PESTICIDE SURFACE WATER QUALITY REPORT

JULY 2011 SAMPLING EVENT

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Pesticide Monitoring Project Report
July 2011 Sampling Event

Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water samples from 25 of the 27 network sites were collected July 11 to July 14, 2011, and analyzed for over 70 pesticides and/or products of their degradation.

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

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

Background and Methods

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

Seventy-one pesticides and degradation products were analyzed in samples from 25 of the 27 network sites (Figure 1). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp.

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

Results

In the surface water samples collected from July 11 to July 14, 2011, at least one pesticide was detected in surface water at 20 of the 25 sites. Modifications to the non-ECP permit changed the requirement for sampling at S142 to only during discharge or flow events. For this sampling event, no sample was obtained due to no discharge at the time of sample collection. Additionally, no sample was collected at US41-25 due to excessive aquatic vegetation which prevented representative sample collection. The concentrations of the pesticides detected at each of the sites are summarized for the surface water in Table 2. All of these compounds have previously been detected in this monitoring program. No harmful impacts are expected from the detected pesticides.

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

Usage and Water Quality Impacts

<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 3 and 4 indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The highest 2,4-D concentration was detected at S5A (0.59 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.

<u>Ametryn</u>: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 μg/L (Verschueren, 1983). Environmental fate and toxicity data in Tables 3 and 4 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.013 to 0.062 μg/L (Table 2). Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

<u>Atrazine</u>: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant

concentration (MATC) of atrazine was 90 and 210 μg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 μg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003). The atrazine surface water concentrations found in this sampling event at 18 of the 25 sampling locations, ranged from 0.013 to 0.31 μg/L (Table 2). Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of groundwater discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1) 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.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC_{50} of 145 mg/L for *Daphnia magna* (U.S. EPA, 1988). The highest surface water concentration detected in this sampling event at FECSR78 (0.14 μg/L) (Table 2) should not have an acute impact on fish or aquatic invertebrates.

Metolachlor: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in Tables 3 and 4 indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The only surface water concentration found in this sampling event (0.13 μg/L 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.

Metribuzin: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in Tables 3 and 4 indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The highest concentration of metribuzin detected was 0.072 µg/L (S8). Using these criteria, this surface water concentration should not have an acute impact on fish or aquatic invertebrates.

Quality Assurance Evaluation

Replicate samples were collected at sites S2 and S331. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No pesticide analytes were detected in the field blanks performed at S177, S191, S31, S8, and S7. All collected samples were shipped and all bottles were received.

