

Pesticide Occurrence in Selected South Florida Canals and Biscayne Bay during High Agricultural Activity

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Climate and soil conditions in South Florida along with an extensive canal system facilitate movement of agricultural pesticides into surface waters. In a two-year study (2002–2004) of the currently used pesticides in South Florida, atrazine, endosulfan, metolachlor, chlorpyrifos, and chlorothalonil were the most frequently detected in the canals and in Biscayne Bay, with average concentrations of 16, 11, 9.0, 2.6, and 6.0 ng/L, respectively. Concentrations of atrazine and chlorpyrifos were highest near corn production. Chlorothalonil and endosulfan concentrations were highest near vegetable production, with no clear trend for metolachlor, which is used on multiple crops. Concentration data were used to calculate an aquatic life hazard potential for the planting period (November) versus the harvest period (March). This analysis indicated that a higher hazard potential occurs during harvest, primarily from the use of endosulfan. These data will also serve to document canal conditions prior to implementation of the Comprehensive Everglades Restoration Plan (CERP).

KEYWORDS: Pesticide; agrochemical; atrazine; endosulfan; chlorothalonil; chlorpyrifos; metolachlor; hazard potential; South Florida; Everglades; Biscayne Bay; Comprehensive Everglades Restoration Plan (CERP)

INTRODUCTION

The South Florida region is a unique combination of highly productive agricultural lands; residential development from the expanding, Miami urban area; critical terrestrial and aquatic wildlife habitat contained in the Everglades and Biscayne and Florida Bays; and 1000 miles of engineered canal structures for flood control (1). 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 (2, 3). Wildlife populations within the Everglades watershed, especially those of wading birds, have declined since the construction of flood control structures in the 1950s, which efficiently move stormwater into canals rather than allowing for natural flows into the Everglades.

Recently, the Comprehensive Everglades Restoration Plan (CERP) was authorized and implementation initiated as part of the Federal Water Resources Development Act of 2000 (4). At an estimated cost of \$15.8 billion over the next 40 years, water from new reservoirs, wetland-based treatment areas, and underground aquifer storage wells will be redirected into the Everglades to bring the hydrologic system closer to historical levels (1). As part of this plan, stormwater will be retained in an attempt to reduce excess nitrogen, phosphorus, and agrochemicals prior to entering the Everglades. However, only limited information is available on pesticide residues present in these canal waters and their potential toxicity to aquatic organisms. Previous studies in the area around the C-111 canal have shown that exposure to the insecticide endosulfan may be causing chronic toxic effects in copepods, clams, and oysters (5), and organophosphate insecticides were suspected of causing acetylcholinesterase inhibition in grass shrimp collected in two South Florida canals (6).

The climate and hydrologic conditions in South Florida are different from those of other major agricultural centers in the United States, thereby limiting the usefulness of previous pesticide fate research data. These conditions include calcareous

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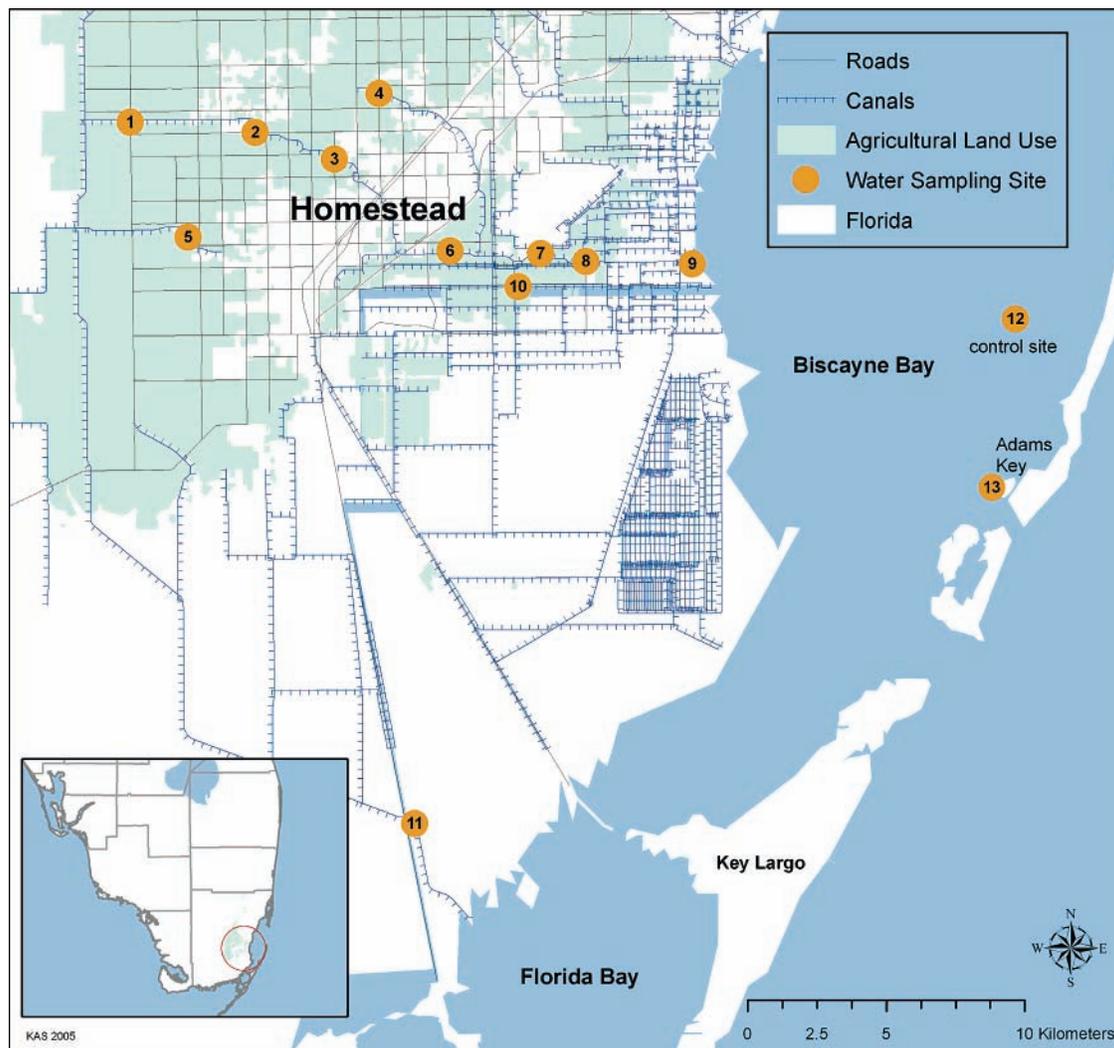


