FLORIDA INTERNATIONAL UNIVERSITY

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AN AQUATIC ECOLOGICAL RISK ASSESSMENT ON PESTICIDES IN SURFACE WATERS OF THE C-111 CANAL SYSTEM AND RELATED ESTUARINE DISCHARGE SITES

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To: Dean R. Bruce Dunlap
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This thesis, written by John Fletcher Carriger, and entitled An Aquatic Ecological Risk Assessment on Pesticides in Surface Waters of the C-111 Canal System and Related Estuarine Discharge Sites, having been approved in respect to style and intellectual content, is referred to you for judgment.

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DEDICATION

I dedicate this thesis to Ann Bailer, my grandmother.

ABSTRACT OF THE THESIS

AN AQUATIC ECOLOGICAL RISK ASSESSMENT ON PESTICIDES IN SURFACE WATERS OF THE C-111 CANAL SYSTEM AND RELATED ESTUARINE DISCHARGE SITES

by

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A screening level ecological risk assessment (SERA) was completed to evaluate the potential risks of pesticides found in water in the lower Canal 111 (C-111) Basin and adjacent tidal zones in South Florida. This risk assessment was conducted under general U.S. EPA guidelines and focuses on effects of water exposure to the herbicides atrazine and metolachlor and to the insecticides chlorpyrifos, endosulfan, and malathion. Results found that the highest potential risk was associated with the acute effects of endosulfan to freshwater arthropods at sites near water control structure S-178 and Canal 111e, a branch of C-111. The highest potential risk of acute effects of endosulfan for saltwater organisms was in Joe Bay, which receives discharges from C-111. Results from evaluations of risk of chronic effects from pesticide exposure show that the highest potential risk is associated with endosulfan in freshwater.

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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 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

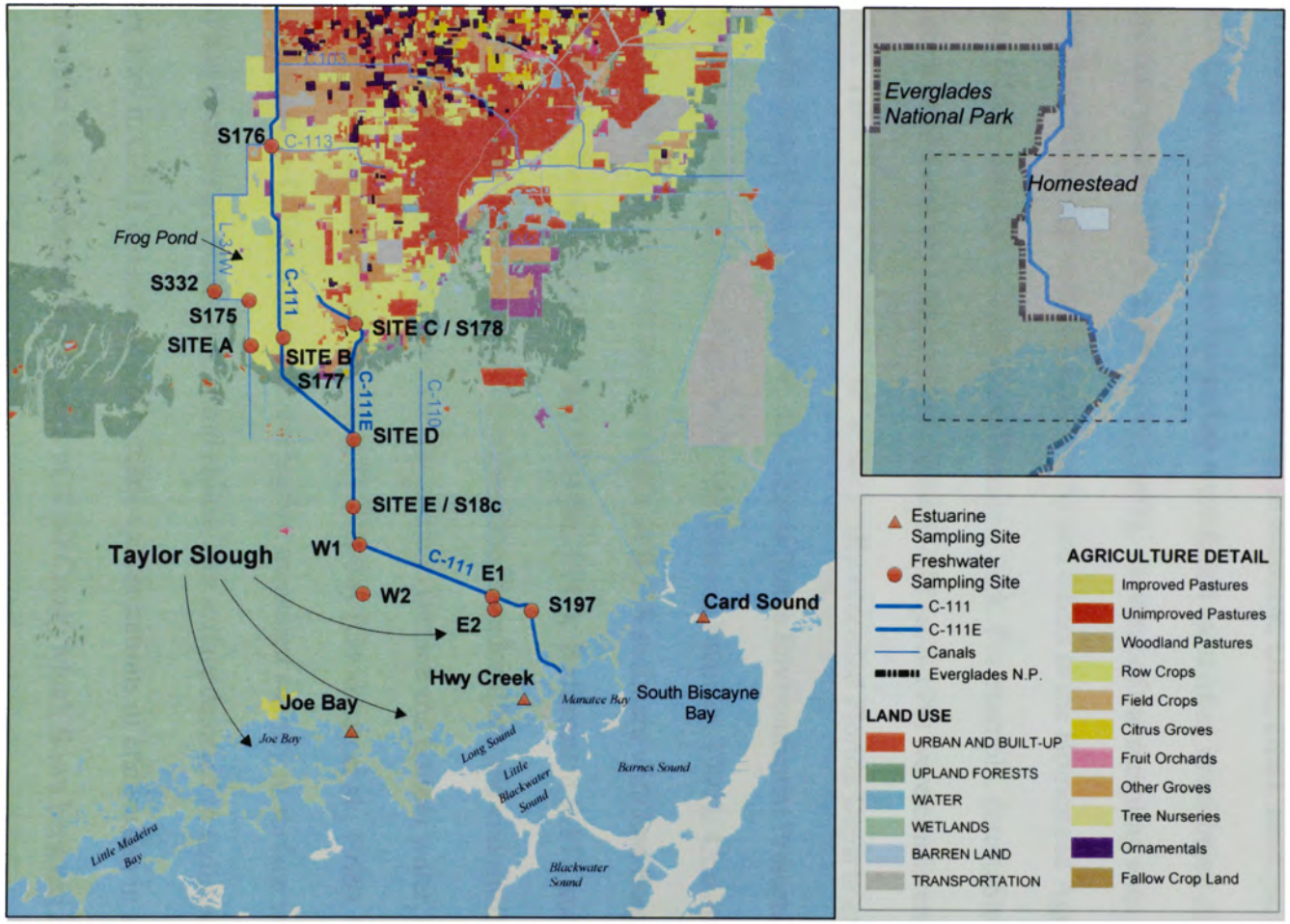


Figure 1. Land use and drainage canals in the C-111 flood control basin in southeast Florida.

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 Everglades National Park. 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 (NSandT) Program 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 NS and T 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 thesis 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 U.S.G.S., 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).

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 Everglades National Park (ENP) (Figure 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 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 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).

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 United States Geological Survey (USGS), NOAA, South Florida Water Management District (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 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,

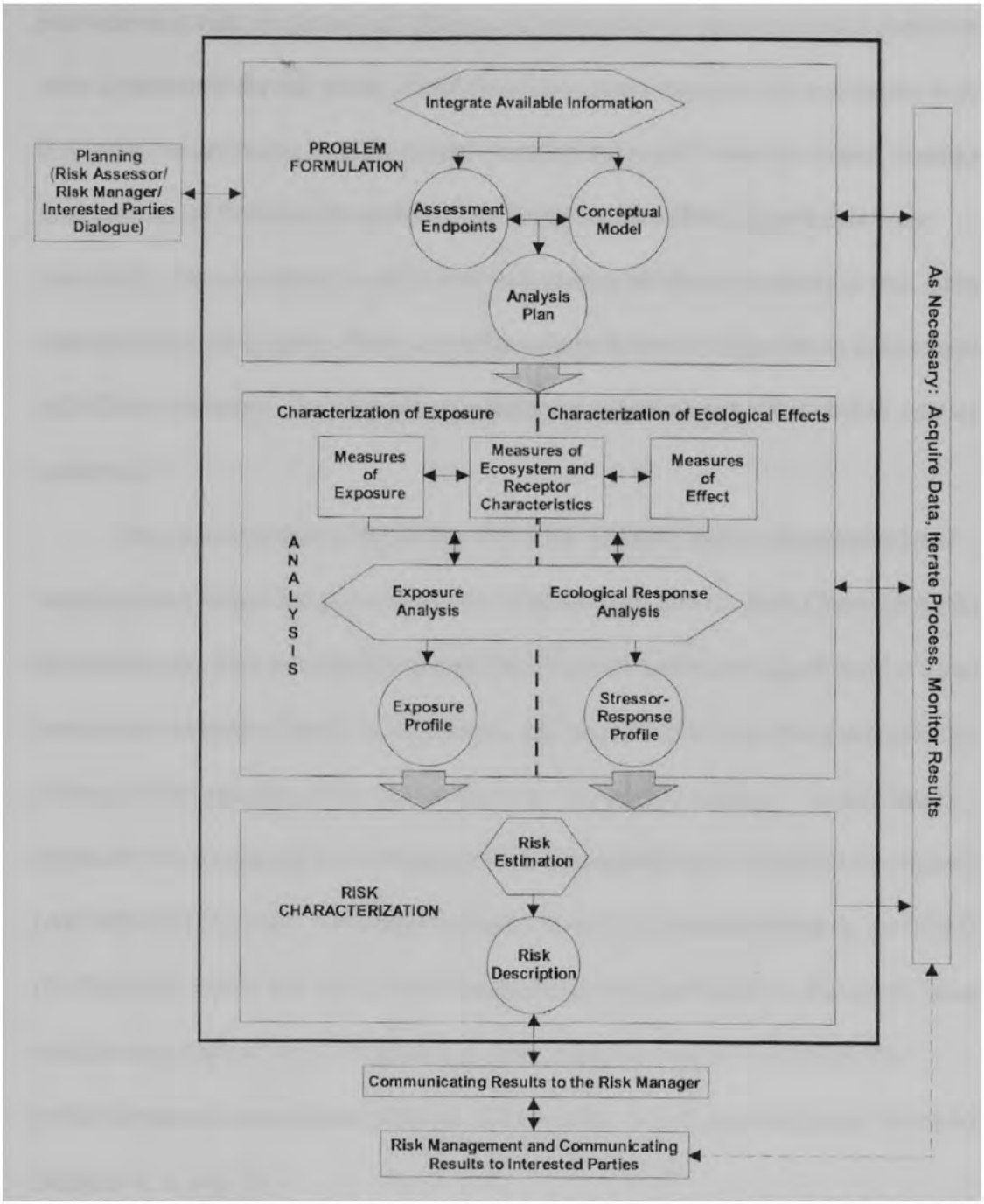


Figure 2. U.S. EPA framework for ecological risk assessment (from U.S.EPA, 1998).

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). (The results of both approaches are discussed in Sections 4, 6, and 7.)

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 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

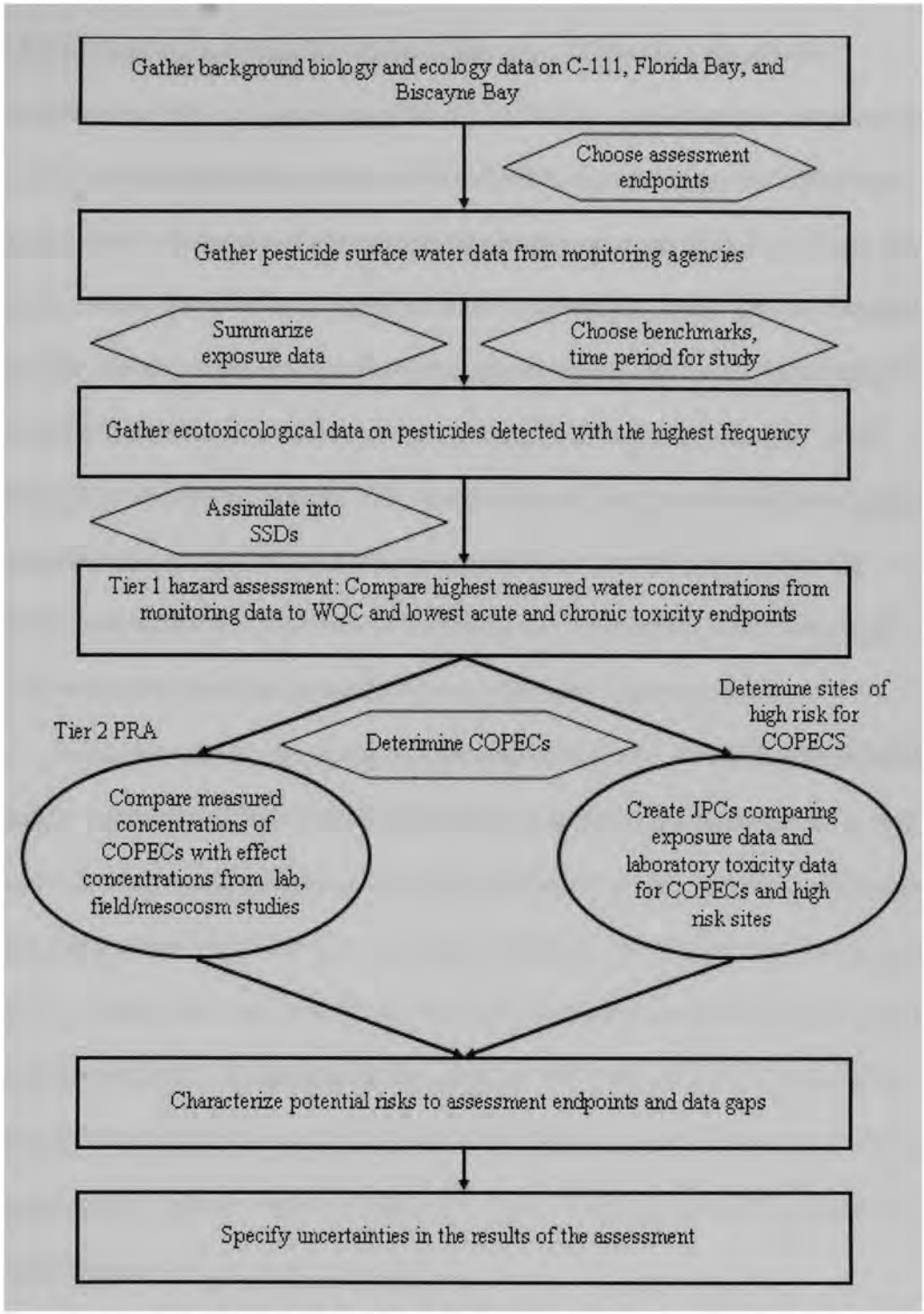


Figure 3. Decision tree for C-111 SERA. SSDs=species sensitivity distributions, COPECs= chemicals of potential ecological concern, JPCs=joint probability curves, PRA=probabilistic risk assessment, WQC=water quality criteria.

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 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).

4. TIER 1 SCREENING ASSESSMENT

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).

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

Table 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)

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 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 2. All quotients were below any designated hazard threshold for aquatic animals and plants/algae from maximum measured concentrations in freshwater or saltwater sites.

Table 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	Plant/Algae
Metolachlor	0.062	0.00	0.01
Acute SW	Peak concentration (µg/L)	Acute hazard quotient	
		Animal	Plant/Algae
Metolachlor	0.00722	0.00	0.00
Chronic FW	Peak concentration (µg/L)	Chronic hazard quotient	
		Animal	Plant/Algae
Metolachlor	0.062	0.00	0.00
Chronic SW	Peak concentration (µg/L)	Chronic hazard quotient	
		Animal	Plant/Algae
Metolachlor	0.00722	0.00	0.00

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 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 hazard quotients or WQC exceeded, atrazine, and metolachlor were also assessed in higher tier work.

5. PROBLEM FORMULATION

5.1. Stressor Characteristics

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 registration 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.

5.1.2. Chlorpyrifos

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).

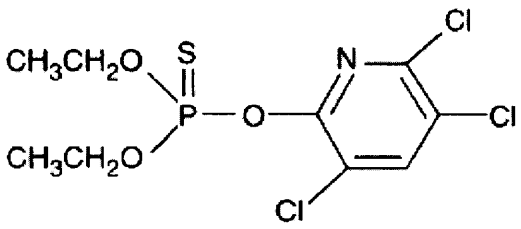
5.1.2.2. Chemical/Physical Properties and Environmental Behavior

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 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 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

Table 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°C
Water solubility	1.39 mg/L @ 25°C
Vapor pressure	2.0×10^{-5} mm Hg @ 25°C
Henry's law constant	6.64×10^{-3} atm-L mol^{-1}
Log K_{ow}	4.7-5.3

*from Giesy et al., 1999
**from ATSDR, 1997

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).

5.1.2.3. 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 (Florida citrus, Georgia corn with spray application, North Carolina tobacco, Mississippi cotton, foliar spray on corn with three aerial applications over a 14 d interval, peanuts, granular post plant corn, and foliar sprayed corn with one aerial application) 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. This occurred in the same eight out of fourteen modeled crop uses that surpassed fish acute toxicity values. 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 10^{th} 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 10^{th} 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.

5.1.2.4. 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).

5.1.3. Endosulfan

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 South Florida Water Management District 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 4 to 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).

5.1.3.2. Chemical/Physical Properties and Environmental Behavior

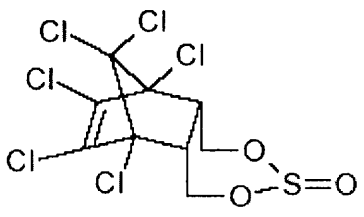
Chemical/Physical Properties

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-

Table 4. Physical and chemical characteristics of technical endosulfan

Structure*:

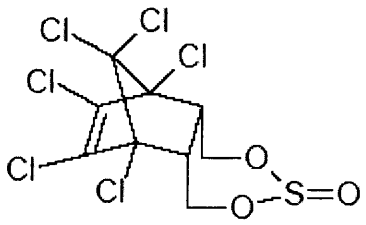


Property	Value*
CAS number	115-29-7
Chemical name	6,7,8,9,10,10-hexachloro-1,5,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo(e)-dioxathiepin-3-oxide
Molecular weight	406.95 g/mol
Molecular formula	$C_9H_6Cl_6O_3S$
Melting point	70-100°C
Water solubility	60-100 μg/L @ 25°C
Vapor pressure	$1x10^{-5}$ mmHg @ 25°C
Henry's law constant	$1x10^{-5}$ atm m^3 mol^{-1} @ 24.8°C
Log K_{ow}	3.55 and 3.62

*from ATSDR, 2000

Table 5. Physical and chemical characteristics of α-endosulfan

Structure*:

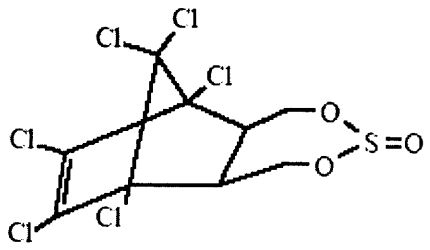


Property	Value*
CAS number	959-98-8
Chemical name	6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide (3α, 5a β, 6α, 9a α, 9β)-
Molecular weight	406.93 g/mol
Molecular formula	$C_9H_6Cl_6O_3S$
Melting point	108–110 °C
Water solubility	0.53 mg/L @ 25°C
Vapor pressure	1 x 10^{-5} mm Hg @ 25°C
Henry's law constant	1.01 x 10^{-4} atm m^3 mol^{-1} @ 25°C
Log K_{ow}	3.83

*from ATSDR, 2000

Table 6. Physical and chemical characteristics of β-endosulfan

Structure*:

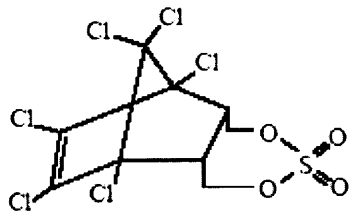


Property	Value*
CAS number	33213-65-9
Chemical name	6,7,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodiozathiepin-3-oxide, (3α, 5aα, 6β, 9β, 9aα)-
Molecular weight	406.9 g/mol
Molecular formula	$C_9H_6Cl_6O_3S$
Melting point	207–212 °C
Water solubility	0.33 mg/L @ 22°C
Vapor pressure	1×10^{-5} mm Hg @ 25°C
Henry's law constant	1.91×10^{-5} atm m^3 mol^{-1} @ 25°C
Log K_{ow}	3.52

*from ATSDR, 2000

Table 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°C
Water solubility	0.22 mg/L @ 22°C
Vapor pressure	$1x10^{-5}$ mmHg @ 25°C
Henry's law constant	$2.61x10^{-5}$ atm m^3 mol^{-1} @ 25°C
Log K_{ow}	3.66

*from ATSDR, 2000

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°C) 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 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 in sterile seawater 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.

5.1.3.3. 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.

5.2. 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) stressor characteristics.

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.

5.4. 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

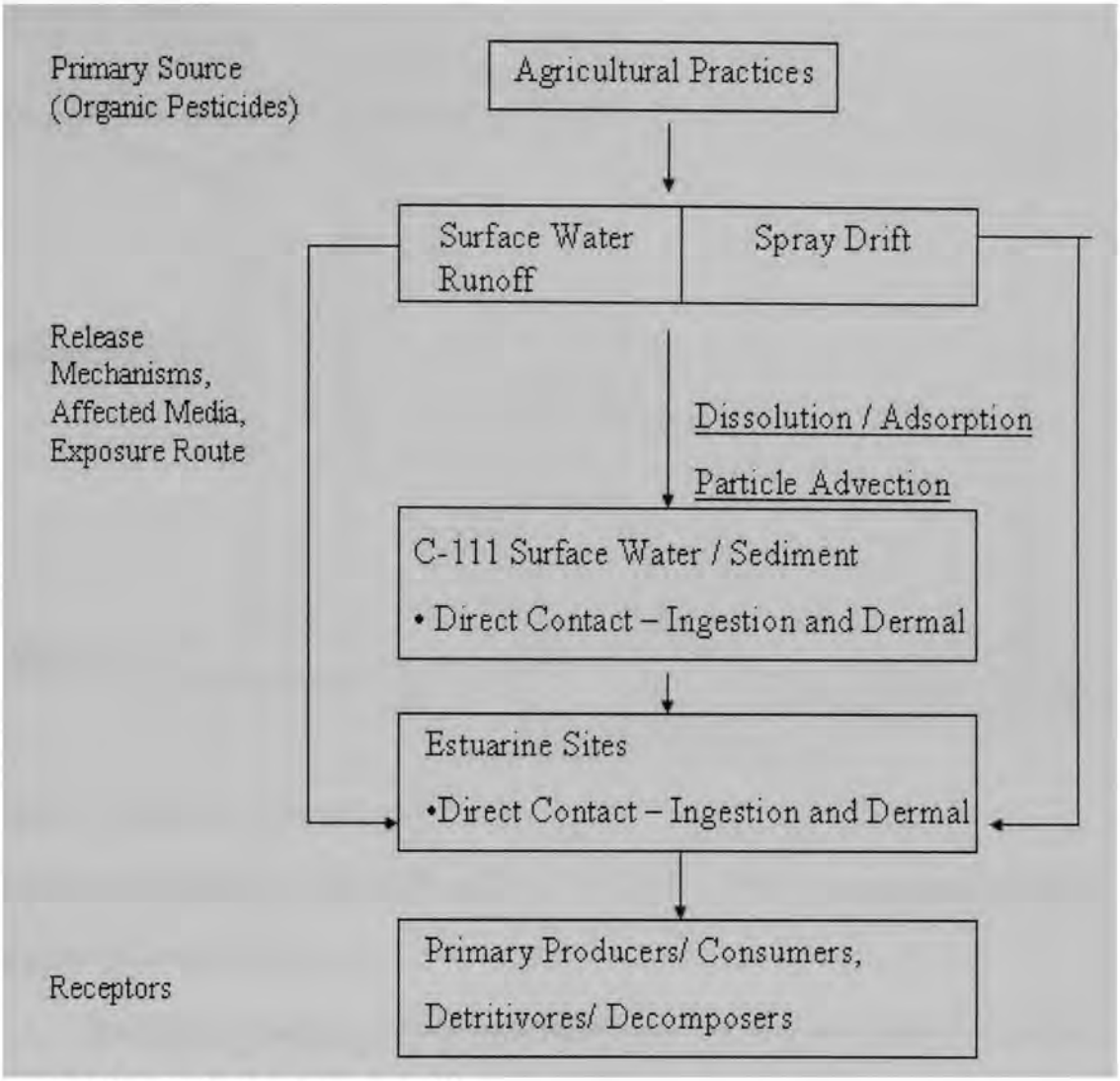


Figure 4. Conceptual exposure model.

