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Occurrence and Distribution of Endosulfan in Water, Sediment, and Fish Tissue: An Ecological Assessment of Protected Lands in South Florida

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ABSTRACT: Over the past 30 years, endosulfan, one of the last polychlorinated pesticides still in use, has received considerable attention and has been the subject of a number of international regulations and restriction action plans worldwide. This study aimed to monitor the presence and to assess the potential transport of endosulfan within the protected areas of Everglades National Park, Biscayne National Park, and Big Cypress National Preserve, South Florida, USA. Endosulfan sulfate was the major metabolite detected in all matrices in areas along the C-111 and C-111E canals, which drain the Homestead agricultural area and discharge to either Florida or Biscayne Bays, both of which are critical wildlife habitats. Endosulfan concentrations of up to 158 ng L^{-1} and 57 ng g^{-1} were observed in surface water and sediments, respectively, which exceeded the U.S. EPA's chronic water quality criteria (56 ng L^{-1}). Elevated levels of up to 371 ng g^{-1} of endosulfan sulfate were detected in whole fish tissue.

KEYWORDS: *endosulfan, insecticide, Everglades, South Florida, aquatic organisms, sediments, surface water, protected environment*

INTRODUCTION

Endosulfan is one of the last remaining organochlorine insecticides used in the United States. Since its introduction in the 1950s, it has been widely used on a variety of crops (including citrus, small fruits, forage crops, grains, and vegetables) and, in some cases, to preserve wood.[1] Technical endosulfan is a mixture of two stereoisomers, endosulfan I (α-endosulfan) and endosulfan II (β-endosulfan), in a 7:3 ratio.[2] Although being phased out in more than 50 countries, including the European Union and several Asian and Western nations, endosulfan is still being used in tropical and subtropical regions.[3] In South Florida, formulations containing technical endosulfan are still applied to control target insects on crops (e.g., tomato, squash) with all uses being phased out by July 31, 2016.[4] Annual usage in South Florida during the 2007−2009 survey was reported to be around 77700 kg of active ingredient endosulfan.[5] More than 76% of the endosulfan used in the southeastern United States had been reported to be released into Florida Bay's watershed.[6]

Endosulfan is one of the most ubiquitous contemporary organochlorine insecticides. It has been detected in surface water, groundwater, sediments,[7−9] atmosphere,[10−12] and biota throughout the world,[13,14] including the Arctic regions, evidencing the long-range atmospheric transport potential of these compounds.[11,15,16] Through oxidation in freshwater and saltwater, including sediments, several metabolites of endosulfan, that is, sulfate, diol, ether, hydroxy ether, and lactone, have been detected;[17,18] however, endosulfan sulfate (ES) is the major metabolite detected in aquatic systems[19] and in biological tissues.[19−21] ES has been shown to be as toxic as the parent α- and β-isomers[22,23] and generally more persistent in soil and sediments with estimated half-lives ranging from months to years.[7]

The South Florida ecosystem is a heterogeneous system of wetlands, uplands, and coastal and marine areas, which encompasses 16 counties and includes two national parks (Everglades and Biscayne) and Big Cypress National Preserve[24] and has been subject to considerable environmental change during the past 100 years due to increased human population and activities.

Significant declines in the ecosystem health of the Biscayne and Florida Bays have been reported in the past two decades with the die-off of seagrass beds; declines in sponge, coral, and shellfish populations; and development of noxious algal blooms.[25,26] Wildlife populations within the Everglades watershed, especially those of wading birds, have also declined (75−95%) since the construction of flood control structures in the 1950s, compartmentalization of the Everglades into water conservation areas in the 1960s, and the change of the rainfall driven sheetflow to an efficient stormwater canal delivery system.[27]

Currently, there is a major effort to restore the south Florida ecosystem by increasing the flow of freshwater to the

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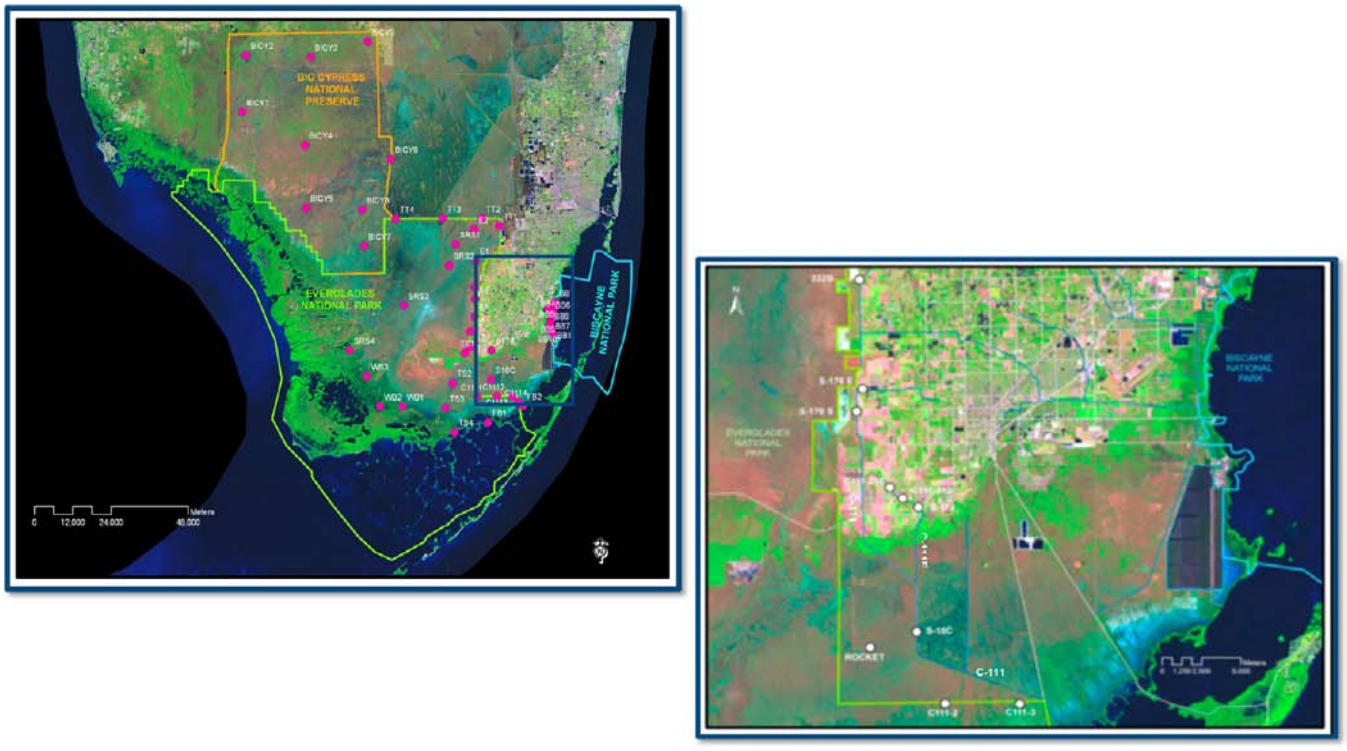

Figure 1. Sampling stations within Everglades National Park (ENP), Big Cypress National Preserve (BICY), Biscayne National Park (BNP/BB), canal and control structures of the C-111 canal, Loveland Slough (C-111E), and one reference station isolated from the network of canals (Rocket). ENP is divided into the following areas: Lower C111 Canal basin (C-111-1/2/3), Highway Creek (C111-4), East Boundary (E), Florida Bay (FB); Shark River Slough (SRS 1/2/3), Shark River (SRS4), Taylor Slough (TS1/2/3), Taylor Slough/Florida Bay (TS4), Tamiami Trail (TT), and West Boundary (WB). Canals and control structures are divided into the following areas: L-31N Canal (332B), C113 Canal (S176E), C111 Canal (S-176S), Structure 178 (S-178), Structure 178 Buffer (S-178B), and Structure 18C (S18C). Loveland Slough is divided into C111-212, C111-217, and C111-217B areas.

