PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

JANUARY 2014 SAMPLING EVENT



Richard J. Pfeuffer
South Florida Water Management District
MSC 4441
3301 Gun Club Road
West Palm Beach, FL 33406

Table of Contents

Summary	2
Background and Methods	
Results	
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 2014 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 2014.	10
Table 3. Summary of pesticides residues (µg/Kg) detected above the method detection limit in sediment samples collected by SFWMD in January 2014.	11
Table 4. Selected properties of pesticides detected during the January 2014 sampling event.	12
Table 5. Toxicity of pesticides detected during the January 2014 sampling event to freshwater aquatic invertebrates and fishes (µg/L).	
Table 6. Atrazine Desethyl (DEA)/Atrazine ratio (DAR) data for January 2014 sampling event	14
Glossary	15
References	16

Summarv

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water and sediment samples were collected January 27 to 30, 2014, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides 2,4-D, ametryn, atrazine, bentazon, diuron, metolachlor, metribuzin, and simazine 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 DDD, and DDE, along with two PCB compounds were found in the sediment at several locations. One DDE compound sediment concentration was 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 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 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 (EC₅₀) or lethal concentration 50 (LC₅₀) 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 27 to January 30, 2014.

Results

At least one pesticide was detected in surface water at 24 of the 26 sites (**Table 2**) and in sediment at 11 of the 16 sites (**Table 3**). After repeated attempts, a sediment sample was not obtained at S3. 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 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 (0.040 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.

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 0.010 to 0.015 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 at 14 micrograms per kilogram (μ g/Kg) (**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 and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μ g/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 μ g/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 13 of the 26 sampling locations, ranged from 0.010 to 0.61 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. 0.04) 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 broad-leaved 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 $0.065 \, \mu g/L$ at S7 (**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.

<u>DDD</u>, <u>DDE</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 $28~\mu g/Kg$ (**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. This 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 μ g/Kg and the PEC is 31 μ g/Kg for DDE in freshwater sediments. The concentration of DDE detected at S6 (**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.

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 LC₅₀ of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48-hour LC₅₀ of 1.4 mg/L for water fleas and a 96-hour LC₅₀ of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 μ g/L (Verschueren, 1983). The highest surface water concentration of diuron found during this sampling event was 0.0056 μ g/L at S140 (**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.

<u>Imidacloprid</u>: 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 $0.009~\mu g/L$ at S140 (**Table 2**) is below any level that would have an acute or chronic detrimental 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 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 highest surface water concentration found in this sampling event $(0.32 \mu g/L \text{ at S6})$ (**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 highest concentration of metribuzin detected was $0.094~\mu g/L$ 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.

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 and PCB-1260 is a commercial grade mixture containing 54 and 60, 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 should not impact 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 μ g/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 S140 (0.020 μ g/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, S331, TAMBR105, S8, S191, S5A, and S4. All of the collected samples were shipped and all bottles were received.

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

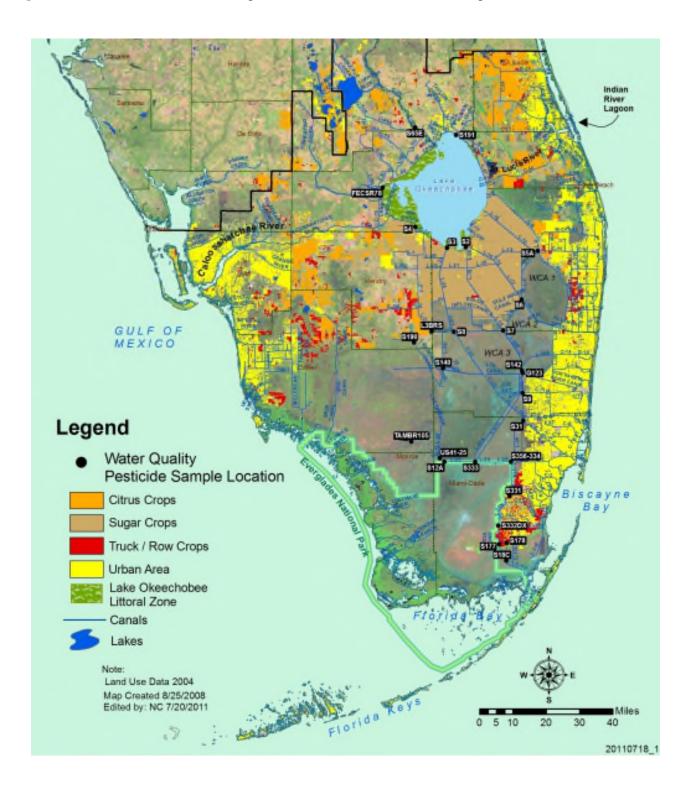


Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for January 2014 sampling event.

