

PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

MARCH 2010 SAMPLING EVENT



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Pesticide Monitoring Program Report March 2010 Sampling Event

Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water and sediment samples were collected March 22 to March 31, 2010, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides 2,4-D, ametryn, atrazine, bromacil, metribuzin, norflurazon, and simazine, along with the insecticide/degradates atrazine desethyl, atrazine desisopropyl, chlorpyrifos ethyl, ethoprop, imidacloprid, and metalaxyl were detected in one or more of these surface water samples. The chlorpyrifos ethyl concentration detected is greater than the calculated acute and chronic toxicity for *Daphnia magna* and at this level, exposure can cause impacts to macroinvertebrate populations. However, the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long-term average exposures. No harmful impacts are expected from the other detected pesticides.

The herbicides, insecticides, and degradates atrazine, chlordane, DDD, DDE, dieldrin, alpha endosulfan, beta endosulfan, endosulfan sulfate, and a PCB compound were found in the sediment at several locations. Two DDE compound sediment concentrations were of a magnitude considered to have a harmful effect to freshwater sediment-dwelling organisms. No harmful impacts are expected from the other detected pesticides.

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

Background and Methods

The SFWMD pesticide monitoring network includes 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-three pesticides and degradation products were analyzed in samples from 33 of the network 34 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 March 22 to March 31, 2010.

Results

At least one pesticide was detected in surface water at 23 of the 33 sites and in sediment at 11 of the 28 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. Sediment samples are not collected at GORDYRD, CR33.5T, S333, S356-334, and TAMBR105, due to access restrictions or no requirement in the respective mandate. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All of these compounds have previously been detected in this monitoring program.

The surface water chlorpyrifos ethyl concentration detected at S2 has the possibility for causing an environmental impact. The sediment DDE concentrations at S2 and S5A were of a magnitude considered to represent detrimental effects to sediment-dwelling organisms in freshwater sediments. All other detected concentrations in the surface water and sediment were below any effect level.

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

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 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 concentration was detected at S191 (4.9 micrograms per liter [$\mu\text{g/L}$]) (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 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 0.0097 to 0.79 µg/L. Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates. Ametryn was not detected in the sediment.

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 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 33 sampling locations, ranged from 0.010 to 23 µg/L. Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates. However, the highest atrazine concentration of 23 µg/L detected at S80, exceeded the previous record value of 18 µg/L detected at S7 in 1993.

Only a TEC level [0.30 micrograms per kilogram (µg/Kg)] has been developed for atrazine concentrations in freshwater sediments. The detected sediment concentrations of atrazine at S4 and S80 (9.5 and 27 µg/Kg, respectively) exceeds this value and it is uncertain if this level will have the possibility for impacting sediment-dwelling freshwater organisms.

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 (e.g. 0.1 to 0.2) at the locations where

both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC₅₀ of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at CR33.5T (0.86 µg/L). Using these criteria, this observed concentration should not have an acute or chronic detrimental impact on fish or aquatic invertebrates. Bromacil was not detected in the sediment.

Chlordane: Chlordane is a chlorinated hydrocarbon previously used as a contact insecticide. 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 µg/Kg and PEC of 18 µg/Kg for chlordane. The detected sediment residue at S3 (16 µg/Kg) is at a concentration where harmful effects to sediment-dwelling organisms may be frequently or always observed. 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.

Chlorpyrifos ethyl: Chlorpyrifos ethyl is a non-systemic insecticide with contact, stomach, and respiratory action, for use on citrus, vegetables, rice, and household insect pests. Environmental fate and toxicity data in Tables 4 and 5 indicate that chlorpyrifos ethyl (1) is not readily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is toxic to mammals and fish; and (3) bioconcentrates to a limited extent. The only concentration of chlorpyrifos ethyl found in this sampling event (0.032 µg/L at S2) could have a harmful impact on aquatic invertebrates, as this level is greater than the calculated acute and chronic toxicity for *Daphnia magna* (Table 5). At this level, exposure can cause impacts to macroinvertebrate populations. However, the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long-term average exposures. Chlorpyrifos ethyl was not detected in the sediment.

DDD, DDE, DDT: DDE is an abbreviation of **d**ichloro**d**iphenyldichloroethylene [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 DDD sediment concentrations detected range from 2.7 to 19 µg/Kg. Any concentration which would fall below the TEC (4.9 µg/Kg) should not impact sediment dwelling organisms while concentrations above the PEC (28 µg/Kg), frequently or always have the possibility for impacting sediment-dwelling organisms. Two of the three sediment concentrations detected were between the TEC and PEC. These concentrations may have the possibility for harmful effects on freshwater sediment-dwelling organisms. DDD was not detected in the surface water.

