Ambient Pesticide Monitoring Network: 1992 to 2007

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Abstract

The South Florida Water Management District has collected surface water and sediment samples for analysis of over 80 pesticides since 1992. Residues of atrazine and p,p'-DDE are nearly ubiquitous throughout the sampling area. Surface water concentrations of atrazine at nine of the fourteen monitoring locations exhibited a downward trend and none of the detected concentrations exceeded established levels of concern. Seventy-five percent of the sampled locations had average sediment residues of p,p'-DDE at levels that may impact sediment-dwelling organisms. Monitoring locations with the highest average p,p'-DDE concentrations (based on detected values) and the highest percentage of pesticide detections did not exhibit consistent trends. Some locations exhibited increasing trends while trends at other locations showed a decrease in concentrations. Additionally, specific location concentrations for ethion, diazinon, and endosulfan documented periods of surface water quality exceedances. However, product label changes and grower education have substantially contributed to the reduced number of exceedances over time.

Introduction

The South Florida Water Management District (SFWMD) is a regional governmental agency responsible for water quality, flood control, water supply, and environmental restoration for 16 counties from Orlando to the Florida Keys. Pesticide monitoring within SFWMD has been ongoing since 1976 (Pfeuffer, 1985) with the routine ambient monitoring program beginning in 1984 (Pfeuffer, 1991). The original monitoring program consisted of 13 locations, but overtime it has grown to 34 sampling sites. The current program includes stations designated in the Settlement Agreement, the Lake Okeechobee Operating Permit, and the non-Everglades Construction Project (non-ECP) permit. The sampling locations are throughout South Florida, and range from Lake Okeechobee through the Everglades Agricultural Area (EAA), and down to the Everglades National Park (Figure 1). Water flow within the monitoring area is generally in a north to south direction.

The main areas of agriculture include citrus (Martin/St. Lucie County area, Caloosahatchee River area), sugarcane (EAA), and the row crop area of South Miami-Dade County. Also the coastal urban areas were an additional source of pesticide residues.

The District's canals and marshes are protected under Florida Administrative Code (F.A.C.) Chapter 62-302 as Class III (fishable and swimmable) surface 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), which encompasses the Arthur R. Marshall Loxahatchee Nation Wildlife Refuge and the Everglades National Park are also designated as Outstanding Florida Waters, under Chapter 62-302, F.A.C., to which anti-degradation standards apply.

The pesticide monitoring program has evolved over time. Sampling for new pesticides and from new locations has been added due to increasing concerns over pesticide use. Over 80 pesticides and degradation products are determined in these samples. This document summarizes pesticide data for surface water and sediment samples collected from April 1992 to December 2007.

Methods

To assess ambient pesticide concentrations, surface water samples were generally collected on a quarterly basis (four times annually) and sediment samples semi-annually (two times per year). The exact sampling date was dependent on staff and equipment availability as well as available capacity of the analytical laboratory. Samples were collected from a small boat or pier, upstream of each water control structure and away from canal banks. Water column samples were unfiltered surface grab samples (0.5 meter depth), while sediment samples were the top layer (approximately 10 centimeters) of sediment and obtained using a stainless steel petite Ponar dredge. Samples were stored on ice before being shipped to the analytical laboratory by overnight courier. All field and sampling procedures are described in current or previous versions of the SFWMD Field Sampling Quality Manual (2008), which requires field quality control checks including field replicates, field blanks, trip spikes (specific concentrations of selected analytes added to deionized or selected sample water), and equipment blanks (sediment only). These quality control samples were handled identically to field samples.

Samples have been analyzed for over 80 pesticides and degradation products (Table 1). The list of compounds has been dynamic over time, with compounds added based on a potential concern or removed after evaluating the compiled data and demonstrating no concern. The current analytical list is divided into chemical groupings (chlorinated [phenoxy acid] herbicides, urea herbicides, organochlorine pesticides, and organonitrogen/phosphorus pesticides) that are used by farmers and homeowners, which also includes restricted-use pesticides. Although listed, polychlorinated biphenyl's are not pesticides, but are generally reported during organochlorine pesticide analysis. Selected compounds with a state-defined numeric water quality standard (Chapter 62-302 F.A.C.) are provided in Table 2. The United States Environmental Protection Agency (USEPA) National Recommended Water Quality Criteria (2006b) are also listed for comparison purposes. For any other compound, an acute or chronic value can be calculated using procedures outlined in state law (62-302.200 (1)(a) and (4)(a) F.A.C.). Section 62-302.200 F.A.C. provides for acute and chronic toxicity standards to be calculated as one-third and one-twentieth, respectively, of the lowest concentration lethal to 50 percent of the test population (LC_{50}) exposed for 96 hours for a species significant to the indigenous aquatic community. The calculated toxicity values are listed for the frequently detected compounds in Table 2. Sediment concentrations were compared to freshwater sediment quality assessment guidelines (MacDonald Environmental Sciences Ltd. and United States Geological Survey, 2003) (Table 3). A value below the threshold effect concentration (TEC) should not have a harmful effect on sediment-dwelling organisms. However, values above the probable effect concentration (PEC) demonstrate that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

All analytical work associated with the pesticide monitoring network was performed by the Florida Department of Environmental Protection Central Laboratory in Tallahassee, Florida. Analytical methods (Chemistry Standard Operating Procedures by Subsection: Organics) are available on the laboratory's Web site (www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp). The reported sediment concentrations were on a dry weight basis.

Since December 1994, modified analytical methods have been used that lowered the method detection limits about tenfold (Miles and Pfeuffer, 1997).

The tables summarizing the detected compounds were compiled using the results the monitoring events from April 1992 to December 2007. Average, geometric mean, and median concentrations were calculated using only the detections for all locations. The number of detections was based on the values above the minimum detection limit for each sampling event at all locations within the land use or drainage basin type. With a few exceptions, as noted below, the summary data presented for the locations represent 68 surface water and 30 sediment sampling events.

Network Results and Discussion

It is important to note that an evaluation of detection limits is critical when assessing pesticide data. For the surface water samples, the average number of compounds detected during a sampling event appeared to increase when the detection limits were decreased (Table 4). Scott et al. (2002) also noted increases in pesticide surface water detections in South Florida when the detection limits were decreased. Conversely, the number of detected concentrations in sediment samples decreased when detection limits were lowered. This apparent discrepancy may be attributed to the fact that only four sampling events occurred during the period of higher detection limits versus 26 for the lower detection limit time period (Table 4). Potentially, the most readily detected compounds (i.e., organochlorine compounds) in the sediment were prevalent during the earlier timeframe, since their use was only recently restricted. Lower detection limits reduces false negatives.

For 44 percent of the monitoring locations, an average of three or more compounds was detected in the surface water during each sampling event (Table 5). The monitoring locations receiving drainage from citrus agriculture had the highest average (4) of different compounds detected, followed by the northern EAA, southern EAA, urban, Lake Okeechobee inflows, South Miami-Dade County, and the reference drainage/land use type basins.

The percentage of detections by month, for the surface water samples ranged from 2.2 to 4.5 percent, with the period of record averaging 3.3 percent (Figure 2). A small seasonal difference in the number of detections was also observed between the wet and dry season averaging 3.1 and 3.4 percent, respectively. No pattern was evident due to the fact that the pesticide application period for the wide range of crops and their locations varies considerably throughout South Florida. For example, pesticide applications for citrus can occur year-round while row crop pesticide applications occur only in the appropriate timeframe during the specific growing season. Additionally, the seasonal temperature ranges for the growing season in the agricultural areas create a difference in the optimal start and end dates from the northern to the southern part of the region.

The percent detections by month, for the sediment ranged from 1.1 to 2.1 percent, with a period of record average of 1.6 percent (Figure 3). The average number of detections for the wet and dry seasons was 1.3 and 1.6 percent, respectively. As was observed for the surface water, no pattern was evident since the application period for the wide variety of crops and locations varied significantly. Additionally, the majority of detections consisted of p,p'-DDE and p,p'-DDE (Table 7).

The most frequently detected pesticides in surface water are the triazine herbicides (atrazine, ametryn, and simazine) (Table 6). These herbicides are applied to significant acreages in South Florida (Miles and Pfeuffer, 1997) and have a higher transport due to surface solution or leaching (Gross and Wauchope, 1992). Atrazine and its associated degradation products, atrazine desethyl and atrazine desisopropyl, were the most frequently detected compounds in the surface water. The most frequently detected pesticides in the sediment included the DDT metabolites (p,p'-DDE and p,p'-DDD) and ametryn (Table 7). Although banned in the early 1970s (USEPA, 1990), DDT and DDD were used widely, degrade slowly, and bind readily to soil. Atrazine, ametryn, atrazine desethyl, norflurazon, and p,p'-DDE were detected in samples from at least one monitoring station during every event. The United States Geological Survey, as part of the South Florida National Ambient Water Quality Assessment (NAWQA), collected samples from 1996 to 1998 and identified similar compounds for the most frequently detected pesticides (McPherson et al., 2000).

Table 8 summarizes the atrazine surface water detections by location. Structure S7 exhibited the highest detected maximum concentration of 18 micrograms per liter [μg/L] (Figure 4). Peak concentrations routinely occurred during April, coinciding with the application season for sugarcane. 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 (USEPA, 2003a). Additionally, the lowest calculated chronic toxicity for the water flea, *Daphnia magna*, is 345 μg/L (Table 2). Based on these criteria, surface water concentrations presented in Table 8 should not have an acute or chronic detrimental impact on fish or invertebrates.

The highest atrazine average location concentration in surface water was observed at S38B, which can receive runoff from an urban drainage basin (Table 8). The peak atrazine detections occur in June, which coincides with the summer application season (Figure 5). The monitoring locations with the next four highest average concentrations received drainage from the EAA. Nine of the top ten monitoring locations with the highest percentage of detections were either receiving runoff from the urban areas or the EAA. The location with the highest percent of detections was observed at S6 with peak concentrations occurring during April, which is the application season for sugarcane (Figure 6).

Results from the NAWQA program (McPherson et al., 2000) for atrazine surface water detections at S7 and S6 were very similar to the SFWMD's detections at the same locations. The peak concentrations measured during the NAWQA program also occurred during the spring months. However, NAWQA's highest detected concentration was 12 μg/L at S6.

Average annual atrazine concentrations from four northern and four southern boundary monitoring locations receiving drainage from the EAA are presented in Figures 7 and 8, respectively. Since 1992, a trend towards lower detectable concentrations was observed for the southern and northern locations. A non-parametric regression (Theil) (Hollander, 1973) identified a significant (p value <0.05) decrease in concentration at all monitoring locations except S3 and S6. Theil regression makes no assumptions about the population distribution and it does not assume the errors are only in the y-direction or are normally distributed.

The average atrazine annual concentration from six monitoring locations receiving drainage from urban areas is presented in Figure 9. A statistically significant (p value <0.05) decrease in concentration based on the Theil regression (Hollander, 1973) was observed at all stations except S38B, G123, and S9.

The number of detections of p,p'-DDE in sediment is summarized by location in Table 9. Sediment samples were not collected at GORDYRD and CR33.5T due to access restrictions. The average concentration at S6, S2, S5A, and S178 for this parameter was higher than the PEC (i.e., 31 µg/Kg) suggesting that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed at these monitoring locations.

The locations with the highest percentage of detections and average concentration of p,p'-DDE were S5A, S2, S178, S177, S3, and S6 (Table 9 and Figure 10). Using a Theil non-parametric regression (Hollander, 1973), significant (p value <0.05) increases in concentration were observed at S2 and S3, while a decreasing trend in concentration was noted at S178 and S177. The thirteen locations exhibited p,p'-DDE detections 50 percent of the time or greater (Table 9) with the majority of sampling locations having average concentrations above the TEC (i.e., 3.2 µg/Kg). Only eight locations (S331, L3BRS, S191, FECSR78, S9, US41-25, S65E, and S140) did not exceed the TEC.

Basin Results and Discussion

Three locations (S65E, S191, and FECSR78) were sampled upstream of potential discharge into Lake Okeechobee (Figure 11). The agricultural activity in this basin is primarily cattle/dairy operations. Atrazine and its major degradation product (atrazine desethyl) were the dominant compounds detected in the surface water followed by the herbicides bromacil, hexazinone, and simazine (Table 10). However, the average concentration for all these compounds were less than 1 ug/L and were appreciably below any level of concern for aquatic invertebrates and fish (Table 2). Only p,p'-DDE was present with any frequency in the sediments (Table 11). The maximum concentration exceeds the Florida freshwater sediment quality assessment guideline TEC but not the PEC. A concentration above the TEC but less than the PEC has a potential for harmful effects on freshwater sediment dwelling organisms.

Six monitoring locations (S99, GORDYRD, S80, S78, CR33.5T, and S79) (Figure 12) were used to evaluate citrus agriculture drainage. Sampling locations GORDYRD and CR33.5T did not have sediment collected for analysis due to access restrictions. A wide variety of herbicides and a few insecticides was detected at low concentrations in the surface water (Table 12). The herbicides norflurazon, simazine, atrazine, and bromacil were most frequently detected. Using a multiple substance risk approach, based on a concentration addition model, Schuler and Rand (2008) identified a high risk to plant and algal communities at S79, S80, and S99 from the herbicide mixtures detected at the respective locations.

The chemical of concern when evaluated on a single chemical to potential species toxicity is the organophosphate pesticide ethion, particularly at the S99 structure. Ethion is a non-systemic acaricide and insecticide previously registered for use on several fruits, citrus, and vegetables. Ethion is acutely toxic to aquatic organisms in low part per billion ranges (Mayer and Ellersieck, 1986, Table 2) and is slightly toxic to mammals (Hartley and Kidd, 1987). Furthermore, it is stable to hydrolytic and photolytic degradation in water (Montgomery, 1993). Ethion is strongly adsorbed to soil and therefore can accumulate in sediments (Gross and Wauchope, 1992). Ethion can bioconcentrate to a limited extent (Lyman et al., 1990).

However, ethion does not have a state numeric standard. The most sensitive species for aquatic macroinvertebrates in acute toxicity tests of ethion is the cladoceran, *Daphnia magna*, with a 48-hour EC_{50} of 0.06 µg/L (Table 2). The acute and chronic standards are 0.02 and 0.003 µg/L, respectively, calculated according to the promulgated procedure (Section 62-302.200 F.A.C.). Based on these values, excursions of ethion concentration above the established acute and chronic standards were observed (Figures 13a-d). Most of the surface water detections occurred during the growing season. Additionally, ethion detections were not routinely preceded by considerable rainfall. With a method detection limit of approximately 0.019 µg/L, any detection will automatically exceed the calculated chronic toxicity. At this level, long-term exposure can cause impacts to macroinvertebrate populations, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long-term average exposures. Since June 1992, 17 out of 41 sampling events at S99 had a detectable level of ethion in the surface water (Figures 13a-d).

The use of ethion on citrus has been banned (Federal Register, March 22, 2002). By December 31, 2004, all use of existing stocks of the end-use products was prohibited. With the voluntary cancellation of all registered products and the availability of alternative pesticides, the last surface water detection occurred during the August 2001 sampling event (Figure 13d). A few sediment detections occurred after this time, with the last ethion residue quantified during the October 2003 sampling event (Figure 13d).

In sediment samples from citrus drainage locations, p,p'-DDE was present along with ethion, PCB-1254, and p,p'-DDD (Table 13). Dieldrin and PCB-1254 were primarily detected at S79. The p,p'-DDE, dieldrin, and all of the PCB compounds had average and maximum concentrations that exceeded the Florida freshwater sediment quality assessment guideline TEC (Table 13). No sediment guidelines are available for ethion.

Four locations, S2, S3, S4, and S235 (Figure 14), were used to evaluate drainage from the northern portion of the EAA, which is predominately sugarcane production, with some row crops such as corn and lettuce (vegetable crops) or rice being grown. The most frequently detected pesticides were the herbicides atrazine, ametryn, hexazinone, and simazine (Table 14). For all of these, the concentrations were below any levels of concern (Table 2). For the sediment samples, p,p'-DDE, p,p'-DDD, p,p'-DDT, chlordane, and the herbicide ametryn dominated the number of detections (Table 15).