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	8.7 - 71	endrin aldehyde	0.0038 - 0.016	0.89 - 9.8
2,4,5-T	0.002 - 0.01	8.7 - 71	ethion	0.0095 - 0.04	2.2 - 24
2,4,5-TP (silvex)	0.002 - 0.01	8.7 - 71	ethoprop	0.0047 - 0.02	1.1 - 12
acifluorfen	0.002 - 0.01	8.7 - 71	fenamiphos	0.028 - 0.12	4.5 - 49
alachlor	0.057 - 0.24	16 - 180	fonofos	0.0095 - 0.04	1.1 - 12
aldrin	0.0019 - 0.008	0.45 - 4.9	heptachlor	0.0019 - 0.008	0.45 - 4.9
ametryn	0.0095 - 0.04	2.2 - 62	heptachlor epoxide	0.0019 - 0.008	0.45 - 4.9
atrazine	0.0095 - 0.04	2.2 - 24	hexazinone	0.028 - 0.12	6.7 - 73
atrazine desethyl	0.0095 - 0.04	N/A	imidacloprid	0.002 - 0.01	N/A
atrazine des is opropyl	0.0095 - 0.04	N/A	linuron	0.002 - 0.01	1.3 - 15
azinphos methyl (guthion)	0.019 - 0.08	6.7 - 73	malathion	0.0095 - 0.04	2.2 - 24
bentazon	0.002 - 0.01	N/A	metalaxyl	0.038 - 0.16	N/A
α-BHC (alpha)	0.0019 - 0.008	0.45 - 4.9	methamidophos	N/A	8.9 - 98
β-BHC (beta)	0.0019 - 0.008	0.45 - 4.9	methoxychlor	0.0095 - 0.04	3.1 - 34
δ-BHC (delta)	0.0019 - 0.008	0.45 - 4.9	metolachlor	0.057 - 0.24	13 - 150
γ-BHC (gamma) (lindane)	0.0019 - 0.008	0.45 - 4.9	metribuzin	0.019 - 0.08	4.5 - 49
bromacil	0.038 - 0.16	13 - 150	mevinphos	0.0095 - 0.04	2.2 - 24
butylate	0.019 - 0.08	N/A	mirex	0.0038 - 0.016	0.89 - 9.8
carbophenothion (trithion)	0.0057 - 0.024	1.3 - 15	monocrotophos	N/A	2.7 - 29
chlordane	0.019 - 0.08	4.5 - 120	naled	0.038 - 0.16	8.9 - 98
chlorothalonil	0.0076 - 0.032	1.3 - 15	norflurazon	0.028 - 0.12	6.7 - 73
chlorpyrifos ethyl	0.0095 - 0.04	2.2 - 24	parathion ethyl	0.019 - 0.08	2.2 - 24
chlorpyrifos methyl	0.0095 - 0.04	2.2 - 24	parathion methyl	0.0095 - 0.04	2.2 - 24
cypermethrin	0.011 - 0.048	2.2 - 24	PCB-1016	0.019 - 0.08	4.5 - 49
DDD-P,P'	0.0038 - 0.016	0.89 - 25	PCB-1221	0.019 - 0.08	8.9 - 98
DDE-P,P'	0.0038 - 0.016	0.89 - 49	PCB-1232	0.019 - 0.08	4.5 - 49
DDT-P,P'	0.0038 - 0.016	1.3 -38	PCB-1242	0.019 - 0.08	4.5 - 49
demeton	0.023 - 0.096	2.7 - 29	PCB-1248	0.019 - 0.08	4.5 - 49
diazinon	0.0095 - 0.04	2.2 - 24	PCB-1254	0.019 - 0.08	6.7 - 73
dicofol (kelthane)	0.023 - 0.096	5.4 - 83	PCB-1260	0.019 - 0.08	4.5 - 49
dieldrin	0.0019 - 0.008	0.45 - 4.9	permethrin	0.0094 - 0.04	2.2 - 24
disulfoton	0.0047 - 0.02	1.1 - 12	phorate	0.0047 - 0.02	1.1 - 22
diuron	0.002 - 0.01	1.3 - 15	prometon	0.019 - 0.08	N/A
α-endosulfan (alpha)	0.0019 - 0.016	0.45 - 4.9	prometryn	0.019 - 0.08	4.5 - 49
β-endosulfan (beta)	0.0019 - 0.016	0.45 - 4.9	simazine	0.0095 - 0.04	2.2 - 24
endosulfan sulfate	0.0038 - 0.016	0.89 - 9.8	toxaphene	0.095 - 0.4	27 - 290
endrin	0.0038 - 0.016	1.4 - 16	trifluralin	0.0076 - 0.032	1.8 - 20