Figure 1. Water sample collection sites in South Florida.

soils, frequent rainfall, high humidity, high temperatures, and a highly transmissive aquifer system. Soils in South Florida's Dade County range from peat and muck in the northwest to medium and fine sand in the central and southeast (7). In some areas soils consist of porous limestone, and cultivated soils represent a thin layer of low-moisture naturally weathered or mechanically crushed limerock (8). The surficial aquifer, called the Biscayne aquifer, has a high transmissivity of $\sim 28\,000\text{ m}^2/\text{day}$ in central and eastern Dade County with a high potential for leaching both nutrients and pesticides. Other areas in the west have lower transmissivities of $\sim 7000\text{ m}^2/\text{day}$ (7). The low water-holding capacity of some South Florida soils and high temperatures also necessitate frequent irrigation of crops, thereby enhancing leaching of agrochemicals. During the dry season, groundwater discharge feeds the canal system, and canal flows feed into Biscayne and Florida Bays and into the Everglades, where sensitive aquatic biota may be affected.

The goals of this study were to determine the types and concentrations of currently used pesticides present in water from several South Florida canals and Biscayne Bay, to examine the impact of land use categories as sources of particular chemicals, and to provide a preliminary assessment of the potential toxicity of the most frequently detected pesticides. To meet these goals, samples were collected during time periods of highest agricultural activity from October to March. This current work was performed prior to the implementation of the CERP. Therefore, these data can be used as a benchmark for comparison with

future measurements after major changes in water quality management in the area. These data will also be useful for regulators, extension specialists, and decision-makers in designing and modifying agricultural management practices to better protect sensitive ecosystems.

MATERIALS AND METHODS

Water Sampling. Thirteen water collection sites were selected in the Homestead, FL, area of South Miami–Dade County, 35 miles south of Miami (Figure 1). Water samples were collected during seven sampling trips on November 13–15, 2002; January 7–9, 2003; March 10–12, 2003; November 10–12, 2003; January 4–6, 2004; February 15–17, 2004; and March 25–27, 2004. A total of 91 water samples were collected (3 samples were lost during the processing steps).

Water was collected from a depth of 1 m using an 1100 GPH submersible marine pump (Rule Industries, Gloucester, MA). The pump was connected directly to two, in-line, high-pressure, stainless steel filter holders (Millipore, Bedford, MA) housing a $2.7\ \mu\text{m}$ pore size GF/D glass fiber prefilter (Whatman, Middlesex, U.K.) and a $0.7\ \mu\text{m}$ pore size GF/F filter (Whatman), respectively, with Teflon and stainless steel tubing. Using a 2 L graduated cylinder, exactly 10 L of filtered sample water was collected in a precleaned, 20 L, stainless steel canister (Pepsi, Hyattsville, MD) with an airtight lid and stored on ice until processing ($\leq 12\text{ h}$). Water quality measurements including pH, salinity, conductivity, dissolved oxygen, and water temperature were recorded at each sample site (Table 1) using a precalibrated, multifunctional, portable probe (model 556 MPS, YSI Environmental, Yellow Springs, OH).

Table 1. Average Measurements of Water Temperature, pH, Dissolved Oxygen, and Salinity between November 2002 and March 2004 ($n = 6$)^a for 13 Sampling Sites in South Florida

site	coordinates	temp (°C)	pH	salinity TDS (g/L)	dissolved oxygen (mg/L)
1	25° 31' 1.54" N 80° 32' 34.05" W	23.7 ± 1.6	6.9 ± 0.6	0.4 ± 0.1	3.2 ± 1.0
2	25° 30' 49.03" N 80° 29' 52.73" W	23.8 ± 1.4	7.1 ± 0.6	0.4 ± 0.1	3.5 ± 1.0
3	25° 30' 17.19" N 80° 28' 10.10" W	23.6 ± 1.9	7.3 ± 0.6	0.4 ± 0.1	5.8 ± 1.0
4	25° 31' 33.85" N 80° 27' 12.50" W	24.3 ± 0.9	7.1 ± 0.5	0.5 ± 0.1	3.6 ± 0.5
5	25° 28' 46.25" N 80° 31' 19.53" W	24.1 ± 2.0	7.0 ± 0.7	0.4 ± 0.1	2.9 ± 1.1
6	25° 28' 28.79" N 80° 25' 41.54" W	24.1 ± 1.3	7.3 ± 0.6	0.5 ± 0.1	5.4 ± 2.1
7	25° 28' 25.18" N 80° 23' 44.71" W	23.9 ± 1.5	7.5 ± 0.5	0.4 ± 0.1	5.4 ± 0.7
8	25° 28' 16.01" N 80° 22' 46.31" W	24.2 ± 1.4	7.3 ± 0.7	0.6 ± 0.2	5.8 ± 1.1
9	25° 28' 12.42" N 80° 20' 28.76" W	23.0 ± 2.7	7.5 ± 0.8	24 ± 10	6.0 ± 1.1
10	25° 27' 46.56" N 80° 24' 13.72" W	23.5 ± 1.9	7.3 ± 0.8	0.4 ± 0.1	5.7 ± 2.0
11	25° 17' 16.54" N 80° 26' 30.18" W	23.6 ± 1.9	7.5 ± 0.9	0.6 ± 0.4	6.2 ± 1.0
12	25° 27' 5.71" N 80° 13' 30.95" W	22.3 ± 3.4	7.8 ± 0.6	37 ± 7.7	6.3 ± 1.6
13	25° 23' 48.54" N 80° 14' 3.01" W	22.3 ± 3.2	7.9 ± 0.5	38 ± 7.3	6.1 ± 1.5

^a Data from March 2003 are unavailable.