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

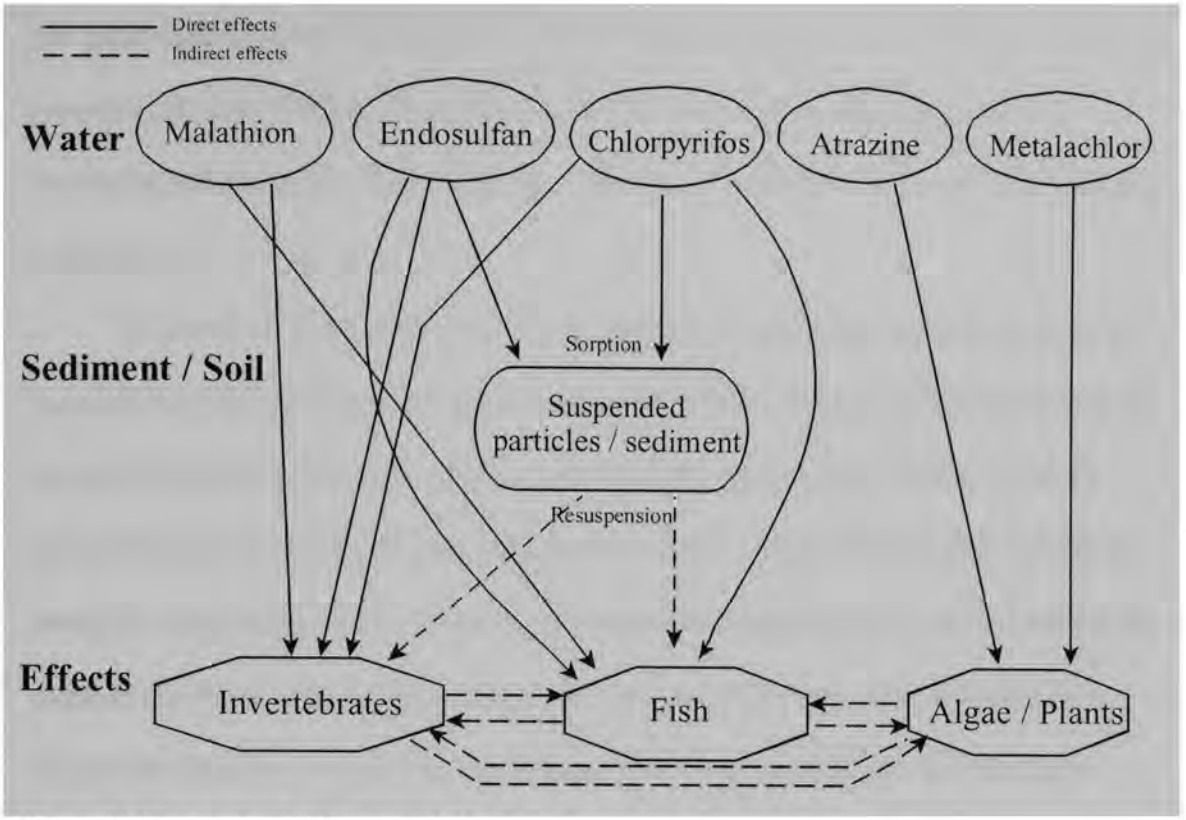


Figure 5. Conceptual effects model.

endpoints and measures of effect (U.S.EPA, 1994, 1997). The site conceptual exposure model is illustrated in Figure 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.

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.

5.5. 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 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).

5.5.1. 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 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 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 (90^{th} 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 90^{th} 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 90^{th} 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 90^{th} 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 90^{th} 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 seagrass effects on atrazine.

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 13 and 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 10^{th} centiles for each distribution were gauged for analysis. Because they are generally conservative, 10^{th} 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:

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

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, 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 13 and 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 10^{th} 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.

5.5.3. Risk Characterization

Risk was assessed by comparing the overlap of the distributions of AMCs and toxicity values for sites and species of concern. The 90^{th} centile of the AMCs for exposure was compared to the 10^{th} 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 10^{th} 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 10^{th} 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):

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

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 90^{th} 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 probabilistic risk assessment 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 99^{th} centile, the 95^{th} centile, the 90^{th} centile, the 75^{th} centile, and the 50^{th} centile concentration estimate. After the 90^{th} 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 90^{th} 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.

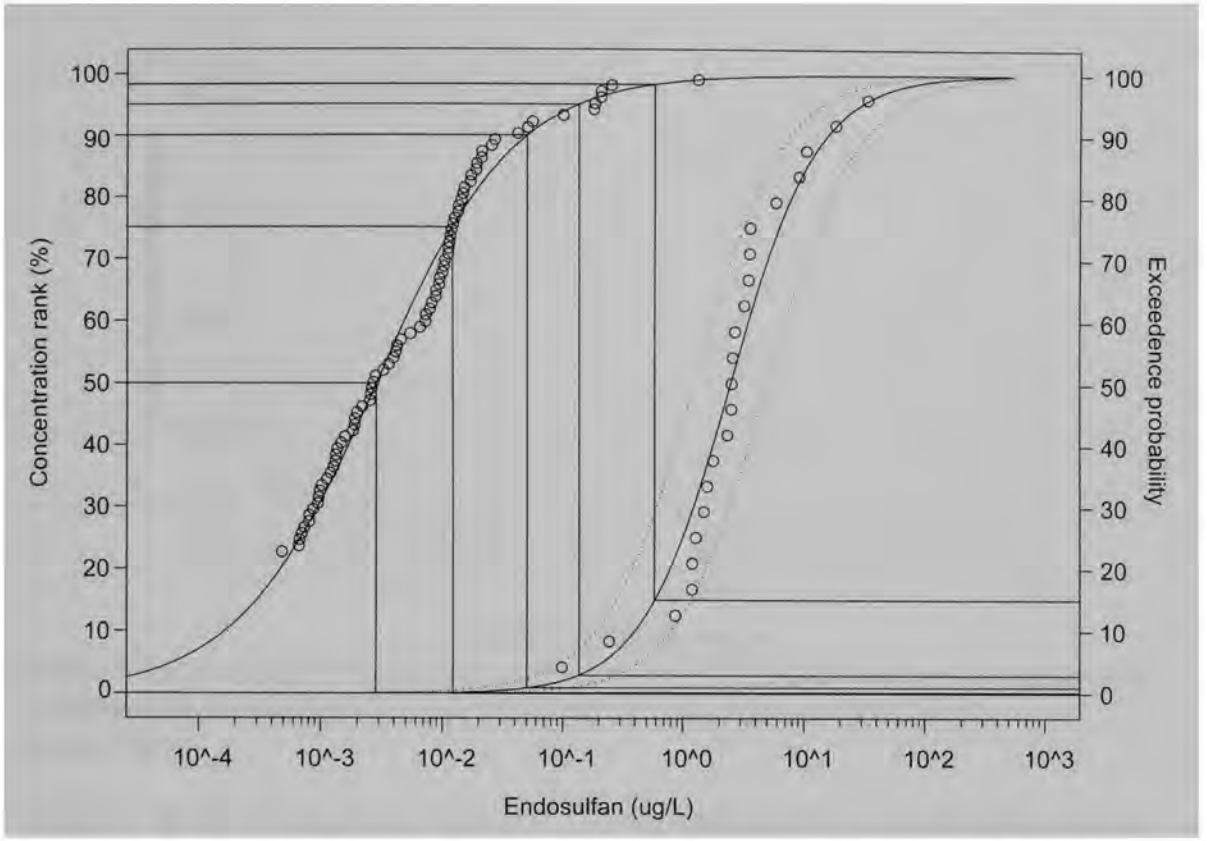


Figure 6. Illustration of the overlap of a distribution of measured concentrations and a distribution of toxicity values for creating a joint probability curve (JPC). Various centile concentrations are estimated from the exposure distribution and their intersection with the response factors from an effects distribution are the essential components in JPC creation.

A visual depiction of the creation of a JPC is presented in Figures 6 and 7. In Figure 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 99^{th}, 95^{th}, 90^{th}, 75^{th}, and 50^{th}) intersect an effects distribution to create a JPC. Figure 7 shows a JPC curve constructed by linear interpolation from Figure 6. From Figure 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

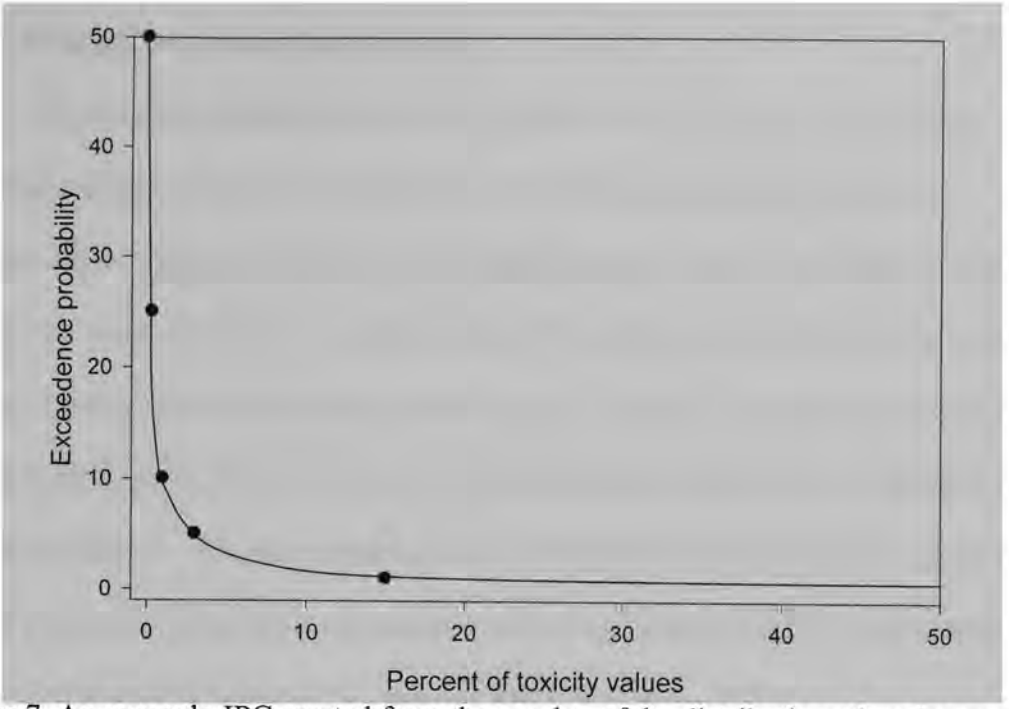


Figure 7. An example JPC created from the overlap of the distribution of environmental concentrations and toxicity values from Figure 6. See Analysis Plan text for interpretation.

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.

5.5.4. 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 toxic mode of action (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 concentration addition 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):

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

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):

$$PAF_{TMoA} = \frac{1}{1+e^{-\log(\Sigma HU_{TMoA})/\beta_{TMoA}}}$$

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 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).

Response addition 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):

$$PAF_{RA} = 1 - \prod_{i}(1 - PAF_i)$$

for $i = 1$ to n pesticides, and PAF_{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 concentration addition 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 concentration addition 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 90^{th} 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.

6. RISK ANALYSIS

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 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. Chlorpyrifos was not analyzed by the SFWMD.

For the assessment of acute risk, 90^{th} centile estimates were chosen as the benchmark level for exposure (SETAC, 1994). Tables 9 and 11 present the 90^{th} centile

estimates for fresh and saltwater sites for the 1999 and 2000 period. Tables 10 and 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:

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

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

Table 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

parameters. Parameter estimates generated from the above model are presented in Tables 13 and 16.

6.2. Exposure Analysis

6.2.1. Data Analysis

The detection limits for pesticides in surface waters from each of the monitoring agencies are listed in Table 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 9 summarizes the various parameters assessed from the monitoring data for freshwater sites in C-111 (e.g., 90^{th} 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 9 to 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.

6.2.2. Measured concentrations in freshwater sites

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.

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.

Table 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 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 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

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 four 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 90^{th} 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.

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 90^{th} 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 90^{th} centile estimate for endosulfan exposures, a value that was approximately an order of magnitude above the concentrations measured in sites in the south.

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 90^{th} 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 fourth highest at S-18C/Site E.

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.

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.

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.

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.

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 1998 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.

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.

6.2.2.12. Annual Distributions of Exposure for Freshwater Sites

Table 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.

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 90^{th} centile estimate for chlorpyrifos was 0.0189 μg/L for measured concentrations in February. For total endosulfan at the same site, the 90^{th} centile estimate was 0.0657 μg/L. At S-178/Site C, the 90^{th} centile estimate for chlorpyrifos in February was 0.00569 μg/L. The 90^{th} centile estimate for total endosulfan at the same site in February was 0.954 μg/L. At S-18C/Site E, measured concentrations

Table 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

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 and total endosulfan than the previous two sites for June exposures. However, 90th centile estimates for both compounds were 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.

6.2.3. Measured Concentrations in Estuarine Sites

Table 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.

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 90^{th} 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 90^{th} centile estimates in Card Sound but not in any other estuarine site. Though endosulfan concentrations in both sites appeared similar, the 90^{th} 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.

Table 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

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 (0.00086 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.

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 concentrations 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.

6.2.3.4. Annual Distributions of Exposure for Estuarine Sites

Annual distributions were created for all estuarine monitoring data (Table 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 centiles

Table 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

estimated for endosulfan increased with time so that 2000 had the highest value and 1999 had the lowest.

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 90^{th} centile estimate for chlorpyrifos was 0.00339 μg/L for measured concentrations in February. For total endosulfan at the same site, the 90^{th} centile estimate was 0.0129 μg/L. At Joe Bay, the 90^{th} centile estimate for chlorpyrifos in February was 0.00514 μg/L. The 90^{th} centile estimate for total endosulfan at the same site in February was 0.0213 μg/L. The 90^{th} 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 90^{th} centile estimate was 0.00169 μg/L. Joe Bay had the highest 90^{th} centile estimates for exposure for chlorpyrifos and 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 estimates 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.

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 8 and 9. Figure 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 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

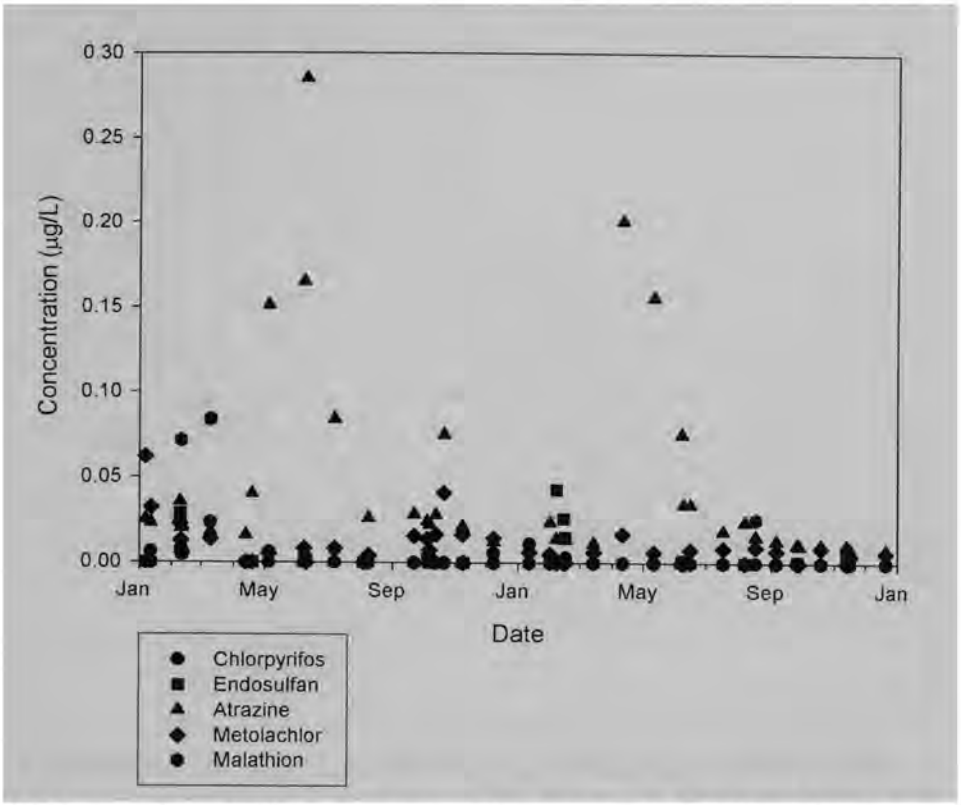


Figure 8. Measured pesticide concentrations in water at S-177/Site B from 1999 to 2000.

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

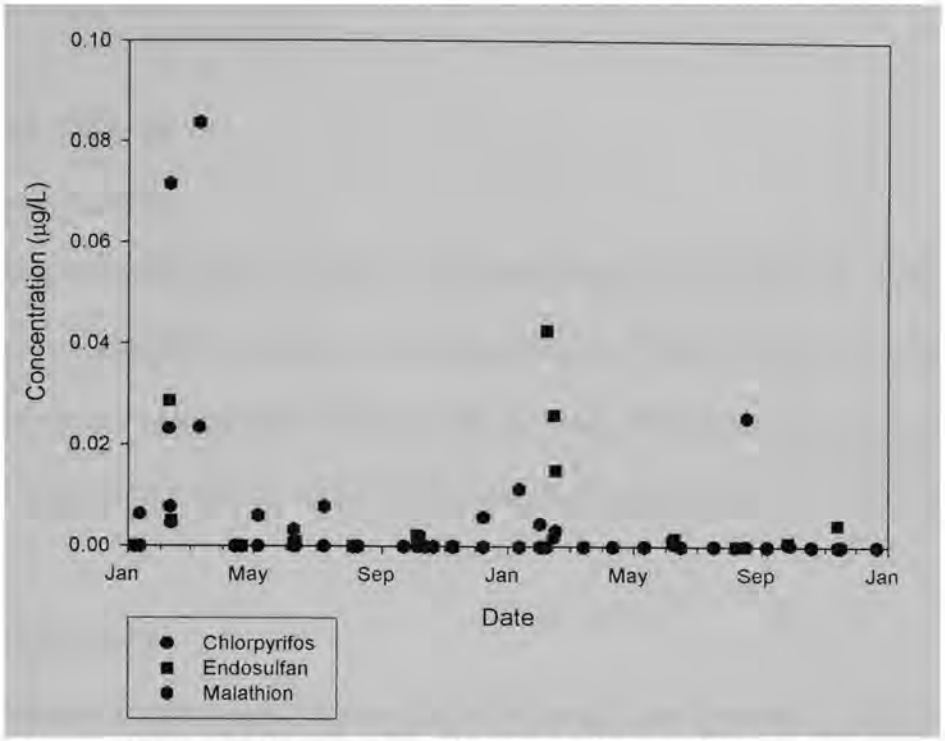


Figure 9. Measured insecticides in water at S-177/Site B from 1999 to 2000.

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.

6.3. Effects Analysis

6.3.1. Acute Toxicity

Statistics for the acute toxicity distributions (SSDs) are presented in Table 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 Appendix 2.

6.3.1.1. Community

The most sensitive species group for chlorpyrifos was arthropods (Table 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 10^{th} 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 10^{th} centile of this distribution was estimated to be 0.11 µg/L. *Americamysis bahia*

Table 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 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 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

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 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 10^{th} 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.

Table 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 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

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.*

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.

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.

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 10^{th} centile for chlorpyrifos was estimated to be 82 µg/L in this category. Since this was the highest 10^{th} 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.

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*.)

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.

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.

6.3.2. Chronic Toxicity

The 10^{th} centile estimates and data for graphs of log-logistically distributed NOECs are presented in Table 16. The 10^{th} centile estimates for chronic effects in increasing order were: chlorpyrifos (0.0180 μg/L), and endosulfan (0.1227 μg/L). Each compound's 10^{th} centile for log-logistically distributed chronic effects distributions were smaller than any of their corresponding acute 10^{th} centiles. Chlorpyrifos had a 10^{th} centile estimate for chronic effects nearly an order of magnitude below the estimated value for endosulfan.

Table 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

6.3.3 Field/Mesocosm Studies

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.

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 osctracods, *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 *Simocephalus*, 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 these 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. 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.

7. RISK CHARACTERIZATION

In contrast with the worst-case scenario hazard quotient 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:

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

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 17 to 20)

and the median exposure concentrations (Tables 21 to 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.

7.1. Acute PAF/msPAF Assessment

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 19 and 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 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 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 18). As mentioned previously, the estimated 10th centile effect concentration for endosulfan and saltwater arthropods was lower than the same value for freshwater arthropods.

Table 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 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	

In S-178/Site C, risks appeared higher for endosulfan over other freshwater sites for 1999 to 2000 (Table 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 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.

7.1.2. Acute Multisubstance Assessment (msPAF)

In 1999, freshwater msPAF values were all below 3% for acute toxicity (Table 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 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 18). In freshwater sites, the msPAF for fish species never exceeded 2% in annual distributions.

Table 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 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 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	

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 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 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 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 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%.

7.2. Chronic PAF/msPAF Assessment

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 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 21). However, chlorpyrifos had higher PAFs for 1999 and 2000 at 1.2% and 1.5%, respectively. Endosulfan PAF values for

Table 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	

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 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 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 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.