Everglades and to Florida and Biscayne Bays. However, increasing water flows in the Everglades may also increase the load of contaminants, particularly pesticides, to the southeastern coasts.

The issue of environmental impacts and water management has been addressed by the South Florida Water Management District (SFWMD) and the Corps of Engineers in a series of remedial actions since the 1980s and, most recently, with the Comprehensive Everglades Restoration Plan (CERP) that seeks to address both hydrology and water quality issues.[28]

Pesticides in the surface waters and sediments of south Florida have been investigated by several agencies. Since 1984, α- and β-endosulfan isomers and endosulfan sulfate have been detected in surface water (fresh- and saltwater) and sediment in monitoring studies conducted by the SFWMD,[29−33] National Oceanic and Atmospheric Administration (NOAA),[6,34,35] U.S. Environmental Protection Agency (U.S. EPA),[36] and U.S. Department of Agriculture.[37] Although the use of endosulfan may appear to have decreased since the late 1990s, U.S. EPA water quality criteria (WQC) for freshwater (56 ng L^{-1}) and marine (8 ng L^{-1}) aquatic wildlife[38] have been exceeded for endosulfan at several sampling sites. Previous studies in the area around the canals have shown that exposure to the insecticide endosulfan might cause chronic toxic effects in copepods, clams, and oysters.[6] A recent aquatic probabilistic risk assessment for endosulfan in surface waters from 1999 to 2000 in South Florida indicated potential acute risks to fish and arthropods in fresh- and saltwaters[39] and, based on exceedences of sediment quality standards[40] and data from 1990 to 2002 in freshwater canals, identified endosulfan as a chemical of potential ecological concern.

The present study comprises the results of comprehensive surveys conducted between August 2001 and March 2004 and between January 2007 and May 2009, to establish the occurrence, distribution, and environmental fate of the pesticide endosulfan and its metabolite, endosulfan sulfate, within the Everglades National Park (ENP), Biscayne National Park (BNP), and Big Cypress National Preserve (BICY). The monitoring network included 65 stations (Figure 1) where surface water, sediment, fish, and benthic organisms were collected on a regular basis from canals and protected parks' lands.

MATERIALS AND METHODS

Study Area Description. ENP is located at the south end of the Florida peninsula and is characterized by a low, flat, wet plain covered by a wide grassy river with alternating ridges and sloughs, covering an area of 6110 km^2. The freshwater portion of the park represents about one-third of the original Everglades, which extended from Lake Okeechobee, in the north, to Florida Bay (FB), in the south, for 160 km and from the Coastal Pineland Ridge, in the east, to the Big Cypress Flatwoods, in the west, for 60 km. This extensive freshwater ecosystem comprised wet prairies, sawgrass marshes, cypress and mangrove forests, and coastal lagoons and bays, which continues to provide a mosaic of wildlife habitats. In the late 1940s, the federal government implemented a major water control project to provide water supply and flood protection for south Florida, which substantially changed the hydrology and ecology of the Everglades. Today in the Everglades, an extensive network of canals and structures allow the rapid redistribution of flows throughout the system but also

facilitate the movement of pollutants, including agricultural pesticides, into surface waters.[6,37] The Canal 111 (C-111) freshwater basin is a buffer zone that separates the wetlands of ENP from highly productive subtropical agricultural lands and urban development areas. Most of the water discharged into ENP and the southern estuaries, as Florida Bay, are a mixture of rainfall and runoff from urban and agricultural areas of southeast Florida.

Water samples were collected between January 2007 and May 2009 in 1 L amber glass bottles from 30 stations within and around ENP, 9 stations within BICY, 11 stations within BNP, 6 stations within the canal and control structures of the C-111 canal, 3 stations in Loveland Slough (C-111E), and 1 reference station completely isolated from the network of canals (Rocket) (Figure 1). ENP samples are divided into the following areas: Lower C111 Canal basin (C-111-1/2/3), Highway Creek (C111-4), East Boundary (E), Florida Bay (FB); Shark River Slough (SRS 1/2/3), Shark River (SRS4), Taylor Slough (TS1/2/3), Taylor Slough/Florida Bay (TS4), Tamiami Trail (TT), and Western Boundary (WB). Canals and control structures are divided into the following areas: L-31N Canal (332B), C113 Canal (S176E), C111 Canal (S-176S), Structure 178 (S-178), Structure 178 Buffer (S-178B, adjacent to S178), and Structure 18C (S18C). The Loveland Slough area includes stations C111-212, C111-217, and C111-217B (located at the same geographical coordinate as C111-217). Some stations were located along areas where anthropogenic inputs were likely, such as the northern (TT) and eastern (E) boundaries of ENP and canals in BNP. Areas in the western side (WB) of ENP not likely to be affected by the implementation of CERP and the resulting changes in water deliveries were also selected as controls. Sediment, surface water, and sunfish were collected at Rocket to act as reference blank samples away from any direct source of pesticide application. Sampling was periodically and generally timed to coincide with agricultural production and included sampling during both growing (high pesticide usage) and nongrowing (low pesticide usage) seasons. The samples were keep refrigerated (<4 °C) until analysis. The sampling points at each location are shown in Figure 1.

The first sediment sampling event was conducted between August 2001 and March 2004 and the second between March 2006 and October 2008. At each station, the top 8 cm of five 6.5 cm cores were collected from within a 100 m^2 area, consolidated, and stored frozen in combusted glass jars with Teflon-lined lids until analysis.

Because of their limited mobility, tissue samples of mosquito fish (*Gambusia holbrooki*), marsh killifish (*Fundulus confluentus*), flag fish (*Jordanella floridae*), Mayan cichlid (*Cichlasoma urophthalmus*), diamond killifish (*Adinia xenica*), jewel cichlid (*Hemichromis* spp.), pike killifish (*Belanesox belizanus*), catfish (*Clarias batrachus*), golden topminnow (*Fundulus chrysotus*), mojarra (*Eucinostomus harengulus*), puffer fish (Tetraodontidae), sunfish (*Lepomis* spp.), rainwater killifish (*Lucania parva*), sailfin molly (*Poecilia latipinna*), sheepshead minnow (*Cyprinodon variegatus variegatus*), bay anchovy, clam, mussel, and tadpole were collected to assess the environmental fate of chemical contaminants in both canal and adjoining estuarine and marine ecosystems.

Tissue sampling was first conducted between December 2001 and March 2004 and then latter between August 2006 and April 2009 using $^1/_4$ and $^1/_8$ in. minnow traps deployed 24 h prior to collection; multiple collections were conducted until an adequate sample size was attained. Fish were identified and sorted at the collection sites, and composite samples of whole tissue ($N > 20$) were homogenized and stored at < −10 °C until ready for analysis. Fish samples were also collected from stations in FB using cast nets. These samples included larger species of fish such as mojarra (*Cichlasoma* spp.) and mullet (*Mugil* spp.). The fish collected feed mainly on zooplankton, small insects, microcrustaceans and microbivalves, organic detritus, and algae (fishbase.org).

Chemicals. All material and glassware used were previously cleaned, combusted in a muffle furnace at 440 °C for at least 6 h, and then rinsed with acetone, methanol, hexane, and dichloromethane prior the analysis to avoid contamination. Certified standards of α- and β-endosulfan and endosulfan sulfate (1000 $\mu g\ mL^{-1}$) were purchased from Ultra Scientific, Analytical Solutions. A mixture of 4,4′-dibromooctafluorobiphenyl (DBOFB), 2,2′,4,5′,6-pentachlorobiphenyl (PCB 103), and 2,2′,3,3′,4,5,5′,6-octachlorobiphenyl (PCB198) at 200 $\mu g\ mL^{-1}$ each in acetone was obtained from Accustandard (New Haven, CT, USA) and used as surrogate (added before extraction) for quality control of the analytical procedure. Tetrachloro-*m*-xylene (TCMX, Supelco, St. Louis, MO, USA) (100 $\mu g\ mL^{-1}$) was used as internal standard (added just before injection) for chromatographic analysis. Stock and working solutions were prepared with optima quality or equivalent solvent, methanol, *n*-hexane, pentane, acetone, and dichloromethane (Fisher Scientific, Fair Lawn, NJ, USA) and stored at −18 °C. Ultrapure water (18.2 MΩ cm^{-1}) was obtained by a Nanopure Infinity Ultrapure Water system.

