PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

JANUARY 2013 SAMPLING EVENT



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Table of Contents

Summary	2
Background and Methods	
Results	3
Usage and Water Quality Impacts	4
Quality Assurance Evaluation	7
Figure 1. South Florida Water Management District Pesticide Monitoring Network.	8
Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for January 2013 sampling event.	9
Table 2. Summary of pesticide residues (µg/L) detected above the method detection limit in surface water samples collected by SFWMD in January 2013.	.10
Table 3. Summary of pesticides residues (µg/Kg) detected above the method detection limit in sediment samples collected by SFWMD in January 2013.	.11
Table 4. Selected properties of pesticides detected during the January 2013 sampling event	.12
Table 5. Toxicity of pesticides detected during the January 2013 sampling event to freshwater aquatic invertebrates and fishes (µg/L).	.13
Table 6. Atrazine Desethyl (DEA)/Atrazine ratio (DAR) data for January 2013 sampling event.	.14
Glossary	15
References	16

Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water and sediment samples were collected January 28 to February 5, 2013, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides 2,4-D, ametryn, atrazine, bromacil, hexazinone, metolachlor, metribuzin, norflurazon, and simazine, along with the insecticide/degradate chlorpyrifos ethyl and atrazine desethyl, were detected in one or more of these surface water samples. The chlorpyrifos ethyl concentration detected is greater than the calculated 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 herbicide ametryn and 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 sites 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. Sediment samples are collected using a petite Ponar® dredge.

Seventy-three pesticides and degradation products were analyzed in samples from 26 of the network 27 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 January 28 to February 5, 2013.

Results

At least one pesticide was detected in surface water at 14 of the 26 sites (**Table 2**) and in sediment at 11 of the 17 sites (**Table 3**). The non-ECP permit requires sampling at S142 only during discharge or flow events. For this sampling event, no sample was obtained due to the lack of discharge at the time of sample collection. A minor modification of the Lake Okeechobee Water Control Structure Operations Permit (#0174552-010, dated December 18, 2011) eliminated sediment sampling at S65E, S191, and FECSR78. Additionally, sediment sampling was reduced to an annual frequency at S2, S3, and S4 for only ametryn, chlordane, DDD, DDE, and DDT analysis, which was performed during this sampling event. Sediment samples are not collected at

S333, S356-334, and TAMBR105, due to no requirement in the respective mandate. All of these compounds have previously been detected in this monitoring program.

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 acute and chronic toxicity and environmental fate impacts are reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

<u>2,4-D</u>: 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 noncrop 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 only 2,4-D residue was detected at S6 (0.41 micrograms per liter [μ g/L]) (**Table 2**). Using these criteria, this observed level should not have an acute or chronic effect on fish or aquatic invertebrates. 2,4-D was not detected in the sediment.

<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 greater than (>) 10 micrograms per liter (μ g/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 LC₅₀ 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 0.072 µg/L (**Table 2**). 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 13 micrograms per kilogram (μ g/Kg) (**Table 3**). However, no sediment guidelines have been developed for ametryn.

<u>Atrazine</u>: 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 LC₅₀ 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 10 of the 26 sampling locations, ranged from 0.027 to 0.35 μ g/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 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, unitless), on a molar basis, has been suggested as an indicator of nonpointsource 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 (Goolsby et al. (1997). The low median DAR ratio (e.g. 0.13) 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.

<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 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 LC₅₀ 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 S65E (0.18 μ g/L) (**Table 2**). Using these criteria, this observed concentration should not have an acute or chronic detrimental impact on fish or aquatic invertebrates.

<u>Chlorpyrifos ethyl</u>: 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 detected in this sampling event (0.015 μ g/L at S177) could have a harmful impact on aquatic invertebrates, as this level is greater than the calculated chronic toxicity for *Daphnia magna* (**Table 4**). 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.

