLB	Nickel	4	4	3.82	1.15	0.95	2.64E-02	22.08
SRS	Arsenic	8	8	3.08	2.01	0.92	1.87E-04	24.33
SRS	Chromium	8	8	1.75	3.09	0.82	2.03E-03	66.17
SRS	Copper	8	8	2.33	3.64	0.77	4.44E-03	13.63
SRS	Lead	8	8	3.02	1.54	0.46	66.18E-03	36.96
SRS	Nickel	8	8	1.88	3.89	0.90	3.56E-04	18.75
TS	Arsenic	4	4	1.81	4.32	0.96	22.3E-03	12.19
TT	arsenic	6	6	2.95	2.01	0.75	2.50E-02	28.11
TT	copper	6	6	2.51	2.21	0.93	1.79E-03	41.98
TT	lead	6	6	4.18	-1.63	0.92	2.39E-03	77.84
TT	nickel	6	6	6.34	-1.00	0.83	1.13E-02	14.10
TT	zinc	6	6	3.55	-1.56	0.91	2.92E-03	160.80

Table 5.4.11
Statistics for Lognormal Distributions of Predicted Pore Water Concentrations for COPECs
Including 90th Centile Concentration (ug/l)

Region	COPEC	Number of times analyzed	Number of Detections	Slope	Intercept	r^2	*p*-value	90th centile ug/l
BB	Arsenic	9	8	2.01	2.42	0.96	2.75E-05	83.37
BB	Copper	9	4	0.64	5.92	0.82	92.54E-03	3.68
C-111	Arsenic	13	13	2.74	1.66	0.96	2.41E-09	48.87
C-111	Chromium	13	13	1.20	6.49	0.91	5.00E-07	0.67
C-111	Copper	13	12	1.03	5.45	0.84	3.07E-05	6.41
C-111	Lead	13	13	1.32	6.41	0.79	4.79E-05	0.80
C-111	Nickel	13	13	3.74	5.90	.90	1.00E-06	1.27
C-111	Zinc	13	13	1.29	5.75	0.91	4.11E-07	2.58
EB	Arsenic	11	11	2.48	2.17	0.84	6.69E-05	45.53
EB	Chromium	11	11	1.42	5.43	0.86	3.96E-05	4.00
EB	Copper	11	11	2.27	4.11	0.94	1.07E-06	8.99
EB	Lead	11	11	1.69	5.38	0.94	6.48E-07	3.42
EB	Nickel	11	11	2.48	4.50	0.90	1.02E-05	5.23
FLB	Arsenic	4	4	1.95	2.14	0.86	7.01E-02	132.68
FLB	Chromium	4	4	2.69	6.06	0.92	3.90E-02	1.21
FLB	Nickel	4	4	3.82	4.59	0.95	2.64E-02	2.78
SRS	Arsenic	8	8	3.08	0.16	0.92	1.87E-04	96.87
SRS	Chromium	8	8	1.75	6.42	0.82	2.03E-03	0.833
SRS	Copper	8	8	2.33	4.80	0.77	4.44E-03	4.31
SRS	Lead	8	8	3.02	6.38	0.46	66.18E-03	0.928
SRS	Nickel	8	8	1.88	5.58	0.90	3.56E-04	2.36
TS	Arsenic	4	4	1.81	3.23	0.96	22.3E-03	48.52
TT	arsenic	6	6	2.95	0.24	0.75	2.50E-02	111.91
TT	copper	6	6	2.51	3.46	0.93	1.79E-03	13.27
TT	lead	6	6	4.18	5.06	0.92	2.39E-03	1.96
TT	nickel	6	6	6.34	4.70	0.83	1.13E-02	1.78
TT	zinc	6	6	3.55	2.35	0.91	2.92E-03	12.77

Table 5.4.12
Probability of Exceedence of the Arthropod Acute 10th Centiles for Pore Water Concentrations in Project Sediment Regions

Region	COPEC	Probability of exceedence of 10th centile (%)
BB	Arsenic	6.59
BB	Copper	12.74
C-111	Arsenic	1.31
C-111	Chromium	0.05
C-111	Copper	21.12
C-111	Lead	0.40
C-111	Nickel	0.00
C-111	Zinc	2.54
EB	Arsenic	1.35
EB	Chromium	0.58
EB	Copper	54.25
EB	Lead	2.44
EB	Nickel	0.00
FLB	Arsenic	13.42
FLB	Chromium	0.00
FLB	Nickel	0.00
SRS	Arsenic	7.69
SRS	Chromium	0.00
SRS	Copper	27.32
SRS	Lead	.00
SRS	Nickel	0.00
Taylor Slough	Arsenic	2.81
TT	Arsenic	10.84
TT	Copper	75.00
TT	Lead	0.00
TT	Nickel	0.00
TT	Zinc	25.45

Table 5.4.13
Probability of Exceedence of the Community Chronic NOEC 10th Centiles for Pore Water Concentrations in Project Sediment Regions

Region	COPEC	Probability of exceedence of 10th centile (%)
BB	Arsenic	NA
BB	Copper	20.89
C-111	Arsenic	NA
C-111	Chromium	NA
C-111	Copper	39.30
C-111	Lead	4.54
C-111	Nickel	.06
C-111	Zinc	0.86
EB	Arsenic	NA
EB	Chromium	NA
EB	Copper	89.85
EB	Lead	22.96
EB	Nickel	14.87
FLB	Arsenic	NA
FLB	Chromium	NA
FLB	Nickel	2.49
SRS	Arsenic	NA
SRS	Chromium	NA
SRS	Copper	72.28
SRS	Lead	2.14
SRS	Nickel	4.01
Taylor Slough	Arsenic	NA
TT	Arsenic	NA
TT	Copper	97.51
TT	Lead	16.94
TT	Nickel	.01
TT	Zinc	3.28

Table 5.4.14
Probability of Exceedence of the Florida SQAG for Bulk Sediment Concentrations

Region	COPEC	Probability of exceedence of TEC (%)	Probability of exceedence of PEC (%)
SRS	4,4 DDE	41.71	0.92
TT	4,4 DDE	29.52	4.27

Table 5.4.15
Probability of Exceedence of the Florida SQAG for Bulk Sediment Concentrations

Region	COPEC	Probability of exceedence of TEC (%)	Probability of exceedence of PEC (%)
BB	Arsenic	36.19	3.00
BB	Copper	7.87	2.86
C-111	Arsenic	15.54	0.70
C-111	Chromium	12.06	4.82
C-111	Copper	6.85	1.46
C-111	Lead	8.83	1.84
C-111	Nickel	0.43	<.01
C-111	Zinc	2.20	0.29
EB	Arsenic	13.24	0.77
EB	Chromium	48.11	26.53
EB	Copper	8.10	0.17
EB	Lead	37.99	10.61
EB	Nickel	25.98	7.23
FLB	Arsenic	50.42	7.09
FLB	Chromium	28.41	3.03
FLB	Nickel	23.05	0.87
SRS	Arsenic	47.47	4.56
SRS	Chromium	17.01	4.76
SRS	Copper	1.60	0.01
SRS	Lead	10.62	0.17
SRS	Nickel	7.38	1.95
TS	Arsenic	13.24	1.95
TT	arsenic	52.70	6.85
TT	copper	16.21	0.38
TT	lead	54.76	1.34
TT	nickel	0.43	<0.01
TT	zinc	20.32	0.19

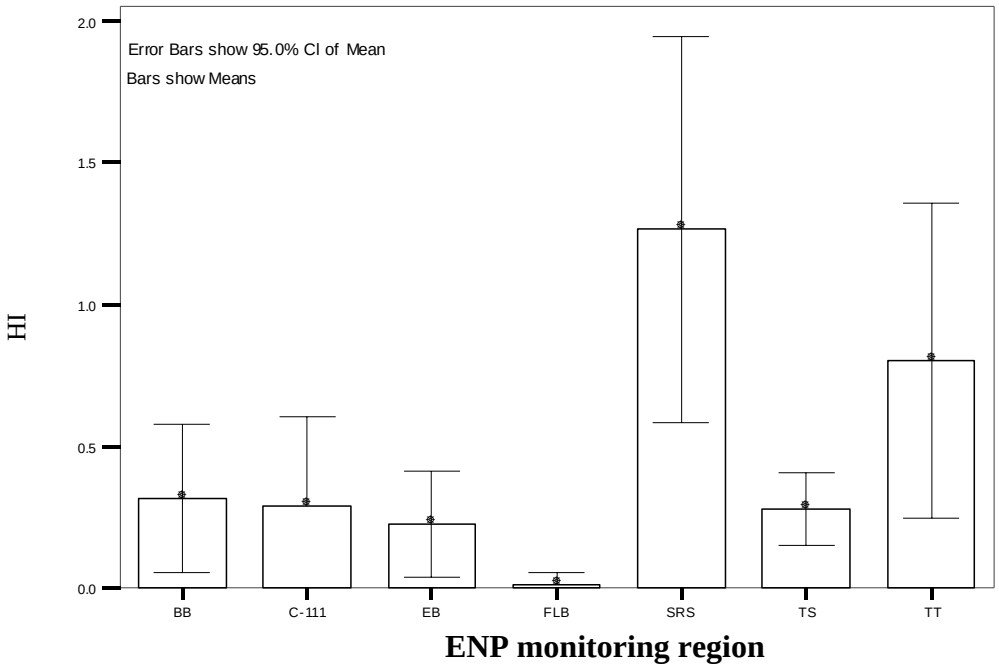


Figure 5.4.1
Summary of mean pesticide hazard indices at regions (n=7) in the 3-year monitoring program.

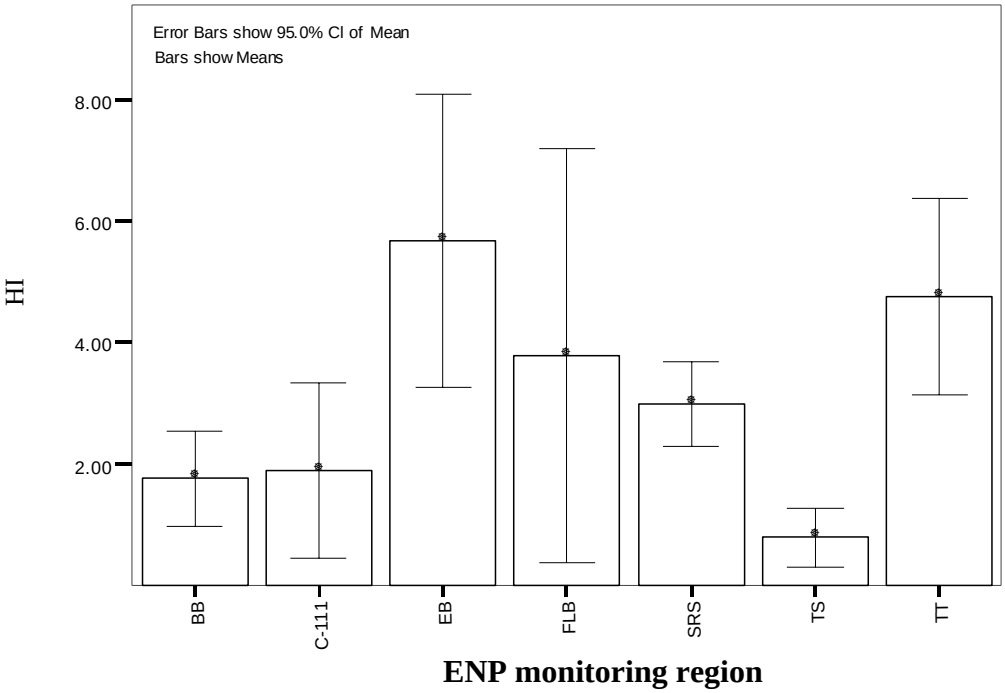


Figure 5.4.2
Summary of mean metal hazard indices at regions (n=7) in the 3-year monitoring program.

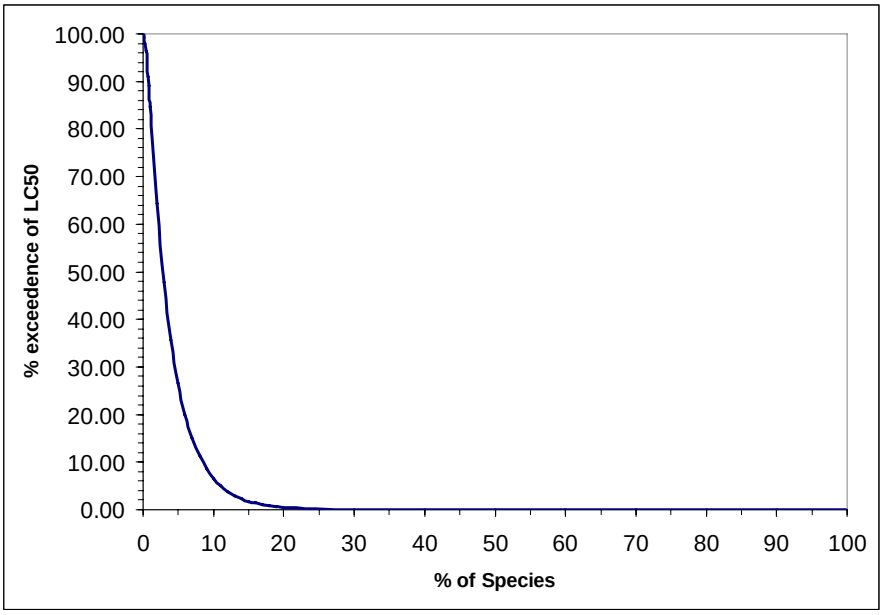


Figure 5.4.3

JPC for predicted pore water concentrations of arsenic for freshwater arthropods at BB

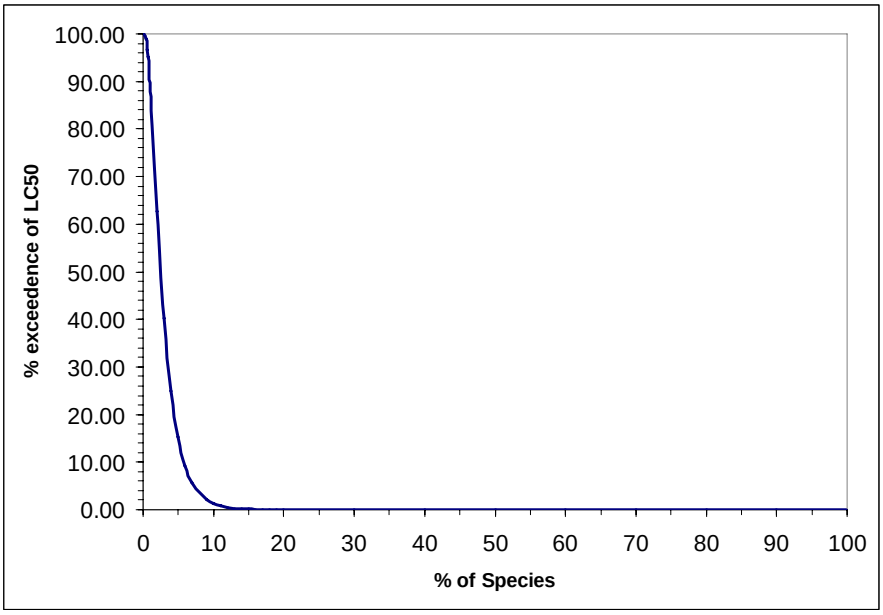


Figure 5.4.4

JPC for predicted pore water concentrations of arsenic for freshwater arthropods at C-111

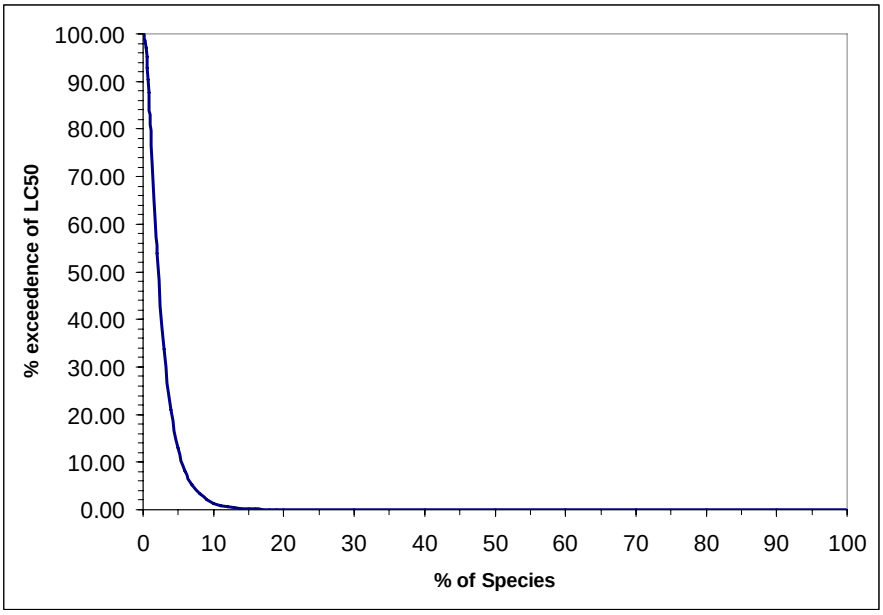


Figure 5.4.5

JPC for predicted pore water concentrations of arsenic for freshwater arthropods at EB

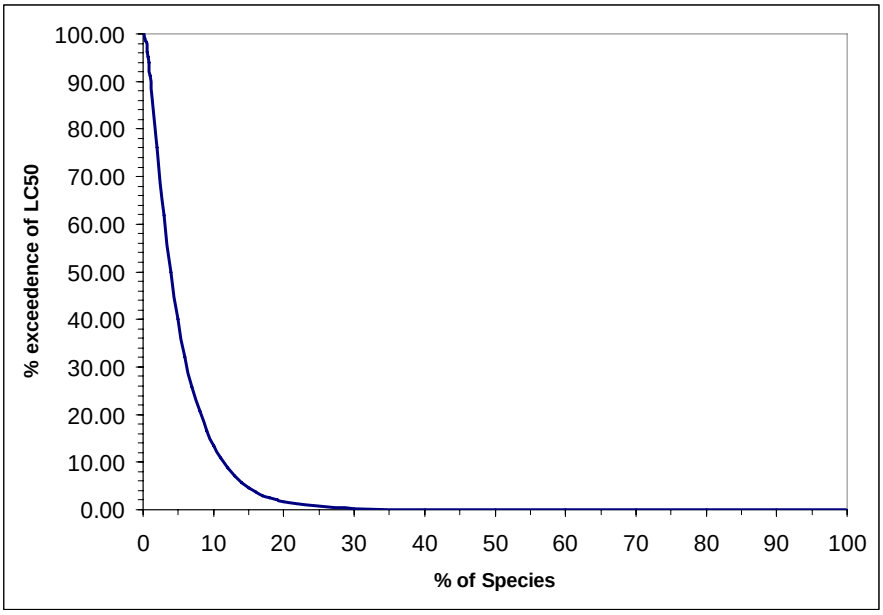


Figure 5.4.6

JPC for predicted pore water concentrations of arsenic for freshwater arthropods at FLB

