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Surface Water Pesticide Movement from the Dade County Agricultural Area to the Everglades and Florida Bay via the C-111 Canal

M. H. Fulton,[1] G. I. Scott,[1] M. E. DeLorenzo,[1] P. B. Key,[1] D. W. Bearden,[1] E. D. Strozier,[1] C. J. Madden[2]

[1] NOAA-National Ocean Service, Center for Coastal Environmental Health and Biomolecular Research, 219 Fort Johnson Road, Charleston, SC 29412, USA
[2] South Florida Water Management District, Everglades Systems Research Division, 3301 Gun Club Road, West Palm Beach, FL 33411, USA

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Pesticide runoff from agricultural fields into estuarine water bodies may lead to significant impacts in sensitive vertebrate and invertebrate populations (Scott et al., 1994). Pesticides often enter surrounding waters through aerial drift, field runoff and groundwater discharge. Intensive agricultural activities in upland areas adjacent to the Everglades National Park and Florida Bay may threaten the health of these sensitive ecosystems. Approximately 14,590 tons of pesticides are used each year in South Florida, mainly in agriculture (Miles and Pfeuffer, 1997). High pesticide use in Dade County has resulted in this area ranking second in the country in terms of hazard-normalized agricultural pesticide application in coastal regions (Pait et al., 1992).

Of particular concern is the runoff of insecticides such as endosulfan, which is highly toxic to fish, crustaceans, and mollusks. This cyclodiene was the primary pesticide involved in coastal fish kills in the U.S. from 1980-89 (Lowe, 1991). Endosulfan is applied at a rate of approximately 36 tons per year in South Florida to control insect pests on vegetable crops (Miles and Pfeuffer, 1997). Other pesticides commonly used in this area include the organophosphate insecticides chlorpyrifos and diazinon, the herbicides atrazine and metolachlor, and the fungicide, chlorothalonil (Miles and Pfeuffer, 1997).

Monitoring studies from 1993-1996 quantified the levels of selected pesticides in Florida Bay and adjacent upland agricultural watersheds (Scott et al., 2002). For example, surface water concentrations of triazine herbicides >100 ng/L and endosulfan as high as 277 ng/L were measured. Levels of endosulfan were found that exceeded the USEPA freshwater water quality criterion (WQC) of 56 ng/L at upland agricultural sites as well as the marine WQC of 8.7 ng/L in Florida Bay. The spatial distribution of endosulfan concentrations suggested that the agricultural areas were a dominant source for the endosulfan measured in Florida Bay (Scott et al., 2002).

In 1997, in an effort to enhance water flow into the Everglades and Florida Bay, an approximately 8 km section of the levee on the C-111 canal was removed, allowing unrestricted sheet flow through the adjacent marsh. The goal of this study was to evaluate the movement of selected agricultural pesticides from the upland agricultural area in South Florida into the Everglades and Florida Bay