<u>DDD</u>, <u>DDE</u>, <u>DDT</u>: 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 (dichlorodiphenyltrichloroethane), 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 (dichlorodiphenyldichloroethane), 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 were from 2.1 to 20 μ g/Kg (**Table 3**). Any concentration which would fall below the TEC (4.9 μ g/Kg) should not impact sediment dwelling organisms while concentrations above the PEC (28 μ g/Kg), frequently or always have the possibility for impacting sediment-dwelling organisms. The DDD concentrations detected at S2, S5A, and S6 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 μ g/Kg and the PEC is 31 μ g/Kg for DDE in freshwater sediments. The concentration of DDE detected at S2, S177, S6, and S5A (**Table 3**) 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 S177 (2.1 μ g/Kg) (**Table 3**) did not exceed the TEC (4.2 μ g/Kg). At this level, there should not be any possibility for impacting sediment-dwelling freshwater organisms. No DDT was detected in the surface water.

<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 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 EC₅₀ of 145 mg/L for *Daphnia magna* (U.S. EPA, 1988). The highest surface water concentration detected in this sampling event of 0.20 μ g/L at S140 (**Table 2**) should not have an acute impact on fish or aquatic invertebrates. Hexazinone was not detected in the sediment.

<u>Metolachlor</u>: 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 (0.10 μ g/L at S65E) (**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. Metolachlor was not detected in the sediment.

<u>Metribuzin</u>: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, 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 $0.076 \ \mu g/L$ at S6 (**Table 2**). Using these criteria, this surface water concentration should not have an acute impact on fish or aquatic invertebrates. Metribuzin was not 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 LC₅₀ for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The highest norflurazon surface water concentration detected (0.050 µg/L at S140) (**Table 2**) 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 S4 (0.020 µg/L) (**Table 2**) was below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

Quality Assurance Evaluation

No pesticide analytes were detected in the equipment blanks or field blank performed at S18C, S191, S331, S4, S8, US41-25, and S5A. All of the collected samples were shipped and all bottles were received.

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

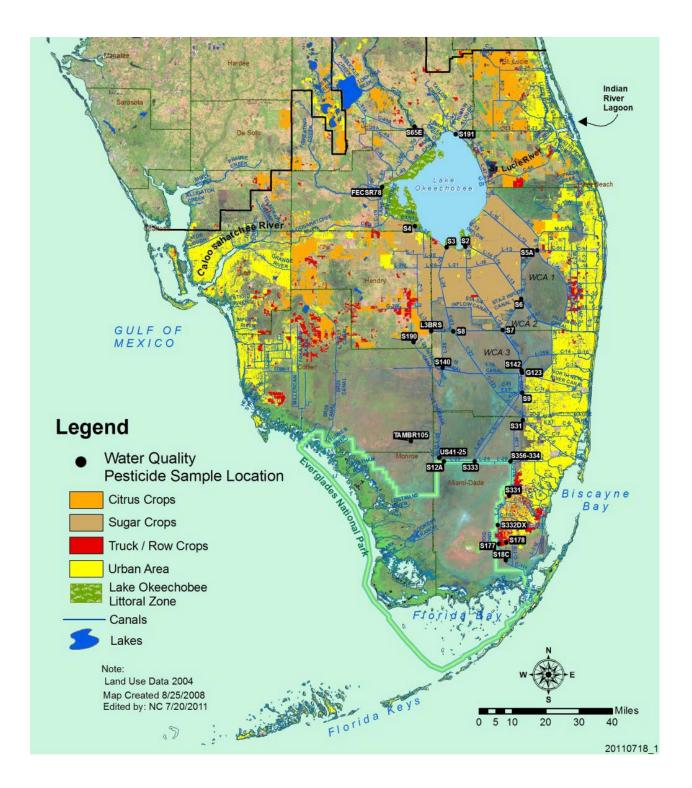


Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for January 2013 sampling event.