The TEC is 3.2 µg/Kg and the PEC is 31 µg/Kg for DDE in freshwater sediments. The concentrations of DDE detected at S2 and S5A exceeded the PEC and frequently or always have the possibility for impacting sediment-dwelling organisms. DDE was not detected in the surface water.

Dieldrin: Dieldrin is a non-systemic insecticide with all uses canceled in the United States. The high K_{oc} and low water solubility accounts for dieldrin's affinity for sediment. The hydrophobicity of this compound also results in a significant bioconcentration factor and the potential for a high degree of accumulation in aquatic organisms (Table 4). Dieldrin is highly toxic to mammals. The dieldrin concentrations detected at S79 (5.3 µg/Kg) and S6 (3.4 µg/Kg) exceeds the TEC (1.9 µg/Kg) but is less than the PEC (62 µg/Kg). It is uncertain if this level will have the possibility for impacting sediment-dwelling freshwater organisms. No dieldrin was detected in the surface water.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, alpha (α) and beta (β). Endosulfan is highly toxic to mammals, with an acute oral LD_{50} for rats of 70 mg/Kg (Table 4). The Soil Conservation Service (SCS) rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 4). Beta endosulfan's water solubility and Henry's law constant ($1.91 \times 10^{-5} \text{ atm} - \text{m}^3/\text{mole}$) (Lyman, et al., 1990) indicate volatilization may be significant in shallow waters. The bioconcentration factors indicate a low to moderate degree of accumulation in aquatic organisms (Table 4). Alpha and beta endosulfan were detected in the sediment at S178 in the South Miami-Dade County farming area (Table 2). However, a sediment quality assessment guideline has not been developed. Endosulfan 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 ($9.63 \times 10^{-8} \text{ atm} - \text{m}^3/\text{mole}$) (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 S177 and S178. However, no sediment quality assessment guideline has been developed for endosulfan sulfate. Endosulfan sulfate was not detected in the surface water.

Ethoprop: Ethoprop is a non-systemic soil insecticide/nematicide used on many crops including

potatoes, tomatoes, sugarcane and turf. Environmental fate and toxicity data in Tables 4 and 5 indicate that ethoprop (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 moderately toxic to mammals and relatively non-toxic to fish; and (3) does not bioconcentrate significantly. Aquatic invertebrate LC₅₀ toxicity ranges from 13 µg/L to 25.3 µg/L for ethoprop (U.S. EPA, 1985). The only surface water concentration of ethoprop found in this sampling event was 0.010 µg/L at S79. This concentration is below a level that would have an acute detrimental impact on fish or aquatic invertebrates. Ethoprop was not detected in the sediment.

Imidacloprid: Imidacloprid is a systemic insecticide registered for use on a variety of row crops and turfgrass 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 only detected concentration of 0.25 µg/L at S80 is below any level that would have an acute or chronic detrimental impact on fish or aquatic invertebrates.

Metalaxyl: Metalaxyl is a systemic fungicide. Registered uses include potatoes, strawberries, citrus, avocados and vegetables. Environmental fate and toxicity data in Tables 4 and 5 indicate that metalaxyl (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 bioaccumulate significantly. The only concentration of metalaxyl detected was 0.062 µg/L at S80 (Table 2). Using these criteria, the concentration of metalaxyl detected should not have an acute, harmful impact 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 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 0.098 µg/L (S78). 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 norflurazon surface water concentrations ranged from 0.032 to 0.98 µg/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these observed concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates. Norflurazon was not detected in the sediment.

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 is a commercial grade mixture containing 54 percent chlorine by weight. Production of PCBs is banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily sorbed 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 residue detected at S79 (220 µg/Kg) is greater than the TEC but less than the PEC. This concentration has a possibility for impacting 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 LC₅₀ of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 µg/L (Verschueren, 1983). Aquatic invertebrate LC₅₀ toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. EPA, 1984). The highest surface water concentration of simazine detected (0.90 µg/L at CR33.5T) was below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

Quality Assurance Evaluation

Replicate samples were collected at locations S2 and S177. All the analytes detected in the surface water had precision ≤ 30 percent relative percent difference. No pesticide analytes were detected in the equipment blanks performed at S99, S191, S331, S4, S18C, S78, S12A, S7, and S5A. 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.

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 atmospheres and S is solubility in 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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Figure 1. South Florida Water Management District Pesticide Monitoring Network.