Some of the p,p'-DDE, p,p'-DDD, chlordane, and toxaphene concentrations exceeded the PEC guideline. However, no sediment guidelines exist for ametryn.

Sampling locations S5A, S6, S7, S8, L3BRS, S190, S142, and S140 (Figure 15) were used to evaluate surface runoff from the southern portion of the EAA. Structures S142 and S140 were added to the monitoring network during the February 1997 sampling event and therefore the summary data represent only 44 events. The surface water pesticide detections in this region consisted primarily of herbicides (Table 16). The concentrations were usually less than 1.0 µg/L, with atrazine, simazine, and diuron being the exceptions. With the exception of the maximum diuron concentration, none of the values exceeded any level of concern (Table 2). The 76 µg/L diuron detection exceeds the calculated chronic toxicity value for the invertebrate, *Daphnia magna*.

Structures S7 and S8 were the only network sampling locations directly impacted by the operation of a Stormwater Treatment Area (STA). Since STA-3/4 was completed in December 2004, flows from the North New River Canal are diverted into the over 16,000-acre treatment area before discharging back to S7 and S8. Within STA-3/4, the vegetative communities were designed to provide water quality treatment through an emergent macrophyte community as well as submerged aquatic vegetation. A comparison of atrazine and ametryn surface water concentrations before and after completion of STA-3/4 showed that the average concentration had decreased (Table 17). However, the percent of detections had increased. STA-3/4 may have attenuated the herbicide concentration peaks and provided a more uniform distribution of the surface water residues.

Herbicides and DDT metabolites were most frequently detected in the sediment samples from the southern portion of the EAA (Table 18). Atrazine and ametryn residues in sediment corresponded with the consistent surface water detections. The average p,p'-DDE, p,p'-DDD, p,p'-DDT, PCB-1242, PCB-1254, and PCB-1260 concentrations exceeded the TEC while the chlordane concentration exceeded the PEC.

The majority of the sampling locations that receive drainage from urban areas have been recently added to the network (S9, G94D, ACME1DS, G123, S31, and S38B) (Figure 16). With the exception of water control structure S9 and S31, the remaining locations have only been sampled since 1997/1998 and only represent 42 to 45 sampling events. After the March 2008 sampling event, the permit mandate for G94D, ACME1DS, and S38B was modified, deleting the requirement for sampling.

A wide variety of pesticides were detected, but the herbicides atrazine (and its major degradation products) and ametryn were most frequently detected in surface water, followed by hexazinone and simazine (Table 19). Like ethion, diazinon can have an acute or chronic toxicity standard calculated based on one-third or one-twentieth of the 96-hour LC_{50} for sensitive aquatic species. The most sensitive species is *Daphnia magna* (i.e., 48-hour EC_{50} = 0.8 µg/L; Table 2) and the calculated acute and chronic standards are 0.3 and 0.04 µg/L, respectively. For the S38B sampling location, four events (9/29/98-0.044; 1/6/99-0.067; 11/8/99-0.059; 8/8/00-0.06; method detection limit for all events: 0.019 µg/L) had detectable concentrations above the chronic calculated standard.

Whenever diazinon was present, it exceeded the 0.04 µg/L calculated chronic criteria. However, the USEPA (USEPA, 2005) derived ambient freshwater quality criteria should not affect aquatic organisms if the one-hour average concentration does not exceed 0.17 µg/L more than once every three years on the average and if the four-day average concentration does not exceed 0.017 µg/L more than once every three years on the average.

The most abundant of the measured sediment contaminants for urban basins were p,p'-DDE and p,p'-DDD (Table 20). The average concentrations of p,p'-DDE and PCB-1016 exceed the TEC for freshwater sediment.

The South Miami-Dade County agricultural area supports a wide variety of predominately row crops (e.g., tomatoes, beans, and squash) and had five sampling locations (S332DX/S176, S177, S178, S18C, and S331) (Figure 17). Endosulfan has been identified as the chemical of concern in this area, especially at S178 (Miles and Pfeuffer, 1997; Scott et al., 2002; Fulton et al., 2004), although atrazine had the highest frequency of detection (Table 21). The maximum atrazine concentration was considerably lower than any levels of concern. Scott et al. (2002) reported atrazine detections over 92 percent of the time from 1996 to 1997 using a substantially lower detection level. Their peak concentration detected for atrazine was similar to the average concentration reported by SFWMD.

Endosulfan is used to control whiteflies on vegetable crops like tomatoes. It is a mixture of two insecticidal stereoisomers: alpha endosulfan and beta endosulfan. Endosulfan can be oxidized to endosulfan sulfate and hydrolyzed to endosulfan diol. These metabolites have been observed in surface waters near agricultural activity (National Research Council Canada, 1975). Endosulfan is highly toxic to aquatic organisms (Johnson and Finley, 1980; Mayer and Ellersieck, 1986). Furthermore, in a national summary of pesticides in coastal areas, endosulfan had the highest hazard rating of pesticides inventoried (Pait et al., 1992).

Endosulfan (alpha and beta) has a promulgated state standard of 0.056 µg/L (Table 2). A plot of the complete period of record of endosulfan detections at water control structure S178 showed eight endosulfan water quality excursions occurring out of the 67 sampling events primarily between early 1993 and 1996 (Figures18a-e). Endosulfan surface water detections were not routinely preceded by significant rainfall. Also the majority of the endosulfan and endosulfan sulfate surface water detections corresponded with the growing season, which runs from September to April. Typically, sediment detections of endosulfan occurred after the surface water detections. However, the frequency and magnitude of endosulfan detections have decreased since the 1994-95 growing seasons. This may be attributed primarily to the availability of an alternative product (imidacloprid), grower education, and product label changes. The March 2007 detection (Figure 18e) was the last excursion since the February 2000 sampling event (Figure 18c). McPherson et al. (2000) reported frequent endosulfan detections at S177 during 1996, but no excursions above the state standard. Detections became less frequent in the following two years of the monitoring program (McPherson et al., 2000).

The DDT family of compounds was most often detected in the sediment in the South Miami-Dade County agricultural area along with numerous endosulfan detections (Table 22). The p,p’-DDE and p,p’-DDD average concentration was greater than the TEC while the p,p’-DDE average maximum concentration was greater than the PEC. A concentration above the TEC but less than the PEC has a possibility of harmful effects on freshwater sediment dwelling organisms. A level above the PEC demonstrates that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed. No sediment guidelines are available for endosulfan. However, a two-tiered ecological risk assessment identified endosulfan as having the highest potential for chronic risk to aquatic arthropods at S178 (Carriger et al., 2006).

The last area of sampling by the SFWMD pesticide monitoring network covered the locations (US41-25 and S12A/S12C) (Figure 19) that are considered relatively pristine, since these locations are the furthest from any agricultural activity. The water source for these structures is primarily the remnant Everglades. These sampling locations are used as reference. However, even at these remote locations atrazine was still present (Table 23). The average maximum concentration however is only 0.52 µg/L, compared to 0.284 to 6.32 µg/L in agricultural areas. Sampling performed by Miller et al. (1999) at S12D over a two year period, detected atrazine concentrations very similar to those detected under the SFWMD monitoring program. Although not determined, atmospheric deposition may be the most probable source of atrazine detected at these locations (USEPA, 2006a). Also present in the sediment at these locations is the ubiquitous p,p’-DDE as well as PCB-1260 (Table 25). Even at these remote locations, the average maximum p,p’-DDE concentration was greater than the TEC.

Conclusions

Due to the diverse variety of crops and the extensive spatial coverage of agriculture and urban areas as well as the large areal coverage of the monitoring program, no discernable pattern of detections was evident unless the data for a specific drainage basin are examined. Pesticide detections occur more frequently during the application season for a crop or location. Due to this diversity, it is critical that the timing of sampling be varied. Although the monitoring was performed on a quarterly basis, sampling could occur any time within that quarter. For the surface water sampling events, each month was sampled between four and seven times (Figure 2). For the sediment sampling, with the exception of September, between two and six sampling events were conducted per month (Figure 3). This randomness captured the varied periods of pesticide application.

The level of detection is also critical for data evaluation. As identified for the insecticides ethion and diazinon, the concentrations at which a pesticide is of concern can be very low. Additionally lower detection limits also reduces the chance of false negatives.

For endosulfan and ethion, SFWMD data were used for the product label changes, which restricted or curtailed pesticide application, helping to reduce environmental exposure. Additionally, SFWMD data were utilized in nine USEPA Reregistration Eligibility Decisions (RED) documents (USEPA, 1996a; USEPA, 1996b; USEPA, 1998c; USEPA, 1998d; USEPA, 1999; USEPA, 2002b; USEPA, 2003b; USEPA, 2006c; and USEPA, 2007). The RED documents summarize the risk assessment conclusions and outline any risk reduction measures necessary for a pesticide to continue to be registered in the United States.

Atrazine and its associated degradation products (atrazine desethyl and atrazine desisopropyl) were the most frequently detected compounds in the surface water while p,p'-DDE (the degradation product of DDT) was most frequently detected in the sediment.

Atrazine was detected at all locations at least once. The top nine locations for detections or those with over 90 percent were locations receiving drainage from either the EAA or urban areas. However, none of the detected concentrations were at a level of concern as they did not exceed the draft ambient aquatic life water quality criterion or the calculated acute or chronic toxicity values. Nine of the 14 locations selected for evaluation demonstrated a decreasing concentration over time for this reporting period.

The p,p'-DDE residues were ubiquitous and the majority of sampling locations had concentrations that could have harmful effects on freshwater sediment-dwelling organisms. Of the 32 locations evaluated, only eight had average location concentrations that were less than the TEC (i.e., the value at which sediment concentration should not have a harmful effect on sediment-dwelling organisms). The average concentration at S6, S2, S5A, and S178 was higher than the PEC, which means that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed. Trend analysis for these structures, as well as S177 and S3, demonstrated increasing concentration at S2 andS3, while decreasing trends were demonstrated at S178 and S177. Although lawful uses of DDT in the United States were curtailed by the USEPA in the early 1970s (USEPA, 1990), the persistence of its predominant environmental metabolite p,p'-DDE, has resulted in residue concentrations that are still at a potentially harmful level.

Since the sediment sampling upstream of the structures was performed at a fixed location, it is difficult to determine what the sediment represents due to potential scouring during pumping or gate openings. Any sediment accumulation or removal upstream is dependent on the operation of the structure. To actually determine contemporary p,p'-DDE residues being transported by the operation of the canal system, a suspended particle trap could be deployed to capture particulate material being transported in the canal. This would help identify which pesticides are being transported via suspended particulates in the respective canal. Sediment traps could be deployed over a specific time period to determine an integrated sediment pesticide contamination.

To determine exceedances of sediment or water quality criteria, pesticides concentrations from grab samples are typically compared to numerical standards or guidelines for sediment or water. However, specific criteria are lacking for most of the pesticides. Calculated criteria are based on the lowest acute toxicity value from the most sensitive aquatic species tested in a short-term test. However, these values are often from species that are not native to south Florida ecosystems. In general, aquatic databases are limited for native species.

Additionally, pesticide detections frequently occur with more than one compound at a time. The most frequently detected pesticides in surface water were the triazine herbicides, while the DDT family was most often detected in the sediment. Although evaluated on a single compound to a single species criterion, a discernable impact is not always evident. However, if the same family of compounds is detected, a synergistic or cumulative impact may be occurring. The current approach can be used to screen for chemicals of potential ecological concern. Probabilistic distributions of the detected concentrations could be compared to a probability distribution of effects data from relevant species. The resulting species sensitivity distributions could be used to characterize acute and chronic effects and the susceptibility of organism to different chemical stressors. This would determine what fraction of species is expected to be potentially affected above its acute or chronic effect level at a given environmental concentration.

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

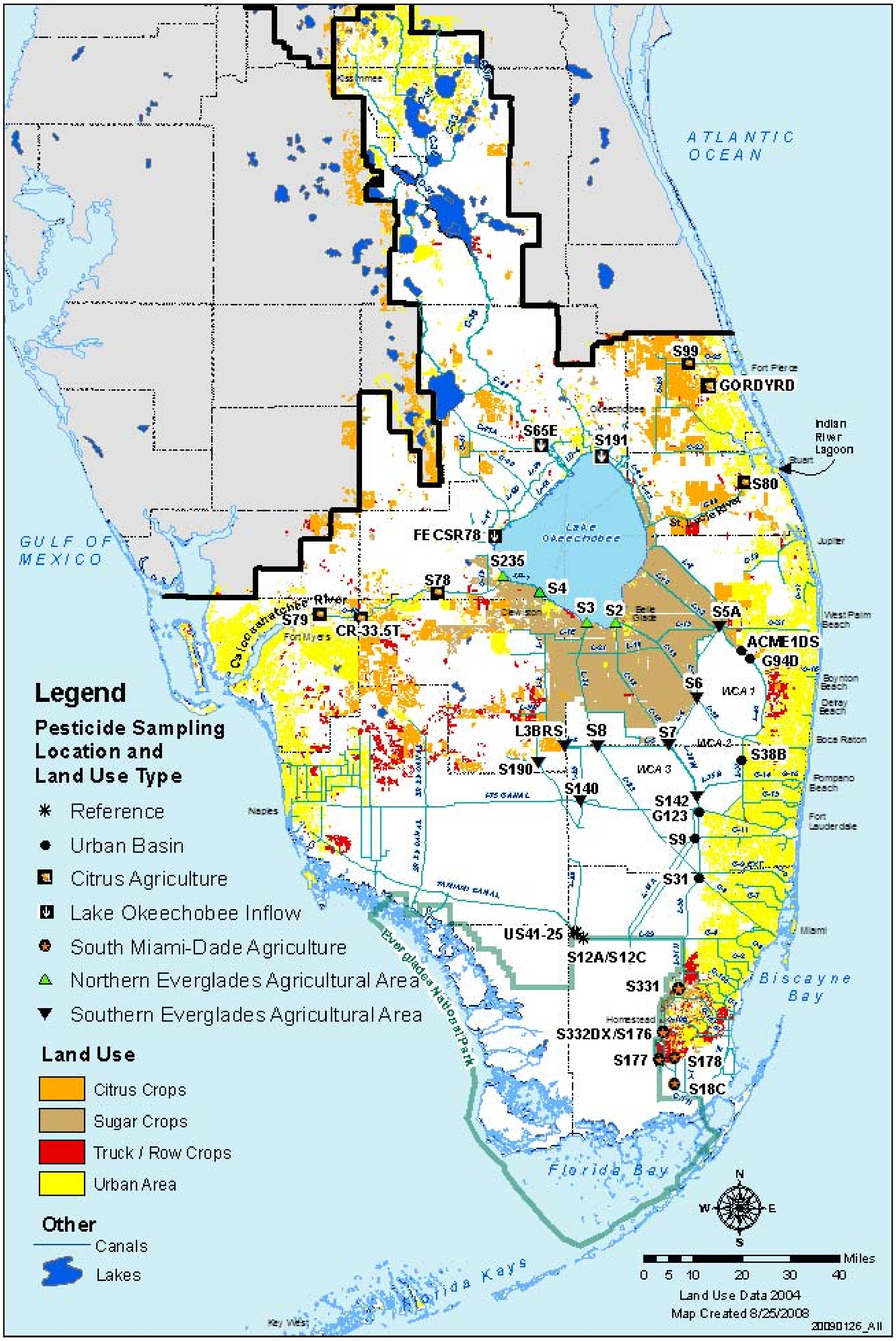

Table 1. Pesticides determined in samples taken by the South Florida Water Management District ambient pesticide monitoring network.