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 - 0.62	10 - 120	endrin aldehyde	0.0038 - 0.016	1 - 17
2,4,5-T	0.2 - 0.62	10 - 120	ethion	0.0094 - 0.04	2.6 - 42
2,4,5-TP (silvex)	0.2 - 0.62	10 - 120	ethoprop	0.0047 - 0.02	1.3 - 21
acifluorfen	0.2 - 0.62	10 - 120	fenamiphos	0.028 - 0.12	5.2 - 83
alachlor	0.056 - 0.24	19 - 300	fonofos	0.0094 - 0.04	1.3 - 21
aldrin	0.0019 - 0.008	0.52 - 8.3	heptachlor	0.0019 - 0.008	0.52 - 8.3
ametryn	0.0094 - 0.04	2.6 - 57	heptachlor epoxide	0.0019 - 0.008	0.52 - 8.3
atrazine	0.0094 - 0.072	2.6 - 42	hexazinone	0.028 - 0.12	7.9 - 120
atrazine desethyl	0.0094 - 0.04	N/A	imidacloprid	0.21 - 0.68	N/A
atrazine desisopropyl	0.0094 - 0.04	N/A	linuron	0.21 - 0.68	9.4 - 110
azinphos methyl (guthion)	0.019 - 0.08	7.9 - 120	malathion	0.0094 - 0.04	2.6 - 42
α-BHC (alpha)	0.0019 - 0.008	0.52 - 8.3	metalaxyl	0.038 - 0.16	N/A
β-BHC (beta)	0.0019 - 0.008	0.52 - 8.3	methamidophos	N/A	10 - 170
δ-BHC (delta)	0.0019 - 0.008	0.52 - 8.3	methoxychlor	0.0094 - 0.04	3.7 - 58
γ-BHC (gamma) (lindane)	0.0019 - 0.008	0.52 - 8.3	metolachlor	0.056 - 0.24	16 - 250
bromacil	0.038 - 0.16	16 - 250	metribuzin	0.019 - 0.08	5.2 - 83
butylate	0.019 - 0.08	N/A	mevinphos	0.0094 - 0.04	2.6 - 42
carbophenothion (trithion)	0.0056 - 0.024	1.6 - 25	mirex	0.0038 - 0.016	1 - 17
chlordane	0.019 - 0.08	5.2 - 110	monocrotophos	N/A	3.1 - 50
chlorothalonil	0.0075 - 0.032	1.6 - 25	naled	0.038 - 0.16	10 - 170
chlorpyrifos ethyl	0.0094 - 0.04	2.6 - 42	norflurazon	0.028 - 0.12	7.9 - 120
chlorpyrifos methyl	0.0094 - 0.04	2.6 - 42	parathion ethyl	0.019 - 0.08	2.6 - 42
cypermethrin	0.011 - 0.048	2.6 - 42	parathion methyl	0.0094 - 0.04	2.6 - 42
DDD-P,P'	0.0038 - 0.016	1 - 23	PCB-1016	0.019 - 0.08	5.2 - 83
DDE-P,P'	0.0038 - 0.016	1 - 23	PCB-1221	0.019 - 0.08	10 - 170
DDT-P,P'	0.0038 - 0.016	1.6 -34	PCB-1232	0.019 - 0.08	5.2 - 83
demeton	0.023 - 0.096	3.1 - 50	PCB-1242	0.019 - 0.08	5.2 - 83
diazinon	0.0094 - 0.04	2.6 - 42	PCB-1248	0.019 - 0.08	5.2 - 83
dicofol (kelthane)	0.023 - 0.096	6.3 - 100	PCB-1254	0.019 - 0.08	7.9 - 120
dieldrin	0.0019 - 0.008	0.52 - 8.3	PCB-1260	0.019 - 0.08	5.2 - 83
disulfoton	0.0047 - 0.02	1.3 - 21	permethrin	0.0094 - 0.04	2.6 - 42
diuron	0.21 - 0.68	9.4 - 110	phorate	0.0047 - 0.02	2.6 - 42
α-endosulfan (alpha)	0.0019 - 0.016	0.52 - 8.3	prometryn	0.019 - 0.08	5.2 - 83
β-endosulfan (beta)	0.0019 - 0.016	0.52 - 8.3	prometon	0.019 - 0.08	N/A
endosulfan sulfate	0.0038 - 0.016	1 - 17	simazine	0.0094 - 0.04	2.6 - 42
endrin	0.0038 - 0.016	1.7 - 27	toxaphene	0.094 - 0.4	31 - 500
			trifluralin	0.0075 - 0.008	2.1 - 33

