PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

NOVEMBER 2014 SAMPLING EVENT



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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 November 3 to 6, 2014, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides 2,4-D, 2,4,5-T, 2,4,5-TP, ametryn, atrazine, bentazon, hexazinone, metolachlor, metribuzin, and norflurazon along with the insecticide/degradate imidacloprid and atrazine desethyl, were detected in one or more of these surface water samples. No harmful impacts are expected from the detected pesticides.

The herbicide ametryn and insecticides/degradates aldrin, chlordane, DDD, DDE, DDT, dieldrin, endosulfan sulfate, and methoxychlor, along with two PCB compounds were found in the sediment at several locations. Two DDE and chlordane compound sediment concentrations were of a magnitude considered to have a harmful effect to freshwater sediment-dwelling organisms or wildlife. 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 is 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-four pesticides and degradation products were analyzed in samples from 24 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 November 3 to November 6, 2014.

Results

At least one pesticide was detected in surface water at 24 of the 26 sites (**Table 2**) and in sediment at 16 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 not performed during this sampling event. Sediment samples are not collected at S333, S356-334, and TAMBR105, due to no requirement in the respective mandate. Structure G123 has been decommissioned and FDEP concurred with terminating all monitoring on

November 7, 2014. This sampling event will be the last one for G123. 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 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 residue was detected at S191 (0.094 micrograms per liter $[\mu g/L]$) (**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>2,4,5-T:</u> 2,4,5-T is a selective systemic herbicide formally used to control woody weeds, brush, and undergrowth in grassland and non-crop areas as well as weed control in rice. Environmental fate and toxicity data in **Tables 4 and 5** indicate that 2,4,5-T (1) can have a large loss from soil by leaching with a small and moderate loss by surface adsorption and surface solution, respectively; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The only detected concentration (**Table 2**) is below any level that would have an acute or chronic detrimental impact on fish. 2,4,5-T was not detected in the sediment.

<u>2,4,5-TP</u>: 2,4,5-TP or silvex is a herbicide which had registered uses for rice, range, and non-crop sites (fencerows, industrial sites, vacant lots, etc.). All uses were canceled in October 1983. Environmental fate and toxicity data in **Tables 4 and 5** indicate that 2,4,5-TP (1) is slightly toxic to mammals and relatively non-toxic to fish; and (2) does not bioaccumulate significantly. The only detected concentration (**Table 2**) is below any level that would have an acute or chronic detrimental impact on fish. 2,4,5-TP was not detected in the sediment.

Aldrin: Aldrin is a non-systemic insecticide with contact, stomach, and respiratory action, used primarily to control soil insects. Its use and manufacture has been discontinued in the United States. Environmental fate and toxicity data in **Tables 4 and 5** indicate that aldrin (1) is relatively toxic to mammals and fish; and (2) due to the large hydrophobicity of this compound, results in a significant bioconcentration factor. Freshwater sediment quality assessment guidelines have not been developed for aldrin due to insufficient data. The highest aldrin concentration detected in sediment was 0.63 micrograms per kilogram (μ g/Kg) at S5A (**Table 3**). No surface water detections of aldrin were found.

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 (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 0.073 μ g/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 S6 and S5A at 11 and 14 μ g/Kg, respectively (**Table 3**). 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 LC₅₀ of 76 mg/L for carp, 16 mg/L for perch, and 4.3 mg/L for guppies (Hartley Also, in a flow-through bioassay, the maximum acceptable toxicant and Kidd, 1987). 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 0.012 to 0.87 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 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 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 (Goolsby et al., (1997). The low median DAR ratio (e.g. 0.04) at the location 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.

Bentazon: Bentazon is a contact herbicide used for post-emergence control of many annual broadleaved weeds in beans, peas, rice, and established turf. Environmental fate and toxicity data in **Tables 4 and 5** indicate that bentazon (1) is easily lost from soil by leaching, with moderate loss from surface solution, and minimum loss by surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The highest detected concentration of $0.25 \mu g/L$ at S178 (**Table 2**), is below any level that would have an acute or chronic detrimental impact on fish or aquatic invertebrates. Bentazon was not detected in the sediment.