 $N/A = not \ analyzed$

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

Date	Location	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	bentazon	diuron	imidacloprid	metolachlor	metribuzin	simazine	Number of compounds detected at location
1/27/2014	S18C	Y	-	-	-	-	0.0026 I	-	-	-	-	-	1
	S178	N	-	-	0.037 I	-	0.055	-	-	-	-	-	2
	S177	Y	-	-	-	-	0.0059 I *	-	-	-	-	-	1
	S331	Y	-	-	-	-	0.0070 I	-	-	-	-	-	1
	S332DX	N	-	-	-	-	0.0055 I	-	-	-	-	-	1
1/28/2014	S65E	N	0.015 *	-	0.021 I *	-	0.011 *	-	0.0078 I*	-	-	-	4
	S31	N	-	-	-	-	0.033	-	-	-	-	-	1
	S356-334	N	-	-	-	-	0.0058 I	-	-	-	-	-	1
	S333	N	-	-	-	-	-	-	-	1	-	-	0
	S12A	N	-	-	-	1	-	-	-	-	-	-	0
	US41-25	Y	-	-	0.013 I	-	-	-	-	-	-	-	1
	TAMBR105	Y	-	-	0.014 I	-	-	-	-	-	-	-	1
1/29/2014	S140	Y	0.0024 I	-	0.014 I	-	0.011	0.0056 I	0.009 I	-	-	0.020 I	6
	S190	N	0.0026 I	-	-	-	-	-	-	-	-	-	1
	L3BRS	N	0.0026 I	0.015 I	-	ı	0.033	-	-	-	-	-	3
	S8	N	-	-	0.065	-	0.039	-	-	-	-	-	2
	G123	N	-	-	-	-	0.027	-	-	-	-	-	1
1/30/2014	S6	Y	0.018	-	0.41	0.029 I	0.061	-	-	0.32	0.094	-	6
	S191	N	0.040	-	0.010 I	-	0.0029 I	-	-	-	-	-	3
	S5A	Y	0.023	-	0.61	0.033 I	0.031	0.0021 I	-	0.22 I	0.045 I	-	7
	S2	N	0.0041 I	0.011 I	0.15	0.012 I	0.0048 I	-	-	-	-	-	5
	S3	N	-	-	0.16	0.031 I	0.0050 I	-	-	-	-	-	3
	S7	N	0.0021 I	0.010 I	0.11	-	0.065	-	-	-	-	-	4
CEB OK	S4	N	0.0099 I	-	0.17	0.025 I	0.0055 I	-	-	-	-	-	4
	FECSR78	N	-	-	0.031 I	1	0.0032 I	-	-	-	-	-	2
	S9	Y	-	-	-	1	0.056	-	-	-	-	-	1
Total number	Γotal number of compound detections			3	14	5	21	2	2	2	2	1	62

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 2014.