Chemical Analyses. All samples were prepared following the procedures described by EPA method 8081B[41] (U.S. EPA, 2007). Prior to water sample extraction, 20−30 g of sodium chloride was added to the samples to increase ionic strength. After addition of the surrogate standards, 1 L water samples were processed by liquid−liquid extraction with 50 mL of methylene chloride. The extraction was repeated two more times using fresh portions of solvent. All extracts were dried over Na_2SO_4, concentrated using a Kuderna−Danish system, and, after addition of internal standard, transferred to GC vials for analysis. An aliquot (15 g) of homogenized freeze-dried or chemically dried sediment sample was extracted for 2 min by accelerated solvent extraction (ASE) using dichloromethane. The extract was then concentrated and solvent exchanged to hexane for cleanup by silica gel/alumina column chromatography. Tissue samples were homogenized, and the sample percent moisture was determined. An aliquot of 0.5−15 g wet weight (depending on tissue type and availability) was extracted three times with fresh portions of 100 mL of dichloromethane in the presence of sodium sulfate (20−50 g) by maceration with a tissumizer. The concentrated extract was then purified using silica gel/alumina column chromatography. The cleanup was performed using a glass chromatographic column (30 cm × 1.1 cm i.d.) packed with 10 g of alumina (deactivated with 1% water) and 20 g of silica gel (deactivated with 5% water) using 30 mL of CH_2Cl_2. Tissue samples required further purification by gel permeation chromatography (GPC) before instrumental analysis. The instrument conditions of GPC were as follows: flow rate, 5−7 mL min^{-1}; detection wavelength, 254 nm; injection volume, 1 mL; GPC column, Phenomenex Phenogel 10 μm, 250 mm × 25 mm; and elution solvent, methylene chloride. The eluted portions of 40 min with 20−22 min rejection volumes ("cutoff time") were collected, and the fractions were transferred to a 250 mL flat-bottom flask, evaporated initially to 10 mL, and then further concentrated to 1 mL in a water bath of 40 °C on a Kuderna−Danish concentrator tube.

Instrumentation. Endosulfan α- and β-isomers and the metabolite ES were quantified on a Hewlett-Packard series II 5890 gas chromatograph fitted with an electron capture detector (ECD) and a DB-5 fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific). A confirmatory chromatographic analysis of standards and samples was performed in a column with a stationary phase of different polarity (30 m × 0.25 mm i.d., 0.25 μm film thickness, Zebron Multiresidue 1, Phenomenex). Chromatographic conditions for endosulfan and endosulfan sulfate determination were the following: 1−4 μL of sample was injected at splitless mode; the column oven was programmed for an initial temperature of 100 °C for 1 min and a rate of 5 °C min^{-1} to 140 °C, then held for 1 min at 140 °C, ramped to 250 °C at a rate of 1.5 °C min^{-1}, held for 1 min, and finally increased at a rate of 10 °C min^{-1} to 300 °C and held for 5 min; with helium as the carrier gas (at a flow rate of 1 mL min^{-1}) and argon/methane or nitrogen as makeup gas (40 mL min^{-1}). The injector and detector temperatures were maintained at 275 and 325 °C, respectively.

Quantitation. Analyte concentrations in the samples were calculated on the basis of the area ratio between the analyte and surrogate standard (PCB 103) and taking into account concentration and/or dilution effects. The internal standard for chromatographic analysis (TCMX) was used to calculate surrogate recoveries. DBOFB or PCB 198 was used to calculate selected analyte concentrations, if it was demonstrated that they produced more reliable data (if matrix