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 21 to 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 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 22). Site E1 had a chronic msPAF of

Table 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 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	

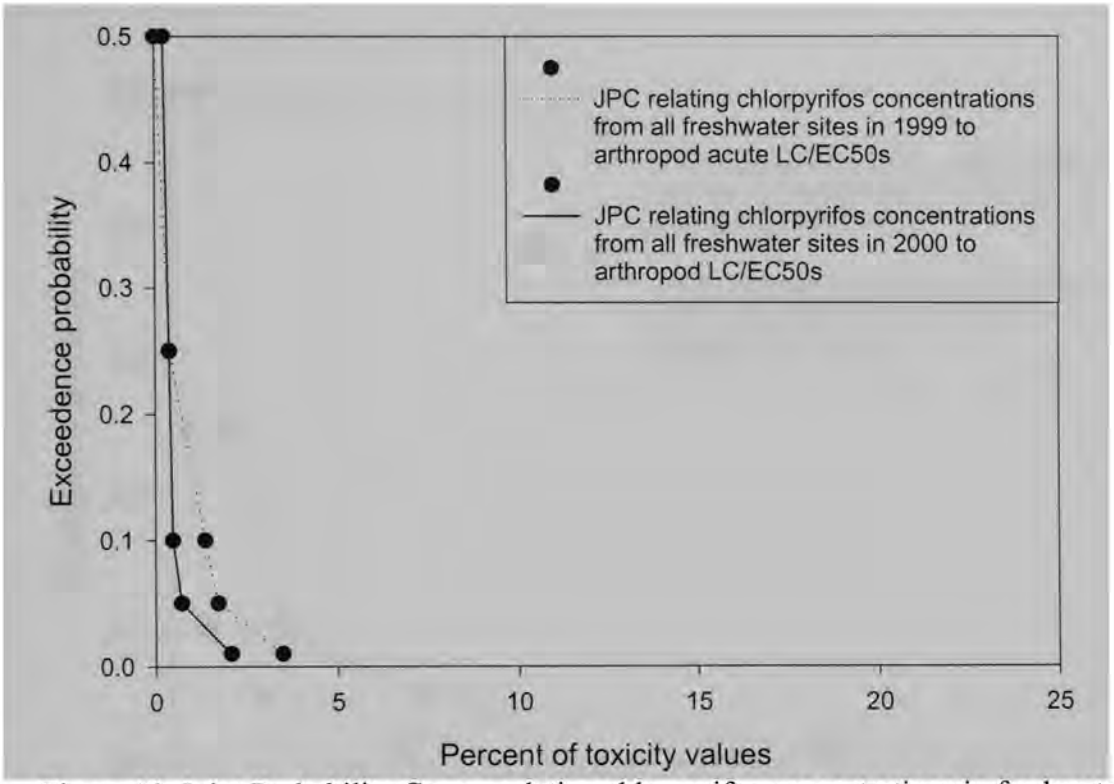


Figure 10. Joint Probability Curves relating chlorpyrifos concentrations in freshwater sites to arthropod acute toxicity data (LC/EC50s).

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 23). The highest value was for Joe Bay at 2.7% and the lowest msPAF values were found at Card Sound and Highway Creek with at 2.1% for each.

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

Figures 10 to 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 10, there is a slight increase in potential risk to freshwater arthropods from

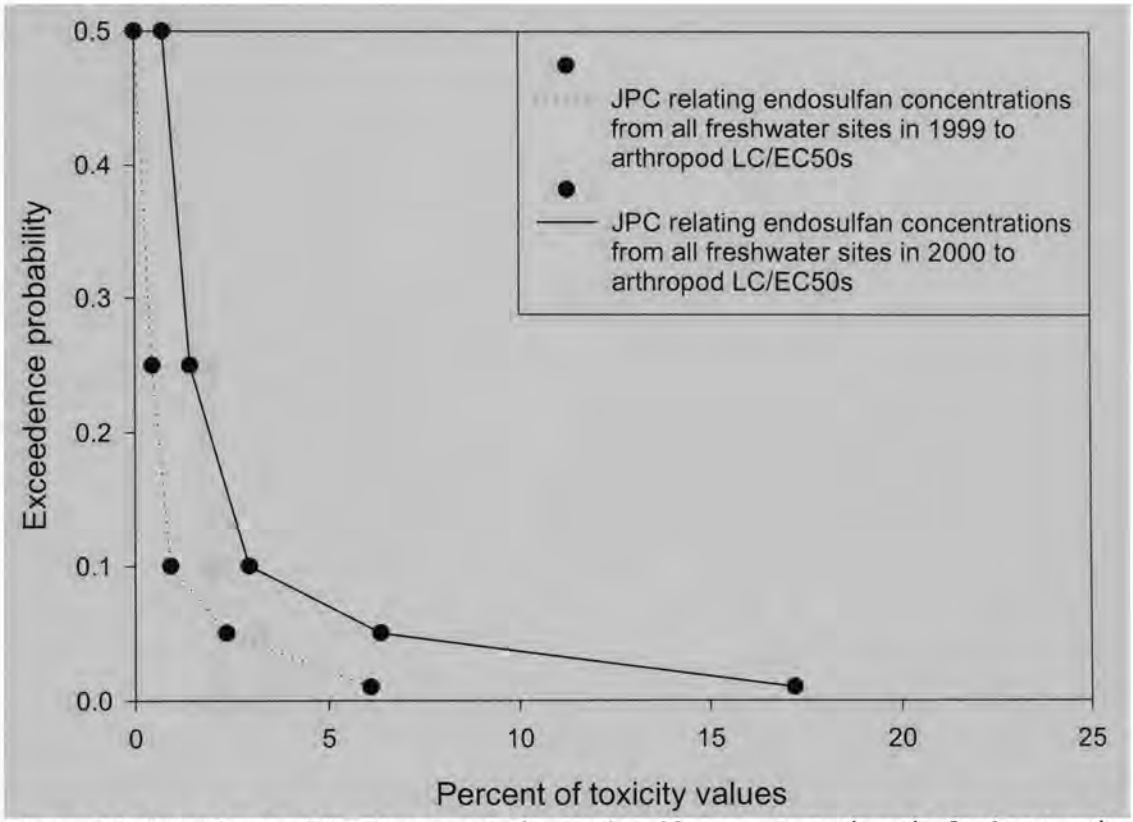


Figure 11. Joint Probability Curves relating endosulfan concentrations in freshwater sites to arthropod acute toxicity data (LC/EC50s).

chlorpyrifos in 1999 over 2000 below the 0.1 exceedence probability. As is apparent from Figure 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 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 13). Thus, the trends illustrated in Figures 10 to 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

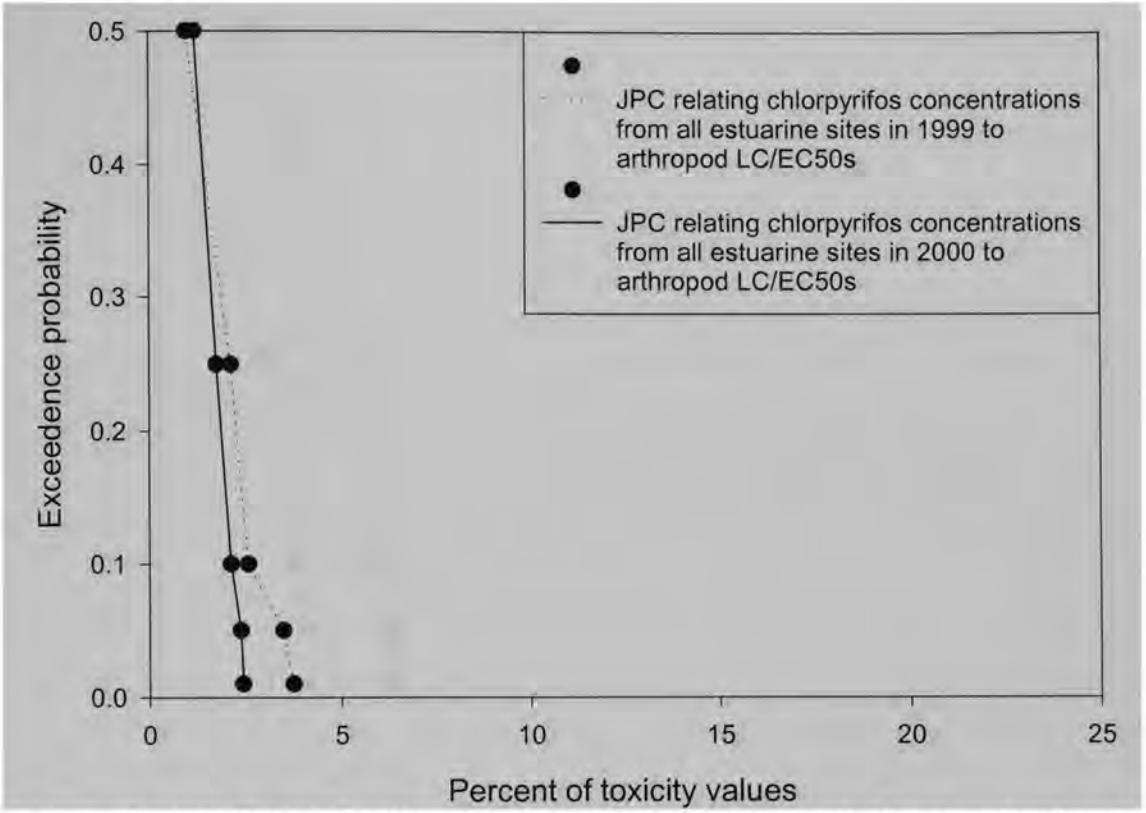


Figure 12. Joint Probability Curves relating chlorpyrifos concentrations in estuarine sites to arthropod acute toxicity data (LC/EC50s).

freshwater sites. JPCs for each site are presented in Figures 14 to 19 for endosulfan and chlorpyrifos over 1999 and 2000. Figures 14 to 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.

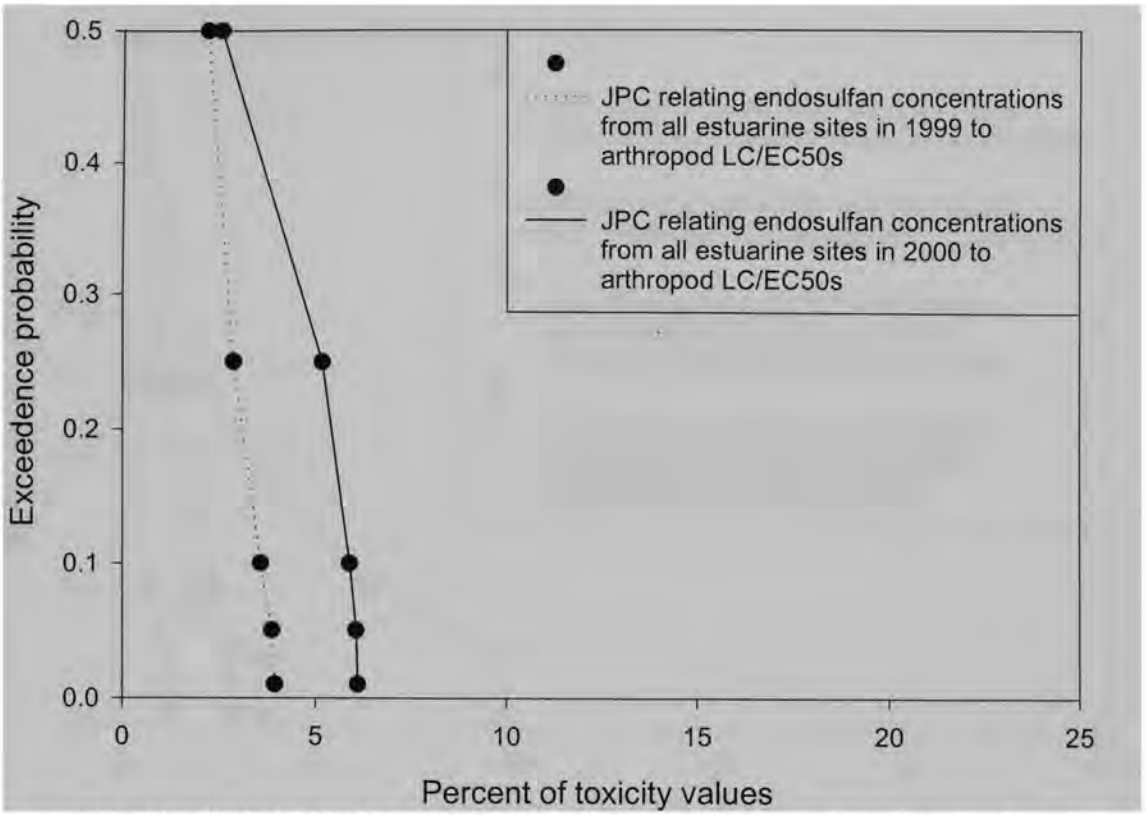


Figure 13. Joint Probability Curves relating endosulfan concentrations in estuarine sites to arthropod acute toxicity data (LC/EC50s).

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

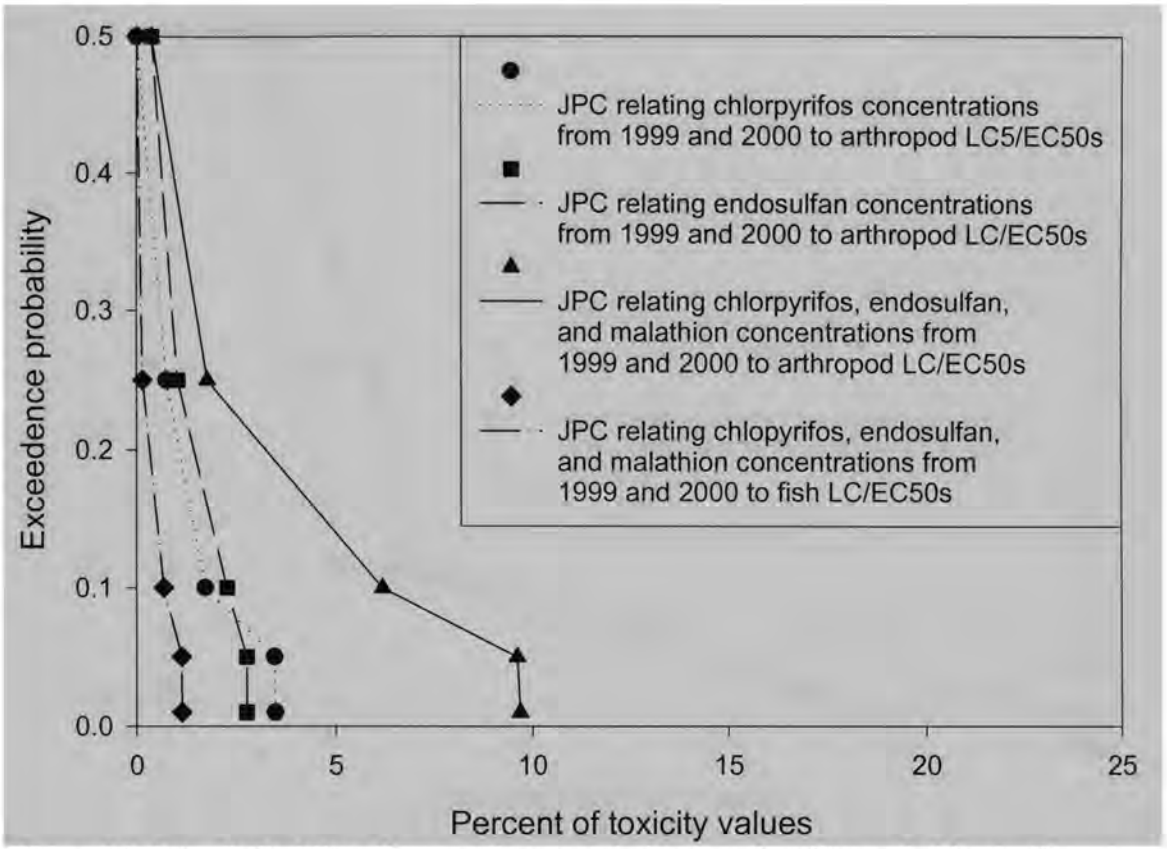


Figure 14. Joint Probability Curves relating malathion, endosulfan and chlorpyrifos concentrations in S-177/Site B to arthropod and fish acute toxicity data (LC/EC50s).

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 14 to 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-

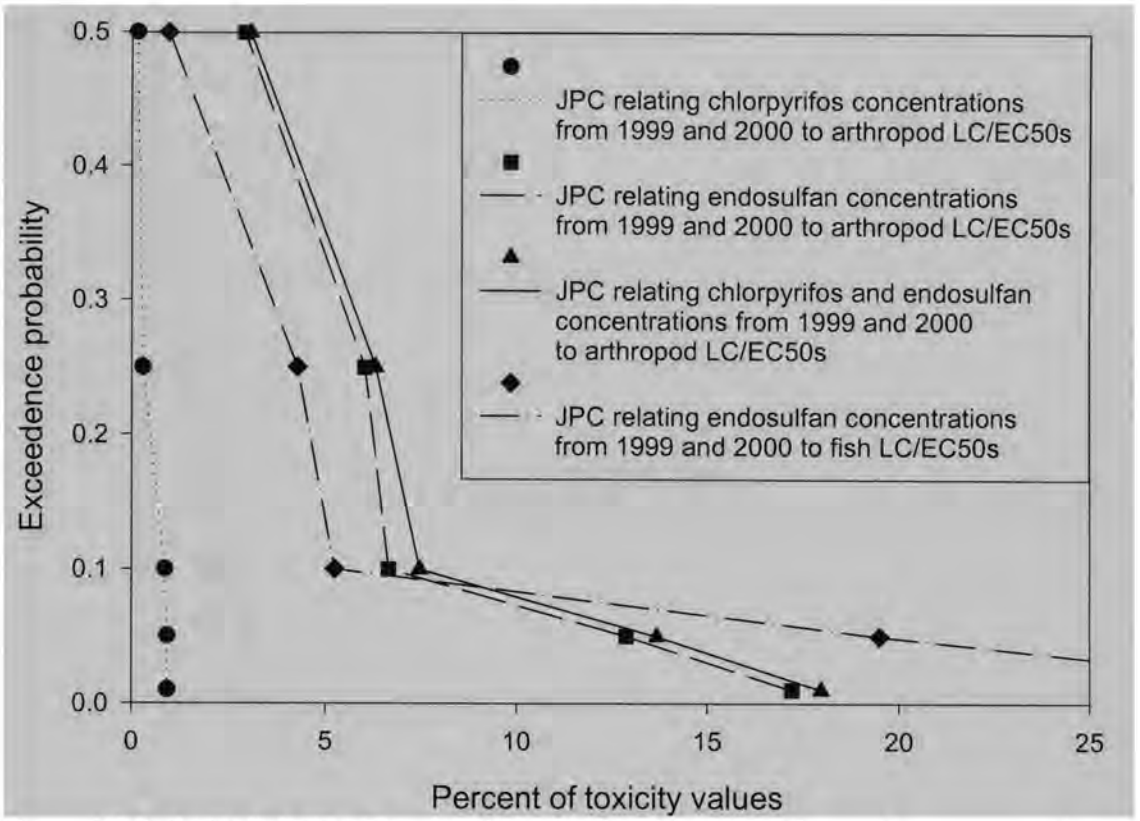


Figure 15. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-178/SiteC to arthropod and fish acute toxicity data (LC/EC50s).

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-

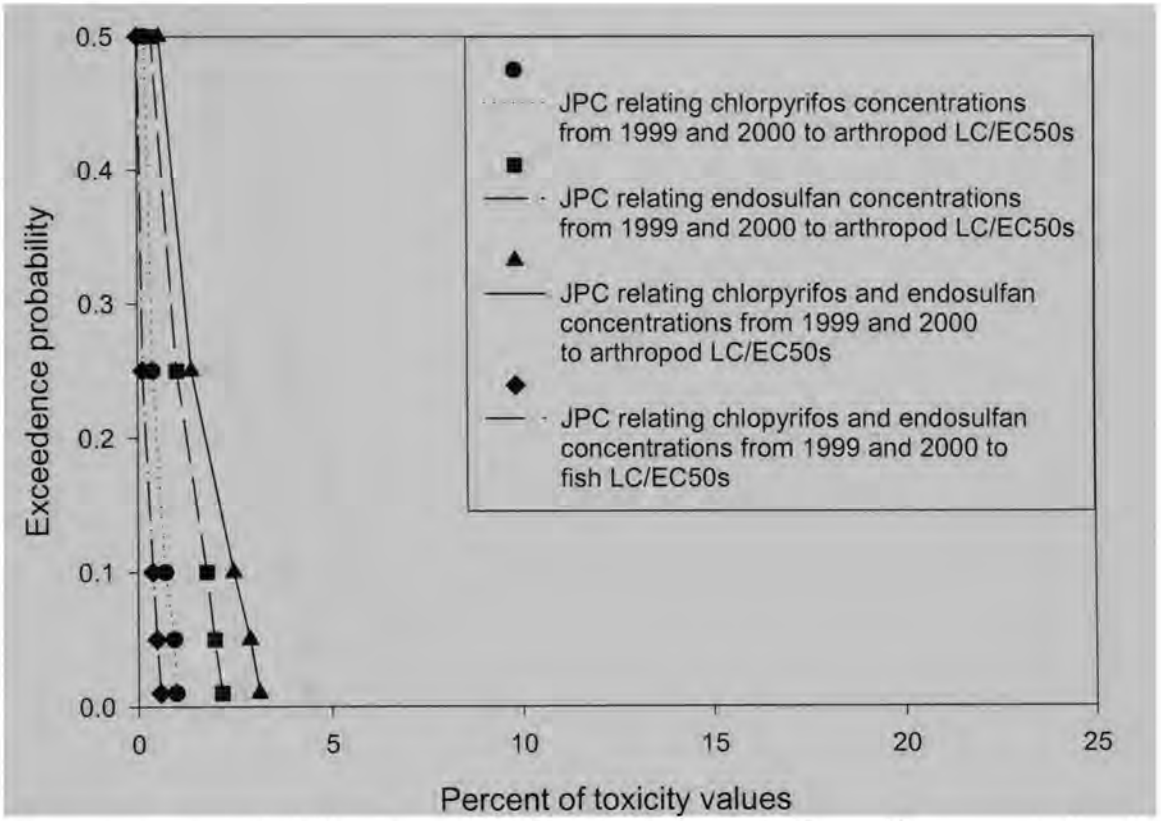


Figure 16. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-18C/Site E to arthropod and fish acute toxicity data (LC/EC50s).

