PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

MARCH 2008 SAMPLING EVENT

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Pesticide Monitoring Project Report
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Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water and sediment samples were collected March 17 to March 20, 2008, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides ametryn, atrazine, bromacil, diuron, hexazinone, metolachlor, metribuzin, norflurazon, and simazine, along with the insecticide/degradates atrazine desethyl, atrazine desisopropyl, alpha endosulfan, and beta endosulfan, were detected in one or more of these surface water samples. No harmful impacts are expected from the detected pesticides.

The herbicide ametryn and the insecticides/degradates chlordane, DDD, DDE, DDT, alpha endosulfan, beta endosulfan, endosulfan sulfate, and one PCB compound were found in the sediment at several locations. The chlordane and three DDE compound sediment concentrations were of a magnitude considered to have a harmful effect to freshwater sediment-dwelling organisms. No harmful impacts are expected from the other detected pesticides.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods

The SFWMD pesticide monitoring network includes stations designated in the Everglades Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction Project (non-ECP) permit. The canals and marshes depicted in Figure 1 are protected as Florida Administrative Code (FAC) 62-302 Class III (fishable and swimmable) waters, while Lake Okeechobee and a segment of the Caloosahatchee River are protected as a Class I drinking water supply. Water Conservation Area 1 (WCA-1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Seventy-three pesticides and degradation products were analyzed in samples from 35 of the network 37 sites (Figure 1). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp.

To evaluate the potential impacts on aquatic life, the observed concentration is compared to the appropriate criterion outlined in FAC 62-302.530. If a pesticide compound is not specifically listed, acute and chronic toxicity criterion are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, using the lowest technical grade EC_{50} or LC_{50} reported in the summarized literature for the species significant to the indigenous aquatic community (FAC 62-302.200). Each pesticide's description and possible uses and sites of application described herein are taken from Hartley and Kidd (1987). Sediment concentrations are compared to freshwater sediment quality assessment guidelines (MacDonald Environmental Sciences, LTD., and United States Geological Survey, 2003). A value below the threshold effects concentration (TEC) should not have a harmful effect on sediment-dwelling organisms. Values above the probable effect concentration (PEC) demonstrate that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed. This summary covers surface water and sediment samples collected from March 17 to March 20, 2008.

Results

At least one pesticide was detected in surface water at 31 of the 35 sites and in sediment at 13 of the 30 sites. Modifications to the non-ECP permit changed the requirement for sampling at S142 and S38B to only during discharge or flow events. For this sampling event, no sample was obtained due to no discharge at the time of sample collection. Sediment samples are not collected at GORDYRD, CR33.5T, S333, S356, and TAMBR105. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All of these compounds have previously been detected in this monitoring program.

The sediment DDE concentrations at S2, S3, and S5A were of a magnitude considered to represent detrimental effects to sediment-dwelling organisms in freshwater sediments. The S5A sediment concentration of chlordane was also at the detrimental effects level. All other detected concentrations in the surface water and sediment were below any effect level.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long-term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

<u>Ametryn</u>: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 micrograms per liter (µg/L) (Verschueren, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.011 to 0.075 µg/L. Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates. Ametryn was detected in the sediment at S3 and S4 at 4.3 and 11 micrograms per kilogram (µg/Kg), respectively. However, no sediment guidelines have been developed for ametryn.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 μg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003a). The atrazine surface water concentrations found in this sampling event at 26 of the 35 sampling locations, ranged from 0.012 to 2.6 μg/L. Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates. Atrazine was not detected in the sediment.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of groundwater discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at S79 (0.12 μg/L). Using these criteria, this observed concentration should not have an acute or chronic detrimental impact on fish. Bromacil was not detected in the sediment.

Chlordane: Chlordane is a chlorinated hydrocarbon previously used as a contact insecticide. Environmental fate and toxicity data in Tables 4 and 5 indicate that chlordane (1) is moderately toxic to mammals and highly toxic to fish; and (2) has the potential for significant bioconcentration. Freshwater sediment quality assessment guidelines identified a TEC of 3.2 μg/Kg and PEC of 18 μg/Kg for chlordane. The detected sediment residue at S5A (45 μg/Kg) is at a concentration where harmful effects to sediment-dwelling organisms are frequently or always observed. While the use of this compound has been discontinued in recent years, its persistence and tendency to accumulate in sediments makes chlordane a compound of concern. Chlordane was not detected in the surface water.

DDD, DDE, DDT: DDE is an abbreviation of **d**ichloro**d**iphenyldichloro**e**thylene [2, 2-bis (4-chlorophenyl)-1, 1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichloro**d**iphenyl**t**richloroethane), a popular insecticide for which the U.S. EPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichloro**d**iphenyl**d**ichloroethane), and the high K_{oc} of these compounds account for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioconcentration factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

The DDD sediment concentrations detected range from 22 to 25 μg/Kg. Any concentration which would fall below the TEC (4.9 μg/Kg) should not impact sediment dwelling organisms while concentrations above the PEC (28 μg/Kg), frequently or always have the possibility for impacting sediment-dwelling organisms. The sediment concentrations detected were between the TEC and PEC. These concentrations may have the possibility for harmful effects on freshwater sediment-dwelling organisms. DDD was not detected in the surface water.

The TEC is 3.2 μg/Kg and the PEC is 31 μg/Kg for DDE in freshwater sediments. The concentrations of DDE detected at S2 (79 μg/Kg), S3 (93 μg/Kg), and S5A (110 μg/Kg) exceeded the PEC and frequently or always have the possibility for impacting sediment-dwelling organisms. DDE was not detected in the surface water.

The DDT concentrations detected at S331, S3, and S5A exceed the TEC (4.2 μg/Kg) but are less than the PEC (63 μg/Kg). It is uncertain if this level will have the possibility for impacting sediment-dwelling freshwater organisms. No DDT was detected in the surface water.

Diuron: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48-hour LC_{50} of 1.4 mg/L for water fleas and a 96-hour LC_{50} of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 μg/L (Verschueren, 1983). The highest surface water concentration of diuron found during this sampling event was 0.66 μg/L at C25S99 (Table 2). Using these criteria, this concentration should not have an acute, harmful impact on fish, aquatic invertebrates, or algae. Diuron was not detected in the sediment.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, alpha (α) and beta (β). Endosulfan is highly toxic to mammals, with an acute oral LD_{50} for rats of 70 mg/Kg (Table 4). The Soil Conservation Service (SCS) rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 4). Beta endosulfan's water solubility and Henry's law constant (1.91 x 10^{-5} atm – m^3/mole) (Lyman, et al. 1990) indicate volatilization may be significant in shallow waters. The bioconcentration factors indicate a low to moderate degree of accumulation in aquatic organisms (Table 4). Endosulfan (α and/or β) was detected in the surface water at S177 and S332DX in the South Miami-Dade County farming area (Table 2). However, none of the concentrations exceeded the FAC 62-302 criteria of 0.056 μg/L. Alpha and beta endosulfan were detected in the sediment at S178. However, a sediment quality assessment guideline has not been developed.

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's law constant (9.63 x 10^{-8} atm – m^3/mole) (Lyman, et al. 1990) indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Table 4). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). Endosulfan sulfate was detected in the sediment at S178 (30 μg/Kg). However, no sediment quality assessment guideline has been developed for endosulfan sulfate. No endosulfan was detected in the surface water.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/L for *Daphnia magna* (U.S. EPA, 1988). The highest surface water concentration detected in this sampling event at CR33.5T (0.13 μg/L) should not have an acute impact on fish or aquatic invertebrates. No hexazinone was detected in the sediment.

Metolachlor: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in Tables 4 and 5 indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The only surface water concentration found in this sampling event (0.084 μg/L at S3) is over three orders of magnitude below the calculated chronic toxicity level. Using these criteria, this observed level should not have a harmful effect on fish or aquatic invertebrates. No metolachlor was detected in the sediment.

Metribuzin: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in Tables 4 and 5 indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The highest concentration of metribuzin detected was 0.054 µg/L (S5A). Using these criteria, this surface water concentration should not have an acute impact on fish or aquatic invertebrates. No metribuzin was detected in the sediment.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC_{50} for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.035 to 0.37 µg/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these observed concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates. Norflurazon was not detected in the sediment.

PCBs: Polychlorinated biphenyls (PCBs) is the generic term for a group of 209 congeners that contain a varying number of substituted chlorine atoms on one or both of the biphenyl rings. PCB-1254 is a commercial grade mixture containing 54 percent chlorine by weight. Production of PCBs was banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily sorbed to suspended sediments due to the very low solubility in water (Callahan et al., 1979). The tendency of PCBs for adsorption increases with the degree of chlorination and with the organic content of the adsorbent. While the production ban, phase out of uses, and stringent spill clean-up requirements have significantly reduced environmental loadings in recent years, the persistence and tendency to accumulate in sediment and bioaccumulate in fish, make this class of organochlorine compounds especially problematic. The TEC and PEC are 60 µg/Kg and 680 µg/Kg, respectively, for total PCBs. The sediment residue detected at S7 (300 µg/Kg) is greater than the TEC but less than the PEC. This concentration has a possibility for impacting freshwater sediment-dwelling organisms. None of the PCB congeners were detected in the surface water.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 µg/L (Verschueren, 1983). Aquatic invertebrate LC_{50} toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. EPA, 1984). The highest surface water concentration of simazine detected at S79 (0.11 µg/L) was below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

Quality Assurance Evaluation

Replicate samples were collected at sites S177 and S4. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No pesticide analytes were detected in the equipment blanks performed at C25S99, S18C, S331, S65E, TAMBR105, FECSR78, S235, S7, and G94D. All collected samples were shipped and all bottles were received with the exception of the chlorophenoxy herbicide bottles from GORDYRD and S18C. Both bottles were broken in transit.

Glossary

Bioconcentration Factor: The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

EC_{50}: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

Henry's law constant (H): Relates the concentration of a compound in the gas phase to its concentration in the liquid phase. The constant is calculated from the formula: $H = P_{vp}/S$ where P_{vp} is pressure in atmospheres and S is solubility in moles/meter^3 for a compound.

K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

LC_{50}: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LD_{50}: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

Method Detection Limit (MDLs): The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.

Practical Quantitation Limit (PQLs): The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.

Probable Effects Concentration (PEC): The probable effects concentration is intended to identify concentrations above which harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

Soil or water half-life: The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

Threshold Effects Concentration (TEC): The threshold effects concentration is intended to identify concentrations below which harmful effects to freshwater sediment-dwelling organisms are unlikely to be observed.

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Figure 1. South Florida Water Management District Pesticide Monitoring Network.

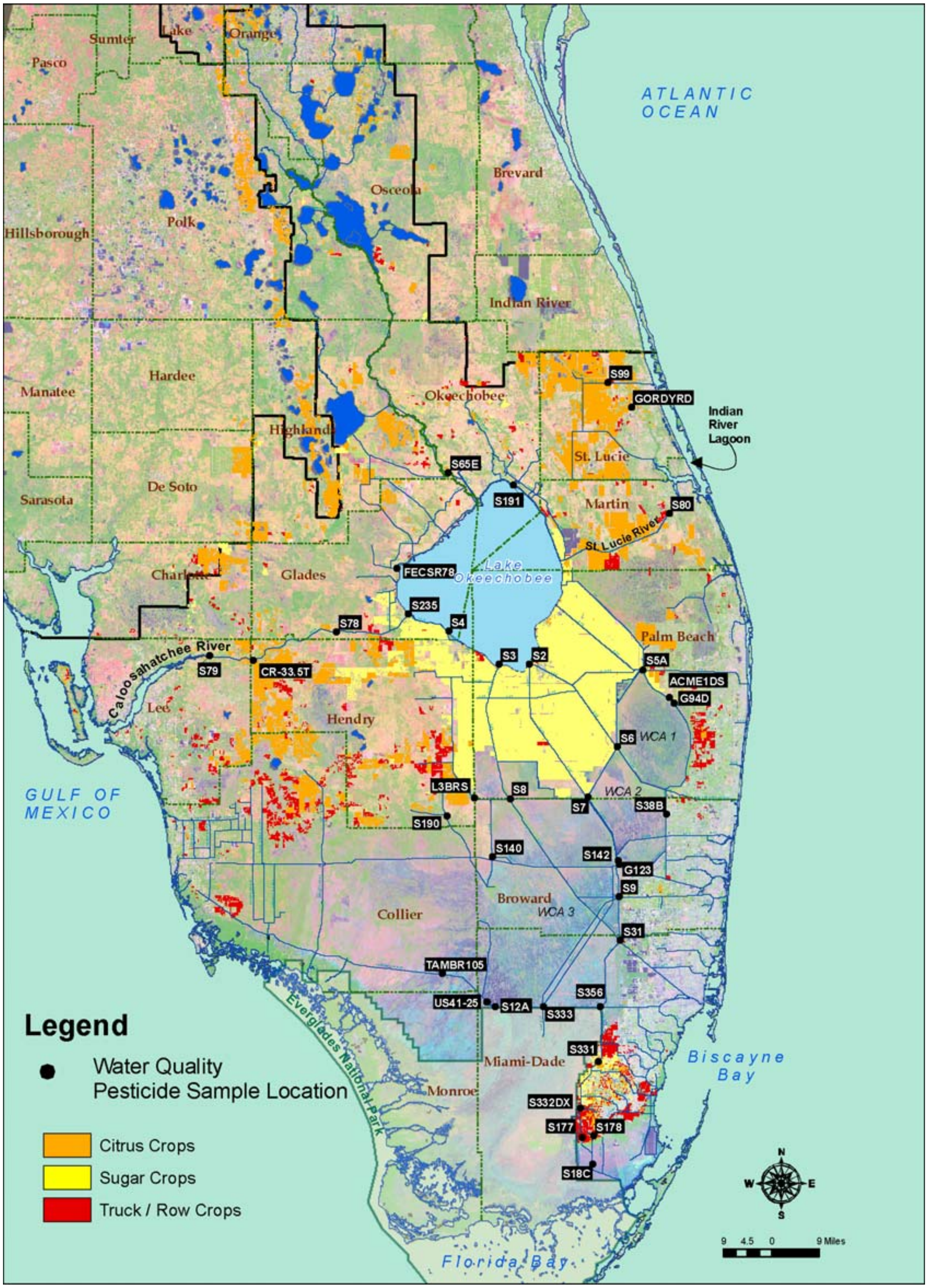

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for March 2008 sampling event.

Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)	Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)
2,4-D	0.2 - 0.6	8.7 - 220	endrin aldehyde	0.0042 - 0.02	0.89 - 30
2,4,5-T	0.2 - 0.6	8.7 - 220	ethion	0.0095 - 0.048	2.2 - 76
2,4,5-TP (silvex)	0.2 - 0.6	8.7 - 220	ethoprop	0.0095 - 0.048	2.2 - 76
acifluorfen	0.2 - 0.6	8.7 - 220	fenamiphos (nemacur)	0.038 - 0.19	8.9 - 300
alachlor	0.057 - 0.28	27 - 880	fonofos (dyfonate)	0.0095 - 0.048	4.5 - 150
aldrin	0.0019 - 0.0092	0.45 - 15	heptachlor	0.0023 - 0.011	0.45 - 15
ametryn	0.0095 - 0.048	2.2 - 76	heptachlor epoxide	0.0019 - 0.0092	0.45 - 15
atrazine	0.0095 - 0.2	2.2 - 76	hexazinone	0.019 - 0.092	2.2 - 76
atrazine desethyl	0.0095 - 0.048	N/A	imidacloprid	0.2 - 0.6	N/A
atrazine desisopropyl	0.0095 - 0.092	N/A	linuron	0.2 - 0.6	8.8 - 200
azinphos methyl (guthion)	0.029 - 0.14	6.7 - 220	malathion	0.029 - 0.14	6.7 - 220
α-BHC (alpha)	0.0021 - 0.01	0.45 - 15	metalaxyl	0.048 - 0.23	N/A
β-BHC (beta)	0.0032 - 0.016	0.45 - 15	methamidophos	N/A	22 - 760
δ-BHC (delta)	0.0019 - 0.0092	0.89 - 30	methoxychlor	0.0095 - 0.048	2.2 - 76
γ-BHC (gamma) (lindane)	0.0019 - 0.0092	0.45 - 15	metolachlor	0.057 - 0.35	22 - 760
bromacil	0.048 - 0.23	8.9 - 300	metribuzin	0.019 - 0.092	4.5 - 150
butylate	0.019 - 0.092	N/A	mevinphos	0.057 - 0.28	8.9 - 300
carbophenothion (trithion)	0.015 - 0.076	2.2 - 76	mirex	0.011 - 0.056	1.8 - 60
chlordane	0.019 - 0.092	6.7 - 220	monocrotophos (azodrin)	N/A	22 - 760
chlorothalonil	0.015 - 0.076	2.2 - 76	naled	0.076 - 0.37	36 - 1200
chlorpyrifos ethyl	0.0095 - 0.048	2.2 - 76	norflurazon	0.019 - 0.092	4.5 - 150
chlorpyrifos methyl	0.019 - 0.092	4.5 - 150	parathion ethyl	0.019 - 0.092	6.7 - 220
cypermethrin	0.019 - 0.092	2.2 - 76	parathion methyl	0.019 - 0.092	6.7 - 220
DDD-P,P'	0.0046 - 0.022	0.89 - 30	PCB-1016	0.019 - 0.092	13 - 440
DDE-P,P'	0.0038 - 0.019	0.89 - 30	PCB-1221	0.019 - 0.092	8.9 - 300
DDT-P,P'	0.0057 - 0.028	1.3 - 44	PCB-1232	0.019 - 0.092	20 - 680
demeton	0.029 - 0.14	45 - 1500	PCB-1242	0.019 - 0.092	13 - 440
diazinon	0.019 - 0.092	4.5 - 150	PCB-1248	0.019 - 0.092	8.9 - 300
dicofol (kelthane)	0.042 - 0.2	6.7 - 220	PCB-1254	0.019 - 0.092	8.9 - 300
dieldrin	0.0019 - 0.0092	0.45 - 15	PCB-1260	0.019 - 0.092	13 - 440
disulfoton	0.019 - 0.092	4.5 - 150	permethrin	0.015 - 0.076	2.7 - 88
diuron	0.2 - 0.6	8.8 - 200	phorate	0.0095 - 0.048	2.2 - 76
α-endosulfan (alpha)	0.0038 - 0.019	0.45 - 15	prometryn	0.019 - 0.092	6.7 - 220
β-endosulfan (beta)	0.0038 - 0.019	0.45 - 19	prometon	0.019 - 0.092	N/A
endosulfan sulfate	0.0046 - 0.022	0.89 - 30	simazine	0.0095 - 0.048	2.2 - 76
endrin	0.0095 - 0.048	2.2 - 76	toxaphene	0.095 - 0.48	33 - 1100
			trifluralin	0.0076 - 0.037	1.8 - 60

N/A - not analyzed

Table 2. Summary of pesticide residues (µg/L) above the method detection limit found in surface water samples collected by SFWMD in March 2008.

Date	Site	Flow	ametryn	atrazine	atrazine desethyl	atrazine desisopropyl	bromacil	diuron	endosulfan (alpha)	endosulfan (beta)	hexazinone	metolachlor	metribuzin	norflurazon	simazine	Number of compounds detected at site
3/17/2008	C25S99	N	-	-	-	-	-	0.66	-	-	-	-	-	0.28	-	2
	GORDYRD	Y	-	-	-	-	-	-	-	-	-	-	-	0.27	-	1
	S177	N	-	0.14 *	-	-	-	-	0.0081 I *	-	-	-	-	-	-	2
	S178	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S18C	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S191	N	-	0.28	0.018 I	-	0.052 I	-	-	-	-	-	-	-	-	3
	S331	N	0.031 I	0.96	0.047	0.012 I	-	-	-	-	-	-	-	-	-	4
	S332DX	N	0.018 I	0.81	0.035 I	0.0096 I	-	-	0.018	0.0062 I	-	-	-	-	-	6
	S65E	N	-	0.041	-	-	0.053 I	-	-	-	-	-	-	-	-	2
	S80	N	-	0.13	0.012 I	-	-	-	-	-	-	-	-	0.27	-	3
3/18/2008	FECSR78	N	-	0.018 I	-	-	-	-	-	-	0.066 I	-	-	-	-	2
	G123	N	-	0.037 I	-	-	-	-	-	-	-	-	-	-	-	1
	S12A	N	0.011 I	0.19	0.011 I	-	-	-	-	-	-	-	-	-	-	3
	S2	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S3	N	0.037 I	1.1	0.040	-	-	-	-	-	-	0.084 I	-	-	-	4
	S31	N	0.036 I	0.90	0.048	-	-	-	-	-	-	-	-	-	0.013 I	4
	S333	Y	0.031 I	0.82	0.047	-	-	-	-	-	-	-	-	-	0.016 I	4
	S356	N	0.032 I	0.53	0.035 I	-	-	-	-	-	-	-	-	-	0.014 I	4
	S4	N	0.045 *	2.7 *	0.061 *	-	-	-	-	-	0.070 I *	-	-	-	-	4
	S9	N	-	0.012 I	-	-	-	-	-	-	-	-	-	-	-	1
	TAMBR105	Y	-	0.013 I	-	-	-	-	-	-	-	-	-	-	-	1
	US41-25	N	-	0.028 I	-	-	-	-	-	-	-	-	-	-	-	1
3/19/2008	CR33.5T	Y	-	-	0.010 I	-	0.10 I	0.44 I	-	-	0.13	-	-	0.37	0.090	6
	L3BRS	N	0.040	2.0	0.11	-	-	-	-	-	-	-	0.023 I	-	-	4
	S140	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S190	N	-	-	-	-	-	-	-	-	-	-	-	0.066 I	-	1
	S235	N	0.031 I	0.44	0.037 I	-	-	-	-	-	0.066 I	-	-	0.035 I	-	5
	S7	N	0.069	2.0	0.096	-	-	-	-	-	-	-	-	-	0.016 I	4
	S78	N	-	0.56	0.036 I	-	0.058 I	-	-	-	0.027 I	-	-	0.065 I	-	5
	S79	N	-	-	-	-	0.12 I	0.39 I	-	-	0.048 I	-	-	0.31	0.11	5
	S8	N	0.075	1.1	0.085	-	-	-	-	-	-	-	0.021 I	-	-	4
3/20/2008	ACME1DS	N	-	0.31	0.022 I	-	-	-	-	-	0.036 I	-	-	-	-	3
	G94D	N	0.012 I	0.15	0.011 I	-	-	-	-	-	0.097	-	-	-	-	4
	S5A	N	0.053	2.6	0.054	-	-	-	-	-	0.029 I	-	0.054 I	-	-	5
	S6	N	0.068	0.90	0.022 I	-	-	-	-	-	-	-	0.044 I	-	-	4
Total number of compound detections			15	26	20	2	5	3	2	1	9	1	4	8	6	102

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples
I - value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit

Table 3. Summary of pesticide residues (µg/Kg) above the method detection limit found in sediment samples collected by SFWMD in March 2008.

Date	Site	Flow	ametryn	chlordane	DDD-P,P'	DDE-P,P'	DDT-P,P'	endosulfan (alpha)	endosulfan (beta)	endosulfan sulfate	PCB-1254	Number of compounds detected at site
3/17/2008	S177	N	-	-	-	4.5 I	-	-	-	-	-	1
	S178	N	-	-	-	8.3 I	-	6.6 I	8.6	30	-	4
	S331	N	-	-	-	-	13	-	-	-	-	1
	S80	N	-	-	-	2.9 I	-	-	-	-	-	1
3/18/2008	S2	N	-	-	25 I	***79***	-	-	-	-	-	2
	S3	N	4.3 I	-	22	***93***	6.5 I	-	-	-	-	4
	S4	N	11 I *	-	-	15 I *	-	-	-	-	-	2
	S9	N	-	-	-	2.4 I	-	-	-	-	-	1
3/19/2008	S7	N	-	-	-	-	-	-	-	-	300	1
	S79	N	-	-	-	6.6 I	-	-	-	-	-	1
	S9	N	-	-	-	2.4 I	-	-	-	-	-	1
3/20/2008	ACME1DS	N	-	-	-	4.3 I	-	-	-	-	-	1
	S5A	N	-	***45 I***	25	***110***	36	-	-	-	-	4
Total number of compound detections			2	1	3	11	3	1	1	1	1	24

N - no Y - yes R - reverse; - denotes that the result is below the method detection limit; * results are the average of replicate samples
I - value reported is less than the practical quantitation limit, and greater than or equal to the minimum detection limit
Values in bold, italicized font are at a concentration that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

Table 4. Selected properties of pesticides found in March 2008 sampling event.

Common Name	Surface Water Standards FAC 62-302 (µg/L)	LD_{50} acute rats oral (mg/kg) (1)	EPA Carcinogenic Potential	Water Solubility (WS) (mg/L) (2, 3)	K_{oc} (mL/g) (2, 3)	Soil Half-life (days) (2, 3)	Soil Conservation Service (SCS) rating (2)			Volatility from Water	Bioconcentration Factor (BCF)
							LE	SA	SS		
ametryn	-	1,110	D	185	300	60	M	M	M	I	33
atrazine	-	3,080	C	33	100	60	L	M	L	I	86
bromacil	-	5,200	C	700	32	60	L	M	M	I	15
chlordane	0.0043	365 - 590	B2	0.056	3,800	-	-	-	-	I	3,141
DDD-p,p'	-	3,400	-	0.055	239,900	-	-	-	-	I	3,173
DDE-p,p'	-	880	-	0.065	243,220	-	-	-	-	S	2,887
DDT-p,p'	0.001	113	-	0.00335	140,000	-	-	-	-	I	15,377
diuron	-	3,400	D	42	480	90	M	M	L	I	75
endosulfan alpha	0.056	70	-	0.53	12,400	50	XS	L	M	S	884
endosulfan beta		70	-	0.28	-	-	-	-	-	S	1,267
endosulfan sulfate	-	-	-	0.117	-	-	-	-	-	I	2,073
hexazinone	-	1,690	D	33,000	54	90	L	M	M	I	2
metolachlor	-	2,780	C	530	200	90	L	M	M	I	18
metribuzin	-	2,200	D	1,220	41	30	L	S	M	I	11
norflurazon	-	9,400	C	28	700	90	M	M	L	I	94
PCB's	0.014	-	B2	-	-	-	-	-	-	-	-
simazine	-	>5,000	C	6.2	130	60	L	M	M	I	221

SCS ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS)
Volatility from water: R = rapid, I = insignificant, S = significant (4)
Bioconcentration Factor (BCF) calculated as BCF = $10^{\wedge(2.791 - 0.564 \log WS)}$ (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP FAC 62-302 surface water standards (12/06) for Class III waters except Class I in ( )
Note: endosulfan usually considered the sum of alpha and beta isomers

(1) Hartley and Kidd (1987).
(2) Goss and Wauchope (1992).
(3) Montgomery (1993).
(4) Lyman, et al. (1990).
(5) U.S. EPA (1996a).

Table 5 . Toxicity of pesticides found in the March 2008 sampling event to freshwater aquatic invertebrates and fishes (ug/L).