Pesticide	Surface Water	Sediment	Pesticide	Surface Water	Sediment
Chlorinated (phenoxy acid) Herbicides			Organochlorine Pesticides		
2,4-D	X	X	*aldrin*	X	X
2,4,5-T	X	X	alpha hexachlorocyclohexane (BHC)	X	X
2,4,5-TP (silvex)	X	X	beta hexachlorocyclohexane (BHC)	X	X
acifluorfen	X(1)	X(2)	delta hexachlorocyclohexane (BHC)	X	X
Urea Herbicides and Imidacloprid			*gamma BHC (lindane)*	X	X
diuron	X	X	carbophenothion	X	X
linuron	X	X	*chlordane*	X	X
imidacloprid	X(3)	-	chlorothalonil	X	X
Organonitrogen and Phosphorus Pesticides			cypermethrin	X	X(6)
alachlor	X	X	p,p'-DDD	X	X
ametryn	X	X	p,p'-DDE	X	X
atrazine	X	X	*p,p'-DDT*	X	X
atrazine desethyl	X(4)	-	dicofol (kelthane)	X	X
atrazine desisopropyl	X(4)	-	*dieldrin*	X	X
azinphos methyl (guthion)	X	X	*alpha endosulfan*	X	X
bromacil	X	X	*beta endosulfan*	X	X
butylate	X	-	endosulfan sulfate	X	X
chlorpyrifos ethyl	X	X	*endrin*	X	X
chlorpyrifos methyl	X	X	endrin aldehyde	X	X
demeton	X	X	*heptachlor*	X	X
diazinon	X	X	heptachlor epoxide	X	X
disulfoton	X	X	*methoxychlor*	X	X
ethion	X	X	*mirex*	X	X
ethoprop	X	X	permethrin	X	X(6)
fenamiphos	X	X	*PCB-1016*	X	X
fonophos	X	X	*PCB-1221*	X	X
hexazinone	X(7)	X(7)	*PCB-1232*	X	X
malathion	X	X	*PCB-1242*	X	X
metalaxyl	X	-	*PCB-1248*	X	X
methamidophos	X(5)	X	*PCB-1254*	X	X
metolachlor	X	X	*PCB-1260*	X	X
metribuzin	X	X	*toxaphene*	X	X
mevinphos	X	X	trifluralin	X	X
monocrotophos	X(5)	X	Dipyridillium Herbicides		
naled	X(8)	X(8)	paraquat	X(5)	X(5)
norflurazon	X(7)	X(7)	diquat	X(5)	X(5)
parathion ethyl	X	X	Water Soluble Pesticides		
parathion methyl	X	X	acephate	X(5)	-
phorate	X	X	dimethoate	X(5)	-
prometon	X(6)	-	monocrotophos	X(5)	X
prometryn	X	X	Phosphonoglycine Herbicide		
simazine	X	X	glyphosate	X(5)	-
Carbamates			Benzimidazole Fungicide		
aldicarb	X(5)	X(5)	benomyl	X(5)	X(5)
carbaryl	X(5)	X(5)	Ethylenebisdithiocarbamate Degradation Product		
carbofuran	X(5)	X(5)	ethylene thiourea	X(5)	-
methomyl	X(5)	X(5)			
oxamyl	X(5)	X(5)			

Compounds in italics have a Florida Administrative Code 62-302 Water Quality Class I or III criterion.
- : pesticide not analyzed in matrix
(1) added November 2002 sampling event
(2) added May 2001 sampling event
(3) added February 1997 sampling event
(4) added November 1999 sampling event
(5) not analyzed after May 1997 sampling event
(6) added December 2001 sampling event
(7) added December 1994 sampling event
(8) added March 2001 sampling event

Table 2. Freshwater surface water quality criteria and toxicity of selected pesticides to freshwater aquatic invertebrates and fishes (µg/L).

Pesticide	Florida Administrative Code 62-302		USEPA[19]		Water Flea *Daphnia magna*			Bluegill *Lepomis macrochirus*			Largemouth Bass *Micropterus salmoides*			Channel Catfish *Ictalurus punctatus*		
	Class I	Class III	CMC*	CCC**	48 hr EC_{50}	Acute Toxicity***	Chronic Toxicity***	96 hr LC_{50}	Acute Toxicity	Chronic Toxicity	96 hr LC_{50}	Acute Toxicity	Chronic Toxicity	96 hr LC_{50}	Acute Toxicity	Chronic Toxicity
2,4-D	≤ 100	-	-	-	25,000 (9)	8,333	1,250	180,000 (8)	60,000	9,000	-	-	-	-	-	-
					-	-	-	900 (48 hr) (6)	113	25	-	-	-	-	-	-
alachlor	-	-	-	-	21,000 (7)	7,000	1,050	2,800 (4)	933	140	-	-	-	-	-	-
					10,000 (24)	3,333	500	4,300 (24)	1,433	215	-	-	-	-	-	-
ametryn	-	-	-	-	28,000 (7)	9,333	1,400	4,100 (4)	1,367	205	-	-	-	-	-	-
atrazine	-	-	-	-	6,900 (7)	2,300	345	16,000 (4)	5,333	800	-	-	-	7,600 (4)	2,533	380
bromacil	-	-	-	-	-	-	-	127,000 (7)	42,333	6,350	-	-	-	-	-	-
					121,000 (18)	40,333	6,050	127,000 (18)	42,333	6,350	-	-	-	-	-	-
chlorpyrifos (ethyl)	-	-	0.083	0.041	1.7 (7)	0.57	0.085	2.6 (4)	0.87	0.13	-	-	-	280 (7)	93	14
					0.1 (7)	0.03	0.005	5.8 (7)	1.9	0.3	-	-	-			
					0.1 (20)	0.03	0.005	1.8 (20)	0.6	0.1	-	-	-			
diazinon	-	-	0.17	0.17	0.8 (1)	0.3	0.04	168 (1)	56	8.4	-	-	-	-	-	-
					0.9 (3)	0.3	0.045	165 (2)	55	8.3	-	-	-	-	-	-
					-	-	-	16,000 (4)	5,333	800	-	-	-	-	-	-
					0.83 (10)	0.28	0.04	460 (10)	153	23	-	-	-	-	-	-
diuron	-	-	-	-	1,400 (7)	457	70	5,900 (4)	1,967	295	-	-	-	-	-	-
					1,400 (11)	457	70	-	-	-	-	-	-	-	-	-
endosulfan	≤ 0.056	≤ 0.056	0.22	0.056	166 (7)	55	8	1 (1)	0.3	0.05	-	-	-	1 (1)	0.3	0.05
					-	-	-	2 (2)	0.67	0.10	-	-	-	1.5 (7)	0.5	0.08
					166 (12)	55	8	1.7 (12)	0.57	0.09	-	-	-	-	-	-
ethion	-	-	-	-	0.06 (1)	0.02	0.003	210 (1)	70	11	173 (1)	58	9	7,600 (1)	2,533	380
					-	-	-	13 (2)	4.3	0.65	150 (3)	50	8	7,500 (3)	2,500	375
					-	-	-	22 (3)	7.3	1.1	-	-	-	-	-	-
					0.056 (15)	0.02	0.003	210 (15)	70	11	173 (15)	58	9	-	-	-
ethoprop	-	-	-	-	93 (7)	31	4.7	-	-	-	-	-	-	-	-	-
hexazinone	-	-	-	-	151,600 (7)	50,533	7,580	100,000 (7)	33,333	5,000	-	-	-	-	-	-
					151,600 (13)	50,533	7,580	505,000 (13)	168,333	25,250	-	-	-	-	-	-
malathion	≤ 0.1	≤ 0.1	-	0.1	1 (1)	0.3	0.05	103 (1)	34	5.2	285 (1)	95	14	8,970 (1)	2,990	449
					1.8 (3)	0.6	0.09	100 (21)	37	5.5	-	-	-	7,620 (7)	2,540	381
								12 (22)	4	0.6	-	-	-	-	-	-
metalaxyl	-	-	-	-	28,000 (7)	9,333	1,400	139,000 (7)	46,333	6,950	-	-	-	-	-	-
					29,000 (14)	9,667	1,450	139,000 (7)	46,333	6,950	-	-	-	-	-	-
metolachlor	-	-	-	-	23,500 (7)	7,833	1,175	15,000 (4)	5,000	750	-	-	-	4,900 (5)	1,633	245
metribuzin	-	-	-	-	4,200 (7)	1,400	210	80,000 (4)	26,667	4,000	-	-	-	100,000 (7)	33,333	5,000
					4,200 (16)	1,400	210	75,900 (16)	25,300	3,795	-	-	-	-	-	-
naled	-	-	-	-	0.3 (25)	0.1	0.02	2,200 (25)	733	110	1,900 (25)	633	95	710 (25)	237	36
norflurazon	-	-	-	-	15,000 (7)	5,000	750	16,300 (7)	5,433	815	-	-	-	>200,000 (4)	>67,000	>10,000
					>15,000 (17)	>5,000	>750	16,300 (17)	5,433	815	-	-	-	-	-	-
prometryn	-	-	-	-	18,590 (23)	6,197	930	10,000 (23)	3,333	500	-	-	-	-	-	-
prometon	-	-	-	-	-	-	-	40,000 (5)	13,333	2,000	-	-	-	-	-	-
simazine	-	-	-	-	1,100 (7)	367	55	90,000 (4)	30,000	4,500	-	-	-	-	-	-

* CMC (criteria maximum concentration) is the highest concentration of a pollutant in surface water to which aquatic life can be exposed for a short period of time (1-hour average) without deleterious effects (40CFR131.36, July 1, 2005)
** CCC (criteria continuous concentration) is the highest concentration of a pollutant in surface water to which aquatic life can be exposed for an extended period of time (4 days) without deleterious effects (40CFR131.36, July 1, 2005)
*** Florida Administrative Code Section 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.
(1) Johnson and Finley, 1980; (2) Schneider, 1979; (3) USEPA, 1972; (4) Hartley and Kidd, 1987; (5) Montgomery, 1993; (6) Verschueren, 1983; (7) USEPA, 1991; (8) Mayer and Ellersieck, 1986; (9) USEPA, 2006a; (10) USEPA, 2004; (11) USEPA, 2003b; (12) USEPA, 2002a; (13) USEPA, 1994a; (14) USEPA, 1994b; (15) USEPA, 1998a; (16) USEPA, 1998b; (17) USEPA, 1996a; (18) USEPA, 1996b; (19) USEPA, 2006b; (20) USEPA, 2002c; (21) USEPA, 1977; (22) Davis, 1970; (23) USEPA, 1996c; (24) USEPA, 1998e; (25) USEPA, 2002d

Table 3. Freshwater sediment assessment guidelines [1].

Parameter	Threshold Effect Concentration[2] (µg/Kg)	Probable Effect Concentration[3] (µg/Kg)
atrazine	0.30	NG
azinphos ethyl	0.018	NG
azinphos methyl	0.062	NG
total chlordane	3.2	18
diazinon	0.38	NG
dieldrin	1.9	62
sum DDD	4.9	28
sum DDE	3.2	31
sum DDT	4.2	63
total DDT	5.3	570
endrin	2.2	210
heptachlor epoxide	2.5	16
lindane	2.4	5.0
malathion	0.67	NG
simazine	0.34	NG
toxaphene	0.10	32
total PCB's	60	680

NG: no guideline
[1] MacDonald Environmental Sciences, Ltd. and United States Geological Survey (2003)
[2] Threshold Effect Concentration: The threshold effect concentration is intended to identify concentrations below which harmful effects on freshwater sediment–dwelling organisms are unlikely to be observed.
[3] Probable Effect Concentration: The probable effect concentration is intended to identify concentrations above which harmful effects on freshwater sediment-dwelling organisms are likely to be frequently or always observed.

Table 4. Number of pesticide detections per sampling event.

	Higher Detection Levels April 1992 to September 1994		Lower Detection Levels December 1994 to December 2007	
	Surface Water	Sediment	Surface Water	Sediment
Number of Sampling Events	15	4	53	26
Average Number of Detections	22	32	84	30
Percent Detections	1.2	2.2	3.7	1.5

Table 5. Number of pesticides detected during a surface water sampling event by location from April 1992 to December 2007.

Land Use or Drainage Basin Type	Location	Average Number of Pesticides Detected per Sampling Event	Median Number of Pesticides Detected per Sampling Event
Lake Okeechobee inflow	S65E	1	1
	S191	1	1
	FECSR78	1	1
citrus	S99	3	3
	GORDYRD	3	3
	S80	3	3
	CR33.5T	5	5
	S78	4	4
	S79	5	5
northern EAA	S2	3	3
	S3	3	3
	S4	3	3
	S235	3	3
southern EAA	S5A	3	3
	S6	3	3
	S7	2	2
	S8	2	2
	L3BRS	2	2
	S190	2	2
	S142	2	2
	S140	2	2
urban	S9	1	1
	G94D	3	3
	ACME1DS	3	3
	G123	1	1
	S31	1	1
	S38B	3	4
South Miami-Dade County	S332DX/S176	1	1
	S177	1	1
	S178	2	2
	S18C	1	1
	S331	1	1
reference	US421-25	0	0
	S12A/S12C	1	1

EAA: Everglades Agricultural Area

Figure 2. Average percentage of pesticide surface water detections by month sampled (April 1992 to December 2007).

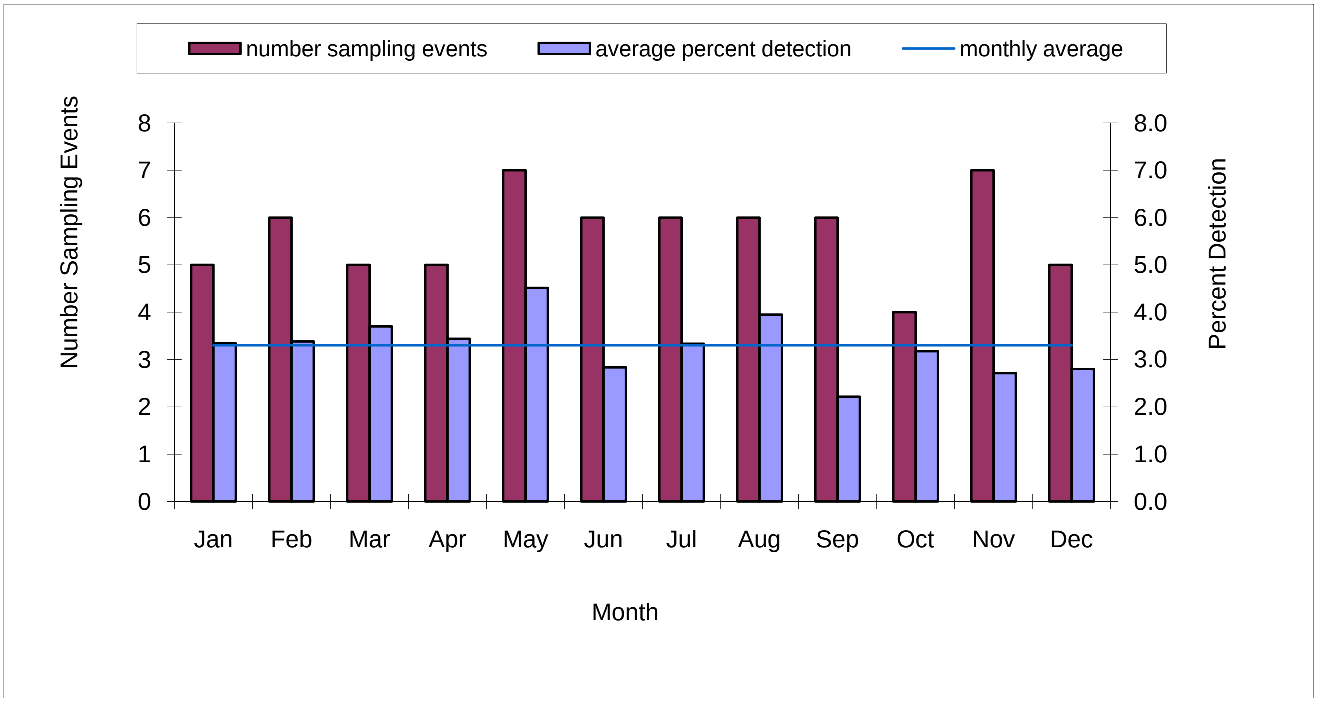

Figure 3. Average percentage of pesticide sediment detections by month sampled (April 1992 to December 2007).