Chlordane: Chlordane is a chlorinated hydrocarbon previously used as a contact insecticide. Chlordane consists of 72% and 23% of the stereoisomers alpha and gamma chlordane, respectively (U.S. EPA, 1997). 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 μ g/Kg and PEC of 18 μ g/Kg for chlordane. The detected sediment residue at S6 and S5A (19 and 14 μ g/Kg, respectively) are at a concentration where harmful effects to sediment-dwelling organisms may be frequently or always observed (**Table 3**). 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.

<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 (**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 highest DDD sediment concentration detected was 7.9 $\mu g/Kg$ at S5A (**Table 3**). Any concentration which would fall below the TEC (4.9 $\mu g/Kg$) should not impact sediment dwelling organisms while concentrations above the PEC (28 $\mu g/Kg$), frequently or always have the possibility for impacting sediment-dwelling organisms. The DDD concentrations detected at S5A and S6 were between the TEC and PEC. These concentration 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 $\mu g/Kg$ and the PEC is 31 $\mu g/Kg$ for DDE in freshwater sediments. The concentration of DDE detected at 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 concentrations detected (**Table 3**) did not exceed the TEC ($4.2 \mu g/Kg$). At this level, there should not be any possibility for impacting sediment-dwelling freshwater organisms. No DDT was detected in the surface water.

<u>Dieldrin</u>: Dieldrin is a non-systemic insecticide with all uses canceled in the United States. Environmental fate and toxicity data in **Tables 4 and 5** indicate that dieldrin (1) is highly toxic to mammals and fish; and (2) bioconcentrates significantly due to this compounds hydrophobicity. The high K_{oc} and low water solubility accounts for dieldrin's affinity for sediment. The dieldrin concentration at S6 (0.83 μ g/Kg) (**Table 3**) is less than the TEC (1.9 μ g/Kg) and should not have an impact on sediment-dwelling freshwater organisms. Dieldrin 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 x 10-8 atm – m3/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 and S177 (**Table 3**). However, no sediment quality assessment guideline has been developed for endosulfan sulfate. Endosulfan sulfate was not 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 0.21 μg/L at S191 (**Table 2**) should not have an acute impact on fish or aquatic invertebrates.

Imidacloprid: Imidacloprid is a systemic insecticide registered for use on a variety of row crops and turf grass 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 detected concentration of $0.0080~\mu g/L$ at S65E (**Table 2**) is below any level that would have an acute or chronic detrimental impact on fish or aquatic invertebrates. Imidacloprid was not detected in the sediment.

Methoxychlor: Methoxychlor is an insecticide formally used on field crops, vegetables, fruits, and ornamentals. All uses were canceled in July 2002. Environmental fate and toxicity data in **Tables 4 and 5** indicate that methoxychlor (1) has an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a medium potential for loss in surface solution; (2) is relatively non-toxic to mammals but very toxic to freshwater invertebrates and fish; and (3) has the potential for bioconcentration. Methoxychlor was only detected in the sediment at S31 (**Table 3**). However, no sediment quality assessment guideline has been developed for methoxychlor.

Methoxychlor was not detected in the surface water.

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 (0.088 μ g/L at S5A) (**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, 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 $0.034 \,\mu\text{g/L}$ at S7 (**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.

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 LC₅₀ for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The only norflurazon surface water concentration detected (0.039 μ g/L at S190) (**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.

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-1016 and PCB-1254 is a commercial grade mixture containing 16 and 54, respectively, 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 absorbed 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 residues detected at S6 (280 μg/Kg) could have an impact freshwater

sediment-dwelling organisms. None of the PCB congeners were detected in the surface water.

Quality Assurance Evaluation

No pesticide analytes were detected in the equipment blanks or field blank performed at S18C, S331, S65E, US41-25, S8, and S5A. All of the collected samples were shipped and all bottles were received.