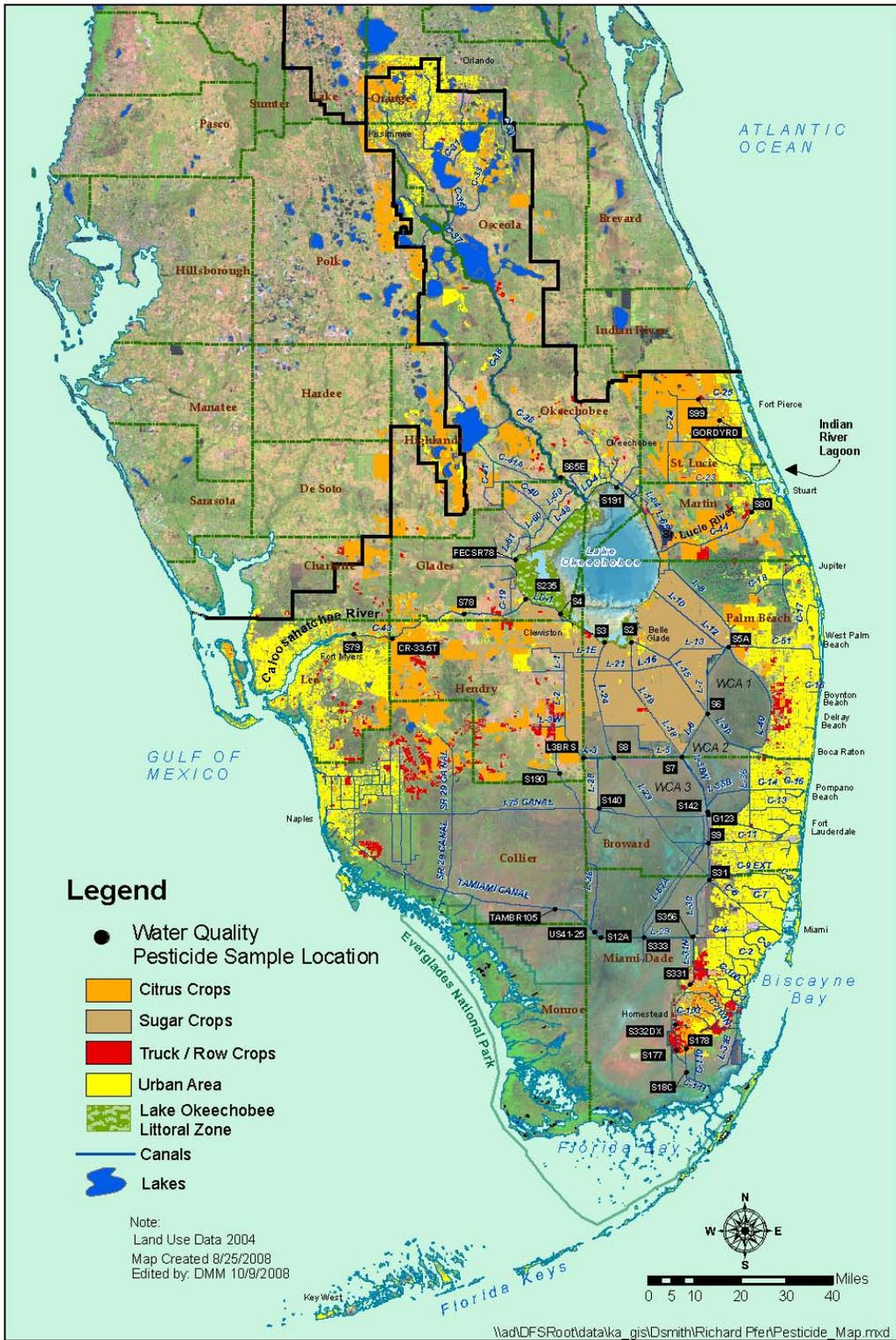


Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for March 2010 sampling event.