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 17, 18 and 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

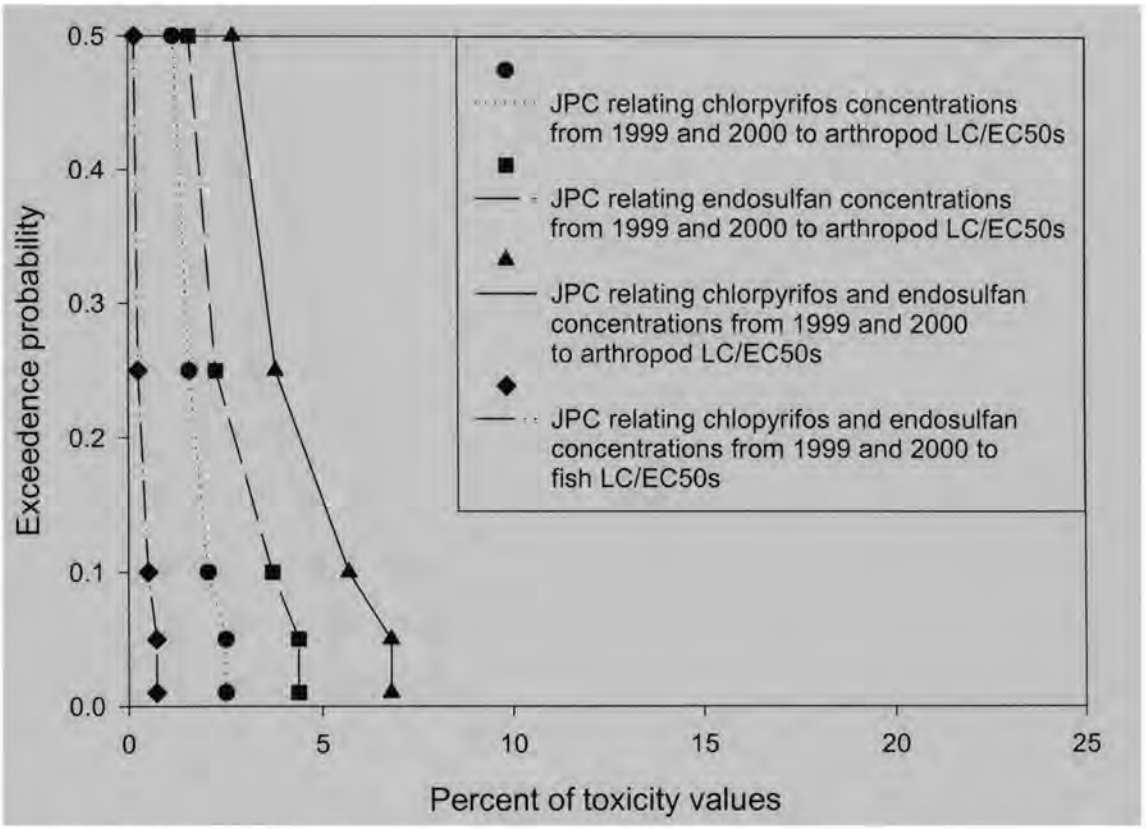


Figure 17. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Card Sound to arthropod and fish acute toxicity data (LC/EC50s).

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 20 to 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

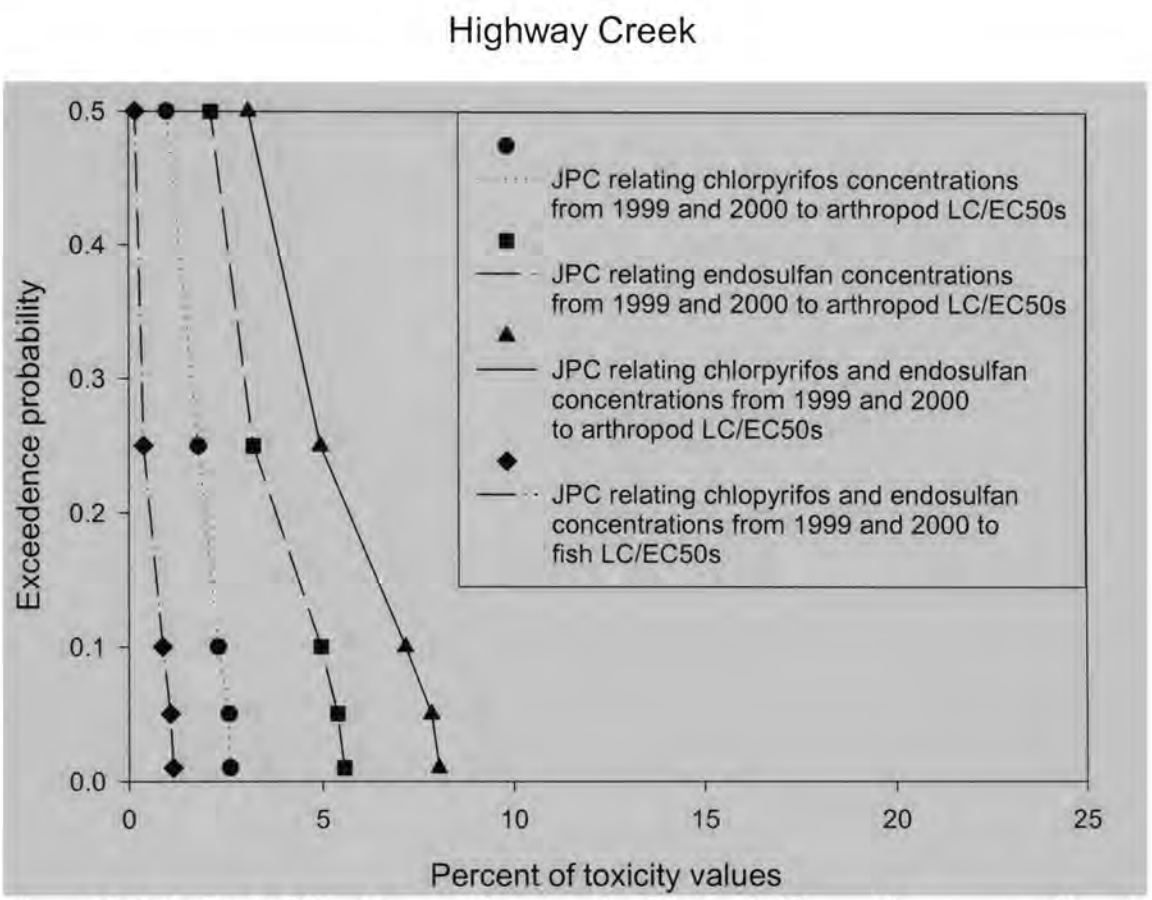


Figure 18. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Highway Creek to arthropod and fish acute toxicity data (LC/EC50s).

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

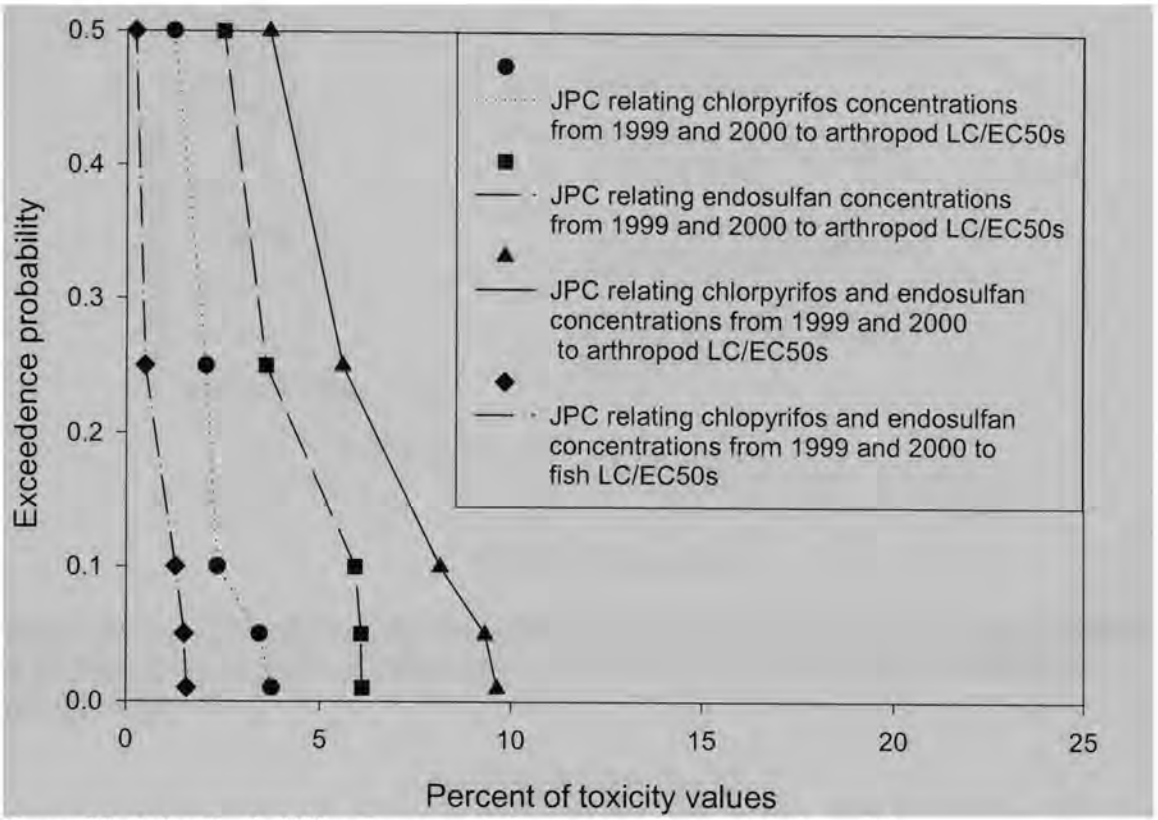


Figure 19. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Joe Bay to arthropod and fish acute toxicity data (LC/EC50s).

substance analyses (Figures 20 to 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 20 and 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 22 and 23). In June, there was an estimated 10% probability that 5% of the

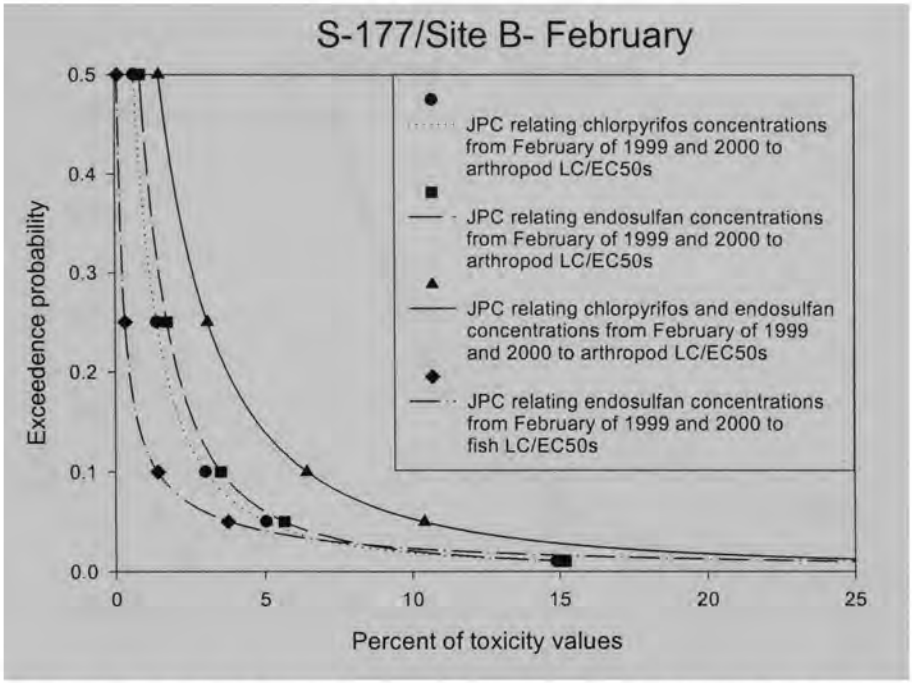


Figure 20. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-177/Site B in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

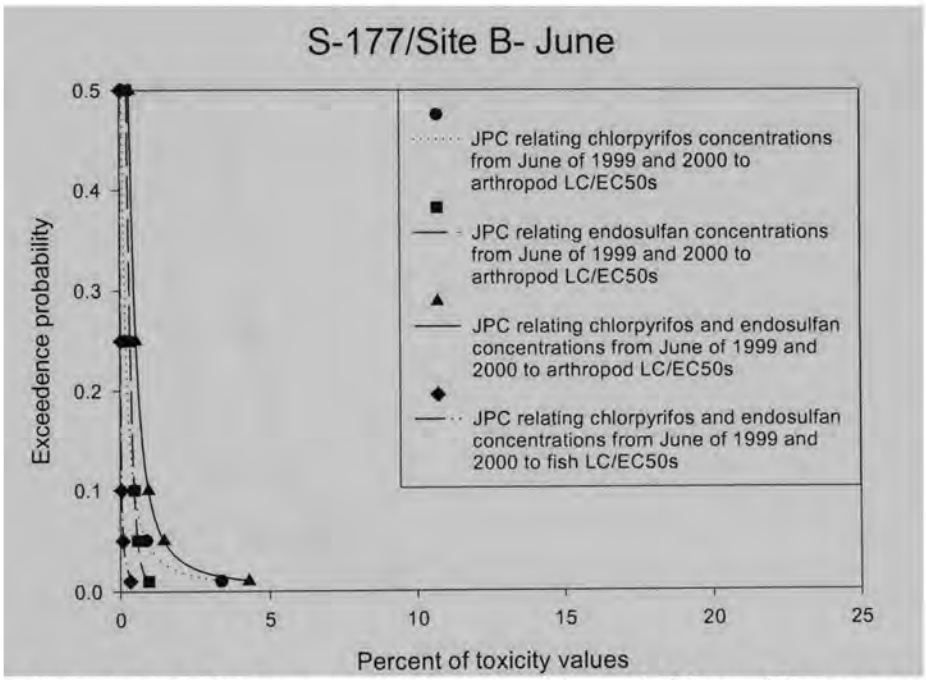


Figure 21. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-177/Site B in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

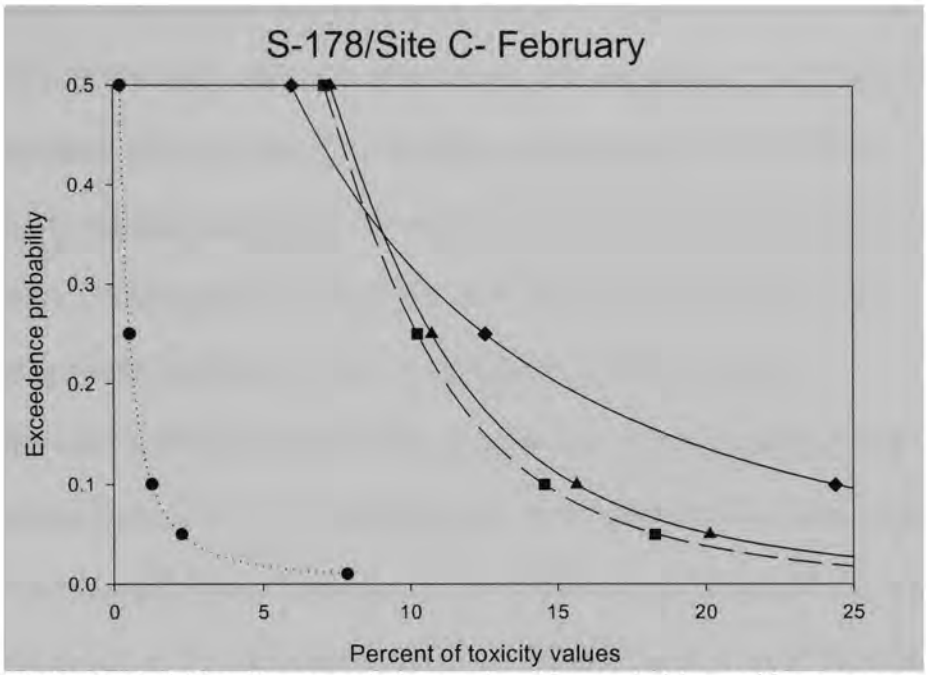


Figure 22. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-178/Site C in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

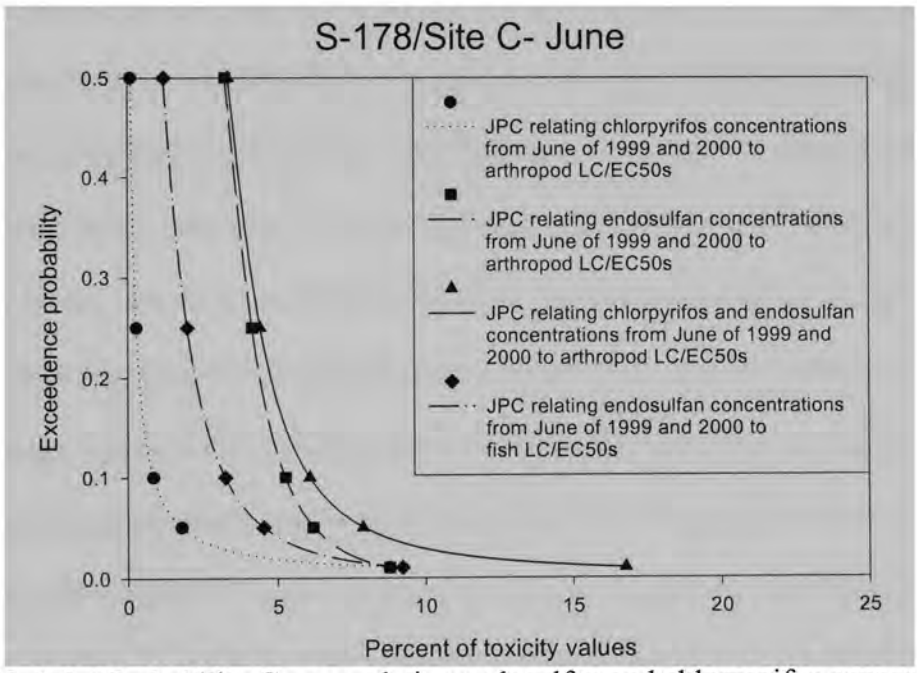


Figure 23. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-178/Site C in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

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 24 and 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 26 to 27). Risks extrapolated from JPCs, however, were usually lower at Card Sound than Highway Creek (Figures 28 and 29) or Joe Bay (Figures 30 and 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 20 to 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 22 and 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

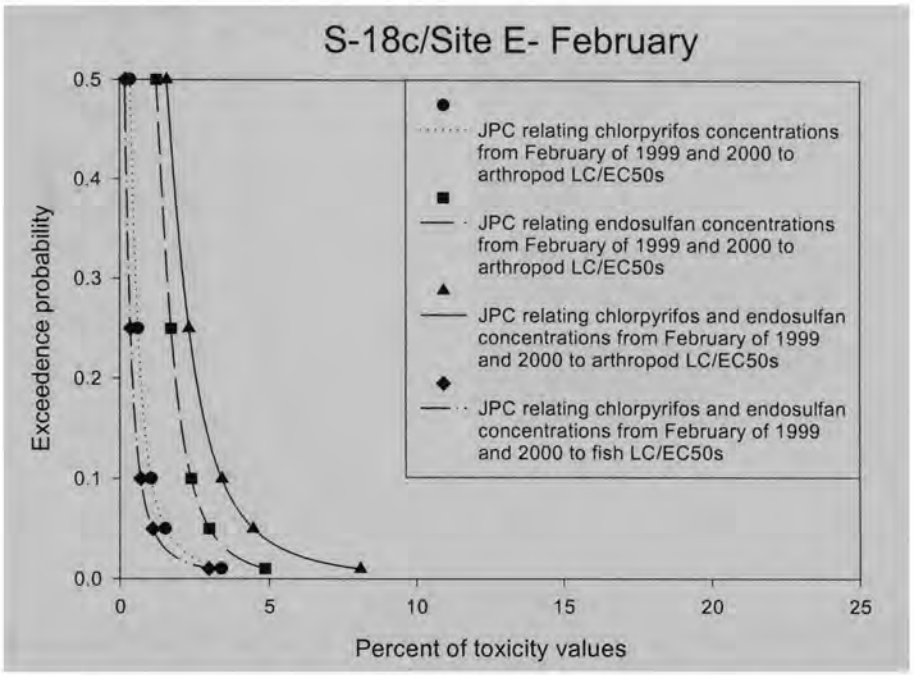


Figure 24. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-18c/Site E in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

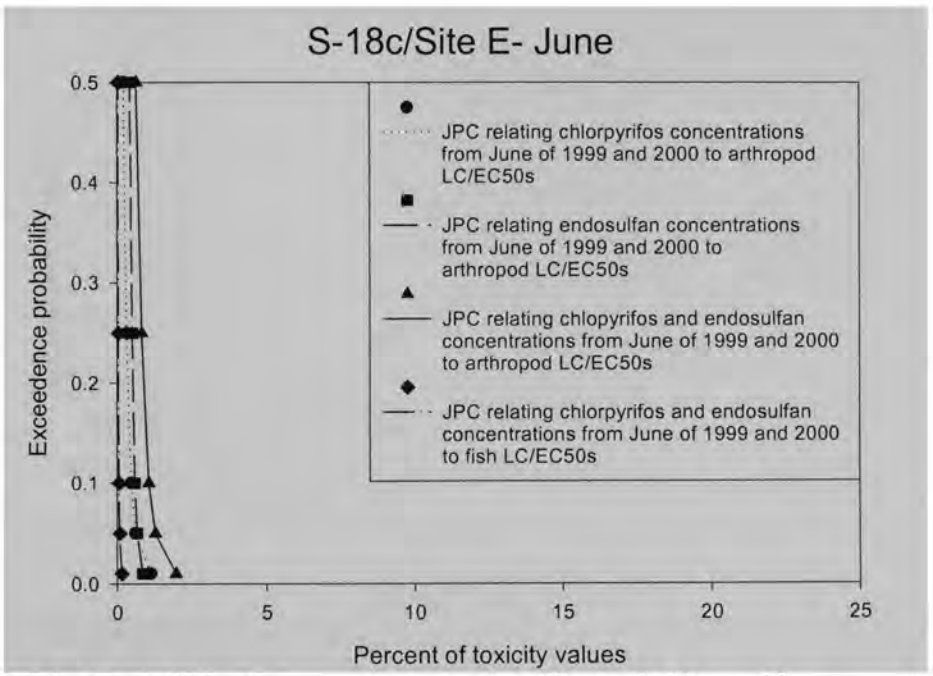


Figure 25. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in S-18c/Site E in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