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

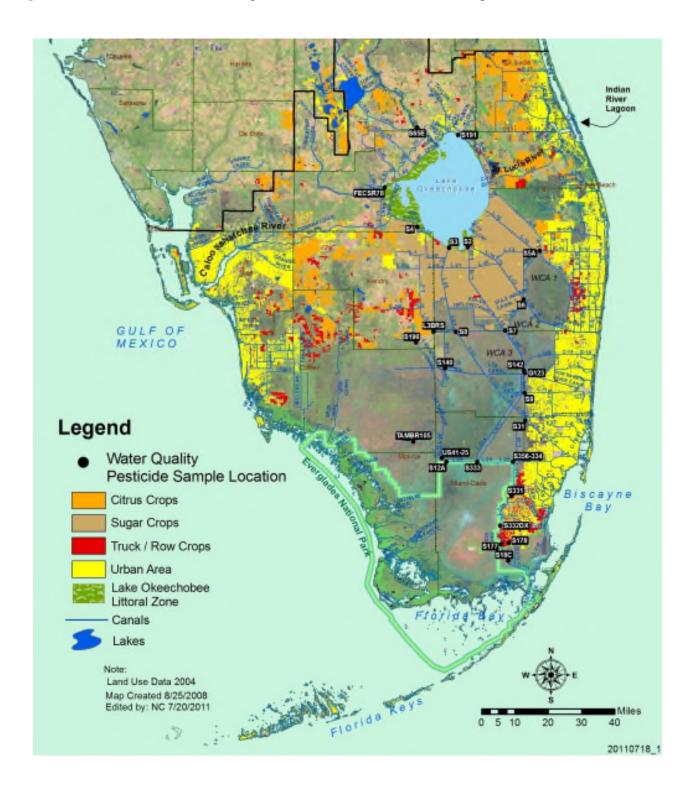


Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for November 2014 sampling event.