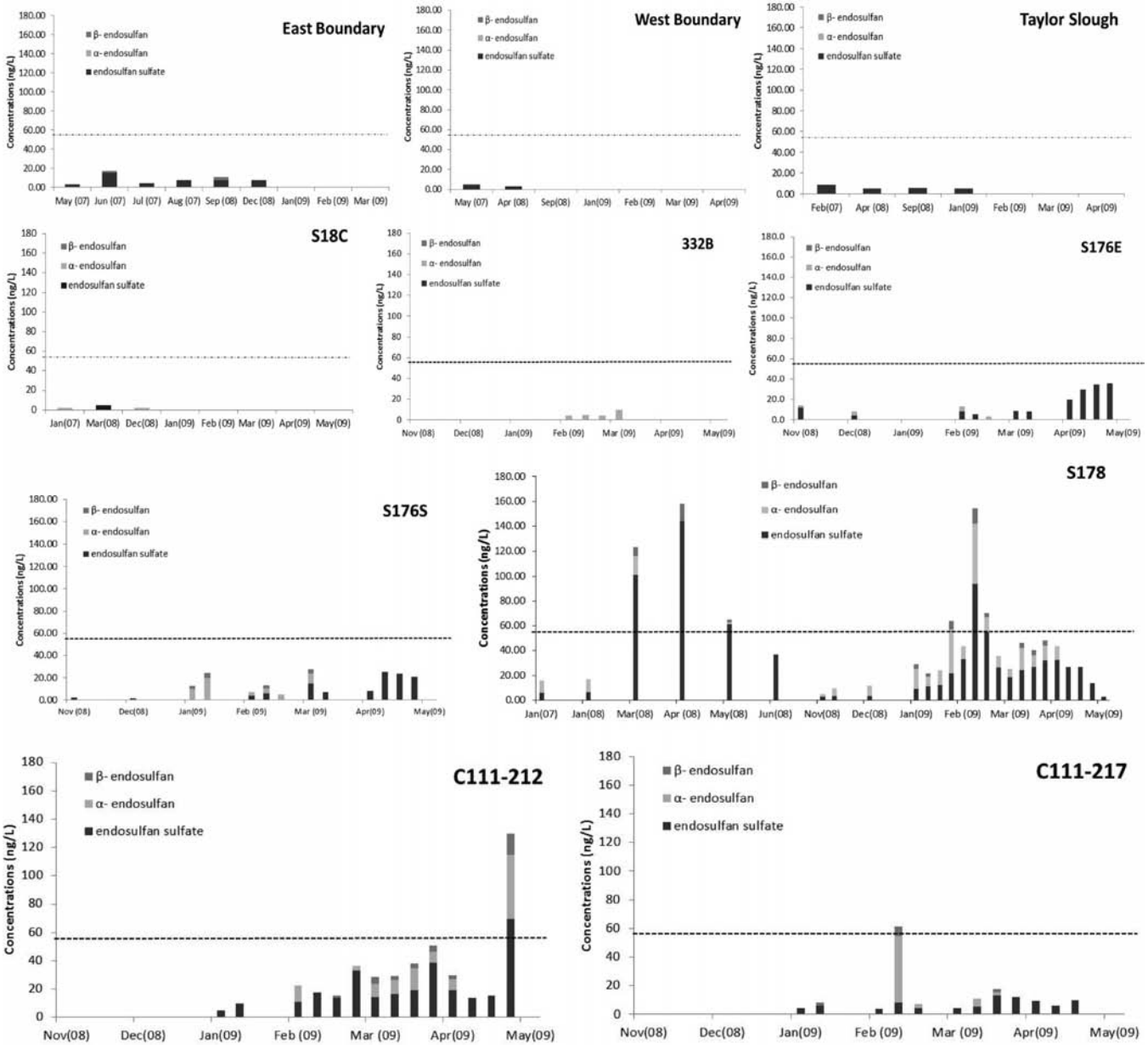

Figure 2. Distribution of endosulfan sulfate and α- and β-endosulfan (ng L^{-1}) in surface water of ENP sampled regions of East (E1-7, n = 28) and West Boundary (WB1-3, n = 25), Taylor Slough (TS1-4, n = 23), Loveland Slough (C111-212 and C111-217, n = 28), L-31N canal (332B, n = 20), C113 canal (S176E, n = 20), C111 canal (S176S, n = 20), and Structure 178 (S178, n = 31). Results showed more than one positive detection for different sampling days in the same month at 332B (Feb09 = 3), S176S (Jan09 = 2, Feb09 = 3, Mar09 = 2, Apr09 = 4), S176E (Feb09 = 2, Mar09 = 2, Apr09 = 4), S178 (Nov08 = 2, Jan09 = 4, Feb09 = 4, Mar09 = 4, Apr09 = 4), C111-212 (Jan09 = 2, Feb09 = 3, Mar09 = 4, Apr09 = 4), and C111-217 (Jan09 = 2, Feb09 = 4, Mar09 = 4, Apr09 = 3).

interference occurs with PCB 103) based on percent recoveries in spiked blanks or matrix spikes.

Quality Control. To control the quality of the analytical data, target compounds were spiked with a mixture of standards at 40 ng L^{-1} and were analyzed through the procedures. Matrix spike recoveries for all target analytes ranged from 56 to 118% (mean ± SD, 97 ± 12%) for water samples, from 59 to 118% (80.4 ± 12%) for sediment samples, and from 54 to 112% (82 ± 16%) for tissue samples. Surrogate recoveries ranged from 54 to 130 (mean ± SD, 86 ± 18%). Calibration standards were prepared in hexane at concentrations ranging from 5 to 200 ng mL^{-1}. Analytical curves were revalidated after every set of 20 samples. All standard calibration curves exhibited excellent linearity (correlation coefficient > 0.99). The method detection limit (MDL) was <1 ng L^{-1} (or ng g^{-1}) for water and sediment samples and <2 ng g^{-1} for fish tissue samples. Quality control samples included a method/procedural blank, a matrix spike, and a matrix spike duplicate with every sample set.

RESULTS AND DISCUSSION

Endosulfan in Surface Water. Water samples have been collected since 1992 at several sites within the studied area. Presently, the U.S. EPA has determined that the concentration of endosulfan sulfate must be summed to that of α- and β-endosulfan to evaluate the risks and toxicity related to the use of endosulfan.[23] Total endosulfan (sum of endosulfan sulfate and α- and β-endosulfan) occurred in 24% of the collected water samples (n = 435), most of those near the canals and structures of ENP. The highest concentrations were at station S-178 followed by those at monitoring stations C111-212 and

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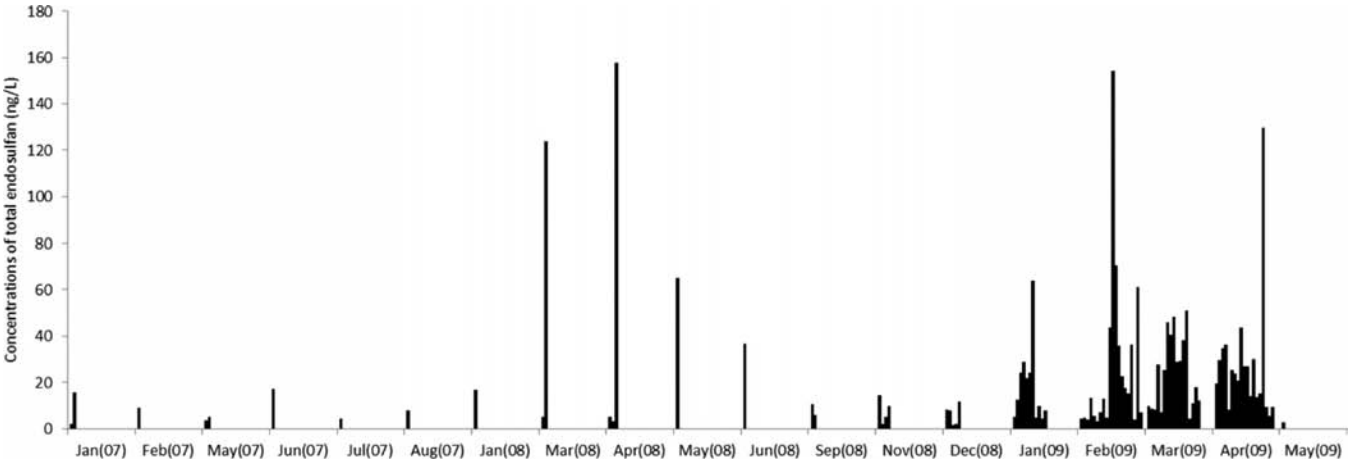

Figure 3. Seasonal distribution of total endosulfan in surface water samples. Sampling sites were BB01-16 (n = 95); BICY01-09 (n = 36); C111-1 to C111-3 (n = 15); C111-4 (n = 6); E1-7 (n = 28); FB1-2 (n = 17); SRS1-3 (n = 12); SRS4 (n = 8); TS1-4 (n = 23); TT1-4 (n = 25); WB1-3 (n = 25); 332B (n = 20); S176E (n = 20); S176S (n = 20); S178 (n = 31); S18C (n = 27); C111-212 (n = 14) and C111-217 (n = 14). Results showed more than one positive detection in Jan(07) = 2, May(07) = 2, Mar(08) = 2, Apr(08) = 3, Sep(08) = 2, Nov(08) = 4, Dec(08) = 5, Jan(09) = 11, Feb(09) = 20, Mar(09) = 17, and Apr(09) = 19.