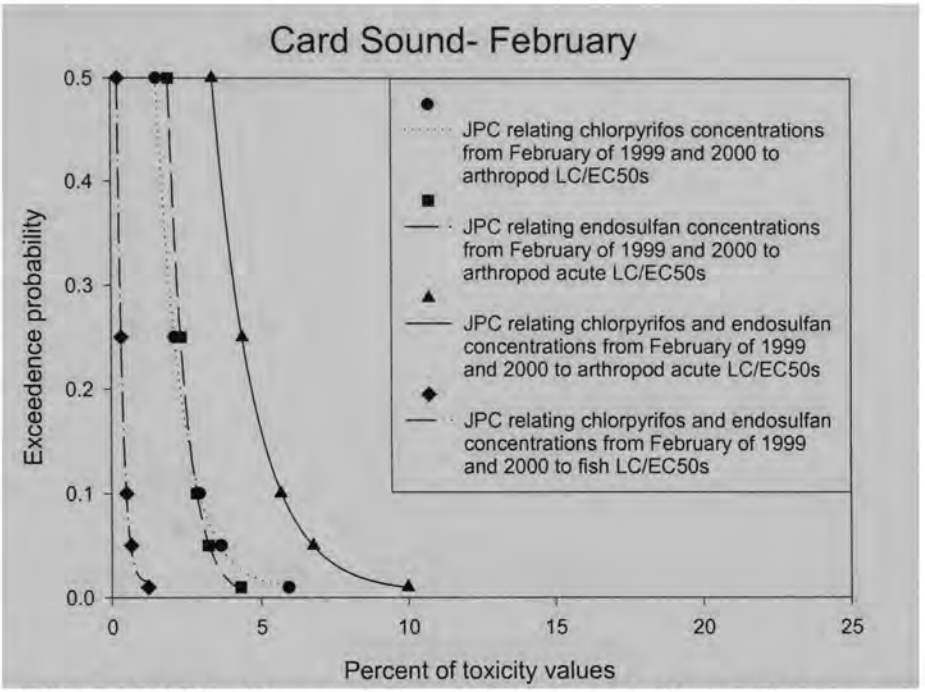


Figure 26. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Card Sound in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

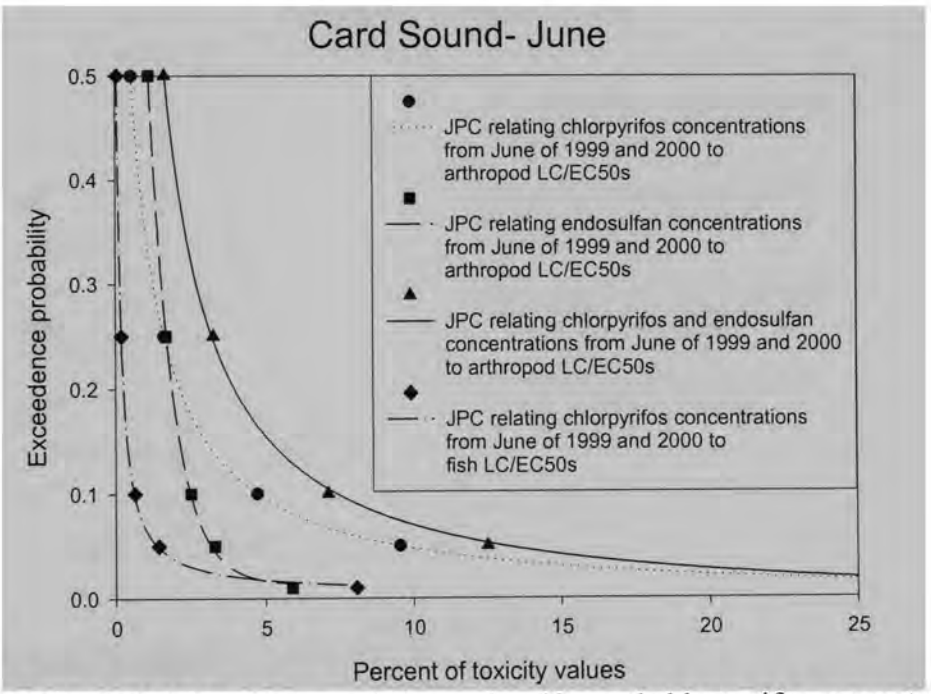


Figure 27. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Card Sound in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

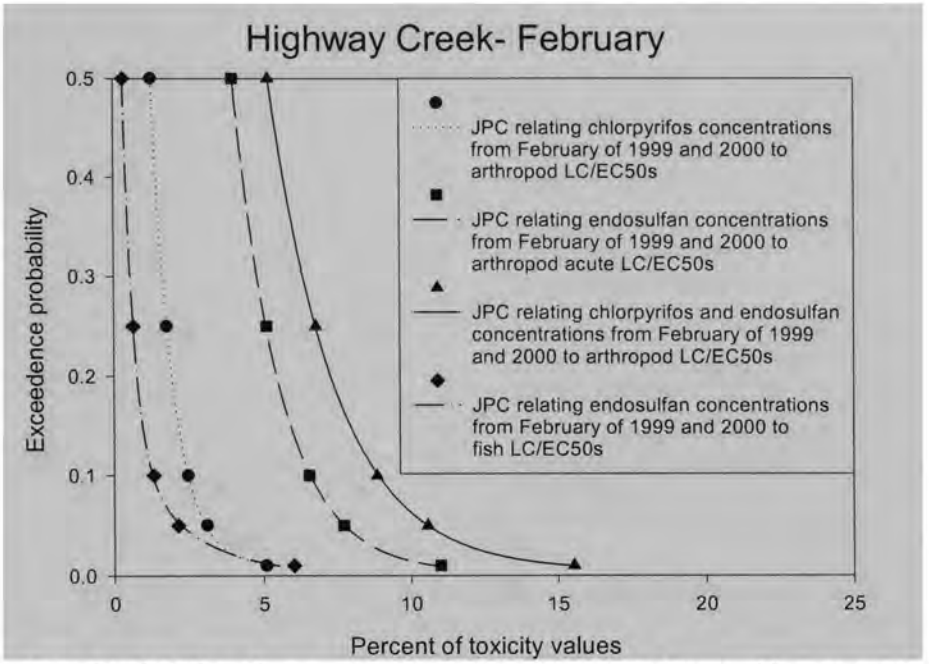


Figure 28. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Highway Creek in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

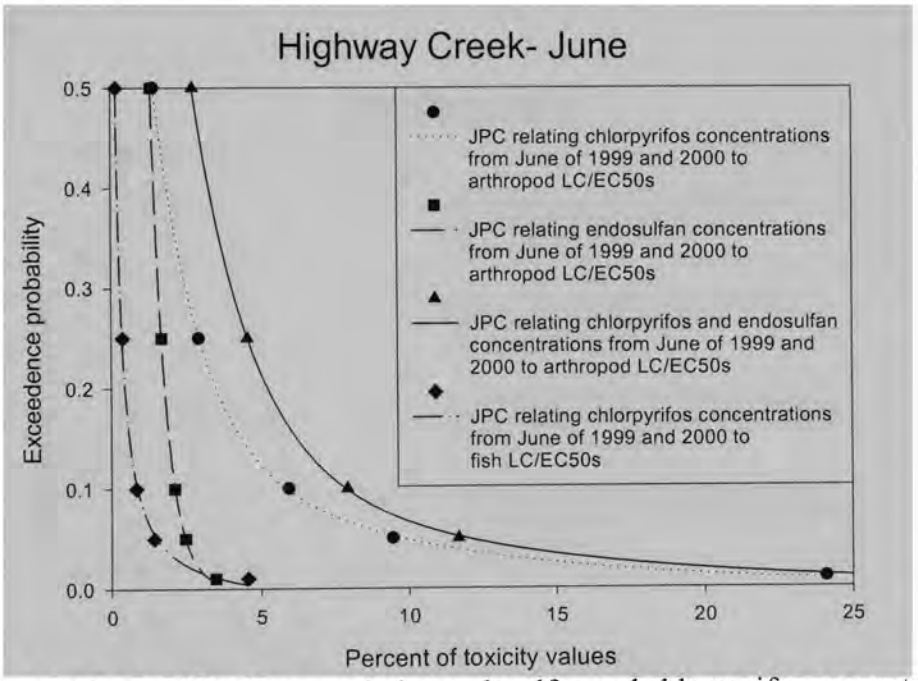


Figure 29. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Highway Creek in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

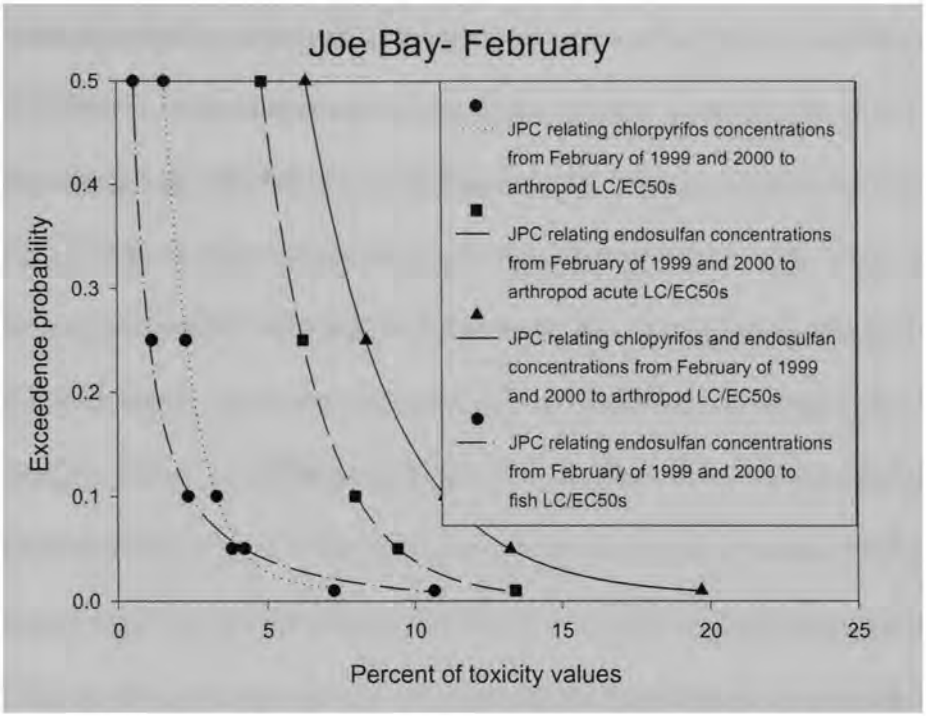


Figure 30. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Joe Bay in February of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

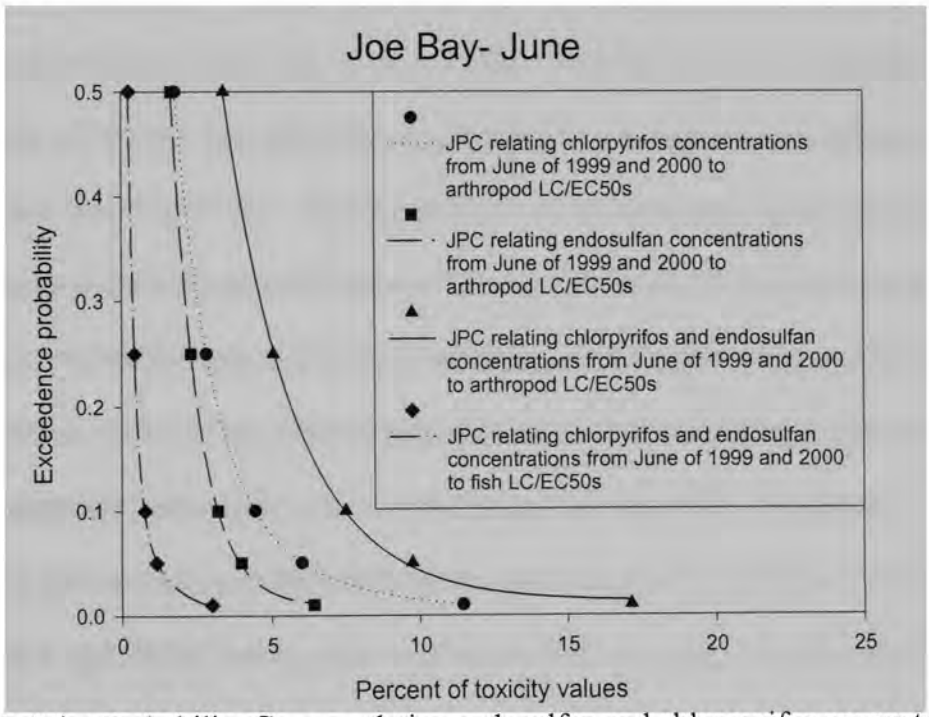


Figure 31. Joint Probability Curves relating endosulfan and chlorpyrifos concentrations in Joe Bay in June of 1999 and 2000 to arthropod and fish acute toxicity data (LC/EC50s).

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 20 and 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 20). In June, there was an estimated 5% exceedence probability for 1% of the acute toxicity data for arthropod species (Figure 21). This same trend was observed at S-18c/Site E at a lower scale (Figures 24 and 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 26 to 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.

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.

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 sites, freshwater regions near S-178 and S-177 had the highest acute PAF values to arthropods from the 90^{th} centile exposure concentration estimate of endosulfan (see Table 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 90^{th} 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 15 and Table 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 (probabilistic risk assessment) 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 10^{th} centile of acute toxicity SSDs was 0% for all sites with monitoring data in 1999 and 2000 and pesticides. Concern, however, can still exist particularly if there are species with sensitivity to biocidal stressors below the 10^{th} 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 Florida Department of Environmental Protection 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.)

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 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.

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).

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 three 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.

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.

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 concentration addition 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).

12. DISCUSSION

This type of probabilistic ecological risk approach should be conducted elsewhere in Florida for contaminants including metals, pesticides, nutrients, etc. This probabilistic risk assessment 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.

REFERENCES

Aldenberg, T., and W. Slob. 1993. Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. Ecotoxicology and Environmental Safety 25: 48-63.

Ali, S. 1978. Degradation and environmental fate of endosulfan isomers and endosulfan sulfate in mouse, insect, and laboratory model ecosystem. Ph. D. Thesis. University of Illinois. 101 pp. Diss. Abstr. Int. B 1978, 39 (5): 2117. University Microfilms, Ann Arbor, MI.

Altenburger, R., T. Backhaus, W. Boedeker, M. Faust, M. Scholze, and L.H. Grimme. 2000. Predictability of the toxicity of multiple chemical mixtures to *Vibrio fischeri*: Mixtures composed of similarly acting chemicals. Environmental Toxicology and Chemistry 19: 2341-2347.

An, K.-G., S.S. Park, and J.-Y. Shin. 2002. An evaluation of a river health using the index of biological integrity along with relations to chemical and habitat conditions. Environment International 28: 411-420.

Antonious, G.F.,and M.E. Byers. 1997. Fate and movement of endosulfan under field conditions. Environmental Toxicology and Chemistry 16 (4): 644-649.

Archer, T.E., I.K. Nazer, and D.G. Crosby. 1972. Photodecomposition of endosulfan and related products in thin films by ultraviolet light irradiation. Journal of Agricultural and Food Chemistry 20 (5): 954-956.

Arrenhius, Å., F. Grönvall, M. Scholze, T. Backhaus, and H. Blanck. 2004. Predictability of the mixture toxicity of 12 similarly acting congeneric inhibitors of photosystem II in marine periphyton and epipsammon communities. Aquatic Toxicology 68: 351-367.

ATSDR. 1997. Toxicological Profile for Chlorpyrifos. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA.

ATSDR. 2000. Toxicological Profile for Endosulfan. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA.

Awasthi, N., N. Manickam, and A. Kumar. 1997. Biodegradation of endosulfan by a bacterial coculture. Bulletin of Environmental Contamination and Toxicology 59: 928-934.

Awasthi, N., R. Ahuja, and A. Kumar. 2000. Factors influencing the degradation of soil-applied endosulfan isomers. Soil Biology and Biochemistry 32: 1697-1705.

Backhaus, T., R. Altenburger, W. Boedeker, M. Faust, M. Scholze, and L.H. Grimme. 2000. Predictability of the toxicity of multiple mixtures of dissimilarly acting chemicals to *Vibrio fischeri*. Environmental Toxicology and Chemistry 19: 2348-2356.

Barbour, M.T., J.B. Stribling, and J.R. Karr. 1995. Multimetric approach for establishing biocriteria and measuring biological condition. In W.S. Davis and T.P. Simon (eds.), Biological Assessment and Criteria: Tools for Water Resource Planning and Decision Making. Lewis Publishers, Boca Raton, FL.

Barron, M.G., S.M. Plakas, P.C. Wilga, and T. Ball. 1993. Absorption, tissue distribution and metabolism of chlorpyrifos in channel catfish following waterborne exposure. Environmental Toxicology and Chemistry 12: 1469-1476.

Barry, M.J., and D.C. Logan. 1998. The use of temporary pond microcosms for aquatic toxicity testing: Direct and indirect effects of endosulfan on community structure. Aquatic Toxicology 41: 101-124.

Boyer, J., J.W. Fourqurean, and R.D. Jones. 1997. Spatial characterization of water quality in Florida Bay and Whitewater Bay by multivariate analyses: Zones of similar influence. Estuaries 20 (4): 743-758.

Browder, J.A., Z. Zein-Eldin, M.M. Criales, M.B. Robblee, S.Wong, T.L. Jackson, and D. Johnson. 2002. Dynamics of pink shrimp (*Farfantepenaeus duorarum*) recruitment potential in relation to salinity and temperature in Florida Bay. Estuaries 25 (6B): 1355-1371.

Caccia, V.G., F.J. Millero, and A. Palanques. 2003. The distribution of trace metals in Florida Bay sediments. Marine Pollution Bulletin 46: 1420-1433.

Callahan, M.A., M.W. Slimak, N.W. Gabel, I.P. May, C.F. Fowler, J.R. Freed, P. Jennings, R.L. Durfree, F.C. Whitmore, B. Maestri, W.R. Mabey, B.R. Holt, and C. Gould. 1979. Water-related fate of 129 priority pollutants: I. Introduction and technical background, metals and inorganics, pesticides and PCBs. EPA-440/4-79-029a, U.S. EPA, Office of Water, Washington, D.C.

Camargo, J.A. 1994. The importance of biological monitoring for the ecological risk assessment of freshwater pollution: A case study. Environment International 20 (2): 229-238.

Cantillo, A.Y., C.G. Lauenstein, T.P. O'Connor, and W.E. Johnson. 1999. Status and Trends of Contaminant Levels in Biota and Sediments of South Florida. National Oceanic and Atmospheric Administration, National Ocean Service, National Centers for Coastal Ocean Science, Center for Coastal Monitoring and Asessment, Silver Spring, MD.

Chambers, H.W. 1992. Organophosphorus compounds: An overview. In, J.E. Chambers and P.E. Levi (eds.), Organophosphates: Chemistry Fate and Effects. Academic Press, San Diego, CA.

Chin Fatt, J., and J.D. Wang. 1987. Canal discharge impacts on Biscayne Bay salinities. Research/Resources Management Report SER-89, United States Department of the Interior, National Park Service, Southeast Region, Atlanta, GA.

Cotham, Jr., W.E., and T.F. Bidleman. 1989. Degradation of malathion, endosulfan, and fenvalerate in seawater and seawater/sediment microcosms. Journal of Agricultural and Food Chemistry 37: 824-828.

Crommentuijn, T., D.F. Kalf, M.D. Polder, R. Posthumus, and E.J. van de Plassche. 1997. Maximum Permissible Concentrations and Negligible Concentrations for Pesticides. Report No. 601501 002, National Institute of Public Health and the Environment, Bilthoven, the Netherlands.

Davis, W.S., B.C. Snyder, J.B. Stribling, and C. Stoughton. 1996. Summary of State Biological Assessment Programs for Streams and Rivers. EPA 230-R-96-007, US Environmental Protection Agency Office of Policy, Planning, and Evaluation, Washington, DC. http://www.epa.gov/owow/monitoring/newmon/bio/

De March, B.G.E. 1987. Simple similar action and independent joint action: Two similar models for the joint effects of toxicants applied as mixtures. Aquatic Toxicology 9: 291-304.

De Wolf, W., J.H. Canton, J.W. Deneer, R.C.C. Wegman, and J.L.M. Hermens. 1988. Quantitative structure-activity relationships and mixture-toxicity studies of alcohols and chlorohydrocarbons: Reproducibility of effects on growth and reproduction of *Daphnia magna*. Aquatic Toxicology 12: 39-49.

De Zwart, D. 2002. Observed regularities in species sensitivity distributions for aquatic species. In, L. Posthuma, G.W. Suter II, and T.P. Traas (eds.), Species Sensitivity Distributions in Ecotoxicology. Lewis Publishers, Boca Raton, FL USA.

DeLorenzo, M.E., G.I. Scott, and P.E. Ross. 1999. Effects of the agricultural pesticides atrazine, deethylatrazine, endosulfan, and chlorpyrifos on an estuarine microbial food web. Environmental Toxicology and Chemistry 18 (12): 2824-2835.

DeLorenzo, M.E., T. Chandler, M.H. Fulton, G.I. Scott, D. Bearden, P.B. Key, K. Chung, H.F. Downing, A.K. Leight, J. Daugomah, S.A. Lund, R. Sumner, D. Wilson, E. Strozier, S. Sivertsen, A. Dias, P. Jenkins, and B. Shaddrix. 2001. An evaluation of pesticide loading from the Dade County agricultural area to the Everglades Panhandle and Florida Bay via the C-111 canal. Final Report. Submitted by NOAA / National Ocean Service Center for Coastal Environmental Health and Biomolecular Research employees to the South Florida Water Management District, West Palm Beach, FL.

Deneer, J.W., T.L. Sinnige, W. Seinen, and J.L.M. Hermens. 1988. The joint acute toxicity to *Daphnia magna* of industrial organic chemicals at low concentrations. Aquatic Toxicology 12: 33-38.

Devi, A.P., D.M.R. Rato, K.S. Tilak, and A.S. Murty. 1981. Relative toxicity of the technical grade material, isomers, and formulations of endosulfan to the fish *Channa punctata*. Bulletin of Environmental Contamination and Toxicology 27: 239-243.

ECOFRAM. 1999. Ecological Committee on FIFRA Risk Assessment Methods: Report of the Aquatic Workgroup. U.S. Environmental Protection Agency, Office of Pesticide Programs, Washington, DC USA.

Eichelberger, J.W., and J.J. Lichtenberg. 1971. Persistence of pesticides in river water. Environmental Science and Technology 5 (6): 541-544.

Ernst, W. 1977. Determination of the bioconcentration potential of marine organisms: A steady state approach. I. Bioconcentration data for seven chlorinated pesticides in mussels (*Mytilus edulis*) and their relation to solubility data. Chemosphere 11: 731-740.

Ernst, W.R., P. Jonah, K. Doe, G. Julien, and P. Hennigar. 1991. Toxicity to aquatic organisms of off-target deposition of endosulfan applied by aircraft. Environmental Toxicology and Chemistry 10: 103-114.

Faust, M., R. Altenburger, T. Backhaus, W. Bödeker, M. Scholze, and L.H. Grimme. 2000. Predictive assessment of the aquatic toxicity of multiple chemical mixtures. Journal of Environmental Quality 29: 1063-1068.

FDOACS. 1999. Summary of Agricultural Pesticide Usage in Florida: 1995-1998. Florida Department Agriculture and Consumer Services, Division of Agricultural Environmental Services, Bureau of Pesticides, Tallahassee, FL.