Common Name	48 hr EC_{50} Water flea *Daphnia magna*	acute toxicity (*)	chronic toxicity (*)	96 hr LC_{50} Fathead Minnow (#) *Pimephales promelas*	acute toxicity	chronic toxicity	96 hr LC_{50} Bluegill *Lepomis macrochirus*	acute toxicity	chronic toxicity	96 hr LC_{50} Largemouth Bass *Micropterus salmoides*	acute toxicity	chronic toxicity	96 hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*	acute toxicity	chronic toxicity	96 hr LC_{50} Channel Catfish *Ictalurus punctatus*	acute toxicity	chronic toxicity
ametryn	28,000 (7)	9,333	1,400	-	-	-	4,100 (4)	1,367	205	-	-	-	8,800 (4)	2,933	440	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	3,600 (8)	1,200	180	-	-	-
atrazine	6,900 (7)	2,300	345	15,000 (7)	5,000	750	16,000 (4)	5,333	800	-	-	-	8,800 (4)	2,933	440	7,600 (4)	2,533	380
	-	-	-	-	-	-	-	-	-	-	-	-	5,300 (9)	1,767	265	-	-	-
bromacil	-	-	-	-	-	-	127,000 (7)	42,333	6,350	-	-	-	36,000 (7)	12,000	1,800	-	-	-
	121,000 (15)	40,333	6,050	-	-	-	127,000 (15)	42,333	6,350	-	-	-	36,000 (15)	12,000	1,800	-	-	-
chlordane	-	-	-	-	-	-	70 (5)	23	3.5		-	-	90 (5)	30	5		-	-
DDD-p,p'	3,200 (6)	1,067	160	4,400 (1)	1,467	220	42 (1)	14	2.1	42 (1)	14	2.1	70 (1)	23.3	3.5	1,500 (1)	500	75
DDE-p,p'	-	-	-	-	-	-	240 (1)	80	12	-	-	-	32 (1)	10.7	1.6	-	-	-
DDT-p,p'	-	-	-	19 (5)	6.3	0.95	8 (5)	2.7	0.4	2 (5)	0.7	0.10	7 (5)	2.3	0.35	16 (5)	5.3	0.8
diuron	1,400 (7)	467	70	14,200 (7)	4,733	710	5,900 (4)	1,967	295	-	-	-	5,600 (4)	1,867	280	-	-	-
	1,400 (10)	467	70	14,000 (10)	4,667	700	-	-	-	-	-	-	-	-	-	-	-	-
endosulfan	166 (7)	55	8	1 (1)	0.3	0.05	1 (1)	0.33	0.05	-	-	-	1 (1)	0.33	0.050	1 (1)	0.3	0.05
	-	-	-	-	-	-	2 (3)	0.67	0.10	-	-	-	3 (2)	1	0.15	1.5 (7)	0.5	0.08
	-	-	-	-	-	-	-	-	-	-	-	-	1 (3)	0.33	0.050	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	0.3 (5)	0.10	0.015	-	-	-
	166 (11)	55	8	1.5 (11)	0.5	0.08	1.7 (11)	0.57	0.09	-	-	-	0.8 (11)	0.27	0.04	-	-	-
hexazinone	151,600 (7)	50,533	7,580	274,000 (4)	91,333	13,700	100,000 (7)	33,333	5,000	-	-	-	180,000 (7)	60,000	9,000	-	-	-
	151,600 (12)	50,533	7,580	274,000 (12)	91,333	13,700	505,000 (12)	168,333	25,250	-	-	-	>320,000 (12)	>106,667	>16,000	-	-	-
metolachlor	23,500 (7)	7,833	1,175	-	-	-	15,000 (4)	5,000	750	-	-	-	2,000 (4)	667	100	4,900 (5)	1,633	245
metribuzin	4,200 (7)	1,400	210	-	-	-	80,000 (4)	26,667	4,000	-	-	-	64,000 (4)	21,333	3,200	100,000 (7)	33,333	5,000
	4,200 (13)	1,400	210	-	-	-	75,900 (13)	25,300	3,795	-	-	-	76,770 (13)	25,590	3,839	-	-	-
norflurazon	15,000 (7)	5,000	750	-	-	-	16,300 (7)	5,433	815	-	-	-	8,100 (7)	2,700	405	>200,000 (4)	>67,000	>10,000
	>15,000 (14)	>5,000	>750	-	-	-	16,300 (14)	5,433	815	-	-	-	8,100 (14)	2,700	405	-	-	-
simazine	1,100 (7)	367	55	100,000 (7)	33,333	5,000	90,000 (4)	30,000	4,500	-	-	-	100,000 (7)	33,333	5,000	-	-	-

(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC50 is the lowest value which has been determined for a species significant to the indigenous aquatic community.
(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson and Finley (1980).
(2) U.S. EPA (1977).
(3) Schneider (1979).
(4) Hartley and Kidd (1987).
(5) Montgomery (1993).
(6) Verschueren (1983).
(7) U.S. EPA (1991).
(8) U.S. EPA (2005).
(9) U.S. EPA (2006).
(10) U.S. EPA (2003b).
(11) U.S. EPA (2002).
(12) U.S. EPA (1994).
(13) U.S. EPA (1998).
(14) U.S. EPA (1996b).
(15) U.S. EPA (1996c).

Table 6. Atrazine desethyl/atrazine ratio (DAR) data for March 2008 sampling event.

Date	Site	Flow*	atrazine		atrazine desethyl		DAR
			µg/L	moles/L	µg/L	moles/L	
3/17/2008	S191	N	0.28	1.29819E-09	0.018	9.59327E-11	0.1
	S331	N	0.96	4.45093E-09	0.047	2.50491E-10	0.1
	S332DX	N	0.81	3.75547E-09	0.035	1.86536E-10	0.0
	S80	N	0.13	6.02731E-10	0.012	6.39551E-11	0.1
3/18/2008	S12A	N	0.19	8.80914E-10	0.011	5.86256E-11	0.1
	S3	N	1.1	5.10003E-09	0.040	2.13184E-10	0.0
	S31	N	0.90	4.17275E-09	0.048	2.55821E-10	0.1
	S333	Y	0.82	3.80184E-09	0.047	2.50491E-10	0.1
	S356	N	0.53	2.45729E-09	0.035	1.86536E-10	0.1
	S4	N	2.7	1.23639E-08	0.061	3.25105E-10	0.0
3/19/2008	L3BRS	N	2.0	9.27278E-09	0.11	5.86256E-10	0.1
	S235	N	0.44	2.04001E-09	0.037	1.97195E-10	0.1
	S7	N	2.0	9.27278E-09	0.096	5.11641E-10	0.1
	S78	N	0.56	2.59638E-09	0.036	1.91865E-10	0.1
	S8	N	1.1	5.10003E-09	0.085	4.53016E-10	0.1
3/20/2008	ACME1DS	N	0.31	1.43728E-09	0.022	1.17251E-10	0.1
	G94D	N	0.15	6.95458E-10	0.011	5.86256E-11	0.1
	S5A	N	2.6	1.20546E-08	0.054	2.87798E-10	0.0
	S6	N	0.90	4.17275E-09	0.022	1.17251E-10	0.0

DAR	All sites	Flow only sites	No flow sites
average	0.1	0.1	0.1
median	0.1	0.1	0.1
minimum	0.0	0.1	0.0

* N - no; Y - yes; R - reverse

PESTICIDE SURFACE WATER QUALITY REPORT

JUNE 2008 SAMPLING EVENT

Richard J. Pfeuffer

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MSC 4642
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West Palm Beach, FL 33406

Pesticide Monitoring Project Report
June 2008 Sampling Event

Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water samples from 33 of the 34 network sites were collected June 16 to June 18, 2008, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides ametryn, atrazine, bromacil, hexazinone, metolachlor, metribuzin, norflurazon, prometon, and simazine, along with the fungicide/degradates metalaxyl, atrazine desethyl, atrazine desisopropyl, and endosulfan sulfate, were detected in one or more of these surface water samples. No harmful impacts are expected from the detected pesticides.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods

The SFWMD pesticide monitoring network includes stations designated in the Everglades Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction Project (non-ECP) permit. The canals and marshes depicted in Figure 1 are protected as Florida Administrative Code (FAC) 62-302 Class III (fishable and swimmable) waters, while Lake Okeechobee and a segment of the Caloosahatchee River are protected as a Class I drinking water supply. Water Conservation Area 1 (WCA-1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Seventy-one pesticides and degradation products were analyzed in samples from 33 of the network 34 sites (Figure 1). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp.

To evaluate the potential impacts on aquatic life, the observed concentration is compared to the appropriate criterion outlined in FAC 62-302.530. If a pesticide compound is not specifically listed, acute and chronic toxicity criterion are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, using the lowest technical grade EC_{50} or LC_{50} reported in the summarized literature for the species significant to the indigenous aquatic community (FAC 62-302.200). Each pesticide's description and possible uses and sites of application described herein are taken from Hartley and Kidd (1987). This summary covers surface water samples collected from June 16 to 18, 2008.

Results

At least one pesticide was detected in surface water at 29 of the 33 sites. Modifications to the non-ECP permit changed the requirement for sampling at S142 to only during discharge or flow events. For this sampling event, no sample was obtained due to no discharge at the time of sample collection. Samples are no longer required to be collected at ACME1DS, G94D, and S38B due to modifications to the non-ECP permit. The concentrations of the pesticides detected at each of the sites are summarized for the surface water in Table 2. All of these compounds have previously been detected in this monitoring program. No harmful impacts are expected from the detected pesticides.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long-term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 micrograms per liter (μg/L) (Verschueren, 1983). Environmental fate and toxicity data in Tables 3 and 4 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.0099 to 0.027 μg/L. Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 μg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003). The atrazine surface water concentrations found in this sampling event at 24 of the 33 sampling locations, ranged from 0.0097 to 0.54 μg/L. Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of groundwater discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.2) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 5). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

<u>Bromacil</u>: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at CR33.5T (0.13 μg/L). Using these criteria, this observed concentration should not have an acute or chronic detrimental impact on fish.

<u>Endosulfan sulfate</u>: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's law constant (9.63×10^{-8} atm-m^3/mole) (Lyman, et al. 1990) indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Table 3). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 3). Endosulfan sulfate was detected in the surface water only at S178 (0.031 μg/L). However, no surface water standard (FAC 62-302) has been developed for endosulfan sulfate.

<u>Hexazinone</u>: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/L for *Daphnia magna* (U.S. EPA, 1988). The highest surface water concentration detected in this sampling event at FECSR78 (2.2 μg/L) should not have an acute impact on fish or aquatic invertebrates.

<u>Metalaxyl</u>: Metalaxyl is a systemic fungicide. Registered uses include potatoes, strawberries, citrus, avocados and vegetables. Environmental fate and toxicity data in Tables 3 and 4 indicate

that metalaxyl (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metalaxyl detected was 0.11 µg/L at S99 (Table 2). Using these criteria, the concentration of metalaxyl detected should not have an acute, harmful impact on fish or aquatic invertebrates.

Metolachlor: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in Tables 3 and 4 indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The only surface water concentration found in this sampling event (0.11 µg/L at S5A) is over two orders of magnitude below the calculated chronic toxicity level. Using these criteria, this observed level should not have a harmful effect on fish or aquatic invertebrates.

Metribuzin: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in Tables 3 and 4 indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The highest concentration of metribuzin detected was 0.023 µg/L (S333). Using these criteria, this surface water concentration should not have an acute impact on fish or aquatic invertebrates.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC_{50} for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.051 to 4.6 µg/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these observed concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Prometon: Prometon is a non-selective systemic herbicide registered for use in non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that prometon (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The only concentration of prometon detected (0.054 µg/L at S5A) is several orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 µg/L (Verschueren, 1983). Aquatic invertebrate LC_{50} toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. EPA, 1984). The highest surface water concentration of simazine detected at CR33.5T (0.23 µg/L) was below any level of concern for fish or aquatic invertebrates.

Quality Assurance Evaluation

Replicate samples were collected at sites S331 and S80. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No pesticide analytes were detected in the field blanks performed at S177, S78, GORDYRD, S8, and S7. All collected samples were shipped and all bottles were received.

Glossary

LD_{50}: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LC_{50}: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

EC_{50}: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:
The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:
The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

Method Detection Limit (MDLs):
The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.

Practical Quantitation Limit (PQLs):
The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20

fortified water samples is < 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.

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Figure 1. South Florida Water Management District Pesticide Monitoring Network.

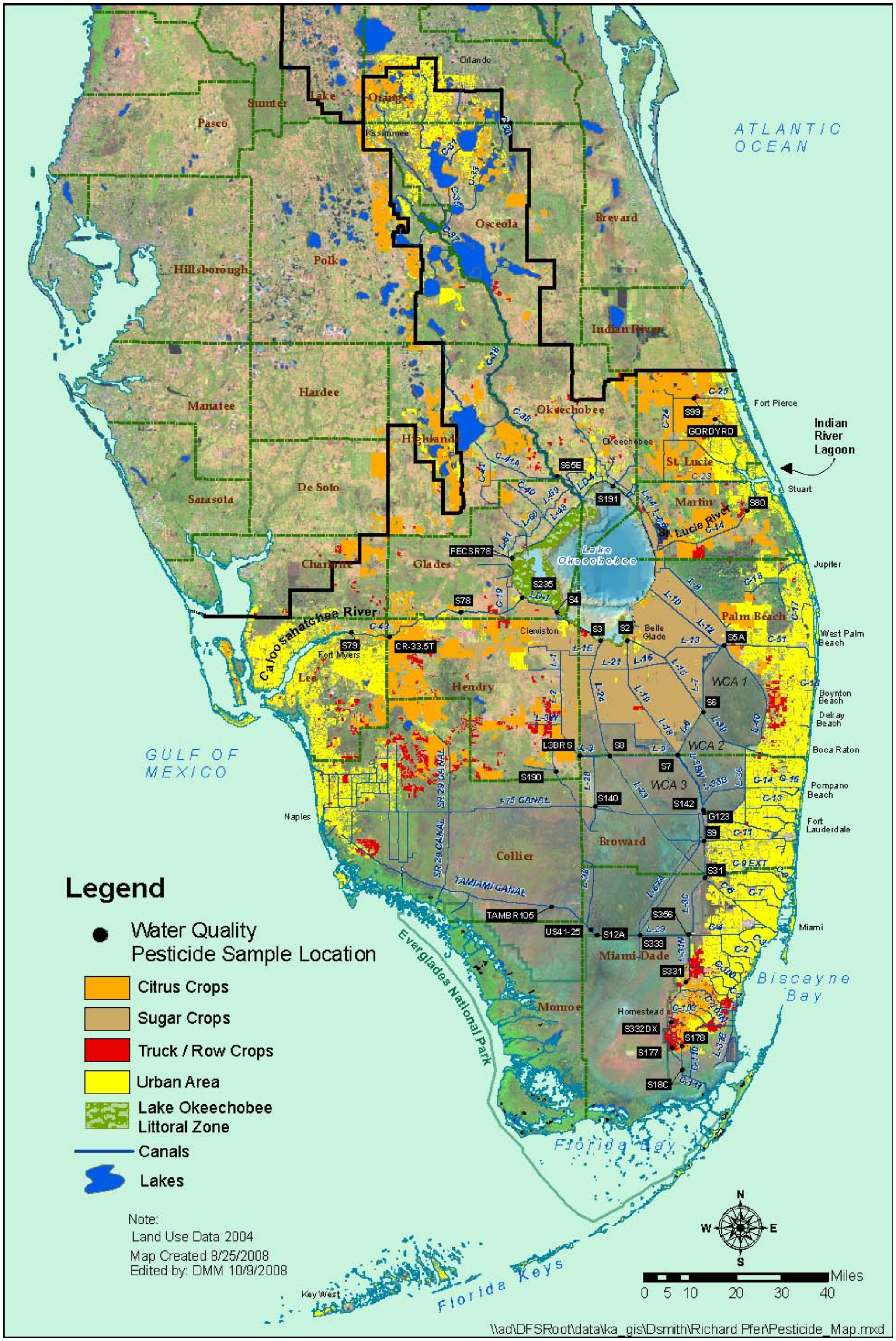

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for June 2008 sampling event.

Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)
2,4-D	0.2 - 0.6	endrin aldehyde	0.004 - 0.024
2,4,5-T	0.2 - 0.6	ethion	0.01 - 0.052
2,4,5-TP (silvex)	0.2 - 0.6	ethoprop	0.01 - 0.072
acifluorfen	0.2 - 0.6	fenamiphos (nemacur)	0.038 - 0.21
alachlor	0.057 - 0.32	fonofos (dyfonate)	0.01 - 0.052
aldrin	0.002 - 0.011	heptachlor	0.002 - 0.013
ametryn	0.01 - 0.052	heptachlor epoxide	0.002 - 0.026
atrazine	0.01 - 0.14	hexazinone	0.019 - 0.38
atrazine desethyl	0.01 - 0.052	imidacloprid	0.2 - 0.6
atrazine desisopropyl	0.01 - 0.052	linuron	0.2 - 0.6
azinphos methyl (guthion)	0.029 - 0.16	malathion	0.029 - 0.16
α-BHC (alpha)	0.002 - 0.017	metalaxyl	0.048 - 0.27
β-BHC (beta)	0.003 - 0.018	methoxychlor	0.001 - 0.052
δ-BHC (delta)	0.002 - 0.011	metolachlor	0.057 - 0.32
γ-BHC (gamma) (lindane)	0.002 - 0.011	metribuzin	0.019 - 0.11
bromacil	0.048 - 0.27	mevinphos	0.057 - 0.32
butylate	0.019 - 0.11	mirex	0.001 - 0.064
carbophenothion (trithion)	0.015 - 0.084	naled	0.076 - 0.44
chlordane	0.019 - 0.11	norflurazon	0.019 - 0.4
chlorothalonil	0.015 - 0.084	parathion ethyl	0.019 - 0.11
chlorpyrifos ethyl	0.01 - 0.052	parathion methyl	0.019 - 0.11
chlorpyrifos methyl	0.019 - 0.11	PCB-1016	0.019 - 0.11
cypermethrin	0.019 - 0.11	PCB-1221	0.019 - 0.11
DDD-P,P’	0.005 - 0.026	PCB-1232	0.019 - 0.11
DDE-P,P’	0.004 - 0.021	PCB-1242	0.019 - 0.11
DDT-P,P’	0.006 - 0.032	PCB-1248	0.019 - 0.11
demeton	0.029 - 0.16	PCB-1254	0.019 - 0.11
diazinon	0.019 - 0.11	PCB-1260	0.019 - 0.11
dicofol (kelthane)	0.042 - 0.24	permethrin	0.015 - 0.084
dieldrin	0.002 - 0.011	phorate	0.01 - 0.052
disulfoton	0.019 - 0.11	prometryn	0.019 - 0.11
diuron	0.2 - 0.6	prometon	0.019 - 0.11
α-endosulfan (alpha)	0.004 - 0.029	simazine	0.01 - 0.052
β-endosulfan (beta)	0.004 - 0.028	toxaphene	0.095 - 0.52
endosulfan sulfate	0.005 - 0.026	trifluralin	0.008 - 0.044
endrin	0.01 - 0.052		

Table 2. Summary of pesticide residues (µg/L) above the method detection limit found in surface water samples collected by SFWMD in June 2008.

Date	Site	Flow	ametryn	atrazine	atrazine desethyl	atrazine desisopropyl	bromacil	endosulfan sulfate	hexazinone	metalaxyl	metolachlor	metribuzin	norflurazon	prometon	simazine	Number of compounds detected at site
6/16/2008	S18C	N	-	0.041	0.0097 I	-	-	-	-	-	-	-	-	-	-	2
	S79	N	-	0.16	0.025 I	0.014 I	0.051 I	-	0.083	-	-	-	0.14	-	0.10	7
	CR33.5T	Y	-	0.22	0.025 I	0.020 I	0.13 I	-	0.049 I	-	-	-	4.6	-	0.23	7
	S177	N	-	0.022 I	-	-	-	-	-	-	-	-	-	-	-	1
	S78	N	0.0099 I	0.29	0.055	0.014 I	-	-	0.027 I	-	-	-	-	-	-	5
	S178	N	-	-	-	-	-	0.031	-	-	-	-	-	-	-	1
	S235	N	0.011 I	0.23	0.055	0.014 I	-	-	0.042 I	-	-	-	-	-	-	5
	S332DX	N	-	0.018 I	-	-	-	-	-	-	-	0.021 I	-	-	-	2
	FECSR78	N	-	0.020 I	-	-	-	-	2.2	-	-	-	-	-	-	2
	S331	N	-	0.017 I *	-	-	-	-	-	-	-	0.017 I *	-	-	-	2
	S356	N	-	0.020 I	-	-	-	-	-	-	-	-	-	-	-	1
	S65E	N	-	0.034 I	0.014 I	-	-	-	-	-	-	-	-	-	-	2
	S191	N	-	0.064	0.014 I	-	0.048 I	-	-	-	-	-	-	-	-	3
	US41-25	N	-	-	-	-	-	-	0.13	-	-	-	-	-	-	1
	S333	Y	-	-	-	-	-	-	-	-	-	0.023 I	-	-	-	1
	S12A	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
6/17/2008	S31	N	-	0.0097 I	-	-	-	-	-	-	-	-	-	-	-	1
	S99	Y	-	-	-	-	-	-	-	0.11 I	-	-	-	-	0.013 I	2
	G123	N	-	0.012 I	-	-	-	-	-	-	-	-	-	-	-	1
	GORDYRD	Y	-	-	-	-	-	-	-	-	-	-	-	-	0.021 I	1
	S9	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	TAMBR105	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S140	N	-	0.034 I	-	-	-	-	-	-	-	-	0.051 I	-	-	2
	S80	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	L3BRS	N	0.020 I	0.51	0.039	-	-	-	-	-	-	-	-	-	-	3
	S2	N	0.017 I	0.27	0.062	0.015 I	-	-	-	-	-	-	-	-	-	4
	S190	N	-	0.22	0.019 I	-	-	-	-	-	-	-	-	-	-	2
	S3	N	0.012 I	0.25	0.058	0.012 I	-	-	-	-	-	-	-	-	-	4
	S4	N	0.017 I	0.26	0.064	0.015 I	-	-	-	-	-	-	-	-	-	4
	S8	N	0.027 I	0.54	0.054	0.013 I	-	-	-	-	-	-	-	-	-	4
6/18/2008	S7	N	0.021 I	0.040	-	-	-	-	-	-	-	-	-	-	-	2
	S6	Y	0.019 I	0.36	0.065	0.017 I	-	-	-	-	-	-	-	-	-	4
	S5A	Y	0.018 I	0.33	0.055	-	-	-	-	-	0.11 I	-	-	0.054 I	-	5
Total number of compound detections			10	24	15	9	3	1	6	1	1	3	3	1	4	81

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples
I - value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit

Table 3. Selected properties of pesticides found in June 2008 sampling event.

Common Name	Surface Water Standards FAC 62-302 (µg/L)	LD_{50} acute rats oral (mg/kg) (1)	EPA Carcinogenic Potential	Water Solubility (WS) (mg/L) (2, 3)	K_{oc} (mL/g) (2, 3)	Soil Half-life (days) (2, 3)	Soil Conservation Service (SCS) rating (2) LE	SA	SS	Volatility from Water	Bioconcentration Factor (BCF)
ametryn	-	1,110	D	185	300	60	M	M	M	I	33
atrazine	-	3,080	C	33	100	60	L	M	L	I	86
bromacil	-	5,200	C	700	32	60	L	M	M	I	15
endosulfan alpha	0.056	70	-	0.53	12,400	50	XS	L	M	S	884
endosulfan beta		70	-	0.28	-	-	-	-	-	S	1,267
endosulfan sulfate	-	-	-	0.117	-	-	-	-	-	I	2,073
hexazinone	-	1,690	D	33,000	54	90	L	M	M	I	2
metalaxyl	-	699	-	7,100	100	70	L	M	M	I	4
metolachlor	-	2,780	C	530	200	90	L	M	M	I	18
metribuzin	-	2,200	D	1,220	41	30	L	S	M	I	11
norflurazon	-	9,400	C	28	700	90	M	M	L	I	94
prometon	-	2,980	-	720	200	500	L	M	M	I	15
simazine	-	>5,000	C	6.2	130	60	L	M	M	I	221

SCS ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS)
Volatility from water: R = rapid, I = insignificant, S = significant
Bioconcentration Factor (BCF) calculated as BCF = $10^{(2.791 - 0.564 \log WS)}$ (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP FAC 62-302 surface water standards (12/06) for Class III waters except Class I in ( )
Note: endosulfan usually considered the sum of alpha and beta isomers

(1) Hartley and Kidd (1987).
(2) Goss and Wauchope (1992).
(3) Montgomery (1993).
(4) Lyman, et al. (1990).
(5) U.S. EPA (1996a).

Table 4 . Toxicity of pesticides found in the June 2008 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

Common Name	48 hr EC_{50} Water flea *Daphnia magna*	acute toxicity (*)	chronic toxicity (*)	96 hr LC_{50} Fathead Minnow (#) *Pimephales promelas*	acute toxicity	chronic toxicity	96 hr LC_{50} Bluegill *Lepomis macrochirus*	acute toxicity	chronic toxicity	96 hr LC_{50} Largemouth Bass *Micropterus salmoides*	acute toxicity	chronic toxicity	96 hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*	acute toxicity	chronic toxicity	96 hr LC_{50} Channel Catfish *Ictalurus punctatus*	acute toxicity	chronic toxicity
ametryn	28,000 (7)	9,333	1,400	-	-	-	4,100 (4)	1,367	205	-	-	-	8,800 (4)	2,933	440	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	3,600 (8)	1,200	180	-	-	-
atrazine	6,900 (7)	2,300	345	15,000 (7)	5,000	750	16,000 (4)	5,333	800	-	-	-	8,800 (4)	2,933	440	7,600 (4)	2,533	380
	-	-	-	-	-	-	-	-	-	-	-	-	5,300 (9)	1,767	265	-	-	-
bromacil	-	-	-	-	-	-	127,000 (7)	42,333	6,350	-	-	-	36,000 (7)	12,000	1,800	-	-	-
	121,000 (15)	40,333	6,050	-	-	-	127,000 (15)	42,333	6,350	-	-	-	36,000 (15)	12,000	1,800	-	-	-
endosulfan	166 (7)	55	8	1 (1)	0.3	0.05	1 (1)	0.33	0.05	-	-	-	1 (1)	0.33	0.050	1 (1)	0.3	0.05
	-	-	-	-	-	-	2 (3)	0.67	0.10	-	-	-	3 (2)	1	0.15	1.5 (7)	0.5	0.08
	-	-	-	-	-	-	-	-	-	-	-	-	1 (3)	0.33	0.050	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	0.3 (5)	0.10	0.015	-	-	-
	166 (11)	55	8	1.5 (11)	0.5	0.08	1.7 (11)	0.57	0.09	-	-	-	0.8 (11)	0.27	0.04	-	-	-
hexazinone	151,600 (7)	50,533	7,580	274,000 (4)	91,333	13,700	100,000 (7)	33,333	5,000	-	-	-	180,000 (7)	60,000	9,000	-	-	-
	151,600 (12)	50,533	7,580	274,000 (12)	91,333	13,700	505,000 (12)	168,333	25,250	-	-	-	>320,000 (12)	>106,667	>16,000	-	-	-
metalaxyl	28,000 (7)	9,333	1,400	-	-	-	139,000 (7)	46,333	6,950	-	-	-	132,000 (7)	44,000	6,600	-	-	-
	29,000 (16)	9,667	1450	9,100 (16)	3,033	455	139,000 (16)	46,333	6,950	-	-	-	132,000 (16)	44,000	6,600	-	-	-
metolachlor	23,500 (7)	7,833	1,175	-	-	-	15,000 (4)	5,000	750	-	-	-	2,000 (4)	667	100	4,900 (5)	1,633	245
metribuzin	4,200 (7)	1,400	210	-	-	-	80,000 (4)	26,667	4,000	-	-	-	64,000 (4)	21,333	3,200	100,000 (7)	33,333	5,000
	4,200 (13)	1,400	210	-	-	-	75,900 (13)	25,300	3,795	-	-	-	76,770 (13)	25,590	3,839	-	-	-
norflurazon	15,000 (7)	5,000	750	-	-	-	16,300 (7)	5,433	815	-	-	-	8,100 (7)	2,700	405	>200,000 (4)	>67,000	>10,000
	>15,000 (14)	>5,000	>750	-	-	-	16,300 (14)	5,433	815	-	-	-	8,100 (14)	2,700	405	-	-	-
prometon	-	-	-	-	-	-	40,000 (5)	13,333	2,000	-	-	-	12,000 (5)	4,000	600	-	-	-
simazine	1,100 (7)	367	55	100,000 (7)	33,333	5,000	90,000 (4)	30,000	4,500	-	-	-	100,000 (7)	33,333	5,000	-	-	-

(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC50 is the lowest value which has been determined for a species significant to the indigenous aquatic community.
(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson and Finley (1980).
(2) U.S. EPA (1977).
(3) Schneider (1979).
(4) Hartley and Kidd (1987).
(5) Montgomery (1993).
(7) U.S. EPA (1991).
(8) U.S. EPA (2005).
(9) U.S. EPA (2006).
(11) U.S. EPA (2002).
(12) U.S. EPA (1994a).
(13) U.S. EPA (1998).
(14) U.S. EPA (1996a).
(15) U.S. EPA (1996b).
(16) U.S. EPA (1994b).

