PESTICIDE SURFACE WATER QUALITY REPORT

OCTOBER 2012 SAMPLING EVENT

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Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered surface water grab samples were collected October 22 to October 25, 2012, and analyzed for over 70 pesticides and/or products of their degradation.

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

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

Background and Methods

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

Seventy-one pesticides and degradation products were analyzed in samples from 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). This summary covers surface water samples collected from October 22 to October 25, 2012.

Results

At least one pesticide was detected in surface water at 12 of the 26 sites. 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. 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

2,4-D: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in **Tables 3 and 4** indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The highest 2,4-D residue was detected at S9 (0.40 micrograms per liter [µg/L]) (**Table 2**). Using these criteria, this observed level should not have an acute or chronic effect on fish or aquatic invertebrates.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations greater than (>) 10 µg/L (Verschueren, 1983). Environmental fate and toxicity data in **Tables 3 and 4** indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate

significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.023 to 0.079 µg/L (**Table 2**). Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf, lawn grasses, and non-crop areas. Environmental fate and toxicity data in **Tables 3 and 4** indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch, and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 µg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 µg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003a). The atrazine surface water concentrations found in this sampling event at 8 of the 26 sampling locations, ranged from 0.029 to 0.38 µg/L (**Table 2**). Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR, 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. 0.05) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (**Table 5**). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

Diuron: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in **Tables 3 and 4** indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 25 mg/L for guppies (Hartley

and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48-hour LC_{50} of 1.4 mg/L for water fleas and a 96-hour LC_{50} of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 µg/L (Verschueren, 1983). The only surface water concentration of diuron found during this sampling event was 0.48 µg/L at S9 (**Table 2**). Using these criteria, this concentration should not have an acute, harmful impact on fish, aquatic invertebrates, or algae.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in **Tables 3 and 4** indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/L for *Daphnia magna* (U.S. EPA, 1988). The highest surface water concentration detected in this sampling event of 0.69 µg/L at S140 (**Table 2**) should not have an acute impact on fish or aquatic invertebrates.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in **Tables 3 and 4** indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC50 for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The only norflurazon surface water concentration detected (0.049 µg/L at S4) (**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.

Quality Assurance Evaluation

No pesticide analytes were detected in the field blanks performed at S177, S3, S31, S8, and S7. All of the 26 collected samples were shipped and all bottles were received.