N/A = not analyzed

Table 2. Summary of pesticide residues $(\mu g/L)$ det	ected above the method detection limit in surface water samples
collected by SFWMD in January 2013.	

Date	Location	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	bromacil	chlorpyrifos ethyl	hexazinone	metolachlor	metribuzin	norflurazon	simazine	Number of compounds detected at location
1/28/2013	S18C	Y	-	-	-	-	-	-	-	-	-	-	-	0
	S178	Ν	-	-	0.26	0.054	-	-	-	-	-	-	-	2
	S177	Ν	-	-	-	-	-	0.015 I	-	-	-	-	-	1
	S331	Ν	-	-	-	-	-	-	-	-	-	-	-	0
	S332DX	Ν	-	-	-	-	-	-	-	-	-	-	-	0
	S191	Ν	-	-	-	-	-	-	-	-	-	-	-	0
	S4	Ν	-	-	0.23	0.020 I	-	-	0.032 I	-	-	-	0.020 I	4
	S2	Ν	-	-	0.18	0.031 I	-	-	0.029 I	-	-	-	-	3
	S3	Ν	-	-	0.20	0.022 I	-	-	0.030 I	-	-	-	-	3
	S65E	Y	1	1	-	-	0.18 *	-	-	0.10 I *	0.041 I*	-	-	3
	FECSR78	Ν	1	1	-	-	-	-	-	-	-	-	-	0
1/29/2013	S31	Ν	-	-	-	-	-	-	-	-	-	-	-	0
	S356-334	Ν	-	-	-	-	-	-	-	-	-	-	-	0
	S333	Y	-	0.011 I	0.027 I	-	-	-	-	-	-	-	-	2
	S12A	Ν	1	1	-	-	-	-	-	-	-	-	-	0
	US41-25	Ν	1	1	-	-	-	-	-	-	-	-	-	0
	TAMBR105	Y	-	-	-	-	-	-	-	-	-	-	-	0
1/30/2013	S140	Ν	-	-	-	-	-	-	0.20	-	-	0.050 I	-	2
	S190	Ν	-	-	-	-	-	-	-	-	-	0.037 I	-	1
	L3BRS	Ν	1	0.023 I	0.15	0.012 I	-	-	-	-	-	-	-	3
	S8	Y	1	0.033 I	0.14	0.014 I	-	-	-	-	-	-	-	3
	G123	Ν	1	1	-	-	-	-	-	-	-	-	-	0
2/5/2013	S6	Ν	0.41 I	0.072	0.17	-	-	-	-	-	0.076 I	-	-	4
	S5A	Ν	-	0.012 I	0.16	-	-	-	0.033 I	-	-	-	-	3
	S7	N	-	0.041	0.35	-	-	-	-	-	0.036 I	-	-	3
	S9	Ν	-	-	-	-	-	-	-	-	-	-	-	0
Total number	Total number of compound detections			6	10	6	1	1	5	1	3	2	1	37

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 method detection limit

* = value is the average of replicate samples

Table 3 . Summary of pesticides residues (µg/Kg) detected above the method detection limit in sediment samples collected
by SFWMD in January 2013.