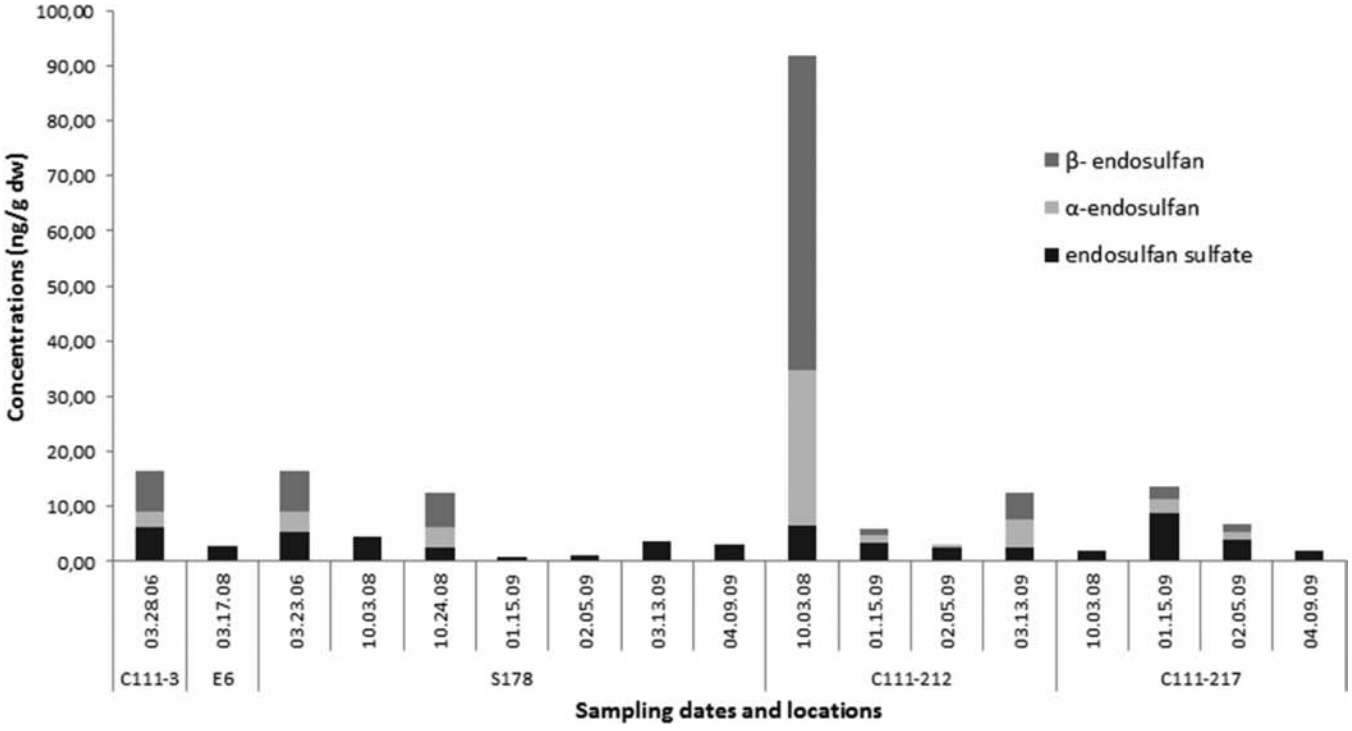

Figure 4. Total endosulfan distribution (ng g^{-1} dw) in sediments collected from 2006 to 2009. Results presented positive detection at C111-3 (n = 1), E6 (n = 1), S178 (n = 7), C111-212 (n = 4), and C111-217 (n = 5).

C111-217 along the Loveland Slough area, located in the upper drainage area of the C111E canal. Figure 2 shows the distribution of endosulfan sulfate and α- and β-endosulfan in surface water of ENP E, WB, and TS regions, Loveland Slough (C111-212 and C111-217), L-31N canal (332B), and structures S176E, S176S, S178, and S18C. Concentrations ranged from <5 to 101 ng L^{-1} (mean, 17.8 ± 22.2 ng L^{-1}), from <5 to 48.4 ng L^{-1} (mean, 10.7 ± 11 ng L^{-1}), and from <5 to 15 ng L^{-1} (mean, 4.8 ± 3.5 ng L^{-1}) for endosulfan sulfate and α- and β-endosulfan, respectively. As observed in Figure 2, some concentrations at S178, C111-212, and C111-217 exceeded the U.S. EPA's chronic water quality criteria (WQC) for fresh waters (56 ng L^{-1}).[38] Other studies have also reported endosulfan in canal and surface waters of Florida Bay, often exceeding the WQC.[32,36,42] However, in the present study, FB samples did not exceed EPA and Florida WQC for saltwater (8.7 ng L^{-1}).[38]

Dry-season (October−March) samples had a higher endosulfan frequency of detection (21%) and higher levels than wet-season samples (Figure 3), with concentrations ranging from <5 to 158 ng L^{-1} (mean, 24 ng L^{-1}) at ENP sites. Downing et al.[43] also noted that dry-season endosulfan concentrations were higher by 3 orders of magnitude than wet-season concentrations. In Figure 3 is presented the seasonal distribution of total endosulfan in surface water, showing the results of all waters sampled within the months. The temporal and spatial

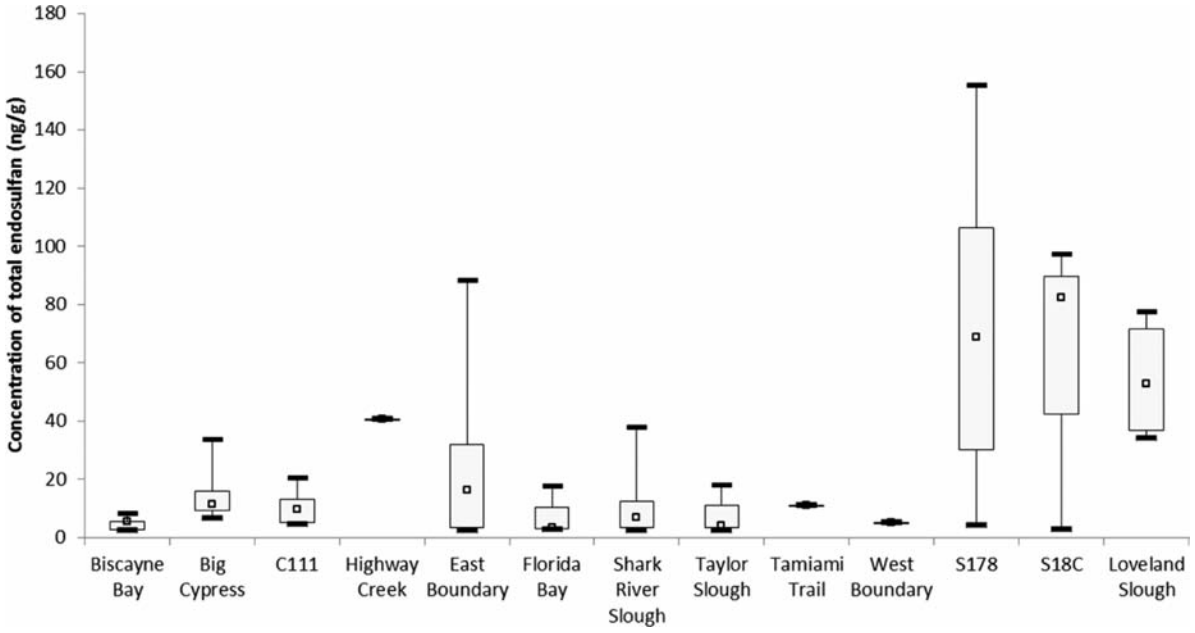

Figure 5. Distribution of total endosulfan (ng g^{-1} dw) in fish tissue collected from 2006 to 2009. The fish species included were sailfin molly, diamond killifish, puffer fish, flag fish, marsh killifish, jewel cichlid, mosquito fish, mojarra, sunfish, Mayan cichlid, and goldentop minnow. Sampling sites were Biscayne Bay stations (n = 26) BB01-11; Big Cypress (n = 20) BICY01-08; C111 stations (n = 10) C111-1, C111-2, and C111-3; Highway Creek (n = 2) C111-4; East Boundary (n = 27) E1-7; Florida Bay (n = 9) FB1 and FB2; Shark River Slough (n = 8) SRS1-4; Taylor Slough (n = 12) TS1-4; Tamiami Trail (n = 9) TT1-4; West Boundary (n = 4) WB1-3; S178 (n = 8); S18C (n = 3); and Loveland Slough (n = 4) C111-212 and C111-217.

distribution of elevated endosulfans may be associated with winter vegetable farming or an infestation of whiteflies that could not be controlled by the use of other insecticides. Concentrations reached 158 ng L^{-1} at S178 and 130 ng L^{-1} at C111-212 station in the C-111E canal (Loveland Slough); both were 3 to 2 times higher than EPA and Florida freshwater chronic criterion of 56 ng L^{-1}, suggesting that aquatic organisms exposed to these elevated levels may be at risk. Similarly, concentrations varied from <5 to 65 ng L^{-1} during the rainy season, although representing only 3% of all water samples. Because α- and β-endosulfan (parent compounds) were detected in surface waters, the source of the endosulfan was probably runoff from nearby agricultural fields.[6,44] It is noteworthy that surface water samples collected from BB and FB sites did not have detectable concentrations of endosulfan in this study.