| Pesticide or metabolite | Water: range of MDLs - PQLs (µg/L) | Sediment: range of MDLs - PQLs (µg/Kg) | Pesticide or metabolite | Water: range of MDLs - PQLs (µg/L) | Sediment: range of MDLs - PQLs (µg/Kg) |
|----------------------------|------------------------------------|--|-------------------------|------------------------------------|--|
| 2,4-D | 0.2 - 0.64 | 9.3 - 230 | endrin aldehyde | 0.0042 - 0.018 | 0.95 - 32 |
| 2,4,5-T | 0.2 - 0.64 | 9.3 - 230 | ethion | 0.0094 - 0.04 | 2.4 - 80 |
| 2,4,5-TP (silvex) | 0.2 - 0.64 | 9.3 - 230 | ethoprop | 0.0094 - 0.04 | 2.4 - 80 |
| acifluorfen | 0.2 - 0.64 | 9.3 - 230 | fenamiphos (nemacur) | 0.038 - 0.16 | 4.8 - 320 |
| alachlor | 0.057 - 0.24 | 14 - 480 | fonofos (dyfonate) | 0.0094 - 0.04 | 2.4 - 80 |
| aldrin | 0.0019 - 0.008 | 0.48 - 16 | heptachlor | 0.0023 - 0.0096 | 0.48 - 16 |
| ametryn | 0.0094 - 0.04 | 2.4 - 80 | heptachlor epoxide | 0.0019 - 0.008 | 0.48 - 16 |
| atrazine | 0.0094 - 3.9 | 2.4 - 80 | hexazinone | 0.019 - 0.14 | 4.8 - 160 |
| atrazine desethyl | 0.0094 - 0.04 | N/A | imidacloprid | 0.2 - 0.67 | N/A |
| atrazine desisopropyl | 0.0094 - 0.12 | N/A | linuron | 0.2 - 0.67 | 8.6 - 220 |
| aziphos methyl (guthion) | 0.028 - 0.12 | 7.1 - 240 | malathion | 0.028 - 0.12 | 4.8 - 160 |
| α-BHC (alpha) | 0.0021 - 0.0088 | 0.48 - 15 | metalaxyl | 0.047 - 0.2 | N/A |
| β-BHC (beta) | 0.0032 - 0.0014 | 0.48 - 16 | methamidophos | N/A | 24 - 800 |
| δ-BHC (delta) | 0.0019 - 0.008 | 0.95 - 32 | methoxychlor | 0.0094 - 0.04 | 2.4 - 80 |
| γ-BHC (gamma) (lindane) | 0.0019 - 0.008 | 0.48 - 16 | metolachlor | 0.057 - 0.24 | 14 - 480 |
| bromacil | 0.047 - 0.2 | 9.5 - 320 | metribuzin | 0.019 - 0.14 | 4.8 - 160 |
| butylate | 0.019 - 0.08 | N/A | mevinphos | 0.057 - 0.24 | 9.5 - 320 |
| carbophenothion (trithion) | 0.015 - 0.064 | 2.4 - 80 | mirex | 0.011 - 0.048 | 1.9 - 64 |
| chlordane | 0.019 - 0.08 | 7.1 - 240 | monocrotophos (azodrin) | N/A | 24 - 800 |
| chlorothalonil | 0.015 - 0.064 | 2.4 - 80 | naled | 0.075 - 0.32 | 19 - 640 |
| chlorpyrifos ethyl | 0.0094 - 0.04 | 2.4 - 80 | norflurazon | 0.019 - 0.08 | 4.8 - 160 |
| chlorpyrifos methyl | 0.019 - 0.08 | 4.8 - 160 | parathion (ethyl) | 0.019 - 0.08 | 4.8 - 160 |
| cypermethrin | 0.019 - 0.08 | 2.4 - 80 | parathion methyl | 0.019 - 0.08 | 4.8 - 160 |
| DDD-p,p' | 0.0045 - 0.019 | 0.95 - 32 | PCB-1016 | 0.019 - 0.08 | 14 - 480 |
| DDE-p,p' | 0.0038 - 0.016 | 0.95 - 32 | PCB-1221 | 0.019 - 0.08 | 9.5 - 320 |
| DDT-p,p' | 0.0057 - 0.024 | 1.4 - 48 | PCB-1232 | 0.019 - 0.08 | 21 - 720 |
| demeton | 0.028 - 0.12 | 7.1 - 240 | PCB-1242 | 0.019 - 0.08 | 14 - 480 |
| diazinon | 0.019 - 0.08 | 2.4 - 80 | PCB-1248 | 0.019 - 0.08 | 9.5 - 320 |
| dicofol (kelthane) | 0.042 - 0.18 | 7.1 - 240 | PCB-1254 | 0.019 - 0.08 | 9.5 - 320 |
| dieldrin | 0.0019 - 0.008 | 0.48 - 16 | PCB-1260 | 0.019 - 0.08 | 14 - 480 |
| disulfoton | 0.019 - 0.08 | 2.4 - 80 | permethrin | 0.015 - 0.064 | 2.9 - 96 |
| diuron | 0.2 - 0.67 | 8.6 - 220 | phorate | 0.0094 - 0.04 | 2.4 - 80 |
| α-endosulfan (alpha) | 0.0038 - 0.016 | 0.48 - 20 | prometryn | 0.019 - 0.08 | 4.8 - 160 |
| β-endosulfan (beta) | 0.0038 - 0.016 | 0.48 - 16 | prometon | 0.019 - 0.08 | N/A |
| endosulfan sulfate | 0.0045 - 0.076 | 0.95 - 32 | simazine | 0.0094 - 0.04 | 2.4 - 80 |
| endrin | 0.0094 - 0.04 | 2.4 - 80 | toxaphene | 0.094 - 0.4 | 36 - 1200 |
| | | | trifluralin | 0.0075 - 0.032 | 1.9 - 64 |