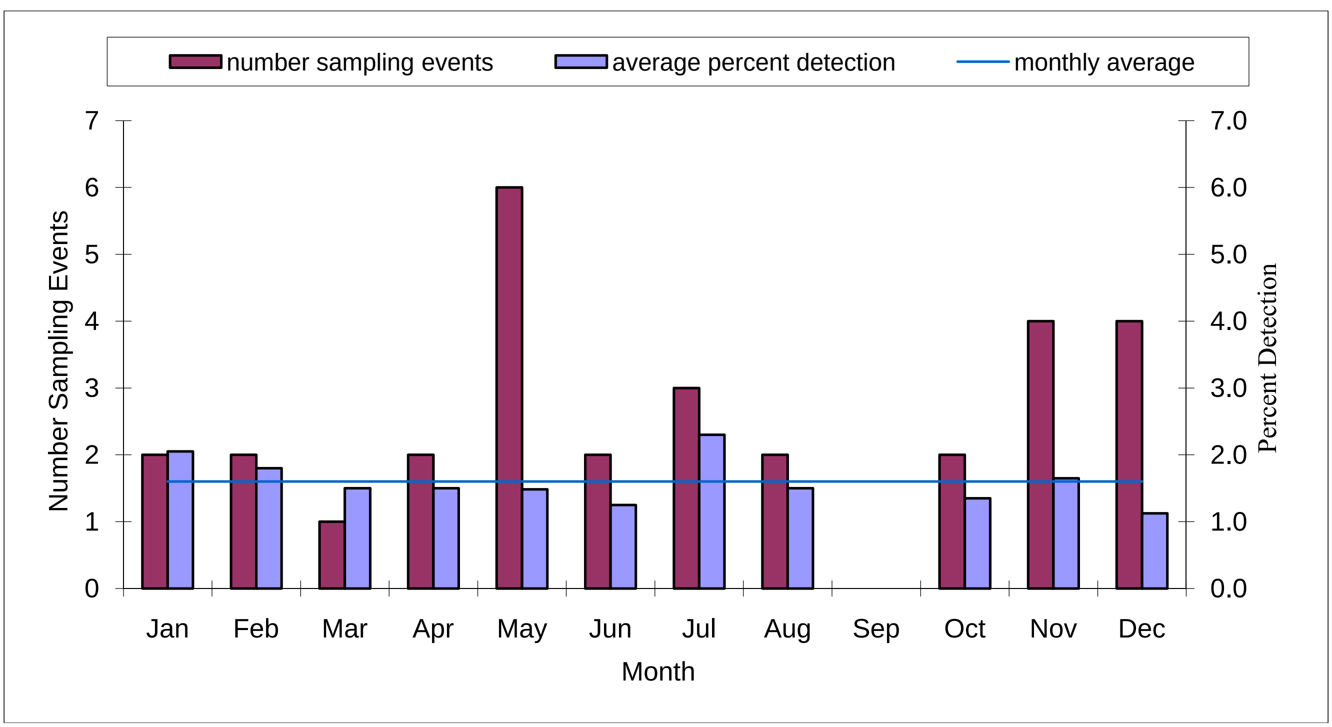

Table 6. Twenty most frequently detected pesticides and degradation products in surface water (April 1992 to December 2007).

Action	Pesticide or Degradation Product	Number Detections	Number Sampling Events With No Detections
herbicide	atrazine	1,517	0
herbicide	ametryn	714	0
herbicide	simazine	472	1
	atrazine desethyl	448	0
herbicide	norflurazon	397	0
herbicide	hexazinone	364	3
herbicide	bromacil	342	3
	atrazine desisopropyl	173	6
herbicide	diuron	97	28
insecticide	alpha endosulfan	82	38
	endosulfan sulfate	81	19
herbicide	metolachlor	58	36
insecticide	beta endosulfan	42	44
herbicide	2,4-D	30	47
insecticide	ethion	27	45
insecticide	ethoprop	22	56
herbicide	metribuzin	18	53
insecticide	metalaxyl	15	54
insecticide	diazinon	15	56
herbicide	prometon	11	19

Table 7. Twenty most frequently detected pesticides and degradation products in sediment (April 1992 to December 2007).

Action	Pesticide or Degradation Product	Number Detections	Number Sampling Events With No Detections
	p,p'-DDE	367	0
insecticide	p,p'-DDD	150	1
herbicide	ametryn	92	3
	PCB-1254	41	9
insecticide	p,p'-DDT	32	7
insecticide	beta endosulfan	26	12
	endosulfan sulfate	26	11
insecticide	ethion	24	13
insecticide	chlordane	23	15
herbicide	atrazine	22	17
insecticide	alpha endosulfan	18	16
insecticide	dieldrin	15	19
	PCB-1260	11	20
insecticide	dicofol	10	27
herbicide	diquat	9	8
herbicide	bromacil	8	25
herbicide	norflurazon	7	20
	PCB-1242	5	27
herbicide	diuron	5	27
	PCB-1016	3	28
insecticide	aldrin	3	27

Table 8. Atrazine surface water detection summary by sampling location from April 1992 to December 2007.

Location	Drainage Basin Type	Percent Detections	Number of Times Sampled	Average Concentration (µg/L)	Maximum Concentration (µg/L)
S6	southern EAA	97	67	0.88	6.8
S38B	urban	95	40	1.42	4.4
ACME1DS	urban	95	42	0.21	1.3
G94D	urban	95	43	0.20	1.5
S3	northern EAA	94	68	0.26	0.78
S5A	southern EAA	93	67	1.07	11
S4	northern EAA	91	68	0.56	7.1
S2	northern EAA	91	68	0.41	4.9
S7	southern EAA	90	67	0.86	18
S78	citrus	90	68	0.36	2.2
S235	northern EAA	88	68	0.48	8.5
S8	southern EAA	87	67	1.01	12
CR33.5T	citrus	87	68	0.67	12
S79	citrus	85	68	0.36	2.3
S142	southern EAA	83	43	0.13	0.58
G123	urban	71	40	0.14	1.9
S80	citrus	68	68	0.17	1
L3BRS	southern EAA	66	67	0.24	1.7
S331	South Miami-Dade County	64	43	0.04	0.22
S65E	Lake Okeechobee inflow	60	68	0.07	0.2
S31	urban	57	67	0.2	1.5
S9	urban	54	67	0.101	0.32
S12A/S12C	reference	53	67	0.08	0.93
S140	southern EAA	53	43	0.062	0.17
S332DX/S178	South Miami-Dade County	50	67	0.062	0.4
S18C	South Miami-Dade County	50	67	0.049	0.31
S177	South Miami-Dade County	47	67	0.058	0.4
S191	Lake Okeechobee inflow	46	68	0.08	0.4
S190	southern EAA	46	67	0.063	0.32
S178	South Miami-Dade County	46	67	0.035	0.089
FECSR78	Lake Okeechobee inflow	40	68	0.07	0.26
US41-25	reference	21	67	0.023	0.10
S99	citrus	9	68	0.018	0.032
GORDYRD	citrus	3	33	0.03	0.03

EAA: Everglades Agricultural Area

Figure 4. Atrazine surface water concentrations detected at S7.

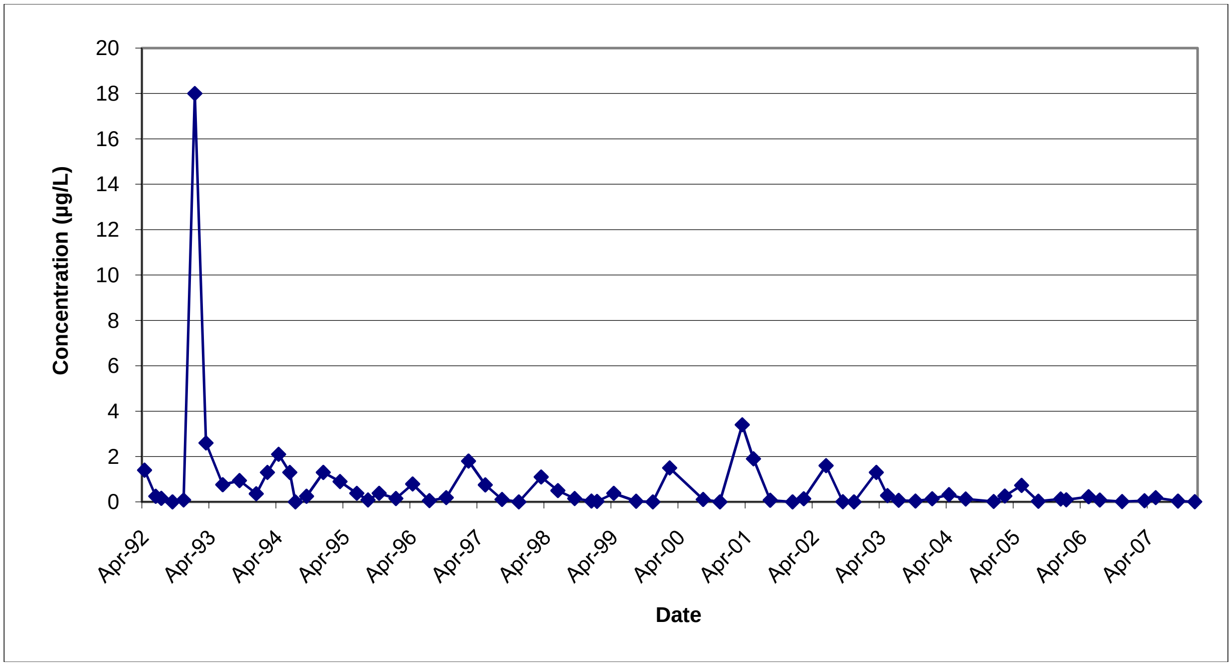

Figure 5. Atrazine surface water concentrations detected at S38B.

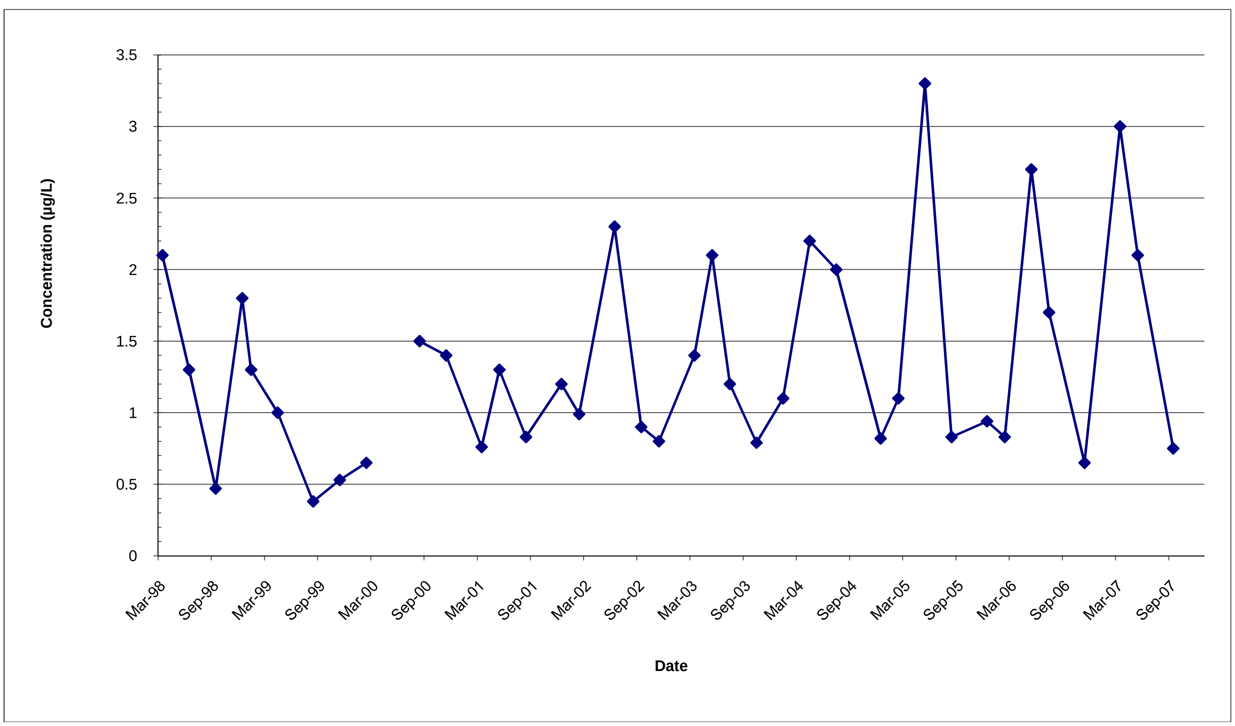

Figure 6. Atrazine surface water concentrations detected at S6.

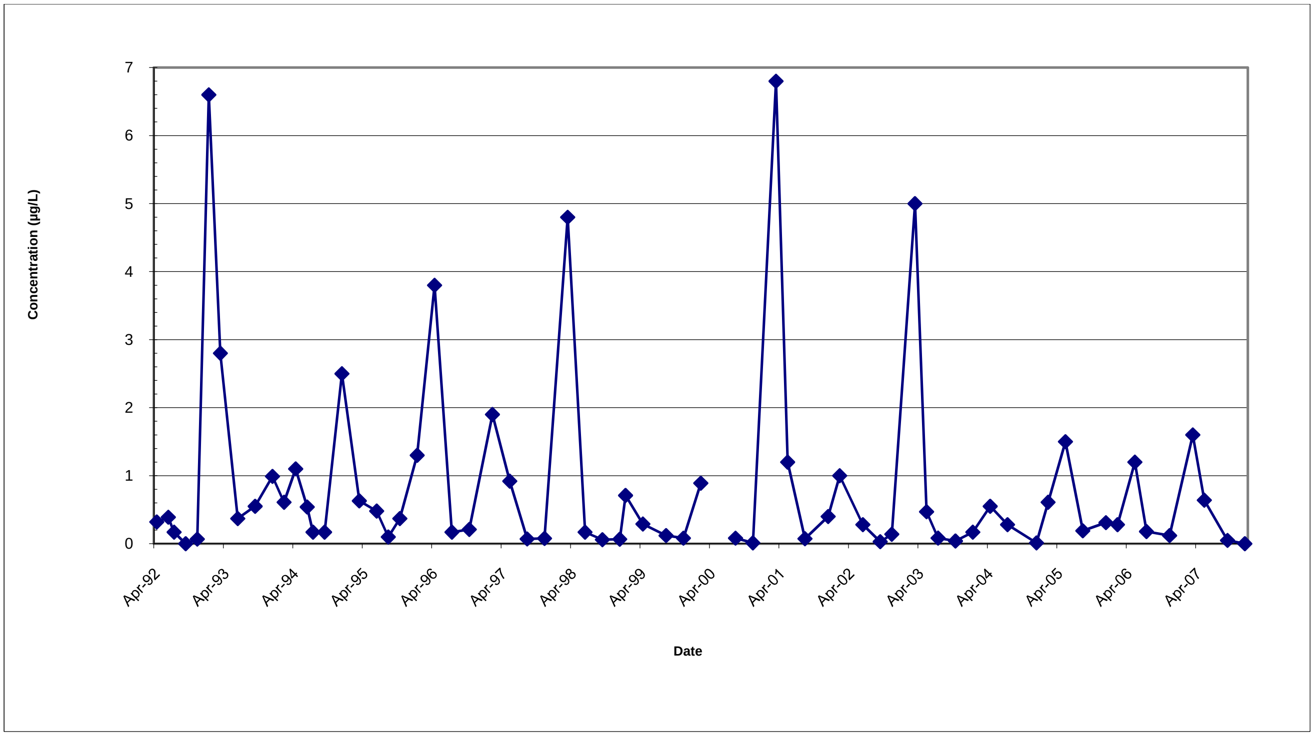

Figure 7. Annual atrazine surface water concentrations at locations receiving drainage from the northern Everglades Agricultural Area.