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	0.002 - 0.01	9 - 200	endrin aldehyde	0.0038 - 0.016	0.37 - 11
2,4,5-T	0.002 - 0.01	9 - 200	ethion	0.0094 - 0.04	2.3 - 66
2,4,5-TP (silvex)	0.002 - 0.01	9 - 200	ethoprop	0.0047 - 0.02	1.2 - 33
acifluorfen	0.002 - 0.01	9 - 200	fenamiphos	0.028 - 0.12	4.6 - 130
alachlor	0.056 - 0.24	17 - 480	fonofos	0.0094 - 0.049	1.2 - 33
aldrin	0.0019 - 0.008	0.093 - 2.6	heptachlor	0.0019 - 0.008	0.046 - 1.3
ametryn	0.0094 - 0.04	2.3 - 66	heptachlor epoxide	0.0019 - 0.008	0.093 - 2.6
atrazine	0.0094 - 0.04	2.3 - 66	hexazinone	0.028 - 0.12	6.9 - 200
atrazine desethyl	0.0094 - 0.04	N/A	imidacloprid	0.002 - 0.01	N/A
atrazine desisopropyl	0.0094 - 0.04	N/A	linuron	0.004 - 0.02	1.4 - 40
azinphos methyl (guthion)	0.019 - 0.08	6.9 - 200	malathion	0.0094 - 0.04	2.3 - 66
bentazon	0.002 - 0.01	N/A	metalaxyl	0.038 - 0.16	N/A
α-BHC (alpha)	0.0019 - 0.008	0.046 - 1.3	methamidophos	N/A	9.3 - 260
β-BHC (beta)	0.0019 - 0.008	0.046 - 1.3	methoxychlor	0.0094 - 0.04	0.046 - 1.3
δ-BHC (delta)	0.0019 - 0.008	0.031 - 0.87	metolachlor	0.056 - 0.24	14 - 400
γ-BHC (gamma) (lindane)	0.0019 - 0.008	0.046 - 1.3	metribuzin	0.019 - 0.08	4.6 - 130
bromacil	0.038 - 0.16	14 - 400	mevinphos	0.0094 - 0.04	2.3 - 66
butylate	0.019 - 0.08	N/A	mirex	0.0038 - 0.016	0.093 - 2.6
carbophenothion (trithion)	0.0056 - 0.024	0.14 - 4	monocrotophos	N/A	2.8 - 79
chlordane	0.019 - 0.08	0.46 - 13	naled	0.038 - 0.16	9.3 - 260
chlorothalonil	0.0075 - 0.032	0.19 - 5.3	norflurazon	0.028 - 0.12	6.9 - 200
chlorpyrifos ethyl	0.0094 - 0.04	2.3 - 66	parathion ethyl	0.019 - 0.08	2.3 - 66
chlorpyrifos methyl	0.0094 - 0.04	2.3 - 66	parathion methyl	0.0094 - 0.04	2.3 - 66
cypermethrin	0.011 - 0.048	0.23 - 6.6	PCB-1016	0.019 - 0.08	0.93 - 26
DDD-P,P'	0.0038 - 0.016	0.046 - 1.3	PCB-1221	0.019 - 0.08	0.93 - 26
DDE-P,P'	0.0038 - 0.016	0.031 - 0.87	PCB-1232	0.019 - 0.08	0.93 - 26
DDT-P,P'	0.0038 - 0.016	0.11 -3.2	PCB-1242	0.019 - 0.08	0.93 - 26
demeton	0.023 - 0.096	2.3 - 66	PCB-1248	0.019 - 0.08	0.93 - 26
diazinon	0.0094 - 0.04	2.2 - 24	PCB-1254	0.019 - 0.08	0.93 - 26
dicofol (kelthane)	0.023 - 0.096	0.093 - 2.6	PCB-1260	0.019 - 0.08	0.93 - 26
dieldrin	0.0019 - 0.008	0.19 - 5.3	permethrin	0.0094 - 0.04	0.11 - 3.2
disulfoton	0.0047 - 0.02	1.2 - 28	phorate	0.0047 - 0.02	1.2 - 33
diuron	0.002 - 0.01	1.4 - 40	prometon	0.019 - 0.08	N/A
α-endosulfan (alpha)	0.0019 - 0.016	0.19 - 5.3	prometryn	0.019 - 0.08	4.5 - 49
β-endosulfan (beta)	0.0019 - 0.016	0.19 - 5.3	simazine	0.0094 - 0.04	2.3 - 66
endosulfan sulfate	0.0038 - 0.016	0.093 - 2.6	toxaphene	0.094 - 0.4	4.6 - 130
endrin	0.0038 - 0.016	0.19 - 5.3	trifluralin	0.0075 - 0.032	0.074 - 2.1

N/A = not analyzed

Table 2. Summary of pesticide residues (µg/L) detected above the method detection limit in surface water samples collected by SFWMD in November 2014.