Date	Location	Flow	ametryn	DDD-P,P'	DDE-P,P'	DDT-P,P'	Number of compounds detected at location
1/28/2013	S2	N	-	16 I	92	-	2
	S178	N	-	-	16	-	1
	S 3	N	-	2.1 I	11	-	2
	S177	N	-	3.6 I	<u>98</u>	2.1 I	3
	S4	N	-	-	1.0 I*	-	1
	S331	N	-	-	2.8 I	-	1
1/30/2013	G123	N	-	-	5.3 I	-	1
	S 8	Y	-	-	3.1 I	-	1
2/5/2013	S9	N	-	-	12	-	1
	S6	N	-	9.5	38	-	2
	S5A	N	13 I*	20 *	71 *	-	3
Total number	of compound de	etections	1	5	11	1	18

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 method detection limit

* = value is the average of replicate samples

Values in bold, italicized font are at a concentration that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

Common Name	Surface Water Standards F.A.C. 62-302 (µg/L)	ndards F.A.C. Acute Oral LD_{50} For Parts (mg/Kg) (1)		Volatility from Water (2)	(S	onservation CS) rating	(3)	K _{oc} (mL/g) (3, 4)	(days)	Water Solubility (WS) (mg/L) (3, 4)	U.S. EPA Carcinogenic Potential (5)
2,4-D (acid)	(100)	375	13	т	LE M	SA S	SS M	20	(3, 4) 10	890	D
ametryn	-	1,110	33	I	M	M	M	300	60	185	D
atrazine	-	3,080	86	I	L	М	L	100	60	33	C
bromacil	-	5,200	15	Ι	L	М	М	32	60	700	С
chlorpyrifos ethyl	-	135 -163	418	-	S	М	М	6,070	30	2	D
DDD-p,p'	-	3,400	3,173	Ι	-	-	-	239,900	-	0.055	-
DDE-p,p'	-	880	2,887	S	-	-	-	243,220	-	0.065	-
DDT-p,p'	0.001	113	15,377	Ι	-	-	-	140,000	-	0.00335	-
hexazinone	-	1,690	2	Ι	L	М	М	54	90	33,000	D
metolachlor	-	2,780	18	Ι	L	М	М	200	90	530	С
metribuzin	-	2,200	11	Ι	L	S	М	41	30	1,220	D
norflurazon	-	9,400	94	Ι	М	М	L	700	90	28	С
simazine	-	>5,000	221	Ι	L	М	Μ	130	60	6.2	С

 Table 4. Selected properties of pesticides detected during the January 2013 sampling event.

- = No data available

FDEP F.A.C. 62-302 surface water standards (7/2012) for Class III waters except Class I noted in ()

Bioconcentration Factor (BCF) calculated as $BCF = 10^{(2.71 - 0.564 \log WS)}$ (2)

Volatility from water: R = rapid, I = insignificant, S = significant

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)

B2 = probable human carcinogen; C = possible human carcinogen; D = not classified; E = evidence of non-carcinogen for humans (5)

(1) Hartley and Kidd (1987)

(2) Lyman, et al. (1990)

(3) Goss and Wauchope (1992)

(4) Montgomery (1993)

(5) U.S. EPA (1996a)