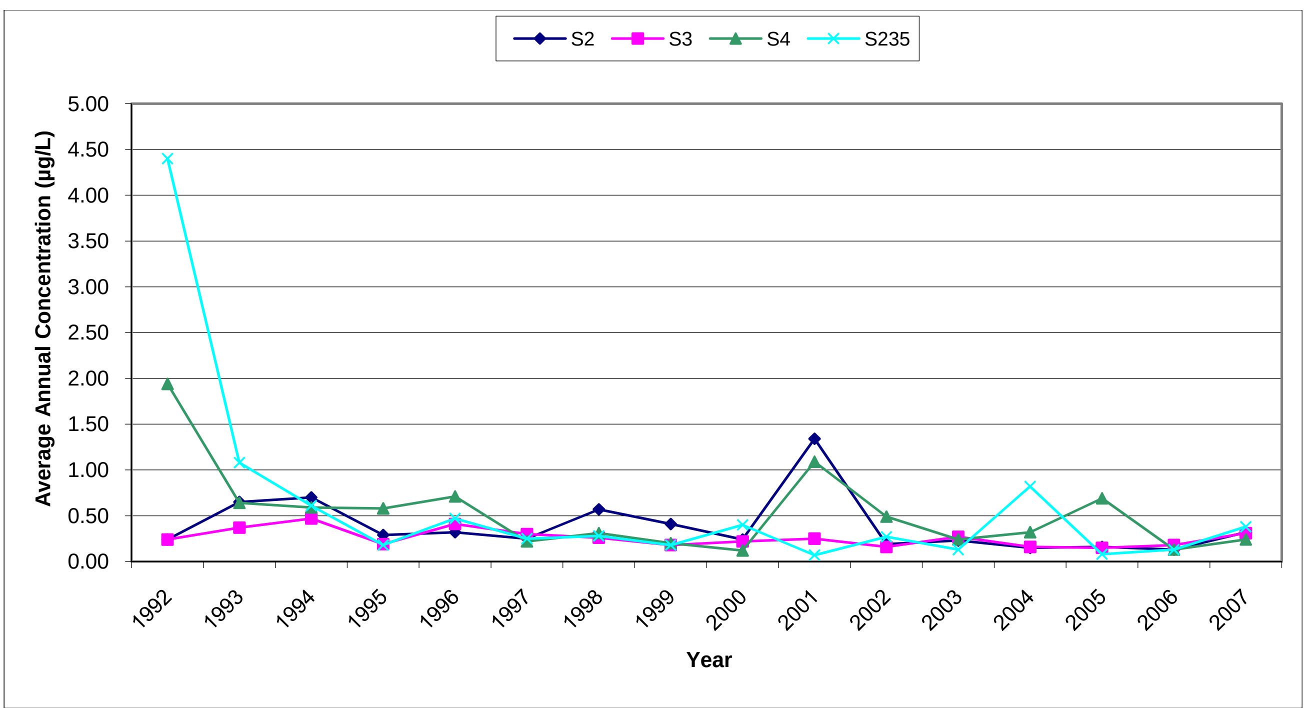

Figure 8. Annual atrazine surface water concentrations at selected locations receiving drainage from the southern Everglades Agricultural Area.

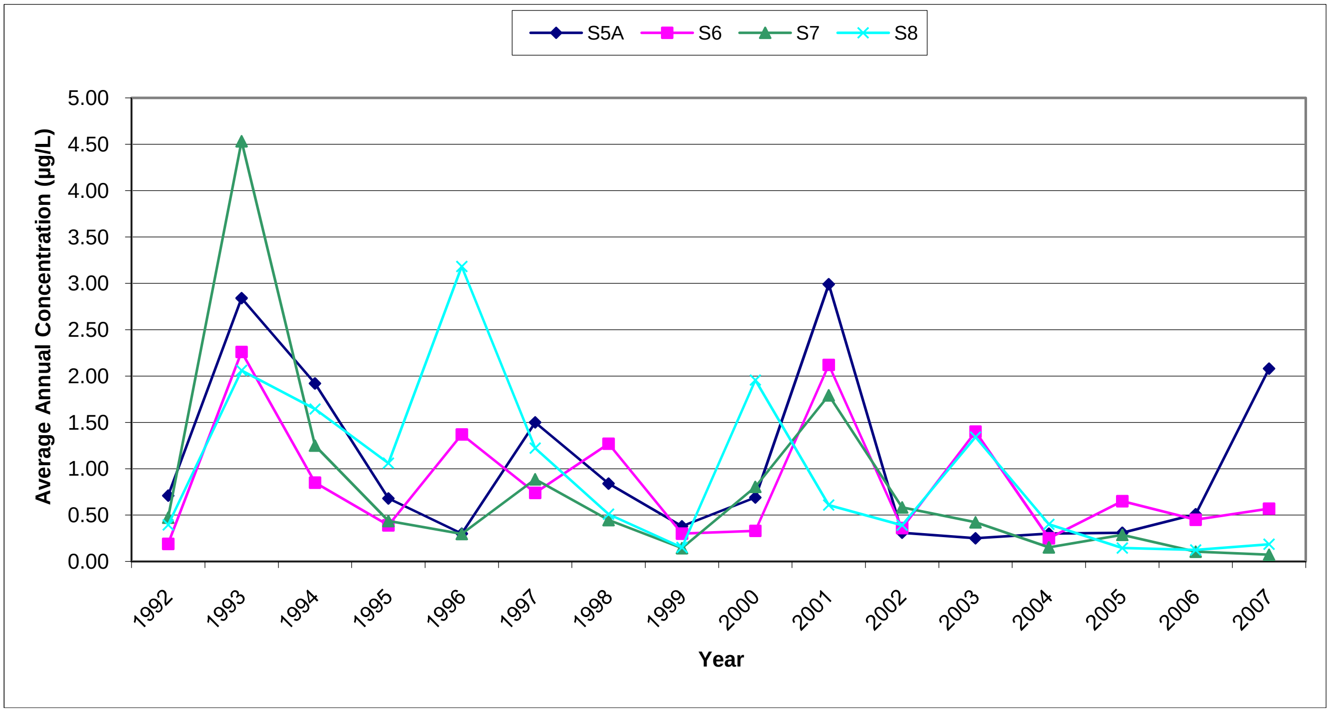

Figure 9. Annual atrazine surface water concentrations at locations receiving drainage from urban areas.

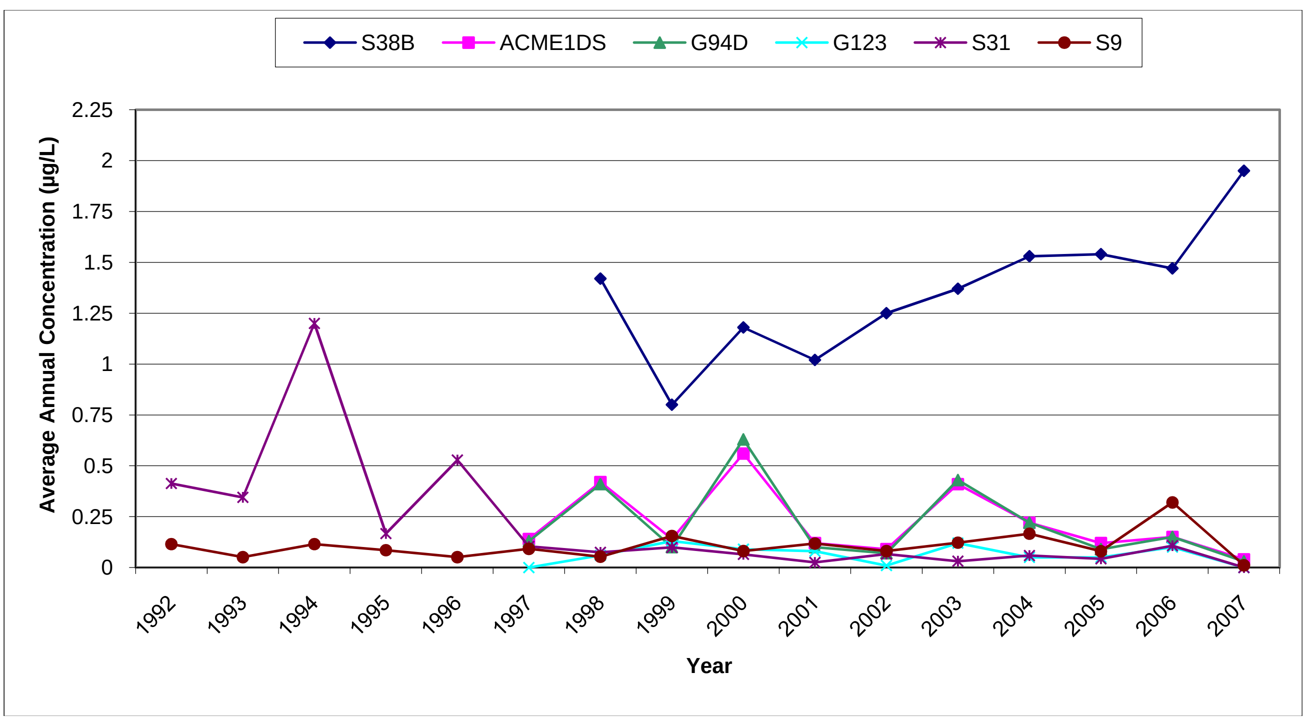

Table 9. Summary of p,p'-DDE sediment detections by sampling location from April 1992 to December 2007.

Location	Percent Detections	Number of Times Sampled	Average Concentration (µg/Kg)	Maximum Concentration (µg/Kg)
S5A	93	30	**53**	**300**
S2	90	30	**78**	**393**
S178	90	30	**40**	**89**
S177	87	30	21.6	**70**
S3	83	30	26	**92**
S6	77	30	**98**	**390**
S4	73	30	*19.3*	**58**
S31	70	30	*9.8*	*21*
S79	63	30	*9.9*	*18*
S80	63	30	*6.2*	*11*
S8	53	30	*4.5*	*13*
S7	50	30	*11*	**55**
G94D	50	22	*4.4*	*10*
S332DX/S176	33	30	*5*	*18*
ACME1DS	48	21	*4.3*	*7.9*
S142	41	22	*8*	*21*
S99	23	30	*4.5*	*11*
S18C	23	30	*3.5*	*8.7*
S331	32	22	2.6	*3.9*
S190	20	30	*4.6*	*15*
L3BRS	13	30	2.7	*3.4*
G123	15	20	*6.9*	*11*
S78	10	30	*3.2*	*4.5*
S191	10	30	2.9	*4.7*
S235	7	30	*10*	*18*
S12A/S12C	7	30	*4.3*	*6.3*
S38B	5	19	*4.6*	*4.6*
FECSR78	3	30	2.8	2.8
S9	3	29	2.2	2.2
US41-25	3	30	1.4	1.4
S65E	0	30	0	0
S140	0	22	0	0

Italicized values exceed the Threshold Effect Concentration (TEC): 3.2 µg/Kg
Bold values exceed the Probable Effect Concentration (PEC): 31 µg/Kg)
(MacDonald Environmental Sciences, Ltd. and United States Geological Survey, 2003)

Figure 10. Biannual p,p'-DDE sediment concentrations from selected locations from April 1992 to December 2007.

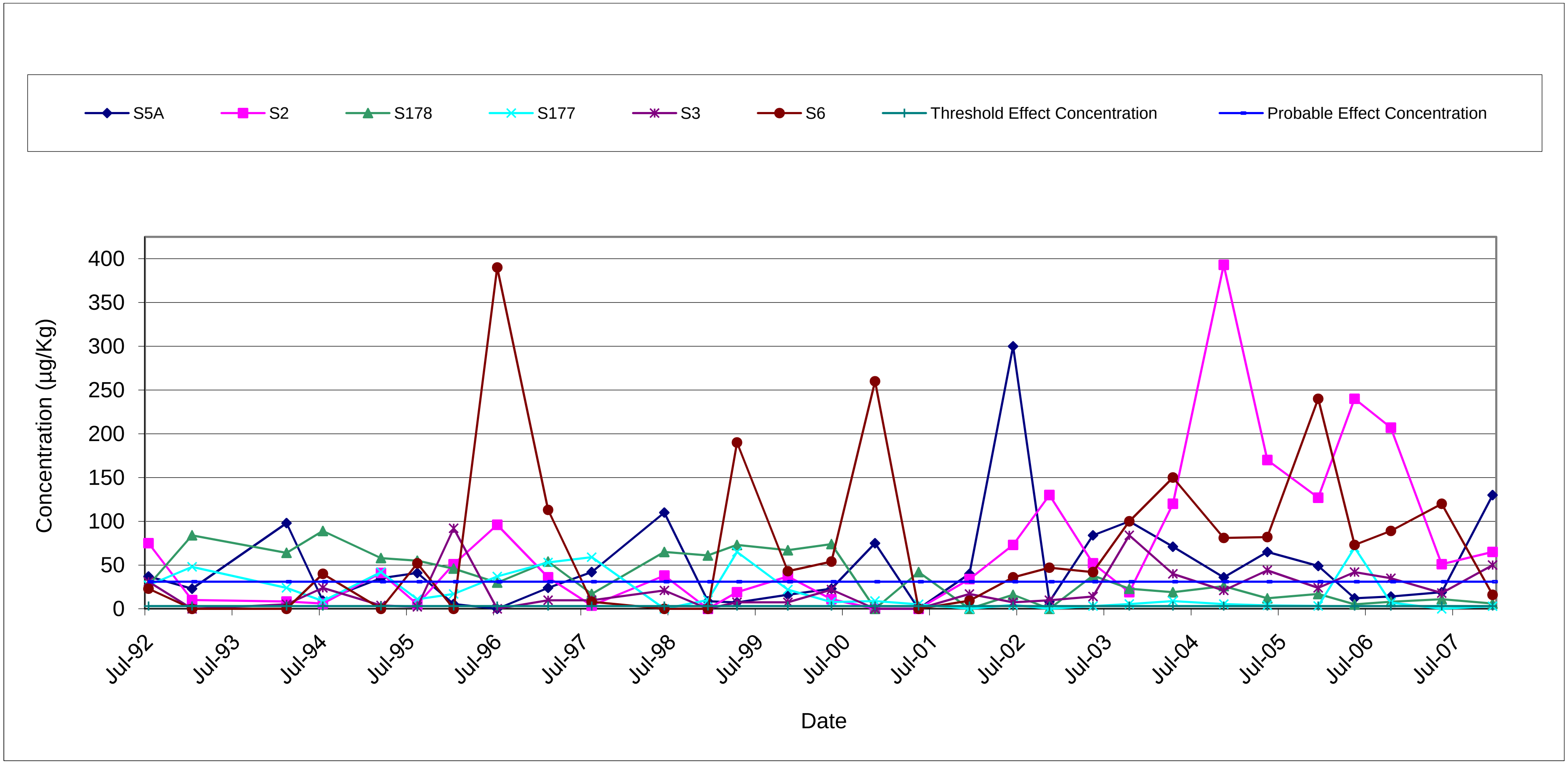

Figure 11. Lake Okeechobee basin sampling locations.