Fischer, R. 1994. Simulated or Actual Field Testing: A Comparison. In, R.L. Graney, J.H. Kennedy, and J.H. Rodgers, Jr. (eds.), Aquatic Mesocosm Studies in Ecological Risk Assessment. Lewis Publishers, Boca Raton, FL.

Fourqurean, J.W., and M.B. Robblee. 1999. Florida Bay: A history of recent ecological changes. Estuaries 22 (2B): 345-357.

Fox, P.J., and P. Matthiessen. 1982. Acute toxicity to fish of low-dose aerosol applications of endosulfan to control tsetse fly in the Okavanga Delta, Botswana. Environmental Pollution (Series A) 27: 129-142.

Froese, R. and D. Pauly. Editors. 2002. FishBase. World Wide Web electronic publication accessible at www.fishbase.org.

Getzin, L.W. 1981. Degradation of chlorpyrifos in soil: Influence of autoclaving, soil moisture, and temperature. Journal of Economic Entomology 74 (2): 158-162.

Ghadiri, H., and C.W. Rose. 2001. Degradation of endosulfan in a clay soil from cotton farms of western Queensland. Journal of Environmental Management 62: 155-169.

Giddings, J.M., R.C. Biever, and K.D. Racke. 1997. Fate of chlorpyrifos in outdoor pond microcosms and effects on growth and survival of bluegill sunfish. Environmental Toxicology and Chemistry 16 (11): 2353-2362.

Giddings, J.M., T.A. Anderson, L.W. Hall, R.J. Kendall, R.P. Richards, K.R. Solomon, and W.M. Williams. 2000a. Aquatic Ecological Risk Assessment of Atrazine: A Tiered Probabilistic Approach., A Report of an Expert Panel. Report nr 709-00. Novartis Crop Protection, Inc. Greensboro, NC.

Giddings, J.M., L.W. Hall, Jr., and K.R. Solomon. 2000b. Ecological risks of diazinon from agricultural use in the Sacramento-San Joaquin River Basins, California. Risk Analysis 20 (5): 545-572.

Giddings, J.M., K.R. Solomon, and S.J. Maund. 2001. Probabilistic risk assessment of cotton pyrethroids: II. Aquatic mesocosm and field studies. Environmental Toxicology and Chemistry 20 (3): 660-668.

Giesy, J.P., K.R. Solomon, J.R. Coats, K.R. Dixon, J.M. Giddings, and E.E. Kenaga. 1999. Chlorpyrifos: Ecological risk assessment in North American aquatic environments. Reviews of Environmental Contamination and Toxicology 160: 1-129.

Gilbert, P.S., T.N. Lee, and G.P. Podestá. 1996. Transport of anomalous low-salinity waters from the Mississippi River flood of 1993 to the Straits of Florida. Continental Shelf Research 16 (8): 1065-1085.

Goebel, H., S. Gorbach, W. Knuaf, R.H. Rimpau, and H. Hüttenbach. 1982. Properties, effects, residues, and analytics of the insecticide endosulfan. Residue Reviews 83: 1-165.

Goodman, L.R., M.A. Lewis, J.M. Macauley, R. Smith, Jr. and J.C. Moore. 1999. Preliminary survey of chemical contaminants in water, sediment, and aquatic biota at selected sites in Northeastern Florida Bay and canal C-111. Gulf of Mexico Science 17 (1): 1-16.

Greve, P.A., and S.L. Wit. 1971. Endosulfan in the Rhine River. Journal of the Water Pollution Control Federation 43 (12): 2338-2348.

Guerin, T.F. 1999. The anaerobic degradation of endosulfan by indigenous microorganisms from low-oxygen soils and sediments. Environmental Pollution 106: 13-21.

Guerin, T.F., and I.R. Kennedy. 1992. Distribution and dissipation of endosulfan and related cyclodienes in sterile aqueous systems: Implications for studies on biodegradation. Journal of Agricultural and Food Chemistry 40: 2315-2323.

Hall, Jr., L.W., M.C. Scott, and W.D. Killen. 1998. Ecological risk assessment of copper and cadmium in surface waters of Chesapeake Bay watershed. Environmental Toxicology and Chemistry 17 (6): 1172-1189.

Hall, M.O., M.J. Durako, J.W. Fourqurean, and J.C. Zieman. 1999. Decadal changes in seagrass distribution and abundance in Florida Bay. Estuaries 22 (2B): 445-459.

Hall, Jr., L.W., M.C. Scott, W.D. Killen, and M.A. Unger. 2000. A probabilistic ecological risk assessment of tributyltin in surface waters of the Chesapeake Bay watershed. Human and Ecological Risk Assessment 6 (1): 141-179.

Hewlett, P.S., and R.L. Plackett. 1979. An Introduction to the Interpretation of Quantal Responses in Biology. Edward Arnold Ltd., London, U.K.

Hose, G.C., R.P. Lim, R.V. Hyne, and F. Pablo. 2002. A pulse of endosulfan-contaminated sediment affects macroinvertebrates in artificial streams. Ecotoxicology and Environmental Safety 51: 44-52.

Hose, G.C., R.P. Lim, R.V. Hyne, and F. Pablo. 2003. Short-term exposure to aqueous endosulfan affects macroinvertebrate assemblages. Ecotoxicology and Environmental Safety 56: 282-294.

Hughes, D.N., M.G. Boyer, M.H. Papst, and C.D. Fowle. 1980. Persistence of three organophosphorus insecticides in artificial ponds and some biological implications. Archives of Environmental Contamination and Toxicology 9: 269-279.

IPCS. 1988. Endosulfan: Health and Safety Guide. International Programme on Chemical Safety, United Nations Environment Programme, International Labor Organization, World Health Organization, Health and Safety Guide No. 17, Geneva, Switzerland. Accessible at http://www.inchem.org/documents/hsg/hsg/hsg017.htm

Jin-Clark, Y., M.J. Lydy, and K.Y. Zhu. 2002. Effects of atrazine and cyanazine on chlorpyrifos toxicity in *Chironomus tentans* (Diptera: Chironomidae). Environmental Toxicology and Chemistry 21 (3): 598-603.

Jonsson, C.M., and M.C.F. Toledo. 1993. Bioaccumulation and elimination of endosulfan in the fish yellow tetra (*Hyphessobrycon bifasciatus*). Bulletin of Environmental Contamination and Toxicology 50: 572-577.

Kamrin, M.A. 1997. Pesticide Profiles: Toxicity, Environmental Impact, and Fate. Lewis Publishers, Boca Raton, FL.

Kang, W.-J., J.H. Trefry, T.A. Nelsen, and H.R. Wanless. 2000. Direct atmospheric inputs versus runoff fluxes of mercury to the Lower Everglades and Florida Bay. Environmental Science and Technology 34: 4058-4063.

Karr, J.R. 1991. Biological integrity: A long neglected aspect of water resource management. Ecological Applications 1 (1): 66-84.

Katayama, A., and F. Matsumura. 1993. Degradation of organochlorine pesticides, particularly endosulfan, by *Trichoderma harzianum*. Environmental Toxicology and Chemistry 12: 1059-1065.

Kaur, I., R.P. Mather, S.N. Tandon, and P. Dureja. 1998. Persistence of endosulfan (technical) in water and soil. Environmental Technology 19: 115-119.

Klepper, O., and D. van de Meent. 1997. Mapping the potentially affected fraction (PAF) of species as an indicator of generic toxic stress. RIVM report 607504 001. National Institute of Public Health and the Environment, Bilthoven, the Netherlands.

Könemann, H. 1981. Fish toxicity tests with mixtures of more than two chemicals: A proposal for a quantitative approach and experimental results. Toxicology 19: 229-238.

Kullman, S.W., and F. Matsumura. 1996. Metabolic pathways utilized by *Phanerochaete chrysosporium* for degradation of the cyclodiene pesticide endosulfan. Applied and Environmental Microbiology 62 (2): 593-600.

LaPoint, T., J. Rodgers Jr., J. Delphino, T. Atkeson, and S. McCutcheon. 1998. Advisory Panel Report on the Workshop: Ecological Risk of Toxic Substances in South Florida Ecosystems; Roz and Cal Kovens Conference Center; Florida International University on October 20 -21, 1998, 20.

Larson, S.J., P.D. Capel, and M.S. Majewski. 1997. Pesticides in Surface Waters: Distributions, Trends, and Governing Factors. Ann Arbor Press, Chelsea, MI.

Leonard, A.W., R.V. Hyne, R.P. Lim, F. Pablo, and P.J. Van den Brink. 2000. Riverine endosulfan concentrations in the Namoi River, Australia: Link to cotton field runoff and macroinvertebrate population densities. Environmental Toxicology and Chemistry 19 (6): 1540-1551.

Liu, B., L.L. McConnell, and A. Torrents. 2001. Hydrolysis of chlorpyrifos in natural waters of the Chesapeake Bay. Chemosphere 44: 1315-1323.

Long, E.R., M.J. Hameedi, G.M. Sloane, and L.B. Read. 2002. Chemical contamination, toxicity, and benthic community indices in sediments of the Lower Miami River and adjoining portions of Biscayne Bay, Florida. Estuaries 25 (4A): 622-637.

Lorenz, J.J. 1999. The response of fishes to physicochemical changes in the mangroves of Northeast Florida Bay. Estuaries 22 (2B): 500-517.

Ludwig, P.D., H.J. Dishburger, J.C. McNeill, IV, W.O. Miller, and J.R. Rice. 1968. Biological effects and persistence of Dursban® insecticide in a salt-marsh habitat. Journal of Economic Entomology 61 (3): 626-633.

Martens, R. 1976. Degradation of [8,9-^{14}C]endosulfan by soil microorganisms. Applied and Environmental Microbiology 31 (6): 853-858.

Martens, R. 1977. Degradation of endosulfan-8,9-^{14}C in soil under different conditions. Bulletin of Environmental Contamination and Toxicology 17 (4): 438-446.

Matheson, Jr., R.E., D.K. Camp, S.M. Sogard, and K.A. Bjorgo. 1999. Changes in seagrass-associated fish and crustacean communities on Florida Bay mud banks: The effect of recent ecosystem changes? Estuaries 22 (2B): 534-551.

Meikle, R.W., and C.R. Youngson. 1978. The hydrolysis rate of chlorpyrifos, *O-O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate, and its dimethyl analog, chorpyrifos-methyl, in dilute aqueous solutions. Archives of Environmental Contamination and Toxicology 7: 13-22.

Miles, C.J., and R.J. Pfeuffer.1997. Pesticides in canals of south Florida. Archives of Environmental Contamination and Toxicology 32: 337-345.

Miles, J.R.W., and P. Moy. 1979. Degradation of endosulfan and its metabolites by a mixed culture of soil microorganisms. Bulletin of Environmental Contamination and Toxicology 23: 13-19.

Miles, J.R.W., C.M. Tu, and C.R. Harris. 1979. Persistence of eight organophosphorus insecticides in sterile and non-sterile mineral and organic soils. Bulletin of Environmental Contamination and Toxicology 22: 312-318.

Montague, B. 2002. EPA One-Liners. United States Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances, Washington DC.

Morrison, M.L., B.G. Marcot, and W.A. Mannan. 1992. Wildlife: Habitat Relationships. University of Wisconsin Press, Madison, WI.

Naddy, R.B., K.A. Johnson, and S.J. Klaine. 2000. Response of *Daphnia magna* to pulsed exposures of chlorpyrifos. Environmental Toxicology and Chemistry 19 (2): 423-431.

Ney, Jr., R. 1998. Fate and Transport of Organic Chemicals in the Environment: A Practical Guide. 3rd ed. Government Institutes, Rockville, MD.

Novak, B., and N. Ahmad. 1989. Residues in fish exposed to sublethal doses of endosulfan and fish collected from cotton growing area. Journal of Environmental Science and Health B24 (1): 97-109.

Nowell, L.H., P.D. Capel, and P.D. Dileanis. 1999. Pesticides in stream sediment and aquatic biota: Distribution, trends and governing factors. Lewis Publishers, Boca Raton, FL.

NRA. 1998. NRA Review of Endosulfan. National Registration Authority for Registration of Agricultural and Vetrinary Chemicals, Australia.

NRC. 2003. Science and the Greater Everglades Ecosystem Restoration: An Assessment of the Critical Ecosystems Initiative. National Research Council of the National Academies, National Academy Press, Washington, DC.

Oliver, L.M., W.S. Fisher, J.T. Winstead, B.L. Hemmer, and E.R. Long. 2001. Relationship between tissue contaminants and defense-related characteristics of oysters (*Crassostrea virginica*) from five Florida Bays. Aquatic Toxicology 55: 203-222.

Pait, A. S., A. E. DeSouza, and D. R. G. Farrow. 1992. Agricultural pesticide use in coastal areas: A national summary. U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Rockville, MD.

Pape-Lindstrom, P.A., and M.J. Lydy. 1997. Synergistic toxicity of atrazine and organophosphate insecticides contravenes the response addition mixture model. Environmental Toxicology and Chemistry 16 (11): 2415-2420.

Peterson, S.M., and G.E. Batley. 1993. The fate of endosulfan in aquatic ecosystems. Environmental Pollution 82: 143-152.

Pfeuffer, R.J. 1985. Pesticide Residue Monitoring in Sediment and Surface Water Within the South Florida Water Management District. Technical Publication 85-2, South Florida Water Management District. West Palm Beach, FL.

Pfeuffer, R.J. 1991. Pesticide Residue Monitoring in Sediment and Surface Water Within the South Florida Water Management District: Volume 2. Technical Publication 91-01, South Florida Water Management District. West Palm Beach, FL

Plackett, R.L., and P.S. Hewlett. 1952. Quantal responses to mixtures of poisons. Journal of the Royal Statistical Society B14: 141-163.

Racke, K.D. 1992. Degradation of organophosphorus insecticides in environmental matrices. In, J.E. Chambers and P.E. Levi (eds.), Organophosphates: Chemistry Fate and Effects. Academic Press, San Diego, CA.

Racke, K.D. 1993. Environmental fate of chlorpyrifos. Reviews of Environmental Contamination and Toxicology 131: 1-154.

Rice, C.P., S.M. Chernyak, and C.J. Hapeman. 1997. Air-water distribution of the endosulfan isomers. Journal of Environmental Quality 26: 1101-1106.

Rao, D.M.R., and A.S. Murty. 1980. Persistence of endosulfan in soils. Journal of Agricultural and Food Chemistry 28: 1099-1101.

Roberts, D. 1972. The assimilation and chronic effects of sub-lethal concentrations of endosulfan on condition and spawning in the common mussel *Mytilus edulis*. Marine Biology 16: 119-125.

Roberts, D. 1975. Differential uptake of endosulfan by the tissues of *Mytilus edulis*. Bulletin of Environmental Contamination and Toxicology 13 (2): 170-175.

Rüdel, H. 1997. Volatilisation of pesticides from soil and plant surfaces. Chemosphere 35 (1-2): 143-152.

S-Plus. 1999. S-Plus 2000 Professional Release 2. MathSoft, Inc., Lucent Technologies, Inc.

Scheidt. D.J. 1989. Pesticides and Everglades National Park: South Florida Use and Threat. Wetlands: Concerns and Successes: 365-375.

Schimmel, S.C., R.L. Garnas, J.M. Patrick, Jr., and J.C. Moore. 1983. Acute toxicity, bioconcentration, and persistence of AC 222, 705, benthiocarb, chlorpyrifos, fenvalerate, methyl parathion, and permethrin in the estuarine environment. Journal of Agricultural and Food Chemistry 31: 104-113.

Science Subgroup. 1996. South Florida Ecosystem Restoration: Scientific Information Needs. Report to the Working Group of the South Florida Ecosystem Restoration Task Force. Miami, FL.

Scott, G.I., M.H. Fulton, E.F. Wirth, G.T. Chandler, P.B. Key, J.W. Daugomah, D. Bearden, K.W. Chung, E.D. Strozier, M. DeLorenzo, S. Sivertsen, A. Dias, M. Sanders, J.M. Macauley, L.R. Goodman, M.W. LaCroix, G.W. Thayer, and J. Kucklick. 2002. Toxicological studies in tropical ecosystems: an ecotoxicological risk assessment of pesticide runoff in South Florida estuarine ecosystems. Journal of Agricultural and Food Chemistry 50: 4400-4408.

Schropp, S.J., F.G. Lewis, H.L. Windom, J.D. Ryan, F.D. Calder, and L.C. Burney. 1990. Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element. Estuaries 13 (3): 227-235.

SETAC. 1994. Pesticide Risk and Mitigation: Final Report of the Aquatic Risk Assessment and Mitigation Dialogue Group. Society of Environmental Toxicology and Chemistry, Foundation for Environmental Education, Pensacola, FL.

SFWMD. 1992. Surface Water Improvement and Management Plan for the Everglades. Supporting Information Document, South Florida Water Management District, West Palm Beach, FL.

Solomon, K.R. 1996. Overview of recent developments in ecotoxicological risk assessment. Risk Analysis 16 (5): 627-633.

Solomon, K.R., D.B. Baker, R.P. Richards, K.R. Dixon, S.J. Klaine, T.W. La Point, R.J. Kendall, C.P. Weisskopf, J.M. Giddings, J.P., Giesy, L.W. Hall, Jr., and W.M. Williams. 1996. Ecological risk assessment of atrazine in North American surface waters. Environmental Toxicology and Chemistry 15 (1): 31-76.

Solomon, K.R., J. Giesy, and P. Jones. 2000. Probabilistic risk assessment of agrochemicals in the environment. Crop Protection 19: 649-655.

Solomon, K.R., J.M. Giddings, and S.J. Maund. 2001. Probabilistic risk assessment of cotton pyrethroids: I. Distributional analyses of laboratory aquatic toxicity data. Environmental Toxicology and Chemistry 20 (3): 652-659.

Stewart, D.K.R., and K.G. Cairns. 1974. Endosulfan persistence in soil and uptake by potato tubers. Journal of Agricultural and Food Chemistry 22 (6): 984-986.

Suter II, G.W. 1993. Ecological Risk Assessment. Lewis Publishers, Boca Raton, FL.

Suter II, G.W., T.P. Traas, and L. Posthuma. 2002. Issues and Practices in the Derivation and Use of Species Sensitivity Distributions. In L. Posthuma, G.W. Suter II, and T.P. Traas (eds.), Species Sensitivity Distributions in Ecotoxicology. Lewis Publishers, Boca Raton, FL.

Swarup, P.A., D.M. Rao, and A.S. Murty. 1981. Toxicity of endosulfan to the freshwater fish *Cirrhinus mrigala*. Bulletin of Environmental Contamination and Toxicology 27: 850-855.

Tabak, H.H., S.A. Quave, C.I. Mashni, and E.F. Barth. 1981. Biodegradability studies with organic priority pollutant compounds. Journal of the Water Pollution Control Federation 53 (10): 1503-1518.

Thayer, G.W., W.F. Hettler, Jr., A.J. Chester, D.R. Colby, and P.J. McElhaney. 1987. Distribution and Abundance of Fish Communities Among Selected Estuarine and Marine Habitats in Everglades National Park. Report SFRC-87/02, Everglades National Park, South Florida Research Center, Homestead, FL.

Toledo, M.C., and C.M. Jonsson. 1992. Bioaccumulation and elimination of endosulfan in zebra fish (*Brachydanio rerio*). Pesticide Science 36: 207-211.

Traas, T.P., D. van de Meent, L. Posthuma, T. Hamers, B.J. Kater, D. de Zwart. and T. Aldenberg. 2002. The Potentially Affected Fraction as a Measure of Ecological Risk. In L. Posthuma, G.W. Suter II, and T.P. Traas (eds.), Species Sensitivity Distributions in Ecotoxicology. Lewis Publishers, Boca Raton, FL.

Trexler, J., J.H.K. Pechmann, and W.G. DeLoach. 1998. Fish and Invertebrates. In R.D. Jones, J. Trexler, and D.L. Childers (Principal Investigators), Numerical Interpretation of Class III Narrative Nutrient Water Criteria for Everglades Wetlands: Annual Report. Southeast Environmental Research Program, Florida International University, Miami, FL.

Trexler, J., J. Chick, and F. Jordan. 2000. Fish and Aquatic Macroinvertebrate Monitoring Studies in Taylor Slough. 2000 Annual Report. Cooperative Agreement CA-5280-6-9011 Between Everglades National Park, United States Department of the Interior, and Florida International University, Miami, FL.

Urban, D.J., and N.J. Cook. 1986. Hazard Evaluation Division Standard Evaluation Procedure: Ecological Risk Assessment. EPA-540/9-85-001, United States Environmental Protection Agency, Office of Pesticide Programs, Washington, DC.

U.S.ACE. 2000. Canal 111 (C-111) South Dade County, Florida: Draft Integrated Reevaluation Report Supplement and Environmental Assessment. U.S. Army Corps of Engineers, Jacksonville, FL.

U.S.ACE and SFWMD. 1999. Central and South Florida Project Comprehensive Review Study: Final Integrated Feasibility Report and Programmatic Environmental Impact Statement. U.S. Army Corps of Engineers and South Florida Water Management District. Available online at http://www.evergladesplan.org/.

U.S.EPA. 1986. Quality Criteria for Water: 1986. EPA-440/5-86-001, United States Environmental Protection Agency, Office of Water, Washington, DC.

U.S.EPA. 1987. Rules and Regulations. *Fed. Reg.* 52: 17954-17955.

U.S.EPA. 1992. Framework for Ecological Risk Assessment. EPA-630-R-92-001. United States Environmental Protection Agency, Risk Assessment Forum, Washington D.C.

U.S.EPA. 1994. Ecological Risk Assessment Issue Papers. EPA/630/R-94-009. United States Environmental Protection Agency, Risk assessment Forum, Washington, D.C.

U.S.EPA. 1997. Ecological Risk Assessment Guidance for Superfund: Processes for Designing and Conducting Ecological Risk Assessments. Interim Final Version, United States Environmental Protection Agency, Environmental Response Team, Edison, NJ.

U.S.EPA. 1998. Guidelines for ecological risk assessment. EPA/630/R-95/002F. United States Environmental Protection Agency, Office of Water, Washington, D.C.

U.S.EPA. 2000. Reregistration Eligibility Science for Chlorpyrifos: Fate and Environmental Risk Assessment Chapter. United States Environmental Protection Agency, Office of Prevention Pesticides and Toxic Substances, Washington DC.

U.S.EPA. 2001. EFED Risk Assessment for the Reregistration Eligibility Decision on Endosulfan (Thiodan®). United States Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances, Washington DC.

U.S.EPA. 2002a. National Recommended WQC: 2002. EPA/822/R-02/047. Office of Water, Washington DC.

U.S.EPA. 2002b. Reregistration Eligibility Science Chapter for Atrazine: Environmental Fate and Effects Chapter. Appendix XV. Comparison of OW and OPP Methods for Aquatic Assessments. United States Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances, Washington DC.