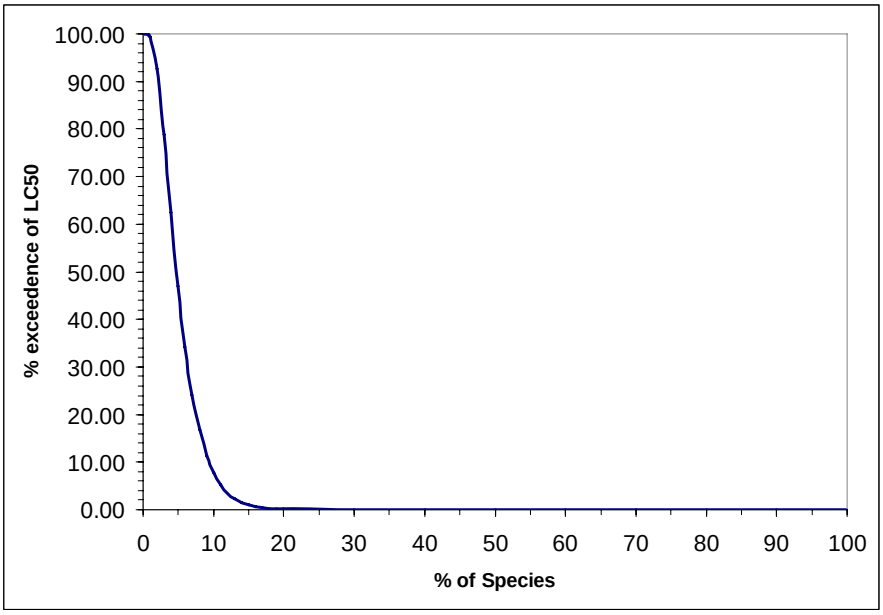


Figure 5.4.7

JPC for predicted pore water concentrations of arsenic for freshwater arthropods at SRS

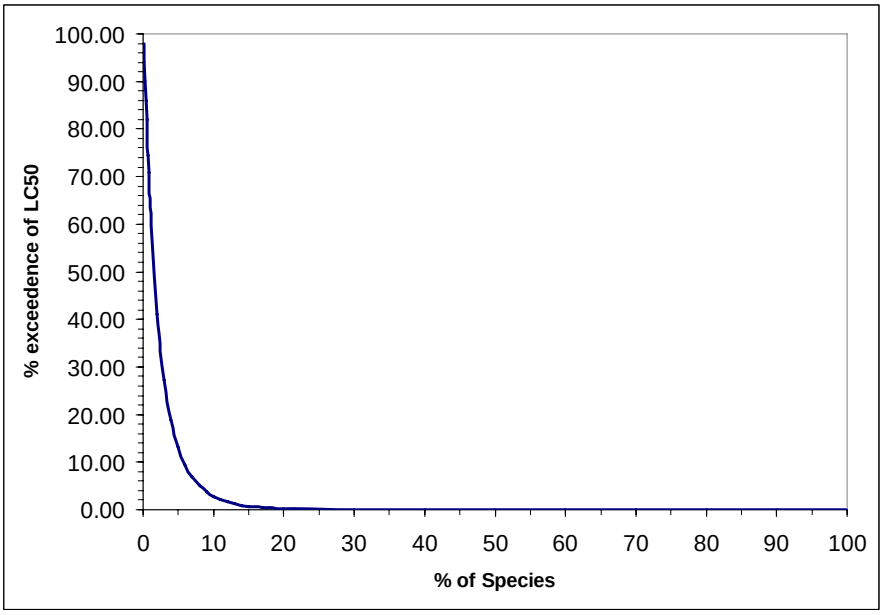


Figure 5.4.8

JPC for predicted pore water concentrations of arsenic for freshwater arthropods at TS

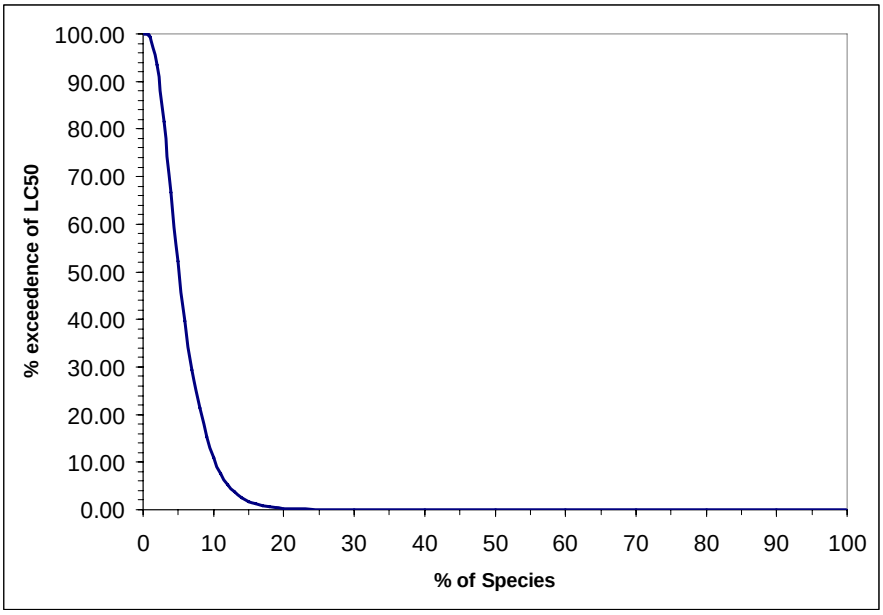


Figure 5.4.9

JPC for predicted pore water concentrations of arsenic for freshwater arthropods at TT

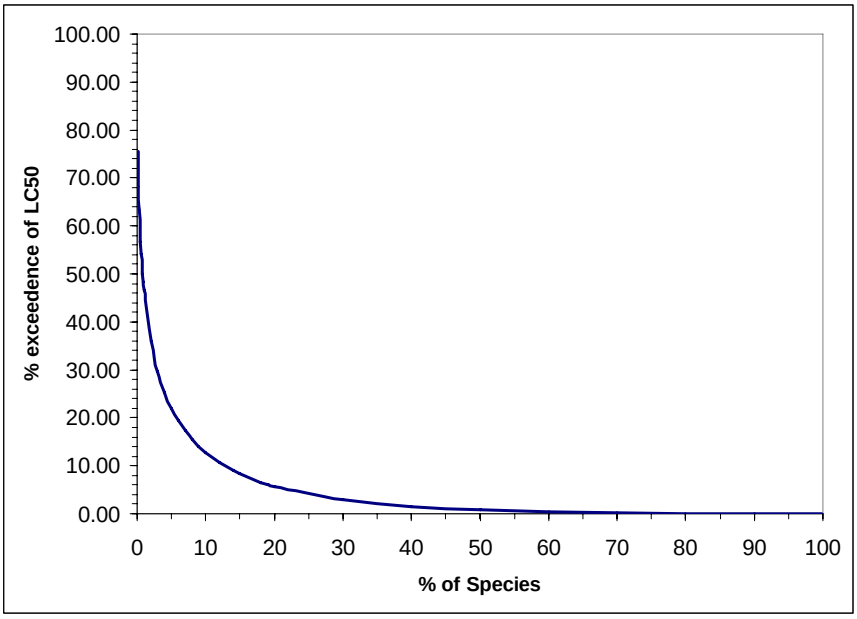


Figure 5.4.10

JPC for predicted pore water concentrations of arsenic for freshwater arthropods at BB

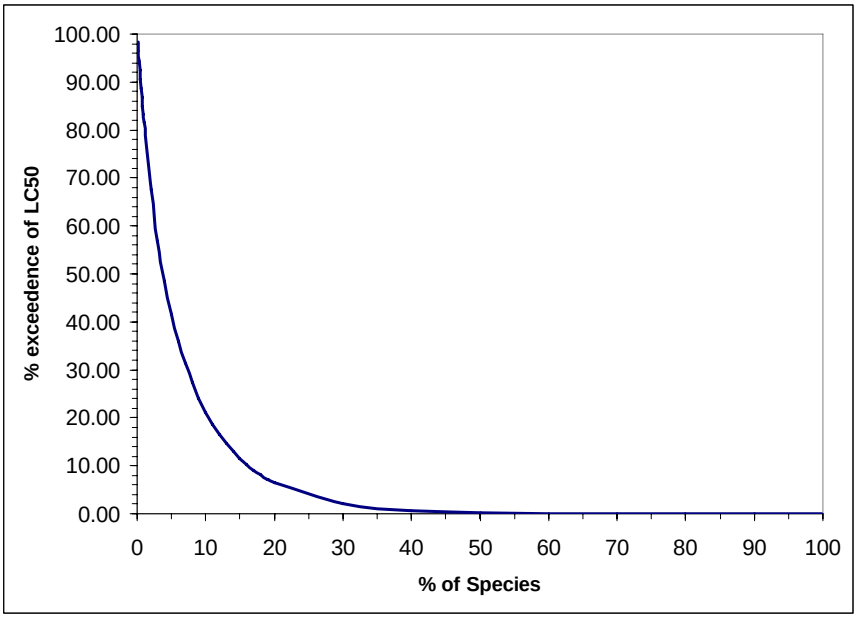


Figure 5.4.11

JPC for predicted pore water concentrations of copper for freshwater arthropods at C-111

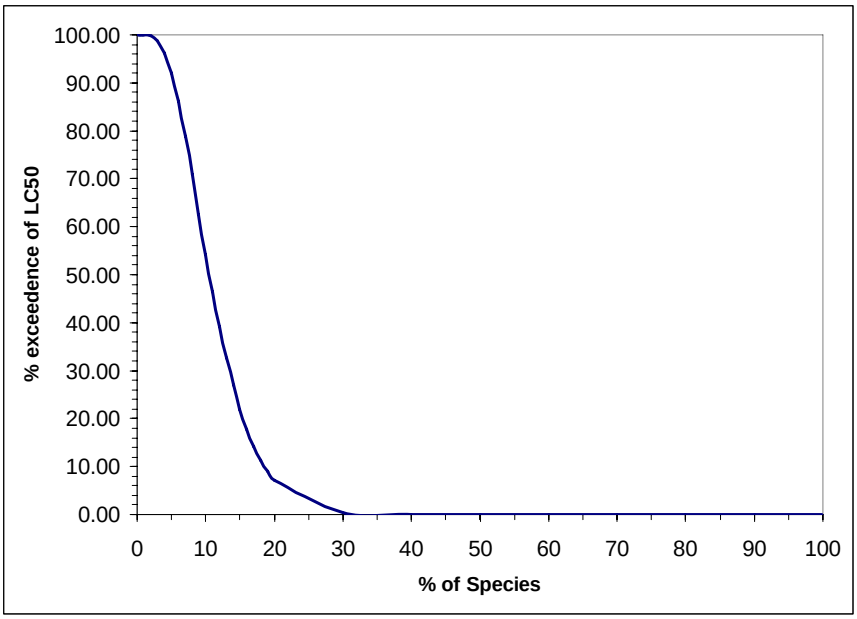


Figure 5.4.12

JPC for predicted pore water concentrations of copper for freshwater arthropods at EB

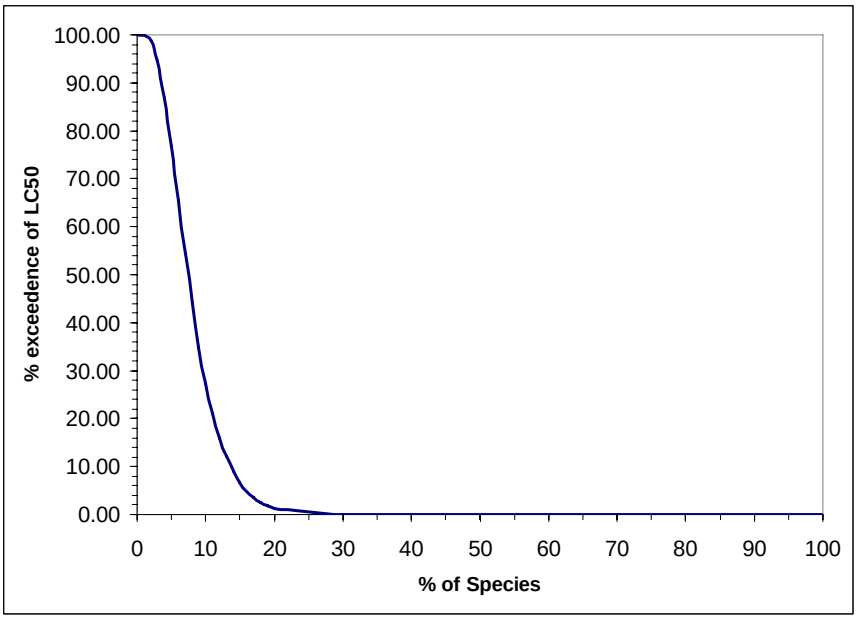


Figure 5.4.13

JPC for predicted pore water concentrations of copper for freshwater arthropods at SRS

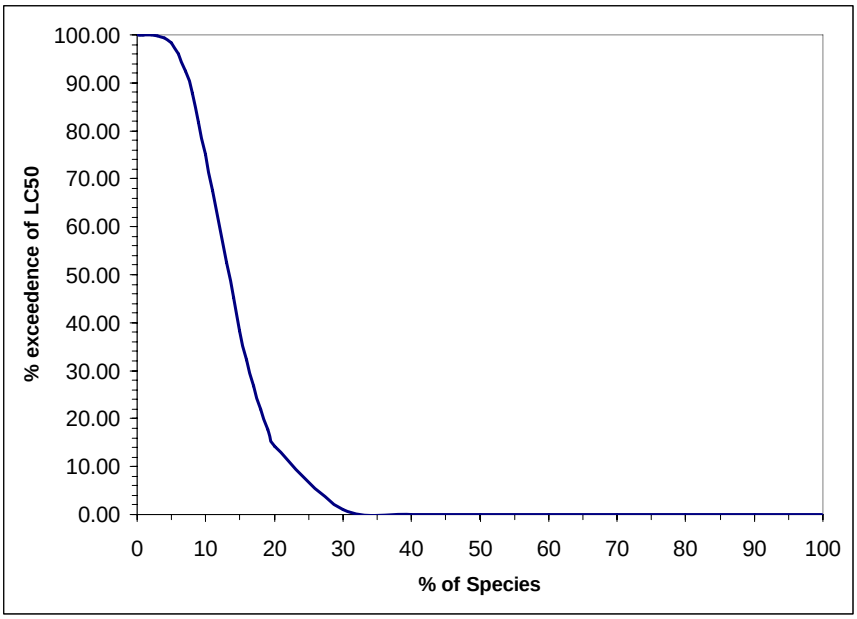


Figure 5.4.14

JPC for predicted pore water concentrations of copper for freshwater arthropods at TT

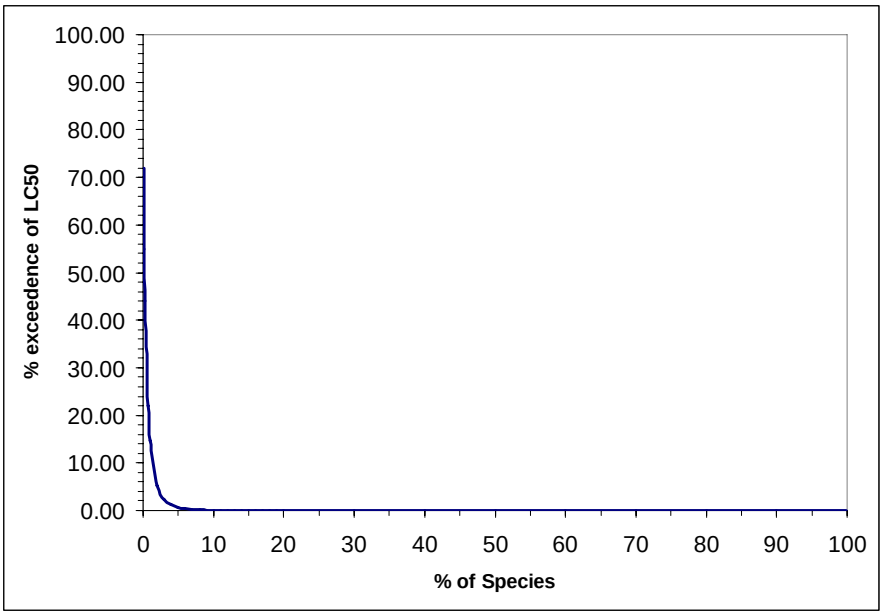


Figure 5.4.15

JPC for predicted pore water concentrations of chromium for freshwater arthropods at C-111

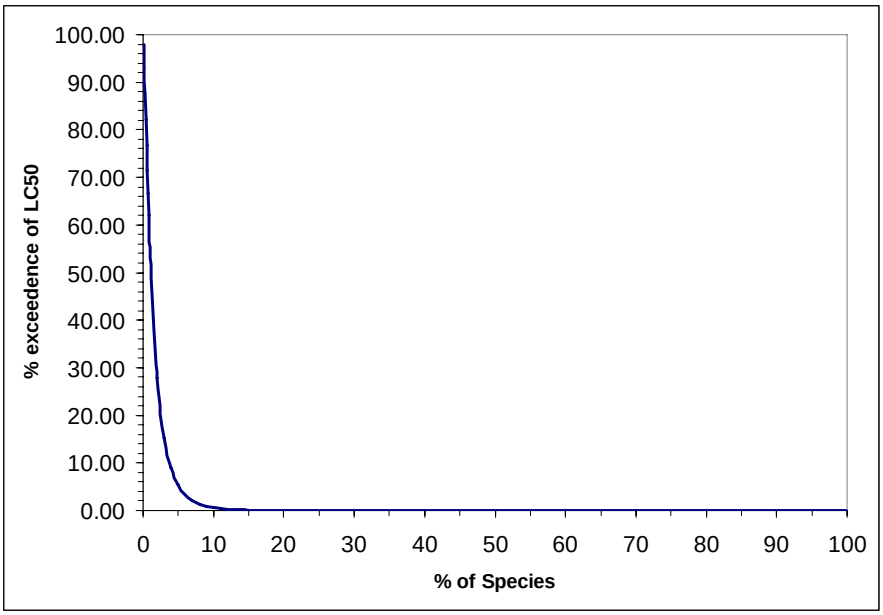


Figure 5.4.16

JPC for predicted pore water concentrations of chromium for freshwater arthropods at EB