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

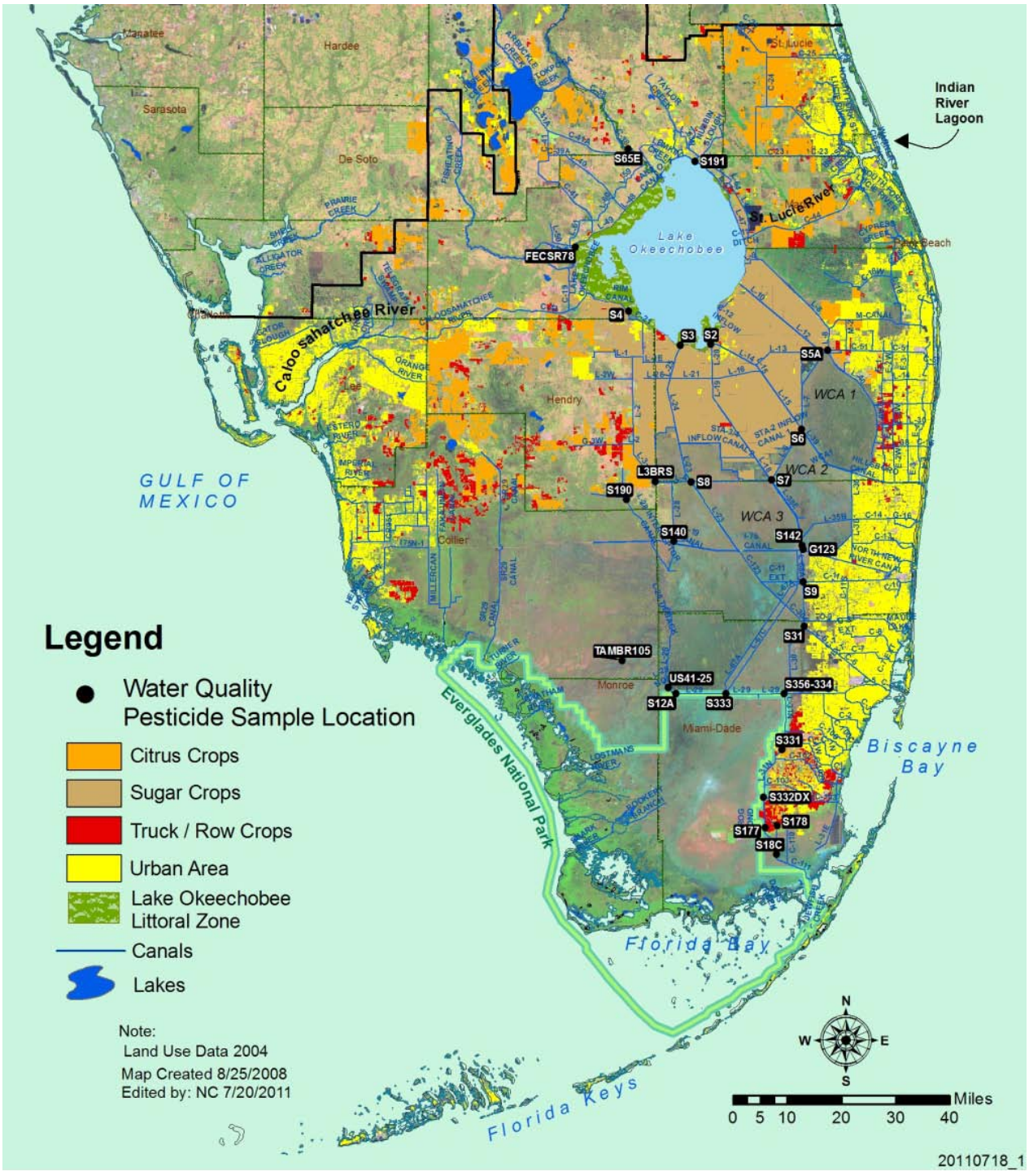

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for October 2012 sampling event.

Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)
2,4-D	0.2 - 0.62	endrin aldehyde	0.0037 - 0.016
2,4,5-T	0.2 - 0.62	ethion	0.0093 - 0.04
2,4,5-TP (silvex)	0.2 - 0.62	ethoprop	0.0047 - 0.02
acifluorfen	0.2 - 0.62	fenamiphos	0.028 - 0.12
alachlor	0.056 - 0.24	fonofos	0.0093 - 0.04
aldrin	0.0019 - 0.0081	heptachlor	0.0019 - 0.076
ametryn	0.0093 - 0.04	heptachlor epoxide	0.0019 - 0.0081
atrazine	0.0093 - 0.04	hexazinone	0.028 - 0.12
atrazine desethyl	0.0093 - 0.084	imidacloprid	0.21 - 0.68
atrazine desisopropyl	0.0093 - 0.04	linuron	0.21 - 0.68
azinphos methyl (guthion)	0.019 - 0.081	malathion	0.0093 - 0.04
α-BHC (alpha)	0.0019 - 0.0081	metalaxyl	0.037 - 0.16
β-BHC (beta)	0.0019 - 0.0081	methoxychlor	0.0093 - 0.04
δ-BHC (delta)	0.0019 - 0.0081	metolachlor	0.056 - 0.48
γ-BHC (gamma) (lindane)	0.0019 - 0.0081	metribuzin	0.019 - 0.081
bromacil	0.037 - 0.16	mevinphos	0.0093 - 0.04
butylate	0.019 - 0.081	mirex	0.0037 - 0.016
carbophenothion (trithion)	0.0056 - 0.024	naled	0.037 - 0.16
chlordane	0.019 - 0.081	norflurazon	0.028 - 0.12
chlorothalonil	0.0074 - 0.032	parathion ethyl	0.019 - 0.081
chlorpyrifos ethyl	0.0093 - 0.04	parathion methyl	0.0093 - 0.04
chlorpyrifos methyl	0.0093 - 0.04	PCB-1016	0.019 - 0.081
cypermethrin	0.011 - 0.048	PCB-1221	0.019 - 0.081
DDD-P,P’	0.0037 - 0.016	PCB-1232	0.019 - 0.081
DDE-P,P’	0.0037 - 0.016	PCB-1242	0.019 - 0.081
DDT-P,P’	0.0037 - 0.016	PCB-1248	0.019 - 0.081
demeton	0.022 - 0.097	PCB-1254	0.019 - 0.081
diazinon	0.0093 - 0.04	PCB-1260	0.019 - 0.081
dicofol (kelthane)	0.022 - 0.097	permethrin	0.0093 - 0.04
dieldrin	0.0019 - 0.0081	phorate	0.0047 - 0.02
disulfoton	0.0047 - 0.02	prometryn	0.019 - 0.081
diuron	0.21 - 0.68	prometon	0.019 - 0.081
α-endosulfan (alpha)	0.0019 - 0.016	simazine	0.0093 - 0.04
β-endosulfan (beta)	0.0019 - 0.021	toxaphene	0.093 - 0.4
endosulfan sulfate	0.0037 - 0.016	trifluralin	0.0074 - 0.032
endrin	0.0037 - 0.016		

Table 2. Summary of pesticide residues (µg/L) detected above the method detection limit in surface water samples collected by SFWMD in October 2012.