N/A - not analyzed

Table 2. Summary of pesticide residues ($\mu\text{g/L}$) above the method detection limit found in surface water samples collected by SFWMD in March 2010.

| Date | Location | Flow | 2,4-D | ametryn | atrazine | atrazine desethyl | atrazine desisopropyl | bromacil | chlorpyrifos ethyl | ethoprop | imidacloprid | metalaxyl | metribuzin | norflurazon | simazine | Number of compounds detected at location |
|-------------------------------------|----------|------|----------|---------|-----------|-------------------|-----------------------|----------|--------------------|----------|--------------|-----------|------------|-------------|----------|--|
| 3/22/2010 | S99 | Y | - | - | - | - | - | 0.11 | - | - | - | - | - | 0.23 | 0.023 | 3 |
| | GORDYRD | Y | - | - | - | - | - | - | - | - | - | - | - | 0.33 | - | 1 |
| | S191 | N | 4.9 | - | - | - | - | 0.055 | - | - | - | - | - | 0.032 | - | 3 |
| | S65E | Y | - | - | 0.040 | - | - | - | - | - | - | - | - | - | - | 1 |
| | S80 | Y | 0.27 | 0.79 | 23 | 0.18 | 0.017 | 0.28 | - | - | 0.25 | 0.062 | - | 0.18 | 0.088 | 10 |
| 3/23/2010 | FECSR78 | Y | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S2 | N | 0.28 * | 0.13 * | 3.3 * | 0.10 * | - | - | 0.032 * | - | - | - | - | - | - | 5 |
| | S3 | N | 0.41 | 0.082 | 2.5 | 0.099 | - | - | - | - | - | - | 0.030 | - | - | 5 |
| | S4 | Y | 0.58 | - | 5.1 | 0.23 | - | - | - | - | - | - | - | - | - | 3 |
| 3/24/2010 | CR33.5T | Y | - | - | 0.087 | - | 0.039 | 0.86 | - | - | - | - | - | 0.98 | 0.90 | 5 |
| | S177 | N | - | - | 0.010 * | - | - | - | - | - | - | - | - | - | - | 1 |
| | S178 | N | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S18C | N | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S235 | N | - | 0.012 | 0.035 | - | - | - | - | - | - | - | - | - | - | 2 |
| | S331 | N | - | 0.010 | - | - | - | - | - | - | - | - | - | - | - | 1 |
| | S332DX | Y | - | - | 0.022 | - | - | - | - | - | - | - | - | - | - | 1 |
| | S78 | Y | 0.40 | 0.064 | - | - | - | 0.55 | - | - | - | - | 0.098 | 0.20 | 0.46 | 6 |
| | S79 | Y | 0.24 | 0.0097 | 2.9 | 0.15 | 0.026 | 0.64 | - | 0.010 | - | - | 0.043 | 0.26 | 0.45 | 10 |
| 3/25/2010 | G123 | N | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S12A | N | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S31 | Y | - | 0.024 | 0.82 | - | - | - | - | - | - | - | 0.048 | - | - | 3 |
| | S333 | Y | - | 0.019 | 0.71 | 0.038 | - | - | - | - | - | - | 0.036 | - | - | 4 |
| | S356-334 | Y | - | 0.020 | 0.91 | 0.028 | - | - | - | - | - | - | - | - | - | 3 |
| | S9 | N | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | TAMBR105 | Y | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | US41-25 | Y | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| 3/29/2010 | L3BRS | Y | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S140 | Y | - | - | 0.013 | - | - | - | - | - | - | - | - | 0.071 | - | 2 |
| | S190 | Y | - | - | - | - | - | - | - | - | - | - | - | - | - | 0 |
| | S7 | Y | - | 0.058 | 1.6 | 0.077 | - | - | - | - | - | - | 0.063 | - | - | 4 |
| | S8 | N | - | 0.015 | 0.55 | 0.035 | - | - | - | - | - | - | - | - | - | 3 |
| 3/31/2010 | S5A | N | 2.8 | 0.29 | 4.5 | - | - | - | - | - | - | - | 0.028 | - | 0.020 | 5 |
| | S6 | N | - | 0.29 | 4.9 | - | - | - | - | - | - | - | 0.059 | - | 0.015 | 4 |
| Total number of compound detections | | | 8 | 14 | 18 | 9 | 3 | 6 | 1 | 1 | 1 | 1 | 8 | 8 | 7 | 85 |

N - no Y - yes R - reverse; - denotes that the result is below the method detection limit; * results are the average of replicate samples
 | - value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit
 Values in bold, italicized font are at a concentration that potential harmful effects to organisms may be observed.