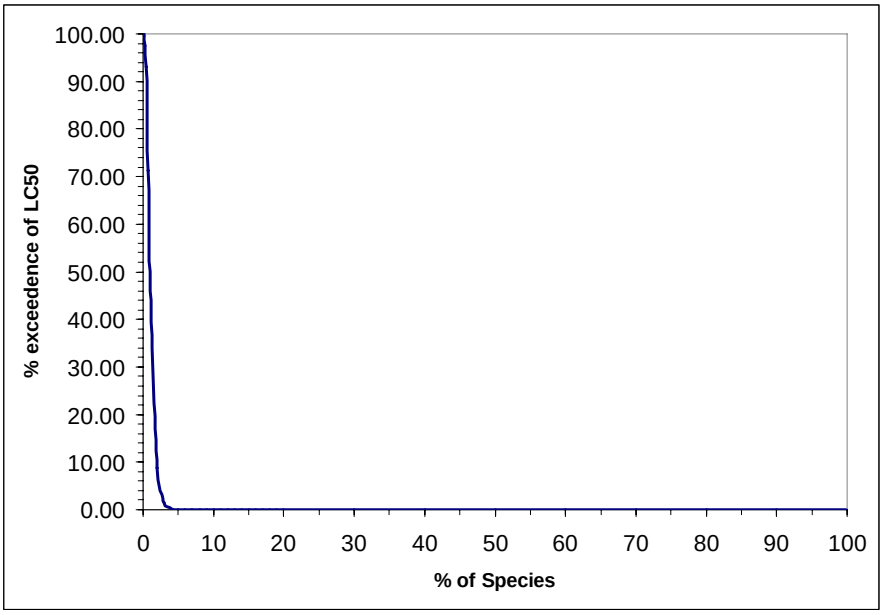


Figure 5.4.17

JPC for predicted pore water concentrations of chromium for freshwater arthropods at FLB

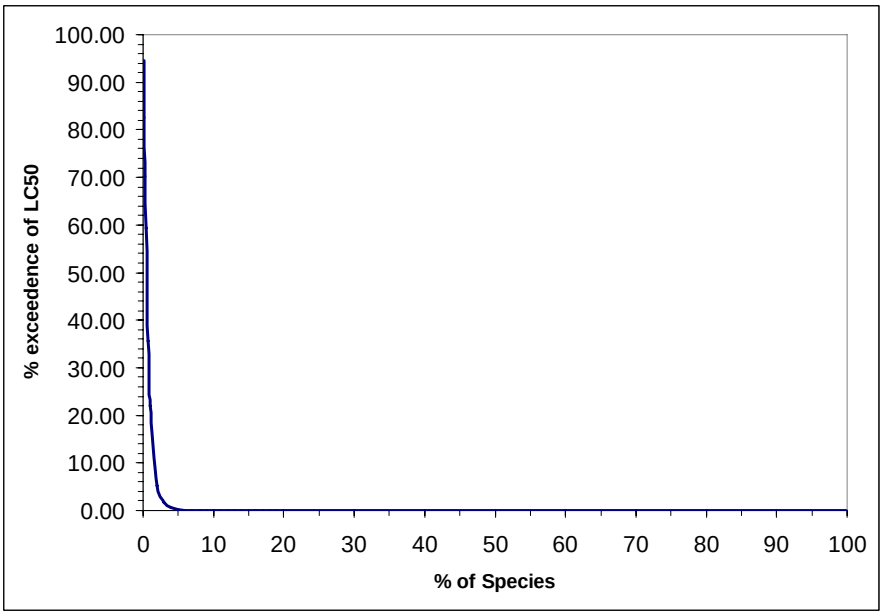


Figure 5.4.18

JPC for predicted pore water concentrations of chromium for freshwater arthropods at SRS

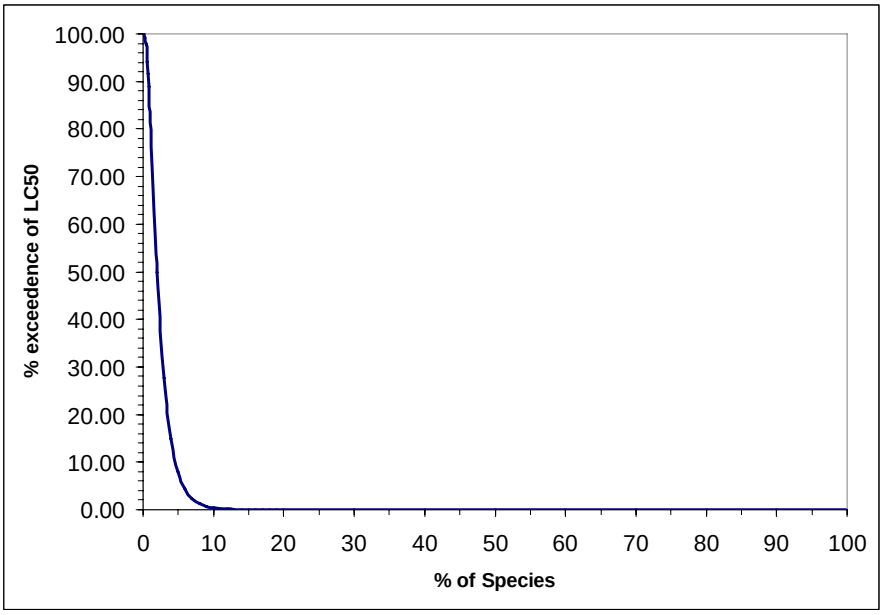


Figure 5.4.19

JPC for predicted pore water concentrations of lead for freshwater arthropods at C-111

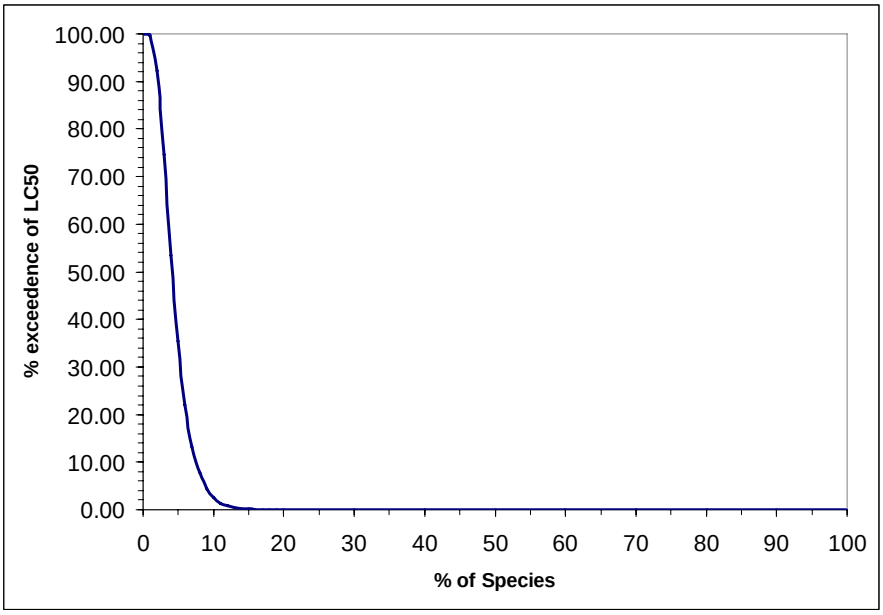


Figure 5.4.20

JPC for predicted pore water concentrations of lead for freshwater arthropods at EB

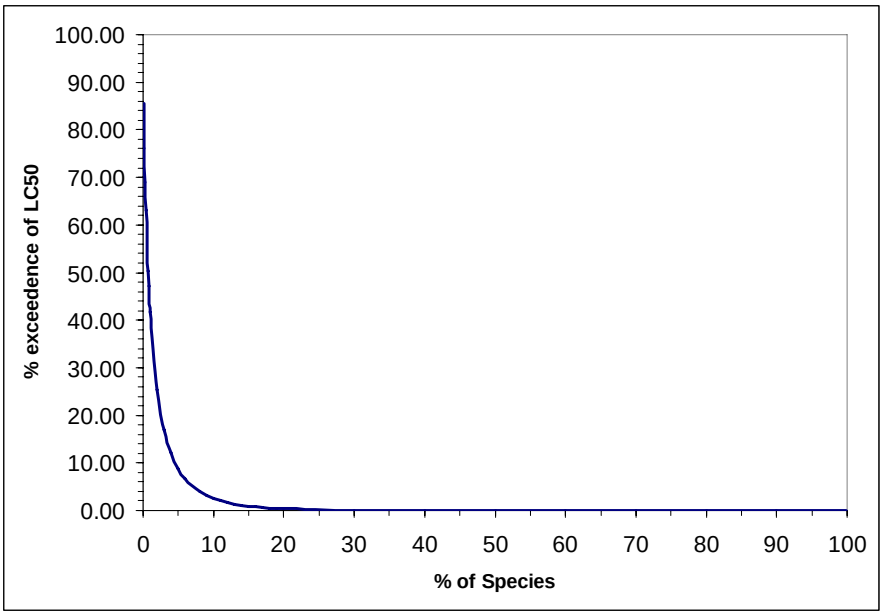


Figure 5.4.21

JPC for predicted pore water concentrations of zinc for freshwater arthropods at C-111

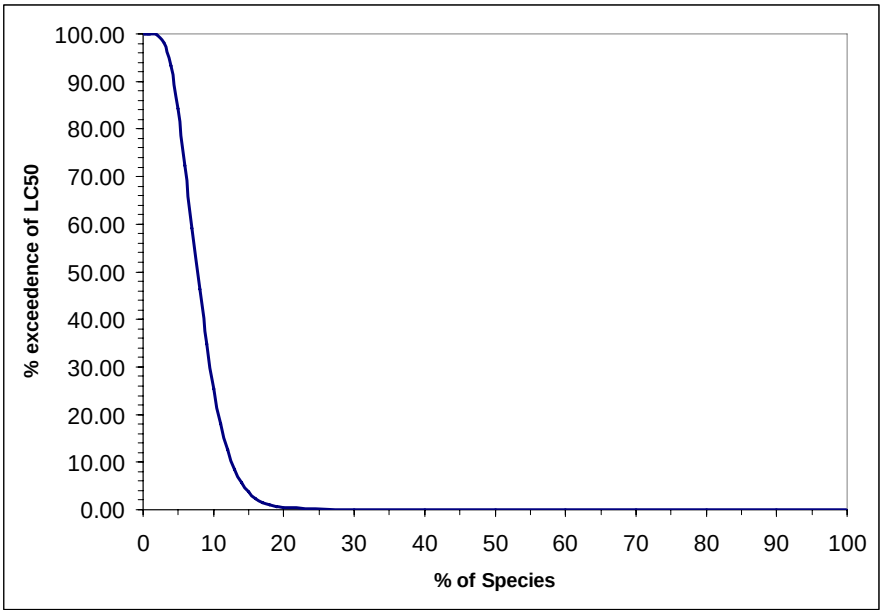


Figure 5.4.22

JPC for predicted pore water concentrations of zinc for freshwater arthropods at TT

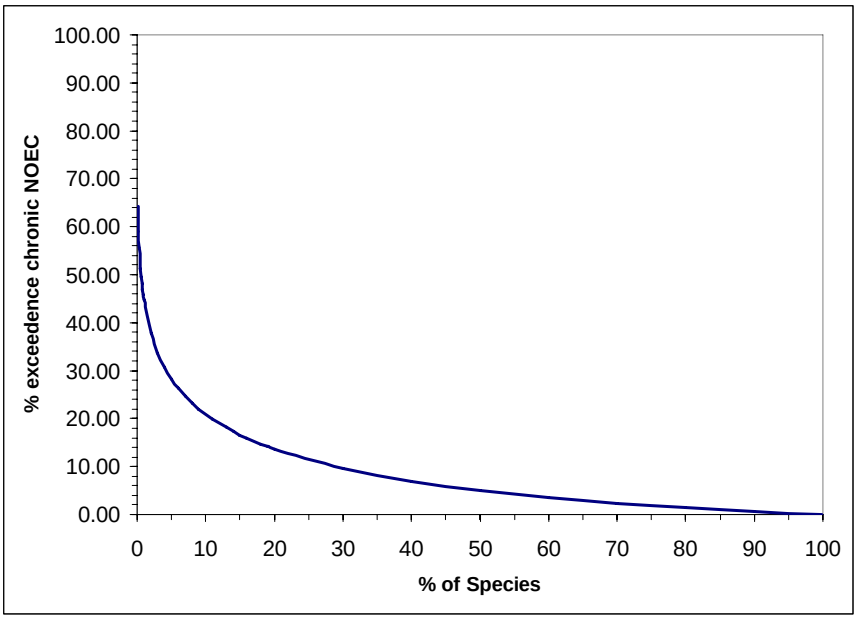


Figure 5.4.23

JPC for predicted pore water concentrations of copper for aquatic community NOECs at BB

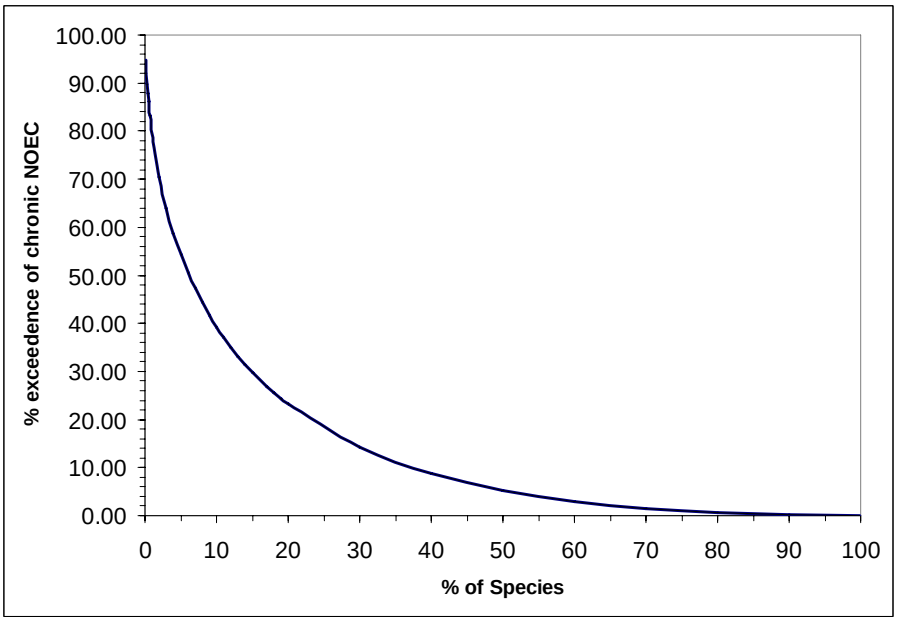


Figure 5.4.24

JPC for predicted pore water concentrations of copper for aquatic community NOECs at C-111

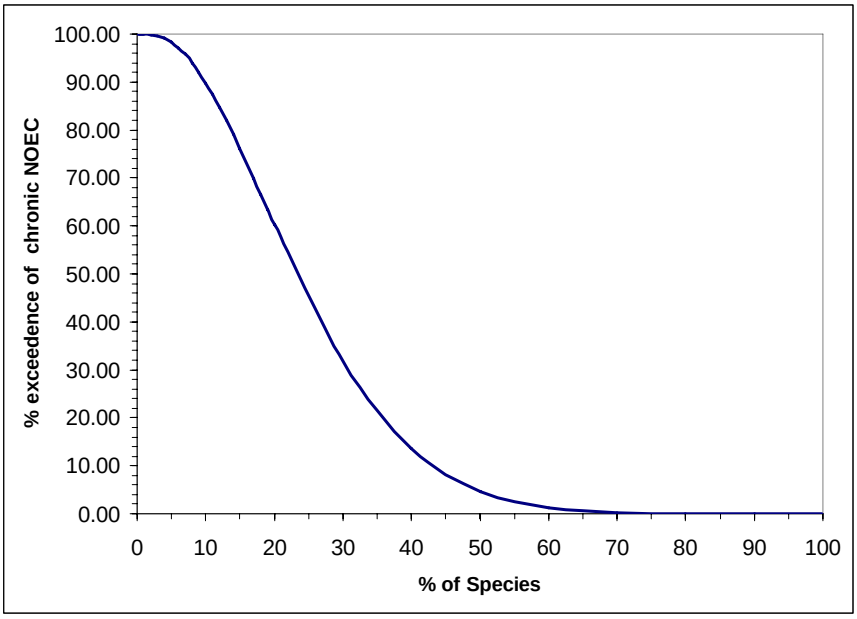


Figure 5.4.25

JPC for predicted pore water concentrations of copper for aquatic community NOECs at EB

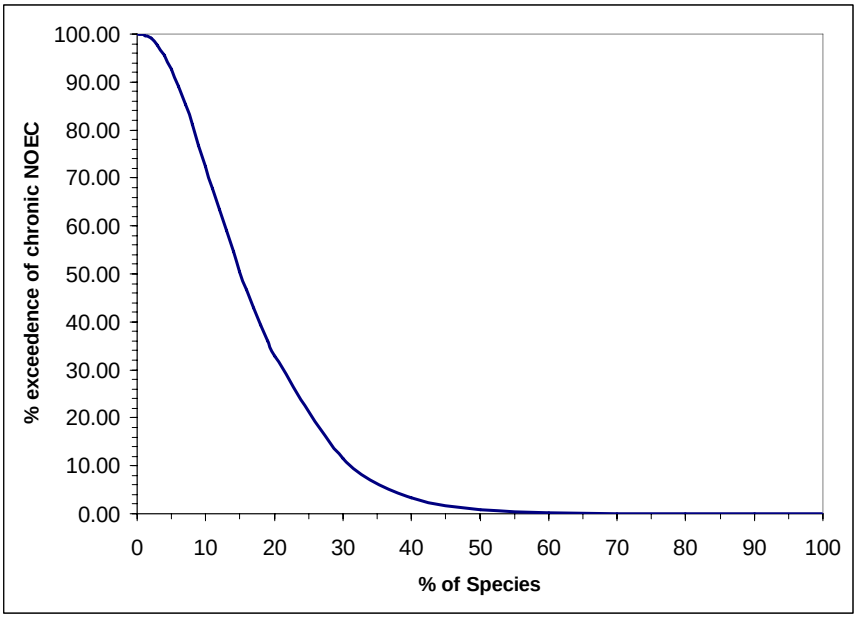


Figure 5.4.26

JPC for predicted pore water concentrations of copper for aquatic community NOECs at SRS

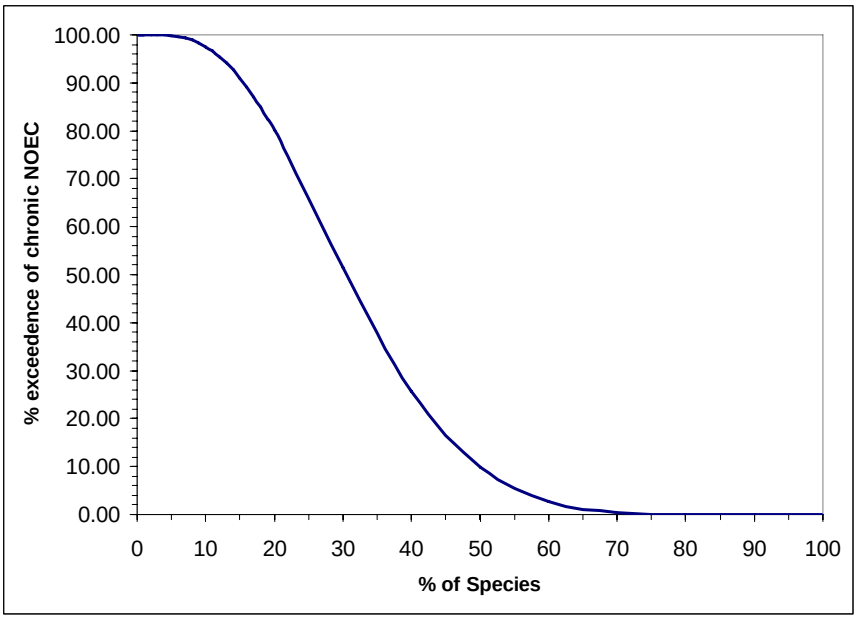


Figure 5.4.27

JPC for predicted pore water concentrations of copper for aquatic community NOECs at TT