Glossary

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

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

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

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

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

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

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

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

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

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

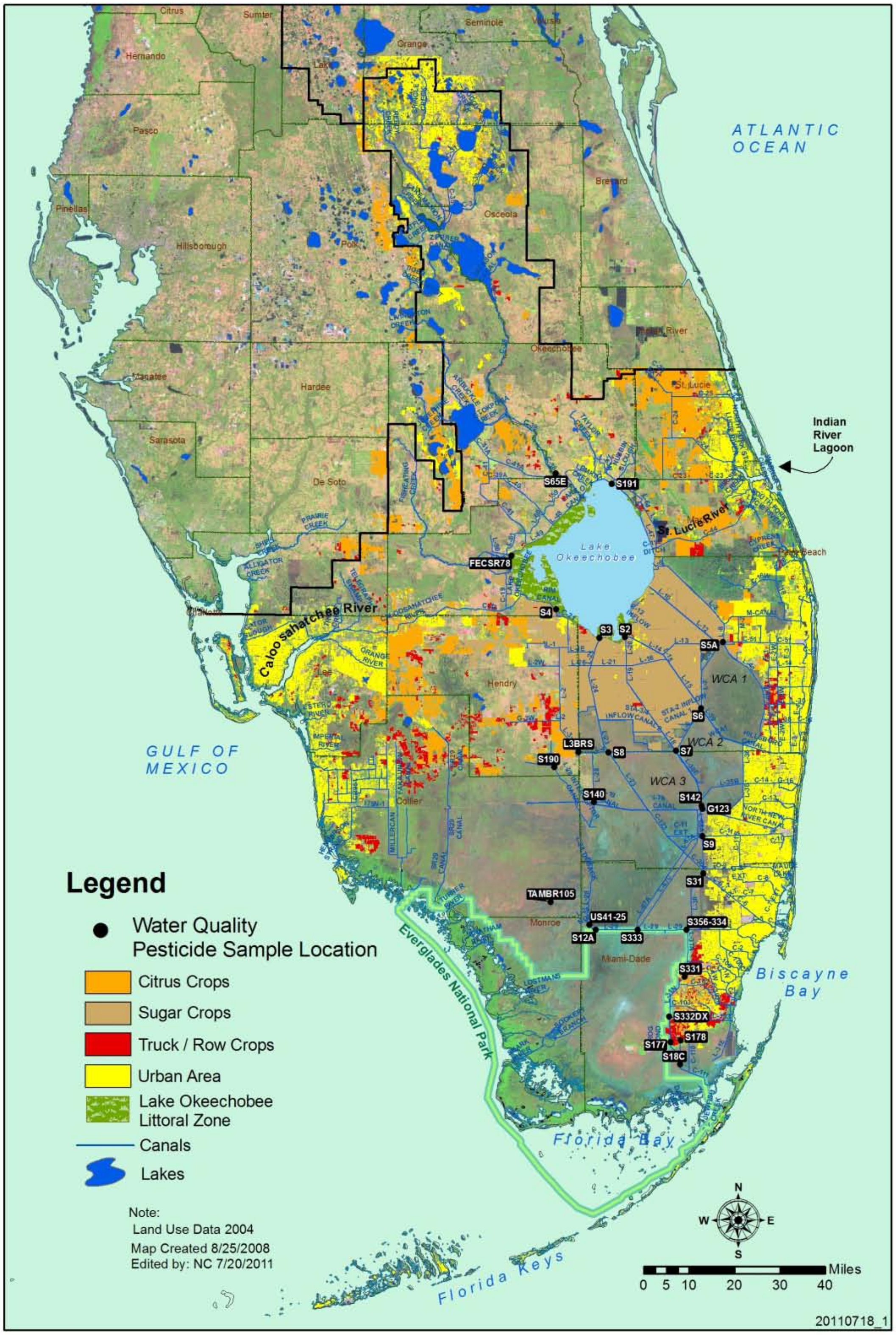

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for July 2011 sampling event.

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	0.0042 - 0.016
2,4,5-T	0.2 - 0.62	ethion	0.0095 - 0.04
2,4,5-TP (silvex)	0.2 - 0.62	ethoprop	0.0095 - 0.04
acifluorfen	0.2 - 0.62	fenamiphos (nemacur)	0.038 - 0.16
alachlor	0.057 - 0.24	fonofos (dyfonate)	0.0095 - 0.04
aldrin	0.0019 - 0.008	heptachlor	0.0023 - 0.0096
ametryn	0.0095 - 0.04	heptachlor epoxide	0.0019 - 0.008
atrazine	0.0095 - 0.04	hexazinone	0.019 - 0.08
atrazine desethyl	0.0095 - 0.04	imidacloprid	0.21 - 0.71
atrazine desisopropyl	0.0095 - 0.044	linuron	0.21 - 0.71
azinphos methyl (guthion)	0.028 - 0.12	malathion	0.028 - 0.12
α-BHC (alpha)	0.0021 - 0.0088	metalaxyl	0.047 - 0.2
β-BHC (beta)	0.0032 - 0.014	methoxychlor	0.0095 - 0.04
δ-BHC (delta)	0.0019 - 0.008	metolachlor	0.057 - 0.24
γ-BHC (gamma) (lindane)	0.0019 - 0.008	metribuzin	0.019 - 0.08
bromacil	0.047 - 0.2	mevinphos	0.057 - 0.24
butylate	0.019 - 0.08	mirex	0.011 - 0.048
carbophenothion (trithion)	0.015 - 0.064	naled	0.076 - 0.32
chlordane	0.019 - 0.08	norflurazon	0.019 - 0.08
chlorothalonil	0.015 - 0.064	parathion ethyl	0.019 - 0.08
chlorpyrifos ethyl	0.0095 - 0.04	parathion methyl	0.019 - 0.08
chlorpyrifos methyl	0.019 - 0.08	PCB-1016	0.019 - 0.08
cypermethrin	0.019 - 0.08	PCB-1221	0.019 - 0.08
DDD-P,P'	0.0046 - 0.019	PCB-1232	0.019 - 0.08
DDE-P,P'	0.0038 - 0.016	PCB-1242	0.019 - 0.08
DDT-P,P'	0.0057 - 0.024	PCB-1248	0.019 - 0.08
demeton	0.028 - 0.12	PCB-1254	0.019 - 0.08
diazinon	0.019 - 0.08	PCB-1260	0.019 - 0.08
dicofol (kelthane)	0.042 - 0.18	permethrin	0.015 - 0.064
dieldrin	0.0019 - 0.008	phorate	0.0095 - 0.04
disulfoton	0.019 - 0.08	prometryn	0.019 - 0.08
diuron	0.21 - 0.71	prometon	0.019 - 0.08
α-endosulfan (alpha)	0.0038 - 0.016	simazine	0.0095 - 0.04
β-endosulfan (beta)	0.0038 - 0.016	toxaphene	0.095 - 0.4
endosulfan sulfate	0.0046 - 0.019	trifluralin	0.0076 - 0.032
endrin	0.0095 - 0.04		