Table 3. Summary of pesticide residues ($\mu\text{g}/\text{Kg}$) above the method detection limit found in sediment samples collected by SFWMD in March 2010.

| Date | Location | Flow | atrazine | chlordane | DDD-p,p' | DDE-p,p' | dieldrin | endosulfan (alpha) | endosulfan (beta) | endosulfan sulfate | PCB-1254 | Number of compounds detected at location |
|-------------------------------------|----------|------|----------|-----------|----------|-------------|----------|--------------------|-------------------|--------------------|----------|--|
| 3/22/2010 | S80 | Y | 27 | - | - | - | - | - | - | - | - | 1 |
| 3/23/2010 | S2 | N | - | - | 18 l* | 75 * | - | - | - | - | - | 2 |
| | S3 | N | - | 16 l | 2.7 l | 10 | - | - | - | - | - | 3 |
| | S4 | Y | 9.5 l | - | - | 4.4 l | - | - | - | - | - | 2 |
| 3/24/2010 | S177 | N | - | - | - | 3.9 l | - | - | - | 2.1 l | - | 2 |
| | S178 | N | - | - | - | 9.4 | - | 1.4 l | 2.4 l | 6.8 l | - | 4 |
| | S332DX | Y | - | - | - | - | - | - | - | - | 15 l | 1 |
| | S79 | Y | - | - | - | 13 l | 5.3 l | - | - | - | 220 | 3 |
| 3/29/2010 | S8 | N | - | - | - | 1.6 l | - | - | - | - | 1 | |
| 3/31/2010 | S5A | N | - | - | 19 | 110 | - | - | - | - | - | 2 |
| | S6 | N | - | - | - | 4.3 l | 3.4 | - | - | - | - | 2 |
| Total number of compound detections | | | 2 | 1 | 3 | 9 | 2 | 1 | 1 | 2 | 2 | 23 |

N - no Y - yes R - reverse; - denotes that the result is below the method detection limit

l - value reported is less than the practical quantitation limit, and greater than or equal to the minimum detection limit

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

* results are the average of replicate samples

Table 4. Selected properties of pesticides found in March 2010 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 (BCF) |
|--------------------|--|---|--|--|-------------------------------------|---------------------------------------|--|----|----|-----------------------------|----------------------------------|
| | | | | | | | 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 |
| bromacil | - | 5,200 | C | 700 | 32 | 60 | L | M | M | I | 15 |
| chlordan | 0.0043 | 365 - 590 | B2 | 0.056 | 3,800 | - | - | - | - | I | 3,141 |
| chlorpyrifos ethyl | - | 135 - 163 | D | 2 | 6,070 | 30 | S | M | M | - | 418 |
| DDD-p,p' | - | 3,400 | - | 0.055 | 239,900 | - | - | - | - | I | 3,173 |
| DDE-p,p' | - | 880 | - | 0.065 | 243,220 | - | - | - | - | S | 2,887 |
| dieldrin | 0.0019 | 37 - 87 | B2 | 0.14 | 10,000 est. | - | - | - | - | I | 1,873 |
| alpha endosulfan | 0.056 | 70 | - | 0.53 | 12,400 | 50 | XS | L | M | S | 884 |
| beta endosulfan | | 70 | - | 0.28 | - | - | - | - | - | S | 1,267 |
| endosulfan sulfate | - | - | - | 0.117 | - | - | - | - | - | I | 2,073 |
| ethoprop | - | 62 | - | 750 | 70 | 25 | L | S | M | I | 15 |
| imidacloprid | - | 424 | E | 510 | - | - | - | - | - | - | 18 |
| metalaxyl | - | 669 | - | 7,100 | 100 | 70 | L | M | M | I | 4 |
| metribuzin | - | 2,200 | D | 1,220 | 41 | 30 | L | S | M | I | 11 |
| norflurazon | - | 9,400 | C | 28 | 700 | 90 | M | M | L | I | 94 |
| PCB's | 0.014 | - | B2 | - | - | - | - | - | - | - | - |
| simazine | - | >5000 | C | 6.2 | 130 | 60 | L | M | M | I | 221 |

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

Bioconcentration Factor (BCF) calculated as $BCF = 10^{(2.791 - 0.564 \log WS)}$ (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 ()

Note: endosulfan usually considered the sum of alpha and beta isomers

(1) Hartley and Kidd (1987)

(2) Goss and Wauchope (1992)