Date	Location	Flow	ametryn	DDD-P,P'	DDE-P,P'	PCB-1254	PCB-1260	Number of compounds detected at location
1/27/2014	S178	N	-	-	13	-	-	1
	S177	N	-	-	4.1 I	-	-	1
1/28/2014	S31	N	-	-	3.3 I	-	-	1
1/29/2014	S140	Y	-	-	-	46	-	1
	S8	N	-	-	2.8 I	-	-	1
1/30/2004	S9	Y	-	-	8 *	-	34 *	2
	S2	N	-	-	6.2 I	-	-	1
	S7	N	-	-	4.4 I	-	-	1
	S6	Y	14 I	28	170	-	-	3
	S4	N	-	6 I*	30 *	-	-	2
	S5A	Y	-	1.3 I	7.5	38	-	3
Total number	Total number of compound detections			3	10	2	1	17

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 January 2014 sampling event.

Common Name	Surface Water Standards F.A.C. 62-302	Acute Oral LD ₅₀ For Rats (mg/Kg) (1)	Bioconcentration Factor (2)	Volatility from Water (2)	(S	onservation CS) rating	(3)	K _{oc} (mL/g) (3, 4)	Soil Half-life (days) (3,	Water Solubility (WS) (mg/L) (3, 4)	U.S. EPA Carcinogenic Potential (5)
	(μg/L)	(. ,	LE	SA	SS		4)	(8) ())	. ,
2,4-D (acid)	(100)	375	13	I	M	S	M	20	10	890	D
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
diuron	-	3,400	75	I	M	M	L	480	90	42	D
DDD-p,p'	-	3,400	3,173	I	-	-	-	239,900	-	0.055	-
DDE-p,p'	-	880	2,887	S	-	-	-	243,220	-	0.065	B2 ⁽⁷⁾
imidacloprid	-	424 ⁽⁶⁾	18	I	-	-	-	178 ⁽⁶⁾	520 ⁽⁶⁾	510 ⁽⁶⁾	Е
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
PCB's	0.014	-	-	-	-	-	-	-	-	-	B2
simazine	-	>5,000	221	I	L	M	M	130	60	6.2	С

- = 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)

(5) U.S. EPA (1996)

(2) Lyman, et al. (1990)

(6) U.S. EPA (1994a)

(3) Goss and Wauchope (1992)

(7) U.S. EPA (1999)

(4) Montgomery (1993)

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

Common Name	48 hour I Water fi Daphnia m	lea	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour I Fathead M (#) Pimep promel	innow hales	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour L Bluegill <i>Lep</i> macrochia	omis	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour LC ₅₀ Largemouth Bass Micropterus salmoides	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour LC ₅₀ Rainbow Trout (# Oncorhynchus mykiss	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour 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	-		-	-	4,100	(2)	1,367	205	-	-	-	8,800 (2		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
	ı		1	-	-		-	-	-		-	-	-	-	-	5,300 (8	1,767	265	-	-	-
bentazon	>100,000	(12)	33,333	5,000	-		-	-	>100,000	(12)	33,333	5,000	-	-	-	>100,000 (12) 33,333	5,000	-	-	-
diuron	1,400	(5)	467	70	14,200	(5)	4733	710	5,900	(2)	1967	295	-	-	-	5,600 (2	1867	280	-	-	
	1,400	(10)	467	70	14,000	(10)	4667	700	-		-	-	-	-	-	-	-	-	-	-	-
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	-	-	-
imidacloprid	85,200	(11)	28,400	4,260	-		-	-	-		-	-	-	-	-	83,000 (1)	27,667	4,150	-	-	-
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	(9)	1,400	210	-		-	-	75,900	(9)	25,300	3,795	-	-	-	76,770 (9	25,590	3,839	-	-	-
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	-	-	-

^{- =} No data available

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

(1) Johnson and Finley (1980)

(6) Mayer and Ellersieck (1986)

(11) U.S. EPA (1994a) (12) U.S. EPA (1994b)

(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 (1998)

(5) U.S. EPA (1991)

(10) U.S. EPA (2003b)

^(*) 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 January 2014 sampling event.