Sample collection equipment was cleaned between stations by pumping several liters of a 1:1 organic-free water/methanol mixture through the entire filtration system to avoid cross-contamination. Field blanks were collected by pumping 10 L of organic-free water through the sampling and filtration system into a clean stainless steel canister to evaluate the equipment for contamination. Replicate samples were collected at sites 11 and 12 with each set of samples for use as matrix spike recovery samples. Two field blanks and two matrix spike recovery samples were collected on each of the seven sampling trips. Duplicate samples were also collected periodically from randomly selected sites to evaluate the precision of the method.

Extraction Method. Prior to extraction, all samples were fortified with an extraction efficiency surrogate standard, diazinon [diethyl-*d*₁₀] (Cambridge Isotope Laboratories, Andover, MA). Each 10 L sample was then drawn by vacuum through a solid-phase extraction (SPE) cartridge containing 500 mg of hyper-cross-linked styrene-divinylbenzene copolymer, ENV+ (Argonaut, Inc., Redwood City, CA), extraction resin. After extraction, ENV+ cartridges were dried with high-purity nitrogen gas and eluted with chromatographic grade solvents (6 mL of dichloromethane followed by 9 mL of 3:1 acetone/acetonitrile) (Fisher Scientific, Fair Lawn, NJ). The 15 mL extract was concentrated to a final volume of 0.5 mL under high-purity nitrogen. Internal standards, atrazine [ethylamine-*d*₅] (Cambridge Isotope Laboratories) and PCB-204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl) (AccuStandard, New Haven CT), were added to the final sample extracts and standards.

Analytical Methodology. Sample extracts were analyzed by gas chromatography-mass spectrometry (GC-MS). Target compounds, instrument mode, ions of interest, minimum detection limits (MDL), detected concentration ranges, percent detection, and spike recovery values are listed in **Table 2**. Full-scan spectra were acquired using a Varian 3800 GC coupled to a Saturn 2000 Ion Trap MS equipped with a DB-17MS (Agilent Technologies, Inc., Palo Alto, CA) 30 m, 0.25

mm i.d., 0.25 μ m in film thickness capillary column. The GC inlet was operated in splitless mode. The carrier gas was ultrahigh-purity helium at a constant flow rate of 1.0 mL/min controlled by a constant flow-pressure program. Operational temperatures were as follows: injection port, 260 °C; oven, 130 °C (1 min), ramped at 5°C/min to 280 °C; interface, 280 °C; and ion trap, 220 °C. The ion trap MS was operated in electron impact (EI)-selective ion storage (SIS) mode, scanning for ions with masses of 70–450.

Better sensitivity for halogenated analytes was achieved using a Hewlett-Packard (HP) 5890 GC coupled to a HP 5989A quadrupole MS in the negative chemical ionization (NCI) mode. The GC inlet was operated in splitless mode with a column identical to that used on the Varian GC-MS. The carrier gas was ultrahigh-purity helium at a constant flow rate of 1.12 mL/min controlled by a constant flow-pressure program. Operational temperatures were as follows: injection port, 280 °C; oven, 130 °C (1 min), ramped at 6 °C/min to 280 °C; interface, 280 °C; source, 150 °C; quadrupole, 100 °C. NCI reagent gas was methane, and the source pressure was 1.6 Torr.

The instruments were calibrated using a mixture of analytes with at least five different concentrations across the expected sample range. Calibration curves were repeated for every 20 sample injections. Sample results were quantified using the internal standard method. In laboratory experiments utilizing fortified organic carbon free water, the extraction method has proven to be efficient at isolating our target compounds (9). Using this same extraction method (10), >80% ($n = 11$) of spiked pesticides were recovered from 10 L water samples. Results for spike recovery samples collected on each sampling trip ($n = 14$) averaged >80% recovery for the majority of target compounds listed in **Table 2**. Aldrin, fipronil, and *p,p'*-DDE were slightly lower (76, 79, and 70%, respectively), but were still within the acceptable range set forth by EPA standard methods (11). Field blank samples ($n = 14$) were devoid of compounds at levels greater than our minimal detection limits. Recovery of the surrogate compound diazinon [diethyl-*d*₁₀] was measured in all sample extracts, blanks, spikes, and replicates with acceptable values (>82 ± 7%, $n = 114$).

RESULTS

In South Florida, pesticides are used intensively for crop protection, mosquito control, and landscape management. U.S. Department of Agriculture (USDA) surveys indicate that in the 16 county region served by the South Florida Water Management District, agriculture accounts for the application of nearly 20 million pounds of pesticide active ingredients (12). Agricultural production in the region is extremely heterogeneous, ranging from numerous vegetable crops, that is, bush and pole beans, tomatoes, squash, okra, peppers, to sweet corn, cabbage, eggplant, potatoes, strawberries, herbs, and ornamental plants (13). This area is sometimes referred to as the nation's "Salad Bowl" (14).

The 13 sites in the study area were chosen because of the high agricultural activity and close proximity to sensitive ecosystems of both Everglades National Park and Biscayne National Park (**Figure 1**). Sites 5 and 10 are located in areas with high agricultural land usage, and site 11 is located to the south, on the C-111 canal, which drains much of the northern agricultural area. Eight sites (1–4 and 6–9) occur along the Mowry canal, which runs through mixed-use areas (agricultural and urban) and empties ultimately into Biscayne Bay. Site 12, located in the middle of Biscayne Bay, is the control site with minimal direct land influence. Site 13 is adjacent to Adams Key, a small remote island that is part of the National Park system.