(3) Montgomery (1993)

(4) Lyman, et al. (1990)

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

Table 5. Toxicity of pesticides found in the March 2010 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

| Common Name | 48 hr EC ₅₀ Water flea <i>Daphnia magna</i> | | Acute Toxicity (*) | Chronic Toxicity (*) | 96 hr LC ₅₀ Fathead Minnow (#) <i>Pimephales promelas</i> | | 96 hr LC ₅₀ Bluegill <i>Lepomis macrochirus</i> | | 96 hr LC ₅₀ Largemouth Bass <i>Micropterus salmoides</i> | | 96 hr LC ₅₀ Rainbow Trout (#) <i>Oncorhynchus mykiss</i> | | 96 hr LC ₅₀ Channel Catfish <i>Ictalurus punctatus</i> | | | | | |
|--------------------|--|----------------------|--------------------|----------------------|--|------------------|--|------------------|---|------------------|---|------------------|---|------------------|--------------|-----------|---------|----|
| | Acute Toxicity (*) | Chronic Toxicity (*) | | | Acute Toxicity | Chronic Toxicity | Acute Toxicity | Chronic Toxicity | Acute Toxicity | Chronic Toxicity | Acute Toxicity | Chronic Toxicity | Acute Toxicity | Chronic Toxicity | | | | |
| 2,4-D | 25,000 (7) | 8,333 | 1,250 | 133,000 (7) | 44,333 | 6,650 | 180,000 (8) | 60,000 | 9,000 | - | - | 100,000 (4) | 33,333 | 5,000 | - | - | - | |
| ametryn | 28,000 (7) | 9,333 | 1,400 | 16,000 (10) | 5,333 | 800 | 900 (48 hr) (6) | 1,367 | 205 | - | - | 110,000 (7) | 36,667 | 5,500 | - | - | - | |
| atrazine | 6,900 (7) | 2,300 | 345 | 15,000 (7) | 5,000 | 750 | 16,000 (4) | 5,333 | 800 | - | - | 8,800 (4) | 2,933 | 440 | 7,600 (4) | 2,533 | 380 | |
| bromacil | - | - | - | - | - | - | 127,000 (7) | 42,333 | 6,350 | - | - | 5,300 (11) | 1,767 | 265 | - | - | - | |
| chlordane | - | - | - | - | - | - | 70 (5) | 23 | 3.5 | - | - | 90 (5) | 30 | 5 | - | - | - | |
| chlorpyrifos ethyl | 1.7 (7) | 0.57 | 0.085 | 203 (7) | 68 | 10 | 2.6 (4) | 0.87 | 0.13 | - | - | 11 (4) | 3.7 | 1 | 280 (7) | 93 | 14 | |
| DDD-p,p' | 3,200 (6) | 1,067 | 160 | 4,400 (1) | 1,467 | 220 | 42 (1) | 14 | 2.1 | 42 (1) | 14 | 2.1 | 70 (1) | 23.3 | 4 | 1,500 (1) | 500 | 75 |
| DDE-p,p' | - | - | - | - | - | - | 240 (1) | 80 | 12 | - | - | 32 (1) | 10.7 | 2 | - | - | - | |
| dieldrin | - | - | - | 16 (5) | 5.3 | 0.80 | 8 (4) | 2.7 | 0.4 | - | - | 10 (5) | 3.3 | 1 | 4.5 (5) | 1.5 | 0.23 | |
| endosulfan | 166 (7) | 55 | 8 | 1 (1) | 0.3 | 0.05 | 1 (1) | 0.33 | 0.05 | - | - | 1 (1) | 0.33 | 0.05 | 1 (1) | 0.3 | 0.05 | |
| | - | - | - | - | - | - | 2 (3) | 0.67 | 0.10 | - | - | 3 (2) | 1 | 0.15 | 1.5 (7) | 0.5 | 0.08 | |
| | - | - | - | - | - | - | - | - | - | - | - | 1 (3) | 0.33 | 0.05 | - | - | - | |
| | - | - | - | - | - | - | - | - | - | - | - | 0.3 (5) | 0.10 | 0.015 | - | - | - | |
| | 166 (12) | 55 | 8 | 1.5 (12) | 0.5 | 0.08 | 1.7 (12) | 0.57 | 0.09 | - | - | 0.8 (12) | 0.27 | 0.04 | - | - | - | |
| ethoprop | 93 (7) | 31 | 4.7 | - | - | - | - | - | - | - | - | 13,800 (4) | 4,600 | 690 | - | - | - | |
| imidacloprid | 85,200 (9) | 28,400 | 4,260 | - | - | - | - | - | - | - | - | 83,000 (9) | 27,667 | 4,150 | - | - | - | |
| metalaxyl | 28,000 (7) | 9,333 | 1,400 | - | - | - | 139,000 (7) | 46,333 | 6,950 | - | - | 132,000 (7) | 44,000 | 6,600 | - | - | - | |
| | 29,000 (13) | 9,667 | 1,450 | 9,100 (13) | 3,033 | 455 | 139,000 (13) | 46,333 | 6,950 | - | - | 132,000 (13) | 44,000 | 6,600 | - | - | - | |
| metribuzin | 4,200 (7) | 1,400 | 210 | - | - | - | 80,000 (4) | 26,667 | 4,000 | - | - | 64,000 (4) | 21,333 | 3,200 | 100,000 (7) | 33,333 | 5,000 | |
| | 4,200 (14) | 1,400 | 210 | - | - | - | 75,900 (14) | 25,300 | 3,795 | - | - | 76,770 (14) | 25,590 | 3,839 | - | - | - | |
| norflurazon | 15,000 (7) | 5,000 | 750 | - | - | - | 16,300 (7) | 5,433 | 815 | - | - | 8,100 (7) | 2,700 | 405 | >200,000 (4) | >67,000 | >10,000 | |
| | >15000 (16) | >5,000 | >750 | - | - | - | 16,300 (16) | 5,433 | 815 | - | - | 8,100 (16) | 2,700 | 405 | - | - | - | |
| simazine | 1,100 (7) | 367 | 55 | 100,000 (7) | 33,333 | 5,000 | 90,000 (4) | 30,000 | 4,500 | - | - | 100,000 (7) | 33,333 | 5,000 | - | - | - | |