Date	Site	Flow*	at	razine	atrazine	desethyl	DAR
Date	Sile	Now	μg/L	moles/L	μg/L	moles/L	DAK
1/30/2014	S 6	Y	0.41	1.90E-09	0.029	1.55E-10	0.08
1/30/2014	S5A	Y	0.61	2.83E-09	0.033	1.76E-10	0.06
1/30/2014	S2	N	0.15	6.95E-10	0.012	6.40E-11	0.09
1/30/2014	S 3	N	0.16	7.42E-10	0.031	1.65E-10	0.22
1/30/2014	S4	N	0.17	7.88E-10	0.025	1.33E-10	0.17
				DAR	All sites	Flow only sites	No flow sites
				average	0.13	0.07	0.16
				median	0.09	0.07	0.17
				minimum	0.06	0.06	0.09
				maximum	0.22	0.08	0.22

^{*} 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.

References

Adams, C.D. and E.M. Thurman. 1991. Formation and Transport of Deethylatrazine in the Soil and Vadose Zone. Journal Environmental Quality, 20: 540-547.

Callahan, M.A., M.W. Slimak, N.W. Gabel, I.P. May, C.F. Fowler, J.R. Freed, P. Jennings, R.L. Durfee, F.C. Witmore, B. Maestri, W.R. Mabey, B.R. Holt, and C. Gould. (1979). *Water-Related Environmental Fate of 129 Priority Pollutants, Volume I.* USEPA 440/4-79-029a.

Goolsby, D.A., E.M. Thurman, M.L. Pomes, M.T. Meyer, and W.A. Battaglin. 1997. *Herbicides and Their Metabolites in Rainfall: Origin, Transport, and Deposition Patterns across the Midwestern and Northeastern United States, 1990-1991*. Environmental Science Technology, 31(5): 1325-1333.

Goss, D. and R. Wauchope. (Eds.) 1992. *The SCS/ARS/CES Pesticide Properties Database: II Using It With Soils Data In A Screening Procedure*. Soil Conservation Service. Fort Worth, TX.

Hartley, D. and H. Kidd. (Eds.) 1987. *The Agrochemicals Handbook*. Second Edition, The Royal Society of Chemistry. Nottingham, England.

Johnson, W.W. and M.T. Finley. 1980. *Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates*. U.S. Department of the Interior, Fish and Wildlife Service Resource Publication 137. Washington, DC.

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. 1990. *Handbook of Chemical Property Estimation Methods*. American Chemical Society, Washington, DC.

MacDonald Environmental Sciences, Ltd. and United States Geological Survey. 2003. Development and Evaluation of Numerical Sediment Quality Assessment Guidelines for Florida Inland Waters. Report to Florida Department of Environmental Protection. Tallahassee, FL.

Mayer, F.L. and M.R. Ellersieck. 1986. *Manual of Acute Toxicity: Interpretation and Database for 410 Chemicals and 66 Species of Freshwater Animals*. United States Fish and Wildlife Service Publication No. 160.

Montgomery, J.H. 1993. Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsea, MI.

Thurman, E.M., D.A. Goolsby, M.T. Meyer, M.S. Mills, M.L. Pomes, and D.W. Kolpin. 1992. A Reconnaissance Study of Herbicides and Their Metabolites in Surface Water of the Midwestern United States Using Immunoassay and Gas Chromatography/Mass Spectrometry. Environmental Science Technology, 26(12): 2440-2447.

United States Environmental Protection Agency. 1984. Chemical Fact Sheet for Simazine. March, 1984. 1991. Pesticide Ecological Effects Database. Ecological Effects Branch, Office of Pesticide Programs, Washington, DC. _____ 1994a. Pesticide Fact Sheet: Imidacloprid 1994b. Reregistration Eligibility Decision (RED) Bentazon. EPA 738-R-94-029 September 1994. _ 1996. Drinking Water Regulations and Health Advisories. Office of Water. EPA 822-B-96-002. ___ 1998. Reregistration Eligibility Decision (RED) Metribuzin, EPA 738-R-37-006 February 1998. 1999 Integrated Risk Information System (IRIS) on p,p-Dichlorodiphenyldichloroethylene. National Center for Environmental Assessment. Office of Research and Development. Washington, DC. 2003a. Ambient Aquatic Life Water Criteria for Atrazine. Revised Draft EPA-822-R-03-023. October 2003. 2003b. Reregistration Eligibility Decision (RED) for Diuron, September 30, 2005. 2005. Reregistration Eligibility Decision (RED) for Ametryn; EPA 738-R-05-006 September 2005. 2006. Decisions Document for Atrazine.

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