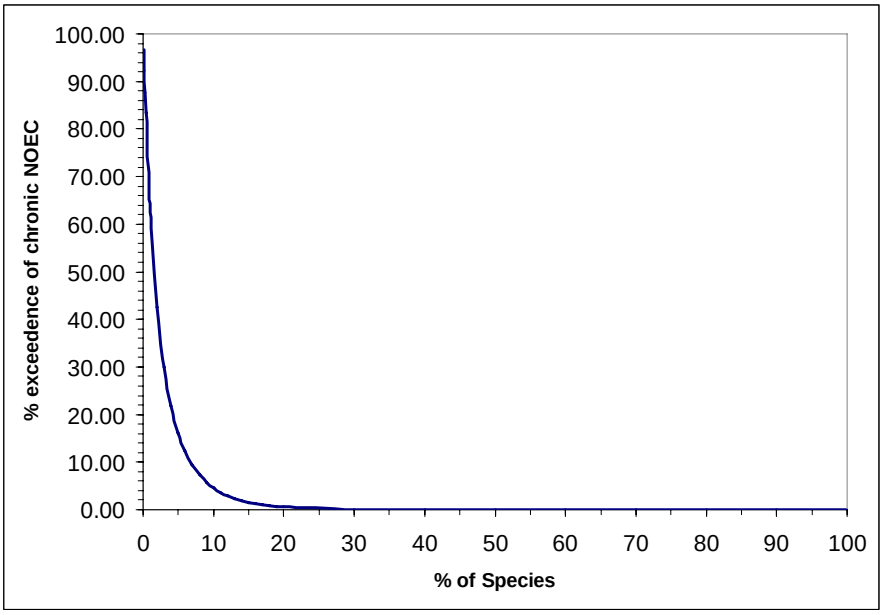


Figure 5.4.28

JPC for predicted pore water concentrations of lead for aquatic community NOECs at C-111

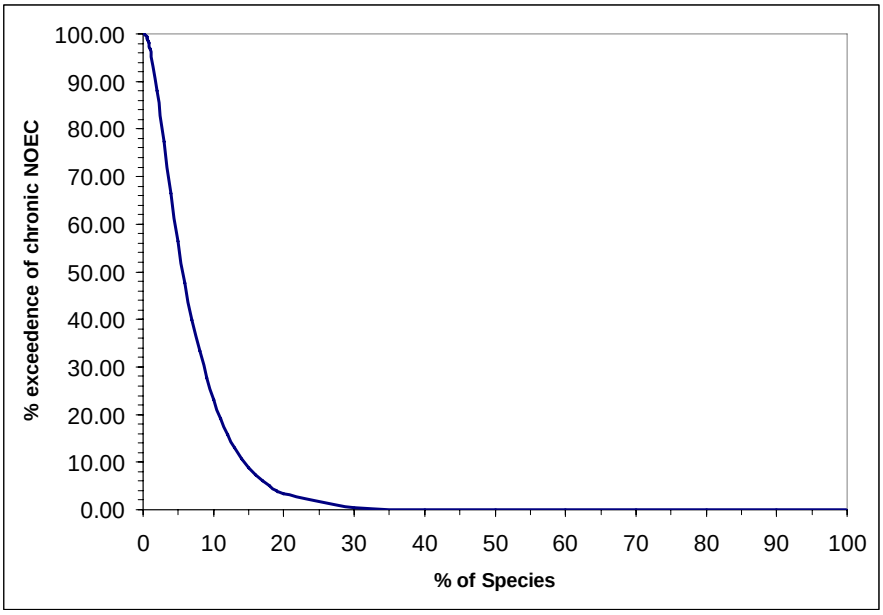


Figure 5.4.29

JPC for predicted pore water concentrations of lead for aquatic community NOECs at EB

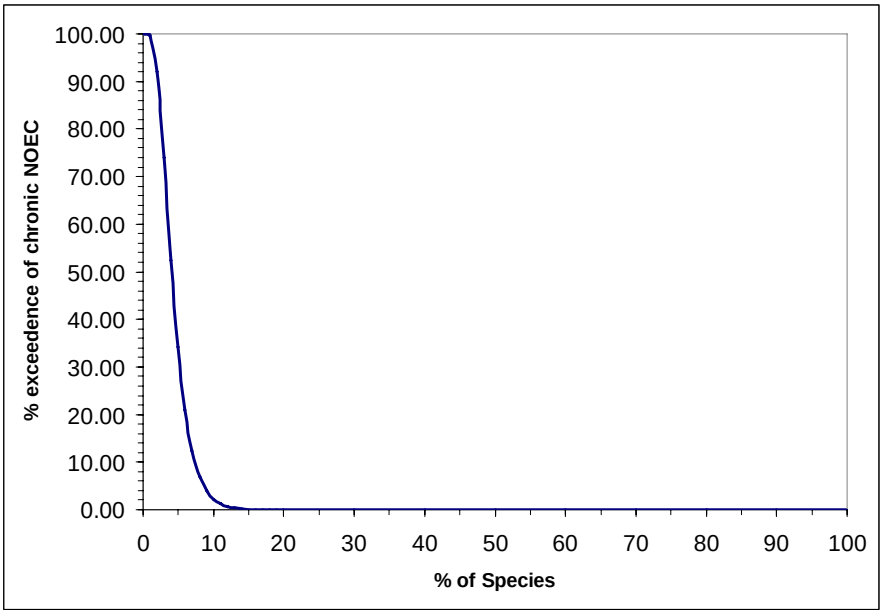


Figure 5.4.30

JPC for predicted pore water concentrations of lead for aquatic community NOECs at SRS

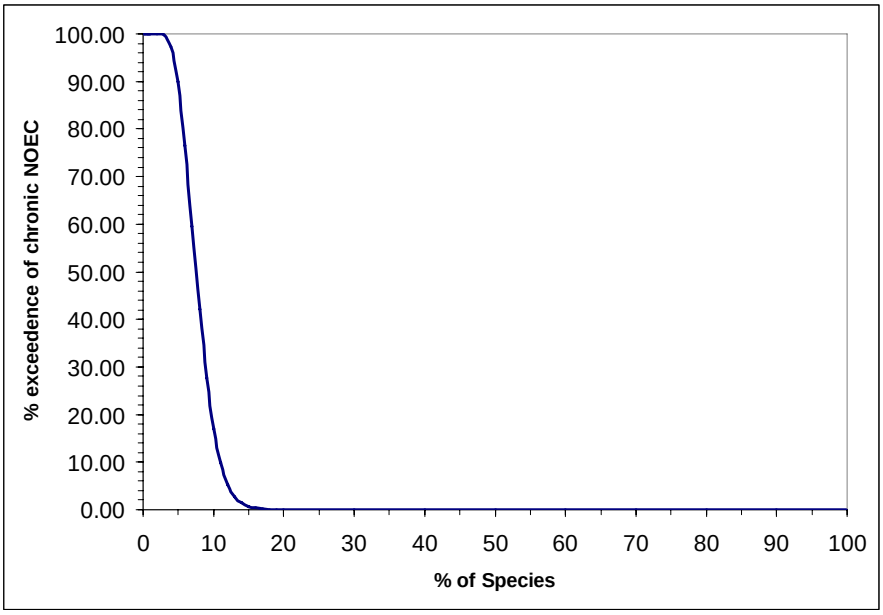


Figure 5.4.31

JPC for predicted pore water concentrations of lead for aquatic community NOECs at TT

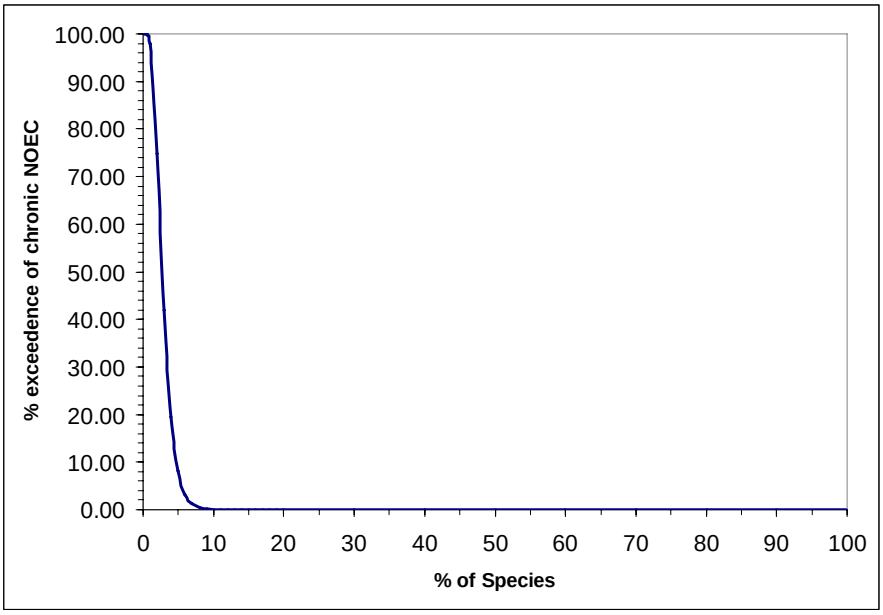


Figure 5.4.32

JPC for predicted pore water concentrations of nickel for aquatic community NOECs at C-111

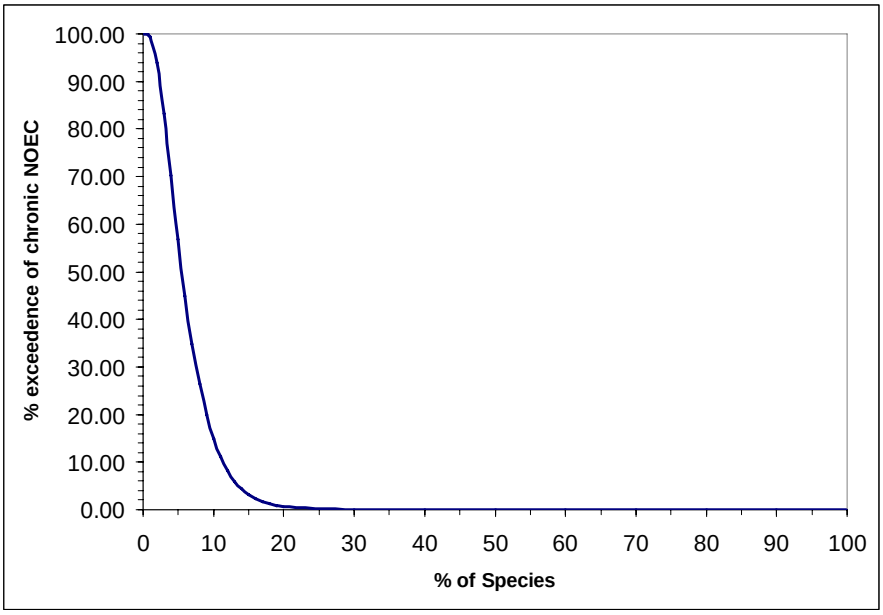


Figure 5.4.33

JPC for predicted pore water concentrations of nickel for aquatic community NOECs at EB

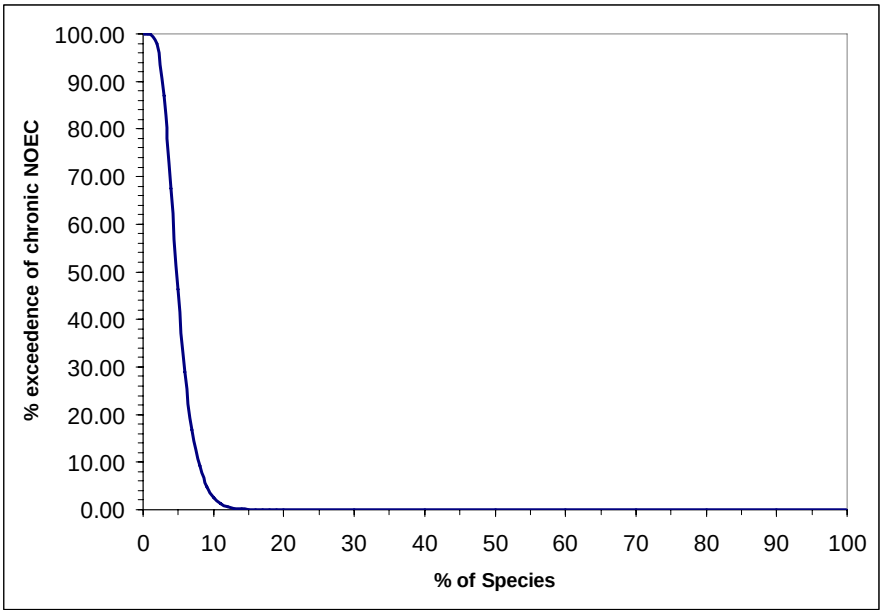


Figure 5.4.34

JPC for predicted pore water concentrations of nickel for aquatic community NOECs at FLB

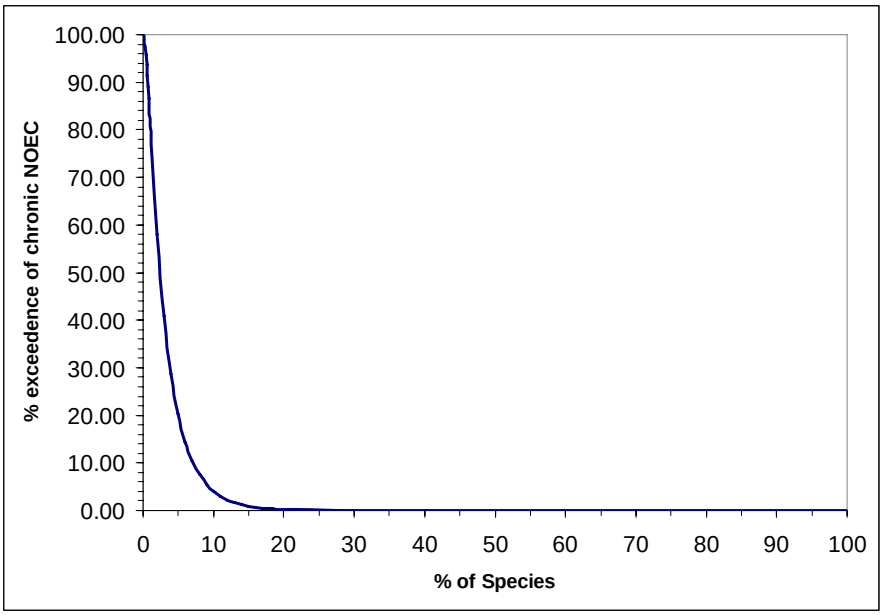


Figure 5.4.35

JPC for predicted pore water concentrations of nickel for aquatic community NOECs at SRS

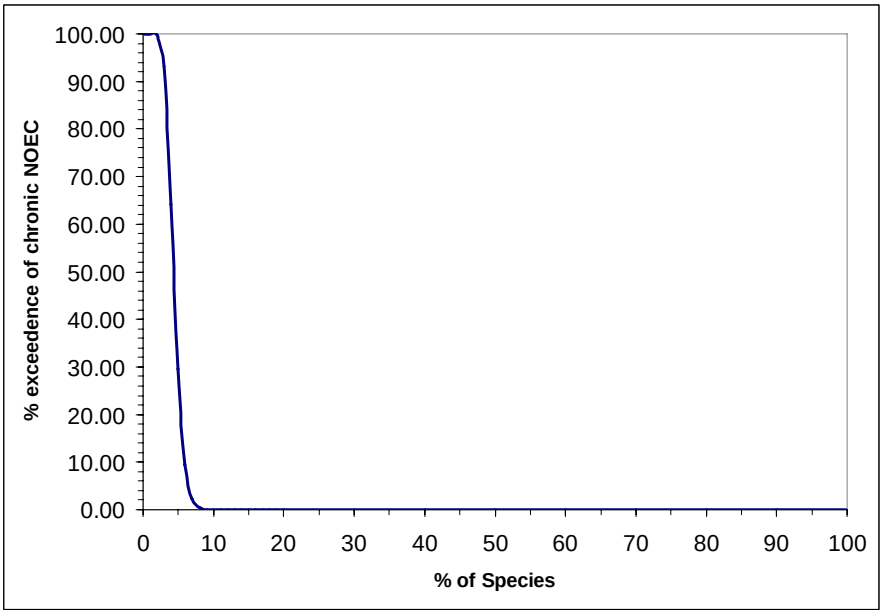


Figure 5.4.36

JPC for predicted pore water concentrations of nickel for aquatic community NOECs at TT

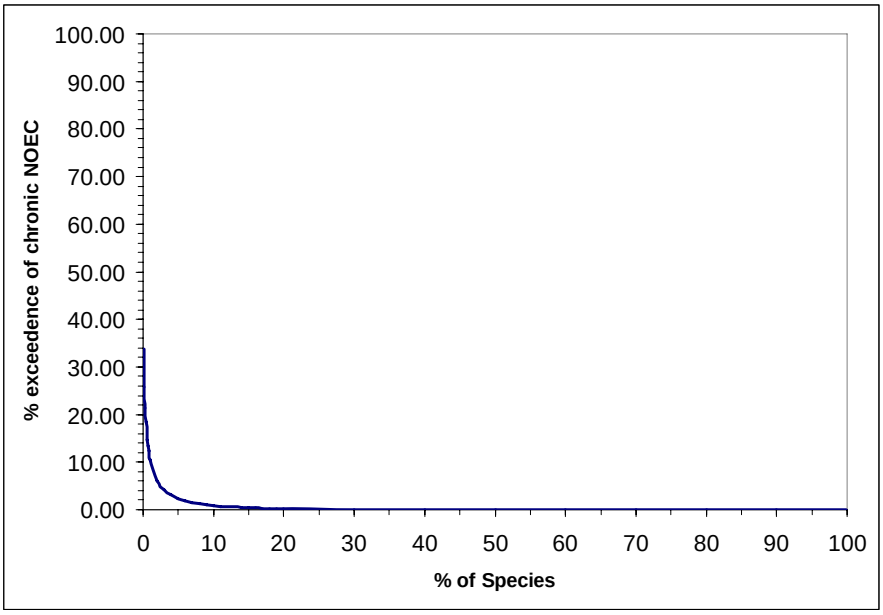


Figure 5.4.37

JPC for predicted pore water concentrations of zinc for aquatic community NOECs at C-111