In the current study (2007−2009), total endosulfan levels ranged from 1.74 to 158 ng L^{-1} and averaged 22.4 ± 28.8 ng L^{-1}. The highest endosulfan concentration previously reported in the C-111 basin was >1300 ng L^{-1}.[35] Previous results in South Miami Dade County indicated the presence of endosulfan in surface water from FB and surrounding environments at concentrations ranging from 103 to 748 ng L^{-1} during the time period from 1992 to 2001,[33] from 0.2 to 477 ng L^{-1} during the 1993−1997 period in a multiyear study of the C-111 canal system of South Florida,[6] and from 12 to 168 ng L^{-1} during the 2002−2003 period, suggesting a possible decrease in application of endosulfan in the area,[45] although concentrations of endosulfan have nearly doubled from the 2002−2003 to the 2004−2007 period.[46]

Similar results were obtained from a monitoring program on insecticide loss to streamwater from agricultural areas in Ontario, Canada, which showed the presence of endosulfan ranging from 10 to 170 ng L^{-1} from agricultural watersheds.[47] Distribution of total endosulfan in a tributary of the Ganges River, in India, ranged from below the detection limit to 94.67 ng L^{-1}.[48] Higher concentration levels ranging from 10 to 2270 ng L^{-1} of detected residual pesticides were found in surface water during the dry and wet seasons from the Warri River and Niger Delta, Nigeria, sampled monthly from January to August 2006.[49] Therefore, the levels found in the present study are consistent with the environmental concentrations in an area of continued use of this particular insecticide.

Endosulfan in Sediments. Endosulfan sulfate was found in sediment samples from the C-111 canal. Concentrations ranged from 5 to 57 ng g^{-1} dry weight (dw) during the 2006−2009 period, with the highest levels in the C111-212 site (Figure 4). In a buffer region between the Loveland Slough (S178B site), upstream of S178, and the adjacent agricultural areas, concentrations were as high as 189 ng g^{-1} dw. The first sampling event during 2001−2004 showed endosulfan in 35% of the samples but at concentrations below the limit of quantification (2 ng g^{-1} dw). Endosulfan isomers were occasionally found in sediment samples. The highest concentrations of α- and β-endosulfan were 28 and 57 ng g^{-1} dw, respectively, at C111-212 (Figure 4). These findings are consistent with the literature, which states that α- and β-endosulfan have relatively short half-lives of 35 and 150 days for sediment and as little as 1 day for water, whereas endosulfan sulfate is more persistent in the environment, showing widespread occurrence. Total endosulfan distribution in sediment (2006−2009 period) is shown in Figure 4.

Previous studies have identified α- and β-endosulfan and endosulfan sulfate as chlorinated pesticides of concern and observed that sediments had multiple endosulfan exceedences in the C-111 basin.[6,40] Sediments from C-111 and FB were collected in 1996, and total endosulfan was 168 and 1.33 ng g^{-1} dw, respectively.[6] Endosulfan sulfate was found in sediment at

S178 in the C-111 canal during a 1991−1995 monitoring event; all three endosulfan residues were found in sediment samples with maximum levels of 1200, 16, and 24 ng g^{-1} for endosulfan sulfate and α- and β-endosulfan, respectively.[32] Endosulfan sulfate was also consistently found in sediments from 1996 to 2000 in the C-111 canal by the SFWMD, whereas the α- and β-isomers were only occasionally found.[38] Total endosulfan concentrations ranged from 3.8 to 152 ng g^{-1} at S-178 during the 1986−2006 period.[46] However, in previous studies conducted by the U.S. EPA in 1995, endosulfan residues occurred at lower concentrations in sediments of the C-111 and in sediments of Shell and Trout Creeks of northeastern Florida Bay.[36]

Elsewhere, Scott et al.[50] found endosulfan concentrations up to 280 ng g^{-1} in sediment from the North Edisto River in South Carolina, and residues were attributed to surface runoff from agricultural lands. Compared to other national parks in the western United States, only endosulfan sulfate has been detected in lake sediments in concentrations ranging from 0.11 to 1.2 ng g^{-1}, suggesting that the parent endosulfan isomers are metabolized in sediments.[8] Endosulfan in bottom sediment has been listed as toxic to aquatic invertebrates,[51] but currently there are no established sediment guidelines for aquatic life.

Endosulfan in Tissue Samples. Fish samples (killifishes, mosquito fish, sailfin molly, cichlids, puffer fish, catfish, flagfish, sunfish, sheepshead minnow, golden topminnow, mojarra, and bay anchovy) and benthic organisms (clam, mussel, and tadpole) were collected from ENP, BNP, and BICY between 2001 and 2009. During the 2001−2004 period, β-endosulfan and endosulfan sulfate were found in 72 and 31% of the samples, respectively, with levels ranging from <5 to 350 ng g^{-1} (mean, 39.1 ± 68 ng g^{-1}) dw for endosulfan sulfate and from <5 to 71.4 ng g^{-1} for β-endosulfan (mean, 4.62 ± 11 ng g^{-1}). During the 2006−2009 period, endosulfan sulfate was found in 59% of the samples; however, both parent compounds, α- and β-endosulfan, were detected in only 12 and 8% of the samples, respectively, and occurred at lower concentrations. Distribution of total endosulfan in fish tissue collected from the 2006−2009 period is presented in Figure 5. Concentrations of the parent α- and β-endosulfan were lower than those observed for their metabolite, ranging from <5 to 55.4 ng g^{-1} dw, and only detected in areas of direct anthropogenic inputs, such as Structures S178 and S18C. Elevated concentrations of endosulfan sulfate, of up to 140 ng g^{-1} dw with a mean of 23 ng g^{-1} (n = 147), were observed in whole fish tissue. Although the distribution of endosulfan in fish tissue seemed to be localized in areas influenced by the system of canals along the C-111 basin and the eastern boundary of ENP near the Homestead Agricultural Area, residues were also detected in the other two parks: BICY (in 70% of 20 samples) and BNP (in 23% of 26 samples). FB sites did not have detectable concentrations of endosulfan in surface waters, but in fish tissues reached a total endosulfan concentration of 8 ng g^{-1} dw.

High levels of total endosulfan were also observed in benthic organisms (clam, mussel, and tadpole) collected from 2006 to 2009 along the S178 site with total concentrations ranging from 48 to 188 ng g^{-1} dw (Figure 6).

The maximum reported total endosulfan tissue concentration for small fish in the C-111 basin was 371 ng g^{-1} in the present study, during the 2001−2004 period. Figure 7 compares the spatial distribution along the study area of endosulfan sulfate in fish tissue collected from 2001 to 2004 versus fish tissue collected from 2006 to 2009. Although a decrease is observed in endosulfan levels from 2001 to 2009 at the east boundary of ENP, concentrations have increased at sites located in Loveland and Shark River Sloughs and showed no change in the C-111 basin.

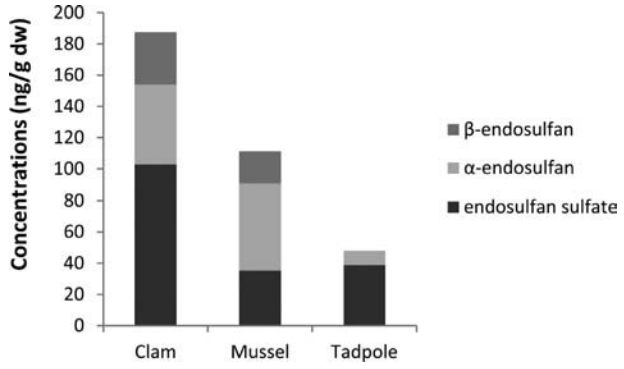

Figure 6. Endosulfan distribution (ng g^{-1} dw) in benthic organisms from S178 (n = 3).