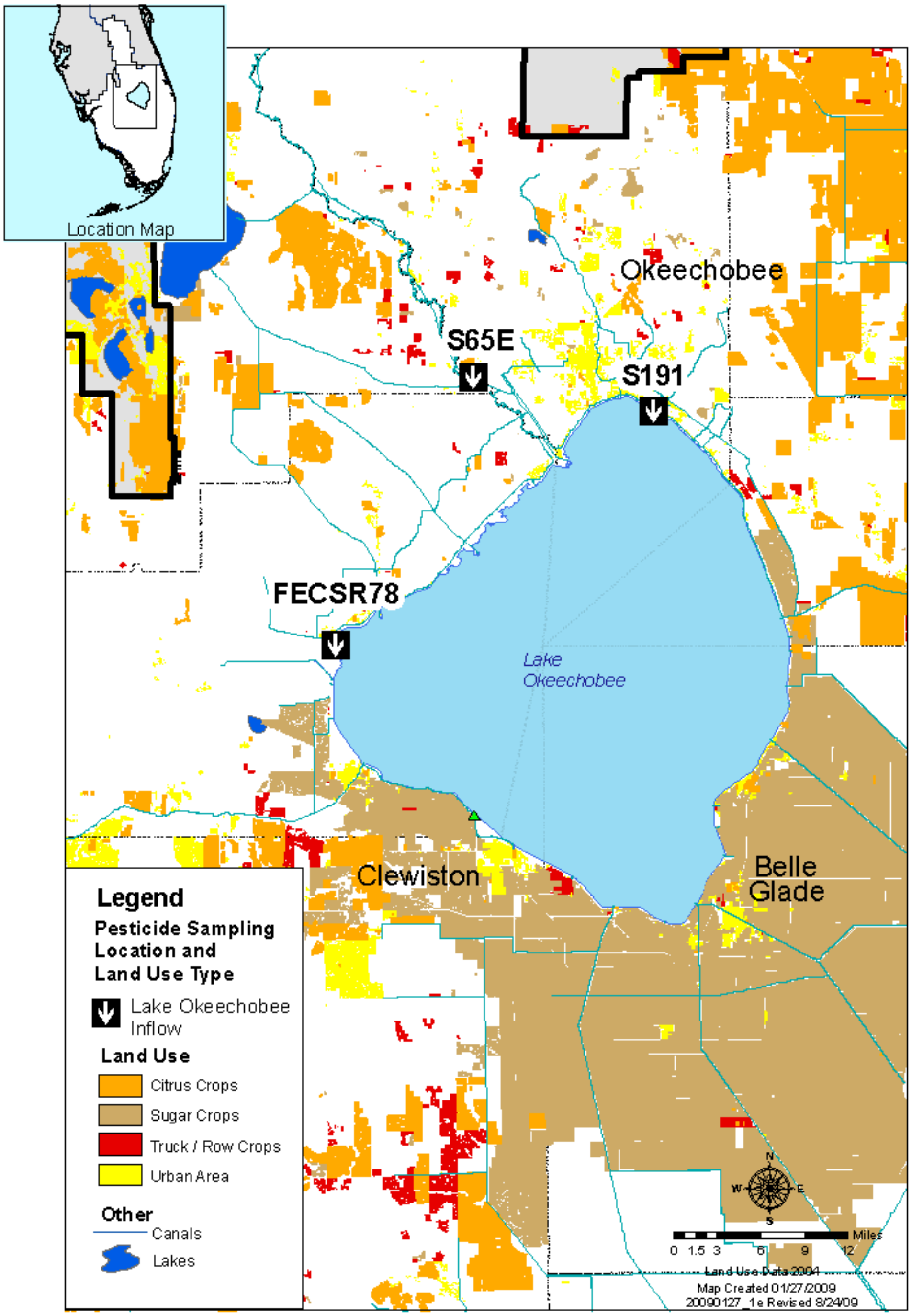

Table 10. Surface water pesticide detections for Lake Okeechobee basin sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/L)	Maximum Concentration (µg/L)	Concentration Geometric Mean	Median Concentration
atrazine	99	0.08	0.40	0.05	0.06
bromacil	57	0.11	1.2	0.08	0.08
hexazinone	37	0.13	1.3	0.07	0.06
atrazine desethyl	25	0.02	0.042	0.023	0.023
simazine	24	0.06	0.50	0.04	0.03
norflurazon	15	0.07	0.16	0.05	0.05
2,4-D	5	0.96	3.3	0.80	0.79
metolachlor	5	0.10	0.24	0.09	0.08
ametryn	2	0.034	0.049	0.034	0.034
metribuzin	2	0.052	0.071	0.048	0.052

Table 11. Sediment pesticide detections for Lake Okeechobee basin sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/Kg)	Maximum Concentration (µg/Kg)	Threshold Effect Concentration (µg/Kg)	Probable Effect Concentration (µg/Kg)
p,p'-DDE	4	2.8	*4.7*	3.2	31
diquat	2	940	1100	-	-

Italicized values exceed the Threshold Effect Concentration (TEC)

- No guideline available

Figure 12. Citrus agriculture sampling locations.

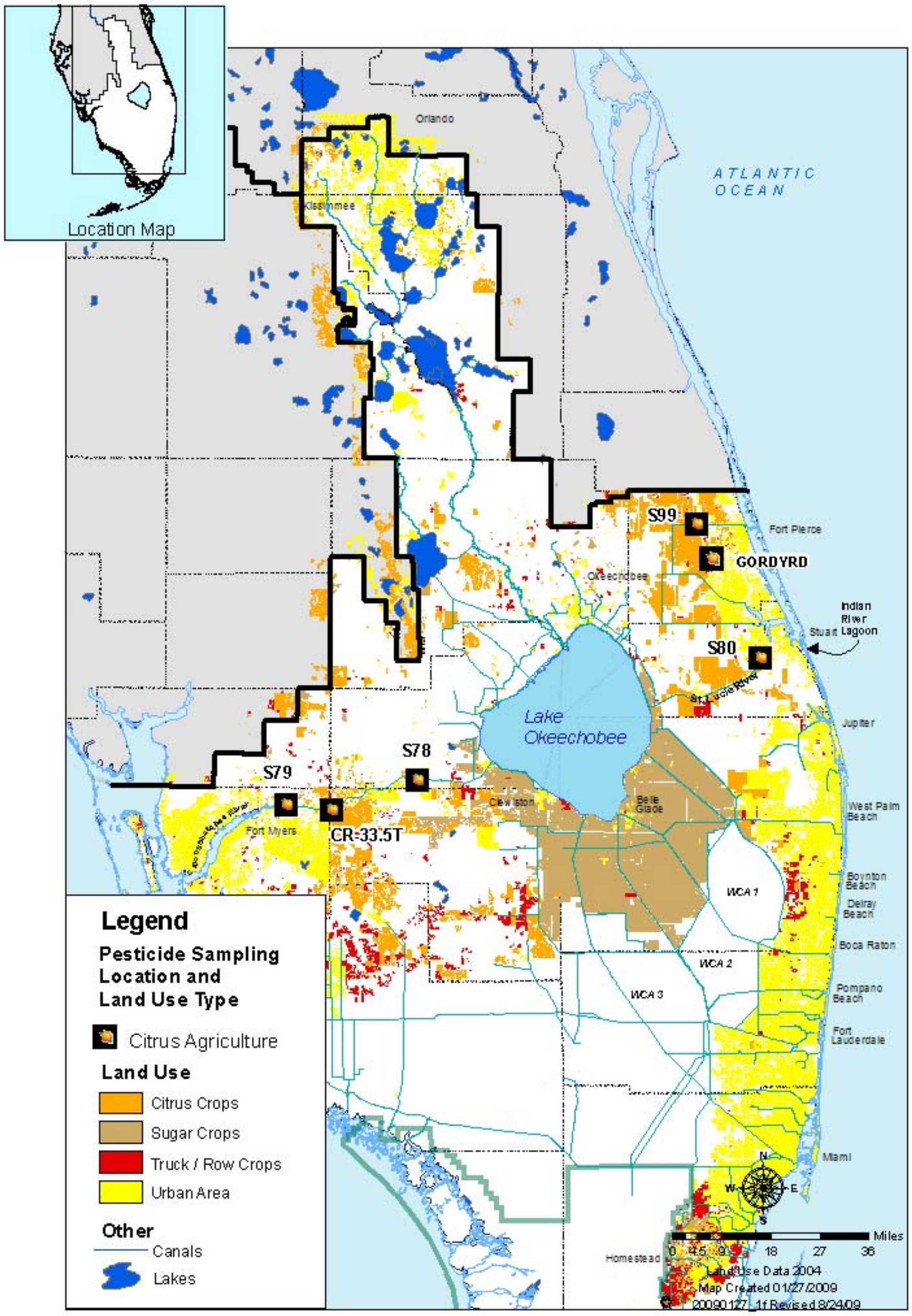

Table 12. Surface water pesticide detections for citrus agriculture sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/L)	Maximum Concentration (µg/L)	Concentration Geometric Mean	Median Concentration
norflurazon	264	0.48	3.9	0.34	0.35
simazine	258	0.22	7.3	0.08	0.07
atrazine	231	0.27	12	0.13	0.13
bromacil	208	0.64	8.6	0.31	0.32
atrazine desethyl	101	0.03	1.0	0.024	0.022
hexazinone	94	0.041	0.75	0.029	0.024
ametryn	85	0.03	0.21	0.022	0.018
diuron	67	0.99	16	0.51	0.49
atrazine desisopropyl	60	0.02	0.13	0.02	0.02
ethion	25	0.11	0.83	0.065	0.055
metolachlor	12	0.16	1.2	0.11	0.11
metalaxyl	9	0.09	0.21	0.11	0.10
2,4-D	6	1.96	4.1	1.7	1.7
endosulfan sulfate	4	0.027	0.048	0.026	0.027
malathion	4	0.06	0.14	0.053	0.048
alpha endosulfan	3	0.0036	0.0065	0.0031	0.0022
metribuzin	3	0.04	0.056	0.041	0.041
beta endosulfan	2	0.0043	0.0052	0.0043	0.0043
ethoprop	2	0.036	0.039	0.036	0.036

Figure 13a. Ethion detections in surface water at S99 from March 1992 to March 1995.

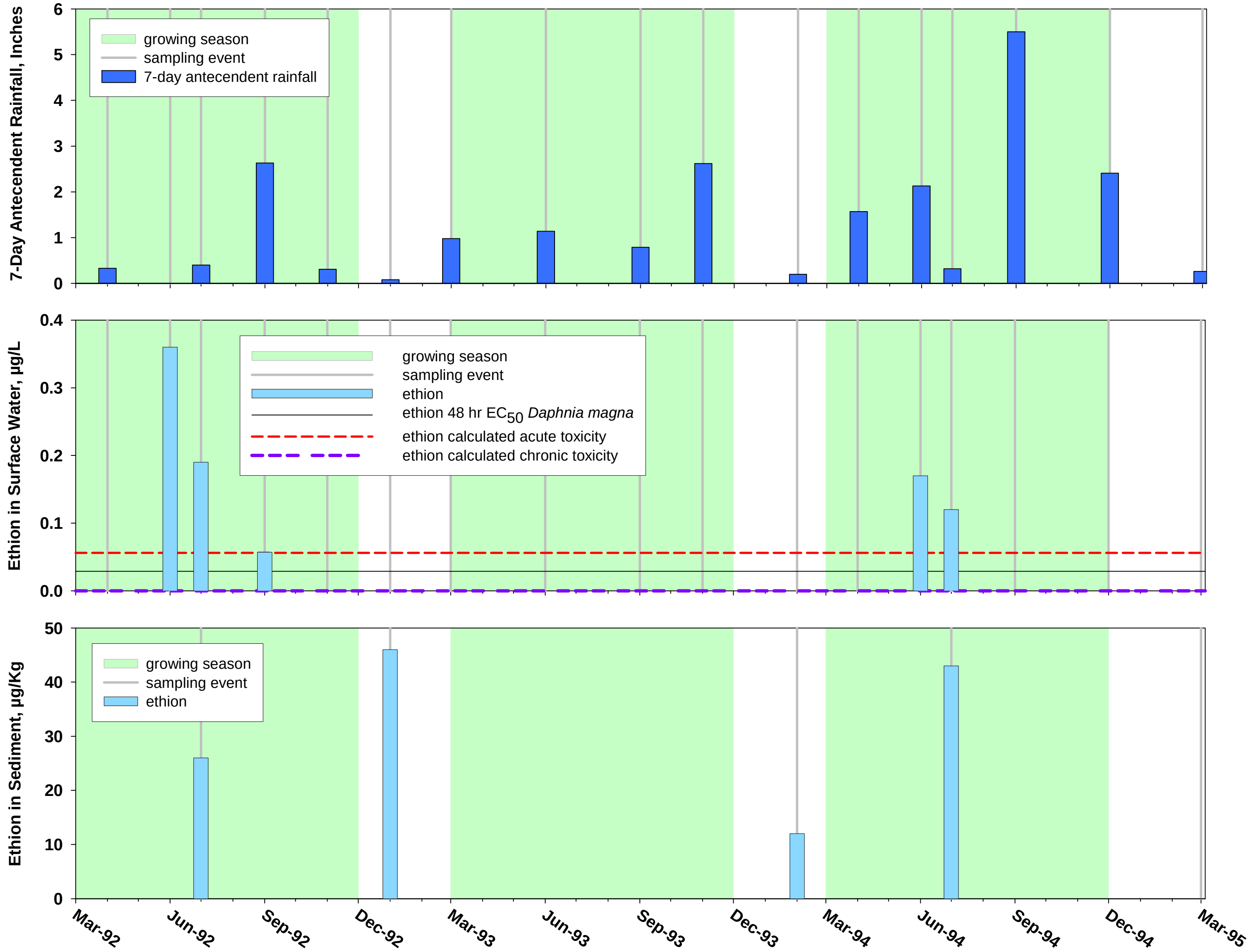

Figure 13b. Ethion detections in surface water at S99 from March 1995 to March 1998.

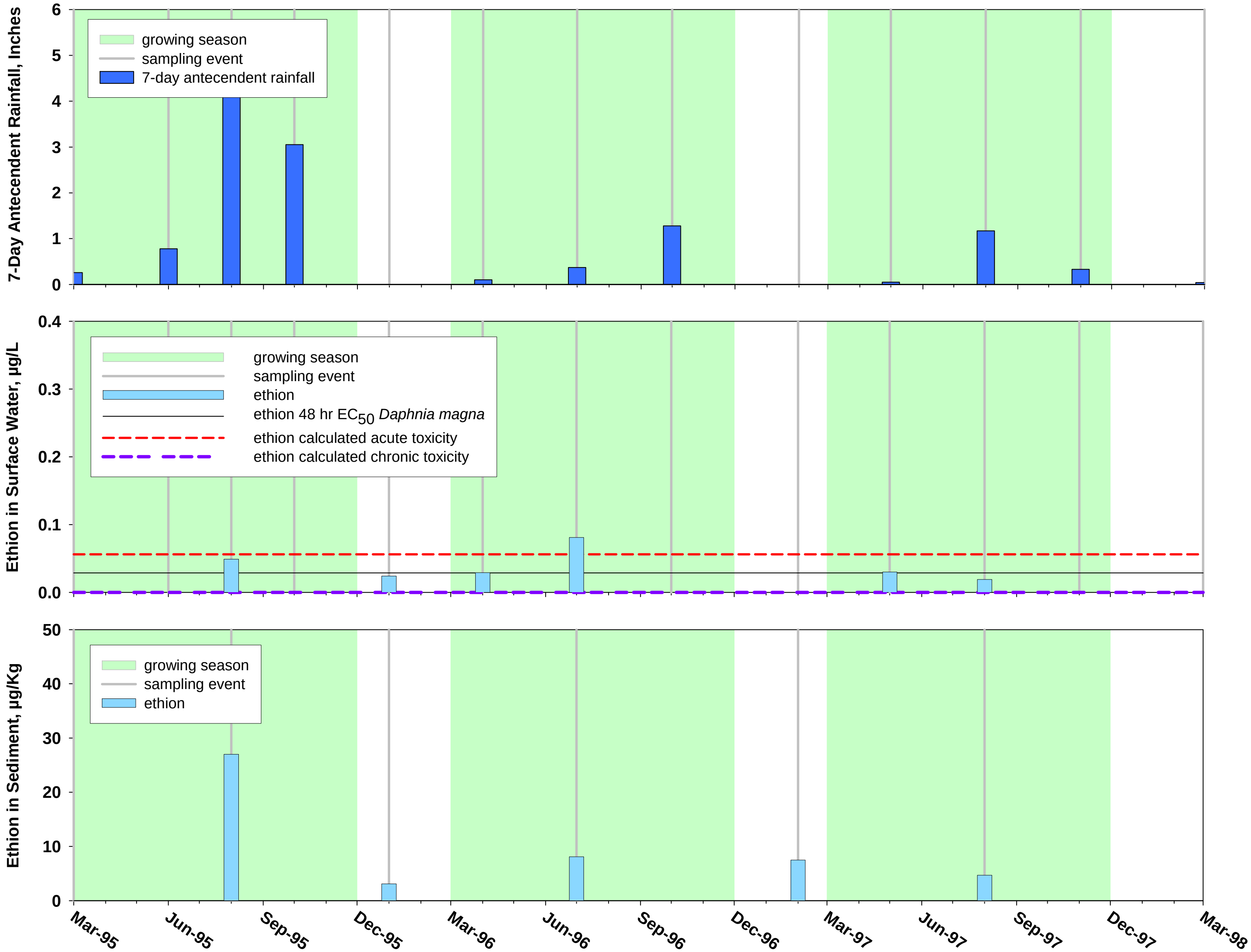

Figure 13c. Ethion detections in surface water at S99 from March 1998 to May 2001.