A narrow range of temperatures was observed in the canals and Biscayne Bay (22–24 °C) over the course of the study, although sampling was not carried out during the summer months (**Table 1**). Water from the canal sites was essentially fresh, with salinity values close to zero except for site 9, at the mouth of the Mowry canal (mean salinity = 24), and higher

Table 2. Quantification Parameters, Quality Assurance Results, and Percent Detection Results Summary for Water Samples Collected in South Florida

target compound	instrument mode ^a	mass ions monitored (<i>m/z</i>)	MDL ^b (ng/L)	recovery (%) <i>n</i> = 14 ^c	concn range ^d (ng/L)	detection (%) <i>n</i> = 88
acetochlor	EI	162, 174, 223, 225	1.5	92 ± 10		0
alachlor	EI	160, 188	1.4	91 ± 9		0
aldrin	NCI	237, 330, 332	0.2	76 ± 20	0.38–1.1	6
ametryn	EI	212, 227, 229	1.4	88 ± 18		0
atrazine	EI	173, 200, 215	0.9	105 ± 13	0.90–108	91
chlorothalonil	NCI	264, 266, 268	0.2	84 ± 33	0.27–14	82
α-chlordane	NCI	408, 410, 412	0.2	87 ± 15	0.21–3.1	9
γ-chlordane	NCI	408, 410, 412	0.2	87 ± 14	0.40–1.1	2
chlorpyrifos	NCI	214, 313, 315	0.2	124 ± 36	0.20–58	66
cyanazine	EI	198, 212, 225	1.8	89 ± 11		0
<i>p,p</i> -DDD	NCI	248, 250, 320	0.2	86 ± 40	0.95–9.0	6
<i>p,p</i> -DDE	NCI	281, 316, 318, 320	0.2	70 ± 12	0.4–2.4	7
<i>p,p</i> -DDT	NCI	71, 248, 318	0.2	86 ± 29	2.1–10	5
diazinon	NCI	169, 303	1.0	107 ± 37	1.0–7.1	19
<i>p,p</i> -dicofol	EI	111, 139	1.5	83 ± 8		0
dieldrin	NCI	237, 346, 380	0.2	230 ± 121	0.20–4.0	16
α-endosulfan	NCI	406, 408, 410	0.2	113 ± 21	0.21–54	81
β-endosulfan	NCI	404, 406, 408	0.2	124 ± 23	0.20–16	75
endosulfan sulfate	NCI	384, 386, 388	0.2	120 ± 15	0.22–28	91
ethion	EI	203, 231, 338	1.5	87 ± 7		0
ethoprop	EI	127, 158	1.5	92 ± 13		0
fipronil	NCI	331, 384, 400	0.2	79 ± 15	0.60–8.6	6
α-HCH	NCI	71, 255, 257	0.2	90 ± 23	0.23–1.3	11
γ-HCH	NCI	71, 255, 257	0.2	95 ± 17	0.20–5.0	6
heptachlor	NCI	266, 300, 232	0.2	102 ± 38	0.28–7.0	16
heptachlor epoxide	NCI	237, 282, 318, 388	0.2	107 ± 13	0.31–1.5	5
malathion	NCI	157, 172	1.6	121 ± 36	6.0	1
metalaxyl	EI	190, 192, 206	1.6	93 ± 15		0
methoxychlor	EI	114, 152, 228, 344	1.8	91 ± 11		0
metolachlor	EI	162, 238	1.0	96 ± 9	1.1–86	89
metribuzin	EI	198	1.5	87 ± 11	0.30–78	8
mirex	NCI	334, 370, 404, 439	0.2	80 ± 20	0.25–1.9	3
<i>cis</i> -nonachlor	NCI	442, 444, 446	0.2	91 ± 15		0
<i>trans</i> -nonachlor	NCI	442, 444, 446	0.2	88 ± 18		0
oxychlordane	NCI	316, 350, 352, 424	0.2	89 ± 18	0.6–0.7	2
pendamethalin	EI	252	1.6	90 ± 9		0
phorate	EI	121, 231	1.5	85 ± 11		0
simazine	EI	138, 186, 201	1.6	101 ± 12	1.7–16	15
trifluralin	NCI	305, 335, 336	0.2	80 ± 27	0.23–3.6	9
diazinon diethyl- <i>d</i> ₁₀	NCI	179	<i>e</i>	91 ± 5	<i>e</i>	100
atrazine ethylamine- <i>d</i> ₅	EI	205, 220	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
PCB-204	NCI	394, 428, 430	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>

^a EI, electron impact; NCI, negative chemical ionization. ^b MDL, method detection limit. ^c Percent spike recovery from surface water samples. ^d Concentration range represents results for samples where levels were above the minimum detection limit. ^e Diazinon-*d*₁₀ was used as an extraction efficiency surrogate in each sample, and MDL values were not determined. ^f Atrazine-*d*₅ and PCB-204 were used as internal standards, and MDL values were not determined.

salinity values at the Biscayne Bay sites (mean salinity values = 37–38). The pH of the canals ranged from 6.3 furthest inland to 8.2 at the more saline Mowry Canal mouth (site 9). As expected, the pH of the Biscayne Bay sites was ~7.8. Average dissolved oxygen measurements were lowest at the most inland sites and ranged from 37 to 84%.

Summary of Pesticide Concentrations. Target analytes included the pesticides most frequently used in this area (excluding methyl bromide and copper hydroxide) and some persistent, banned pesticides. Results for the 88 water samples analyzed during the growing seasons from 2002 to 2004 indicated that several target compounds (acetochlor, alachlor, ametryn, cyanazine, *p,p*-dicofol, ethion, ethoprop, metalaxyl, methoxychlor, *cis*- and *trans*-nonachlor, pendamethalin, and phorate) were never present at concentration levels above the limits of detection (Table 2). Fifteen of the target compounds (aldrin, α-chlordane, γ-chlordane, *p,p*-DDD, *p,p*-DDE, *p,p*-DDT, fipronil, α-HCH, γ-HCH, heptachlor epoxide, malathion, metribuzin, mirex, and trifluralin) were present at detectable concentrations in fewer than 11% of the 88 samples analyzed. Diazinon, dieldrin, heptachlor, and simazine were present in

fewer than 19% of the water samples. Atrazine, metolachlor, chlorothalonil, chlorpyrifos, and total endosulfan (α-endosulfan + β-endosulfan + endosulfan sulfate) were detected in greater than 66% of all samples analyzed. These chemicals will be used in the remaining sections to assess trends, sources, and potential toxicity to aquatic organisms.