Correspondence to: M. H. Fulton

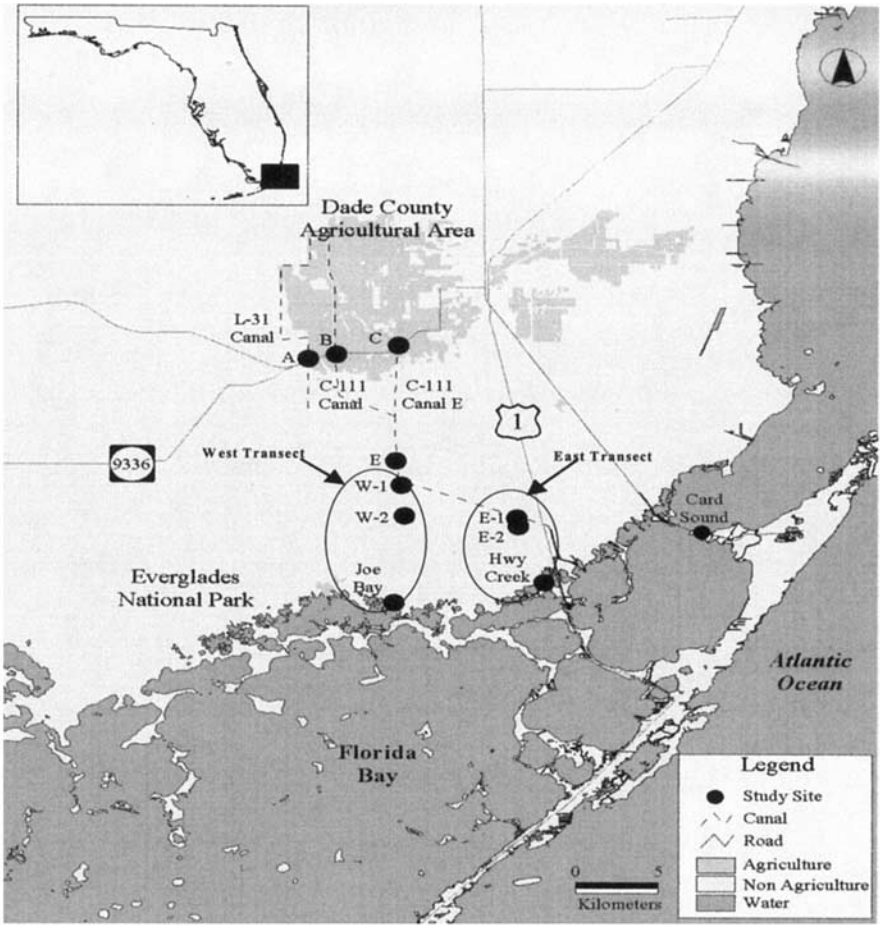

Figure 1. Map of study area and sample locations.

to examine the influence of season and rainfall on the movement and distribution of these pesticides.

MATERIALS AND METHODS

Study sites included three locations on each of two transects in the Everglades Panhandle south of the C-111 canal terminating in Florida Bay (Figure 1). The eastern transect stations were designated as E-1, E-2 and Highway Creek while the western transect stations were W-1, W-2 and Joe Bay. Water samples were also collected at a series of upstream canal sites located on the L-31 (station A), C-111 (stations B and E) and C-111E (station C) canals. Station C is located directly adjacent to a large agricultural field while Station E is located approximately 8 km downstream from Station C and receives water from both the main C-111 canal and C-111E. Sites W-1 and E-1 are located approximately 10 and 14 km downstream from Site C, respectively. The terminal site of the western

transect (Joe Bay) is located approximately 9 km to the south of W-1 while the terminal site of the eastern transect (Highway Creek) is located about 5 km southeast of E-1. A reference marine site in Card Sound was sampled to provide background pesticide concentrations at a site away from the influence of the C-111 canal system. Sampling was conducted three times per year (beginning of the wet season-June; end of the wet season-October; and the dry season-February) from October, 1998 to October, 2000. Typically, these intensive sampling events were conducted over a 5 d period.

Water samples (~4L) were collected daily at each site using a combination of grab sampling and autosampling techniques. Autosamplers were programmed to sample in the composite mode and a single composite sample was collected. Samples were processed and analyzed based on the method of Lehotay et al. (1998). Samples were poured into 20 L stainless steel pressurized containers. An acetone solution containing the internal standards atrazine-d_5 and endosulfan-d_4 was added. Samples were filtered under pressure through a 90 mm glass fiber filter (Gelman GF/F). Pesticides were extracted from the water by passing through a 0.5 g ENV+ solid-phase extraction cartridge that was pre-eluted with the extraction solvents. Following extraction, cartridges and filters were frozen until they were eluted and analyzed (within two months). Cartridges were eluted using ~20 mL of acetone followed by ~25 mL dichloromethane. Endosulfan I (detection limit (DL) = 0.23 ng/L), endosulfan II (DL = 0.07 ng/L), endosulfan sulfate (DL = 0.03 ng/L) and chlorpyrifos (DL = 0.04 ng/L) were quantified by dual column capillary gas chromatography (GC) with electron capture detection (ECD). Atrazine (DL = 2.2 ng/L), diazinon (DL = 2.9 ng/L) and metolachlor (DL = 6.7 ng/L) were quantified from the sample extracts using GC ion trap mass spectrometry (GC/MS). The detection limits were derived through a statistical treatment of background noise in field blank extracts. The standard deviation of the integrated noise was multiplied by the appropriate Student's-t factor to estimate detection limits. Appropriate quality control measures were taken, including the analysis of field blanks and matrix spikes. Total endosulfan is reported as the sum of endosulfan I, endosulfan II, and endosulfan sulfate.