Date	Location	Flow	2,4-D	2,4,5-T	2,4,5-TP	ametryn	atrazine	atrazine desethyl	bentazon	hexazinone	imidacloprid	metolachlor	metribuzin	norflurazon	Number of compounds detected at location
11/3/2014	S18C	Y	-	-	-	-	-	-	0.011	-	-	-	-	-	1
	S178	Y	-	-	-	-	-	-	0.25	-	0.0068 I	-	-	-	2
	S177	Y	-	-	-	-	-	-	0.012 *	-	0.0038 I*	-	-	-	2
	S331	Y	-	-	-	-	-	-	0.015	-	-	-	-	-	1
	S332DX	Y	-	-	-	-	-	-	0.012	-	-	-	-	-	1
	S4	N	0.031	-	-	0.073	0.87	0.044	0.0040 I	-	-	-	-	-	5
	S2	N	0.013	-	-	0.013 I	0.083	0.022 I	0.0025 I	-	-	-	-	-	5
	S3	N	0.0097 I	-	-	0.011 I	0.12	0.036 I	-	-	-	-	-	-	4
	S65E	Y	0.013	-	-	-	0.069	-	0.036	0.031 I	0.0080 I	-	-	-	5
	S191	N	0.094	-	-	-	-	-	-	0.21	-	-	-	-	2
	FECSR78	N	0.0076 I	-	-	-	-	-	-	0.070 I	0.0059 I	-	-	-	3
11/4/2014	S31	N	-	-	-	0.016 I	0.012 I	-	0.17	-	-	-	-	-	3
	S356-334	N	-	-	-	-	-	-	0.015	-	-	-	-	-	1
	S333	Y	-	-	-	-	-	-	0.095	-	-	-	-	-	1
	S12A	N	0.035	-	-	-	-	-	0.028	-	-	-	-	-	2
	US41-25	N	-	-	-	-	-	-	-	-	-	-	-	-	0
	TAMBR105	Y	-	-	-	-	-	-	-	-	-	-	-	-	0
11/5/2014	S140	Y	0.0044 I	-	-	-	-	-	0.0043 I	-	0.0038 I	-	-	-	3
	S190	N	-	-	-	-	-	-	-	-	-	-	-	0.039 I	1
	L3BRS	N	0.0078 I	-	-	0.012 I	0.015 I	-	0.035	-	0.0066 I	-	-	-	5
	S8	N	-	-	-	0.033 I	0.030 I	-	0.10	-	-	-	-	-	3
	G123	N	-	0.0026 I	0.0058 I	-	-	-	0.013	-	-	-	-	-	3
11/6/2014	S6	N	0.020	-	-	0.031 I	0.10	0.024 I	0.025	-	-	-	-	-	5
	S7	N	0.0030 I	-	-	0.052	0.18	-	0.061	-	-	-	0.034 I	-	5
	S5A	N	0.065	-	-	0.037 I	0.40	0.027 I	0.043	-	0.0039 I	0.088 I	-	-	7
	S9	N	-	-	-	-	-	-	0.016	-	-	-	-	-	1
	nber of compour detections	nd	12	1	1	9	10	5	20	3	7	1	1	1	71

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 ($\mu g/Kg$) detected above the method detection limit in sediment samples collected by SFWMD in November 2014.

Date	Location	Flow	aldrin	ametry n	chlordane	DDD-P,P'	DDE-P,P'	DDT-P,P'	dieldrin	endosulfan sulfate	methoxy chlor	PCB-1016	PCB-1254	Number of compounds detected at location
11/3/2014	S18C	Y	-	-	1	-	1.1	-	-	-	-	-	-	1
	S178	N	-	-	5.2	-	6.6	-	-	0.65 I	-	-	-	3
	S177	N	-	-	1.9 I	0.43	6.8	0.46 I	-	0.16 I	-	-	-	5
	S332DX	Y	-	-	-	0.11 I	2.0	-	-	-	-	-	-	2
	S331	Y	-	-	•	0.087 I	1.1	-	-	-	-	-	-	2
11/4/2014	S31	N	-	-	-	0.25 I	7	-	-	1	0.17 I	-	4.1 I	4
	S12A	N	-	-	i	-	0.24	-	-	-	-	-	-	1
	US41-25	N	-	-	-	-	0.21	-	-	1	-	-	-	1
11/5/2014	G123	N	-	-	-	-	0.21	-	-	ı	1	-	-	1
	S190	N	-	-	-	-	0.67 I	-	-	ı	1	-	-	1
	L3BRS	N	-	-	1.9 I	0.084 I	0.48	-	-	ı	1	12	-	4
	S8	N	-	-	1	0.22 I	3.1	-	-	ı	ı	-	-	2
11/6/2014	S9	N	-	-	1	-	0.073 I	-	-	ı	ı	-	-	1
	S7	N	-	-	1	-	0.85	-	-	ı	ı	-	-	1
	S6	N	0.54 I	11 I	19	4.9	46	0.90 I	0.83 I	-	-		280	8
	S5A	N	0.63 I*	14 I*	14 *	7.9 *	62 *	2.5 I*	-	ı	ı	-	-	6
	nber of comp letections	ound	2	2	5	8	16	3	1	2	1	1	2	43

N = no, Y = yes, R = reverse

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

^{- =} 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 4. Selected properties of pesticides detected during the November 2014 sampling event.