Table 5. Atrazine desethyl/atrazine ratio (DAR) data for June 2008 sampling event.

Date	Site	Flow*	atrazine		atrazine desethyl		DAR
			µg/L	moles/L	µg/L	moles/L	
6/16/2008	S18C	N	0.041	1.90E-10	0.0097	5.17E-11	0.3
	S79	N	0.16	7.42E-10	0.025	1.33E-10	0.2
	CR33.5T	Y	0.22	1.02E-09	0.025	1.33E-10	0.1
	S78	N	0.29	1.34E-09	0.055	2.93E-10	0.2
	S235	N	0.23	1.07E-09	0.055	2.93E-10	0.3
	S65E	N	0.034	1.58E-10	0.014	7.46E-11	0.5
	S191	N	0.064	2.97E-10	0.014	7.46E-11	0.3
6/17/2008	L3BRS	N	0.51	2.36E-09	0.039	2.08E-10	0.1
	S2	N	0.3	1.25E-09	0.062	3.30E-10	0.3
	S190	N	0.22	1.02E-09	0.019	1.01E-10	0.1
	S3	N	0.25	1.16E-09	0.058	3.09E-10	0.3
	S4	N	0.26	1.21E-09	0.064	3.41E-10	0.3
	S8	N	0.54	2.50E-09	0.054	2.88E-10	0.1
	S6	Y	0.36	1.67E-09	0.065	3.46E-10	0.2
	S5A	Y	0.33	1.53E-09	0.055	2.93E-10	0.2

DAR	All sites	Flow only sites	No flow sites
average	0.2	0.2	0.2
median	0.2	0.2	0.3
minimum	0.1	0.1	0.1
maximum	0.5	0.2	0.5

* N - no; Y - yes; R - reverse

PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

SEPTEMBER 2008 SAMPLING EVENT

Richard J. Pfeuffer

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Pesticide Monitoring Project Report
September 2008 Sampling Event

Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water and sediment samples were collected September 15 to September 18, 2008, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides ametryn, atrazine, bromacil, hexazinone, metribuzin, norflurazon, and simazine, along with the insecticide/degradates atrazine desethyl and chlorpyrifos ethyl were detected in one or more of these surface water samples. The chlorpyrifos ethyl concentration detected should not have an acute, harmful impact on fish. However, for aquatic invertebrates, this level is greater than the calculated acute and chronic toxicity for *Daphnia magna*. At this level, exposure can cause impacts to macroinvertebrate populations, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long-term average exposures.

The herbicide ametryn and the insecticides/degradates chlordane, DDD, DDE, dieldrin, alpha endosulfan, beta endosulfan, and endosulfan sulfate were found in the sediment at several locations. Two chlordane and DDE compound sediment concentrations were of a magnitude considered to have a harmful effect to freshwater sediment-dwelling organisms. No harmful impacts are expected from the other detected pesticides.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods

The SFWMD pesticide monitoring network includes stations designated in the Everglades Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction Project (non-ECP) permit. The canals and marshes depicted in Figure 1 are protected as Florida Administrative Code (FAC) 62-302 Class III (fishable and swimmable) waters, while Lake Okeechobee and a segment of the Caloosahatchee River are protected as a Class I drinking water supply. Water Conservation Area 1 (WCA-1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Seventy-three pesticides and degradation products were analyzed in samples from 33 of the network 34 sites (Figure 1). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp.

To evaluate the potential impacts on aquatic life, the observed concentration is compared to the appropriate criterion outlined in FAC 62-302.530. If a pesticide compound is not specifically listed, acute and chronic toxicity criterion are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, using the lowest technical grade EC_{50} or LC_{50} reported in the summarized literature for the species significant to the indigenous aquatic community (FAC 62-302.200). Each pesticide's description and possible uses and sites of application described herein are taken from Hartley and Kidd (1987). Sediment concentrations are compared to freshwater sediment quality assessment guidelines (MacDonald Environmental Sciences, LTD., and United States Geological Survey, 2003). A value below the threshold effect concentration (TEC) should not have a harmful effect on sediment-dwelling organisms. Values above the probable effect concentration (PEC) demonstrate that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed. This summary covers surface water and sediment samples collected from September 15 to September 18, 2008.

Results

At least one pesticide was detected in surface water at 22 of the 33 sites and in sediment at 12 of the 29 sites. Modifications to the non-ECP permit changed the requirement for sampling at S142 to only during discharge or flow events. For this sampling event, no sample was obtained due to no discharge at the time of sample collection. Sediment samples are not collected at GORDYRD, CR33.5T, S333, S356, and TAMBR105. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All of these compounds have previously been detected in this monitoring program.

The surface water chlorpyrifos ethyl concentration detected at CR33.5T has the possibility for causing an environmental impact. The sediment DDE concentrations at S2 and S5A were of a magnitude considered to represent detrimental effects to sediment-dwelling organisms in freshwater sediments. The S2 and S5A sediment concentration of chlordane was also at the detrimental effects level. All other detected concentrations in the surface water and sediment were below any effect level.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long-term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

<u>Ametryn</u>: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 micrograms per liter (µg/L) (Verschueren, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1

milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.014 to 0.041 μg/L. Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates. Ametryn was detected in the sediment at S4 at 7.0 micrograms per kilogram (μg/Kg). However, no sediment guidelines have been developed for ametryn.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 μg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003). The atrazine surface water concentrations found in this sampling event at 14 of the 33 sampling locations, ranged from 0.01 to 0.077 μg/L. Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates. Atrazine was not detected in the sediment.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of groundwater discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at CR33.5T (0.20 µg/L). Using these criteria, this observed concentration should not have an acute or chronic detrimental impact on fish. Bromacil was not detected in the sediment.

Chlordane: Chlordane is a chlorinated hydrocarbon previously used as a contact insecticide. Environmental fate and toxicity data in Tables 4 and 5 indicate that chlordane (1) is moderately toxic to mammals and highly toxic to fish; and (2) has the potential for significant bioconcentration. Freshwater sediment quality assessment guidelines identified a TEC of 3.2 µg/Kg and PEC of 18 µg/Kg for chlordane. The detected sediment residue at S2 (63 µg/Kg) and S5A (73 µg/Kg) is at a concentration where harmful effects to sediment-dwelling organisms are frequently or always observed. While the use of this compound has been discontinued in recent years, its persistence and tendency to accumulate in sediments makes chlordane a compound of concern. Chlordane was not detected in the surface water.

Chlorpyrifos ethyl: Chlorpyrifos ethyl is a non-systemic insecticide with contact, stomach, and respiratory action, for use on citrus, vegetables, rice, and household insect pests. Environmental fate and toxicity data in Tables 4 and 5 indicate that chlorpyrifos ethyl (1) is not readily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is toxic to mammals and fish; and (3) bioconcentrates to a limited extent. The only concentration of chlorpyrifos ethyl found in this sampling event (0.034 µg/L at CR33.5T) should not have an acute or chronic harmful impact on fish. However, for aquatic invertebrates, this level is greater than the calculated acute and chronic toxicity for *Daphnia magna* (Table 5). At this level, exposure can cause impacts to macroinvertebrate populations, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long-term average exposures. Chlorpyrifos ethyl was not detected in the sediment.

DDD, DDE: DDE is an abbreviation of **d**ichloro**d**iphenyldichloro**e**thylene [2, 2-bis (4-chlorophenyl)-1, 1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichloro**d**iphenyl**t**richloroethane), a popular insecticide for which the U.S. EPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichloro**d**iphenyl**d**ichloroethane), and the high K_{oc} of these compounds account for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioconcentration factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

The DDD sediment concentrations detected range from 5.9 to 27 µg/Kg. Any concentration which would fall below the TEC (4.9 µg/Kg) should not impact sediment dwelling organisms while concentrations above the PEC (28 µg/Kg), frequently or always have the possibility for impacting sediment-dwelling organisms. The sediment concentrations detected were between the TEC and PEC. These concentrations may have the possibility for harmful effects on freshwater sediment-dwelling organisms. DDD was not detected in the surface water.

The TEC is 3.2 µg/Kg and the PEC is 31 µg/Kg for DDE in freshwater sediments. The concentrations of DDE detected at S2 (108 µg/Kg) and S5A (130 µg/Kg) exceeded the PEC and frequently or always have the possibility for impacting sediment-dwelling organisms. DDE was not detected in the surface water.

Dieldrin: Dieldrin is a non-systemic insecticide with all uses canceled in the United States. The high K_{oc} and low water solubility accounts for dieldrin's affinity for sediment. The hydrophobicity of this compound also results in a significant bioconcentration factor and the potential for a high degree of accumulation in aquatic organisms (Table 4). Dieldrin is highly toxic to mammals. The dieldrin concentration detected at S5A (4.6 μg/Kg) exceeds the TEC (1.9 μg/Kg) but is less than the PEC (62 μg/Kg). It is uncertain if this level will have the possibility for impacting sediment-dwelling freshwater organisms. No dieldrin was detected in the surface water.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, alpha (α) and beta (β). Endosulfan is highly toxic to mammals, with an acute oral LD_{50} for rats of 70 mg/Kg (Table 4). The Soil Conservation Service (SCS) rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 4). Beta endosulfan's water solubility and Henry's law constant (1.91×10^{-5} atm – m^3/mole) (Lyman, et al., 1990) indicate volatilization may be significant in shallow waters. The bioconcentration factors indicate a low to moderate degree of accumulation in aquatic organisms (Table 4). Alpha and beta endosulfan were detected in the sediment at S178. However, a sediment quality assessment guideline has not been developed. Endosulfan was not detected in the surface water.

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's law constant (9.63×10^{-8} atm – m^3/mole) (Lyman, et al., 1990) indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Table 4). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). Endosulfan sulfate was detected in the sediment at S178 (13 μg/Kg). However, no sediment quality assessment guideline has been developed for endosulfan sulfate. No endosulfan sulfate was detected in the surface water.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/L for *Daphnia magna* (U.S. EPA, 1988). The highest surface water concentration detected in this sampling event at S4 (0.17 μg/L) should not have an acute impact on fish or aquatic invertebrates. No hexazinone was detected in the sediment.

Metribuzin: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in Tables 4 and 5 indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metribuzin detected was 0.061 µg/L (S190). Using these criteria, this surface water concentration should not have an acute impact on fish or aquatic invertebrates. No metribuzin was detected in the sediment.

<u>Norflurazon</u>: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC_{50} for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.021 to 0.46 µg/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these observed concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates. Norflurazon was not detected in the sediment.

<u>Simazine</u>: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 µg/L (Verschueren, 1983). Aquatic invertebrate LC_{50} toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. EPA, 1984). The only surface water concentration of simazine detected at S191 (0.036 µg/L) was below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

Quality Assurance Evaluation

Replicate samples were collected at locations S177 (surface water only), S18C (sediment only), and S2. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No pesticide analytes were detected in the equipment blanks performed at C25S99, S18C, S331, S191, S3, TAMBR105, S79, and S5A. All collected samples were shipped and all bottles were received.

Glossary

Bioconcentration Factor: The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

EC_{50}: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

Henry's law constant (H): Relates the concentration of a compound in the gas phase to its concentration in the liquid phase. The constant is calculated from the formula: $H = P_{vp}/S$ where P_{vp} is pressure in atmospheres and S is solubility in moles/meter^3 for a compound.

K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

LC_{50}: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LD_{50}: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

Method Detection Limit (MDLs): The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.

Practical Quantitation Limit (PQLs): The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.

Probable Effect Concentration (PEC): The probable effect concentration is intended to identify concentrations above which harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

Soil or water half-life: The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

Threshold Effect Concentration (TEC): The threshold effect concentration is intended to identify concentrations below which harmful effects to freshwater sediment-dwelling organisms are unlikely to be observed.

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Figure 1. South Florida Water Management District Pesticide Monitoring Network.

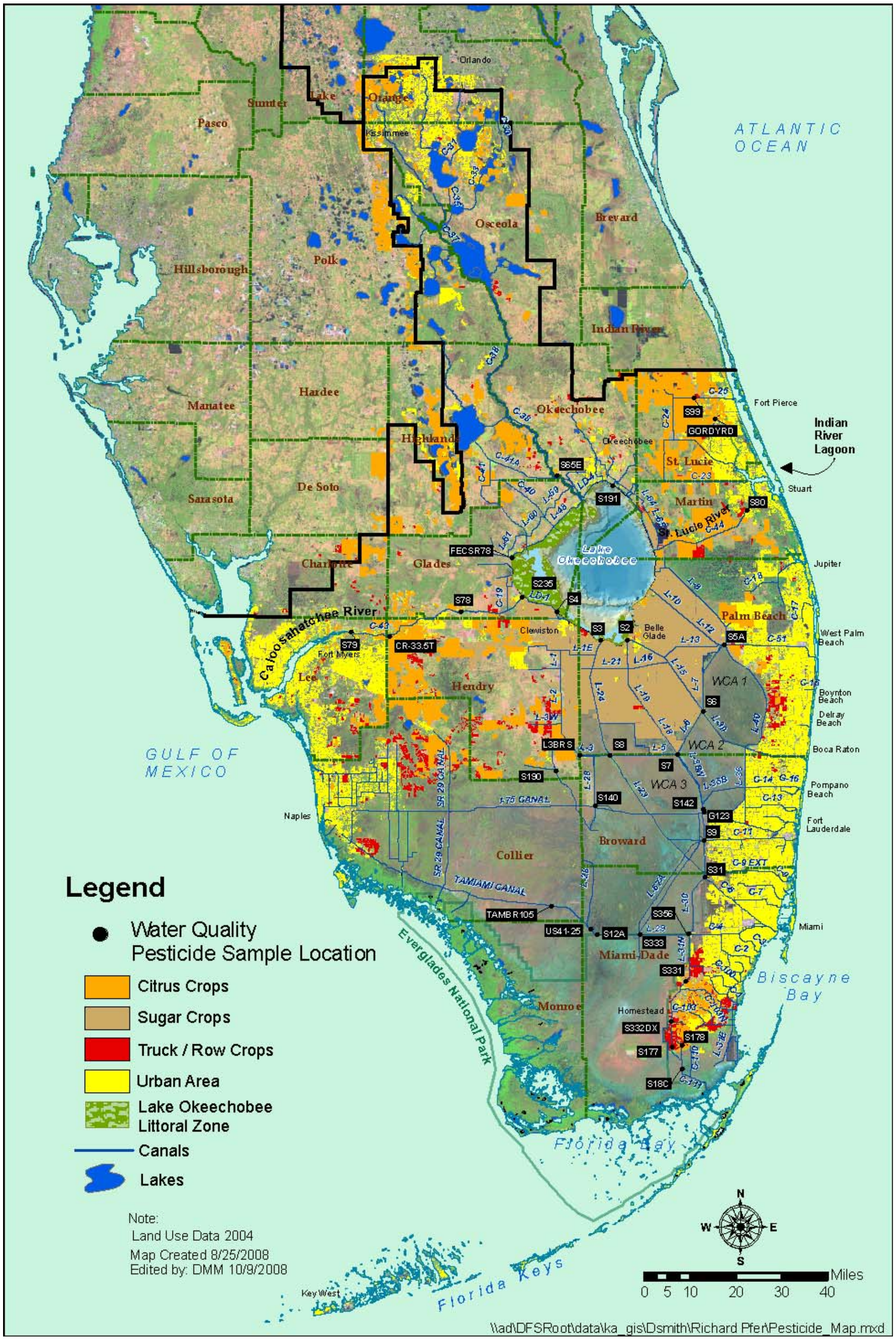

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for Septermber 2008 sampling event.

Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)	Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)
2,4-D	0.2 - 0.6	8.7 - 220	endrin aldehyde	0.0042 - 0.018	0.89 - 30
2,4,5-T	0.2 - 0.6	8.7 - 220	ethion	0.0094 - 0.04	2.2 - 76
2,4,5-TP (silvex)	0.2 - 0.6	8.7 - 220	ethoprop	0.0094 - 0.04	2.2 - 76
acifluorfen	0.2 - 0.6	8.7 - 220	fenamiphos (nemacur)	0.038 - 0.16	4.5 - 150
alachlor	0.057 - 0.24	13 - 440	fonofos (dyfonate)	0.0094 - 0.04	2.2 - 76
aldrin	0.0019 - 0.008	0.45 - 15	heptachlor	0.0023 - 0.0096	0.45 - 15
ametryn	0.0094 - 0.04	2.2 - 76	heptachlor epoxide	0.0019 - 0.017	0.45 - 15
atrazine	0.0094 - 0.04	2.2 - 76	hexazinone	0.019 - 0.08	4.5 - 150
atrazine desethyl	0.0094 - 0.04	N/A	imidacloprid	0.2 - 0.6	N/A
atrazine desisopropyl	0.0094 - 0.04	N/A	linuron	0.2 - 0.6	8.1 - 220
azinphos methyl (guthion)	0.028 - 0.12	6.7 - 220	malathion	0.028 - 0.12	4.5 - 150
α-BHC (alpha)	0.0021 - 0.0088	0.45 - 15	metalaxyl	0.047 - 0.2	N/A
β-BHC (beta)	0.0032 - 0.014	0.45 - 15	methamidophos	N/A	22 - 760
δ-BHC (delta)	0.0019 - 0.008	0.89 - 30	methoxychlor	0.0094 - 0.04	2.2 - 76
γ-BHC (gamma) (lindane)	0.0019 - 0.008	0.45 - 15	metolachlor	0.057 - 0.24	13 - 440
bromacil	0.047 - 0.22	8.9 - 300	metribuzin	0.019 - 0.08	4.5 - 150
butylate	0.019 - 0.08	N/A	mevinphos	0.057 - 0.24	8.9 - 300
carbophenothion (trithion)	0.015 - 0.064	2.2 - 76	mirex	0.011 - 0.048	1.8 - 60
chlordane	0.019 - 0.08	6.7 - 220	monocrotophos (azodrin)	N/A	22 - 760
chlorothalonil	0.015 - 0.064	2.2 - 76	naled	0.075 - 0.32	18 - 600
chlorpyrifos ethyl	0.0094 - 0.04	2.2 - 76	norflurazon	0.019 - 0.08	4.5 - 150
chlorpyrifos methyl	0.019 - 0.08	4.5 - 150	parathion ethyl	0.019 - 0.08	4.5 - 150
cypermethrin	0.019 - 0.08	2.2 - 76	parathion methyl	0.019 - 0.08	4.5 - 150
DDD-P,P'	0.0045 - 0.019	0.89 - 30	PCB-1016	0.019 - 0.08	13 - 440
DDE-P,P'	0.0038 - 0.016	0.89 - 30	PCB-1221	0.019 - 0.08	8.9 - 300
DDT-P,P'	0.0057 - 0.024	1.3 - 44	PCB-1232	0.019 - 0.08	20 - 680
demeton	0.028 - 0.12	6.7 - 220	PCB-1242	0.019 - 0.08	13 - 440
diazinon	0.019 - 0.08	2.2 - 76	PCB-1248	0.019 - 0.08	8.9 - 300
dicofol (kelthane)	0.042 - 0.18	6.7 - 220	PCB-1254	0.019 - 0.08	8.9 - 300
dieldrin	0.0019 - 0.008	0.45 - 15	PCB-1260	0.019 - 0.08	13 - 440
disulfoton	0.019 - 0.08	2.2 - 76	permethrin	0.015 - 0.064	2.7 - 88
diuron	0.2 - 0.6	8.1 - 220	phorate	0.0094 - 0.04	2.2 - 76
α-endosulfan (alpha)	0.0038 - 0.016	0.45 - 15	prometon	0.019 - 0.08	N/A
β-endosulfan (beta)	0.0038 - 0.016	0.45 - 15	prometryn	0.019 - 0.08	4.5 - 150
endosulfan sulfate	0.0045 - 0.02	0.89 - 30	simazine	0.0094 - 0.04	2.2 - 76
endrin	0.0094 - 0.04	2.2 - 76	toxaphene	0.0094 - 0.04	33 - 1100
			trifluralin	0.0075 - 0.032	1.8 - 60

N/A - not analyzed

Table 2. Summary of pesticide residues (µg/L) above the method detection limit found in surface water samples collected by SFWMD in September 2008.

Date	Location	Flow	ametryn	atrazine	atrazine desethyl	bromacil	chlorpyrifos ethyl	hexazinone	metribuzin	norflurazon	simazine	Number of compounds detected at location
9/15/2008	C25S99	Y	-	-	-	-	-	-	-	0.28	-	1
	GORDYRD	Y	-	-	-	-	-	-	-	0.34	-	1
	S177	N	-	-	-	-	-	-	-	-	-	0
	S178	N	-	-	-	-	-	-	-	-	-	0
	S18C	Y	-	-	-	-	-	-	-	-	-	0
	S191	N	-	-	-	-	-	-	-	-	0.036 I	1
	S331	Y	-	-	-	-	-	-	-	-	-	0
	S332DX	Y	-	-	-	-	-	-	-	-	-	0
	S65E	Y	-	0.018 I	-	-	-	0.12	-	-	-	2
	S80	Y	-	-	0.016 I	-	-	-	-	0.11	-	2
9/16/2008	FECSR78	Y	-	-	-	-	-	-	-	-	-	0
	G123	N	-	-	-	-	-	-	-	-	-	0
	S12A	Y	-	-	-	-	-	-	-	-	-	0
	S2	N	0.041 *	0.056 *	-	-	-	-	-	-	-	2
	S3	N	0.025 I	0.072	-	-	-	-	-	-	-	2
	S31	N	-	0.01 I	-	-	-	-	-	-	-	1
	S333	N	-	0.01 I	-	-	-	-	-	-	-	1
	S356	N	-	-	-	-	-	-	-	-	-	0
	S4	N	0.014 I	0.032 I	-	-	-	0.17	-	-	-	3
	S9	Y	-	0.017 I	-	-	-	-	-	-	-	1
	TAMBR105	Y	-	-	-	-	-	-	-	-	-	0
	US41-25	Y	-	-	-	-	-	-	-	-	-	0
9/17/2008	CR33.5T	Y	-	-	-	0.20 I	***0.034 I***	0.020 I	-	0.46	-	4
	L3BRS	N	-	-	-	-	-	-	-	0.077	-	1
	S140	Y	-	-	-	-	-	0.03 I	-	0.032 I	-	2
	S190	Y	-	-	-	-	-	-	0.061 I	0.021 I	-	2
	S235	N	0.030 I	0.018 I	-	-	-	0.071 I	-	-	-	3
	S7	Y	0.026 I	0.077	0.011 I	-	-	-	-	-	-	3
	S78	Y	-	0.023 I	-	-	-	-	-	0.076 I	-	2
	S79	Y	-	0.017 I	-	0.13 I	-	0.024 I	-	0.21	-	4
	S8	Y	-	0.01 I	-	-	-	-	-	-	-	1
9/18/2008	S5A	N	0.041	0.025 I	-	-	-	-	-	-	-	2
	S6	N	0.04	0.028 I	-	-	-	-	-	-	-	2
Total number of compound detections			7	14	2	2	1	6	1	9	1	43

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples
I - value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit
Values in bold, italicized font are at a concentration that potential harmful effects to organisms may be observed.

Table 3. Summary of pesticide residues (μg/Kg) above the method detection limit found in sediment samples collected by SFWMD in September 2008.

Date	Location	Flow	ametryn	chlordane	DDD-P,P'	DDE-P,P'	dieldrin	endosulfan (alpha)	endosulfan (beta)	endosulfan sulfate	Number of compounds detected at location
9/15/2008	S177	N	-	-	-	2.9 I	-	-	-	-	1
	S178	N	-	-	-	9.3 I	-	3.7 I	4.9 I	13 I	4
	S80	Y	-	-	-	3.6 I	-	-	-	-	1
9/16/2008	S2	N	-	***63 ****	24 I *	***108 ****	-	-	-	-	3
	S3	N	-	-	7.4 I	30	-	-	-	-	2
	S31	N	-	-	-	1.9 I	-	-	-	-	1
	S4	N	7.0 I	-	-	4.5 I	-	-	-	-	2
9/17/2008	S7	Y	-	-	-	2.8 I	-	-	-	-	1
	S78	Y	-	-	-	1.6 I	-	-	-	-	1
	S8	Y	-	-	-	3.4 I	-	-	-	-	1
9/18/2008	S5A	N	-	***73 I***	27	***130***	4.6 I	-	-	-	4
	S6	N	-	13 I	5.9	18	-	-	-	-	3
Total number of compound detections			1	3	4	12	1	1	1	1	24

N - no Y - yes R - reverse; - denotes that the result is below the method detection limit; * results are the average of replicate samples
I - value reported is less than the practical quantitation limit, and greater than or equal to the minimum detection limit
Values in bold, italicized font are at a concentration that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

Table 4. Selected properties of pesticides found in Septermber 2008 sampling event.