Atrazine had the highest observed concentration of any of the target analytes at 108 ng/L, well below the EPA maximum allowable contamination level (MCL) (3000 ng/L). Total endosulfans had a maximum concentration of 98 ng/L followed by metolachlor at 86 ng/L, chlorpyrifos (58 ng/L), and chlorothalonil (14 ng/L). No MCL values exist for the other compounds of interest; however, the World Health Organization has published acceptable daily intake (ADI) levels for chlorpyrifos, chlorothalonil, and endosulfan of 0.01, 0.03, and 0.006 mg/kg/day, respectively (15). For comparison, Table 3 lists the LC₅₀ (96 h) for freshwater fish. The mean and median concentrations for these five chemicals were all below 20 ng/L (Figure 2). Examining concentration results for these five chemicals across all stations reveals a large amount of variability

Table 3. Comparison of Pesticide Concentration Measurements in South Florida Canals from 1992 to 2004 with Corresponding Toxicity Data

study reference	dates	concn range (ng/L)				
		atrazine	chlorpyrifos	chlorothalonil	endosulfans	metolachlor
Pfeuffer and Rand (16)	1992–2001	9.9–400	— ^a	—	103–748	—
Scott et al. (5) ^b	1993–1997	1.0–48	0.1–2.42	0.4–2.70	0.2–477	— ^c
Key et al. (6)	Dec 1999	7.9–29.4	5.2	—	—	2.5–119
Pfeuffer and Matson (17–20)	Nov 2002–May 2003	10–56	—	—	12–168	—
current study	Nov 2002–March 2004	0.90–108	0.20–58	0.27–14	0.22–17	1.1–86
		toxicity data (ng/L)				
LC ₅₀ (96 h) for rainbow trout		5.3e ⁶ (27)	1.8e ^{3d} (28)	4.23e ⁶ (24)	800 (29)	3.9e ^{6d} (30)
hazard rating coefficient (25, 26)		0.09	7.18	2.60	42.8	0.11

^a No data reported above the limit of detection values. ^b Lower range limit is equal to reported method detection limits. ^c Compound not measured in this study. ^d LC₅₀ (96 h) for freshwater fish; species not specified.

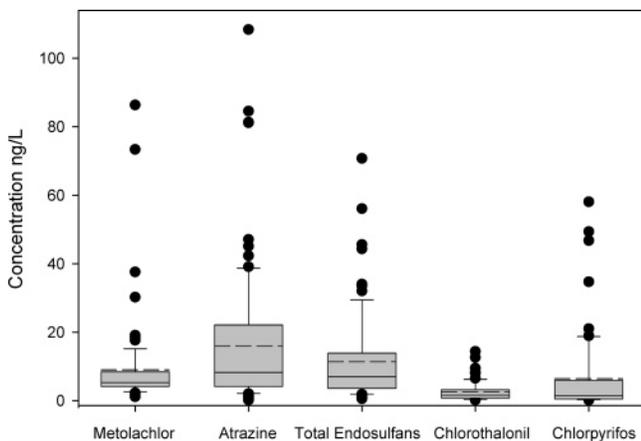


Figure 2. Data summary of atrazine, chlorpyrifos, chlorothalonil, total endosulfans, and metolachlor for all 88 samples analyzed over the course of the study. Medians and means are indicated by the solid and dashed lines, respectively. Boxes indicate the 25th–75th percentiles, whiskers show the 10th and 90th percentiles, and outliers are indicated by dots.

with many outliers above the 90th percentile, suggesting a recent, local pesticide application.

DISCUSSION

Concentration results from this study compare well with results from other researchers (Table 3). As part of the South Florida Water Management District's (SFWMD) water quality monitoring program (16–20), grab samples have been collected quarterly since 1992 at 34 sites and analyzed for nearly 70 pesticides. The sample volumes were not listed in the reports nor were specific details of the analytical methods. Results for the SFWMD study sites in South Dade County indicated the presence of atrazine and endosulfans with concentrations ranging from 9.9 to 400 ng/L and from 103 to 748 ng/L, respectively, during the time period from 1992 to 2001 (16). Lower concentrations were found during 2002 and 2003, 10–56 and 12–168 ng/L, respectively (17–20), suggesting a possible decrease in application of these two chemicals in the area. Neither chlorpyrifos, chlorothalonil, nor metolachlor was detected during the entire monitoring period. The maximum concentrations for atrazine and endosulfans for the 2002 and 2003 SFWMD study fall within a factor of ~2 of those observed in our study.

In a multiyear study of the C-111 canal system of South Florida from 1993 to 1997, observed concentrations of atrazine, chlorpyrifos, chlorothalonil, and endosulfans in water samples ranged from 1 to 48 ng/L, from 0.1 to 2.4 ng/L, from 0.4 to 2.7 ng/L, and from 0.2 to 477 ng/L, respectively (5). A comparison

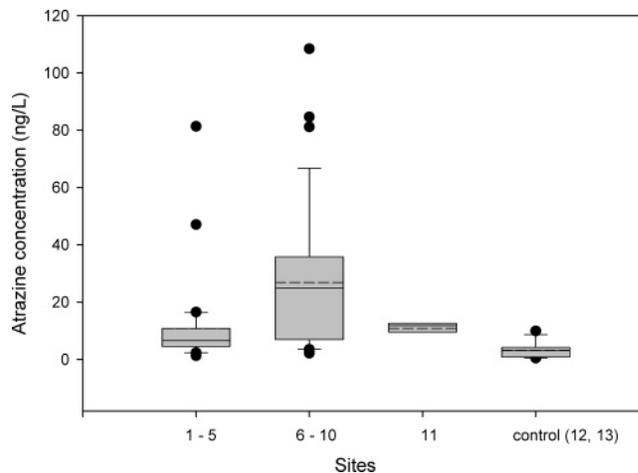


Figure 3. Spatial dependence of atrazine concentrations using all sampling events. Corn is principally grown near sites 6–10. Medians and means are indicated by the solid and dashed lines, respectively. Boxes indicate the 25th–75th percentiles, whiskers show the 10th and 90th percentiles, and outliers are indicated by dots.