Common Name	Surface Water Standards F.A.C. 62-302 (µg/L)	Acute Oral LD ₅₀ For Rats (mg/Kg) (1)	Bioconcentration Factor (2)	Volatility from Water (2)		nservation CS) rating SA		K _{oc} (mL/g) (3, 4)	Soil Half-life (days) (3, 4)	Water Solubility (WS) (mg/L) (3, 4)	U.S. EPA Carcinogenic Potential (5)
2.4-D (acid)	(100)	375	13	I	M	S	M	20	10	890	D
2,4,5-T	-	500	30	I	L	S	M	80	24	220	D
2,4,5-TP	(10)	650	33	I	-	-	-	-	-	176	D
aldrin	3	38 - 67	3,348	S	-	-	-	48,500	-	0.05	B2
ametryn	-	1,110	33	I	M	M	M	300	60	185	D
atrazine	-	3,080	86	I	L	M	L	100	60	33	С
bentazon	-	1,100	19	I	L	S	M	34	20	500	С
chlordane	0.0043	365 - 590	3141	I	-	-	-	3,800	-	0.056	B2
DDD-P,P'	-	3,400	3,173	I	-	-	-	239,900	-	0.055	B2 ⁽⁸⁾
DDE-P,P'	-	880	2,887	S	-	-	-	243,220	-	0.065	B2 ⁽⁷⁾
DDT-P,P'	0.001	113	15,377	I	-	-	-	140,000	-	0.00335	B2 ⁽⁸⁾
dieldrin	0.0019	37 - 87	1,873	I	-	-	-	10,000 est.	-	0.14	B2
endosulfan sulfate	-	-	2,073	I	-	-	-	-	-	0.117	-
hexazinone	-	1,690	2	I	L	M	M	54	90	33,000	D
imidacloprid	-	424 ⁽⁶⁾	18	I	-	-	-	178 ⁽⁶⁾	520 ⁽⁶⁾	510 ⁽⁶⁾	Е
methoxy chlor	0.03	6,000	2265	S	XS	L	M	80,000	120	0.1	D
metolachlor	-	2,780	18	I	L	M	M	200	90	530	С
metribuzin	-	2,200	11	I	L	S	M	41	30	1,220	D
norflurazon	-	9,400	94	I	M	M	L	700	90	28	-
PCB's	0.014	-	-	-	-	-	-	-	-	-	B2

- = 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)
- (3) Goss and Wauchope (1992)
- (5) U.S. EPA (1996)
- (7) U.S. EPA (1999)

- (2) Lyman, et al. (1990)
- (4) Montgomery (1993)
- (6) U.S. EPA (1994a)
- (8) U.S. Department of Health (1994)

Table 5. Toxicity of pesticides detected during the November 2014 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