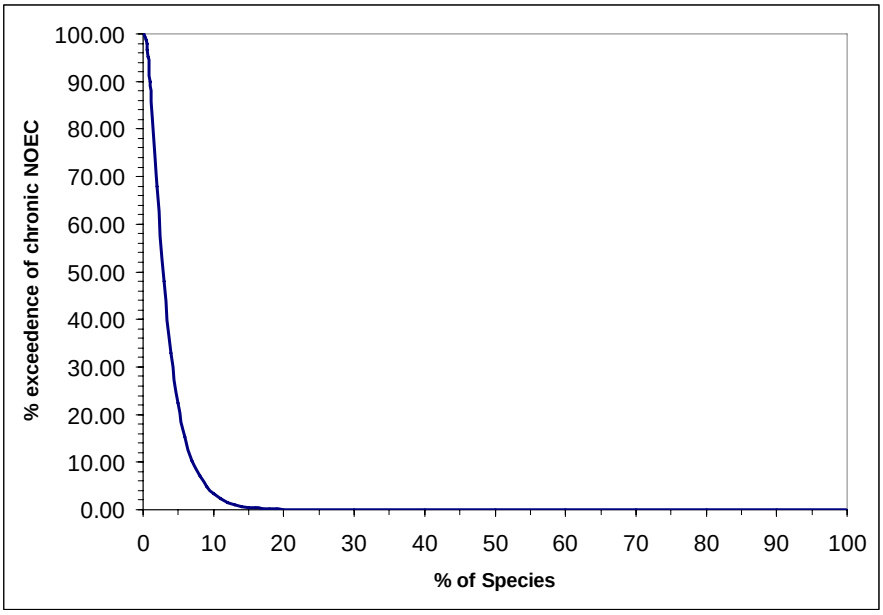


Figure 5.4.38

JPC for predicted pore water concentrations of zinc for aquatic community NOECs at TT

6.0. CONCLUSIONS AND RECOMMENDATIONS

7.0. REFERENCES

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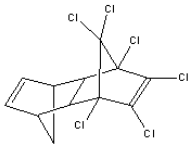
8.0. APPENDICES

APPENDIX I. Chemical Structure of Organochlorine Pesticides



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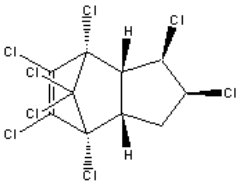

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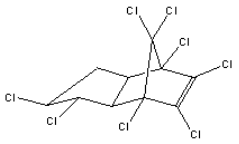

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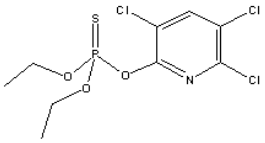

Chlorpyrifos
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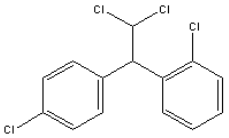

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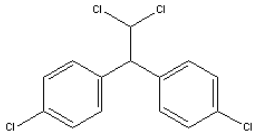

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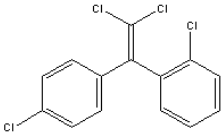

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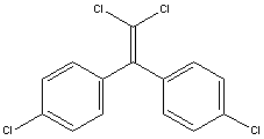

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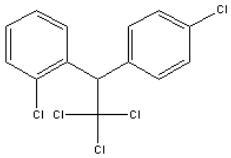

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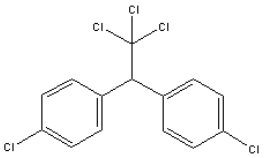

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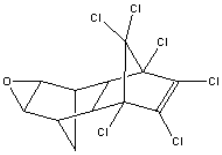

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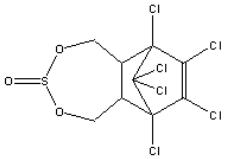

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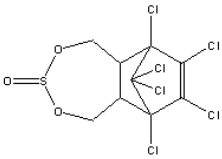

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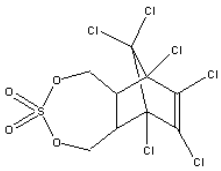
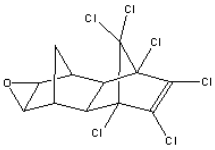
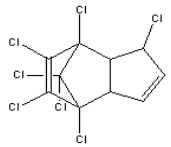


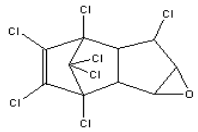
Endosulfane sulfate
$C_9H_6Cl_6O_4S$ M.W.422.922



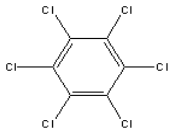
Endrin
C12H8Cl6O M.W.380.9126



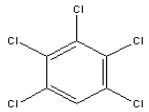
Heptachlor
$C_{10}H_5Cl_7$ M.W. 373.3205



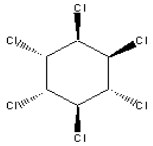
Heptachlor epoxide
$C_{10}H_5Cl_7O$ M.W. 389.3199



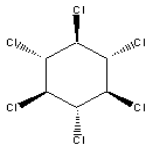
Hexachlorobenzene
C_6Cl_6 M.W. 284.784



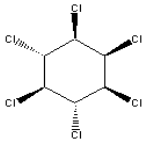
Pentachlorobenzene
C6HCl5 M.W.250.3389



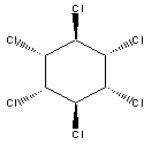
alpha-hexachlorocyclohexane
$C_6H_6Cl_6$ M.W. 290.8314



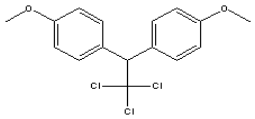
beta-hexachlorocyclohexane
$C_6H_6Cl_6$ M.W. 290.8314



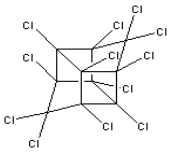
delta-Hexachlorocyclohexane
C6H6Cl6 M.W. 290.8314



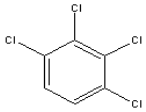
Lindane (gamma-HCH)
$C_6H_6Cl_6$ M.W.290.8314



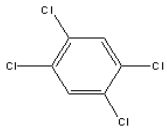
Metoxychlor
$C_{16}H_{15}Cl_3O_2$ M.W. 345.6523



Mirex
$C_{10}Cl_{12}$ M.W. 545.546



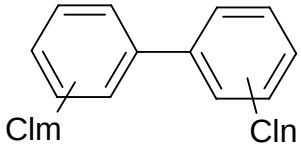
1,2,3,4-Tetrachlorobenzene
$C_6H_2Cl_4$ M.W. 215.8938



1,2,4,5-Tetrachlorobenzene
$C_6H_2Cl_4$ M.W. 215.8938

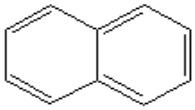
APPENDIX II. Chemical Structure of Polychlorinated Biphenyls

PCBs have the chemical formula $C_{12}H_{10-n}Cl_{n,}$ where n=1-10 (Figure 1).

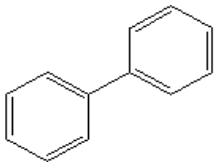


m + n = 1 to 10

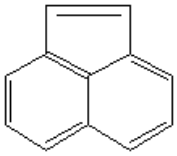
APPENDIX III. Chemical Structure of Polycyclic Aromatic Hydrocarbons



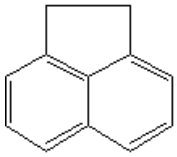
Naphthalene
C10H8 M.W. 128.2



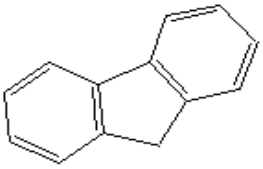
Biphenyl
C12H10 M.W. 154.2



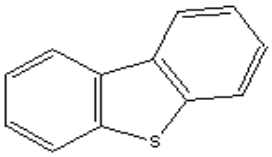
Acenaphthylene
C12H8 M.W. 152.2



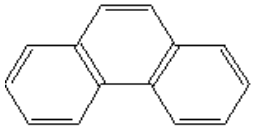
Acenaphthene
C12H10 M.W. 154.2



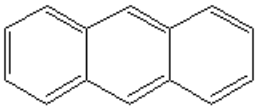
Fluorene
C13H10 M.W. 166.2



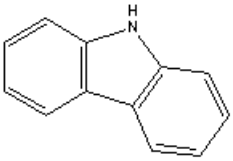
Dibenzothiophene
C12H8S M.W. 184.2



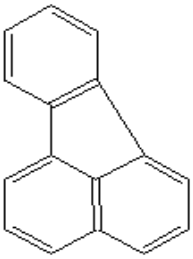
Phenanthrene
C14H10 M.W. 178.2



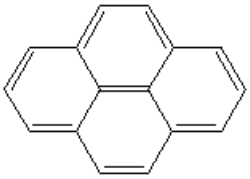
Anthracene
C14H10 M.W. 178.2



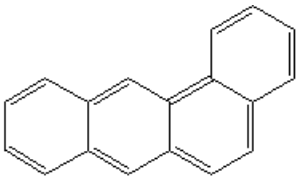
Carbazole
C12H9N M.W. 167.2



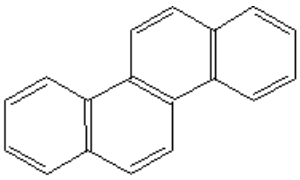
Fluoranthene
C16H10 M.W. 202.2



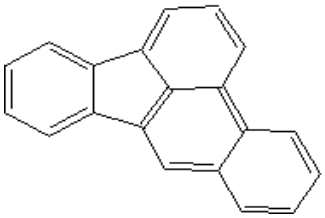
Pyrene
C16H10 M.W. 202.2



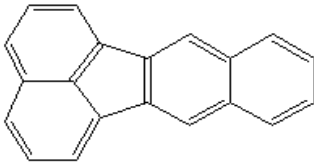
Benz(a)anthracene
C18H12 M.W. 228.2



Chrysene
C18H12 M.W. 228.3



Benzo(b)fluoranthene
C20H12 M.W. 252.3



Benzo(k)fluoranthene
C20H12 M.W. 252.3

APPENDIX IV. List of Common Acronyms

AChE
Acetylcholinesterase

AMC
Actual measured concentration

ARAMDGP
Aquatic Risk Assessment and Mitigation Dialogue Group

BCF
Bioconcentration factor

C-111
Canal 111

CandSF
Central and Southern Florida

CA
Concentration addition

CCC
Criterion Continuous Concentration

CERP
Comprehensive Everglades Restoration Plan

CMC
Criterion Maximum Concentration

COPEC
Chemical of potential ecological concern

DOI
Department of the Interior

EAA
Everglades Agricultural Area

EC50
Effect concentration for 50% of the sample population

EEC
Expected environmental concentration

EFED
United States Environmental Protection Agency Environmental Fate and Effects Division

ENP
Everglades National Park

FDEP
Florida Department of Environmental Protection

FIFRA
Federal Insecticide, Fungicide, and Rodenticide Act

GIS
Geographic Information System

HAA
Homestead Agricultural Area

HQ
Hazard quotient

HU
Hazard unit

JPC
Joint probability curve

K_{oc}
Adsorption coefficient based on organic carbon

K_{ow}
Octanol/water partition coefficient

LC50
Lethal concentration for 50% of the sample population

LOC
Level of concern

MDL
Method detection limit

MEC

Maximum measured environmental concentration

MSE
Mean square error

msPAF
Multiple substance potentially affected fraction

NAWQA
National Ambient Water-Quality Assessment Program

NOAA
National Oceanographic and Atmospheric Administration

NOAEC
No observed adverse effect concentration

NOEC
No observed effect concentration

NSandT
National Oceanographic and Atmospheric Administration's National Status and Trends Program

OM
Organic matter

OP
Organophosphate

OW
United States Environmental Protection Agency's Office of Water

PAF
Potentially affected fraction

PDF
Probability density function

PRA
Probabilistic risk assessment

RA
Response addition

RED
Reregistration eligibility document

SERA
Screening-level ecological risk assessment

SFWMD
South Florida Water Management District

SSD
Species sensitivity distribution

TBC
Toxicological benchmark concentration

TCP
3,5,6-Trichloro-2-pyridinol

TMoA
Toxic mode of action

TRV
Toxicity reference value

U.S.EPA
United States Environmental Protection Agency

USGS
United States Geological Survey

WQC
Water quality criteria

APPENDIX V. SPECIES SENSITIVITY DISTRIBUTIONS FOR CHLORPYRIFOS AND ENDOSULFAN

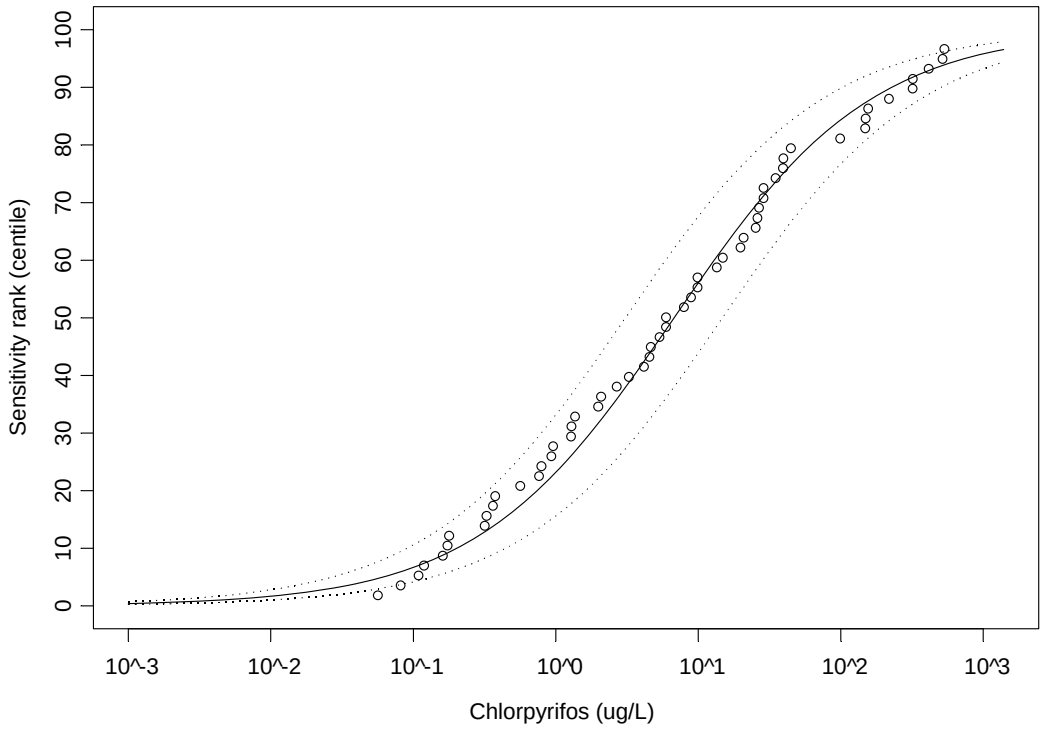


Figure 5.1.32. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for freshwater organisms.

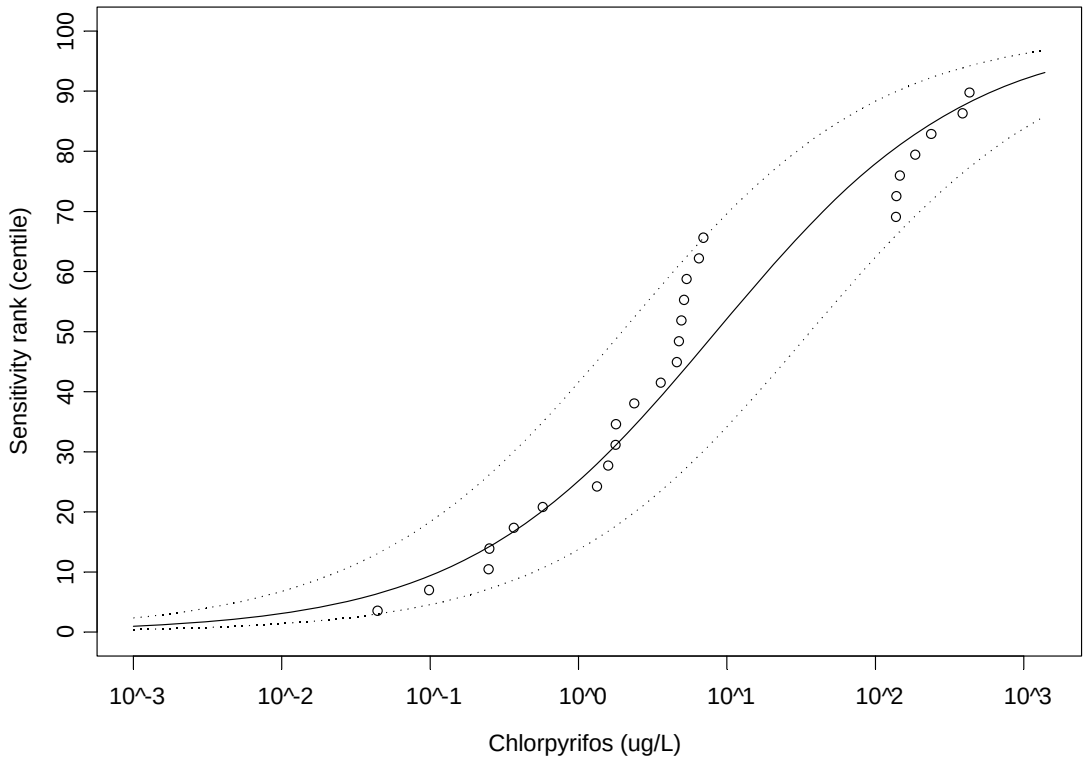


Figure 5.1.33. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for saltwater organisms.

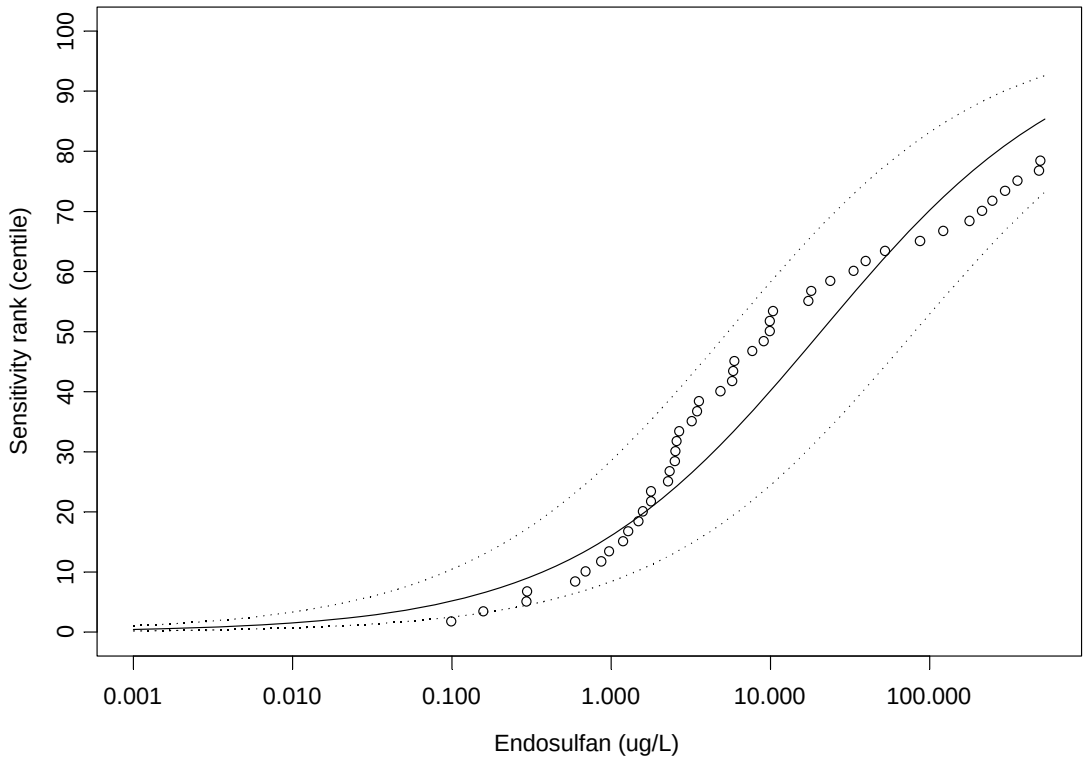


Figure 5.1.34. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for freshwater organisms.