RESULTS AND DISCUSSION

Pesticide concentrations measured in South Florida surface waters varied both spatially and temporally. Endosulfan, chlorpyrifos, metolachlor and atrazine followed a noticeable gradient in pesticide contamination, with the highest concentrations occurring in the upper canal sites and levels generally decreasing toward the bay sites (Figures 2-5). Maximum concentrations of each pesticide detected over the course of the study were 1345 ng/L total endosulfan, 23 ng/L chlorpyrifos, 337 ng/L atrazine, and 34 ng/L metolachlor. Diazinon was not detected in any of the water samples. Endosulfan, chlorpyrifos and metolachlor concentrations were typically highest during the dry season (February; Figures 2-4) whereas atrazine concentrations were generally most elevated in June, during the onset of the wet season (Figure 5).

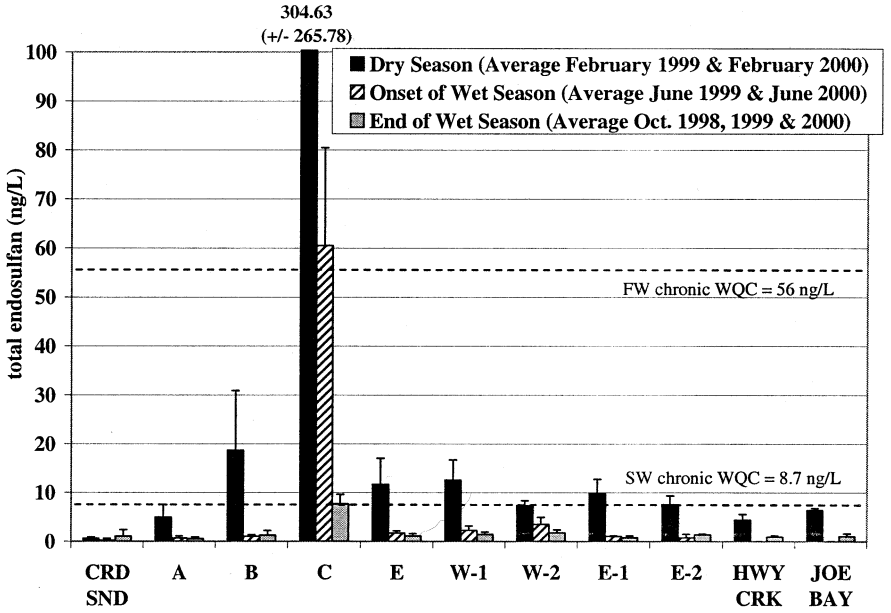

Figure 2. Average total endosulfan concentrations (± S.D.) measured at each site.

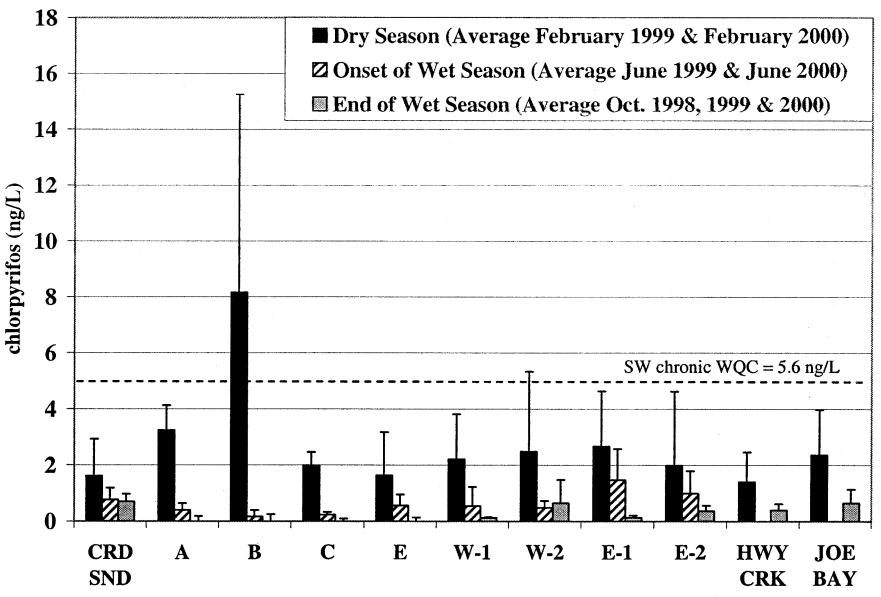

Figure 3. Average chlorpyrifos concentrations (± S.D.) measured at each site.