Date	Site	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	diuron	hexazinone	norflurazon	Number of compounds detected at site
10/22/2012	S18C	Y	-	-	-	-	-	-	-	0
	S178	N	-	-	-	-	-	-	-	0
	S177	Y	-	-	-	-	-	-	-	0
	S331	N	-	-	-	-	-	-	-	0
	S332DX	Y	-	-	-	-	-	-	-	0
	S4	N	-	-	-	-	-	0.033 I	0.049 I	2
	S2	N	-	0.079	0.21	-	-	-	-	2
	S3	N	0.23 I	0.064	0.37	0.013 I	-	-	-	4
	S65E	Y	-	-	-	-	-	0.031 I*	-	1
	S191	N	0.26 I	-	0.033 I	-	-	-	-	2
	FECSR78	Y	-	-	-	-	-	0.065 I	-	1
10/23/2012	S31	Y	-	-	0.015 I	-	-	-	-	1
	S356-334	N	-	-	-	-	-	-	-	0
	S333	N	-	-	-	-	-	-	-	0
	S12A	Y	-	-	-	-	-	-	-	0
	US41-25	Y	-	-	-	-	-	-	-	0
	TAMBR105	Y	-	-	-	-	-	-	-	0
10/24/2012	G123	N	-	-	-	-	-	-	-	0
	S140	Y	-	-	-	-	-	0.69	-	1
	S190	N	-	-	-	-	-	-	-	0
	L3BRS	N	-	-	-	-	-	-	-	0
	S8	N	-	-	-	-	-	-	-	0
10/25/2012	S6	Y	-	0.040	0.029 I	-	-	-	-	2
	S5A	Y	-	0.065	0.38	0.016 I	-	-	-	3
	S7	Y	-	0.023 I	0.036 I	-	-	-	-	2
	S9	Y	0.40 I	-	0.13	-	0.48 I	-	-	3
Total number of compound detections			3	5	8	2	1	4	1	24

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

Table 3. Selected properties of pesticides detected during the October 2012 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)	Soil Conservation Service (SCS) rating (3)			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)
					LE	SA	SS				
2,4-D	(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	C
diuron	-	3,400	75	I	M	M	L	480	90	42	D
hexazinone	-	1,690	2	I	L	M	M	54	90	33,000	D
norflurazon	-	9,400	94	I	M	M	L	700	90	28	C

- = No data available
FDEP F.A.C. 62-302 surface water standards (4/2008) for Class III waters except Class I noted in ( )
Bioconcentration Factor (BCF) calculated as BCF = $10^{\wedge(2.71 - 0.564 \log WS)}$ (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)

Table 4. Toxicity of pesticides detected during the October 2012 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

Common Name	48 hour EC_{50} Water flea *Daphnia magna*	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour LC_{50} Fathead Minnow (#) *Pimephales promelas*	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour LC_{50} Bluegill *Lepomis macrochirus*	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*
2,4-D	25,000 (3)	8,333	1,250	133,000 (3)	44,333	6,650	180,000 (9)	60,000	9,000	-	-	-	100,000 (1)	33,333	5,000	-
	-	-	-	-	-	-	900 (48 hour) (2)	300	45	-	-	-	110,000 (3)	36,667	5,500	-
ametryn	28,000 (3)	9,333	1,400	16,000 (4)	5,333	800	4,100 (1)	1,367	205	-	-	-	8,800 (1)	2,933	440	-
	-	-	-	-	-	-	-	-	-	-	-	-	3,600 (4)	1,200	180	-
atrazine	6,900 (3)	2,300	345	15,000 (3)	5,000	750	16,000 (1)	5,333	800	-	-	-	8,800 (1)	2,933	440	7,600 (1)
	-	-	-	-	-	-	-	-	-	-	-	-	5,300 (5)	1,767	265	-
diuron	1,400 (3)	467	70	14,200 (3)	4,733	710	5,900 (1)	1,967	295	-	-	-	5,600 (1)	1,867	280	-
	1,400 (8)	467	70	14,000 (8)	4,667	700	-	-	-	-	-	-	-	-	-	-
hexazinone	151,600 (3)	50,533	7,580	274,000 (1)	91,333	13,700	100,000 (3)	33,333	5,000	-	-	-	180,000 (3)	60,000	9,000	-
	151,600 (6)	50,533	7,580	274,000 (6)	91,333	13,700	505,000 (6)	168,333	25,250	-	-	-	>320,000 (6)	>106,667	>16,000	-
norflurazon	15,000 (3)	5,000	750	-	-	-	16,300 (3)	5,433	815	-	-	-	8,100 (3)	2,700	405	>200,000 (1)
	>15000 (7)	>5,000	>750	-	-	-	16,300 (7)	5,433	815	-	-	-	8,100 (7)	2,700	405	-

- = 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 LC_{50} is the lowest value which has been determined for a species significant to the indigenous aquatic community.

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

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

Table 5. Atrazine Desethyl (DEA)/Atrazine ratio (DAR) data for October 2012 sampling event.

Date	Site	Flow*	atrazine		atrazine desethyl		DAR
			µg/L	moles/L	µg/L	moles/L	
10/22/2012	S3	N	0.37	1.72E-09	0.013	6.93E-11	0.04
10/25/2012	S5A	Y	0.38	1.76E-09	0.016	8.53E-11	0.05

DAR	All sites	Flow only sites	No flow sites
average	0.04	0.05	0.04
median	0.04	0.05	0.04
minimum	0.04	0.05	0.04
maximum	0.05	0.05	0.04

* 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.

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

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

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

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

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

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

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

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

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