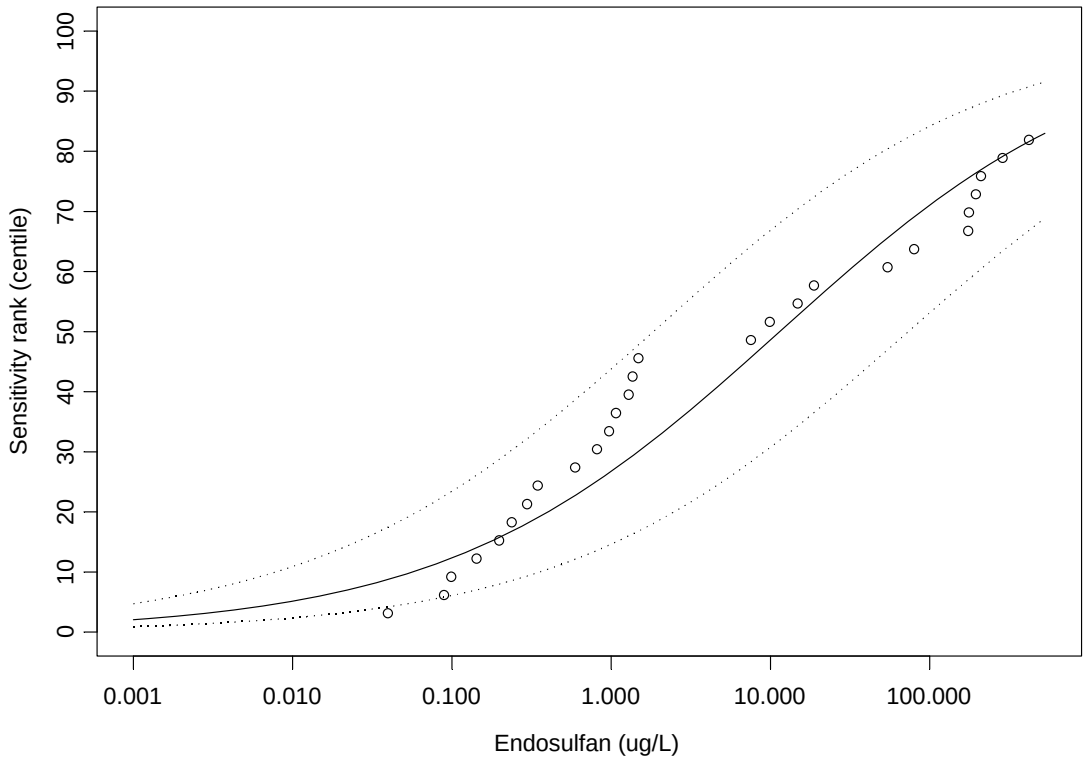


Figure 5.1.35. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for saltwater organisms.

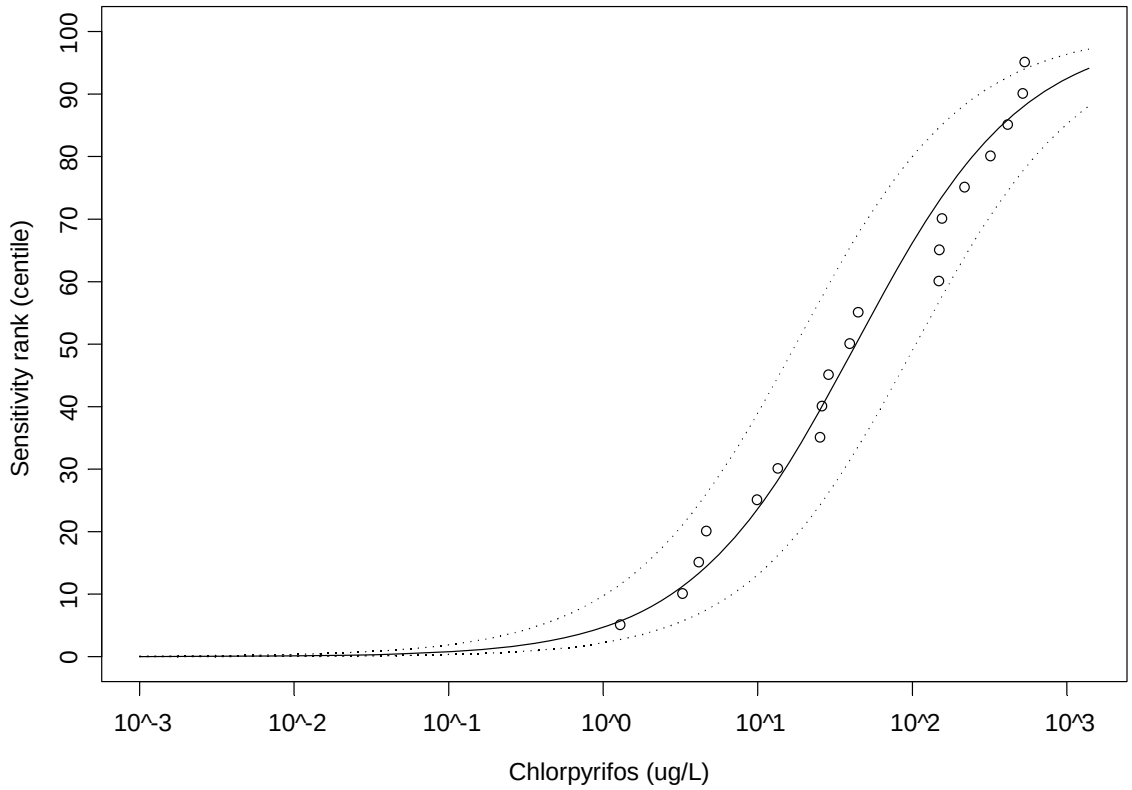


Figure 5.1.36. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for freshwater fish.

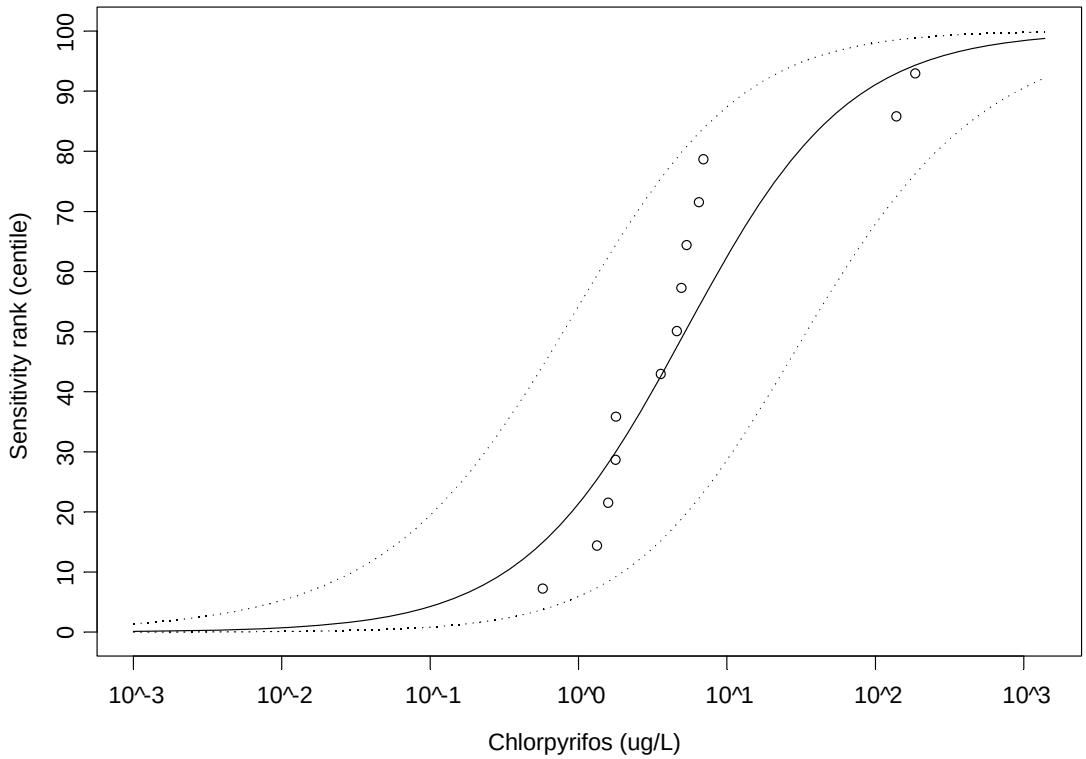


Figure5.1.37. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for saltwater fish.

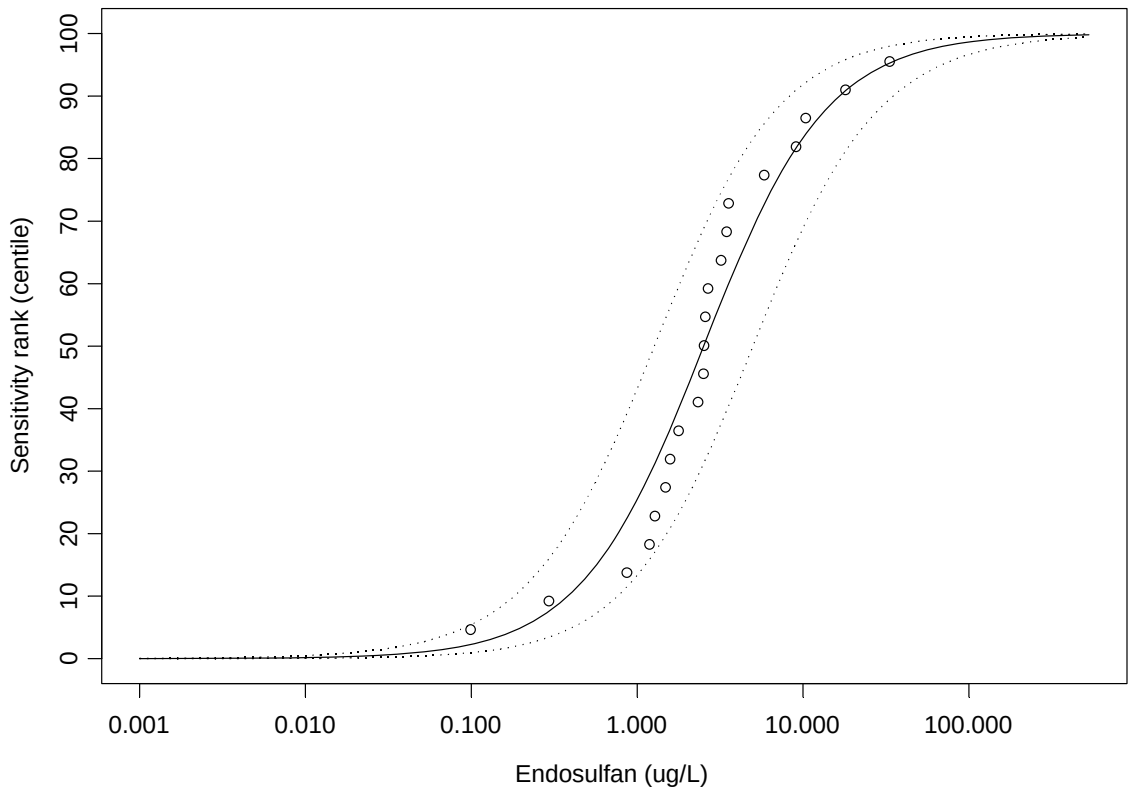


Figure 5.1.38. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for freshwater fish.

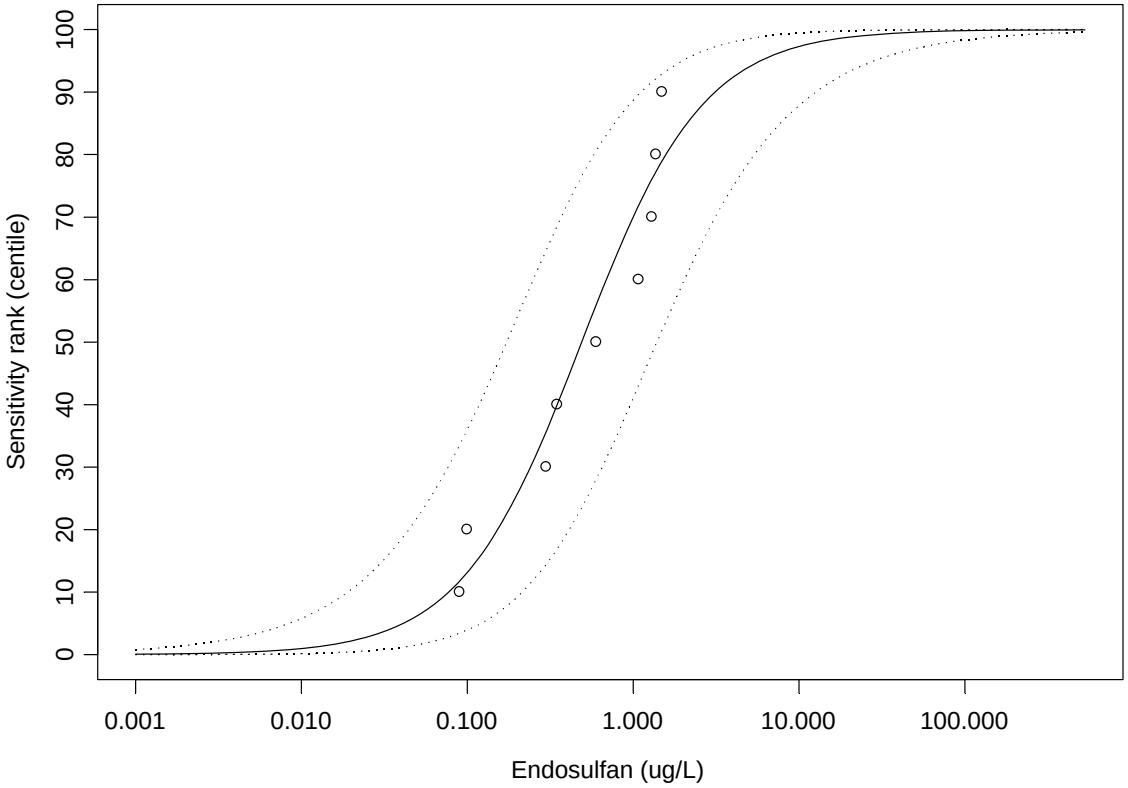


Figure 5.1.39. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for saltwater fish.

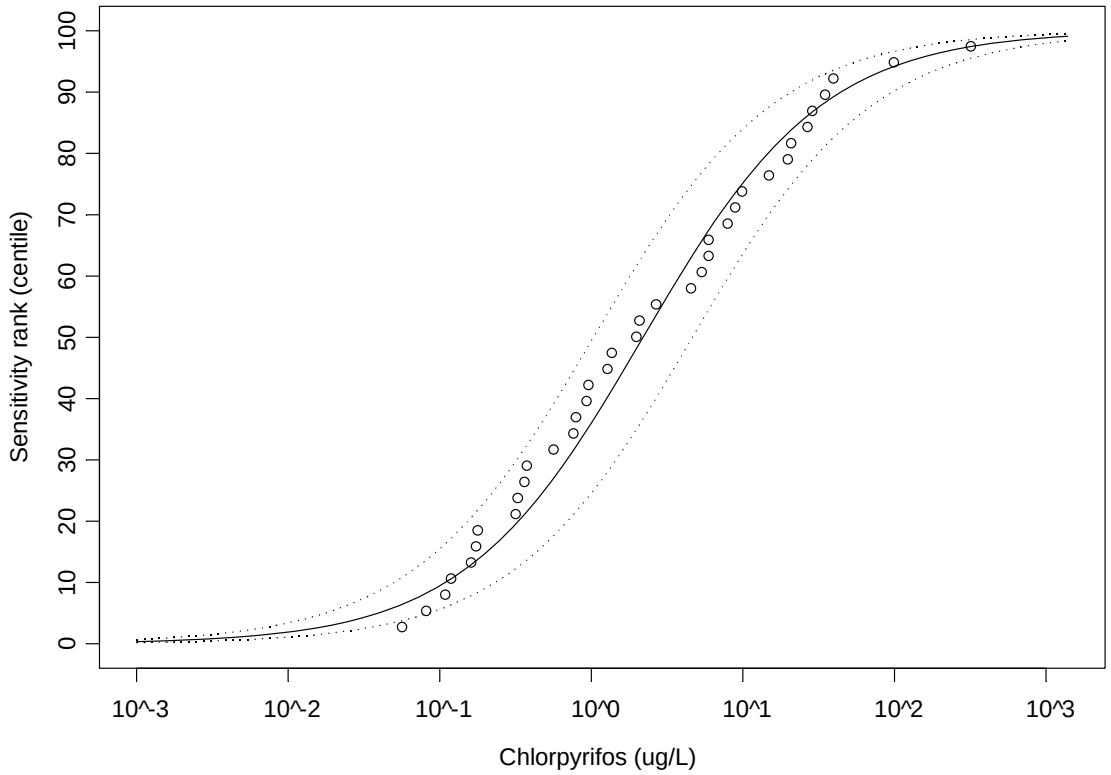


Figure 5.1.40. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for freshwater arthropods.