	Water Flea (Daphnia magna)			a)	Fathead Minnow # (Pimephales promelas)				Bluegill (Lepomis macrochirus)			Largemouth Bass (Micropterus salmoides)			Rainbow Trout [#] (Oncorthynchus mykiss)				Channel Catfish (Ictgalurus punctatus)					
Pesticide Common Name	48 hour l	EC ₅₀	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour I	.C ₅₀	Acute Toxicity	Chronic Toxicity	96 hour L	C ₅₀	Acute Toxicity	Chronic Toxicity	96 hour LC	e 0	cute	Chronic Toxicity	96 hour L	C ₅₀	Acute Toxicity	Chronic Toxicity	96 hour LO	C ₅₀	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	_		_	_
2,4-D	23,000	(3)	0,333	1,230	133,000	(3)	77,333	0,050	900 (48 hr)	(4)	-	-				_	110,000	(5)	36,667	5,500			_	_
2,4,5-T	-		-	-	-		-	-	10,400	(1)	3,467	520	-		-	-	17,200	(1)	5,733	860	19,400	(1)	6,467	970
2,4,5-TP	-		-	-	-		-	-	9,600	(2)	3,200	480	-		-	-	14,800	(2)	4,933	740	-			-
aldrin	-		-	-	28	(3)	9.3	1.4	13	(3)	4.3	0.7	1		-	-	17.7	(3)	5.9	0.9	i		-	-
ametryn	28,000	(5)	9,333	1,400	16,000	(7)	5,333	800	4.100	(2)	1.367	205			-	-	8,800	(2)	2,933	440				_
	-,	· · /		,	-,	.,	- /		,	. ,	,						3,600	(7)	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
bentazon	>100,000	(12)	33,333	5,000					>100,000	(12)	33,333	5,000			_	_	5,300 >100,000	(8)	1,767 33,333	265 5,000				
chlordane	>100,000	(12)	33,333	3,000	-		-	-	70	(3)	23	3,000	-		-	-	>100,000 90	(3)	30,333	5,000	-		-	-
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	4	1,500	(1)	500	75
DDE-P.P'	5,200	(+)	1,007	-	-,400	(1)	1,407	-	240	(1)	80	12	- (1	.,	-	2.1	32	(1)	11	2	1,500	(1)	-	-
DDT-P.P'	_			_	19	(3)	6	1	8	(3)	2.7	0.4	2 (3	8) (8	0.7	0.1	7	(3)	2	0.4	16	(3)	5.3	0.8
dieldrin	-		-	-	16	(3)	5.3	0.8	8	(3)	2.7	0.4	-	7	-	-	10	(3)	3.3	0.5	4.5	(3)	1.5	0.2
	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		(-)		
hexzinone	151,600	(10)	50,533	7,580	274,000	(10)	91,333	13,700	505,000	(10)	168,333	25,250	-		-	-	>320,000	(10)	>106,667	>16,000	-		-	-
imidacloprid	85,200	(11)	28,400	4,260	-		-	-	-		-	-	-		-	-	83,000	(11)	27,667	4,150	-		-	-
methoxy chlor	0.78	(13)	0.3	0.04	-		-	-	-		-	-	-		-	-	52	(13)	17	3	-		-	-
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
methouzin	4,200	(9)	1,400	210	-		_	_	75,900	(9)	25,300	3,795	-			-	76,770	(9)	25,590	3,839	100,000	(3)	55,555	3,000
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

^{- =} No data available

(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson and Finley (1980) (5) U.S. EPA (1991) (9) U.S. EPA (1998) (13) U.S. EPA (2004) (2) Hartley and Kidd (1987) (6) Mayer and Ellersieck (1986) (10) U.S. EPA (1994c) (11) U.S. EPA (1994a)

(4) Verschueren (1983) (8) U.S. EPA (2006) (11) U.S. EPA (1994a) (12) U.S. EPA (1994b)

^(*) 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.

Table 6. Atrazine Desethyl (DEA)/Atrazine ratio (DAR) data for November 2014 sampling event.

Date	Site	Flow*	at	razine	atrazine	desethyl	DAR
Date	Site	LIOW.	μg/L	moles/L	μg/L	moles/L	DAK
11/3/2014	S4	N	0.87	4.03E-09	0.044	2.35E-10	0.06
11/3/2014	S2	N	0.083	3.85E-10	0.022	1.17E-10	0.30
11/3/2014	S3	N	0.12	5.56E-10	0.036	1.92E-10	0.34
11/6/2014	S6	N	0.10	4.64E-10	0.024	1.28E-10	0.28
11/6/2014	S5A	N	0.40	1.85E-09	0.027	1.44E-10	0.08
				DAR	All sites	Flow only sites	No flow sites
				average	0.21	-	0.21
				median	0.28	-	0.28
				minimum	0.06	-	0.06
				maximum	0.34	-	0.34

^{*} 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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