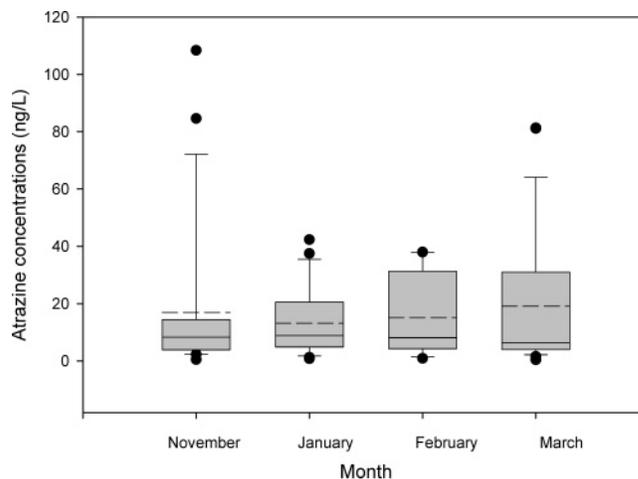


Figure 4. Temporal variation in atrazine concentration using data from all sites. Medians and means are indicated by the solid and dashed lines, respectively. Boxes indicate the 25th–75th percentiles, whiskers show the 10th and 90th percentiles, and outliers are indicated by dots.

of this SFWMD study with the current study also suggests that the use of endosulfan may have decreased since the late 1990s. This observation is supported by data from a 2002 Miami–Dade County agricultural land retention study conducted by the University of Florida's Agricultural Market Research Center (21), which states that tomato acreage and production have

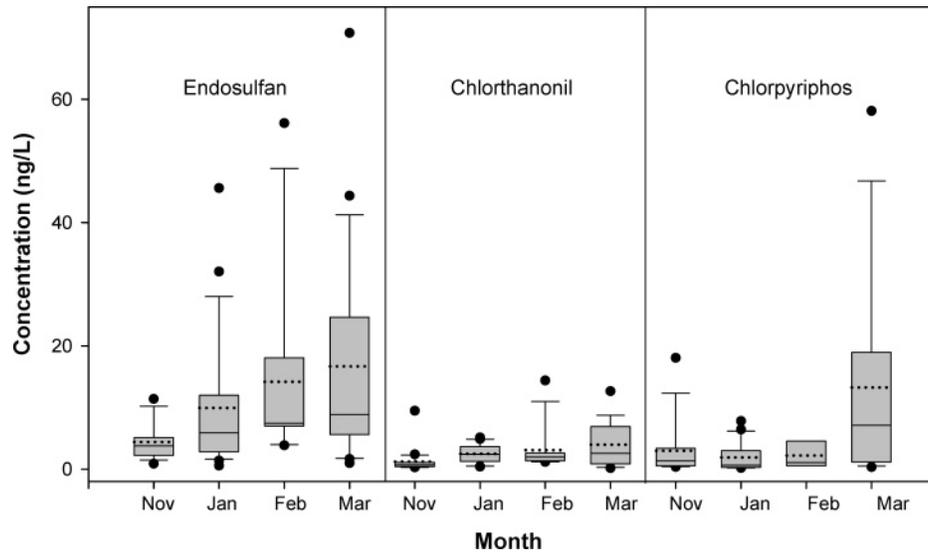


Figure 5. Temporal variation of endosulfan, chlorthalonil, and chlorpyrifos concentrations using data from all locations. Medians and means are indicated by the solid and dotted lines, respectively. Boxes indicate the 25th–75th percentiles, whiskers show the 10th and 90th percentiles, and outliers are indicated by dots.