Previous studies have reported endosulfan sulfate concentrations in mussel tissue of 3.4 ng g^{-1} dw in eastern Florida Bay and 8.1 ng g^{-1} dw at the Goulds Canal in Biscayne Bay.[52] The average concentration of total endosulfan, from 1993 to 1998, ranged from 0.3 to 20.1 ng g^{-1} dw for small fish and from 3.3 to 21.3 ng g^{-1} dw in mangrove oysters,[6] being slightly lower than in fish tissue and benthic organisms from the present study. A recent report on oyster tissue had maximum concentrations for α-endosulfan of 41.4 and 16.8 ng g^{-1} dw at sites in Joe Bay, Florida Bay.[53]

On the basis of a recently reported lethal dose of endosulfan in fish tissue of 31 ng g^{-1} (ww),[54] critical levels above this threshold were found in 5% of fish samples (n = 135), representing potential acute and chronic risks of total endosulfan to aquatic organisms. Mussel, tadpole, and clam accumulated endosulfan at high concentrations (up to 188 ng/g dw), indicating that the endosulfan contamination source and any potential effects may be realized locally. The highest risk of acute effects is associated with endosulfan exposure on athropods at the S-178 site.[54]

The literature shows that α-endosulfan may be more acutely toxic than β-endosulfan and endosulfan sulfate to fish and invertebrates, but a combination of (α + β)-endosulfan plus endosulfan sulfate appears to be more toxic than any single isomer.[55] However, the half-life of the endosulfan sulfate is longer than that of the two isomers, making chronic exposure to the former a real threat to fish and invertebrates.[56]

Accumulation Patterns. Bioconcentration factors (BCFs) were estimated on the basis of the average concentration of total endosulfan measured in water and in whole body fish collected at the same sampling station. The estimation did not take into consideration the different fish species, because they had similar sizes and feeding habits.

On the basis of the water concentration available at limited stations, the total endosulfan BCF ranged from 441 to 5285 L kg^{-1} dw. Mean BCF values were estimated at 2245 and 4435 L kg^{-1} dw for endosulfan sulfate and total endosulfan, respectively. Previous studies with similar species reported a range from 318 to 2963,[57] which is in good agreement with the above estimates. In benthic organisms, BCFs were estimated at 1844 and 2595 L kg^{-1} dw for endosulfan sulfate and total endosulfan, respectively.

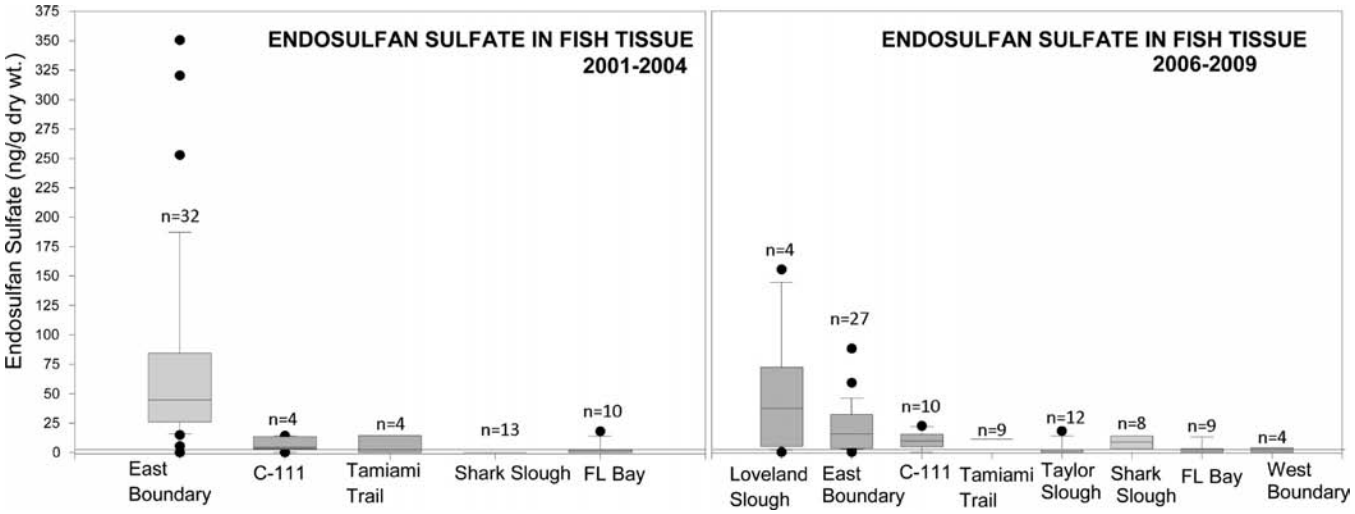

Figure 7. Spatial distribution of endosulfan sulfate in fish tissue collected from 2001 to 2004 versus fish tissue collected from 2006 to 2009. Sampling sites included were C111 stations C111-1 to C111-4; East Boundary E1-E7; Florida Bay FB1 and FB2; Shark Slough SRS1-4; Taylor Slough TS1-4; Tamiami Trail TT1-4; West Boundary WB1-3; and Loveland Slough C111-212 and C11-217. Sample size (n) is presented in the figure.

In the absence of environmental criterion to evaluate the potential risk from endosulfan sulfate exposure to fish, an indirect assessment based on the estimated BCF was used. A median lethal concentration (LC_{50}) of 84 ng L^{-1} was derived from the equation proposed by McCarty,[58] which represents the surface water total endosulfan concentration to achieve a body burden of 371 ng g^{-1} dw (the highest total endosulfan concentration observed in fish). This threshold is even higher than the water quality criteria for endosulfan in fresh waters (56 ng L^{-1}). Concentrations above the threshold value were found at S-178 and C111-212 and represent conditions where exposure to endosulfan in surface waters may be conducive to high risk to the aquatic environment.

Alternatively, if the LC_{50} is assumed to be equal to the water quality criteria, a lethal body burden of 250 ng g^{-1} dw is obtained for total endosulfan. In the present study, 4% of analyzed fish exceeded the estimated critical body residues of endosulfan in fish tissue of 250 ng g^{-1} dw. However, until reliable toxicological data based on endosulfan sulfate become available, the question of risk associated with the observed body burdens remains largely unanswered. Because these small fish are an intermediary link in the Everglades' food chain, monitoring of top predators such as wading birds should be explored.

Higher BCFs ranging from approximately 20 to 11600 L kg^{-1}[16] have been reported for seven species of fish, including sheepshead minnow (*Cyprinodon variegatus*), zebra fish (*Brachydanio rerio*), yellow tetra (*Hyphessobrycon bifasciatus*), striped mullet (*Mugil cephalus*), pinfish (*Lagodon rhomboids*), long whiskers catfish (*Mystus gulio*), and spot croaker (*Leiostomus xanthurus*). In most cases, BCF values appeared to be in the 1000[59] to 3000 range,[57] which are within the range observed in this study. Bioconcentration studies were also available for invertebrates (blue mussel, grass shrimp, oyster, clam, and red swamp crayfish) and the BCF ranged from 12 to 600.[16] More recently, average BCFs of 2682 and 3278 were determined for freshwater green algae (*Pseudokirchneriella subcapitatum*) and the cladoceran (*Daphnia magna*), respectively,[60] which is in the same range of the values observed for clam, mussel, and tadpole in the present study.

Endosulfan Environmental Fate and Temporal Trends. Endosulfan sulfate was more frequently detected than the α- and β-isomers in all sample matrices. Endosulfan sulfate typically is more persistent in aqueous environments than either parent isomer because of its longer half-life in water and soil.[61] Endosulfan α-isomer is more volatile than the β-isomer and therefore is transported as vapor and spray drift, presenting higher atmospheric concentrations.[62] However, β-endosulfan has a lower Henry's law constant, which favors its removal from the atmosphere by wet deposition and air−water exchange.[63−65] Isomer conversion from endosulfan β to α can also occur.[66] Increasing concentrations of endosulfan sulfate in aquatic mammals from the Artic have been reported,[67,68] whereas endosulfan sulfate concentrations in male belugas from southeastern Baffin Island in 2002 did not differ from those in 1996.