Common Name	Surface Water Standards FAC 62-302 (µg/L)	LD_{50} acute rats oral (mg/kg) (1)	EPA Carcinogenic Potential	Water Solubility (WS) (mg/L) (2, 3)	K_{oc} (mL/g) (2, 3)	Soil Half-life (days) (2, 3)	Soil Conservation Service (SCS) rating (2)			Volatility from Water	Bioconcentration Factor (BCF)
							LE	SA	SS		
ametryn	-	1,110	D	185	300	60	M	M	M	I	33
atrazine	-	3,080	C	33	100	60	L	M	L	I	86
bromacil	-	5,200	C	700	32	60	L	M	M	I	15
chlordane	0.0043	365 - 590	B2	0.056	3,800	-	-	-	-	I	3,141
chlorpyrifos ethyl	-	135 - 163	D	2	6,070	30	S	M	M	-	418
DDD, p,p'	-	3,400	-	0.055	239,900	-	-	-	-	I	3,173
DDE, p,p'	-	880	-	0.065	243,220	-	-	-	-	S	2,887
dieldrin	0.0019	37 - 87	B2	0.14	10,000 est.	-	-	-	-	I	1,873
endosulfan-alpha	0.056	70	-	0.53	12,400	50	XS	L	M	S	884
endosulfan-beta		70	-	0.28	-	-	-	-	-	S	1,267
endosulfan-sulfate	-	-	-	0.117	-	-	-	-	-	I	2,073
hexazinone	-	1,690	D	33,000	54	90	L	M	M	I	2
metribuzin	-	2,200	D	1,220	41	30	L	S	M	I	11
norflurazon	-	9,400	C	28	700	90	M	M	L	I	94
simazine	-	>5,000	C	6.2	130	60	L	M	M	I	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS)
Volatility from water: R = rapid, I = insignificant, S = significant
Bioconcentration Factor (BCF) calculated as BCF = $10^{\wedge(2.791 - 0.564 \log WS)}$ (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP FAC 62-302 surface water standards (12/06) for Class III waters except Class I in ( )
Note: endosulfan usually considered the sum of alpha and beta isomers

(1) Hartley and Kidd (1987)
(2) Goss and Wauchope (1992)
(3) Montgomery (1993)
(4) Lyman, et al. (1990)
(5) U.S. EPA (1996a)

Table 5. Toxicity of pesticides found in the September 2008 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

Common Name	48 hr EC_{50} Water flea *Daphnia magna*	Acute Toxicity (*)	Chronic Toxicity (*)	96 hr LC_{50} Fathead Minnow (#) *Pimephales promelas*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Bluegill *Lepomis macrochirus*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Largemouth Bass *Micropterus salmoides*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Channel Catfish *Ictalurus punctatus*	Acute Toxicity	Chronic Toxicity
ametryn	28,000 (7)	9,333	1,400	-	-	-	4,100 (4)	1,367	205	-	-	-	8,800 (4)	2,933	440	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	3,600 (8)	1,200	180	-	-	-
atrazine	6,900 (7)	2,300	345	15,000 (7)	5,000	750	16,000 (4)	5,333	800	-	-	-	8,800 (4)	2,933	440	7,600 (4)	2533	380
	-	-	-	-	-	-	-	-	-	-	-	-	5,300 (9)	1,767	265	-	-	-
bromacil	-	-	-	-	-	-	127,000 (7)	42,333	6,350	-	-	-	36,000 (7)	12,000	1,800	-	-	-
	121,000 (10)	40,333	6,050	-	-	-	127,000 (10)	42,333	6,350	-	-	-	36,000 (10)	12,000	1,800	-	-	-
chlordane	-	-	-	-	-	-	70 (5)	23	3.5	-	-	-	90 (5)	30	5	-	-	-
chlorpyrifos ethyl	1.7 (7)	0.57	0.085	203 (7)	68	10	2.6 (4)	0.87	0.13	-	-	-	11 (4)	3.7	0.55	280 (7)	93	14
	0.1 (7)	0.03	0.005	-	-	-	5.8 (7)	1.93	0.29	-	-	-	-	-	-	-	-	-
	0.1 (11)	0.03	0.005	-	-	-	1.8 (11)	0.60	0.09	-	-	-	-	-	-	-	-	-
DDD, p,p'	3,200 (6)	1,067	160	4,400 (1)	1467	220	42 (1)	14	2.1	42 (1)	14	2.1	70 (1)	23.3	3.5	1,500 (1)	500	75
DDE, p,p'	-	-	-	-	-	-	240 (1)	80	12	-	-	-	32 (1)	10.7	1.6	-	-	-
dieldrin	-	-	-	16 (5)	5.3	0.80	8 (4)	2.7	0.4	-	-	-	10 (5)	3.3	0.5	4.5 (5)	1.5	0.23
endosulfan	166 (7)	55	8	1 (1)	0.3	0.05	1 (1)	0.33	0.05	-	-	-	1 (1)	0.33	0.050	1 (1)	0.3	0.05
	-	-	-	-	-	-	2 (3)	0.67	0.10	-	-	-	3 (2)	1	0.15	1.5 (7)	0.5	0.08
	-	-	-	-	-	-	-	-	-	-	-	-	1 (3)	0.33	0.050	-	-	-
	166 (12)	55	8	1.5 (12)	0.5	0.08	1.7 (12)	0.57	0.09	-	-	-	0.8 (12)	0.27	0.04	-	-	-
hexazinone	151,600 (7)	50,533	7,580	274,000 (4)	91,333	13,700	100,000 (7)	33,333	5,000	-	-	-	180,000 (7)	60,000	9,000	-	-	-
	151,600 (13)	50,533	7,580	274,000 (13)	91,333	13,700	505,000 (13)	168,333	25,250	-	-	-	>320,000 (13)	>106,667	>16,000	-	-	-
metribuzin	4,200 (7)	1,400	210	-	-	-	80,000 (4)	26,667	4,000	-	-	-	64,000 (4)	21,333	3,200	100,000 (7)	33,333	5,000
	4,200 (14)	1,400	210	-	-	-	75,900 (14)	25,300	3,795	-	-	-	76,770 (14)	25,590	3,839	-	-	-
norflurazon	15,000 (7)	5,000	750	-	-	-	16,300 (7)	5,433	815	-	-	-	8,100 (7)	2,700	405	>200,000 (4)	>67,000	>10,000
	>15,000 (15)	>5,000	>750	-	-	-	16,300 (15)	5,433	815	-	-	-	8,100 (15)	2,700	405	-	-	-
simazine	1,100 (7)	367	55	100,000 (7)	33,333	5,000	90,000 (4)	30,000	4,500	-	-	-	100,000 (7)	33,333	5,000	-	-	-

(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC50 is the lowest value which has been determined for a species significant to the indigenous aquatic community.
(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson and Finley (1980)
(2) U.S. EPA (1977)
(3) Schneider (1979)
(4) Hartley and Kidd (1987)
(5) Montgomery (1993)
(6) Verschueren (1983)
(7) U.S. EPA (1991)
(8) U.S. EPA (2005)
(9) U.S. EPA (2006)
(10) U.S. EPA (1996c)
(11) U.S. EPA (2002a)
(12) U.S. EPA (2002b)
(13) U.S. EPA (1994)
(14) U.S. EPA (1998)
(15) U.S. EPA (1996b)

Table 6. Atrazine desethyl/atrazine ratio (DAR) data for September 2008 sampling event.

Date	Location	Flow*	atrazine		atrazine desethyl		DAR
			µg/l	moles/l	µg/l	moles/l	
9/17/2008	S7	Y	0.077	3.57002E-10	0.011	5.86256E-11	0.2

DAR	All sites	Flow only sites	No flow sites
average	0.2	0.2	-
median	0.2	0.2	-
minimum	0.2	0.2	-
maximum	0.2	0.2	-

* N - no; Y - yes; R - reverse

PESTICIDE SURFACE WATER QUALITY REPORT

DECEMBER 2008 SAMPLING EVENT

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Pesticide Monitoring Project Report
December 2008 Sampling Event

Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water samples from 33 of the 34 network sites were collected December 8 to December 10, 2008, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides 2,4-D, ametryn, atrazine, bromacil, diuron, hexazinone, metolachlor, metribuzin, norflurazon, and simazine, along with the insecticides/degradates atrazine desethyl, atrazine desisopropyl, alpha endosulfan, beta endosulfan, and malathion, were detected in one or more of these surface water samples. The malathion concentration of 0.14 µg/L at S99 exceeds the Florida Administrative Code 62-302 Class III surface water quality standard of 0.1 µg/L. No harmful impacts are expected from the other detected pesticides.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods

The SFWMD pesticide monitoring network includes stations designated in the Everglades Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction Project (non-ECP) permit. The canals and marshes depicted in Figure 1 are protected as Florida Administrative Code (F.A.C.) 62-302 Class III (fishable and swimmable) waters, while Lake Okeechobee and a segment of the Caloosahatchee River are protected as a Class I drinking water supply. Water Conservation Area 1 (WCA-1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Seventy-one pesticides and degradation products were analyzed in samples from 33 of the 34 network sites (Figure 1). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp.

To evaluate the potential impacts on aquatic life, the observed concentration is compared to the appropriate criterion outlined in F.A.C. 62-302.530. If a pesticide compound is not specifically listed, acute and chronic toxicity criterion are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, using the lowest technical grade effective concentration 50 (EC_{50}) or lethal concentration 50 (LC_{50}) reported in the summarized literature for the species significant to the indigenous aquatic community (F.A.C. 62-302.200). Each pesticide's description and possible uses and sites of application described herein are taken from Hartley and Kidd (1987). This summary covers surface water samples collected from December 8 to December 10, 2008.

Results

At least one pesticide was detected in surface water at 23 of the 33 sites. Modifications to the non-ECP permit changed the requirement for sampling at S142 to only during discharge or flow events. For this sampling event, no sample was obtained due to no discharge at the time of sample collection. The concentrations of the pesticides detected at each of the sites are summarized for the surface water in Table 2. All of these compounds have previously been detected in this monitoring program. Only the malathion concentration detected at S99 has the possibility for causing an environmental impact. No harmful impacts are expected from the other detected pesticides.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long-term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

2,4-D: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The only 2,4-D concentration was detected at S99 (0.41 micrograms per liter [μg/L]) (Table 2). Using these criteria, this observed level should not have an acute or chronic effect on fish or aquatic invertebrates.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 micrograms per liter (μg/L) (Verschueren, 1983). Environmental fate and toxicity data in Tables 3 and 4 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.010 to 0.037 μg/L. Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies

(Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 μg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003a). The atrazine surface water concentrations found in this sampling event at 19 of the 33 sampling locations, ranged from 0.013 to 0.18 μg/L. Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of groundwater discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1 to 0.2) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 5). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

<u>Bromacil</u>: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at CR33.5T (0.95 μg/L). Using these criteria, this observed concentration should not have an acute or chronic detrimental impact on fish.

<u>Diuron</u>: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48-hour LC_{50} of 1.4 mg/L for water fleas and a 96-hour LC_{50} of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 μg/L (Verschueren, 1983). The only surface water concentration of diuron found during this sampling event was 0.37 μg/L at

CR33.5T (Table 2). Using these criteria, this concentration should not have an acute, harmful impact on fish, aquatic invertebrates, or algae.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, alpha (α) and beta (β). Endosulfan is highly toxic to mammals, with an acute oral LD_{50} for rats of 70 mg/Kg (Table 3). The Soil Conservation Service (SCS) rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 3). Beta endosulfan's water solubility and Henry's law constant (1.91×10^{-5} atm – m^3/mole) (Lyman, et al. 1990) indicate volatilization may be significant in shallow waters. The bioconcentration factors indicate a low to moderate degree of accumulation in aquatic organisms (Table 3). Endosulfan (α and/or β) was detected in the surface water at S178 and CR33.5T (Table 2). However, none of the concentrations exceeded the F.A.C. 62-302 standard of 0.056 µg/L.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/L for *Daphnia magna* (U.S. EPA, 1988). The highest surface water concentration detected in this sampling event at S191 (0.23 µg/L) should not have an acute impact on fish or aquatic invertebrates.

Malathion: Malathion is an insecticide/acaricide used on a variety of crops including fruits, vines, ornamentals, vegetables, and field crops (Hartley and Kidd, 1987). Environmental fate and toxicity data in Tables 3 and 4 indicate that malathion (1) has a small potential for loss from soil by leaching, surface adsorption or surface solution; (2) is relatively non-toxic to mammals but highly toxic to fish; and (3) does not bioaccumulate significantly. The only concentration of malathion found in the surface water from this sampling event was 0.14 µg/L at S99. This concentration exceeded the F.A.C. 62-302 standard of 0.1 µg/L.

Metolachlor: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in Tables 3 and 4 indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The only surface water concentration found in this sampling event (0.10 µg/L at CR33.5T) is over two orders of magnitude below the calculated chronic toxicity level. Using these criteria, this observed level should not have a harmful effect on fish or aquatic invertebrates.

Metribuzin: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in Tables 3 and 4 indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The highest concentration of metribuzin detected was 0.034 μg/L (CR33.5T). Using these criteria, this surface water concentration should not have an acute impact on fish or aquatic invertebrates.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC_{50} for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.038 to 1.2 μg/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these observed concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 μg/L (Verschueren, 1983). Aquatic invertebrate LC_{50} toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. EPA, 1984). The highest surface water concentration of simazine detected at CR33.5T (0.18 μg/L) was below any level of concern for fish or aquatic invertebrates.

Quality Assurance Evaluation

Replicate samples were collected at sites S331 and S80. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No pesticide analytes were detected in the field blanks performed at S177, S78, GORDYRD, S8, and S7. All collected samples were shipped and all bottles were received.

Glossary

LD_{50}: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LC_{50}: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

EC_{50}: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:
The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:
The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

Method Detection Limit (MDLs):
The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.

Practical Quantitation Limit (PQLs):
The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is $<$ 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.

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Figure 1. South Florida Water Management District Pesticide Monitoring Network.

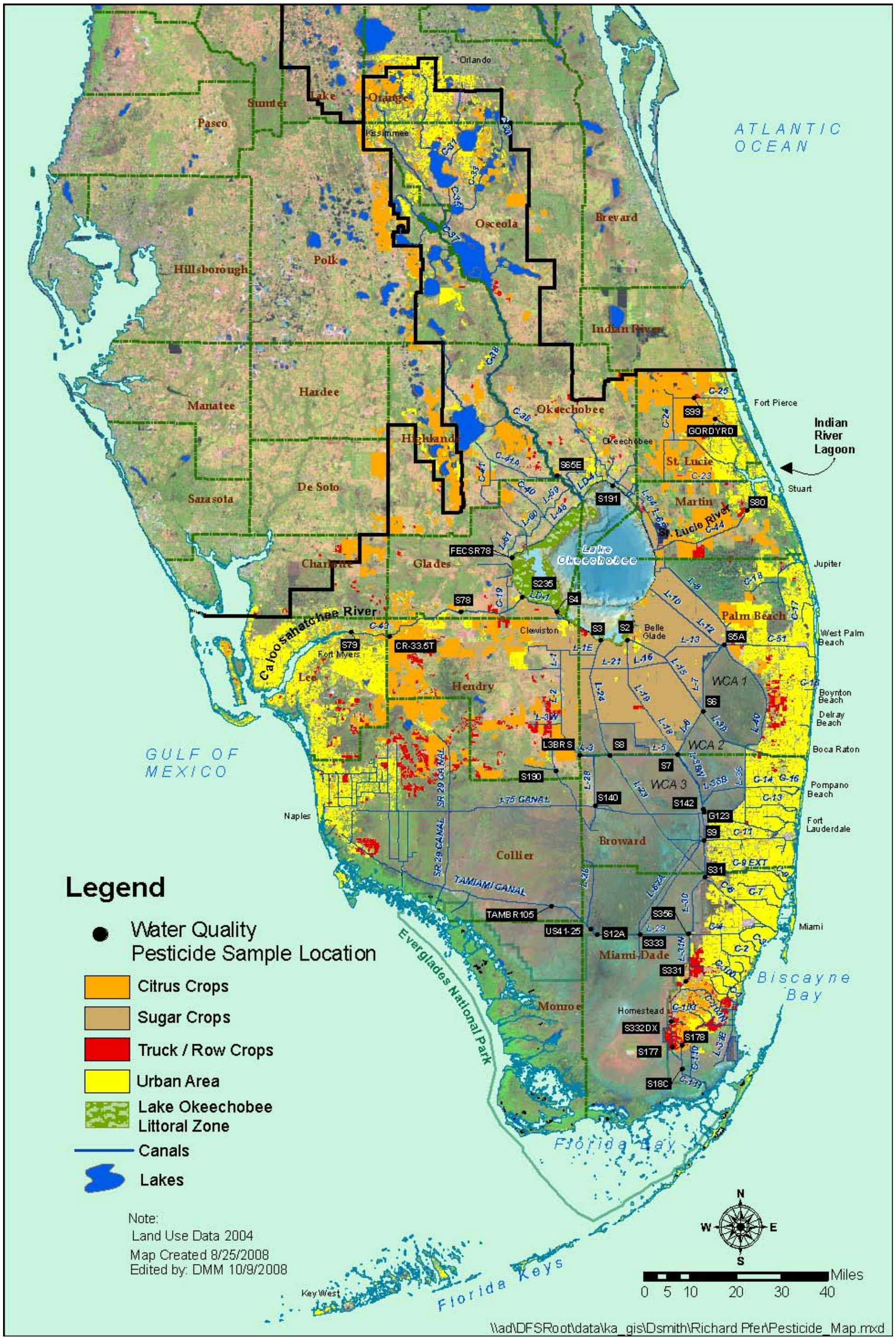

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for December 2008 sampling event.

Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)
2,4-D	0.2 - 0.6	endrin aldehyde	0.0041 - 0.018
2,4,5-T	0.2 - 0.6	ethion	0.0094 - 0.04
2,4,5-TP (silvex)	0.2 - 0.6	ethoprop	0.0094 - 0.04
acifluorfen	0.2 - 0.6	fenamiphos (nemacur)	0.038 - 0.16
alachlor	0.056 - 0.24	fonofos (dyfonate)	0.0094 - 0.04
aldrin	0.0019 - 0.008	heptachlor	0.0023 - 0.0096
ametryn	0.0094 - 0.04	heptachlor epoxide	0.0019 - 0.008
atrazine	0.0094 - 0.04	hexazinone	0.019 - 0.08
atrazine desethyl	0.0094 - 0.04	imidacloprid	0.2 - 0.6
atrazine desisopropyl	0.0094 - 0.04	linuron	0.2 - 0.6
azinphos methyl (guthion)	0.028 - 0.12	malathion	0.028 - 0.12
α-BHC (alpha)	0.0021 - 0.0088	metalaxyl	0.047 - 0.2
β-BHC (beta)	0.0032 - 0.014	methoxychlor	0.0094 - 0.04
δ-BHC (delta)	0.0019 - 0.008	metolachlor	0.056 - 0.24
γ-BHC (gamma) (lindane)	0.0019 - 0.008	metribuzin	0.019 - 0.08
bromacil	0.047 - 0.31	mevinphos	0.056 - 0.24
butylate	0.019 - 0.08	mirex	0.011 - 0.048
carbophenothion (trithion)	0.015 - 0.064	naled	0.075 - 0.32
chlordane	0.019 - 0.08	norflurazon	0.019 - 0.08
chlorothalonil	0.015 - 0.064	parathion ethyl	0.019 - 0.08
chlorpyrifos ethyl	0.0094 - 0.04	parathion methyl	0.019 - 0.08
chlorpyrifos methyl	0.019 - 0.08	PCB-1016	0.019 - 0.08
cypermethrin	0.019 - 0.08	PCB-1221	0.019 - 0.08
DDD-P,P'	0.0045 - 0.02	PCB-1232	0.019 - 0.08
DDE-P,P'	0.0038 - 0.016	PCB-1242	0.019 - 0.08
DDT-P,P'	0.0056 - 0.024	PCB-1248	0.019 - 0.08
demeton	0.028 - 0.12	PCB-1254	0.019 - 0.08
diazinon	0.019 - 0.08	PCB-1260	0.019 - 0.08
dicofol (kelthane)	0.041 - 0.18	permethrin	0.015 - 0.064
dieldrin	0.0019 - 0.008	phorate	0.0094 - 0.04
disulfoton	0.019 - 0.08	prometryn	0.019 - 0.08
diuron	0.2 - 0.6	prometon	0.019 - 0.08
α-endosulfan (alpha)	0.0038 - 0.016	simazine	0.0094 - 0.04
β-endosulfan (beta)	0.0038 - 0.016	toxaphene	0.094 - 0.4
endosulfan sulfate	0.0045 - 0.02	trifluralin	0.0075 - 0.032
endrin	0.0094 - 0.04		

Table 2. Summary of pesticide residues (µg/L) above the method detection limit found in surface water samples collected by SFWMD in December 2008.

Date	Location	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	atrazine desisopropyl	bromacil	diuron	alpha endosulfan	beta endosulfan	hexazinone	malathion	metolachlor	metribuzin	norflurazon	simazine	Number of compounds detected at location
12/8/2008	CR33.5T	N	-	-	0.13	0.021 I	0.021 I	0.95	0.37 I	0.0040 I	0.010 I	-	-	0.10 I	0.034 I	1.2	0.18	11
	FECSR78	N	-	-	0.044	-	-	0.093 I	-	-	-	-	-	-	-	-	-	2
	S12A	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S177	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S178	N	-	-	-	-	-	-	-	0.0064 I	-	-	-	-	-	-	-	1
	S18C	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S191	N	-	-	0.046	-	-	-	-	-	-	0.23	-	-	-	-	-	2
	S235	N	-	0.028 I	0.064	-	-	-	-	-	-	0.063 I	-	-	-	-	-	3
	S331	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S332DX	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S333	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S356-334	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S65E	Y	-	-	0.033 I	-	-	-	-	-	-	0.030 I	-	-	-	-	-	2
	S78	N	-	-	0.18	0.015 I	-	-	-	-	-	-	-	-	-	-	-	2
	S79	N	-	0.011 I	0.051	-	-	0.080 I	-	-	-	-	-	-	0.032 I	0.16	0.021 I	6
	TAMBR105	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	US41-25	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
12/9/2008	S99	N	0.41 I	-	0.013 I	-	-	-	-	-	-	-	***0.14***	-	-	0.26	-	4
	G123	N	-	0.011 I	-	-	-	-	-	-	-	-	-	-	-	-	-	1
	GORDYRD	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	0.33	-	1
	L3BRS	N	-	-	0.030 I	-	-	-	-	-	-	-	-	-	-	-	-	1
	S140	N	-	-	-	-	-	-	-	-	-	-	-	-	-	0.038 I	-	1
	S190	N	-	-	0.014 I	-	-	-	-	-	-	-	-	-	-	-	-	1
	S2	N	-	-	0.10	0.020 I	-	-	-	-	-	0.026 I	-	-	-	-	0.012 I	4
	S3	N	-	-	0.13	0.021 I	-	-	-	-	-	0.033 I	-	-	-	-	0.016 I	4
	S31	N	-	0.010 I	0.025 I	-	-	-	-	-	-	-	-	-	-	-	-	2
	S4	N	-	0.013 I	0.13	0.019 I	-	-	-	-	-	0.037 I	-	-	-	-	0.013 I	5
	S8	N	-	-	0.026 I	-	-	-	-	-	-	-	-	-	-	-	-	1
	S80	Y	-	-	0.12 *	0.029 I *	-	-	-	-	-	0.02 I *	-	-	-	0.091 *	0.010 I *	5
	S9	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
12/10/2008	S5A	Y	-	-	0.14	0.035 I	-	-	-	-	-	0.025 I	-	-	-	-	0.012 I	4
	S6	N	-	0.037 I	0.019 I	-	-	-	-	-	-	-	-	-	-	-	-	2
	S7	N	-	0.020 I	0.053	-	-	-	-	-	-	-	-	-	-	-	-	2
Total number of compound detections			1	7	19	7	1	3	1	2	1	8	1	1	2	6	7	67

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples
I - value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit
Values in bold, italicized font are at a concentration that potential harmful effects to organisms may be observed.

Table 3. Selected properties of pesticides found in December 2008 sampling event.