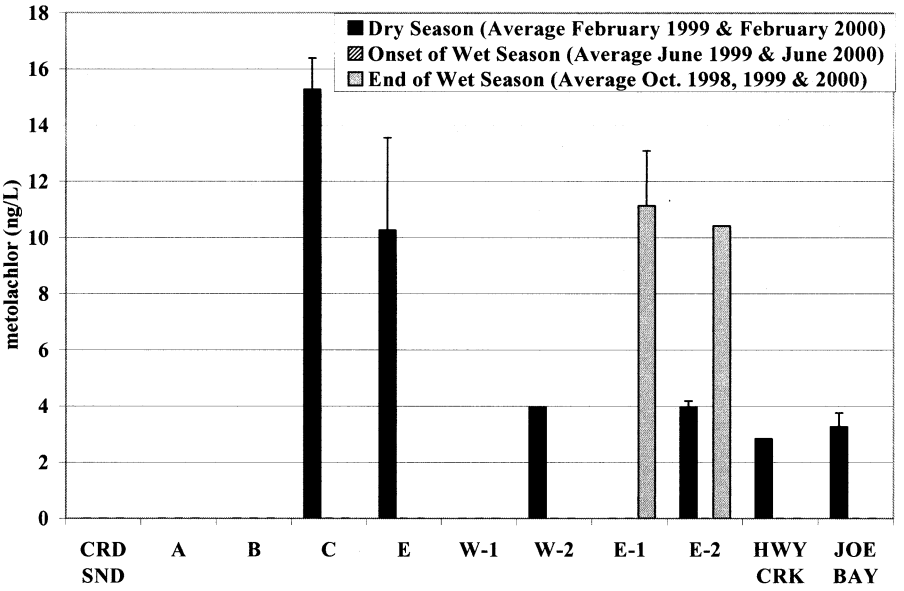

Figure 4. Average metolachlor concentrations (± S.D.) measured at each site.

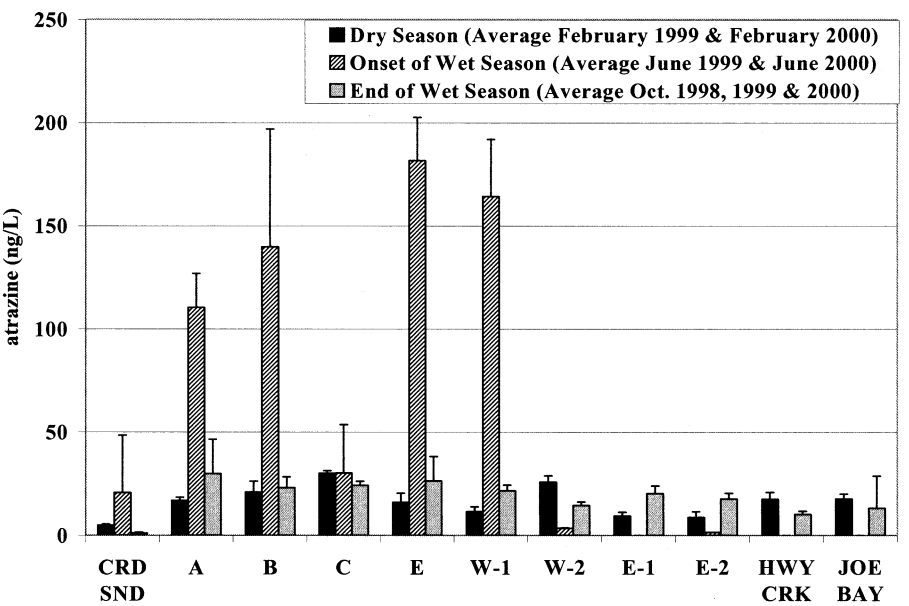

Figure 5. Average atrazine concentrations (± S.D.) measured at each site.

February coincides with the time of highest agricultural pesticide use in the study area. February is also considered to be the dry season for this region, when pesticide runoff from fields should be reduced. However, since the agricultural operations in the area utilize intensive spray irrigation, the potential for runoff in the dry season still exists. Rainfall amounts (range for all sites) for the study period were 0.25-12.19 cm in the onset of the wet season-June, 0-1.5 cm in the end of wet season-October, and 0-1.0 cm in the dry season-February.