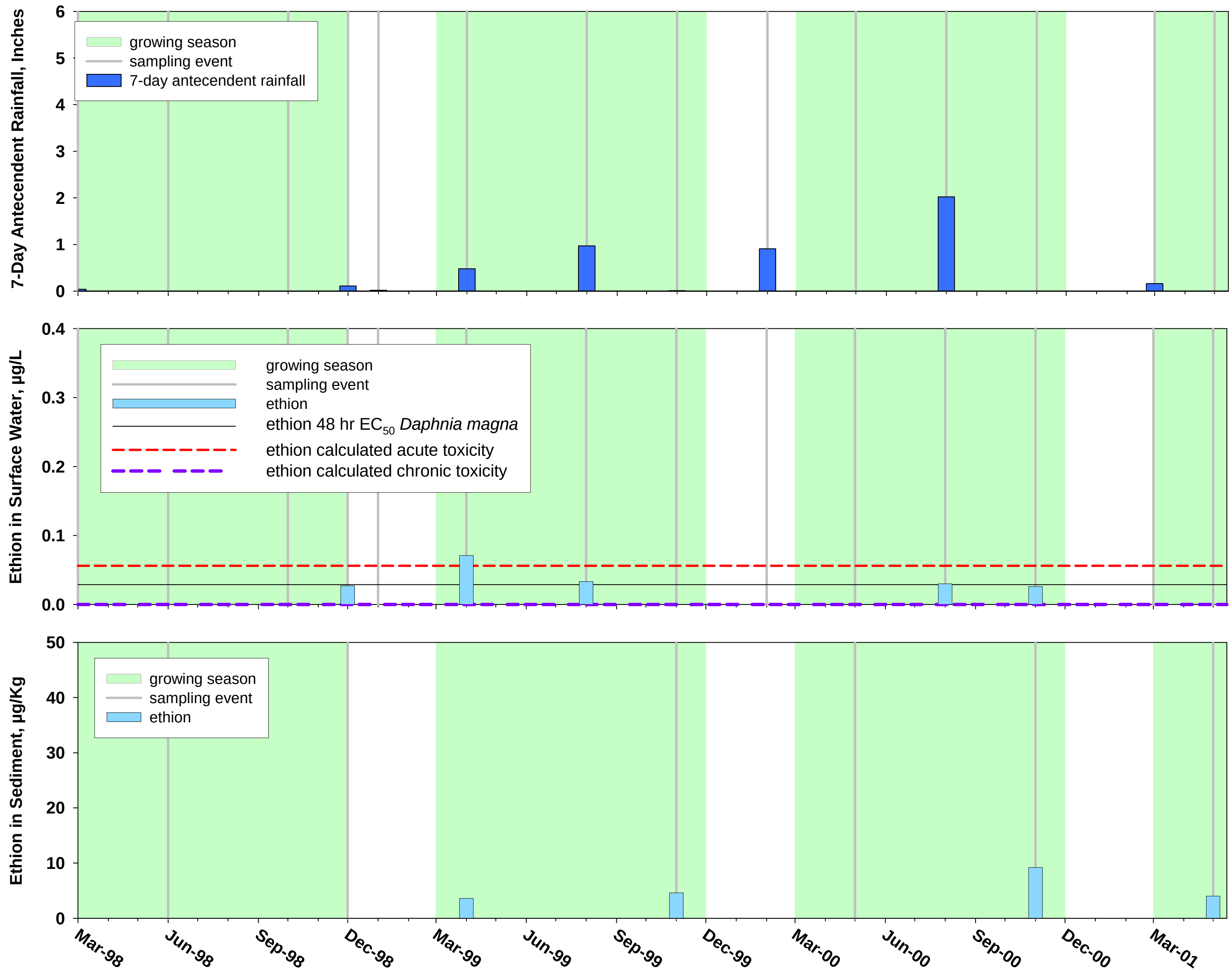

Figure 13d. Ethion detections in surface water at S99 from June 2001 to May 2004.

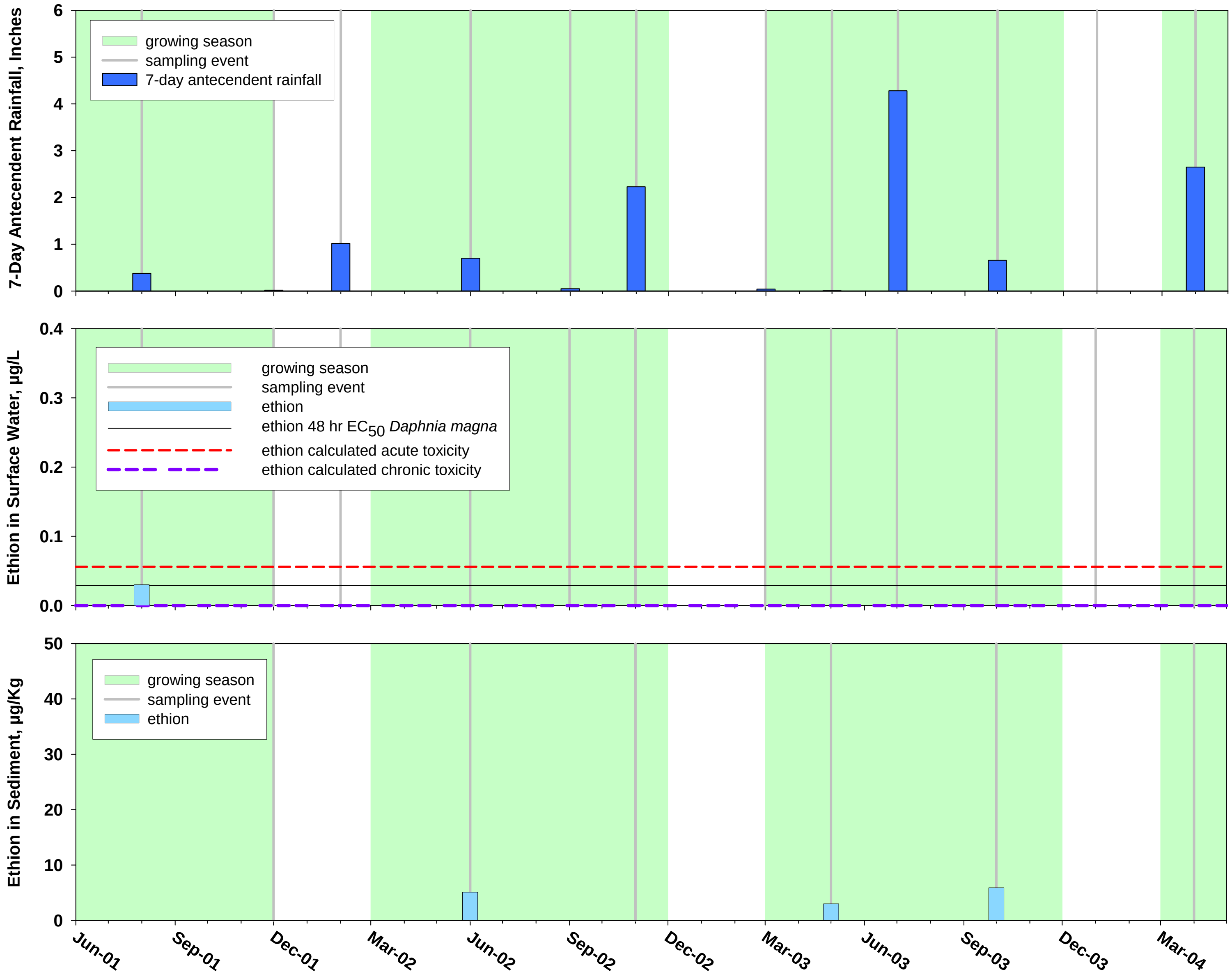

Table 13. Sediment pesticide detections for citrus agriculture sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/Kg)	Maximum Concentration (µg/Kg)	Threshold Effect Concentration (µg/Kg)	Probable Effect Concentration (µg/Kg)
p,p'-DDE	41	*6.4*	*18*	3.2	31
ethion	20	9.8	46	-	-
PCB-1254	20	*133*	*290*	60	680
p,p'-DDD	11	4	*11*	4.9	28
norflurazon	7	17.9	15	-	-
dicofol	5	12.9	26	-	-
dieldrin	5	*7.0*	*11*	1.9	62
diuron	2	19.5	21	-	-
PCB-1242	2	*79.5*	*89*	60	680

Italicized values exceed the Threshold Effect Concentration (TEC)
- No guideline available

Figure 14. Everglades Agricultural Area northern sampling locations.

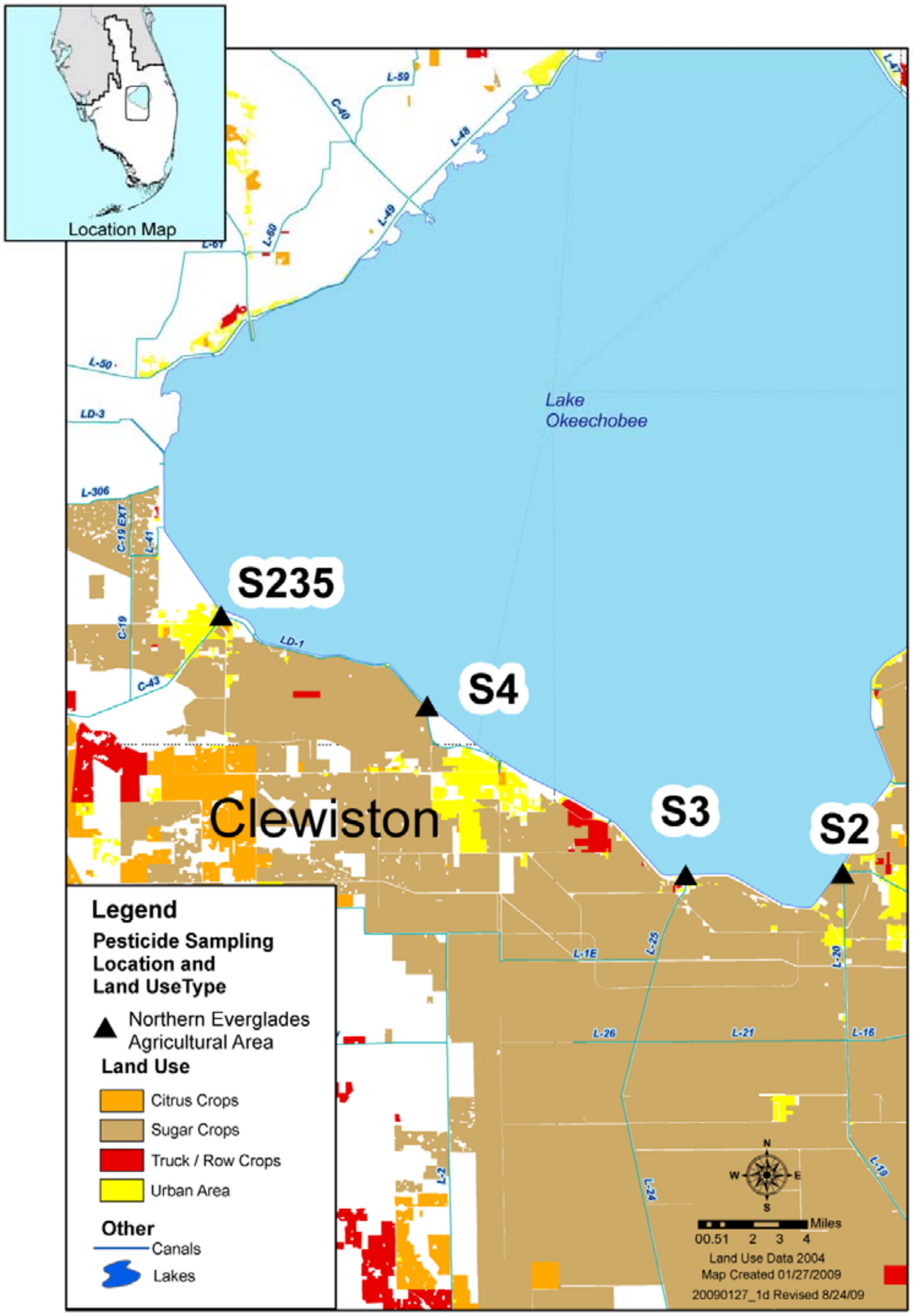

Table 14. Surface water pesticide detections for Everglades Agricultural Area northern sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/L)	Maximum Concentration (µg/L)	Concentration Geometric Mean	Median Concentration
atrazine	248	0.43	8.5	0.24	0.23
ametryn	174	0.11	1.0	0.05	0.05
atrazine desethyl	110	0.03	0.1	0.028	0.029
hexazinone	80	0.03	0.41	0.03	0.03
simazine	65	0.06	0.79	0.03	0.02
atrazine desisopropyl	36	0.02	0.079	0.015	0.014
norflurazon	15	0.11	1.3	0.07	0.07
bromacil	12	0.13	1.1	0.09	0.08
ethoprop	12	0.07	0.22	0.05	0.06
metolachlor	7	0.30	1.4	0.17	0.14
diazinon	3	1.05	1.9	1.0	1.0
diuron	3	0.61	0.8	0.6	0.6
2,4-D	2	3.1	4.9	3.1	3.1
chlorpyrifos ethyl	2	0.051	0.085	0.051	0.051
metribuzin	2	0.021	0.022	0.021	0.021

Table 15. Sediment pesticide detections for Everglades Agricultural Area northern sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/Kg)	Maximum Concentration (µg/Kg)	Threshold Effect Concentration (µg/Kg)	Probable Effect Concentration (µg/Kg)
p,p'-DDE	76	**33**	**393**	3.2	31
p,p'-DDD	57	*12*	**80**	4.9	28
ametryn	39	20	56	-	-
p,p'-DDT	12	*14*	*78*	4.2	63
chlordane	10	**64**	**260**	3.2	18
atrazine	6	8	17	-	-
dieldrin	4	*7*	*20*	1.9	62
aldrin	2	7	11	-	-
PCB-1254	2	*66*	*82*	60	680

Italicized values exceed the Threshold Effect Concentration (TEC)
Bold values exceed the Probable Effect Concentration (PEC)
- No guideline available

Figure 15. Everglades Agricultural Area southern sampling locations.