(*) Florida Administrative Code (F.A.C.) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC₅₀ is the lowest value which has been determined for a species significant to the indigenous aquatic community.

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

- (1) Johnson and Finley (1980)
- (2) U.S. EPA (1977)
- (3) Schneider (1979)
- (4) Hartley and Kidd (1987)
- (5) Montgomery (1993)
- (6) Verschueren (1983)
- (7) U.S. EPA (1991)
- (8) Mayer and Ellersieck (1986)
- (9) U.S. EPA (1994a)
- (10) U.S. EPA (2005)
- (11) U.S. EPA (2006)
- (12) U.S. EPA (2002b)
- (13) U.S. EPA (1994b)
- (14) U.S. EPA (1998)
- (15) U.S. EPA (2002a)
- (16) U.S. EPA (1996b)
- (17) U.S. EPA (1996c)

Table 6. Atrazine Desethyl/Atrazine ratio (DAR) data for March 2010 sampling event.

| Date | Location | Flow* | atrazine | | atrazine desethyl | | DAR | |
|-----------|----------|-------|----------|-------------|-------------------|-------------|-----------------|---------------|
| | | | µg/L | moles/l | µg/L | moles/l | | |
| 3/22/2010 | S80 | Y | 23 | 1.06637E-07 | 0.18 | 9.59327E-10 | 0.0 | |
| 3/23/2010 | S2 | N | 3.3 | 1.53001E-08 | 0.10 | 5.34558E-10 | 0.0 | |
| | S3 | N | 2.5 | 1.15910E-08 | 0.099 | 5.2763E-10 | 0.0 | |
| | S4 | Y | 5.1 | 2.36456E-08 | 0.23 | 1.22581E-09 | 0.1 | |
| 3/24/2010 | S79 | Y | 2.9 | 1.34455E-08 | 0.15 | 7.99439E-10 | 0.1 | |
| 3/25/2010 | S333 | Y | 0.71 | 3.29184E-09 | 0.038 | 2.02525E-10 | 0.06 | |
| | S356-334 | Y | 0.91 | 4.21911E-09 | 0.028 | 1.49229E-10 | 0.04 | |
| 3/29/2010 | S7 | Y | 1.6 | 7.41822E-09 | 0.077 | 4.10379E-10 | 0.1 | |
| | S8 | N | 0.55 | 2.55001E-09 | 0.035 | 1.86536E-10 | 0.07 | |
| 3/31/2010 | S5A | N | 4.5 | 2.08637E-08 | 0.095 | 5.06312E-10 | 0.0 | |
| | S6 | N | 4.9 | 2.27183E-08 | 0.097 | 5.16971E-10 | 0.0 | |
| | | | | | DAR | All sites | Flow only sites | No flow sites |
| | | | | | average | 0.0 | 0.0 | 0.0 |
| | | | | | median | 0.1 | 0.1 | 0.0 |
| | | | | | minimum | 0.0 | 0.0 | 0.0 |
| | | | | | maximum | 0.1 | 0.1 | 0.1 |

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