Common Name	48 hour l Water f Daphnia m	lea	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour L Fathead Mi (#) Pimeph promelo	innow hales	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour l Bluegill Lep macroch	pomis	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour LC ₅₀ Largemouth Bass <i>Micropterus</i> salmoides	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour LO Rainbow Troi Oncorhynci mykiss	ut (#)	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour Le Channel Cat Ictalurus punctatu	fish s	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	-		-	-
ametry n	28,000	(5)	9,333	1,400	-		-	-	4,100	(2)	1,367	205	-	-	-	8,800	(2)	2,933	440	-		-	-
	-		-	-	-		-	-	-		-	-	-	-	-	3,600	(7)	1,200	180	-		-	-
atrazine	6900	(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	(8)	1,767	265	-		-	-
bromacil	-		-	-	-		-	-	127,000	(5)	42,333	6,350	-	-	-	36,000	(5)	12,000	1,800	-		-	-
	121,000	(13)	40,333	6,050	-		-	-	127,000	(13)	42,333	6,350	-	-	-	36,000	(13)	12,000	1,800	-		-	-
chlorp y rifos	1.7	(5)	0.57	0.085	203	(5)	68	10	2.6	(2)	0.87	0.13	-	-	-	11	(2)	3.7	0.55	280	(5)	93	14
ethy1	0.1	(5)	0.03	0.005	-		-	-	5.8	(5)	1.93	0.29	-	-	-	-		-	-	-		-	-
	0.1	(11)	0.03	0.005	-		-	-	1.8	(11)	0.60	0.09	-	-	-	-		-	-	-		-	-
DDD-p,p'	3,200	(4)	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	(3)	6.3	0.95	8	(3)	2.7	0.4	2 (3)	0.7	0.10	7	(3)	2.3	0.35	16	(3)	5.3	0.8
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	(9)	50,533	7,580	274,000	(9)	91,333	13,700	505,000	(9)	168,333	25,250	-	-	-	>320,000	(9)	>106,667	>16,000	-		-	-
metolachlor	23,500	(5)	7,833	1,175	-		-	-	15,000	(2)	5,000	750	-	-	-	2,000	(2)	667	100	4,900	(3)	1,633	245
metribuzin	4,200	(5)	1,400	210	-		-	-	80,000	(2)	26,667	4,000	-	-	-	64,000	(2)	21,333	3,200	100,000	(5)	33,333	5,000
	4,200	(10)	1,400	210	-		-	-	75,900	(10)	25,300	3,795	-	-	-	76,770	(10)	25,590	3,839	-		-	-
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
	>15000	(12)	>5,000	>750	-		-	-	16,300	(12)	5,433	815	-	-	-	8,100	(12)	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	-		-	-

Table 5. Toxicity of pesticides detected during the January 2013 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

- = No data available

(*) 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 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)	(6) Mayer and Ellersieck (1986)
(2) Hartley and Kidd (1987)	(7) U.S. EPA (2005)
(3) Montgomery (1993)	(8) U.S. EPA (2006)
(4) Verschueren (1983)	(9) U.S. EPA (1994)
(5) U.S. EPA (1991)	(10) U.S. EPA (1998)

(11) U.S. EPA (2002)
(12) U.S. EPA (1996b)
(13) U.S. EPA (1996c)

Date	Site	Flow*	at	razine	atrazine	desethyl	DAR
Date	Sile	FIOW.	µg/L	moles/L	μg/L	moles/L	DAK
1/28/2013	S178	N	0.26	1.21E-09	0.054	2.88E-10	0.24
1/28/2013	S4	Ν	0.23	1.07E-09	0.020	1.07E-10	0.10
1/28/2013	S2	Ν	0.18	8.35E-10	0.031	1.65E-10	0.20
1/28/2013	S3	N	0.2	9.27E-10	0.022	1.17E-10	0.13
1/30/2013	L3BRS	N	0.15	6.95E-10	0.012	6.40E-11	0.09
1/30/2013	S 8	Y	0.14	6.49E-10	0.014	7.46E-11	0.11
				DAR	Allsites	Flow only sites	No flow sites
				average	0.15	0.11	0.15
			median	0.12	0.11	0.13	
				minimum	0.09	0.11	0.09
				maximum	0.24 0.11		0.24

Table 6. Atrazine Desethyl (DEA)/Atrazine ratio (DAR) data for January 2013 sampling event.

* N = no, Y = yes, R = reverse

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.
- EC₅₀: 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 units of atmospheres and S is solubility in units of moles/meter³ 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.
- LC₅₀: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- LD₅₀: 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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