U.S.EPA. 2003. Ambient Aquatic Life WQC for Atrazine: Revised Draft. EPA/822/R-03/023. United States Environmental Protection Agency, Office of Water, Washington DC.

U.S.GAO. 2003. South Florida Ecosystem Restoration: Task Force Needs to Improve Science Coordination to Increase the Likelihood of Success. GAO-03-345 South Florida Science, United States General Accounting Office, Report to Subcommittee on Interior and Related Agencies, Committee on Appropriations, House of Representatives, Washington DC.

Van de Plassche, E.J., J.H. Canton, Y.A. Eijs, J.W. Everts, P.J.C.M. Janssen, J.E.M. v. Koten-Vermeulen, M.D. Polder, R. Posthumus, and J.M. de Stoppelaar. 1994. Towards Integrated Environmental Quality Objectives for Several Compounds with a Potential for Secondary Poisoning: Underlying Data. Report No. 679101 012, National Institute of Public Health and Environmental Protection, Bilthoven, the Netherlands.

Van den Brink, P.J., R.P.A. van Wijngaarden, W.G.H. Lucassen, T.C.M. Brock, and P. Leeuwangh. 1996. Effects of the insecticide Dursban[7] 4E (active ingredient chlorpyrifos) in outdoor experimental ditches: II. Invertebrate community responses and recovery. Environmental Toxicology and Chemistry 15 (7): 1143-1153.

Van Dolah, R.F., J.L. Hyland, A.F. Holland, J.S. Rosen, and T.R. Snoots. 1999. A benthic index of biological integrity for assessing habitat quality in estuaries of the southeastern USA. Marine Environmental Research 48: 269-283.

Van Dyk, L.P., and A. Van der Linde. 1976. Persistence of endosulfan in soils of the Loskop Dam irrigation area. Agrochemophysica 8: 31-34.

Van Wijngaarden, R.P.A., P.J. van den Brink, S.J.H. Crum, J.H.O. Voshaar, T.C.M. Brock, and P. Leeuwangh. 1996. Effects of the insecticide Dursban[7] 4E (active ingredient chlorpyrifos) in outdoor experimental ditches: I. Comparison of short-term toxicity between the laboratory and the field. Environmental Toxicology and Chemistry 15 (7): 1133-1142.

Walker, W.W., C.R. Cripe, P.H. Pritchard, and A.W. Bourquin. 1988. Biological and abiotic degradation of xenobiotic compounds in *in vitro* estuarine water and sediment/water systems. Chemosphere 17 (12): 2255-2270.

Wang, J.D., M.D. Ernest Daddio, and M.D. Horwitz. 1978. Canal discharges into south Biscayne Bay: Report to the Department of Environmental Resources Management., Metro Dade County, FL. University of Miami, RSMAS.

Warren-Hicks, W.J., B.R. Parkhurst, and J.B. Butcher. 2002. Methodology for aquatic ecological risk assessment. In, L. Posthuma, G.W. Suter II, and T.P. Traas (eds.), Species Sensitivity Distributions in Ecotoxicology. Lewis Publishers, Boca Raton, FL USA.

Welling, W., and J.W. de Vries. 1992. Bioconcentration kinetics of the organophosphorus insecticide chlorpyrifos in guppies (*Poecilia reticulata*). Ecotoxicology and Environmental Safety 23: 64-75.

APPENDIX 1. ACRONYMS.

AMC
actual measured concentration

AChE
Acetylcholinesterase

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

EECs
Expected environmental concentrations

EFED
United States Environmental Protection Agency Environmental Fate and Effects Division

ENP
Everglades National Park

FIFRA
Federal Insecticide, Fungicide, and Rodenticide Act

GIS
Geographic Information System

HQ
Hazard quotient

HU
Hazard unit

JPC
Joint probability curve

K_{oc}
Adsorption coefficient based on organic carbon

K_{ow}
Octanol/water partition coefficient

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

OM
Organic matter

OP
Organophosphate

OW
United States Environmental Protection Agency's Office of Water

PAF
Potentially affected fraction

PDF
Probability density function

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

USGS
United States Geological Survey

Water quality criteria
WQC

APPENDIX 2. SPECIES SENSITIVITY DISTRIBUTIONS FOR CHLORPYRIFOS AND ENDOSULFAN

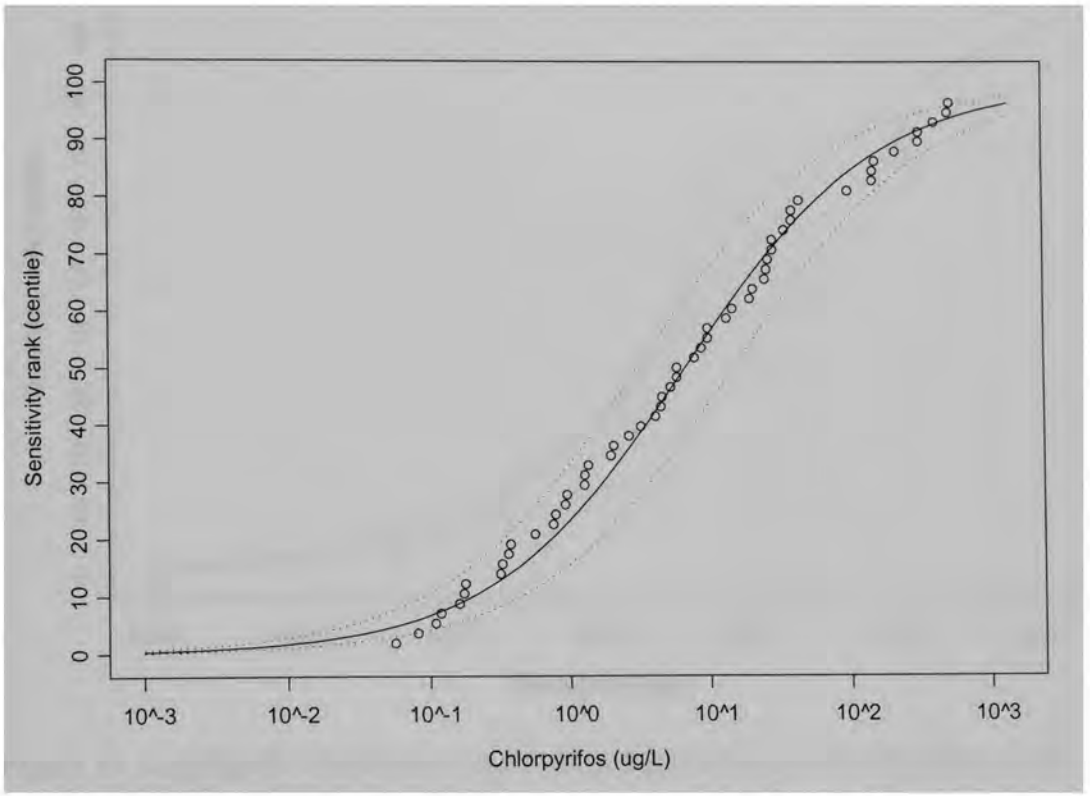


Figure 32. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for freshwater organisms.

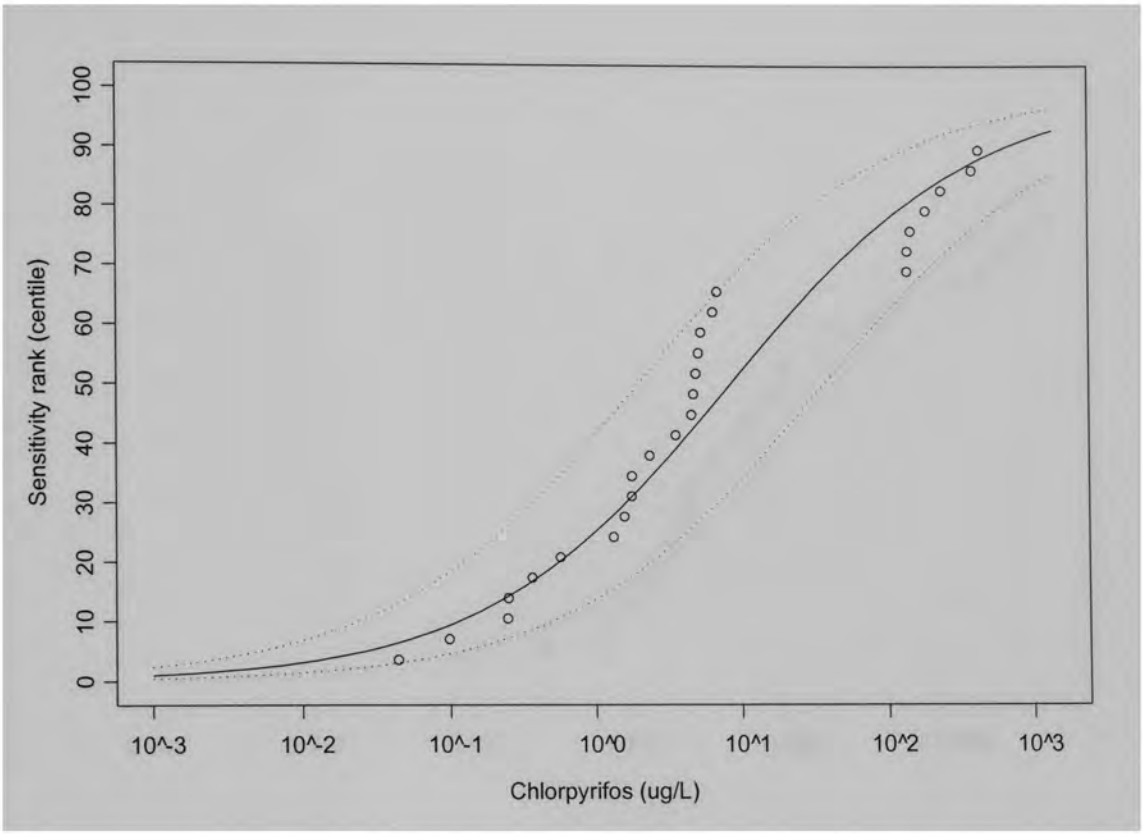


Figure 33. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for saltwater organisms.

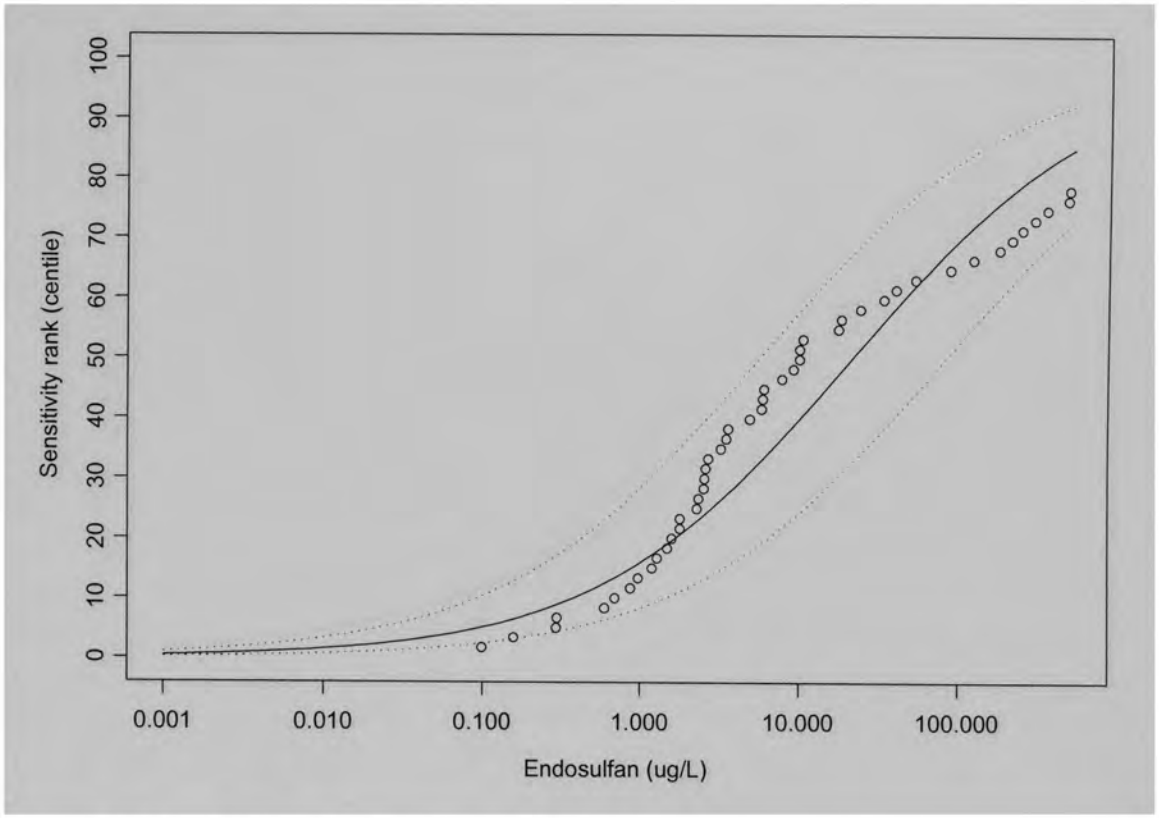


Figure 34. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for freshwater organisms.

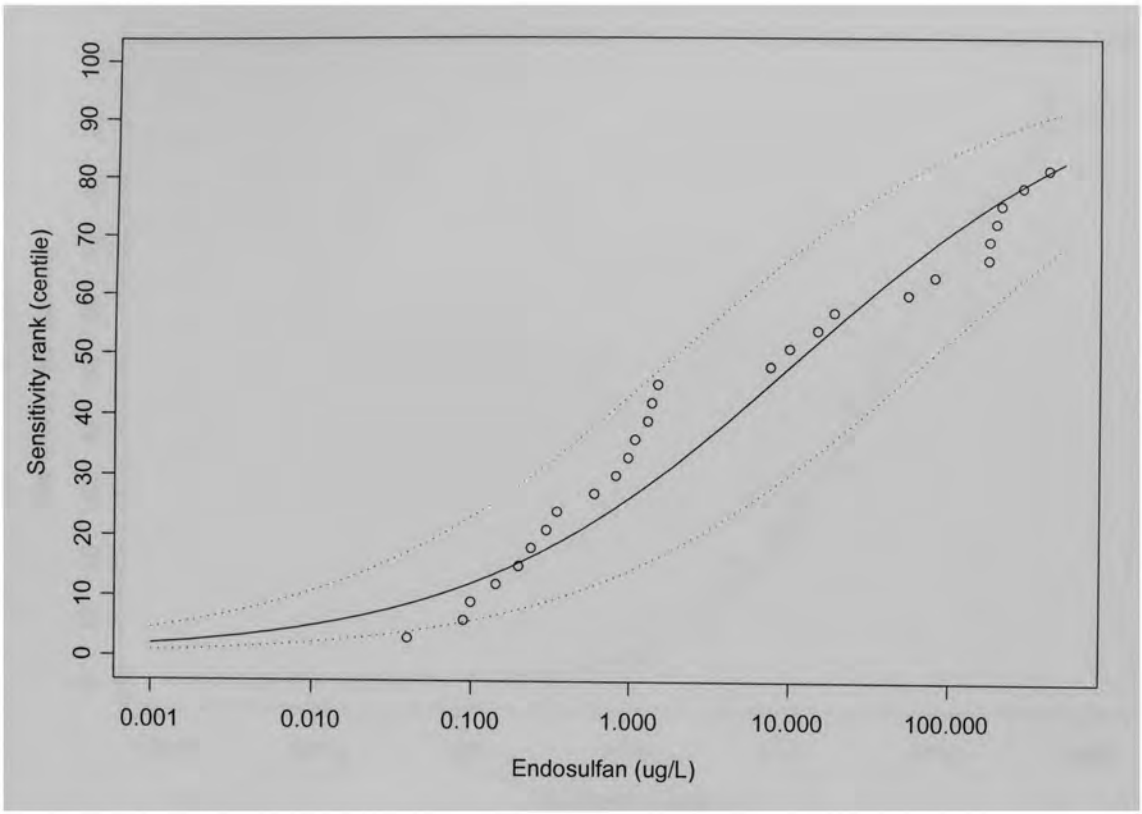


Figure 35. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for saltwater organisms.

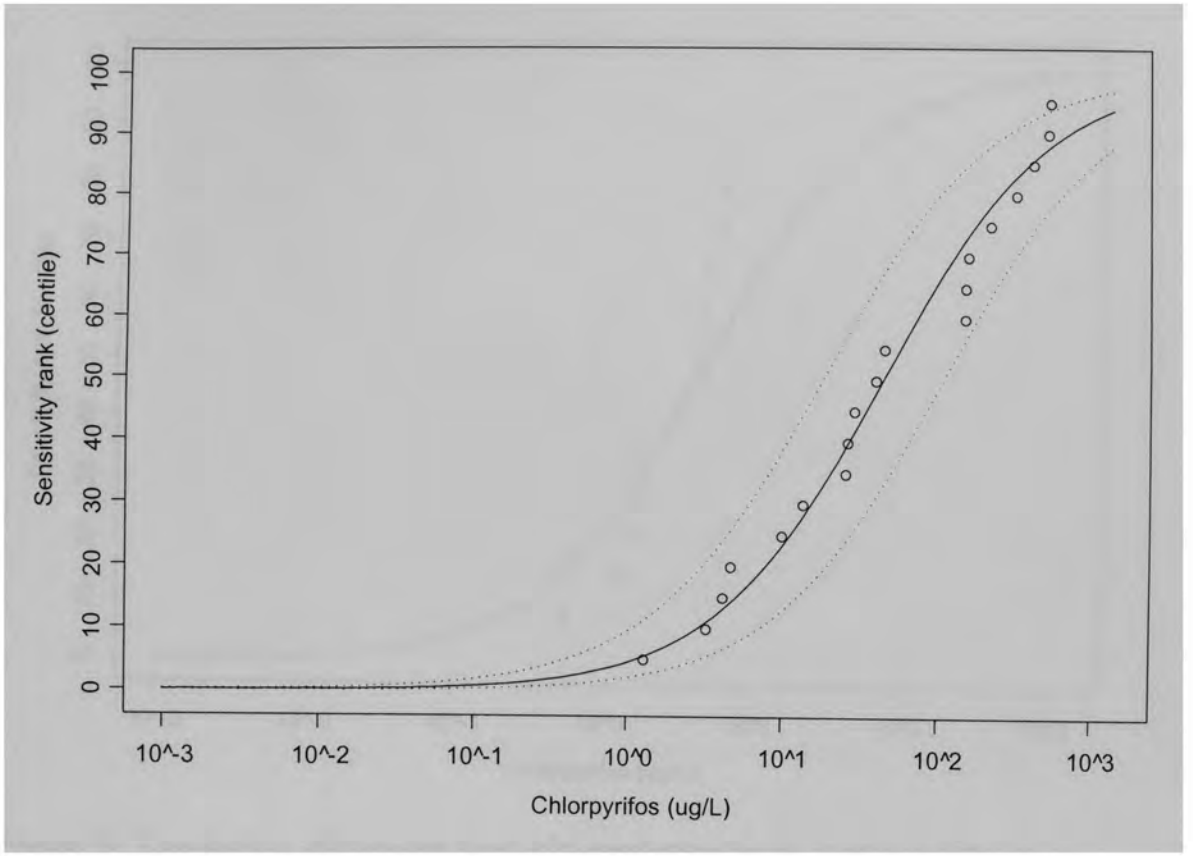


Figure 36. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for freshwater fish.

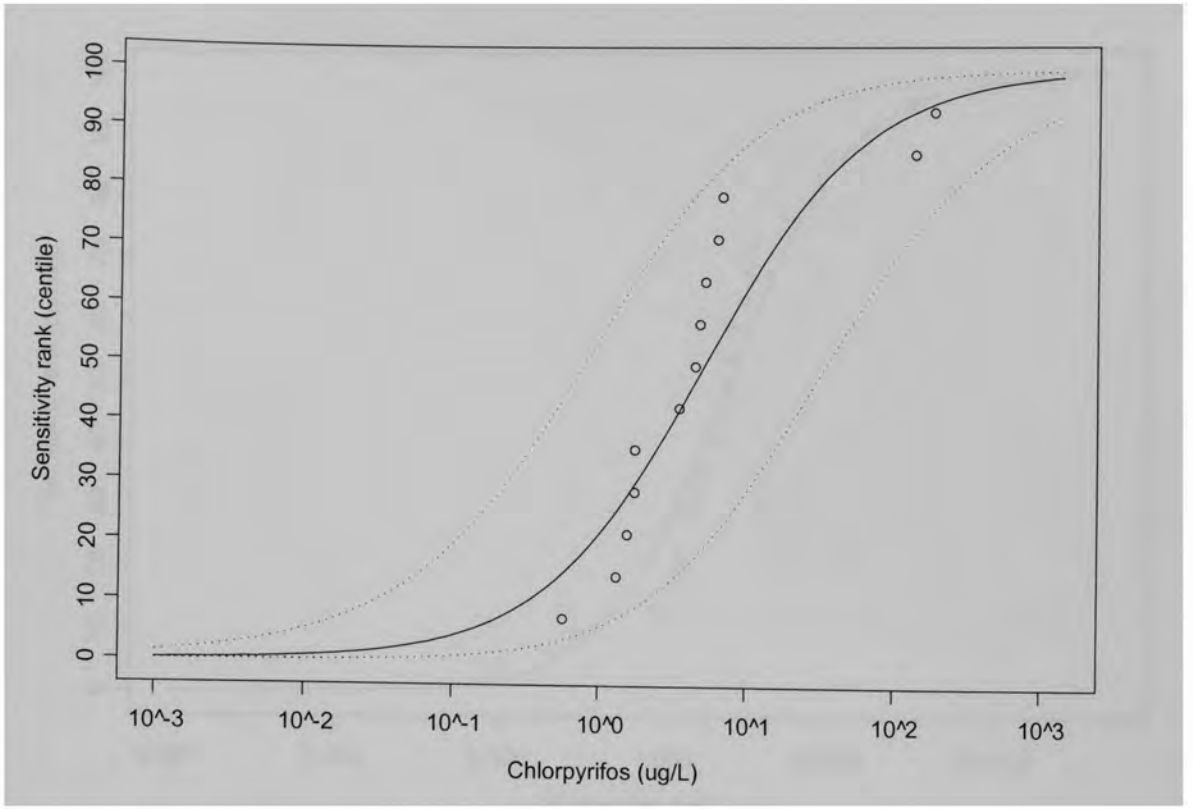


Figure 37. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for saltwater fish.