Common Name	Surface Water Standards F.A.C. 62-302 (µg/L)	Acute Oral LD_{50} For Rats (mg/kg) (1)	U.S. EPA Carcinogenic Potential	Water Solubility (WS) (mg/L) (2, 3)	K_{oc} (mL/g) (2, 3)	Soil Half-life (days) (2, 3)	Soil Conservation Service (SCS) rating (2)			Volatility from Water	Bioconcentration Factor (BCF)
							LE	SA	SS		
2,4-D (acid)	(100)	375	D	890	20	10	M	S	M	I	13
ametryn	-	1,110	D	185	300	60	M	M	M	I	33
atrazine	-	3,080	C	33	100	60	L	M	L	I	86
bromacil	-	5,200	C	700	32	60	L	M	M	I	15
diuron	-	3,400	D	42	480	90	M	M	L	I	75
endosulfan alpha	0.056	70	-	0.53	12,400	50	XS	L	M	S	884
endosulfan beta		70	-	0.28	-	-	-	-	-	S	1,267
endosulfan sulfate	-	-	-	0.117	-	-	-	-	-	I	2,073
hexazinone	-	1,690	D	33,000	54	90	L	M	M	I	2
malathion	0.1	2,800	D	145	1,800	1	S	S	S	I	37
metolachlor	-	2,780	C	530	200	90	L	M	M	I	18
metribuzin	-	2,200	D	1,220	41	30	L	S	M	I	11
norflurazon	-	9,400	C	28	700	90	M	M	L	I	94
simazine	-	>5,000	C	6.2	130	60	L	M	M	I	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS)
Volatility from water: R = rapid, I = insignificant, S = significant

Bioconcentration Factor (BCF) calculated as BCF = $10^{\wedge(2.791 - 0.564 \log WS)}$ (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP F.A.C. 62-302 surface water standards (12/06) for Class III waters except Class I in ( )
Note: endosulfan usually considered the sum of alpha and beta isomers

(1) Hartley and Kidd (1987)
(2) Goss and Wauchope (1992)
(3) Montgomery (1993)
(4) Lyman, et al. (1990)
(5) U.S. EPA (1996a)

Table 4. Toxicity of pesticides found in the December 2008 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

Common Name	48 hr EC_{50} Water flea *Daphnia magna*	Acute Toxicity (*)	Chronic Toxicity (*)	96 hr LC_{50} Fathead Minnow (#) *Pimephales promelas*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Bluegill *Lepomis macrochirus*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Largemouth Bass *Micropterus salmoides*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Channel Catfish *Ictalurus punctatus*	Acute Toxicity	Chronic Toxicity
2,4-D	25,000 (9)	8,333	1,250	133,000 (9)	44,333	6,650	180,000 (10)	60,000	9,000	-	-	-	100,000 (6)	33,333	5,000	-	-	-
	-	-	-	-	-	-	900 (48 hr) (8)	-	-	-	-	-	110,000 (9)	36,667	5,500	-	-	-
ametryn	28,000 (9)	9,333	1,400	16,000 (11)	5,333	800	4,100 (6)	1,367	205	-	-	-	8,800 (6)	2,933	440	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	3,600 (11)	1,200	180	-	-	-
atrazine	6,900 (9)	2,300	345	15,000 (9)	5,000	750	16,000 (6)	5,333	800	-	-	-	8,800 (6)	2,933	440	7,600 (6)	2,533	380
	-	-	-	-	-	-	-	-	-	-	-	-	5,300 (12)	1,767	265	-	-	-
bromacil	-	-	-	-	-	-	127,000 (9)	42,333	6,350	-	-	-	36,000 (9)	12,000	1,800	-	-	-
	121,000 (19)	40,333	6,050	-	-	-	127,000 (19)	42,333	6,350	-	-	-	36,000 (19)	12,000	1,800	-	-	-
diuron	1,400 (9)	467	70	14,200 (9)	4,733	710	5,900 (6)	1,967	295	-	-	-	5,600 (6)	1,867	280	-	-	-
	1,400 (13)	467	70	14,000 (13)	4,667	700	-	-	-	-	-	-	-	-	-	-	-	-
endosulfan	166 (9)	55	8	1 (1)	0.3	0.05	1 (1)	0.33	0.05	-	-	-	1 (1)	0.33	0	1 (1)	0.3	0.05
	-	-	-	-	-	-	2 (4)	0.67	0.10	-	-	-	3 (2)	1	0	1.5 (9)	0.5	0.08
	-	-	-	-	-	-	-	-	-	-	-	-	1 (4)	0.33	0	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	0.3 (7)	0.10	0	-	-	-
	166 (14)	55	8	1.5 (14)	0.5	0.08	1.7 (14)	0.57	0.09	-	-	-	0.8 (14)	0.27	0	-	-	-
hexazinone	151,600 (9)	50,533	7,580	274,000 (6)	91,333	13,700	100,000 (9)	33,333	5,000	-	-	-	180,000 (9)	60,000	9,000	-	-	-
	151,600 (15)	50,533	7,580	274,000 (15)	91,333	13,700	505,000 (15)	168,333	25,250	-	-	-	>320,000 (15)	>106,667	-	-	-	-
malathion	1 (1)	0.3	0.05	8,650 (1)	2,883	433	103 (1)	34	5.2	285 (1)	95	14	200 (1)	67	10	8,970 (1)	2,990	449
	1.8 (5)	0.6	0.09	9,000 (2)	3,000	450	110 (2)	37	5.5	-	-	-	170 (2)	57	9	7,620 (9)	2,540	381
	-	-	-	-	-	-	12 (3)	4	0.6	-	-	-	100 (3)	33	5	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	29 (4)	10	1	-	-	-
	1.0 (16)	0.33	0.05	-	-	-	30 (16)	10	1.5	-	-	-	4 (16)	1.3	0	-	-	-
metolachlor	23,500 (9)	7,833	1,175	-	-	-	15,000 (6)	5,000	750	-	-	-	2,000 (6)	667	100	4,900 (7)	1,633	245
metribuzin	4,200 (9)	1,400	210	-	-	-	80,000 (6)	26,667	4,000	-	-	-	64,000 (6)	21,333	3,200	100,000 (9)	33,333	5,000
	4,200 (17)	1,400	210	-	-	-	75,900 (17)	25,300	3,795	-	-	-	76,770 (17)	25,590	3,839	-	-	-
norflurazon	15,000 (9)	5,000	750	-	-	-	16,300 (9)	5,433	815	-	-	-	8,100 (9)	2,700	405	>200,000 (6)	>67,000	>10,000
	>15,000 (18)	>5,000	>750	-	-	-	16,300 (18)	5,433	815	-	-	-	8,100 (18)	2,700	405	-	-	-
simazine	1,100 (9)	367	55	100,000 (9)	33,333	5,000	90,000 (6)	30,000	4,500	-	-	-	100,000 (9)	33,333	5,000	-	-	-

(*) Florida Administrative Code (F.A.C.) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC_{50} is the lowest value which has been determined for a species significant to the indigenous aquatic community.
(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson and Finley (1980)
(2) U.S. EPA (1977)
(3) Davis (1970)
(4) Schneider (1979)
(5) U.S. EPA (1972)
(6) Hartley and Kidd (1987)
(7) Montgomery (1993)
(8) Verschueren (1983)
(9) U.S. EPA (1991)
(10) Mayer and Ellersieck (1986)
(11) U.S. EPA (2005)
(12) U.S. EPA (2006a)
(13) U.S. EPA (2003b)
(14) U.S. EPA (2002)
(15) U.S. EPA (1994)
(16) U.S. EPA (2006b)
(17) U.S. EPA (1998)
(18) U.S. EPA (1996b)
(19) U.S. EPA (1996c)

Table 5. Atrazine desethyl/atrazine ratio (DAR) data for December 2008 sampling event.

Date	Location	Flow*	atrazine		atrazine desethyl		DAR
			µg/L	moles/L	µg/L	moles/L	
12/8/2008	CR33.5T	N	0.13	6.02731E-10	0.021	1.11922E-10	0.2
	S78	N	0.18	8.34550E-10	0.015	7.99439E-11	0.1
12/9/2008	S2	N	0.10	4.63639E-10	0.020	1.06592E-10	0.2
	S3	N	0.13	6.02731E-10	0.021	1.11922E-10	0.2
	S4	N	0.13	6.02731E-10	0.019	1.01262E-10	0.2
	S80	Y	0.12	5.41067E-10	0.029	1.54558E-10	0.3
12/10/2008	S5A	Y	0.14	6.49094E-10	0.035	1.86536E-10	0.3

DAR	All sites	Flow only sites	No flow sites
average	0.2	0.3	0.2
median	0.2	0.3	0.2
minimum	0.1	0.3	0.1
maximum	0.3	0.3	0.2

* N - no; Y - yes; R - reverse

PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

FEBRUARY 2009 SAMPLING EVENT

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Pesticide Monitoring Program Report
February 2009 Sampling Event

Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water and sediment samples were collected February 23 to February 26, 2009, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides ametryn, atrazine, bromacil, hexazinone, metribuzin, norflurazon, and simazine, along with the insecticide/degradates atrazine desethyl, alpha endosulfan, beta endosulfan, and endosulfan sulfate were detected in one or more of these surface water samples. No harmful impacts are expected from the detected pesticides.

The herbicide ametryn and the insecticides/degradates DDD, DDE, DDT, endosulfan sulfate, along with one PCB compound were found in the sediment at several locations. Five DDE compound sediment concentrations were of a magnitude considered to have a harmful effect to freshwater sediment-dwelling organisms. No harmful impacts are expected from the other detected pesticides.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods

The SFWMD pesticide monitoring network includes stations designated in the Everglades Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction Project (non-ECP) permit. The canals and marshes depicted in Figure 1 are protected as Florida Administrative Code (F.A.C.) 62-302 Class III (fishable and swimmable) waters, while Lake Okeechobee and a segment of the Caloosahatchee River are protected as a Class I drinking water supply. Water Conservation Area 1 (WCA-1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Seventy-three pesticides and degradation products were analyzed in samples from 33 of the network 34 sites (Figure 1). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp.

To evaluate the potential impacts on aquatic life, the observed concentration is compared to the appropriate criterion outlined in F.A.C. 62-302.530. If a pesticide compound is not specifically listed, acute and chronic toxicity criterion are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, using the lowest technical grade effective concentration 50 (EC_{50}) or lethal concentration 50 (LC_{50}) reported in the summarized literature for the species significant to the indigenous aquatic community (F.A.C. 62-302.200). Each pesticide's description and possible uses and sites of application described herein are taken from Hartley and Kidd (1987). Sediment concentrations are compared to freshwater sediment quality assessment guidelines (MacDonald Environmental Sciences, Ltd., and United States Geological Survey, 2003). A value below the threshold effect concentration (TEC) should not have a harmful effect on sediment-dwelling organisms. Values above the probable effect concentration (PEC) demonstrate that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed. This summary covers surface water and sediment samples collected from February 23 to February 26, 2009.

Results

At least one pesticide was detected in surface water at 23 of the 33 sites and in sediment at 14 of the 28 sites. Modifications to the non-ECP permit changed the requirement for sampling at S142 to only during discharge or flow events. For this sampling event, no sample was obtained due to no discharge at the time of sample collection. Sediment samples are not collected at GORDYRD, CR33.5T, S333, S356-334, and TAMBR105. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All of these compounds have previously been detected in this monitoring program.

The sediment DDE concentrations at S2, S3, S4, S5A, and S6 were of a magnitude considered to represent detrimental effects to sediment-dwelling organisms in freshwater sediments. All other detected concentrations in the surface water and sediment were below any effect level.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long-term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations greater than (>) 10 micrograms per liter (µg/L) (Verschueren, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.013 to 0.089 µg/L. Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates. Ametryn was detected in the sediment at S5A at 9.2 micrograms per kilogram (µg/Kg). However, no sediment guidelines have been developed for ametryn.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch, and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 μg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003). The atrazine surface water concentrations found in this sampling event at 19 of the 33 sampling locations, ranged from 0.014 to 2.1 μg/L. Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates. Atrazine was not detected in the sediment.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of groundwater discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1 to 0.2) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 164 mg/L for carp (Hartley and Kidd, 1987). The only concentration of bromacil detected in the surface water during this sampling event was at S79 (0.050 μg/L). Using these criteria, this observed concentration should not have an acute or chronic detrimental impact on fish. Bromacil was not detected in the sediment.

DDD, DDE, DDT: DDE is an abbreviation of **d**ichloro**d**iphenyldichloro**e**thylene [2, 2-bis (4-chlorophenyl)-1, 1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichloro**d**iphenyl**t**richloroethane), a popular insecticide for which the U.S. EPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichloro**d**iphenyl**d**ichloroethane), and the high K_{oc} of these compounds account for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioconcentration factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

The DDD sediment concentrations detected range from 9.7 to 25 µg/Kg. Any concentration which would fall below the TEC (4.9 µg/Kg) should not impact sediment dwelling organisms while concentrations above the PEC (28 µg/Kg), frequently or always have the possibility for impacting sediment-dwelling organisms. The sediment concentrations detected were between the TEC and PEC. These concentrations may have the possibility for harmful effects on freshwater sediment-dwelling organisms. DDD was not detected in the surface water.

The TEC is 3.2 µg/Kg and the PEC is 31 µg/Kg for DDE in freshwater sediments. The concentrations of DDE detected at S2, S3, S4, S5A, and S6 exceeded the PEC and frequently or always have the possibility for impacting sediment-dwelling organisms. DDE was not detected in the surface water.

The DDT concentration detected at S5A did not exceed the TEC (4.2 µg/Kg). At this level, there should not be any possibility for impacting sediment-dwelling freshwater organisms. No DDT was detected in the surface water.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, alpha (α) and beta (β). Endosulfan is highly toxic to mammals, with an acute oral LD_{50} for rats of 70 mg/Kg (Table 4). The Soil Conservation Service (SCS) rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 4). Beta endosulfan's water solubility and Henry's law constant (1.91×10^{-5} atm – m^3/mole) (Lyman, et al., 1990) indicate volatilization may be significant in shallow waters. The bioconcentration factors indicate a low to moderate degree of accumulation in aquatic organisms (Table 4). Endosulfan (α and/or β) was detected in the surface water at S178 and S177 in the South Miami-Dade County farming area (Table 2). However, none of the concentrations exceeded the F.A.C. 62-302 criterion of 0.056 µg/L.

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's law constant (9.63×10^{-8} atm – m^3/mole) (Lyman, et al., 1990) indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Table 4). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). Endosulfan sulfate was detected in the surface water and sediment at S178. However, no surface water criteria or sediment quality assessment guideline has been developed for endosulfan sulfate.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/L for *Daphnia magna* (U.S. EPA, 1988). The highest surface water concentration detected in this sampling event at S191 (0.076 μg/L) should not have an acute impact on fish or aquatic invertebrates. No hexazinone was detected in the sediment.

Metribuzin: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in Tables 4 and 5 indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metribuzin detected was 0.020 μg/L (S6). Using these criteria, this surface water concentration should not have an acute impact on fish or aquatic invertebrates. No metribuzin was detected in the sediment.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC_{50} for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.034 to 0.44 μg/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these observed concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates. Norflurazon was not detected in the sediment.

PCBs: Polychlorinated biphenyls (PCBs) is the generic term for a group of 209 congeners that contain a varying number of substituted chlorine atoms on one or both of the biphenyl rings. PCB-1254 is a commercial grade mixture containing 54 percent chlorine by weight. Production of PCBs was banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily sorbed to suspended sediments due to the very low solubility in water (Callahan et al., 1979). The tendency of PCBs for adsorption increases with the degree of chlorination and with the organic content of the adsorbent. While the production ban, phase out of uses, and stringent spill clean-up requirements have significantly reduced environmental loadings in recent years, the persistence and tendency to accumulate in sediment and bioaccumulate in fish, make this class of organochlorine compounds especially problematic. The TEC and PEC are 60 μg/Kg and 680 μg/Kg, respectively, for total PCBs. The sediment residue detected at S6 and S79 is greater than the TEC but less than the PEC. This concentration has a possibility for impacting freshwater sediment-dwelling organisms. None of the PCB congeners were detected in the surface water.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and

5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 µg/L (Verschueren, 1983). Aquatic invertebrate LC_{50} toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. EPA, 1984). The highest surface water concentration of simazine detected (0.040 µg/L at S79) was below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

Quality Assurance Evaluation

Replicate samples were collected at locations S177, S18C and S2. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No pesticide analytes were detected in the equipment blanks performed at S99, S18C, S331, S191, S3, US41-25, S78, S7, and S5A. All collected samples were shipped and all bottles were received.

Glossary

Bioconcentration Factor: The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

EC_{50}: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

Henry's law constant (H): Relates the concentration of a compound in the gas phase to its concentration in the liquid phase. The constant is calculated from the formula: $H = P_{vp}/S$ where P_{vp} is pressure in atmospheres and S is solubility in moles/meter^3 for a compound.

K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

LC_{50}: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LD_{50}: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

Method Detection Limits (MDLs): The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.

Practical Quantitation Limits (PQLs): The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.

Probable Effect Concentration (PEC): The probable effect concentration is intended to identify concentrations above which harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

Soil or water half-life: The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

Threshold Effect Concentration (TEC): The threshold effect concentration is intended to identify concentrations below which harmful effects to freshwater sediment-dwelling organisms are unlikely to be observed.

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Figure 1. South Florida Water Management District Pesticide Monitoring Network.

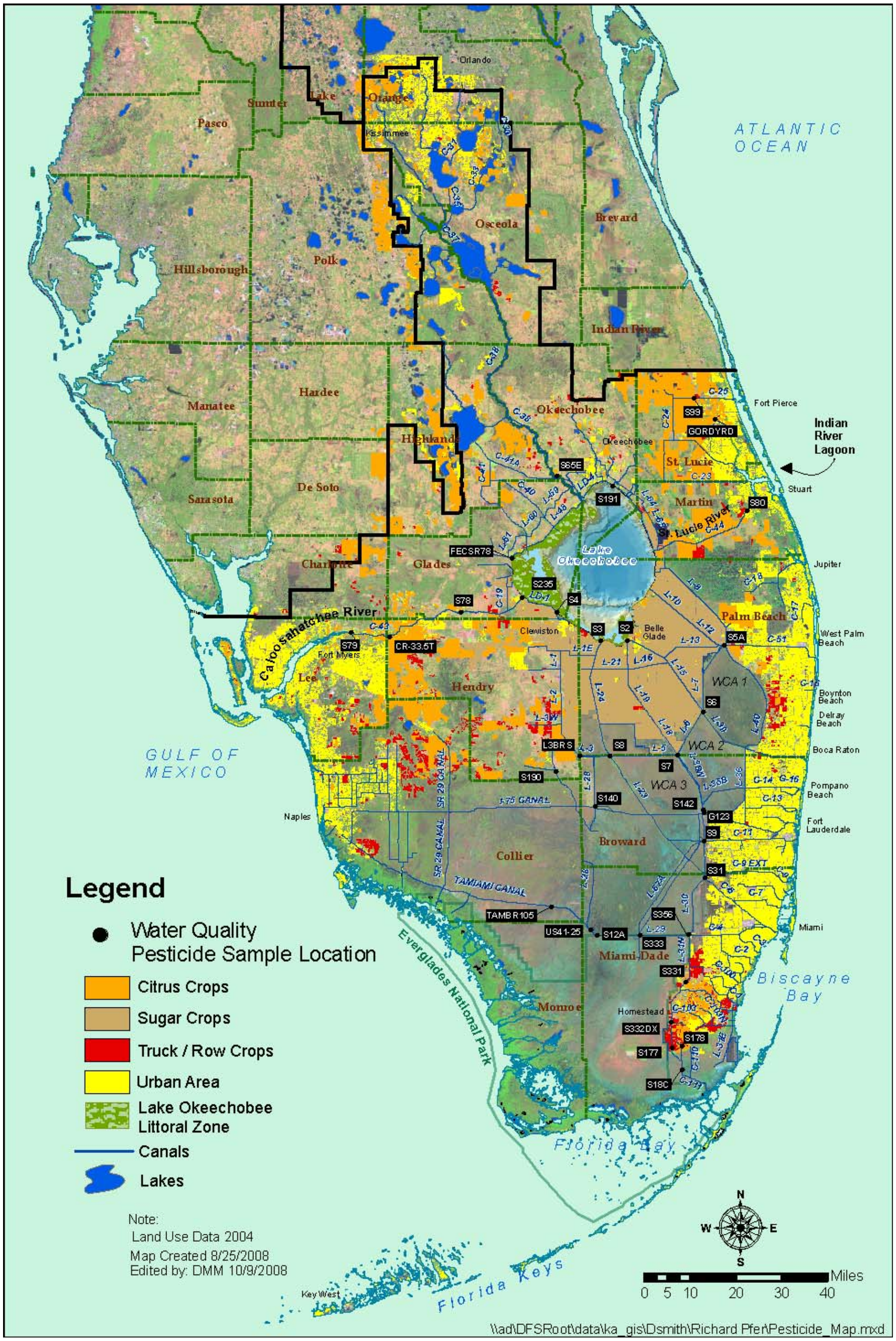

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for February 2009 sampling event.

Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)	Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)
2,4-D	0.2 - 0.64	8 - 310	endrin aldehyde	0.0042 - 0.018	0.82 - 44
2,4,5-T	0.2 - 0.64	8 - 310	ethion	0.0095 - 0.04	2 - 100
2,4,5-TP (silvex)	0.2 - 0.64	8 - 310	ethoprop	0.0095 - 0.04	2 - 100
acifluorfen	0.2 - 0.64	8 - 310	fenamiphos (nemacur)	0.038 - 0.16	4.1 - 210
alachlor	0.057 - 0.24	12 - 640	fonofos (dyfonate)	0.0095 - 0.04	2 - 100
aldrin	0.0019 - 0.008	0.41 - 21	heptachlor	0.0023 - 0.017	0.41 - 21
ametryn	0.0095 - 0.04	2 - 100	heptachlor epoxide	0.0019 - 0.008	0.41 - 21
atrazine	0.0095 - 0.04	2 - 100	hexazinone	0.019 - 0.08	4.1 - 210
atrazine desethyl	0.0095 - 0.04	N/A	imidacloprid	0.2 - 0.62	N/A
atrazine desisopropyl	0.0095 - 0.04	N/A	linuron	0.2 - 0.62	7.3 - 300
azinphos methyl (guthion)	0.028 - 0.12	6.1 - 320	malathion	0.028 - 0.12	4.1 - 210
α-BHC (alpha)	0.0021 - 0.0088	0.41 - 21	metalaxyl	0.047 - 0.2	N/A
β-BHC (beta)	0.0032 - 0.014	0.41 - 21	methamidophos	N/A	20 - 1000
δ-BHC (delta)	0.0019 - 0.008	0.82 - 44	methoxychlor	0.0095 - 0.04	2 - 100
γ-BHC (gamma) (lindane)	0.0019 - 0.008	0.41 - 21	metolachlor	0.057 - 0.24	12 - 640
bromacil	0.047 - 0.2	8.2 - 440	metribuzin	0.019 - 0.08	4.1 - 210
butylate	0.019 - 0.08	N/A	mevinphos	0.057 - 0.24	8.2 - 440
carbophenothion (trithion)	0.015 - 0.064	2 - 100	mirex	0.011 - 0.048	1.6 - 84
chlordane	0.019 - 0.08	6.1 - 320	monocrotophos (azodrin)	N/A	20 - 1000
chlorothalonil	0.015 - 0.064	2 - 100	naled	0.076 - 0.32	16 - 840
chlorpyrifos ethyl	0.0095 - 0.04	2 - 100	norflurazon	0.019 - 0.08	4.1 - 210
chlorpyrifos methyl	0.019 - 0.08	4.1 - 210	parathion ethyl	0.019 - 0.08	4.1 - 210
cypermethrin	0.019 - 0.08	2 - 100	parathion methyl	0.019 - 0.08	4.1 - 210
DDD-P,P'	0.0045 - 0.02	0.82 - 44	PCB-1016	0.019 - 0.08	12 - 640
DDE-P,P'	0.0038 - 0.016	0.82 - 44	PCB-1221	0.019 - 0.08	8.2 - 440
DDT-P,P'	0.0057 - 0.024	1.2 - 64	PCB-1232	0.019 - 0.08	18 - 960
demeton	0.028 - 0.12	6.1 - 320	PCB-1242	0.019 - 0.08	12 - 640
diazinon	0.019 - 0.08	2 - 100	PCB-1248	0.019 - 0.08	8.2 - 440
dicofol (kelthane)	0.042 - 0.18	6.1 - 320	PCB-1254	0.019 - 0.08	8.2 - 440
dieldrin	0.0019 - 0.008	0.41 - 21	PCB-1260	0.019 - 0.08	12 - 640
disulfoton	0.019 - 0.08	2 - 100	permethrin	0.015 - 0.064	2.5 - 130
diuron	0.2 - 0.62	7.3 - 300	phorate	0.0095 - 0.04	2 - 100
α-endosulfan (alpha)	0.0038 - 0.022	0.41 - 21	prometryn	0.019 - 0.08	4.1 - 210
β-endosulfan (beta)	0.0038 - 0.016	0.41 - 21	prometon	0.019 - 0.08	N/A
endosulfan sulfate	0.0045 - 0.02	0.82 - 44	simazine	0.0095 - 0.04	2 - 100
endrin	0.0095 - 0.04	2 - 100	toxaphene	0.095 - 0.4	31 - 1600
			trifluralin	0.0076 - 0.032	1.6 - 84

N/A - not anlayzed

Table 2. Summary of pesticide residues (µg/L) above the method detection limit found in surface water samples collected by SFWMD in February 2009.

Date	Location	Flow	ametryn	atrazine	atrazine desethyl	bromacil	alpha endosulfan	beta endosulfan	endosulfan sulfate	hexazinone	metribuzin	norflurazon	simazine	Number of compounds detected at location
2/23/2009	S99	N	-	-	-	-	-	-	-	-	-	0.44	-	1
	GORDYRD	Y	-	-	-	-	-	-	-	-	-	0.23	0.012 I	2
	S177	N	-	-	-	-	0.015 I *	-	-	-	-	-	-	1
	S178	N	-	-	-	-	0.011 I	0.011 I	0.026	-	-	-	-	3
	S18C	N	-	-	-	-	-	-	-	-	-	-	-	0
	S191	N	-	0.023 I	-	-	-	-	-	0.076	-	-	-	2
	S331	N	-	-	-	-	-	-	-	-	-	-	-	0
	S332DX	N	-	-	-	-	-	-	-	-	-	-	-	0
	S65E	N	-	0.026 I	-	-	-	-	-	-	-	-	-	1
	S80	Y	-	0.075	0.015 I	-	-	-	-	-	-	0.16	-	3
2/24/2009	FECSR78	Y	-	0.016 I	-	-	-	-	-	-	-	-	-	1
	G123	N	-	-	-	-	-	-	-	-	-	-	-	0
	S12A	N	-	0.014 I	-	-	-	-	-	-	-	-	-	1
	S2	N	-	0.14 *	0.021 I *	-	-	-	-	0.026 I *	-	-	0.012 I *	4
	S3	N	-	0.15	0.024 I	-	-	-	-	0.025 I	-	-	-	3
	S31	N	-	-	-	-	-	-	-	-	-	-	-	0
	S333	Y	-	-	-	-	-	-	-	-	-	-	-	0
	S356-334	N	-	-	-	-	-	-	-	-	-	-	-	0
	S4	N	-	0.13	0.017 I	-	-	-	-	0.023 I	-	-	-	3
	S9	N	-	-	-	-	-	-	-	-	-	-	-	0
	TAMBR105	N	-	-	-	-	-	-	-	-	-	-	-	0
	US41-25	N	-	-	-	-	-	-	-	-	-	-	-	0
2/25/2009	CR33.5T	N	-	0.16	0.019 I	-	-	-	-	0.025 I	-	0.057 I	0.025 I	5
	S235	Y	-	0.13	0.022 I	-	-	-	-	0.026 I	-	-	0.011 I	4
	S78	Y	-	0.13	0.021 I	-	-	-	-	0.025 I	-	-	0.010 I	4
	S79	N	-	0.13	0.019 I	0.050 I	-	-	-	0.023 I	-	0.075 I	0.040	6
	L3BRS	Y	-	0.17	0.014 I	-	-	-	-	-	-	-	-	2
	S140	N	-	0.019 I	-	-	-	-	-	-	-	0.034 I	-	2
	S190	N	-	0.11	-	-	-	-	-	-	-	-	-	1
	S7	N	0.013 I	0.24	0.022 I	-	-	-	-	0.021 I	-	-	-	4
	S8	N	0.089	2.1	0.033 I	-	-	-	-	0.022 I	-	-	0.016 I	5
2/26/2009	S5A	N	0.019 I	0.34	0.029 I	-	-	-	-	0.029 I	-	-	0.012 I	5
	S6	N	0.048	0.16	-	-	-	-	-	-	0.020 I	-	-	3
Total number of compound detections			4	19	12	1	2	1	1	11	1	6	8	66

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples
I - value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit

Table 3. Summary of pesticide residues (µg/Kg) above the method detection limit found in sediment samples collected by SFWMD in February 2009.

Date	Location	Flow	ametryn	DDD-P,P'	DDE-P,P'	DDT-P,P'	endosulfan sulfate	PCB-1254	Number of compounds detected at location
2/23/2009	S177	N	-	-	11	-	-	-	1
	S178	N	-	-	9.8 I	-	23	-	2
	S191	N	-	-	1.8 I	-	-	-	1
	S331	N	-	-	3.0 I	-	-	-	1
	S80	Y	-	-	5.3 I	-	-	-	1
2/24/2009	G123	N	-	-	2.0 I	-	-	-	1
	S2	N	-	11 I *	***33 I****	-	-	-	2
	S3	N	-	9.7 I	***35***	-	-	-	2
	S31	N	-	-	2.1 I	-	-	-	1
	S4	N	-	25 I	***72***	-	-	-	2
2/25/2009	S7	Y	-	-	1.5 I	-	-	-	1
	S79	N	-	-	-	-	-	240	1
2/26/2009	S5A	N	9.2 I	14	***73***	3.7 I	-	-	4
	S6	N	-	11	***39***	-	-	74	3
Total number of compound detections			1	5	13	1	1	2	23

N - no Y - yes R - reverse; - denotes that the result is below the method detection limit; * results are the average of replicate samples
I - value reported is less than the practical quantitation limit, and greater than or equal to the minimum detection limit
Values in bold, italicized font are at a concentration that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

Table 4. Selected properties of pesticides found in February 2009 sampling event.