Table 2. Summary of pesticide residues (µg/L) detected above the method detection limit in surface water samples collected by SFWMD in July 2011.

Date	Location	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	hexazinone	metolachlor	metribuzin	Number of compounds detected at location
7/11/2011	FECSR78	Y	-	-	-	-	0.14	-	-	1
	S177	N	-	-	0.055	-	-	-	-	1
	S178	N	-	-	-	-	-	-	-	0
	S18C	N	-	-	0.061	-	-	-	-	1
	S191	N	-	-	0.018 I	-	0.13	-	-	2
	S2	N	0.28 I *	0.047 *	0.24 *	0.033 I *	-	-	0.030 I *	5
	S3	N	0.22 I	0.043	0.31	0.058	-	-	-	4
	S331	N	-	-	0.053 *	-	-	-	-	1
	S332DX	N	-	-	0.051	-	-	-	-	1
	S4	N	-	0.062	0.094	0.011 I	0.024 I	-	-	4
	S65E	Y	-	-	0.042	-	-	-	-	1
7/12/2011	S12A	N	-	-	-	-	0.11	-	-	1
	S31	N	-	0.013 I	0.041	-	-	-	-	2
	S333	Y	-	-	-	-	-	-	-	0
	S356-334	N	-	-	0.021 I	-	-	-	-	1
	TAMBR105	N	-	-	-	-	-	-	-	0
7/13/2011	G123	N	-	-	-	-	-	-	-	0
	L3BRS	N	-	-	0.12	0.034 I	-	-	-	2
	S140	Y	-	-	-	-	-	-	-	0
	S190	Y	-	-	0.15	0.027 I	-	-	-	2
	S8	Y	-	0.020 I	0.16	0.029 I	-	-	0.072 I	4
	S9	Y	-	-	0.013 I	-	-	-	-	1
7/14/2011	S5A	Y	0.59 I	0.042	0.16	-	-	-	0.027 I	4
	S6	Y	0.47 I	0.049	0.24	0.023 I	-	0.13 I	-	5
	S7	Y	-	0.040	0.10	0.024 I	-	-	0.032 I	4
Total number of compound detections			4	8	18	8	4	1	4	47

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

Table 3. Selected properties of pesticides detected during the July 2011 sampling event.