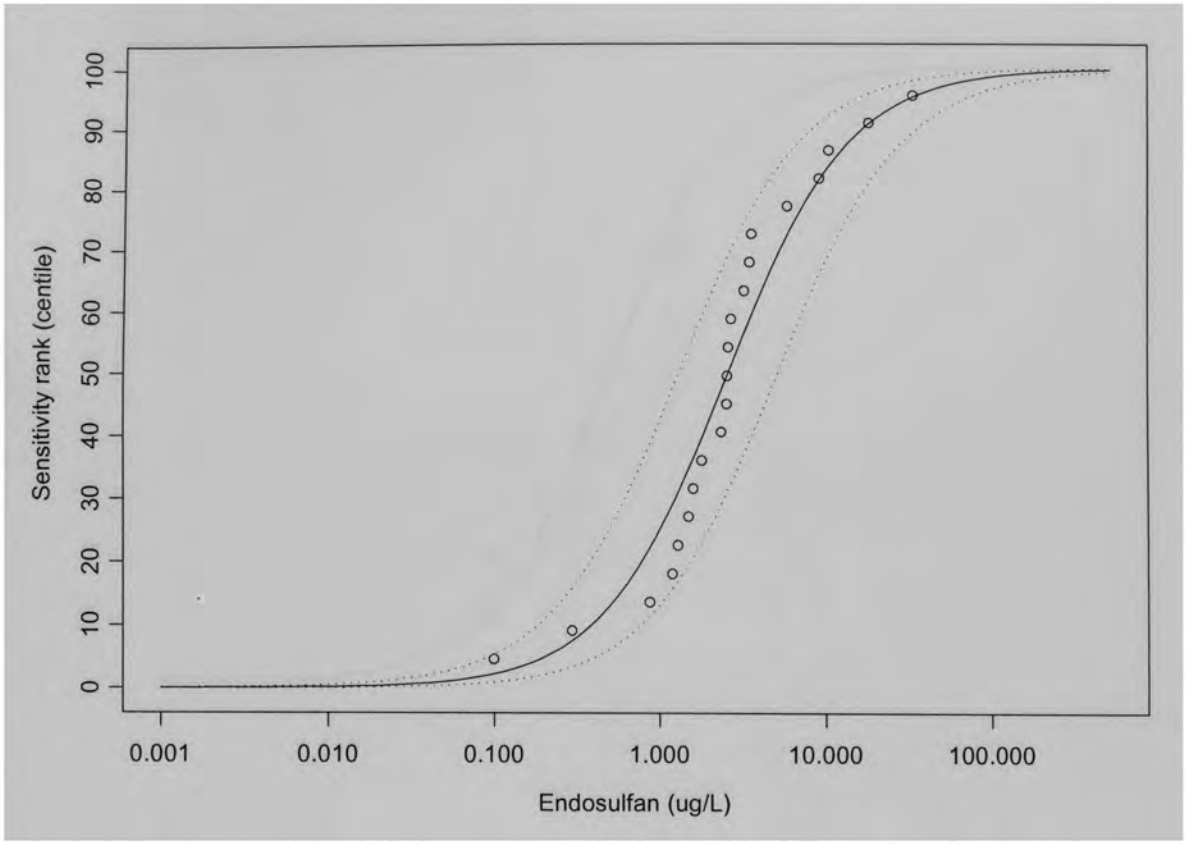


Figure 38. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for freshwater fish.

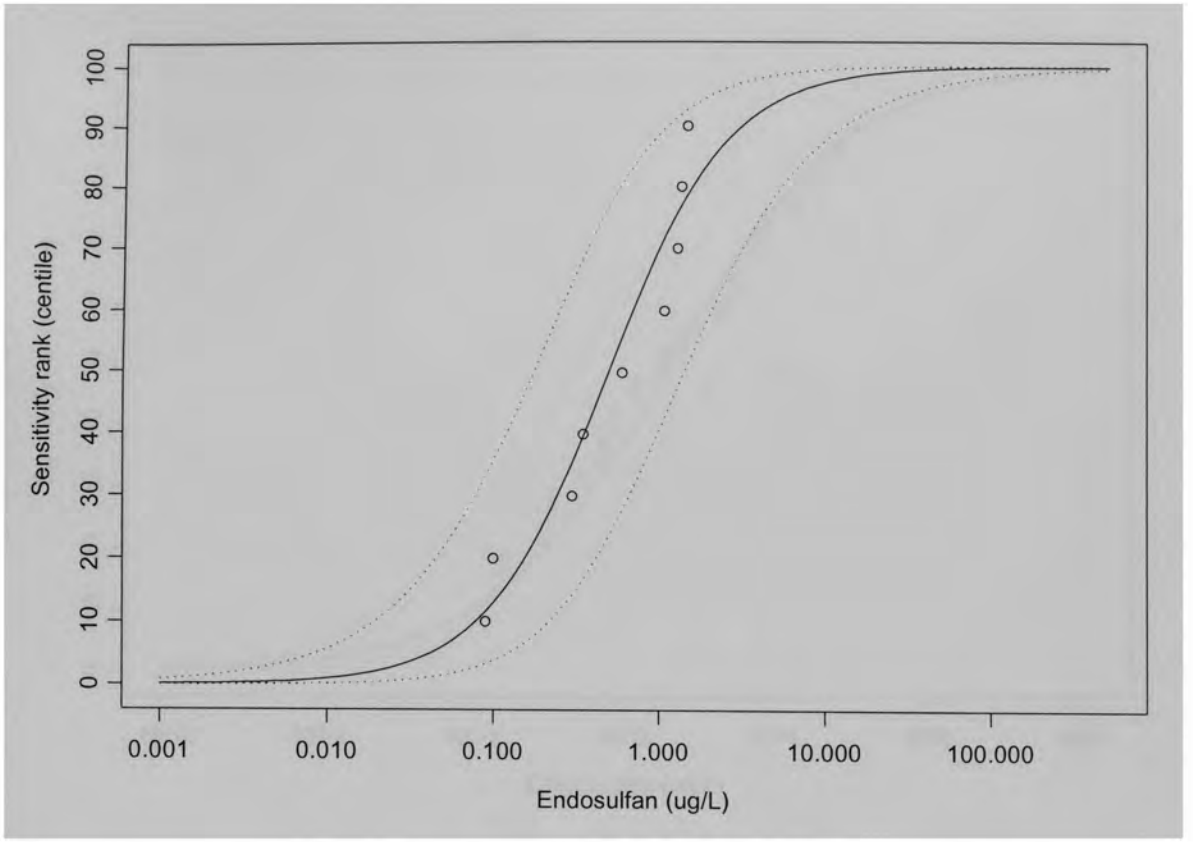


Figure 39. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for saltwater fish.

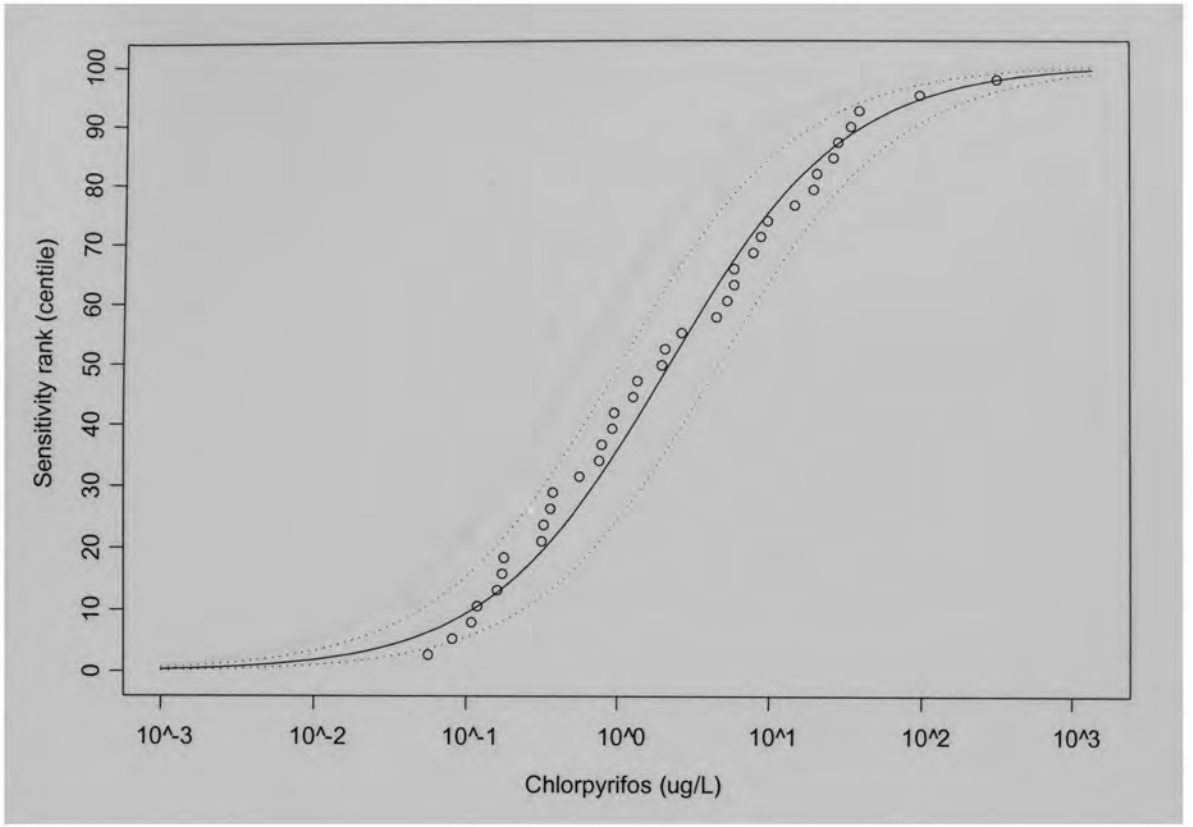


Figure 40. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for freshwater arthropods.

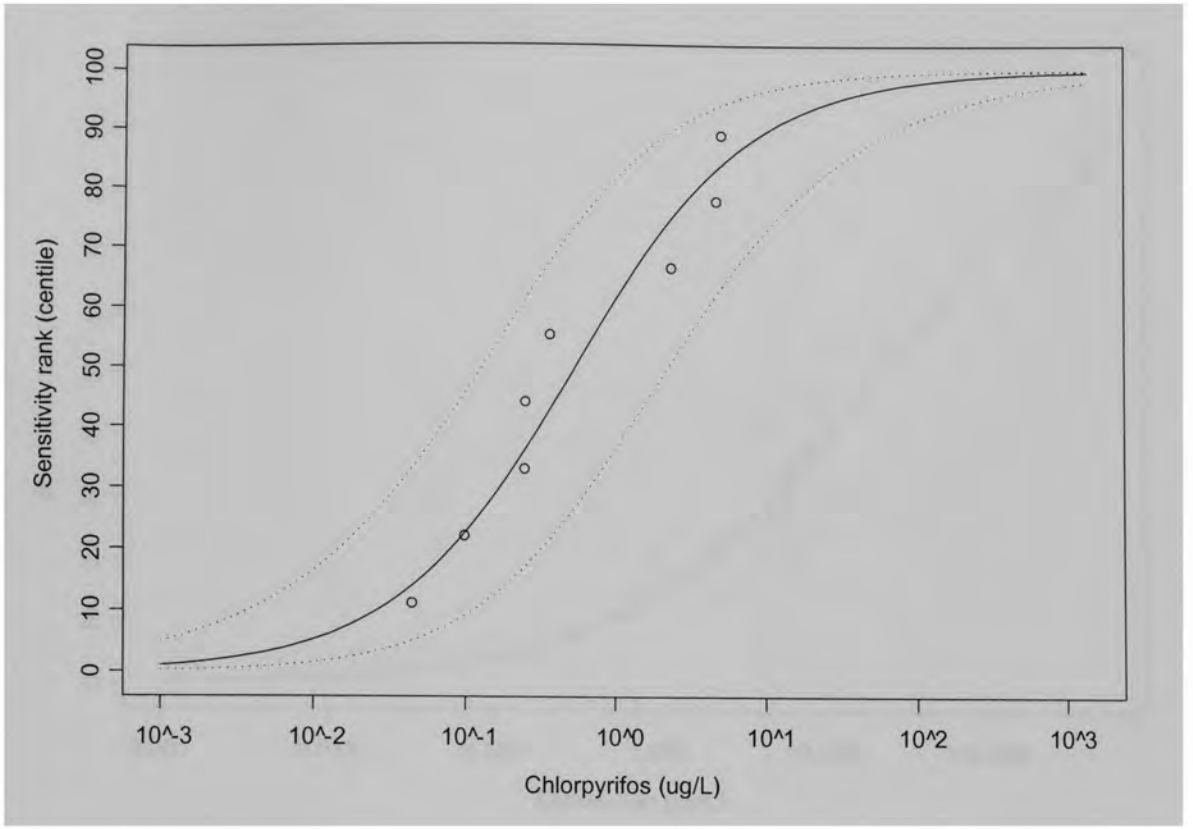


Figure 41. Log-logistic distribution (and 95% prediction band) of chlorpyrifos acute toxicity values for saltwater arthropods.

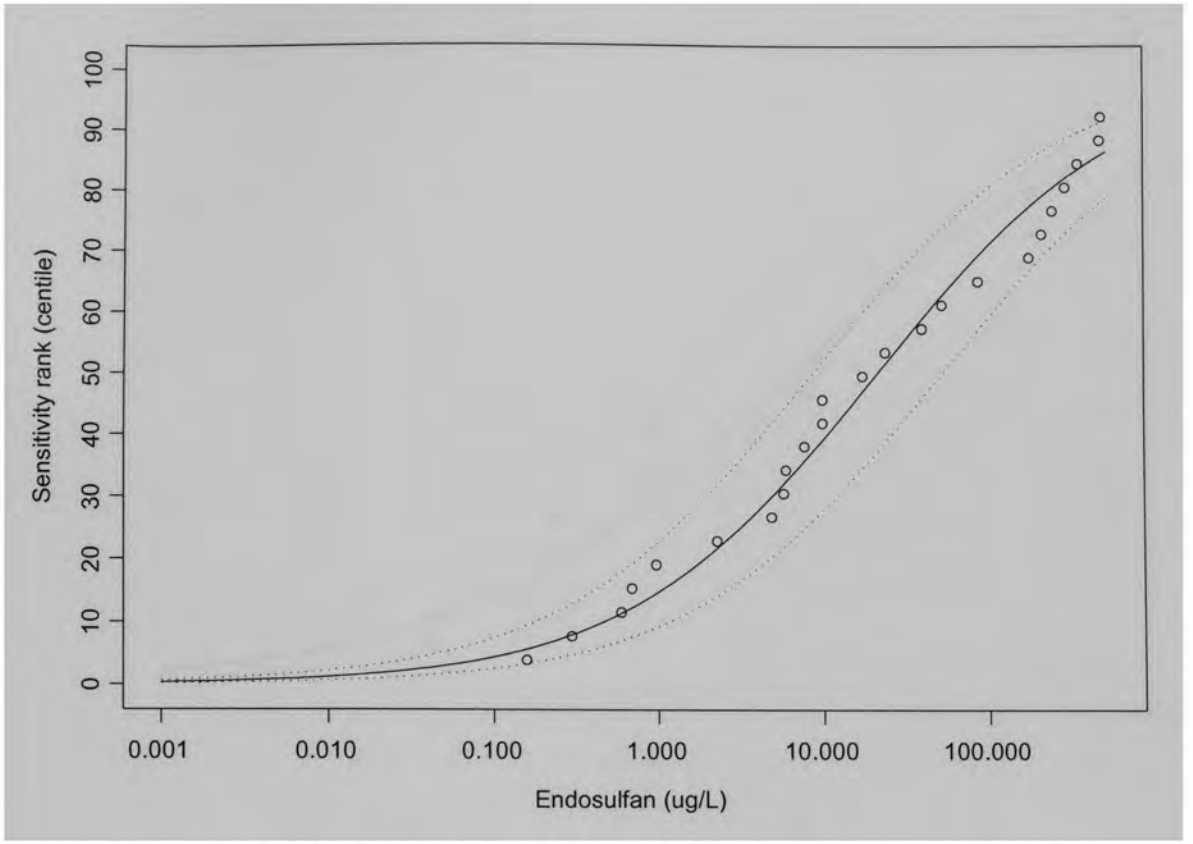


Figure 42. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for freshwater arthropods.

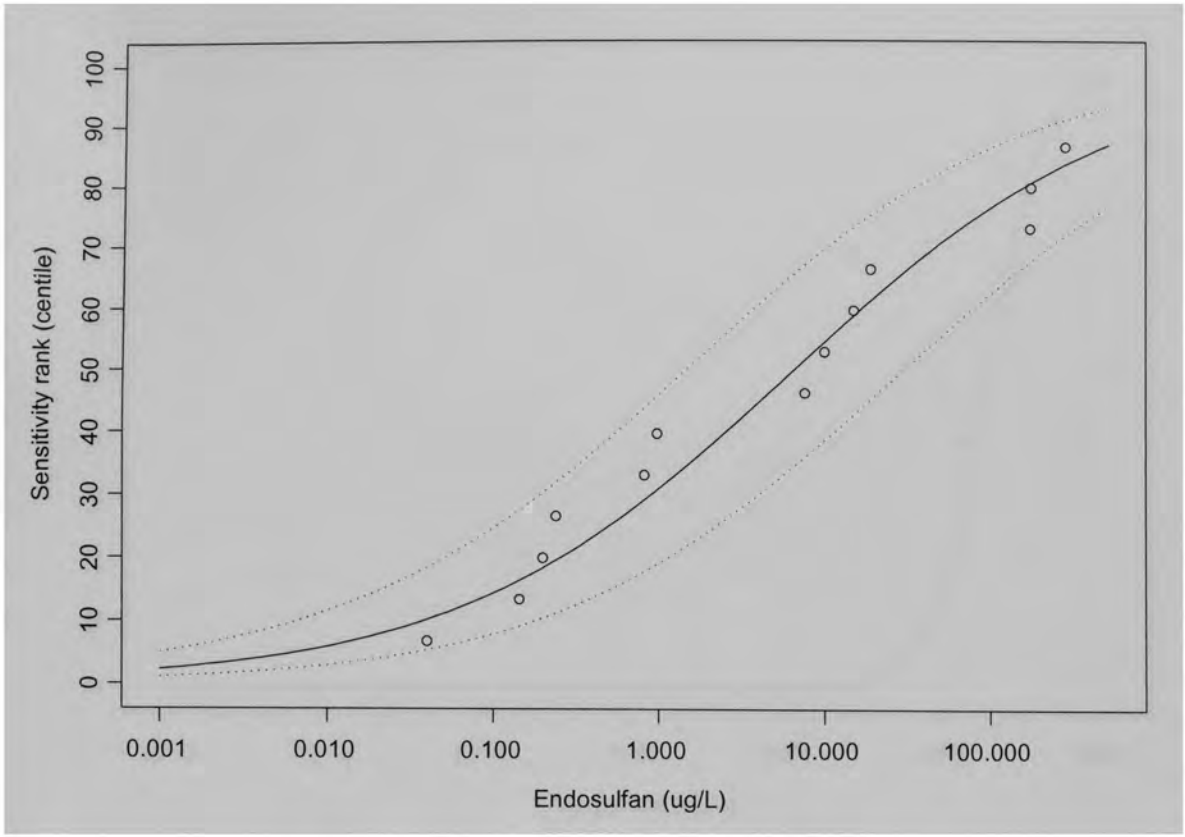


Figure 43. Log-logistic distribution (and 95% prediction band) of endosulfan acute toxicity values for saltwater arthropods.

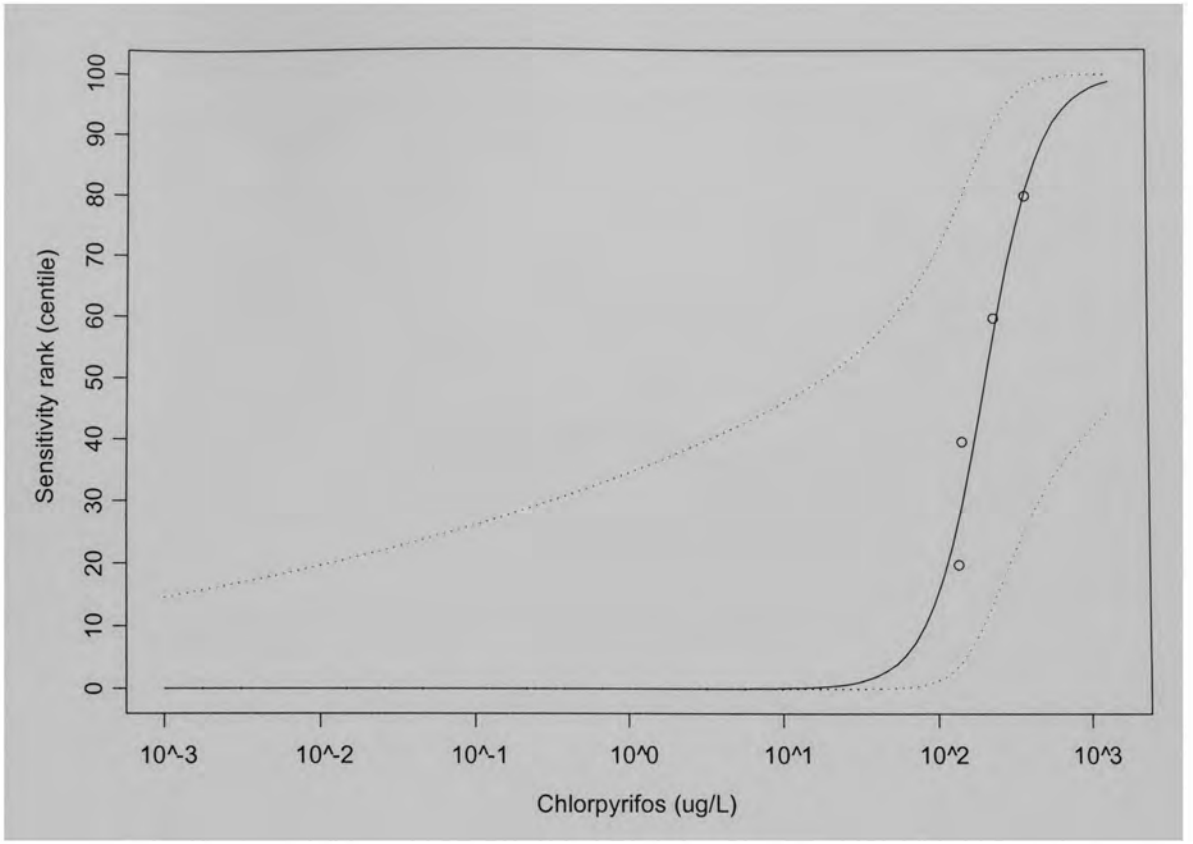


Figure 44. Log-logistic distribution (and 95% prediction band) of chlorpyrifos LC/EC50 values for saltwater plants/phytoplankton.