Common Name	Surface Water Standards F.A.C. 62-302 (µg/L)	Acute Oral LD_{50} For Rats (mg/kg) (1)	U.S. EPA Carcinogenic Potential	Water Solubility (WS) (mg/L) (2, 3)	K_{oc} (mL/g) (2, 3)	Soil Half-life (days) (2, 3)	Soil Conservation Service (SCS) rating (2) LE	SA	SS	Volatility from Water	Bioconcentration Factor (BCF)
ametryn	-	1,110	D	185	300	60	M	M	M	I	33
atrazine	-	3,080	C	33	100	60	L	M	L	I	86
bromacil	-	5,200	C	700	32	60	L	M	M	I	15
DDD-p,p'	-	3,400	-	0.055	239,900	-	-	-	-	I	3,173
DDE-p,p'	-	880	-	0.065	243,220	-	-	-	-	S	2,887
DDT-p,p'	0.001	113	-	0.00335	140,000	-	-	-	-	I	15,377
alpha endosulfan	0.056	70	-	0.53	12,400	50	XS	L	M	S	884
beta endosulfan		70	-	0.28	-	-	-	-	-	S	1,267
endosulfan sulfate	-	-	-	0.117	-	-	-	-	-	I	2,073
hexazinone	-	1,690	D	33,000	54	90	L	M	M	I	2
metribuzin	-	2,200	D	1,220	41	30	L	S	M	I	11
norflurazon	-	9,400	C	28	700	90	M	M	L	I	94
PCB's	0.014	-	B2	-	-	-	-	-	-	-	-
simazine	-	>5,000	C	6.2	130	60	L	M	M	I	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA), or surface solution (SS) and grouped as large(L), medium (M), small (S), or extra small (XS)
Volatility from water: R = rapid, I = insignificant, S = significant
Bioconcentration Factor (BCF) calculated as BCF = $10^{\wedge(2.791 - 0.564 \log WS)}$ (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP F.A.C. 62-302 surface water standards (12/06) for Class III waters except Class I in ( )
Note: endosulfan usually considered the sum of alpha and beta isomers

(1) Hartley and Kidd (1987)
(2) Goss and Wauchope (1992)
(3) Montgomery (1993)
(4) Lyman, et al. (1990)
(5) U.S. EPA (1996a)

Table 5. Toxicity of pesticides found in the February 2009 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

Common Name	48 hr EC_{50} Water flea *Daphnia magna*	Acute Toxicity (*)	Chronic Toxicity (*)	96 hr LC_{50} Fathead Minnow (#) *Pimephales promelas*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Bluegill *Lepomis macrochirus*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Largemouth Bass *Micropterus salmoides*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Channel Catfish *Ictalurus punctatus*	Acute Toxicity	Chronic Toxicity
ametryn	28,000 (7)	9,333	1,400	16,000 (8)	5,333	800	4,100 (4)	1,367	205	-	-	-	8,800 (4)	2,933	440	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	3,600 (8)	1,200	180	-	-	-
atrazine	6900 (7)	2,300	345	15,000 (7)	5,000	750	16,000 (4)	5,333	800	-	-	-	8,800 (4)	2,933	440	7,600 (4)	2,533	380
	-	-	-	-	-	-	-	-	-	-	-	-	5,300 (9)	1,767	265	-	-	-
bromacil	-	-	-	-	-	-	127,000 (7)	42,333	6,350	-	-	-	36,000 (7)	12,000	1,800	-	-	-
	121,000 (14)	40,333	6,050	-	-	-	127,000 (14)	42,333	6,350	-	-	-	36,000 (14)	12,000	1,800	-	-	-
DDD-p,p'	3,200 (6)	1,067	160	4,400 (1)	1,467	220	42 (1)	14	2.1	42 (1)	14	2.1	70 (1)	23.3	3.5	1,500 (1)	500	75
DDE-p,p'	-	-	-	-	-	-	240 (1)	80	12	-	-	-	32 (1)	10.7	1.6	-	-	-
DDT-p,p'	-	-	-	19 (5)	6.3	0.95	8 (5)	2.7	0.4	2 (5)	0.7	0.10	7 (5)	2.3	0.35	16 (5)	5.3	0.8
endosulfan	166 (7)	55	8	1 (1)	0.3	0.05	1 (1)	0.33	0.05	-	-	-	1 (1)	0.33	0.05	1 (1)	0.3	0.05
	-	-	-	-	-	-	2 (3)	0.67	0.10	-	-	-	3 (2)	1	0.15	1.5 (7)	0.5	0.08
	-	-	-	-	-	-	-	-	-	-	-	-	1 (3)	0.33	0.05	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	0.3 (5)	0.10	0.02	-	-	-
	166 (10)	55	8	1.5 (10)	0.5	0.08	1.7 (10)	0.57	0.09	-	-	-	0.8 (10)	0.27	0.04	-	-	-
hexazinone	151,600 (7)	50,533	7,580	274,000 (4)	91,333	13,700	100,000 (7)	33,333	5,000	-	-	-	180,000 (7)	60,000	9,000	-	-	-
	151,600 (11)	50,533	7,580	274,000 (11)	91,333	13,700	505,000 (11)	168,333	25,250	-	-	-	>320,000 (11)	>106,667	>16,000	-	-	-
metribuzin	4,200 (7)	1,400	210	-	-	-	80,000 (4)	26,667	4,000	-	-	-	64,000 (4)	21,333	3,200	100,000 (7)	33,333	5,000
	4,200 (12)	1,400	210	-	-	-	75,900 (12)	25,300	3,795	-	-	-	76,770 (12)	25,590	3,839	-	-	-
norflurazon	15,000 (7)	5,000	750	-	-	-	16,300 (7)	5,433	815	-	-	-	8,100 (7)	2,700	405	>200,000 (4)	>67,000	>10,000
	>15,000 (13)	>5,000	>750	-	-	-	16,300 (13)	5,433	815	-	-	-	8,100 (13)	2,700	405	-	-	-
simazine	1,100 (7)	367	55	100,000 (7)	33,333	5,000	90,000 (4)	30,000	4,500	-	-	-	100,000 (7)	33,333	5,000	-	-	-

(*) Florida Administrative Code (F.A.C.) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC_{50} is the lowest value which has been determined for a species.
(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson and Finley (1980)
(2) U.S. EPA (1977)
(3) Schneider (1979)
(4) Hartley and Kidd (1987)
(5) Montgomery (1993)
(6) Verschueren (1983)
(7) U.S. EPA (1991)
(8) U.S. EPA (2005)
(9) U.S. EPA (2006)
(10) U.S.EPA (2002)
(11) U.S. EPA (1994)
(12) U.S. EPA (1998)
(13) U.S. EPA (1996b)
(14) U.S. EPA (1996c)

Table 6. Atrazine desethyl/atrazine ratio (DAR) data for February 2009 sampling event.

Date	Location	Flow *	atrazine		atrazine desethyl		DAR
			µg/L	moles/L	µg/L	moles/L	
2/23/2009	S80	Y	0.075	3.48E-10	0.015	7.99E-11	0.2
2/24/2009	S2	N	0.14	6.49E-10	0.021	1.12E-10	0.2
	S3	N	0.15	6.95E-10	0.024	1.28E-10	0.2
	S4	N	0.13	6.03E-10	0.017	9.06E-11	0.2
2/25/2009	CR33.5T	N	0.16	7.42E-10	0.019	1.01E-10	0.1
	S235	Y	0.13	6.03E-10	0.022	1.17E-10	0.2
	S78	Y	0.13	6.03E-10	0.021	1.12E-10	0.2
	S79	N	0.13	6.03E-10	0.019	1.01E-10	0.2
	L3BRS	Y	0.17	7.88E-10	0.014	7.46E-11	0.1
	S7	N	0.24	1.11E-09	0.022	1.17E-10	0.1
	S8	N	2.1	9.74E-09	0.033	1.76E-10	0.02
2/26/2009	S6	N	1.6	7.42E-09	0.024	1.28E-10	0.02
				DAR	All sites	Flow only sites	No flow sites
				average	0.1	0.2	0.1
				median	0.2	0.2	0.1
				minimum	0.02	0.1	0.02
				maximum	0.2	0.2	0.2

* No - no; Y - yes; R- reverse

PESTICIDE SURFACE WATER QUALITY REPORT

APRIL 2009 SAMPLING EVENT

Richard J. Pfeuffer

South Florida Water Management District
MSC 4642
3301 Gun Club Road
West Palm Beach, FL 33406

Pesticide Monitoring Project Report
April 2009 Sampling Event

Summary
As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water samples from 33 of the 34 network sites were collected April 27 to April 30, 2009, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides ametryn, atrazine, diuron, hexazinone, metribuzin, norflurazon, and simazine, along with the insecticides/degradates atrazine desethyl, endosulfan sulfate, and malathion, were detected in one or more of these surface water samples. The malathion concentration of 0.10 µg/L at S178 equals the Florida Administrative Code 62-302 Class III surface water quality standard of 0.1 µg/L. No harmful impacts are expected from the other detected pesticides.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods
The SFWMD pesticide monitoring network includes stations designated in the Everglades Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction Project (non-ECP) permit. The canals and marshes depicted in Figure 1 are protected as Florida Administrative Code (F.A.C.) 62-302 Class III (fishable and swimmable) waters, while Lake Okeechobee and a segment of the Caloosahatchee River are protected as a Class I drinking water supply. Water Conservation Area 1 (WCA-1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Seventy-one pesticides and degradation products were analyzed in samples from 33 of the 34 network sites (Figure 1). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp.

To evaluate the potential impacts on aquatic life, the observed concentration is compared to the appropriate criterion outlined in F.A.C. 62-302.530. If a pesticide compound is not specifically listed, acute and chronic toxicity criterion are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, using the lowest technical grade effective concentration 50 (EC_{50}) or lethal concentration 50 (LC_{50}) reported in the summarized literature for the species significant to the indigenous aquatic community (F.A.C. 62-302.200). Each pesticide's description and possible uses and sites of application described herein are taken from Hartley and Kidd (1987). This summary covers surface water samples collected from April 27 to April 30, 2009.

Results

At least one pesticide was detected in surface water at 29 of the 33 sites. Modifications to the non-ECP permit changed the requirement for sampling at S142 to only during discharge or flow events. For this sampling event, no sample was obtained due to no discharge at the time of sample collection. The concentrations of the pesticides detected at each of the sites are summarized for the surface water in Table 2. All of these compounds have previously been detected in this monitoring program. Only the malathion concentration detected at S178 has the possibility for causing an environmental impact. No harmful impacts are expected from the other detected pesticides.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long-term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 micrograms per liter (µg/L) (Verschueren, 1983). Environmental fate and toxicity data in Tables 3 and 4 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.013 to 0.039 µg/L. Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 µg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 µg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003a). The atrazine surface water concentrations found in this sampling event at 24 of the 33 sampling locations, ranged from 0.012 to 1.5 µg/L. Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of groundwater discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1 to 0.2) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 5). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

Diuron: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48-hour LC_{50} of 1.4 mg/L for water fleas and a 96-hour LC_{50} of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 µg/L (Verschueren, 1983). The only surface water concentration of diuron found during this sampling event was 0.25 µg/L at S178 (Table 2). Using these criteria, this concentration should not have an acute, harmful impact on fish, aquatic invertebrates, or algae.

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's law constant (9.63×10^{-8} atm – m^3/mole) (Lyman, et al., 1990) indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Table 3). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 3). Endosulfan sulfate was detected in the surface water at S177 and S178. However, no surface water standard (F.A.C. 62-302) has been developed for endosulfan sulfate.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/L for *Daphnia magna* (U.S. EPA, 1988). The highest surface water concentration detected in this sampling event at FECSR78 (0.32 µg/L) should not have an acute impact on fish or aquatic invertebrates.

Malathion: Malathion is an insecticide/acaricide used on a variety of crops including fruits, vines, ornamentals, vegetables, and field crop. Environmental fate and toxicity data in Tables 3 and 4 indicate that malathion (1) has a small potential for loss from soil by leaching, surface adsorption or surface solution; (2) is relatively non-toxic to mammals but highly toxic to fish; and (3) does not bioaccumulate significantly. The only concentration of malathion found in the surface water from this sampling event was 0.10 µg/L at S178. This concentration equals the F.A.C. 62-302 standard of 0.1 µg/L. At this level, impacts could occur to the fish and wildlife.

Metribuzin: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in Tables 3 and 4 indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metribuzin detected was 0.036 µg/L (S6). Using these criteria, this surface water concentration should not have an acute impact on fish or aquatic invertebrates.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC_{50} for norflurazon is > 200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.034 to 0.47 µg/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these observed concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 µg/L (Verschueren, 1983). Aquatic invertebrate LC_{50} toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. EPA, 1984). The highest surface water concentration of simazine detected at GORDYRD (0.033 µg/L) was below any level of concern for fish or aquatic invertebrates.

Quality Assurance Evaluation

Replicate samples were collected at sites S4 and S331. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No pesticide analytes were detected in the field blanks performed at S99, S177, S65E, S8, and S7. All collected samples were shipped and all bottles were received.

Glossary

Bioconcentration Factor: The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

EC_{50}: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

Henry's law constant (H): Relates the concentration of a compound in the gas phase to its concentration in the liquid phase. The constant is calculated from the formula: $H = P_{vp}/S$ where P_{vp} is pressure in atmospheres and S is solubility in moles/meter^3 for a compound.

K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

LC_{50}: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LD_{50}: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

Method Detection Limits (MDLs): The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.

Practical Quantitation Limits (PQLs): The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.

Soil or water half-life: The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

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Figure 1. South Florida Water Management District Pesticide Monitoring Network.

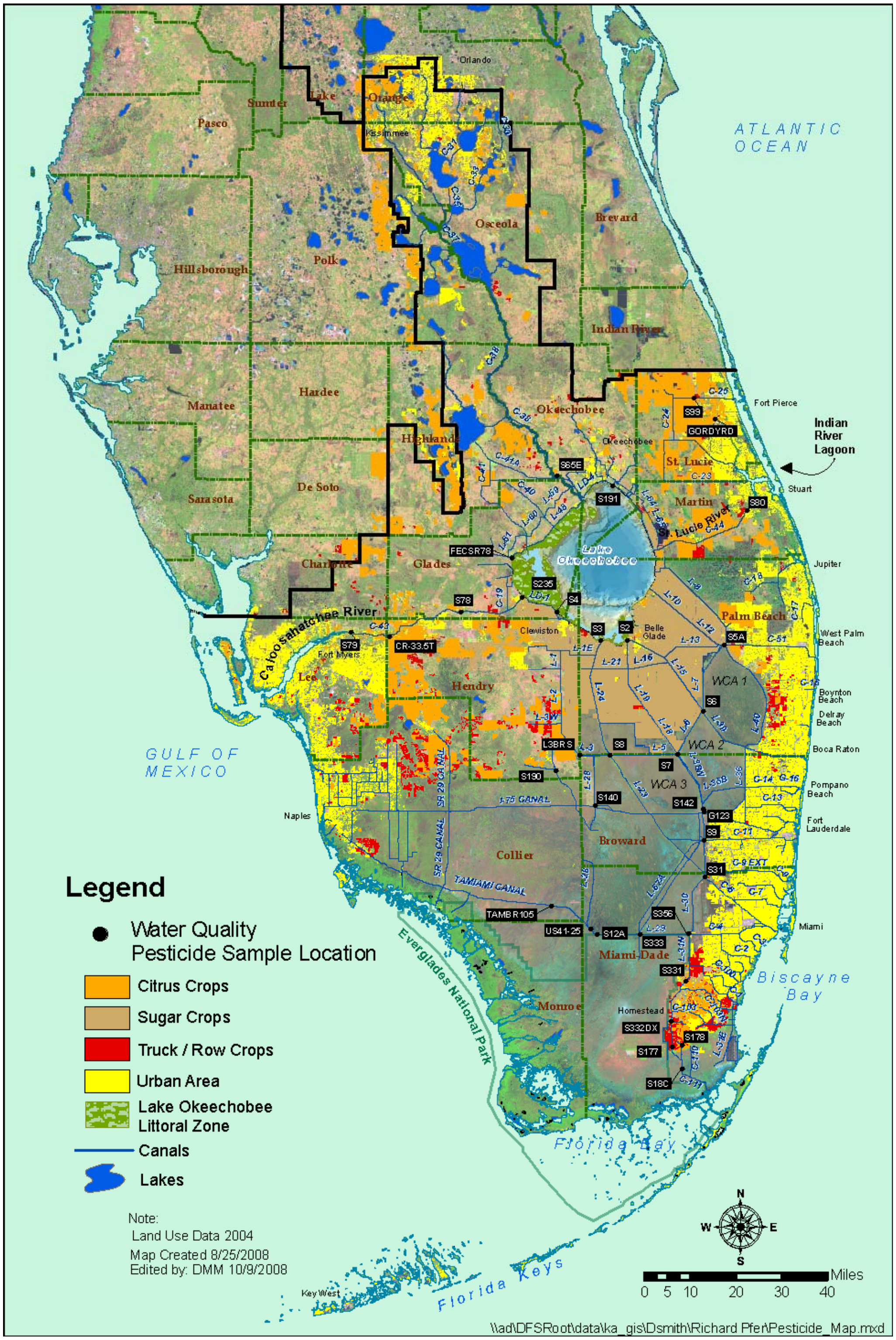

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for April 2009 sampling event.

Pesticide or metabolite	Water: range of MDLs - PQLs (μg/L)	Pesticide or metabolite	Water: range of MDLs - PQLs (μg/L)
2,4-D	0.2 - 0.63	endrin aldehyde	0.0042 - 0.018
2,4,5-T	0.2 - 0.63	ethion	0.0094 - 0.04
2,4,5-TP (silvex)	0.2 - 0.63	ethoprop	0.0094 - 0.04
acifluorfen	0.2 - 0.63	fenamiphos (nemacur)	0.038 - 0.16
alachlor	0.057 - 0.24	fonofos (dyfonate)	0.0094 - 0.04
aldrin	0.0019 - 0.008	heptachlor	0.0023 - 0.0096
ametryn	0.0094 - 0.04	heptachlor epoxide	0.0019 - 0.008
atrazine	0.0094 - 0.076	hexazinone	0.019 - 0.08
atrazine desethyl	0.0094 - 0.04	imidacloprid	0.2 - 0.78
atrazine desisopropyl	0.0094 - 0.048	linuron	0.2 - 0.78
azinphos methyl (guthion)	0.028 - 0.12	malathion	0.028 - 0.12
α-BHC (alpha)	0.0021 - 0.0088	metalaxyl	0.047 - 0.2
β-BHC (beta)	0.0032 - 0.014	methoxychlor	0.0094 - 0.04
δ-BHC (delta)	0.0019 - 0.008	metolachlor	0.057 - 0.24
γ-BHC (gamma) (lindane)	0.0019 - 0.008	metribuzin	0.019 - 0.08
bromacil	0.047 - 0.2	mevinphos	0.057 - 0.24
butylate	0.019 - 0.08	mirex	0.011 - 0.048
carbophenothion (trithion)	0.015 - 0.064	naled	0.076 - 0.32
chlordane	0.019 - 0.08	norflurazon	0.019 - 0.08
chlorothalonil	0.015 - 0.064	parathion ethyl	0.019 - 0.08
chlorpyrifos ethyl	0.0094 - 0.04	parathion methyl	0.019 - 0.08
chlorpyrifos methyl	0.019 - 0.08	PCB-1016	0.019 - 0.08
cypermethrin	0.019 - 0.08	PCB-1221	0.019 - 0.08
DDD-P,P’	0.0045 - 0.019	PCB-1232	0.019 - 0.08
DDE-P,P’	0.0038 - 0.016	PCB-1242	0.019 - 0.08
DDT-P,P’	0.0057 - 0.024	PCB-1248	0.019 - 0.08
demeton	0.028 - 0.12	PCB-1254	0.019 - 0.08
diazinon	0.019 - 0.08	PCB-1260	0.019 - 0.08
dicofol (kelthane)	0.042 - 0.18	permethrin	0.015 - 0.064
dieldrin	0.0019 - 0.008	phorate	0.0094 - 0.04
disulfoton	0.019 - 0.08	prometon	0.019 - 0.08
diuron	0.2 - 0.78	prometryn	0.019 - 0.08
α-endosulfan (alpha)	0.0038 - 0.016	simazine	0.0094 - 0.04
β-endosulfan (beta)	0.0038 - 0.016	toxaphene	0.094 - 0.4
endosulfan sulfate	0.0045 - 0.019	trifluralin	0.0076 - 0.032
endrin	0.0094 - 0.04		

Table 2. Summary of pesticide residues (μg/L) above the method detection limit found in surface water samples collected by SFWMD in April 2009.

Date	Location	Flow	ametryn	atrazine	atrazine desethyl	diuron	endosulfan sulfate	hexazinone	malathion	metribuzin	norflurazon	simazine	Number of compounds detected at location
4/27/2009	S99	N	-	0.025 I	0.019 I	-	-	-	-	-	0.47	-	3
	GORDYRD	Y	-	0.022 I	0.015 I	-	-	-	-	-	0.12	0.033 I	4
	S2	N	-	0.26	0.034 I	-	-	-	-	-	-	-	2
	S3	N	-	-	0.036 I	-	-	-	-	-	-	-	1
	S4	N	-	0.26 *	0.040 *	-	-	-	-	-	-	0.01 I	3
	S80	N	-	0.095	0.017 I	-	-	-	-	-	0.16	-	3
4/28/2009	CR33.5T	Y	-	-	0.030 I	-	-	-	-	-	0.041 I	0.016 I	3
	FECSR78	N	-	-	0.011 I	-	-	0.32	-	-	-	-	2
	S12A	N	-	0.033 I	0.013 I	-	-	-	-	-	-	-	2
	S177	N	-	0.012 I	-	-	0.019	-	-	-	-	-	2
	S178	N	-	-	-	0.25 I	0.018	-	***0.10 I***	-	-	-	3
	S18C	N	-	-	-	-	-	-	-	-	-	-	0
	S191	N	-	0.026 I	-	-	-	-	-	-	-	-	1
	S235	N	-	0.11	0.020 I	-	-	-	-	-	-	-	2
	S331	N	-	0.022 I *	-	-	-	-	-	-	-	-	1
	S332DX	N	-	0.034 I	-	-	-	-	-	-	-	-	1
	S333	N	-	0.039	-	-	-	-	-	-	-	-	1
	S356-334	N	-	0.038	-	-	-	-	-	-	-	-	1
	S65E	Y	-	0.023 I	-	-	-	-	-	-	-	-	1
	S78	Y	-	-	0.032 I	-	-	-	-	-	-	-	1
	S79	Y	-	0.17	0.025 I	-	-	-	-	-	0.044 I	0.017 I	4
	TAMBR105	N	-	-	-	-	-	-	-	-	-	-	0
	US41-25	N	-	0.017 I	0.0097 I	-	-	-	-	-	-	-	2
4/29/2009	G123	N	-	-	-	-	-	-	-	-	-	-	0
	L3BRS	Y	0.013 I	0.43	0.047	-	-	0.024 I	-	-	-	0.013 I	5
	S140	N	-	0.053	-	-	-	-	-	-	0.034 I	-	2
	S190	N	0.038	0.80	0.072	-	-	0.021 I	-	-	-	0.011 I	5
	S31	N	-	0.025 I	-	-	-	-	-	-	-	-	1
	S8	N	-	0.30	0.028 I	-	-	-	-	-	-	-	2
	S9	N	-	-	-	-	-	-	-	-	-	-	0
4/30/2009	S5A	Y	-	0.22	0.043	-	-	-	-	-	-	-	2
	S6	N	0.039	1.5	0.070	-	-	-	-	0.036 I	-	0.011 I	5
	S7	N	-	1.5	0.081	-	-	-	-	-	-	-	2
Total number of compound detections			3	24	19	1	2	3	1	1	6	7	67

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples
I - value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit.
Values in bold, italicized font are at a concentration that potential harmful effects to organisms may be observed.

Table 3. Selected properties of pesticides found in April 2009 sampling event.

Common Name	Surface Water Standards F.A.C. 62-302 (µg/L)	Acute Oral LD_{50} For Rats (mg/kg) (1)	U.S. EPA Carcinogenic Potential	Water Solubility (WS) (mg/L) (2, 3)	Koc (mL/g) (2, 3)	Soil Half-life (days) (2, 3)	Soil Conservation Service (SCS) rating (2)			Volatility from Water	Bioconcentration Factor (BCF)
							LE	SA	SS		
ametryn	-	1,110	D	185	300	60	M	M	M	I	33
atrazine	-	3,080	C	33	100	60	L	M	L	I	86
diuron	-	3,400	D	42	480	90	M	M	L	I	75
endosulfan sulfate	-	-	-	0.117	-	-	-	-	-	I	2,073
hexazinone	-	1,690	D	33,000	54	90	L	M	M	I	2
metribuzin	-	2,200	D	1,220	41	30	L	S	M	I	11
malathion	0.1	2,800	D	145	1,800	1	S	S	S	I	37
norflurazon	-	9,400	C	28	700	90	M	M	L	I	94
simazine	-	>5,000	C	6.2	130	60	L	M	M	I	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA), or surface solution (SS) and grouped as large(L), medium (M), small (S), or extra small (XS)
Volatility from water: R = rapid, I = insignificant, S = significant

Bioconcentration Factor (BCF) calculated as $BCF = 10^{(2.791 - 0.564 \log WS)}$ (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP F.A.C. 62-302 surface water standards (12/06) for Class III waters except Class I in ( )

(1) Hartley and Kidd (1987)
(2) Goss and Wauchope (1992)
(3) Montgomery (1993)
(4) Lyman, et al. (1990)
(5) U.S. EPA (1996a)

Table 4. Toxicity of pesticides found in the April 2009 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

Common Name	48 hr EC_{50} Water Flea *Daphnia magna*	Acute Toxicity (*)	Chronic Toxicity (*)	96 hr LC_{50} Fathead Minnow (#) *Pimephales promelas*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Bluegill *Lepomis macrochirus*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Largemouth *Micropterus salmoides*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Channel *Ictalurus punctatus*	Acute Toxicity	Chronic Toxicity
ametryn	28,000 (8)	9,333	1,400	16,000 (9)	5,333	800	4,100 (6)	1,367	205	-	-	-	8,800 (6)	2,933	440	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	3,600 (9)	1,200	180	-	-	-
atrazine	6,900 (8)	2,300	345	15,000 (8)	5,000	750	16,000 (6)	5,333	800	-	-	-	8,800 (6)	2,933	440	7,600 (6)	2,533	380
	-	-	-	-	-	-	-	-	-	-	-	-	5,300 (10)	1,767	265	-	-	-
diuron	1,400 (8)	467	70	14,200 (8)	4,733	710	5,900 (6)	1,967	295	-	-	-	5,600 (6)	1,867	280	-	-	-
	1,400 (11)	467	70	14,000 (11)	4,667	700	-	-	-	-	-	-	-	-	-	-	-	-
endosulfan	166 (8)	55	8	1 (1)	0.3	0.05	1 (1)	0.3	0.05	-	-	-	1 (1)	0.3	0.05	1 (1)	0.3	0.05
	-	-	-	-	-	-	2 (4)	0.7	0.10	-	-	-	3 (2)	1	0.15	1.5 (8)	0.5	0.08
	-	-	-	-	-	-	-	-	-	-	-	-	1 (4)	0.3	0.05	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	0.3 (7)	0.10	0.02	-	-	-
	166 (12)	55	8	1.5 (12)	0.5	0.08	1.7 (12)	0.57	0.09	-	-	-	0.8 (12)	0.27	0.04	-	-	-
hexazinone	151,600 (8)	50,533	7,580	274,000 (6)	91,333	13,700	100,000 (8)	33,333	5,000	-	-	-	180,000 (8)	60,000	9,000	-	-	-
	151,600 (13)	50,533	7,580	274,000 (13)	91,333	13,700	505,000 (13)	168,333	25,250	-	-	-	>320,000 (13)	>106,667	> 16,000	-	-	-
malathion	1 (1)	0.3	0.05	8,650 (1)	2,883	433	103 (1)	34	5.2	285 (1)	95	14	200 (1)	67	10	8,970 (1)	2,990	449
	1.8 (5)	0.6	0.09	9,000 (2)	3,000	450	110 (2)	37	5.5	-	-	-	170 (2)	57	9	7,620 (8)	2,540	381
	-	-	-	-	-	-	12 (3)	4	0.6	-	-	-	100 (3)	33	5	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	29 (4)	10	1	-	-	-
	1.0 (14)	0.33	0.05	-	-	-	30 (14)	10	1.5	-	-	-	4 (14)	1.3	0.2	-	-	-
metribuzin	4,200 (8)	1,400	210	-	-	-	80,000 (6)	26,667	4,000	-	-	-	64,000 (6)	21,333	3,200	100,000 (7)	33,333	5,000
	4,200 (16)	1,400	210	-	-	-	75,900 (16)	25,300	3,795	-	-	-	76,770 (16)	25,590	3,839	-	-	-
norflurazon	15,000 (8)	5,000	750	-	-	-	16,300 (8)	5,433	815	-	-	-	8,100 (8)	2,700	405	>200,000 (6)	>67,000	>10,000
	>15,000 (15)	>5,000	>750	-	-	-	16,300 (15)	5,433	815	-	-	-	8,100 (15)	2,700	405	-	-	-
simazine	1,100 (8)	367	55	100,000 (8)	33,333	5,000	90,000 (6)	30,000	4,500	-	-	-	100,000 (8)	33,333	5,000	-	-	-

(*) Florida Administrative Code (F.A.C.) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC_{50} is the lowest value which has been determined for a species significant to the indigenous aquatic community.
(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson and Finley (1980)
(2) U.S. EPA (1977)
(3) Davis (1970)
(4) Schneider (1979)
(5) U.S. EPA (1972)
(6) Hartley and Kidd (1987)
(7) Montgomery (1993)
(8) U.S. EPA (1991)
(9) U.S. EPA (2005)
(10) U.S. EPA (2006a)
(11) U.S. EPA (2003b)
(12) U.S. EPA (2002)
(13) U.S. EPA (1994)
(14) U.S. EPA (2006b)
(15) U.S. EPA (1996b)
(16) U.S. EPA (1998)

Table 5. Atrazine desethyl/atrazine ratio (DAR) data for April 2009 sampling event.