Concentrations of endosulfan have been detected in snow samples of western U.S. national parks ranging from 0.20 to 2.5 ng L^{-1} and from 0.07 to 1.18 ng L^{-1} for α- and β-endosulfan, respectively, whereas for endosulfan sulfate, concentrations ranged from 0.15 to 0.21 ng L^{-1},[8] providing clear evidence of airborne transport of endosulfan into these ecosystems and reinforcing the concerns expressed by ENP regarding the threat that endosulfan exposure poses to flora and fauna in national parks.[69] These compounds also were detected in precipitation, confirming that pesticides entering aquatic ecosystems through atmospheric deposition are persistent enough to be accumulated in lake sediments and potentially in aquatic biota as well.[8,62,65]

The ubiquity of endosulfan along the environmental compartments near ENP seems to be directly linked to agricultural activities and has some of the highest historical surface water concentrations of endosulfan sulfate in all of South Florida, suggesting that runoff of pesticides is the main contamination route.[53] The trend of these compounds is still unclear; although the use of endosulfan may have decreased worldwide since 1990s, contaminant levels in sediments, fish, and surface water are still high in some areas. Trend analyses of canal water data (1990−2010) at Station S-178 in Loveland Slough based on DBHYDRO database show that endosulfan concentrations have not exactly decreased over time (Figure 8).

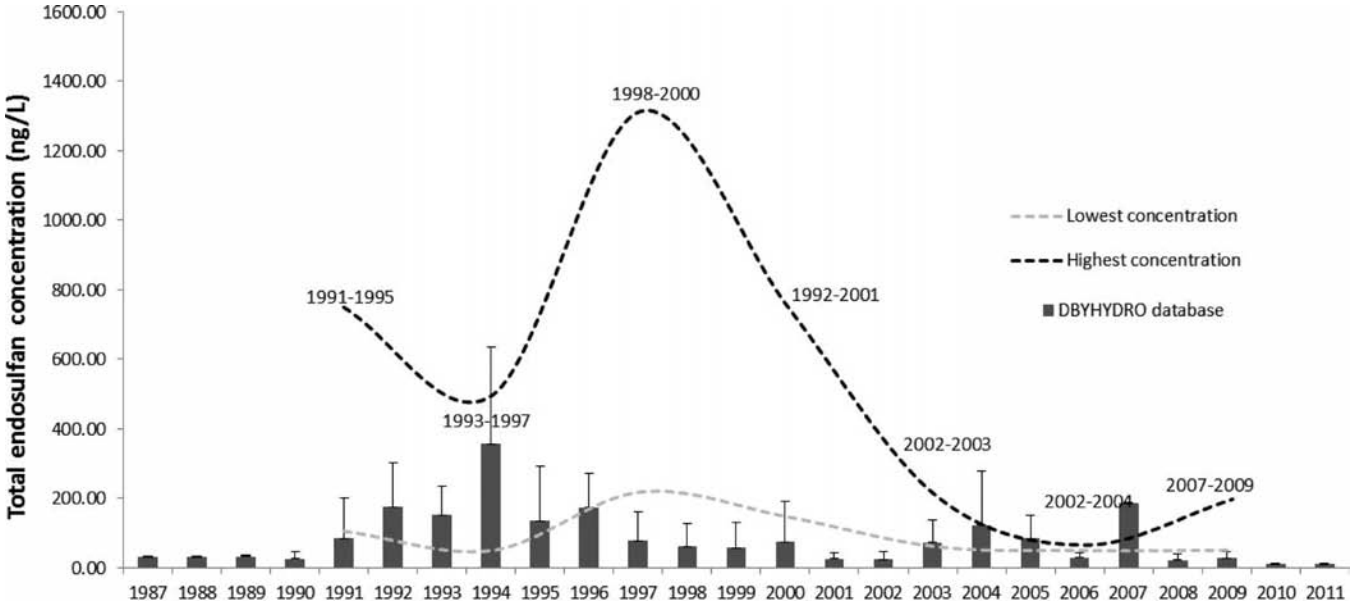

Figure 8. Comparison of endosulfan DBHYDRO database (bars) to previous studies in the ENP area of Miles and Pfeuffer, 1997 (1991−1995); Pfeuffer and Rand, 2004 (1992−2001); Scott et al., 2002 (1993−1997); Downing et al., 2004 (1998−2000); Pfeuffer and Matson, 2003 (2002−2003); Harman Fetcho et al., 2005 (2002−2004); and the present study (2007−2009) (dashed line).

The DBHYDRO database is the SFWMD corporate environmental database, which stores hydrologic, meteorologic, hydrogeologic, and water quality data; this database is the source of historical and up-to-date environmental data for the 16 county region covered by the district.

Comparison to other studies on total endosulfan levels found in surface water from South Florida canals over the years is also shown in Figure 8. It appears that decades of agricultural activity have built a reservoir of soil endosulfan that is replenished every growing season. Local farming practices of crushing the limestone cap rock with heavy plows may facilitate soil erosion and transport of endosulfan-absorbed soil particles to nearby water bodies and canals.[40,70] Such practices also have the potential for enhancing volatilization, atmospheric transport, and redeposition of endosulfan in areas away from the source. This is evident in sites on the east boundary of ENP, Loveland Slough, and C-111 canal, where the chronic risk of exposure is particularly high to fish and invertebrates because of elevated endosulfan concentrations that have not significantly changed over the past few years.

In summary, the analysis of surface waters and sediments showed a similar geographic distribution of endosulfan. Endosulfan was detected in 24% of the water samples (n = 437) and had a high concentration of 158 ng/L and in 14% of sediment samples (n = 144) with a high of 189 ng/g. Elevated concentrations of endosulfan sulfate were detected in whole fish tissue of up to 140 ng g^{-1} (dw) with a mean of 23 ng g^{-1} (n = 147) during the 2006−2009 period and up to 350 ng g^{-1} dw with a mean of 39 ng g^{-1} (n = 68) during the 2001−2004 period. Endosulfan sulfate was the major endosulfan metabolite detected in the samples, whereas α and β-endosulfan were normally observed at concentrations considerably lower. The distribution of endosulfan in all types of samples seems to be localized in areas influenced by the system of canals and along the C-111 and C-111E canals.

Although the use of endosulfan may have decreased, levels found along the C-111 canal and structures (S178) still exceeded the U.S. EPA's WQC for fresh waters (56 ng L^{-1}).[38] Overall, it is evident that there is not significant widespread contamination in the protected parklands of southeast Florida, although the endosulfan levels encountered especially along the C111 canal might pose a threat to the biota and the aquatic ecosystem. In terms of the current project of restoration and the efforts to continue to increase freshwater flow into the Everglades from the C-111 canal system, attention should be drawn to the increasing endosulfan usage in South Florida,[4] which contributes to the potential for agriculturally associated pesticide contamination in this area. Another fact is that endosulfan will continue to be used by growers for the next few years until existing stocks are exhausted; therefore, continuous monitoring is recommended to ensure that no further harzard is realized in this environmentally sensitive region.

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Notes

The authors declare no competing financial interest.

ABBREVIATIONS USED

332B, L-31N Canal; BCFs, bioconcentration factors; BICY, Big Cypress National Preserve; BNP, Biscayne National Park; C-111, C111 Canal; C111-4, Highway Creek; CARE, contaminant, assessment, and risk evaluation; CERP, Comprehensive Everglades Restoration Plan; dw, dry weight; E, East Boundary; ENP, Everglades National Park; FB, Florida Bay; LC_{50}, median lethal concentration; NOAA, National Oceanic and Atmospheric Administration; S-176E, C113 Canal; S-176S, C111 Canal; S-178, Structure 178; S-178B, Structure 178 Buffer;

S18C, Structure 18C; SFWMD, South Florida Water Management District; SRS, Shark River Slough; SRS4, Shark River; TS, Taylor Slough; TS4, Taylor Slough/Florida Bay; TT, Tamiami Trail; U.S. EPA, United States Environmental Protection Agency; WB, West Boundary; WQC, chronic water quality criteria

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