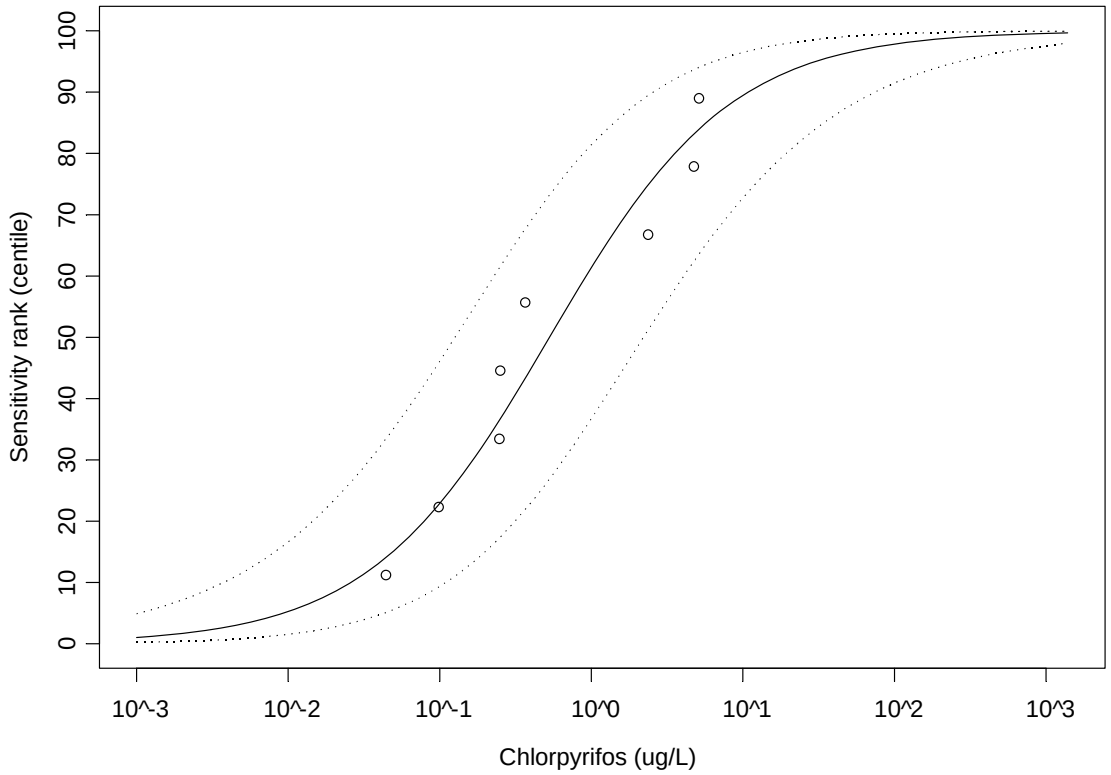


Figure 5.1.41. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for saltwater arthropods.

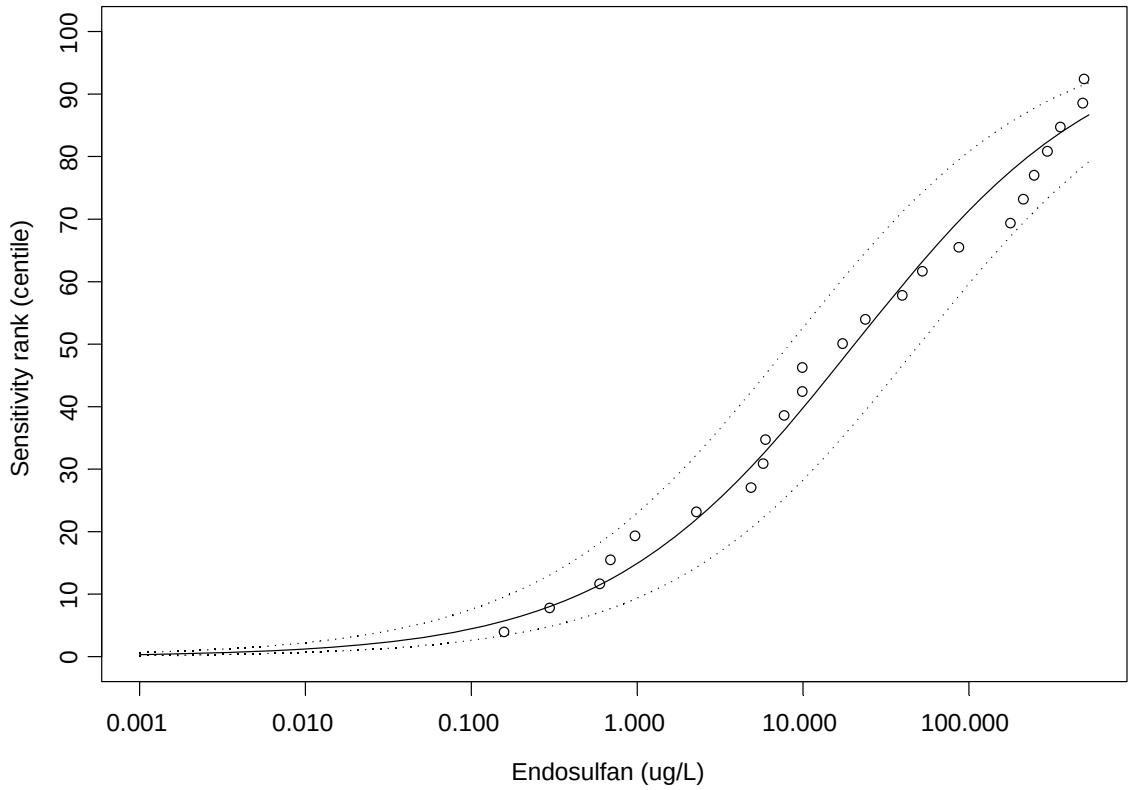


Figure 5.1.42. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for freshwater arthropods.

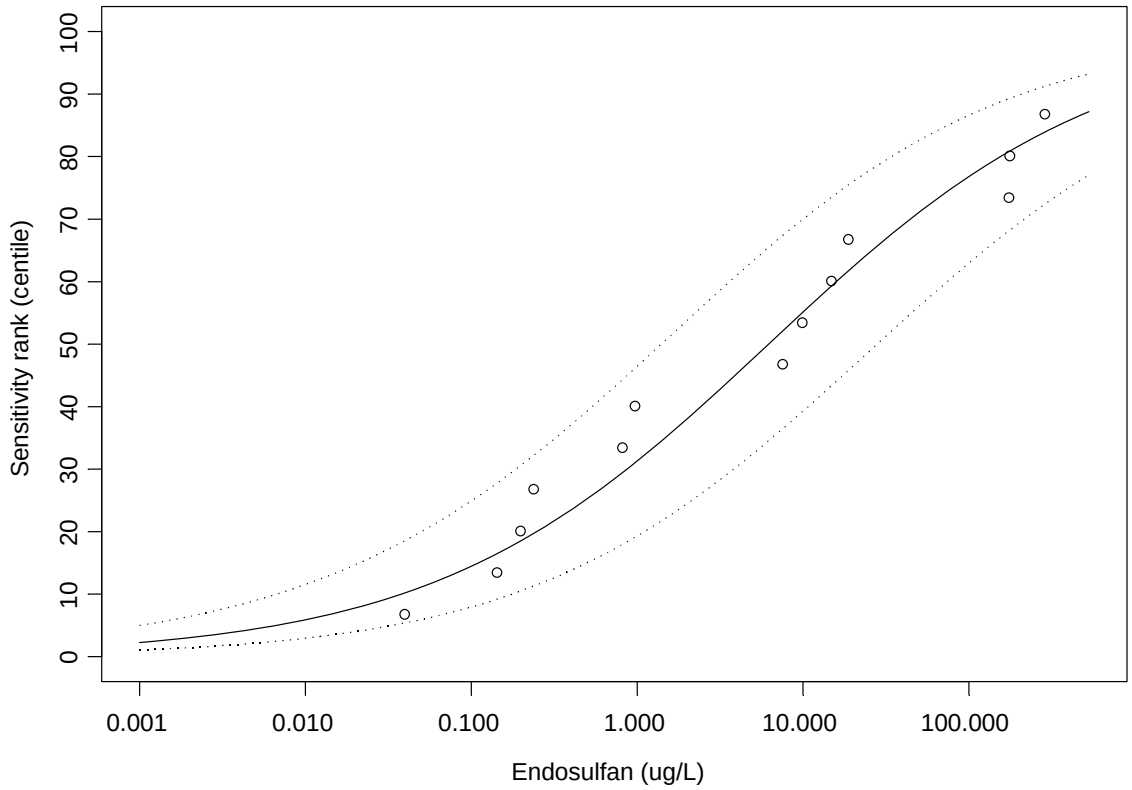


Figure 5.1.43. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for saltwater arthropods.

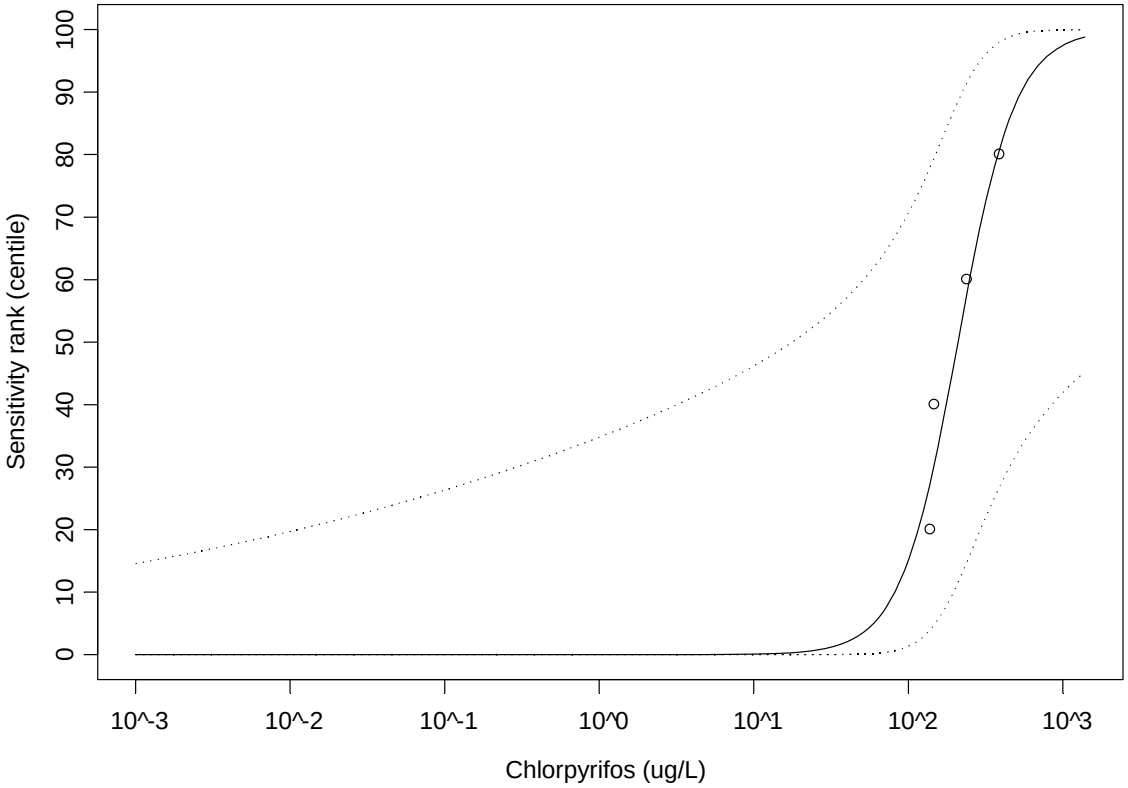


Figure 5.1.44. Log-logistic distribution (and 95% prediction band) of chlorpyrifos LC/EC50 values for saltwater plants/phytoplankton.

APPENDIX VI. PESTICIDE SEDIMENT QUALITY GUIDELINES USED IN THE SERA'S.

Freshwater*	Criteria source	Saltwater*	Criteria source	Compound	SFWMD measured	3-year project measured
1273	RCRA ESL[1]	NG		2,4 D	Y	N
58700	RCRA ESL	NG		2,4,5 T	Y	N
675	RCRA ESL	NG		2,4,5 TP	Y	N
2	RCRA ESL	9.5	NOOA UET	Aldrin	Y	Y
0.3	FL TEC[2]	NG		Atrazine	Y	N
NG[6]		NG		Alpha Chlordane	N	Y
NG		NG		Gamma Chlordane	N	Y
3.2	FL TEC	2.26	FL TEL[4]	Total Chlordanes	Y	Y
NG		NG		Chlorpyrifos	Y	Y
NG		NG		2,4' DDD	N	Y
NG		NG		2,4' DDE	N	N
NG		NG		2,4' DDT	N	Y
NG		1.22	FL TEL	4,4' DDD	Y	Y
NG		2.07	FL TEL	4,4' DDE	Y	Y
NG		1.19	FL TEL	4,4' DDT	Y	Y
4.9	FL TEC	NG		sum DDD	N	Y
3.2	FL TEC	NG		sum DDE	N	N
4.2	FL TEC	NG		sum DDT	N	Y
5.3	FL TEC	3.89	FL TEL	Total DDTs	N	Y
1.9	FL TEC	0.715	FL TEL	Dieldrin	Y	Y
3.26	RCRA ESL	NG		Endosulfan I	Y	N
1.94	RCRA ESL	NG		Endosulfan II	Y	Y
34.6	RCRA ESL	NG		Endosulfan Sulfate	Y	Y
2.2	FL TEC	NG		Endrin	Y	Y
6	RCRA ESL	NG		Alpha HCH	Y	Y
5	RCRA ESL	NG		Beta HCH	Y	Y
71500	RCRA ESL	NG		Delta HCH	Y	Y
2.4	FL TEC	0.32	FL TEL	Gamma HCH	Y	Y
NG		NG		Total HCHs	N	Y
0.6	RCRA ESL	0.3	NOOA UET	Heptachlor	Y	Y
2.5	FL TEC	NG		Heptachlor Epoxide	Y	N
20	FL TEC	6	NOOA AET[5]	Hexachlorobenzene	Y	Y
800	NOAA UET[3]	NG		Mirex	Y	Y
24	RCRA	NG		Pentachlorobenzene	N	Y
0.861	RCRA	NG		Phorate	Y	N
NG		NG		Tetrachlorobenzene 1,2,3,4	N	Y
1252	RCRA	NG		Tetrachlorobenzene 1,2,4,5	N	Y
60	FL TEC	21.6	FL TEL	Total PCBs	N	Y
0.1	Fl TEC	NG		Toxaphene	Y	N

*All units ug/kg dw

1. Resource conservation recovery act (RCRA) ecological screening level (ESL)
2. Florida threshold effect concentration (TEC)
3. NOAA upper effect threshold (UET)
4. Florida threshold effect level (TEL)
5. NOAA apparent effect threshold (AET)
6. No guidance for compound

APPENDIX VII. NATIVE AND NONNATIVE SPECIES INCLUDED IN SPECIES SENSITIVITY DISTRIBUTIONS (SSDS) - PESTICIDES.

* indicates genus is nonnative to Florida

DDD

Scientific Name	Common Name
Asellus brevicaudus	Aquatic sowbug
Chironomus tentans	Midge
Cypridopsis vidua	Ostracod, Seed shrimp
Daphnia magna	Water flea
Daphnia pulex	Water flea
Gammarus fasciatus	Scud
Gammarus lacustris	Scud
Hyalella azteca	Scud
Ischnura verticalis	Damselfly
Palaemonetes kadiakensis	Grass shrimp,freshwater prawn
Pteronarcys californicus	Stonefly
Simocephalus serrulatus	Water flea

Chlordane

Scientific Name	Common Name
Chironomus tentans	Midge
Daphnia magna	Water flea
Daphnia pulex	Water flea
Gammarus fasciatus	Scud
Hyalella azteca	Scud
Idotea balthica	Aquatic sowbug, Isopod
Orconectes nais	Crayfish
Pteronarcys californicus	Stonefly
Simocephalus serrulatus	Water flea

DDE

Scientific Name	Common Name
Bosmina longirostris	Water flea
Chironomus tentans	Midge
Chironomus thummi	Midge
Diacyclops thomasi	Calanoid copepod*
Hyalella azteca	Scud

DDT

Scientific Name	Common Name
Arctopsyche grandis	Caddisfly
Asellus brevicaudus	Aquatic sowbug
Astacus astacus	European crayfish*

Atherix variegata	Snipefly
Baetis	Mayfly
Barytelphusa cunicularis	Crab*
Bosmina longirostris	Water flea
Ceriodaphnia cornuta	Water flea
Ceriodaphnia reticulata	Water flea
Chaoborus	Phantom midge
Chironomus plumosus	Midge
Chironomus tentans	Midge
Chironomus thummi	Midge
Claassenia sabulosa	Stonefly*
Cloeon dipterum	Mayfly
Cypridopsis vidua	Ostracod, Seed shrimp
Daphnia carinata	Water flea
Daphnia magna	Water flea
Daphnia pulex	Water flea
Decapoda	Crayfish,crab order
Drunella grandis	Mayfly*
Echinogammarus tibaldii	Amphipod*
Ephemerella	Mayfly
Eretes sticticus	Beetle*
Gammarus fasciatus	Scud
Gammarus italicus	Scud
Gammarus lacustris	Scud
Hesperoperla pacifica	Golden stonefly, Willow fly*
Hexagenia bilineata	Mayfly
Hyalella azteca	Scud
Hydropsyche californica	Caddisfly
Ischnura verticalis	Damselfly
Isoperla	Stonefly
Macrobrachium kistnensis	Shrimp
Moina brachiata	Water flea*
Neodiaptomus kamakhiae	Calanoid copepod*
Notonecta undulata	Backswimmer
Ophiogomphus	Dragonfly
Orconectes nais	Crayfish*
Palaemonetes kadiakensis	Grass shrimp,freshwater prawn
Paratelphusa jacquemontii	Crab*
Peltodytes	Beetle
Pentaneura	Midge
Procambarus clarkii	Red swamp crayfish
Procladius	Midge
Pteronarcella badia	Stonefly*
Pteronarcys californicus	Stonefly
Simocephalus serrulatus	Water flea

Endosulfan

Scientific Name	**Common Name**
Asellus aquaticus	Aquatic sowbug
Atalophlebia australis	Mayfly*
Cambarus	Crayfish
Caridina weberi	Pugnose caridina*
Ceriodaphnia dubia	Water flea
Cheumatopsyche	Caddisfly
Chironomus plumosus	Midge
Chironomus riparius	Midge
Daphnia carinata	Water flea
Daphnia longispina	Water flea
Daphnia magna	Water flea
Daphnia pulex	Water flea
Enallagma	Damselfly
Eretes sticticus	Beetle*
Gammarus fasciatus	Scud
Gammarus lacustris	Scud
Ischnura	Damselfly
Jappa kutera	Mayfly nymph*
Macrobrachium rosenbergii	Giant river prawn
Moinodaphnia macleayi	Water flea*
Oziotelphusa senex senex	Crab*
Paratelphusa jacquemontii	Crab*
Potamonautes	Crab*
Procambarus clarkii	Red swamp crayfish
Pteronarcys californicus	Stonefly
Spicodiaptomus chilospinus	Calanoid copepod*

APPENDIX VIII. ORGANIC CARBON CONTENTS FOR ALL SFWMD SAMPLES

Mean Organic Carbon Content in Sediment at All District Sites (mg/kg)