Date	Location	Flow*	atrazine		atrazine desethyl		DAR
			µg/l	moles/l	µg/l	moles/l	
4/27/2009	S99	N	0.025	1.16E-10	0.019	1.01E-10	0.9
	GORDYRD	Y	0.022	1.02E-10	0.015	7.99E-11	0.8
	S2	N	0.26	1.21E-09	0.034	1.81E-10	0.2
	S4	N	0.26	1.21E-09	0.040	2.13E-10	0.2
	S80	N	0.095	4.40E-10	0.017	9.06E-11	0.2
4/28/2009	S12A	N	0.033	1.53E-10	0.013	6.93E-11	0.5
	S235	N	0.11	5.10E-10	0.020	1.07E-10	0.2
	S79	Y	0.17	7.88E-10	0.025	1.33E-10	0.2
	US41-25	N	0.017	7.88E-11	0.0097	5.17E-11	0.7
4/29/2009	L3BRS	Y	0.43	1.99E-09	0.047	2.50E-10	0.1
	S190	N	0.80	3.71E-09	0.072	3.84E-10	0.1
	S8	N	0.30	1.39E-09	0.028	1.49E-10	0.1
4/30/2009	S5A	Y	0.22	1.02E-09	0.043	2.29E-10	0.2
	S6	N	1.5	6.95E-09	0.070	3.73E-10	0.1
	S7	N	1.5	6.95E-09	0.081	4.32E-10	0.1
				DAR	All sites	Flow only sites	No flow sites
				average	0.3	0.3	0.3
				median	0.2	0.2	0.2
				minimum	0.1	0.1	0.1
				maximum	0.9	0.8	0.9

* No - no; Y - yes; R- reverse

PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

AUGUST 2009 SAMPLING EVENT

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Pesticide Monitoring Program Report
August 2009 Sampling Event

Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water and sediment samples were collected August 3 to August 6, 2009, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides 2,4-D, ametryn, atrazine, bromacil, diuron, hexazinone, norflurazon, and simazine, along with the insecticide/degradates atrazine desethyl, chlorpyrifos ethyl and imidacloprid were detected in one or more of these surface water samples. The chlorpyrifos ethyl concentration detected could have a chronic, harmful impact on fish. Also, for aquatic invertebrates, this level is greater than the calculated acute and chronic toxicity for *Daphnia magna* and at this level, exposure can cause impacts to macroinvertebrate populations. However, the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long-term average exposures. No harmful impacts are expected from the other detected pesticides.

The insecticides/degradates DDD, DDE, and DDT, were found in the sediment at several locations. Four DDE compound sediment concentrations were of a magnitude considered to have a harmful effect to freshwater sediment-dwelling organisms. No harmful impacts are expected from the other detected pesticides.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods

The SFWMD pesticide monitoring network includes stations designated in the Everglades Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction Project (non-ECP) permit. The canals and marshes depicted in Figure 1 are protected as Florida Administrative Code (F.A.C.) 62-302 Class III (fishable and swimmable) waters, while Lake Okeechobee and a segment of the Caloosahatchee River are protected as a Class I drinking water supply. Water Conservation Area 1 (WCA-1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Seventy-three pesticides and degradation products were analyzed in samples from 33 of the network 34 sites (Figure 1). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp.

To evaluate the potential impacts on aquatic life, the observed concentration is compared to the appropriate criterion outlined in F.A.C. 62-302.530. If a pesticide compound is not specifically listed, acute and chronic toxicity criterion are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, using the lowest technical grade effective concentration 50 (EC_{50}) or lethal concentration 50 (LC_{50}) reported in the summarized literature for the species significant to the indigenous aquatic community (F.A.C. 62-302.200). Each pesticide's description and possible uses and sites of application described herein are taken from Hartley and Kidd (1987). Sediment concentrations are compared to freshwater sediment quality assessment guidelines (MacDonald Environmental Sciences, Ltd., and United States Geological Survey, 2003). A value below the threshold effect concentration (TEC) should not have a harmful effect on sediment-dwelling organisms. Values above the probable effect concentration (PEC) demonstrate that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed. This summary covers surface water and sediment samples collected from August 3 to August 6, 2009.

Results

At least one pesticide was detected in surface water at 24 of the 33 sites and in sediment at 8 of the 28 sites. Modifications to the non-ECP permit changed the requirement for sampling at S142 to only during discharge or flow events. For this sampling event, no sample was obtained due to no discharge at the time of sample collection. Sediment samples are not collected at GORDYRD, CR33.5T, S333, S356-334, and TAMBR105, due to access restrictions or no requirement in the respective mandate. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All of these compounds have previously been detected in this monitoring program.

The surface water chlorpyrifos ethyl concentration detected at CR33.5T has the possibility for causing an environmental impact. The sediment DDE concentrations at S2, S3, S5A, and S6 were of a magnitude considered to represent detrimental effects to sediment-dwelling organisms in freshwater sediments. All other detected concentrations in the surface water and sediment were below any effect level.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long-term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

2,4-D: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The highest 2,4-D concentration was detected at S99 (1.2 micrograms per liter [μg/L]) (Table 2). Using these criteria, this observed level should not have an acute or chronic effect on fish or aquatic invertebrates.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations greater than (>) 10 μg/L (Verschueren, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.013 to 0.042 μg/L. Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates. Ametryn was not detected in the sediment.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch, and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 μg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003a). The atrazine surface water concentrations found in this sampling event at 15 of the 33 sampling locations, ranged from 0.014 to 0.71 μg/L. Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates. Atrazine was not detected in the sediment.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of groundwater discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (e.g. 0.1 to 0.2) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at CR33.5T (0.22 μg/L). Using these criteria, this observed concentration should not have an acute or chronic detrimental impact on fish or aquatic invertebrates. Bromacil was not detected in the sediment.

Chlorpyrifos ethyl: Chlorpyrifos ethyl is a non-systemic insecticide with contact, stomach, and respiratory action, for use on citrus, vegetables, rice, and household insect pests. Environmental fate and toxicity data in Tables 4 and 5 indicate that chlorpyrifos ethyl (1) is not readily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is toxic to mammals and fish; and (3) bioconcentrates to a limited extent. The only concentration of chlorpyrifos ethyl found in this sampling event (0.18 μg/L at CR33.5T) could have a chronic, harmful impact on fish. Also, for aquatic invertebrates, this level is greater than the calculated acute and chronic toxicity for *Daphnia magna* (Table 5). At this level, exposure can cause impacts to macroinvertebrate populations. However, the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long-term average exposures. Chlorpyrifos ethyl was not detected in the sediment.

DDD, DDE, DDT: DDE is an abbreviation of **d**ichloro**d**iphenyldichloro**e**thylene [2, 2-bis (4-chlorophenyl)-1, 1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichloro**d**iphenyl**t**richloroethane), a popular insecticide for which the U.S. EPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichloro**d**iphenyl**d**ichloroethane), and the high K_{oc} of these compounds account for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioconcentration factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

The DDD sediment concentrations detected range from 10 to 27 micrograms per kilogram (μg/Kg). Any concentration which would fall below the TEC (4.9 μg/Kg) should not impact sediment dwelling organisms while concentrations above the PEC (28 μg/Kg), frequently or always have the possibility for impacting sediment-dwelling organisms. The sediment concentrations detected were between the TEC and PEC. These concentrations may have the possibility for harmful effects on freshwater sediment-dwelling organisms. DDD was not detected in the surface water.

The TEC is 3.2 μg/Kg and the PEC is 31 μg/Kg for DDE in freshwater sediments. The concentrations of DDE detected at S2, S3, S5A, and S6 exceeded the PEC and frequently or always have the possibility for impacting sediment-dwelling organisms. DDE was not detected in the surface water.

The DDT concentrations detected at S2 and S5A exceeded the TEC (4.2 μg/Kg) but not the PEC (63 μg/Kg). At these levels, there may be a possibility for impacting sediment-dwelling freshwater organisms. No DDT was detected in the surface water.

Diuron: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48-hour LC_{50} of 1.4 mg/L for water fleas and a 96-hour LC_{50} of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 μg/L (Verschueren, 1983). The only surface water concentration of diuron found during this sampling event was 0.25 μg/L at CR33.5T (Table 2). Using these criteria, this concentration should not have an acute, harmful impact on fish, aquatic invertebrates, or algae. Diuron was not detected in the sediment.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/L for *Daphnia magna* (U.S. EPA, 1988). The highest surface water concentration detected in this sampling event at S4 (0.075 μg/L) should not have an acute impact on fish or aquatic invertebrates. No hexazinone was detected in the sediment.

Imidacloprid: Imidacloprid is a systemic insecticide registered for use on a variety of row crops and turfgrass applications as well as for flea control. Environmental fate and toxicity data in Tables 4 and 5 indicate that imidacloprid (1) is soluble in water; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioconcentrate significantly. The highest concentration of 0.28 μg/L detected at CR33.5T is below a level that would have an acute or chronic detrimental impact on fish or aquatic invertebrates. Imidacloprid was not detected in the sediment.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC_{50} for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.031 to 1.1 μg/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these observed concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates. Norflurazon was not detected in the sediment.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 μg/L (Verschueren, 1983). Aquatic invertebrate LC_{50} toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. EPA, 1984). The highest surface water concentration of simazine detected (0.38 μg/L at CR33.5T) was below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

Quality Assurance Evaluation

Replicate samples were collected at locations S177 and S235. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No pesticide analytes were detected in the equipment blanks performed at S99, S331, S2, US41-25, CR33.5T, S7, and S5A. All collected samples were shipped and all bottles were received.

Glossary

Bioconcentration Factor: The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

EC_{50}: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

Henry's law constant (H): Relates the concentration of a compound in the gas phase to its concentration in the liquid phase. The constant is calculated from the formula: $H = P_{vp}/S$ where P_{vp} is pressure in atmospheres and S is solubility in moles/meter^3 for a compound.

K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

LC_{50}: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LD_{50}: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

Method Detection Limits (MDLs): The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.

Practical Quantitation Limits (PQLs): The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.

Probable Effect Concentration (PEC): The probable effect concentration is intended to identify concentrations above which harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

Soil or water half-life: The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

Threshold Effect Concentration (TEC): The threshold effect concentration is intended to identify concentrations below which harmful effects to freshwater sediment-dwelling organisms are unlikely to be observed.

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Verschueren, K. 1983. *Handbook of Environmental Data on Organic Chemicals*. Second Edition, Van Nostrand Reinhold Co. Inc. New York, NY.

Figure 1. South Florida Water Management District Pesticide Monitoring Network.

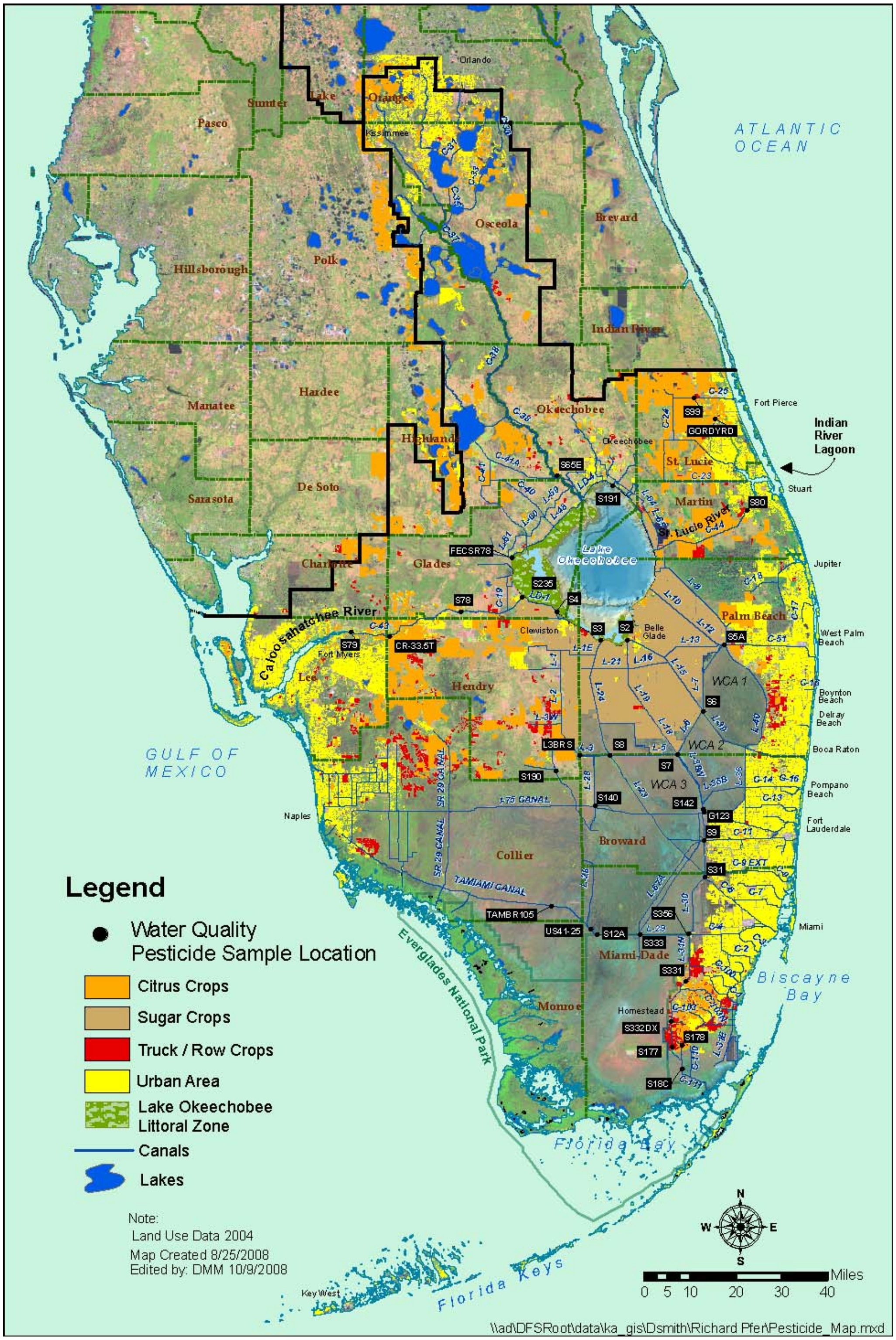

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for August 2009 sampling event.

Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)	Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)
2,4-D	0.2 - 0.68	7.8 - 200	endrin aldehyde	0.0042 - 0.018	0.8 - 28
2,4,5-T	0.2 - 0.68	7.8 - 200	ethion	0.0094 - 0.04	1.7 - 68
2,4,5-TP (silvex)	0.2 - 0.68	7.8 - 200	ethoprop	0.0094 - 0.04	1.7 - 68
acifluorfen	0.2 - 0.68	7.8 - 200	fenamiphos	0.038 - 0.16	3.3 - 140
alachlor	0.057 - 0.24	10 - 400	fonofos	0.0094 - 0.04	1.7 - 68
aldrin	0.0019 - 0.008	0.4 - 14	heptachlor	0.0023 - 0.0096	0.4 - 14
ametryn	0.0094 - 0.04	1.7 - 68	heptachlor epoxide	0.0019 - 0.013	0.4 - 14
atrazine	0.0094 - 0.04	1.7 - 68	hexazinone	0.019 - 0.08	3.3 - 140
atrazine desethyl	0.0094 - 0.04	N/A	imidacloprid	0.2 - 0.63	N/A
atrazine desisopropyl	0.0094 - 0.04	N/A	linuron	0.2 - 0.63	7.1 - 180
azinphos methyl (guthion)	0.028 - 0.12	5 - 210	malathion	0.028 - 0.12	3.3 - 140
α-BHC (alpha)	0.0021 - 0.0096	0.4 - 14	metalaxyl	0.047 - 0.2	N/A
β-BHC (beta)	0.0032 - 0.035	0.4 - 14	methamidophos	N/A	17 - 680
δ-BHC (delta)	0.0019 - 0.008	0.8 - 28	methoxychlor	0.0094 - 0.04	2 - 68
γ-BHC (gamma) (lindane)	0.0019 - 0.008	0.4 - 14	metolachlor	0.057 - 0.24	10 - 400
bromacil	0.047 - 0.2	6.7 - 280	metribuzin	0.019 - 0.08	3.3 - 140
butylate	0.019 - 0.08	N/A	mevinphos	0.057 - 0.24	6.7 - 280
carbophenothion (trithion)	0.015 - 0.064	2 - 68	mirex	0.011 - 0.048	1.6 - 56
chlordane	0.019 - 0.08	6 - 210	monocrotophos	N/A	17 - 680
chlorothalonil	0.015 - 0.064	2 - 68	naled	0.076 - 0.32	13 - 560
chlorpyrifos ethyl	0.0094 - 0.04	1.7 - 68	norflurazon	0.019 - 0.08	3.3 - 140
chlorpyrifos methyl	0.019 - 0.08	3.3 - 140	parathion ethyl	0.019 - 0.08	3.3 - 140
cypermethrin	0.019 - 0.08	2 - 68	parathion methyl	0.019 - 0.08	3.3 - 140
DDD-P,P’	0.0045 - 0.019	0.8 - 28	PCB-1016	0.019 - 0.08	12 - 400
DDE-P,P’	0.0038 - 0.016	0.8 - 28	PCB-1221	0.019 - 0.08	8 - 280
DDT-P,P’	0.0057 - 0.024	1.2 - 40	PCB-1232	0.019 - 0.08	18 - 640
demeton	0.028 - 0.12	5 - 210	PCB-1242	0.019 - 0.08	12 - 400
diazinon	0.019 - 0.08	1.7 - 68	PCB-1248	0.019 - 0.08	8 - 280
dicofol (kelthane)	0.042 - 0.18	6 - 210	PCB-1254	0.019 - 0.08	8 - 280
dieldrin	0.0019 - 0.0088	0.4 - 14	PCB-1260	0.019 - 0.08	12 - 400
disulfoton	0.019 - 0.08	1.7 - 68	permethrin	0.015 - 0.064	2.4 - 84
diuron	0.2 - 0.63	7.1 - 180	phorate	0.0094 - 0.04	1.7 - 68
α-endosulfan (alpha)	0.0038 - 0.016	0.4 - 14	prometon	0.019 - 0.08	N/A
β-endosulfan (beta)	0.0038 - 0.016	0.4 - 14	prometryn	0.019 - 0.08	3.3 - 140
endosulfan sulfate	0.0045 - 0.019	0.8 - 28	simazine	0.0094 - 0.04	1.7 - 68
endrin	0.0094 - 0.04	2 - 68	toxaphene	0.094 - 0.4	30 - 1000
			trifluralin	0.0076 - 0.032	1.6 - 56

N/A - not analyzed

Table 2. Summary of pesticide residues (µg/L) above the method detection limit found in surface water samples collected by SFWMD in August 2009.

Date	Location	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	bromacil	chlorpyrifos ethyl	diuron	hexazinone	imidacloprid	norflurazon	simazine	Number of compounds detected at location
8/3/2009	S99	Y	1.2	-	-	-	-	-	-	0.020 I	0.20 I	0.30	0.027 I	5
	GORDYRD	Y	0.25 I	-	-	-	-	-	-	-	-	0.34	0.21	3
	S191	N	0.30 I	-	-	-	-	-	-	-	-	-	-	1
	S65E	Y	-	-	0.015 I	-	-	-	-	-	-	-	-	1
	S80	N	-	-	-	0.019 I	-	-	-	-	-	0.095	-	2
	S177	N	-	-	-	-	-	-	-	-	-	-	-	0
	S178	Y	-	-	-	-	-	-	-	-	-	-	-	0
	S18C	Y	-	-	-	-	-	-	-	-	-	-	-	0
	S331	Y	-	-	0.014 I	-	-	-	-	-	-	-	-	1
	S332DX	Y	-	-	0.014 I	-	-	-	-	-	-	-	-	1
8/4/2009	FECSR78	Y	-	-	-	-	-	-	-	0.036 I	-	-	-	1
	G123	N	-	-	-	-	-	-	-	-	-	-	-	0
	S12A	Y	-	-	-	-	-	-	-	-	-	-	-	0
	S2	N	-	0.013 I	0.096	0.025 I	-	-	-	0.023 I	-	-	-	4
	S3	N	-	0.015 I	0.073	0.025 I	-	-	-	0.028 I	-	-	-	4
	S31	N	-	0.014 I	0.029 I	-	-	-	-	-	-	-	-	2
	S333	Y	-	-	0.018 I	-	-	-	-	-	-	-	-	1
	S356-334	Y	-	-	0.022 I	-	-	-	-	-	-	-	-	1
	S4	N	-	0.018 I	-	0.015 I	-	-	-	0.075 I	-	-	-	3
	S9	N	-	-	0.027 I	-	-	-	-	-	-	-	-	1
	TAMBR105	N	-	-	-	-	-	-	-	-	-	-	-	0
	US41-25	Y	-	-	-	-	-	-	-	-	-	-	-	0
8/5/2009	CR33.5T	Y	0.38 I	-	0.71	0.039	0.22	***0.18***	0.25 I	-	0.28 I	1.1	0.38	9
	L3BRS	N	-	-	-	-	-	-	-	-	-	0.031 I	-	1
	S140	Y	-	-	-	-	-	-	-	-	0.21 I	0.042 I	-	2
	S190	Y	-	-	-	-	-	-	-	-	-	-	-	0
	S235	Y	-	0.042 *	0.050 *	-	-	-	-	0.059 I *	-	-	-	3
	S7	N	-	0.039	0.053	0.015 I	-	-	-	-	-	-	-	3
	S78	Y	-	0.018 I	-	-	0.072 I	-	-	0.025 I	-	0.20	0.0096 I	5
	S79	N	0.35 I	-	0.030 I	-	0.11 I	-	-	0.023 I	-	0.23	0.019 I	6
	S8	N	-	-	-	-	-	-	-	-	-	-	-	0
8/6/2009	S5A	N	-	0.032 I	0.63	0.017 I	-	-	-	-	-	-	-	3
	S6	N	-	0.041	0.093	0.013 I	-	-	-	-	-	-	-	3
Total number of compound detections			5	9	15	8	3	1	1	8	3	8	5	66

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of replicate samples
I - value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit
Values in bold, italicized font are at a concentration that potential harmful effects to organisms may be observed.

Table 3. Summary of pesticide residues (μg/Kg) above the method detection limit found in sediment samples collected by SFWMD in August 2009.