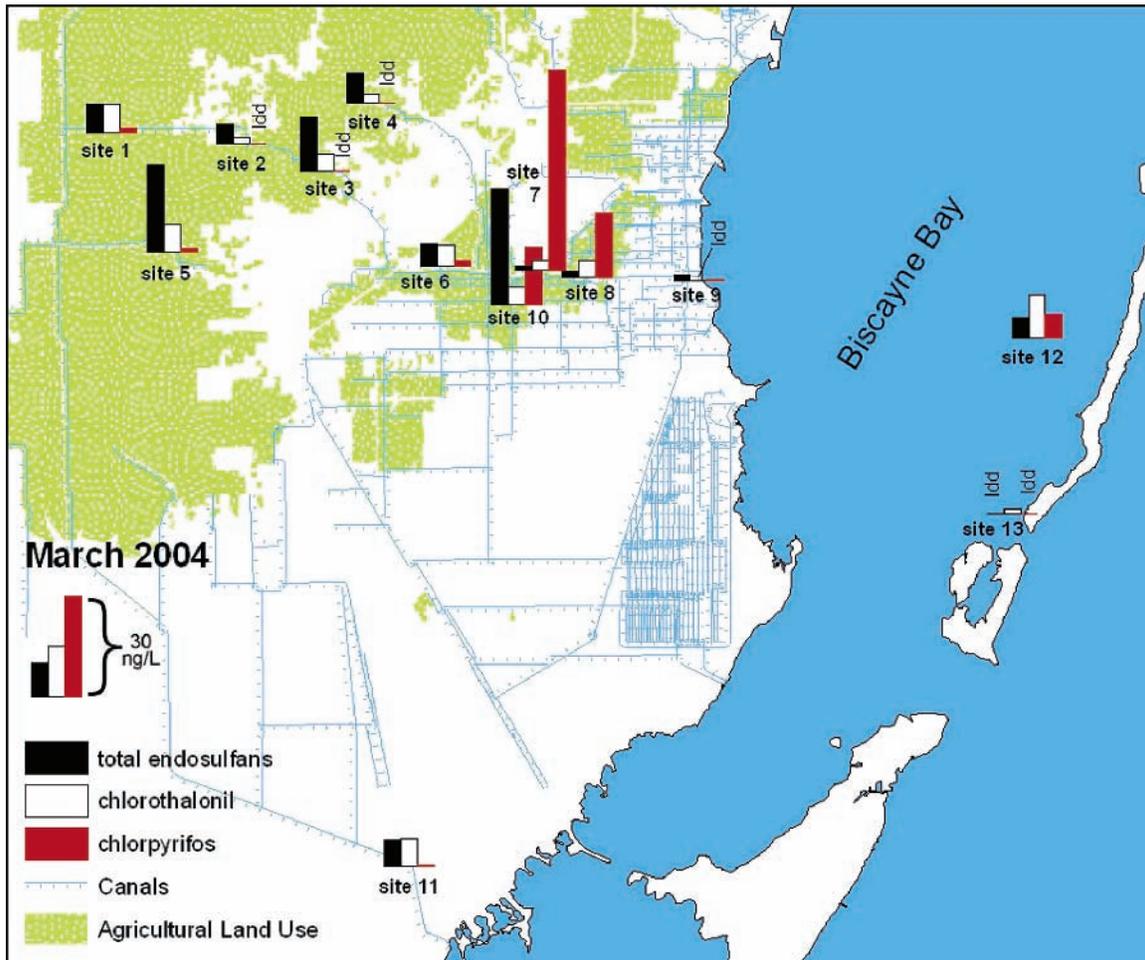


Figure 6. Spatial variation of the insecticides endosulfan, chlorthalonil, and chlorpyrifos for March 2003.

declined over the past 20 years at a rate of ~ 230 ha per year. Specifically, the area of land devoted to tomato production dropped from nearly 4500 ha per season in the mid-1980s to ~ 1500 ha in 2001 (21). Assuming the recommended manufacturer application rates for endosulfan were followed, estimated usage on tomatoes has declined by a factor of 3 (nearly 6000 kg of active ingredient/growing season) in South Florida.

Lower concentrations of chlorpyrifos and chlorthalonil observed by Scott et al. indicate that their stations, generally south of this study area, may have been further removed from sources. In an NOAA–USDA cooperative study conducted in December 1999, atrazine, chlorpyrifos, and metolachlor were measured in water samples from drainage canals of South Florida ranging in concentration from 7.9 to 29.4 ng/L, from

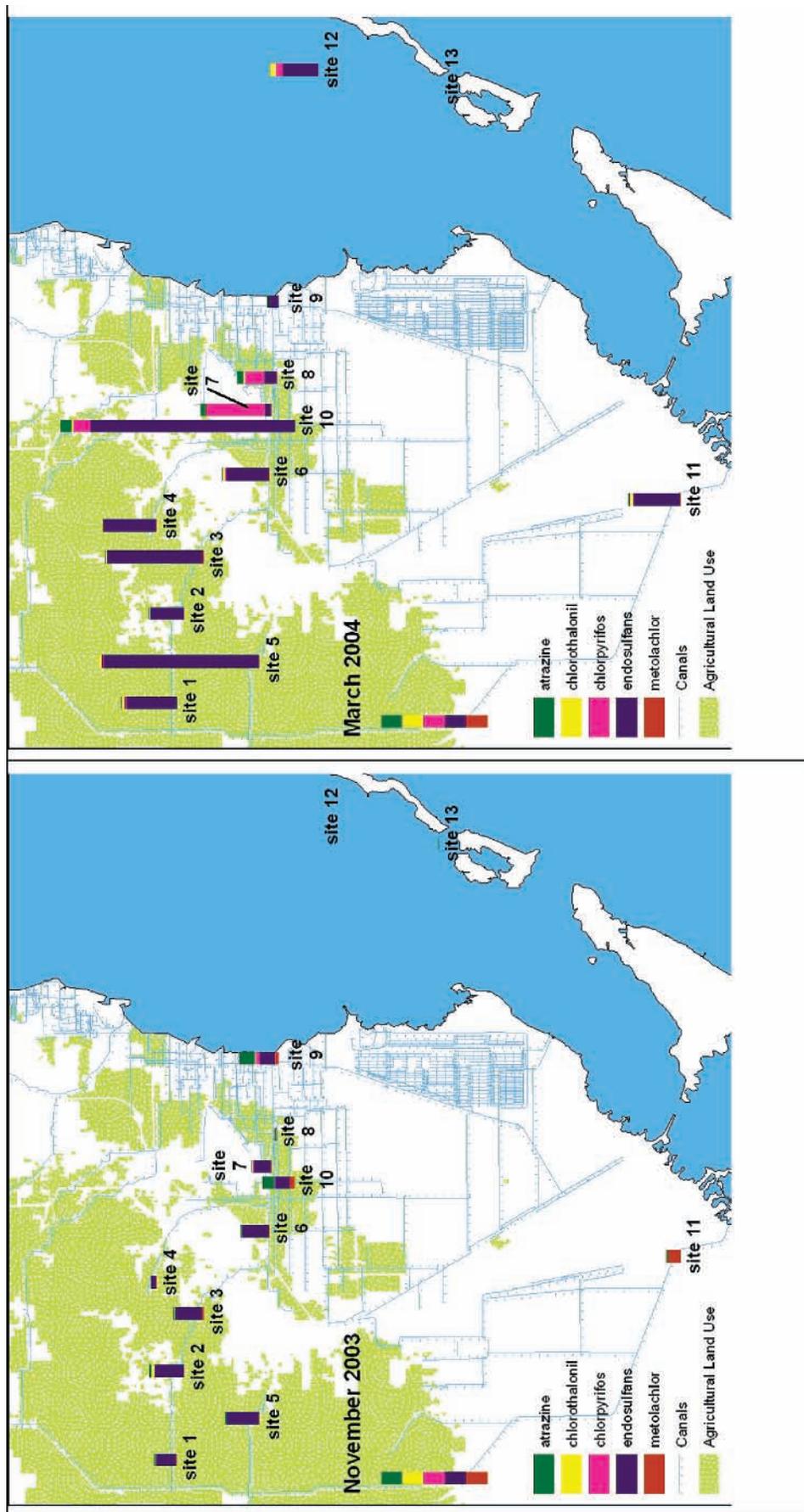


Figure 7. Comparison of spatial cumulative hazard potentials for November (planting; left) versus March (harvest; right).