Site	Mean	N	Std. Deviation	Minimum	Maximum	Median
C25S99	22000	2	11314	14000	30000	22000
CA2-15	446750	4	19050	431000	474000	441000
CA3-15	485750	4	17056	468000	506000	484500
CA3-3	285500	4	169740	122000	434000	293000
GORDYRD	0	1	.	0	0	0
HOLYSD1	292000	6	165785	47000	461000	323500
HOLYSD2	206500	6	175230	66000	450000	113000
HOLYSD3	334667	6	173820	61000	465000	433000
HOLYSD4	332667	6	159064	60000	474000	387500
L28I	13500	1	.	13500	13500	13500
L-38-1	10000	1	.	10000	10000	10000
LO308C	156000	1	.	156000	156000	156000
LOX10	478500	4	27197	440000	502000	486000
LOX8	502500	4	4203	497000	507000	503000
MARSH-2	15150	1	.	15150	15150	15150
S12C	11389	4	10876	856	26500	9100
S176	6454	4	4202	1250	11000	6783
S177	7870	4	8777	2710	21000	3885
S178	13967	4	11600	2266	30000	11800
S18C	7665	4	7151	2000	18000	5330
S2	12650	3	4729	8051	17500	12400
S3	9892	3	12273	1676	24000	4000
S332	10328	4	9735	2040	24000	7635
S34	13900	1	.	13900	13900	13900
S4	15367	3	12023	3800	27800	14500
S6	51040	5	60492	2698	150000	22000
S7	10859	3	7083	3478	17600	11500
S8	12522	3	8119	3765	19800	14000
S80	64500	2	7778	59000	70000	64500
S9	8354	3	2849	5121	10500	9440
STA2C1SD	206000	1	.	206000	206000	206000
US41-25	10421	4	7341	385	17500	11900
WCA2F1	435500	4	30730	400000	465000	438500
WHTCYPRK	0	1	.	0	0	0
Total	169883	111	200616	0	507000	30000

APPENDIX IX. METAL SEDIMENT QUALITY CRITERIA/GUIDELINES USED IN THE SERA'S

Fresh Water*	Criteria source	Saltwater*	Criteria Source	Compound	SFWMD measured	3-year Project measured
58000	ARCS/ERM[1]	NG		Aluminum	Y	Y
3	NOAA UET[2]	9.3	NOAA AET[4]	Antimony	Y	N
9.8	FL TEC[3]	7.24	FL TEL[5]	Arsenic	Y	Y
NG[6]		NG		beryllium	Y	Y
1	FL TEC	0.676	FL TEL	Cadmium	Y	Y
43	FL TEC	52.3	FL TEL	Chromium	Y	Y
50	FL TEC	10	NOAA AET	Cobalt	N	Y
32	FL TEC	18.7	FL TEL	Copper	Y	Y
36	FL TEC	30.2	FL TEL	Lead	Y	Y
23	FL TEC	15.9	FL TEL	Nickel	Y	Y
1	FL TEC	0.733	FL TEL	Silver	Y	Y
NG		57	NOAA AET	Vanadium	N	Y
120	FL TEC	124	FL TEL	Zinc	Y	Y

* all units mg/kg dw

1. Assessment and remediation of contaminated sediments program(ARCS): effects range median (ERM)
2. NOAA; upper effect threshold (UET)
3. Florida threshold effect concentration (TEC)
4. NOAA apparent effect threshold (AET)
5. Florida threshold effect level (TEL)
6. No guidance for compound

APPENDIX X. NATIVE AND NONNATIVE SPECIES INCLUDED IN SPECIES SENSITIVITY DISTRIBUTIONS (SSDS) – METALS.

* indicates genus is nonnative to Florida

Arsenic Community

Scientific Name	Common Name	SMAV ug/l
Bosmina longirostris	Water flea	850
Gammarus pseudolimnaeus	Scud	874
Esox masquinongy	Muskellunge	1100
Ceriodaphnia dubia	Water flea	1448
Daphnia magna	Water flea	1500
Jordanella floridae	Flagfish	3040
*Aplexa hypnorum**	Snail	9280
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	10800
*Philodina roseola**	Rotifer	11517
Morone saxatilis	Striped bass	11665
*Coregonus hoyi**	Bloater	16125
*Pimephales promelas**	Fathead minnow	25243
*Salvelinus fontinalis**	Brook trout	25800
Notropis hudsonius	Spottail shiner	27000
Selenastrum capricornutum	Green algae	31200
*Potamopyrgus antipodarum**	Snail	32485
Tanytarsus dissimilis	Midge	36700
Carassius auratus	Goldfish	44900
Lepomis macrochirus	Bluegill	47396
Daphnia pulex	Water flea	49600

Arsenic Arthropods

Scientific Name	Common Name	SMAV ug/l
Bosmina longirostris	Water flea	850
Gammarus pseudolimnaeus	Scud	874
Ceriodaphnia dubia	Water flea	1448
Daphnia magna	Water flea	1500
Tanytarsus dissimilis	Midge	36700
Daphnia pulex	Water flea	49600

Arsenic Fish

Scientific Name	Common Name	SMAV ug/l
Esox masquinongy	Muskellunge	1100
Jordanella floridae	Flagfish	3040
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	10800
Morone saxatilis	Striped bass	11665
*Coregonus hoyi**	Bloater	16125
*Pimephales promelas**	Fathead minnow	25243
*Salvelinus fontinalis**	Brook trout	25800
Notropis hudsonius	Spottail shiner	27000
Carassius auratus	Goldfish	44900
Lepomis macrochirus	Bluegill	47396

Arsenic Non-Vertebrate Animal

Scientific Name	Common Name	SMAV ug/l
Bosmina longirostris	Water flea	850
Gammarus pseudolimnaeus	Scud	874
Ceriodaphnia dubia	Water flea	1448
Daphnia magna	Water flea	1500
*Aplexa hypnorum**	Snail	9280
*Philodina roseola**	Rotifer	11517
*Potamopyrgus antipodarum**	Snail	32485
Tanytarsus dissimilis	Midge	36700
Daphnia pulex	Water flea	49600

Chromium III (N) Fish

Scientific Name	Common Name	SMAV ug/l
Poecilia reticulata	Guppy	21950
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	24159
Carassius auratus	Goldfish	27026
*Pimephales promelas**	Fathead minnow	27643
Anguilla rostrata	American eel	40013
Morone americana	White perch	41452
Lepomis macrochirus	Bluegill	46741
Fundulus diaphanus	Banded killifish	48649
Lepomis gibbosus	Pumpkinseed	48937
Morone saxatilis	Striped bass	50952
Cyprinus carpio	Common Carp	82717

Chromium III (N) Arthropods

Scientific Name	Common Name	SMAV ug/l
Ceriodaphnia reticulata	Water flea	153
Daphnia pulex	Water flea	163
Simocephalus vetulus	Water flea	170
Gammarus sp.	Scud, Amphipod	9959
Daphnia magna	Water flea	30060
Chironomus sp.	Midge	34236
Zygoptera	Damselfly order	134142
Trichoptera	Caddisfly order	155617

Chromium III (N) Community

Scientific Name	Common Name	SMAV ug/l
Anodonta imbecillis	Mussel	149
Ceriodaphnia reticulata	Water flea	153
Daphnia pulex	Water flea	163
Simocephalus vetulus	Water flea	170
Dugesia tigrina	Turbellarian, flatworm	6909
Gammarus sp.	Scud, Amphipod	9959
Poecilia reticulata	Guppy	21950
Oncorhynchus mykiss*	Rainbow trout,donaldson trout	24159
Carassius auratus	Goldfish	27026
Pimephales promelas*	Fathead minnow	27643
Nais sp.	Oligochaete	28945
Daphnia magna	Water flea	30060
Amnicola sp.	Spire snail	31764
Chironomus sp.	Midge	34236
Anguilla rostrata	American eel	40013
Morone americana	White perch	41452
Lepomis macrochirus	Bluegill	46741
Fundulus diaphanus	Banded killifish	48649
Lepomis gibbosus	Pumpkinseed	48937
Morone saxatilis	Striped bass	50952
Cyprinus carpio	Common carp	82717
Zygoptera	Damselfly order	134142
Trichoptera	Caddisfly order	155617

Copper (N) Fish

Scientific Name	Common Name	SMAV ug/l
Etheostoma rubrum	Fountain darter	71
*Oncorhynchus clarki henshawi**	Lahontan cutthroat trout	81
*Oncorhynchus apache**	Apache trout	82
*Oncorhynchus mykiss**	Rainbow trout	116
*Oncorhynchus tshawystcha**	Chinook salmon	140
*Salvelinus confluentus**	Bull trout	151
*Scaphirhynchus platorynchus**	Shovelnose sturgeon	190
*Poeciliposis occidentalis**	Gila topminnow	190
*Ptychocheilus oregonensis**	Northern squawfish	222
*Gila elegans**	Bonytail chub	229
*Oncorhynchus clarki **	Cutthroat trout	289
Etheostoma lepidum	Greenthroat darter	308
*Oncorhynchus gorbuscha**	Pink salmon	309
*Xyrauchen texanus**	Razorback sucker	314
*Oncorhynchus nerka**	Sockeye salmon	373
*Pimephales promelas**	Fathead minnow	381
Etheostoma flabellare	Fantail darter	417
*Oncorhynchus kisutch**	Coho salmon	439
*Acrocheilus alutaceus**	Chiselmouth	491
Etheostoma nigrum	Johnny darter	617
Lepomis macrochirus	Bluegill	5547
Notemigonus crysoleucas	Golden shiner	220946

Copper Fish NOEC

Scientific Name	Common Name	SMCV ug/l
Danio rerio	Zebra danio	0.10
*Pimephales promelas**	Fathead minnow	8
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	12
*Salvelinus fontinalis**	Brook trout	109
*Oncorhynchus kisutch**	Coho salmon,silver salmon	282

Copper (N) Arthropods

Scientific Name	Common Name	SMAV ug/l
Ceriodaphnia dubia	Water flea	41
Daphnia magna	Water flea	50
Hyalella azteca	Scud, Amphipod	61
*Scapholeberis sp.**	Water flea	64
Gammarus	Scud, Amphipod	84
Daphnia pulicaria	Water flea	111
Chironomus decorus	Midge	3078
Acroneuria lycorias	Stonefly	36115

Copper Arthropods NOEC

Scientific Name	Common Name	SMCV ug/l
Daphnia pulex	Water flea	5
Gammarus pulex	Scud	11
Ceriodaphnia dubia	Water flea	15
Chironomus tentans	Midge	29

Copper (N) Community

Scientific Name	Common Name	SMAV ug/l
Ceriodaphnia dubia	Water flea	41
Daphnia magna	Water flea	50
*Actinonaias**	Freshwater mussel	54
Hyalella azteca	Scud, Amphipod	61
*Scapholeberis sp.**	Water flea	64
*lithoglypus virens**	snail	67
Etheostoma rubrum	Fountain darter	71
*Oncorhynchus clarki henshawi**	Lahontan cutthroat trout	81
*Oncorhynchus apache**	Apache trout	82
Gammarus	Scud, Amphipod	84
Daphnia pulicaria	Water flea	111
*Oncorhynchus mykiss**	Rainbow trout	116
*Juga plicifera**	Snail	125
*Oncorhynchus tshawystcha**	Chinook salmon	140
Bufo boreas	Boreal Toad	142
*Salvelinus confluentus**	Bull trout	151
Physa integra	Snail	159
*Utterbackia imbecillis**	Freshwater mussel	177
lumbriculus variegatus	Worm	183
*Scaphirhynchus platorynchus**	Shovelnose sturgeon	190
*Poeciliposis occidentalis**	Gila topminnow	190
*Ptychocheilus oregonensis**	Northern squawfish	222
*Gila elegans**	Bonytail chub	229
*Oncorhynchus clarki **	Cutthroat trout	289
Etheostoma lepidum	Greenthroat darter	308
*Oncorhynchus gorbuscha**	Pink salmon	309
*Xyrauchen texanus**	Razorback sucker	314
*Oncorhynchus nerka**	Sockeye salmon	373
*Pimephales promelas**	Fathead minnow	381
Etheostoma flabellare	Fantail darter	417
*Oncorhynchus kisutch**	Coho salmon	439
*Acrocheilus alutaceus**	Chiselmouth	491
Etheostoma nigrum	Johnny darter	617
Chironomus decorus	Midge	3078
Lepomis macrochirus	Bluegill	5547
Campeloma decisum	Snail	6837
Acroneuria lycorias	Stonefly	36115
Notemigonus crysoleucas	Golden shiner	220946

Copper Community NOEC

Scientific Name	Common Name	SMCV ug/l
Danio rerio	Zebra danio	0.10
Daphnia pulex	Water flea	5
*Juga plicifera**	Snail	6
*Fluminicola virens***	Columbia-river spire snail	> 6
*Pimephales promelas**	Fathead minnow	8
Protozoa	Protozoan phylum	9
Gammarus pulex	Scud	11
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	12
Ceriodaphnia dubia	Water flea	15
Chlamydomonas reinhardtii	Green algae	22
Chironomus tentans	Midge	29
Lemna minor	Duckweed	60
Chlorella vulgaris	Green algae	100
*Salvelinus fontinalis**	Brook trout	109
*Oncorhynchus kisutch**	Coho salmon,silver salmon	282

** Species only included in ranking not in regression because of inequality in SMCV

Lead (N) Community

Scientific Name	Common Name	SMAV ug/l
Cyprinus carpio	Common Carp	344
Ceriodaphnia dubia	Water flea	599
Gammarus pseudolimnaeus	Scud	829
Daphnia magna	Water flea	2229
*Aplexa hypnorum**	Snail	6088
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	12479
*Pimephales promelas**	Fathead minnow	14473
*Salmo salar**	Atlantic salmon	28094
Carassius auratus	Goldfish	95151
*Enallagma sp.***	Damselfly	> 1582159
Procambarus clarkii	Red swamp crayfish	8297349

** Species only included in ranking not in regression because of inequality in SMAV

Lead Community

Scientific Name	Common Name	SMCV ug/l
*Oncorhynchus mykiss**	Rainbow trout	15.3
Danio rerio	Zebra danio	24.5
Daphnia magna	Water flea	270
*Salvelinus fontinalis**	Brook trout	2466

Lead (N) Arthropods

Scientific Name	Common Name	SMAV ug/l
Ceriodaphnia dubia	Water flea	599
Gammarus pseudolimnaeus	Scud	829
Daphnia magna	Water flea	2229
*Enallagma sp.***	Damselfly	> 1582159
Procambarus clarkii	Red swamp crayfish	8297349

** Species only included in ranking not in regression because of inequality in SMAV

Lead (N) Fish

Scientific Name	Common Name	SMAV ug/l
Cyprinus carpio	Common carp	344
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	12479
*Pimephales promelas**	Fathead minnow	14473
*Salmo salar**	Atlantic salmon	28094
Carassius auratus	Goldfish	95151

Nickel (N) Community

Scientific Name	Common Name	SMAV ug/l
Anodonta imbecillis	Mussel	758
*Juga plicifera**	Snail	945
Lemna minor	Duckweed	1093
Daphnia pulex	Water flea	1340
Daphnia magna	Water flea	4086
Daphnia pulicaria	Water flea	6096
Morone saxatilis	Striped bass	6774
Cyprinus carpio	Common carp	8986
Dugesia tigrina	Turbellarian, flatworm	9951
Ambloplites rupestris	Rock bass	13933
Poecilia reticulata	Guppy	14460
*Pimephales promelas**	Fathead minnow	25699
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	43818
*Salmo salar**	Atlantic salmon	290799

Nickel Community NOEC

Scientific Name	Common Name	SMCV ug/l
Danio rerio	Zebra danio	57
Daphnia magna	Water flea	90
*Juga plicifera**	Snail	124
Chlorella pyrenoidosa	Green algae	4000

Nickel (N) Fish

Scientific Name	Common Name	SMAV ug/l
Morone saxatilis	Striped bass	6774
Cyprinus carpio	Common carp	8986
Ambloplites rupestris	Rock bass	13933
Poecilia reticulata	Guppy	14460
*Pimephales promelas**	Fathead minnow	25699
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	43818
*Salmo salar**	Atlantic salmon	290799

Nickel (N) Invertebrates

Scientific Name	Common Name	SMAV ug/l
Anodonta imbecillis	Mussel	758
*Juga plicifera**	Snail	945
Daphnia pulex	Water flea	1340
Daphnia magna	Water flea	4086
Daphnia pulicaria	Water flea	6096

Zinc (N) Community

Scientific Name	Common Name	SMAV ug/l
Ceriodaphnia reticulata	Water flea	83
Daphnia magna	Water flea	98
Morone saxatilis	Striped bass	136
Ceriodaphnia dubia	Water flea	155
Cyprinus carpio	Common carp	253
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	581
*Oncorhynchus tshawytscha**	Chinook salmon	593
Daphnia pulex	Water flea	643
*Agosia chrysogaster**	Longfin dace	737
Anodonta imbecillis	Mussel	1071
*Oncorhynchus nerka**	Sockeye salmon	4861
Poecilia reticulata	Guppy	4873
Physa gyrina	Pouch snail	5447
*Salvelinus fontinalis**	Brook trout	6378
Hydra vulgaris	Hydra	7277
*Oncorhynchus kisutch**	Coho salmon,silver salmon	8644
Lirceus alabamale	Aquatic sowbug	10805
*Pimephales promelas**	Fathead minnow	11731
Corbicula manilensis	Asiatic clam	15966
*Catostomus commersoni**	White sucker	16924
*Ptychocheilus oregonensis**	Northern squawfish	20931
Dugesia tigrina	Turbellarian, flatworm	21430
Lepomis macrochirus	Bluegill	21636
*Xenopus laevis**	Clawed toad	62070

Zinc Community NOEC

Scientific Name	Common Name	SMCV ug/l
Jordanella floridae	Flagfish	26
Daphnia magna	Water flea	69
Lemna minor	Duckweed	160
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	212
*Pimephales promelas**	Fathead minnow	247
Physa gyrina	Pouch snail	570
Danio rerio	Zebra danio	2847

Zinc (N) Fish

Scientific Name	Common Name	SMAV ug/l
Morone saxatilis	Striped bass	136
Cyprinus carpio	Common carp	253
*Oncorhynchus mykiss**	Rainbow trout,donaldson trout	581
*Oncorhynchus tshawytscha**	Chinook salmon	593
*Oncorhynchus nerka**	Sockeye salmon	4861
Poecilia reticulata	Guppy	4873
*Salvelinus fontinalis**	Brook trout	6378
*Oncorhynchus kisutch**	Coho salmon,silver salmon	8644
*Pimephales promelas**	Fathead minnow	11731
*Catostomus commersoni**	White sucker	16924
*Ptychocheilus oregonensis**	Northern squawfish	20931
Lepomis macrochirus	Bluegill	21636

Zinc (N) Arthropods

Scientific Name	Common Name	SMAV ug/l
Ceriodaphnia reticulata	Water flea	83
Daphnia magna	Water flea	98
Ceriodaphnia dubia	Water flea	155
Daphnia pulex	Water flea	643
Lirceus alabamale	Aquatic sowbug	10805