Date	Location	Flow	DDD-p,p'	DDE-p,p'	DDT-p,p'	Number of compounds detected at location
8/3/2009	S177	N	-	11	-	1
	S178	Y	-	13 I	-	1
8/4/2009	S2	N	19 I	***66***	17 I	3
	S3	N	10 I	***37***	-	2
	S4	N	-	2.6 I	-	1
8/5/2009	S79	N	-	7.3 I	-	1
8/6/2009	S5A	N	16	***65***	5.1 I	3
	S6	N	27	***97***	-	2
Total number of compound detections			4	8	2	14

N - no Y - yes R - reverse; - denotes that the result is below the method detection limit
I - value reported is less than the practical quantitation limit, and greater than or equal to the minimum detection limit
Values in bold, italicized font are at a concentration that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

Table 4. Selected properties of pesticides found in August 2009 sampling event

common name	Surface Water Standards F.A.C. 62-302 (µg/L)	Acute Oral LD_{50} For Rats (mg/kg) (1)	U.S. EPA Carcinogenic Potential	Water Solubility (WS) (mg/L) (2, 3)	K_{oc} (mL/g) (2, 3)	Soil Half-life (days) (2, 3)	Soil Conservation Service (SCS) rating (2)			Volatility from Water	Bioconcentration Factor (BCF)
							LE	SA	SS		
2,4-D (acid)	(100)	375	D	890	20	10	M	S	M	I	13
ametryn	-	1,110	D	185	300	60	M	M	M	I	33
atrazine	-	3,080	C	33	100	60	L	M	L	I	86
bromacil	-	5,200	C	700	32	60	L	M	M	I	15
chlorpyrifos ethyl	-	135 - 163	D	2	6,070	30	S	M	M	-	418
DDD-p,p'	-	3,400	-	0.055	239,900	-	-	-	-	I	3,173
DDE-p,p'	-	880	-	0.065	243,220	-	-	-	-	S	2,887
DDT-p,p'	0.001	113	-	0.00335	140,000	-	-	-	-	I	15,377
diuron	-	3,400	D	42	480	90	M	M	L	I	75
hexazinone	-	1,690	D	33,000	54	90	L	M	M	I	2
imidacloprid	-	424	E	510	-	-	-	-	-	-	18
norflurazon	-	9,400	C	28	700	90	M	M	L	I	94
simazine	-	>5000	C	6.2	130	60	L	M	M	I	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA), or surface solution (SS) and grouped as large(L), medium (M), small (S), or extra small (XS)
Volatility from water: R = rapid, I = insignificant, S = significant

Bioconcentration Factor (BCF) calculated as BCF = $10^{\wedge(2.791 - 0.564 \log WS)}$ (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP F.A.C. 62-302 surface water standards (12/06) for Class III waters except Class I in ( )

(1) Hartley and Kidd (1987)
(2) Goss and Wauchope (1992)
(3) Montgomery (1993)
(4) Lyman, et al. (1990)
(5) U.S. EPA (1996a)

Table 5 . Toxicity of pesticides found in the August 2009 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

Common Name	48 hr EC_{50} Water Flea *Daphnia magna*	Acute Toxicity (*)	Chronic Toxicity (*)	96 hr LC_{50} Fathead Minnow (#) *Pimephales promelas*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Bluegill *Lepomis macrochirus*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Largemouth Bass *Micropterus salmoides*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Channel Catfish *Ictalurus punctatus*	Acute Toxicity	Chronic Toxicity
2,4-D	25,000 (5)	8,333	1,250	133,000 (5)	44,333	6,650	180,000 (6)	60,000	9,000	-	-	-	100,000 (2)	33,333	5,000	-	-	-
	-	-	-	-	-	-	900 (48 hr) (4)	-	-	-	-	-	110,000 (5)	36,667	5,500	-	-	-
ametryn	28,000 (5)	9,333	1,400	16,000 (8)	5,333	800	4,100 (2)	1,367	205	-	-	-	8,800 (2)	2,933	440	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	3,600 (8)	1,200	180	-	-	-
atrazine	6,900 (5)	2,300	345	15,000 (5)	5,000	750	16,000 (2)	5,333	800	-	-	-	8,800 (2)	2,933	440	7,600 (2)	2,533	380
	-	-	-	-	-	-	-	-	-	-	-	-	5,300 (9)	1,767	265	-	-	-
bromacil	-	-	-	-	-	-	127,000 (5)	42,333	6,350	-	-	-	36,000 (5)	12,000	1,800	-	-	-
	121,000 (14)	40,333	6,050	-	-	-	127,000 (14)	42,333	6,350	-	-	-	36,000 (14)	12,000	1,800	-	-	-
chlorpyrifos ethyl	1.7 (5)	0.57	0.085	203 (5)	68	10	2.6 (2)	0.87	0.13	-	-	-	11 (2)	3.7	1	280 (5)	93	14
	0.1 (5)	0.03	0.005	-	-	-	5.8 (5)	1.93	0.29	-	-	-	-	-	-	-	-	-
	0.1 (12)	0.03	0.005	-	-	-	1.8 (12)	0.60	0.09	-	-	-	-	-	-	-	-	-
DDD-p,p'	3,200 (4)	1,067	160	4,400 (1)	1,467	220	42 (1)	14	2	42 (1)	14	2.1	70 (1)	23.3	4	1,500 (1)	500	75
DDE-p,p'	-	-	-	-	-	-	240 (1)	80	12	-	-	-	32 (1)	11	2	-	-	-
DDT-p,p'	-	-	-	19 (3)	6.3	0.95	8 (3)	2.7	0.4	2 (3)	0.7	0.10	7 (3)	2.3	0.4	16 (3)	5.3	0.8
diuron	1,400 (5)	467	70	14,200 (5)	4,733	710	5,900 (2)	1,967	295	-	-	-	5,600 (2)	1,867	280	-	-	-
	1,400 (10)	467	70	14,000 (10)	4,667	700	-	-	-	-	-	-	-	-	-	-	-	-
hexazinone	151,600 (5)	50,533	7,580	274,000 (2)	91,333	13,700	100,000 (5)	33,333	5,000	-	-	-	180,000 (5)	60,000	9,000	-	-	-
	151,600 (11)	50,533	7,580	274,000 (11)	91,333	13,700	505,000 (11)	168,333	25,250	-	-	-	>320,000 (11)	>106,667	-	-	-	-
imidacloprid	85,200 (7)	28,400	4,260	-			-			-			83,000 (7)	27,667	4,150			
norflurazon	15,000 (5)	5,000	750	-	-	-	16,300 (5)	5,433	815	-	-	-	8,100 (5)	2,700	405	>200,000 (2)	>67,000	>10,000
	>15,000 (13)	>5,000	>750	-	-	-	16,300 (13)	5,433	815	-	-	-	8,100 (13)	2,700	405	-	-	-
simazine	1,100 (5)	367	55	100,000 (5)	33,333	5,000	90,000 (2)	30,000	4,500	-	-	-	100,000 (5)	33,333	5,000	-	-	-

(*) Florida Administrative Code (F.A.C.) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC_{50} is the lowest value which has been determined for a species significant to the indigenous aquatic community.
(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson and Finley (1980)
(2) Hartley and Kidd (1987)
(3) Montgomery (1993)
(4) Verschueren (1983)
(5) U.S. EPA (1991)
(6) Mayer and Ellersieck (1986)
(7) U.S. EPA (1994a)
(8) U.S. EPA (2005)
(9) U.S. EPA (2006)
(10) U.S. EPA (2003b)
(11) U.S. EPA (1994b)
(12) U.S. EPA (2002)
(13) U.S. EPA (1996b)
(14) U.S. EPA (1996c)

Table 6. Atrazine Desethyl/Atrazine ratio (DAR) data for August 2009 sampling event.

Date	Location	Flow	atrazine		atrazine desethyl		DAR
			µg/L	moles/L	µg/L	moles/L	
8/4/2009	S2	N	0.096	4.45E-10	0.025	1.33E-10	0.3
	S3	N	0.073	3.38E-10	0.025	1.33E-10	0.4
8/5/2009	CR33.5T	Y	0.71	3.29E-09	0.039	2.08E-10	0.1
	S7	N	0.053	2.46E-10	0.015	7.99E-11	0.3
8/6/2009	S5A	N	0.63	2.92E-09	0.017	9.06E-11	0.03
	S6	N	0.093	4.31E-10	0.013	6.93E-11	0.2

DAR	All sites	Flow only sites	No flow sites
average	0.2	0.1	0.2
median	0.3	0.1	0.3
minimum	0.0	0.1	0.03
maximum	0.4	0.1	0.4

N - no; Y - yes; R- reverse

PESTICIDE SURFACE WATER QUALITY REPORT

OCTOBER 2009 SAMPLING EVENT

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Pesticide Monitoring Project Report
October 2009 Sampling Event

Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water samples from 33 of the 34 network sites were collected October 26 to October 28, 2009, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides 2,4-D, ametryn, atrazine, bromacil, diuron, hexazinone, metolachlor, norflurazon, and simazine, along with the insecticide/degradate atrazine desethyl, were detected in one or more of these surface water samples. No harmful impacts are expected from the detected pesticides.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods

The SFWMD pesticide monitoring network includes stations designated in the Everglades Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction Project (non-ECP) permit. The canals and marshes depicted in Figure 1 are protected as Florida Administrative Code (F.A.C.) 62-302 Class III (fishable and swimmable) waters, while Lake Okeechobee and a segment of the Caloosahatchee River are protected as a Class I drinking water supply. Water Conservation Area 1 (WCA-1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Seventy-one pesticides and degradation products were analyzed in samples from 33 of the 34 network sites (Figure 1). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp.

To evaluate the potential impacts on aquatic life, the observed concentration is compared to the appropriate criterion outlined in F.A.C. 62-302.530. If a pesticide compound is not specifically listed, acute and chronic toxicity criterion are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, using the lowest technical grade effective concentration 50 (EC_{50}) or lethal concentration 50 (LC_{50}) reported in the summarized literature for the species significant to the indigenous aquatic community (F.A.C. 62-302.200). Each pesticide's description and possible uses and sites of application described herein are taken from Hartley and Kidd (1987). This summary covers surface water samples collected from October 26 to October 28, 2009.

Results

At least one pesticide was detected in surface water at 21 of the 33 sites. Modifications to the non-ECP permit changed the requirement for sampling at S142 to only during discharge or flow events. For this sampling event, no sample was obtained due to no discharge at the time of sample collection. The concentrations of the pesticides detected at each of the sites are summarized for the surface water in Table 2. All of these compounds have previously been detected in this monitoring program. No harmful impacts are expected from the detected pesticides.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long-term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

2,4-D: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The highest 2,4-D concentration was detected at S80 (1.4 micrograms per liter [μg/L]) (Table 2). Using these criteria, this observed level should not have an acute or chronic effect on fish or aquatic invertebrates.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 micrograms per liter (μg/L) (Verschueren, 1983). Environmental fate and toxicity data in Tables 3 and 4 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.01 to 0.038 μg/L (Table 2). Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 µg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003a). The atrazine surface water concentrations found in this sampling event at 12 of the 33 sampling locations, ranged from 0.013 to 0.43 µg/L (Table 2). Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of groundwater discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1 to 0.2) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 5). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at CR33.5T (0.082 µg/L) (Table 2). Using these criteria, this observed concentration should not have an acute or chronic detrimental impact on fish or aquatic invertebrates.

Diuron: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48-hour LC_{50} of 1.4 mg/L for water fleas and a 96-hour LC_{50} of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 µg/L (Verschueren, 1983). The only surface water concentration of diuron found during this sampling event was 0.23 µg/L at S79 (Table 2). Using these criteria, this concentration should not have an acute, harmful impact on fish, aquatic invertebrates, or algae.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/L for *Daphnia magna* (U.S. EPA, 1988). The highest surface water concentration detected in this sampling event at S99 (0.14 μg/L) (Table 2) should not have an acute impact on fish or aquatic invertebrates.

Metolachlor: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in Tables 3 and 4 indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The only surface water concentration found in this sampling event (0.08 μg/L at S178; Table 2) is over two orders of magnitude below the calculated chronic toxicity level. Using these criteria, this observed level should not have a harmful effect on fish or aquatic invertebrates.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC_{50} for norflurazon is > 200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.024 to 0.30 μg/L (Table 2). Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these observed concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 μg/L (Verschueren, 1983). Aquatic invertebrate LC_{50} toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. EPA, 1984). The highest surface water concentration of simazine detected at S99 (0.13 μg/L; Table 2) was below any level of concern for fish or aquatic invertebrates.

Quality Assurance Evaluation

Replicate samples were collected at sites GORDYRD and S331. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No pesticide analytes were detected in the field blanks performed at S99, S177, S235, S8, and S7. All collected samples were shipped and all bottles were received.

Glossary

Bioconcentration Factor: The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

EC_{50}: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

Henry's law constant (H): Relates the concentration of a compound in the gas phase to its concentration in the liquid phase. The constant is calculated from the formula: $H = P_{vp}/S$ where P_{vp} is pressure in atmospheres and S is solubility in moles/meter^3 for a compound.

K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

LC_{50}: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LD_{50}: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

Method Detection Limits (MDLs): The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.

Practical Quantitation Limits (PQLs): The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.

Soil or water half-life: The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

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Figure 1. South Florida Water Management District Pesticide Monitoring Network.

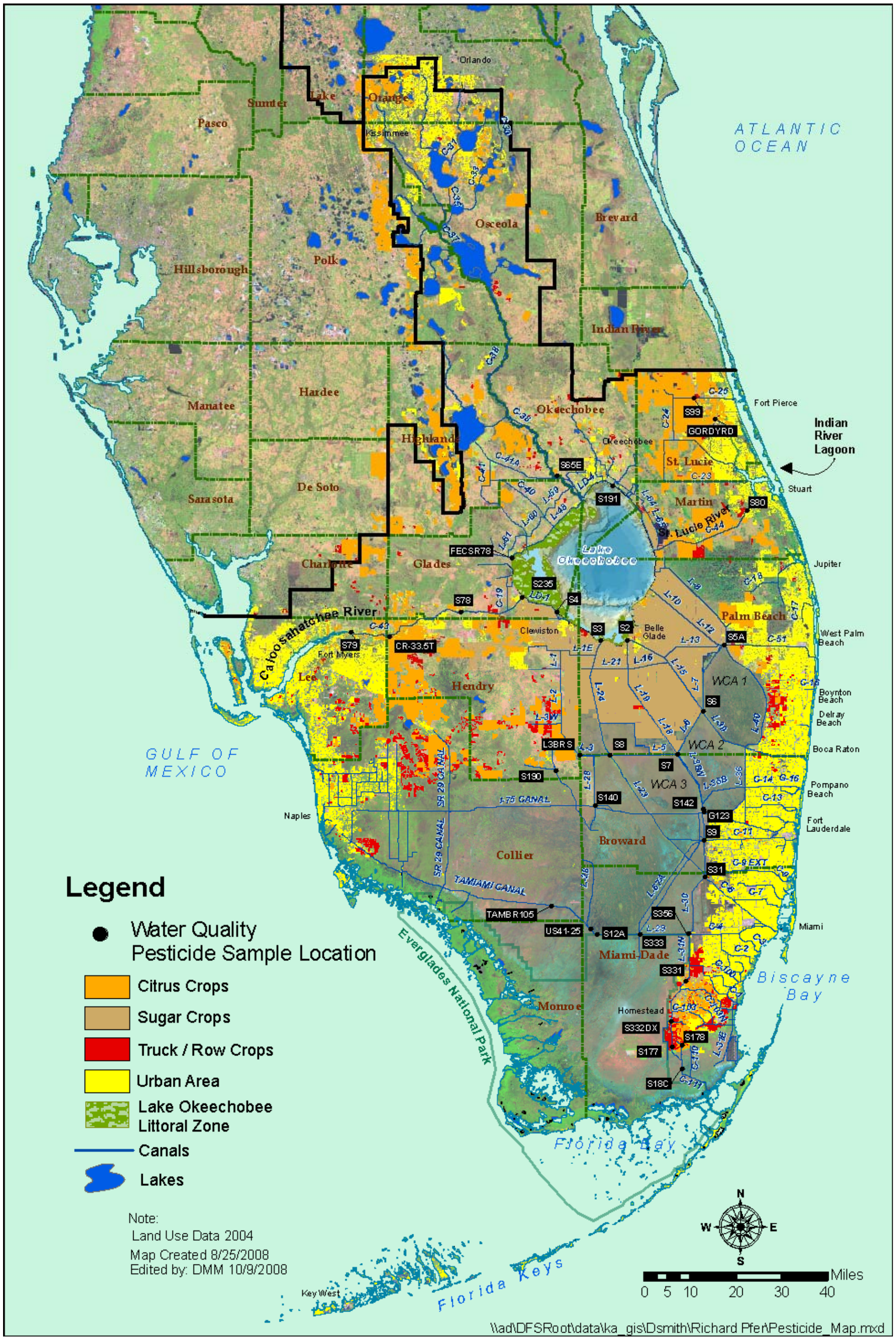

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for October 2009 sampling event.

Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)
2,4-D	0.2 - 0.68	endrin aldehyde	0.0042 - 0.018
2,4,5-T	0.2 - 0.68	ethion	0.0094 - 0.04
2,4,5-TP (silvex)	0.2 - 0.68	ethoprop	0.0094 - 0.04
acifluorfen	0.2 - 0.68	fenamiphos (nemacur)	0.038 - 0.16
alachlor	0.057 - 0.24	fonofos (dyfonate)	0.0094 - 0.04
aldrin	0.0019 - 0.008	heptachlor	0.0023 - 0.0096
ametryn	0.0094 - 0.04	heptachlor epoxide	0.0019 - 0.013
atrazine	0.0094 - 0.04	hexazinone	0.019 - 0.08
atrazine desethyl	0.0094 - 0.04	imidacloprid	0.2 - 0.63
atrazine desisopropyl	0.0094 - 0.04	linuron	0.2 - 0.63
azinphos methyl (guthion)	0.028 - 0.12	malathion	0.028 - 0.12
α-BHC (alpha)	0.0021 - 0.0096	metalaxyl	0.047 - 0.2
β-BHC (beta)	0.0032 - 0.035	methoxychlor	0.0094 - 0.04
δ-BHC (delta)	0.0019 - 0.008	metolachlor	0.057 - 0.24
γ-BHC (gamma) (lindane)	0.0019 - 0.008	metribuzin	0.019 - 0.08
bromacil	0.047 - 0.2	mevinphos	0.057 - 0.24
butylate	0.019 - 0.08	mirex	0.011 - 0.048
carbophenothion (trithion)	0.015 - 0.064	naled	0.076 - 0.32
chlordane	0.019 - 0.08	norflurazon	0.019 - 0.08
chlorothalonil	0.015 - 0.064	parathion ethyl	0.019 - 0.08
chlorpyrifos ethyl	0.0094 - 0.04	parathion methyl	0.019 - 0.08
chlorpyrifos methyl	0.019 - 0.08	PCB-1016	0.019 - 0.08
cypermethrin	0.019 - 0.08	PCB-1221	0.019 - 0.08
DDD-p,p'	0.0045 - 0.019	PCB-1232	0.019 - 0.08
DDE-p,p'	0.0038 - 0.016	PCB-1242	0.019 - 0.08
DDT-p,p'	0.0057 - 0.024	PCB-1248	0.019 - 0.08
demeton	0.028 - 0.12	PCB-1254	0.019 - 0.08
diazinon	0.019 - 0.08	PCB-1260	0.019 - 0.08
dicofol (kelthane)	0.042 - 0.18	permethrin	0.015 - 0.064
dieldrin	0.0019 - 0.0088	phorate	0.0094 - 0.04
disulfoton	0.019 - 0.08	prometryn	0.019 - 0.08
diuron	0.2 - 0.63	prometon	0.019 - 0.08
α-endosulfan (alpha)	0.0038 - 0.016	simazine	0.0094 - 0.04
β-endosulfan (beta)	0.0038 - 0.016	toxaphene	0.094 - 0.4
endosulfan sulfate	0.0045 - 0.019	trifluralin	0.0076 - 0.032
endrin	0.0094 - 0.04		

Table 2. Summary of pesticide residues (µg/L) above the method detection limit found in surface water samples collected by SFWMD in October 2009.

Date	Location	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	bromacil	diuron	hexazinone	metolachlor	norflurazon	simazine	Number of compounds detected at location
10/26/2009	S99	N	-	-	-	-	-	-	0.14	-	0.20	0.13	3
	GORDYRD	Y	-	-	-	-	-	-	-	-	0.30 *	-	1
	S12A	N	-	-	-	-	-	-	-	-	-	-	0
	S177	N	-	-	-	-	-	-	-	-	-	-	0
	S178	N	-	-	-	-	-	-	-	0.08 I	-	-	1
	S18C	Y	-	-	-	-	-	-	-	-	-	-	0
	S2	N	-	0.026 I	0.065	0.012 I	-	-	-	-	-	-	3
	S3	N	-	-	0.097	0.024 I	-	-	-	-	-	-	2
	S331	Y	-	-	-	-	-	-	-	-	-	-	0
	S332DX	Y	-	-	-	-	-	-	-	-	-	-	0
	S333	Y	-	-	-	-	-	-	-	-	-	-	0
	S356-334	Y	-	-	-	-	-	-	-	-	-	-	0
	S4	N	-	-	0.057	0.015 I	-	-	-	-	-	-	2
	S80	N	1.4	-	-	-	-	-	-	-	0.23	0.021 I	3
	TAMBR105	N	-	-	-	-	-	-	-	-	-	-	0
	US41-25	Y	-	-	-	-	-	-	-	-	-	-	0
10/27/2009	CR33.5T	R	-	-	0.037 I	-	0.082 I	-	0.021 I	-	0.21	-	4
	FECSR78	Y	-	-	-	-	-	-	0.036 I	-	-	-	1
	G123	N	-	-	-	-	-	-	-	-	-	-	0
	L3BRS	Y	-	-	-	-	-	-	-	-	0.024 I	-	1
	S140	Y	-	-	-	-	-	-	-	-	0.058 I	-	1
	S190	N	-	-	-	-	-	-	-	-	-	-	0
	S191	Y	-	-	-	-	-	-	-	-	-	-	0
	S235	R	-	-	0.058	0.017 I	-	-	-	-	-	-	2
	S31	N	-	0.01 I	0.021 I	-	-	-	-	-	-	-	2
	S65E	N	0.24 I	-	-	-	-	-	0.089	-	-	-	2
	S78	Y	0.27 I	0.011 I	0.43	0.021 I	0.059 I	-	-	-	0.12	-	6
	S79	N	-	-	0.040	-	0.051 I	0.23 I	-	-	0.18	-	4
	S8	N	-	0.028 I	0.029 I	-	-	-	-	-	-	-	2
	S9	N	-	-	0.013 I	-	-	-	-	-	-	-	1
10/28/2009	S5A	N	-	0.017 I	0.15	0.029 I	-	-	0.031 I	-	-	-	4
	S6	N	-	0.038	0.023 I	-	-	-	-	-	-	-	2
	S7	R	-	0.036 I	-	-	-	-	-	-	-	-	1
Total number of compound detections			3	7	12	6	3	1	5	1	8	2	48

N - no Y - yes R - reverse; - denotes that the result is below the method detection limit; * results are the average of replicate samples
I - value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit

Table 3. Selected properties of pesticides found in October 2009 sampling event.

Common Name	Surface Water Standards F.A.C. 62-302 (µg/L)	Acute Oral LD_{50} For Rats (mg/kg) (1)	U.S. EPA Carcinogenic Potential	Water Solubility (WS) (mg/L) (2, 3)	K_{oc} (mL/g) (2, 3)	Soil Half-life (days) (2, 3)	Soil Conservation Service (SCS) rating (2) LE	SA	SS	Volatility from Water	Bioconcentration Factor (BCF)
2,4-D (acid)	(100)	375	D	890	20	10	M	S	M	I	13
ametryn	-	1,110	D	185	300	60	M	M	M	I	33
atrazine	-	3,080	C	33	100	60	L	M	L	I	86
bromacil	-	5,200	C	700	32	60	L	M	M	I	15
diuron	-	3,400	D	42	480	90	M	M	L	I	75
hexazinone	-	1,690	D	33,000	54	90	L	M	M	I	2
metolachlor	-	2,780	C	530	200	90	L	M	M	I	18
norflurazon	-	9,400	C	28	700	90	M	M	L	I	94
simazine	-	>5000	C	6.2	130	60	L	M	M	I	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS)
Volatility from water: R = rapid, I = insignificant, S = significant

Bioconcentration Factor (BCF) calculated as BCF = $10^{(2.791 - 0.564 \log WS)}$ (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP F.A.C. 62-302 surface water standards (12/06) for Class III waters except Class I in ( )

(1) Hartley and Kidd (1987)
(2) Goss and Wauchope (1992)
(3) Montgomery (1993)
(4) Lyman, et al. (1990)
(5) U.S. EPA (1996a)

Table 4. Toxicity of pesticides found in the October 2009 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

Common Name	48 hr EC_{50} Water Flea *Daphnia magna*	Acute Toxicity (*)	Chronic Toxicity (*)	96 hr LC_{50} Fathead Minnow (#) *Pimephales promelas*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Bluegill *Lepomis macrochirus*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Largemouth Bass *Micropterus salmoides*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Channel Catfish *Ictalurus punctatus*	Acute Toxicity	Chronic Toxicity
2,4-D	25,000 (4)	8,333	1,250	133,000 (4)	44,333	6,650	180,000 (5)	60,000	9,000	-	-	-	100,000 (1)	33,333	5,000	-	-	-
	-	-	-	-	-	-	900 (48 hr) (3)	-	-	-	-	-	110,000 (4)	36,667	5,500	-	-	-
ametryn	28,000 (4)	9,333	1,400	16,000 (6)	5,333	800	4,100 (1)	1,367	205	-	-	-	8,800 (1)	2,933	440	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	3,600 (6)	1,200	180	-	-	-
atrazine	6,900 (4)	2,300	345	15,000 (4)	5,000	750	16,000 (1)	5,333	800	-	-	-	8,800 (1)	2,933	440	7,600 (1)	2,533	380
	-	-	-	-	-	-	-	-	-	-	-	-	5,300 (7)	1,767	265	-	-	-
bromacil	-	-	-	-	-	-	127,000 (4)	42,333	6,350	-	-	-	36,000 (4)	12,000	1,800	-	-	-
	121,000 (11)	40,333	6,050	-	-	-	127,000 (11)	42,333	6,350	-	-	-	36,000 (11)	12,000	1,800	-	-	-
diuron	1,400 (4)	467	70	14,200 (4)	4,733	710	5,900 (1)	1,967	295	-	-	-	5,600 (1)	1,867	280	-	-	-
	1,400 (8)	467	70	14,000 (8)	4,667	700	-	-	-	-	-	-	-	-	-	-	-	-
hexazinone	151,600 (4)	50,533	7,580	274,000 (1)	91,333	13,700	100,000 (4)	33,333	5,000	-	-	-	180,000 (4)	60,000	9,000	-	-	-
	151,600 (9)	50,533	7,580	274,000 (9)	91,333	13,700	505,000 (9)	168,333	25,250	-	-	-	>320,000 (9)	>106,667	-	-	-	-
metolachlor	23,500 (4)	7,833	1,175	-	-	-	15,000 (1)	5,000	750	-	-	-	2,000 (1)	667	100	4,900 (2)	1,633	245
norflurazon	15,000 (4)	5,000	750	-	-	-	16,300 (4)	5,433	815	-	-	-	8,100 (4)	2,700	405	>200,000 (1)	>67,000	>10,000
	>15,000 (10)	>5,000	>750	-	-	-	16,300 (10)	5,433	815	-	-	-	8,100 (10)	2,700	405	-	-	-
simazine	1,100 (4)	367	55	100,000 (4)	33,333	5,000	90,000 (1)	30,000	4,500	-	-	-	100,000 (4)	33,333	5,000	-	-	-

(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC50 is the lowest value which has been determined for a species significant to the indigenous aquatic community.
(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Hartley and Kidd (1987)
(2) Montgomery (1993)
(3) Verschueren (1983)
(4) U.S. EPA (1991)
(5) Mayer and Ellersieck (1986)
(6) U.S. EPA (2005)
(7) U.S. EPA (2006)
(8) U.S. EPA (2003b)
(9) U.S. EPA (1994)
(10) U.S. EPA (1996b)
(11) U.S. EPA (1996c)

Table 5. Atrazine Desethyl/Atrazine ratio (DAR) data for October 2009 sampling event.

Date	Location	Flow*	atrazine		atrazine desethyl		DAR
			µg/l	moles/l	µg/l	moles/l	
10/26/2009	S2	N	0.065	3.01365E-10	0.012	6.39551E-11	0.2
	S3	N	0.097	4.49730E-10	0.024	1.2791E-10	0.3
	S4	N	0.057	2.64274E-10	0.015	7.99439E-11	0.3
10/27/2009	S235	R	0.058	2.68911E-10	0.017	9.06031E-11	0.3
	S78	Y	0.43	1.99365E-09	0.021	1.11922E-10	0.1
10/28/2009	S5A	N	0.15	6.95458E-10	0.029	1.54558E-10	0.2

DAR	All sites	Flow only sites	No flow sites
average	0.2	0.1	0.3
median	0.3	0.1	0.3
minimum	0.1	0.1	0.2
maximum	0.3	0.1	0.3

*N - no; Y - yes; R - reverse