Table 4. Major South Florida Crops and Usage of the Five Most Commonly Detected Pesticides in This Study^a

crop	herbicides		insecticides		fungicide
	atrazine	metolachlor	chlorpyrifos	endosulfan	chlorothalonil
bean, snap		X		X	X
cabbage		X	X	X	X
corn	X	X	X		
cucumber		X		X	X
pepper		X		X	X
squash		X		X	X
tomato		X		X	X
watermelon				X	X

^a Pesticide use data from USDA-NASS (21).

5.2 to 11 ng/L, and from 2.5 to 119 ng/L, respectively (6). With the exception of metolachlor, these concentrations are generally lower than those found in the current study, but they represent only one sample collection time point at multiple sites. Although chlorothalonil and endosulfan were not detected in the Key et al. study, this is likely due to higher detection limits for these chemicals using an ion-trap GC-MS instrument. Limits of detection in the Key et al. study were 3.1 ng/L for chlorothalonil, 9.4 ng/L for α -endosulfan, and 18.8 ng/L for β -endosulfan and endosulfan sulfate as compared to a 0.2 ng/L MDL for these compounds in the current study (Table 2).

Spatial and Temporal Distribution of Pesticides. Corn is generally grown east of site 6, and higher concentrations of atrazine, a corn herbicide, were generally observed at site 6 on each of the seven sampling trips with the exception of March 2003, when atrazine concentrations of 81 and 47 ng/L were found at sites 1 and 5, respectively. Atrazine was found in lower concentrations at sites 1–5 where vegetables (tomato, pepper, snap bean, and squash) were the predominant crops. Ornamentals are produced near sites 6–8 in addition to corn. Very little atrazine was found in the remote locations or at the control site (Figure 3). The lowest concentrations of atrazine were observed during the middle part of the growing season, whereas the highest concentrations were observed in the beginning, although mean concentration in each month did not vary (Figure 4). Not surprisingly, a similar analysis of metolachlor concentrations revealed no discernible trend. This indicates either remote or multiple sources in the region as this product is used on all of the major crops in this area except watermelon (Table 4) (22).

Temperatures and humidity begin to rise toward the end of the growing season, increasing insect and fungal pressures. As a result, increased insecticide and fungicide (e.g. chlorothalonil, chlorpyrifos, and endosulfan) use would be expected to protect the harvest. Figure 5 indicates that chlorpyrifos and endosulfan concentrations were highest in the latter part of the growing season. Furthermore, chlorpyrifos is primarily used on corn, whereas endosulfan is used on other vegetables. This spatial difference is shown in Figure 6, where higher concentrations of chlorpyrifos are observed at sites 10 and eastward, and, concomitantly, endosulfan is more likely to be found west of site 10. Although chlorothalonil was frequently detected (82%), no discernible trends were observed. This may be a function of its fairly rapid degradation rate in soil, $t_{1/2} = 0.5$ –3.5 days (23), following application as compared to the reported hydrolysis half-life of 49 days (24).

Evaluation of Potential Risk to Aquatic Organisms. South Florida is a critical wildlife area as well as being an intensely cultivated region. A preliminary evaluation of potential risk to aquatic organisms was conducted using measured pesticide concentration data. A hazard rating system was developed that

uses subcoefficients calculated for a number of pesticides to rank the potential impact of the pesticides on aquatic systems (25, 26). The coefficients are a function of toxicity of the pesticide to fish and crustaceans, bioconcentration potential represented by the octanol–water partition coefficient (K_{ow}), and soil half-life (Table 3). Endosulfan has by far the highest coefficient value at 42.8, followed by chlorpyrifos at 7.18. The remaining three compounds display much lower potential risk (<2.6). A relative comparison of potential toxicity from various pesticides may be obtained by multiplying the coefficient by the observed concentration.

The coefficients were multiplied by observed concentrations for each of the five pesticides at each site at the beginning and end of the growing season. These values were used to estimate the potential risk associated with pesticide use. The cumulative values for each site are shown in Figure 7. Although atrazine was present at the highest concentrations, endosulfan presents a much larger hazard to aquatic organisms. The toxicity contribution from endosulfan increases in magnitude toward the end of the growing season with heavier insecticide usage and higher observed concentrations (March 2004). Chlorpyrifos also contributes to the potential toxicity in March at sites 7, 8, and 10. Thus, these data suggest the largest threat to aquatic organisms is not during planting but just prior to harvest.

Although this exercise provides some insight into the potential toxicity issues associated with pesticide use, more detailed studies to determine the length of exposure to high-risk pesticides, that is, continuous monitoring at key sites, not just grab samples, would provide a more complete picture. Risk calculations could also be carried out for other ecosystem components such as phytoplankton, submerged aquatic vegetation, wading birds, and aquatic mammals. In addition, the hazard potential calculations used here do not address synergistic interactions between pesticides, which may enhance the toxicity of certain pesticides, nor do they address the potential impact on the life cycle of particular species. Pesticide fate studies under soil, climate, and surface water conditions found in South Florida combined with advanced toxicological studies are required to accurately assess the risk from commonly used pesticides. Specially designed agricultural management strategies may be required to mitigate the off-site movement of pesticides and to protect especially sensitive species in the region.

ACKNOWLEDGMENT

We acknowledge the dedicated contributions from field technician Michael S. Gutierrez and collection volunteer Sally Mitchell.

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Received for review December 28, 2004. Revised manuscript received March 31, 2005. Accepted April 1, 2005. Mention of specific products or supplies is for identification and does not imply endorsement by the U.S. Department of Agriculture to the exclusion of other suitable products or suppliers.

JF047803G