Endosulfan was present at every sampling location during every sampling event. Endosulfan concentrations were always highest at Site C, which was located directly adjacent to an agricultural field on the C-111E canal. Endosulfan concentrations declined rapidly at sites downstream from Site C during all seasons (Figure 2). For example, the mean dry season concentration at Site C was ~ 300 ng/L while that at Site E (located 8 km downstream) was ~ 11 ng/L. This represents a 96% reduction in total endosulfan concentration. In general, endosulfan concentrations were further reduced downstream and across the marsh gradient stations (W-1, W-2, Joe Bay, E-1, E-2, Highway Creek). The rapid reduction in endosulfan concentrations observed downstream (Site E) is likely due to the fact that the S-178 structure at Site C was rarely open; reducing the movement of contaminants from this site to downstream locations (Miles and Pfeuffer, 1997). The ratio of the parent isomers (endosulfan I and II) to the primary degradation product (endosulfan sulfate) was much higher at Site C than at the downstream stations, implicating the upstream agricultural activities as the primary source of endosulfan in the estuarine waters. Mean total endosulfan concentrations at Site C always exceeded freshwater acute (220 ng/L) and chronic (56 ng/L) WQC during February. Endosulfan concentrations at the Bay sites (Highway Creek and Joe Bay) were also highest during February, further suggesting a relationship between endosulfan concentrations at the Bay sites and upstream endosulfan inputs into the C-111E (Site C) canal. During February of 2000, mean endosulfan concentrations at the Joe Bay site were above the saltwater WQC (8.7 ng/L), and were approximately equal to the saltwater WQC at the Highway Creek site.

Chlorpyrifos concentrations were highest at Sites A (located on the L-31 canal) and B (located on the C-111 canal). Chlorpyrifos concentrations were similar at all remaining sites, including Site C (Figure 3). The differences in the distribution patterns for endosulfan and chlorpyrifos suggest that the agricultural activities directly adjacent to Site C represent the dominant source for endosulfan at this site and the downstream stations. Chlorpyrifos concentrations however, appear unrelated to the agricultural operations adjacent to Site C. Concentrations at Sites A and B appear to be related to upstream inputs while chlorpyrifos concentrations at the remaining sites appear to reflect a more diffuse environmental source; possibly atmospheric deposition (McConnell et al. 1997). None of the chlorpyrifos concentrations measured at any of the freshwater sites exceeded WQC; however, one sample collected from Joe Bay during February of 1999 was slightly above the saltwater chronic WQC of 5.6 ng/L. Chlorpyrifos was detected in 83% of the samples collected from the Joe Bay site during the study period.

Metolachlor was detected sporadically at the freshwater stations and was only detected in the bay sites during February 2000 (Figure 4). Metolachlor concentrations were well below the toxicity threshold for the most sensitive aquatic species tested (96 h EC_{50} of 70 μg/L for an aquatic macrophyte (Fairchild et al., 1998)). Highest concentrations were measured at Site C during the growing season (February).

Concentrations of the triazine herbicide atrazine were highest at Sites A, B, E, and W-1 (Figure 5). Since atrazine concentrations were higher at Site B on the main C-111 canal and Site E downstream from both Sites B and C, these findings suggest a dominant atrazine source upstream from Site B. Maximum measured atrazine concentrations (337 ng/L at Site E) were below levels (10-20 μg/L) that might be expected to cause ecological impacts in freshwater or saltwater systems (Solomon et al., 1996).

This study demonstrated detectable levels of agricultural pesticides year-round in the surface waters of the C-111 canal and Florida Bay. While detectable quantities of atrazine, metolachlor and chlorpyrifos were also found, the primary chemical of concern in this area is endosulfan. Endosulfan is extremely toxic to many marine organisms (96 h LC_{50} values ranging from 0.04 – 1.3 μg/L for larval shrimp and juvenile fish; Mayer, 1987). Local agricultural activities adjacent to the C-111E canal provide significant inputs of endosulfan into the receiving waters. Endosulfan concentrations measured in the canal were high enough to be both an acute and chronic hazard for local fish and invertebrate populations. Peak endosulfan concentrations at estuarine stations located approximately 20 km down-gradient did appear to be correlated with peak inputs at Site C and were, on occasion, above the chronic WQC for saltwater. These findings suggest that endosulfan inputs may be sufficient to be a potential chronic risk for sensitive species and life history stages of estuarine vertebrates and invertebrates. These down-gradient concerns are likely to be magnified when gates on the water control structure at Site C are opened, and particularly during the winter-dry season, when endosulfan concentrations are highest in the C-111 canal. Given the heavy usage of endosulfan in South Florida, and the detection of toxicologically significant levels in surface waters, careful management of freshwater flows is recommended to assure that water diverted into the Everglades and Florida Bay is environmentally safe.

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