Common Name	Surface Water Standards F.A.C. 62-302 (µg/L)	Acute Oral LD_{50} For Rats (mg/Kg) (1)	U.S. EPA Carcinogenic Potential	Water Solubility (WS) (mg/L) (2, 3)	K_{oc} (mL/g) (2, 3)	Soil Half-life (days) (2, 3)	Soil Conservation Service (SCS) rating (2)			Volatility from Water	Bioconcentration Factor
							LE	SA	SS		
2,4-D (acid)	(100)	375	D	890	20	10	M	S	M	I	13
ametryn	-	1,110	D	185	300	60	M	M	M	I	33
atrazine	-	3,080	C	33	100	60	L	M	L	I	86
hexazinone	-	1,690	D	33,000	54	90	L	M	M	I	2
metolachlor	-	2,780	C	530	200	90	L	M	M	I	18
metribuzin	-	2,200	D	1,220	41	30	L	S	M	I	11

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

Bioconcentration Factor (BCF) calculated as BCF = $10^{\wedge(2.791 - 0.564 \log WS)}$ (4)
B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)
FDEP F.A.C. 62-302 surface water standards (4/2008) for Class III waters except Class I in ( )

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

Table 4. Toxicity of pesticides detected during the July 2011 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

Common Name	48 hr EC_{50} Water flea *Daphnia magna*	Acute Toxicity (*)	Chronic Toxicity (*)	96 hr LC_{50} Fathead Minnow (#) *Pimephales promelas*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Bluegill *Lepomis macrochirus*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Largemouth Bass *Micropterus salmoides*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Rainbow Trout (#) *Oncorhynchus mykiss*	Acute Toxicity	Chronic Toxicity	96 hr LC_{50} Channel Catfish *Ictalurus punctatus*	Acute Toxicity	Chronic Toxicity
2,4-D	25,000 (4)	8,333	1,250	133,000 (4)	44,333	6,650	180,000 (5)	60,000	9,000	-	-	-	100,000 (1)	33,333	5,000	-	-	-
	-	-	-	-	-	-	900 (48 hr) (3)	-	-	-	-	-	110,000 (4)	36,667	5,500	-	-	-
ametryn	28,000 (4)	9,333	1,400	16,000 (6)	5,333	800	4,100 (1)	1,367	205	-	-	-	8,800 (1)	2,933	440	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	3,600 (6)	1,200	180	-	-	-
atrazine	6900 (4)	2,300	345	15,000 (4)	5,000	750	16,000 (1)	5,333	800	-	-	-	8,800 (1)	2,933	440	7,600 (1)	2,533	380
	-	-	-	-	-	-	-	-	-	-	-	-	5,300 (7)	1,767	265	-	-	-
hexazinone	151,600 (4)	50,533	7,580	274,000 (1)	91,333	13,700	100,000 (4)	33,333	5,000	-	-	-	180,000 (4)	60,000	9,000	-	-	-
	151,600 (8)	50,533	7,580	274,000 (8)	91,333	13,700	505,000 (8)	168,333	25,250	-	-	-	>320,000 (8)	>106,667	-	-	-	-
metolachlor	23,500 (4)	7,833	1,175	-	-	-	15,000 (1)	5,000	750	-	-	-	2,000 (1)	667	100	4,900 (2)	1,633	245
metribuzin	4,200 (4)	1,400	210	-	-	-	80,000 (1)	26,667	4,000	-	-	-	64,000 (1)	21,333	3,200	100,000 (4)	33,333	5,000
	4,200 (9)	1,400	210	-	-	-	75,900 (9)	25,300	3,795	-	-	-	76,770 (9)	25,590	3,839	-	-	-

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

Table 5. Atrazine Desethyl/Atrazine ratio (DAR) data for July 2011 sampling event.

Date	Location	Flow*	atrazine		atrazine desethyl		DAR
			µg/L	moles/L	µg/L	moles/L	
7/11/2011	S2	N	0.24	1.09743E-09	0.033	2.13184E-10	0.2
	S3	N	0.31	1.43728E-09	0.058	3.09117E-10	0.2
	S4	N	0.094	4.35821E-10	0.011	5.86256E-11	0.1
7/13/2011	L3BRS	N	0.12	5.56367E-10	0.034	1.81206E-10	0.3
	S190	Y	0.15	6.95458E-10	0.027	1.43899E-10	0.2
	S8	Y	0.16	7.41822E-10	0.029	1.54558E-10	0.2
7/14/2011	S6	Y	0.24	1.11273E-09	0.023	1.22581E-10	0.1
	S7	Y	0.10	4.63639E-10	0.024	1.2791E-10	0.3

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

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