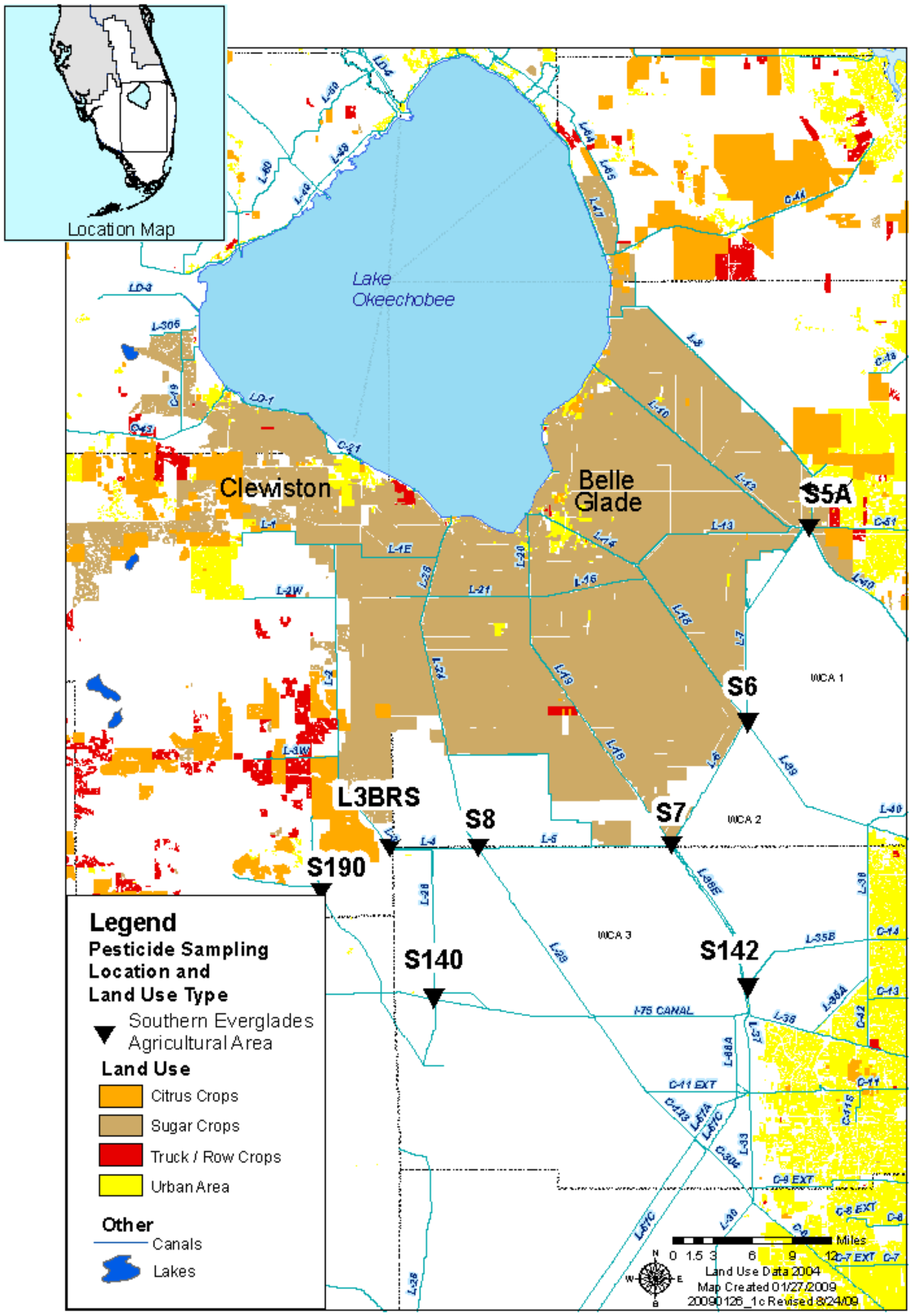

Table 16. Surface water pesticide detections for Everglades Agricultural Area southern sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/L)	Maximum Concentration (µg/L)	Concentration Geometric Mean	Median Concentration
atrazine	378	0.53	18	0.19	0.17
ametryn	257	0.052	0.67	0.03	0.03
norflurazon	95	0.061	0.21	0.05	0.05
atrazine desethyl	79	0.05	0.37	0.02	0.02
hexazinone	90	0.06	1.7	0.03	0.03
simazine	82	0.105	9.3	0.03	0.02
bromacil	49	0.163	1.4	0.10	0.11
metolachlor	32	0.158	0.44	0.14	0.15
atrazine desisopropyl	20	0.019	0.031	0.017	0.018
metribuzin	7	0.19	0.51	0.19	0.17
diuron	6	9.69	76	1.5	3.3
ethoprop	6	0.136	0.67	0.09	0.09
prometryn	6	0.139	0.59	0.06	0.03
endosulfan sulfate	5	0.010	0.015	0.010	0.010
p,p'-DDE	4	0.0042	0.0051	0.0041	0.0040
chlorpyrifos ethyl	3	0.021	0.023	0.020	0.021
2,4-D	2	0.37	0.40	0.37	0.37
alachlor	2	0.040	0.068	0.027	0.040

Table 17. Selected pesticide data at S7 and S8 structures before and after Stormwater Treatment Area 3/4 completion.

		Ametryn		Atrazine	
		Pre-operation	Post-operation	Pre-operation	Post-operation
S7	Average Concentration (µg/L)	0.08	0.05	1.18	0.43
	Percent Detections	69	82	87	93
S8	Average Concentration (µg/L)	0.13	0.04	1.31	0.47
	Percent Detections	54	64	82	93

Table 18. Sediment pesticide detections for Everglades Agricultural Area southern sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/Kg)	Maximum Concentration (µg/Kg)	Threshold Effect Concentration (µg/Kg)	Probable Effect Concentration (µg/Kg)
p,p'-DDE	92	*29*	**390**	3.2	31
p,p'-DDD	63	*15*	**180**	4.9	28
ametryn	48	14	100	-	-
PCB-1254	18	*124*	**890**	60	680
atrazine	14	14	50	-	-
p,p'-DDT	14	*21*	**150**	4.2	63
chlordane	10	**55**	**190**	3.2	18
PCB-1260	8	*76*	*190*	60	680
dieldrin	6	*7*	*22*	1.9	62
dicofol	3	5.8	9.1	-	-
diquat	3	1717	2750	-	-
PCB-1242	2	*67*	*101*	60	680

Italicized values exceed the Threshold Effect Concentration (TEC)
Bold values exceed the Probable Effect Concentration (PEC)
- No guideline available

Figure 16. Urban basin sampling locations.

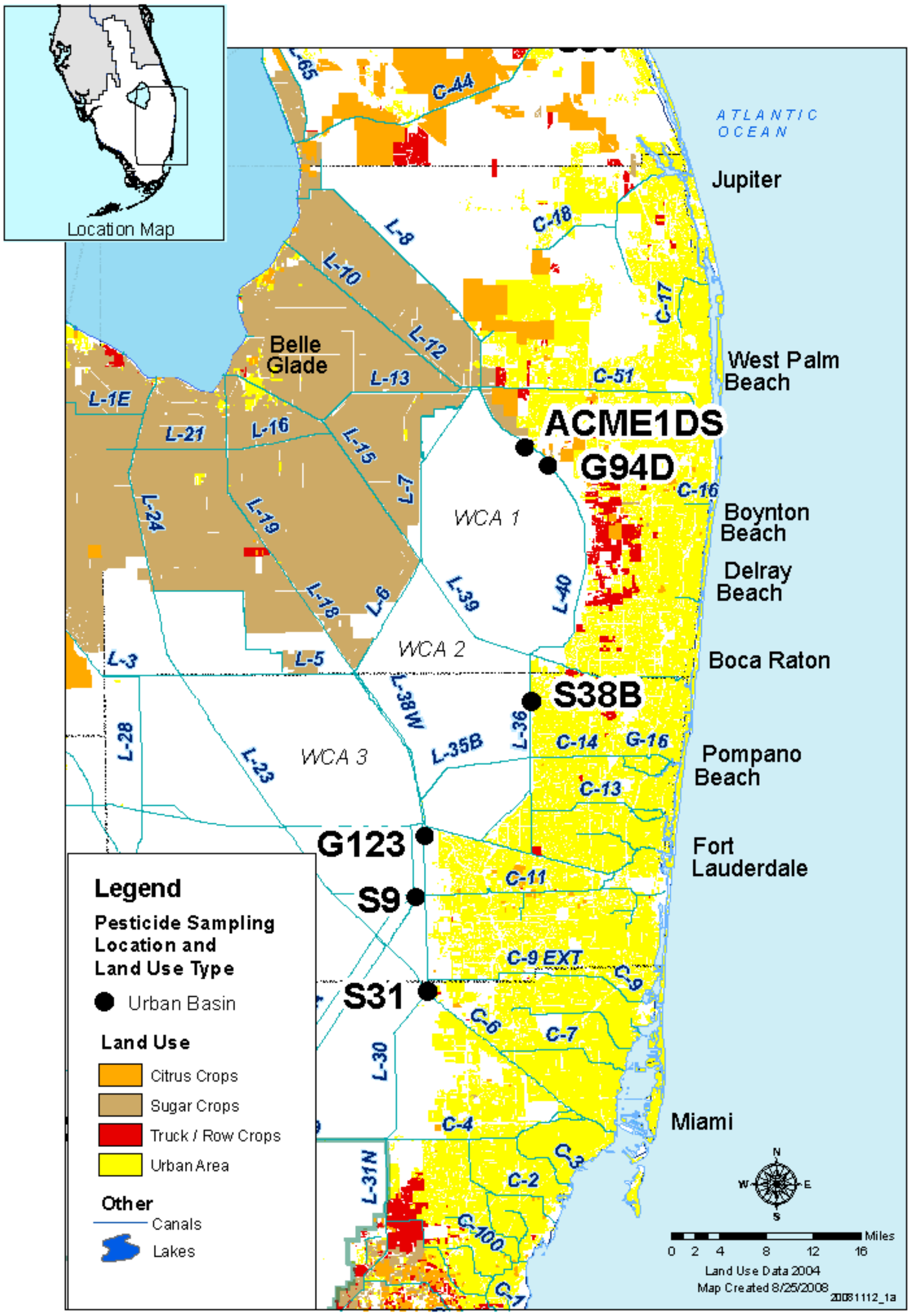

Table 19. Surface water pesticide detections for urban basin sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/L)	Maximum Concentration (µg/L)	Concentration Geometric Mean	Median Concentration
atrazine	223	0.35	3.3	0.26	0.26
ametryn	149	0.02	0.17	0.02	0.02
atrazine desethyl	76	0.04	0.21	0.03	0.03
hexazinone	48	0.08	1.7	0.04	0.03
atrazine desisopropyl	24	0.020	0.029	0.020	0.021
simazine	15	0.07	0.43	0.05	0.04
diuron	13	0.65	1.4	0.61	0.62
2,4-D	10	7.7	29	5.6	6.8
endosulfan sulfate	8	0.029	0.11	0.018	0.017
diazinon	7	0.041	0.097	0.61	0.62
alpha endosulfan	5	0.022	0.076	0.016	0.014
prometon	5	0.029	0.043	0.028	0.023
beta endosulfan	4	0.026	0.077	0.019	0.026
metolachlor	3	0.09	0.11	0.1	0.1
naled	2	0.22	0.24	0.22	0.22

Table 20. Sediment pesticide detections for urban basin sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/Kg)	Maximum Concentration (µg/Kg)	Threshold Effect Concentration (µg/Kg)	Probable Effect Concentration (µg/Kg)
p,p'-DDE	47	*5.4*	*21*	3.2	31
p,p'-DDD	9	2.5	4.3	4.9	28
bromacil	3	92	200	-	-
PCB-1016	2	*60*	*78*	60	680

Italicized values exceed the Threshold Effect Concentration (TEC)
- No guideline available

Figure 17. South Miami-Dade County agriculture sampling locations.

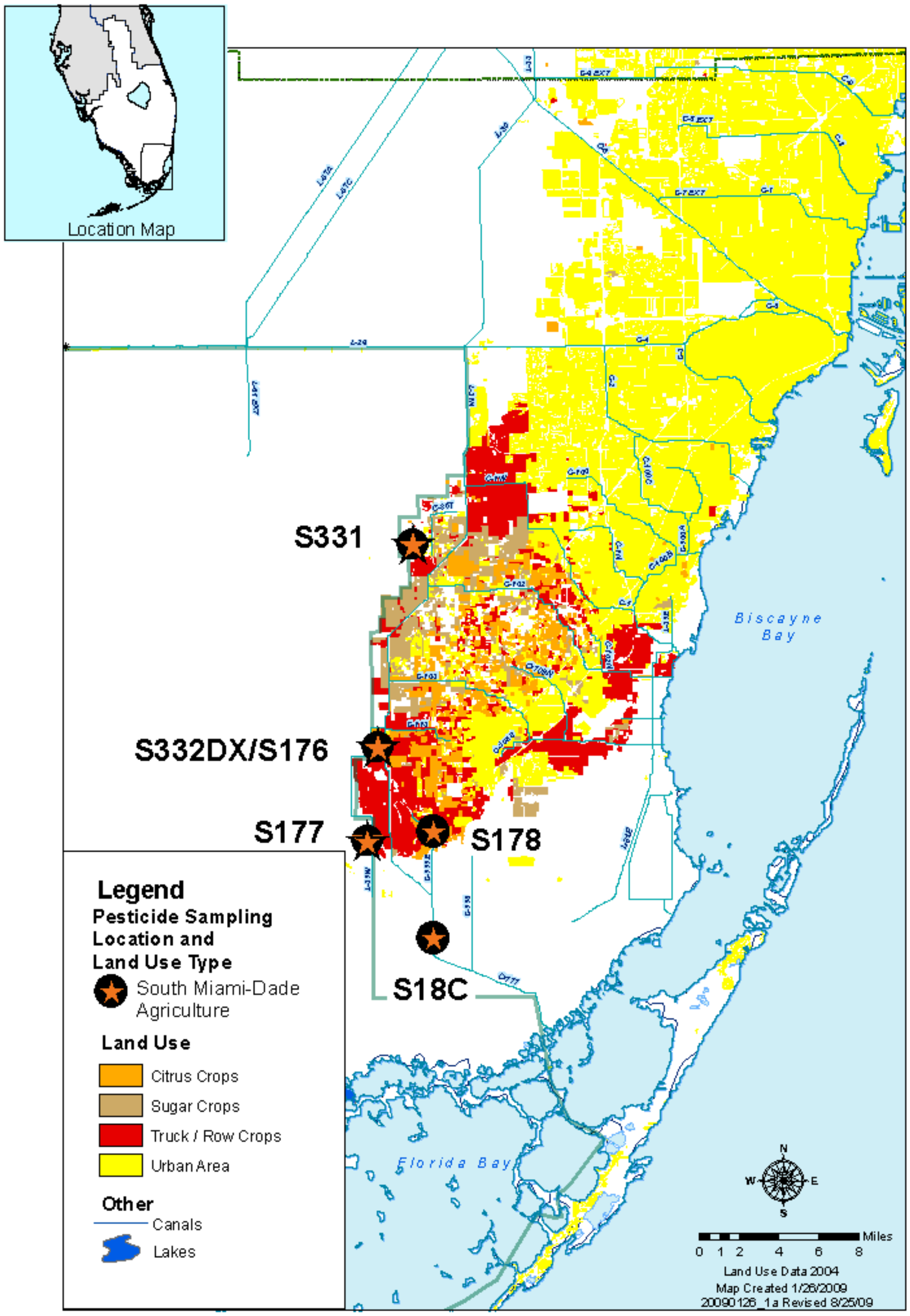

Table 21. Surface water pesticide detections for South Miami-Dade County agriculture sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/L)	Maximum Concentration (µg/L)	Concentration Geometric Mean	Median Concentration
atrazine	159	0.049	0.4	0.031	0.025
alpha endosulfan	63	0.014	0.22	0.011	0.010
endosulfan sulfate	59	0.039	0.45	0.028	0.025
beta endosulfan	32	0.010	0.078	0.008	0.009
hexazinone	9	0.027	0.052	0.025	0.028
atrazine desethyl	7	0.016	0.033	0.015	0.014
chlorpyrifos ethyl	4	0.035	0.056	0.031	0.028
metolachlor	4	0.11	0.22	0.10	0.10
metribuzin	3	0.11	0.29	0.60	0.30
2,4-D	3	0.95	1.7	0.95	0.95
atrazine desisopropyl	2	0.014	0.016	0.014	0.014
ethion	2	0.037	0.053	0.037	0.037

Figure 18a. Endosulfan detections at S178 from March 1992 to April 1995.

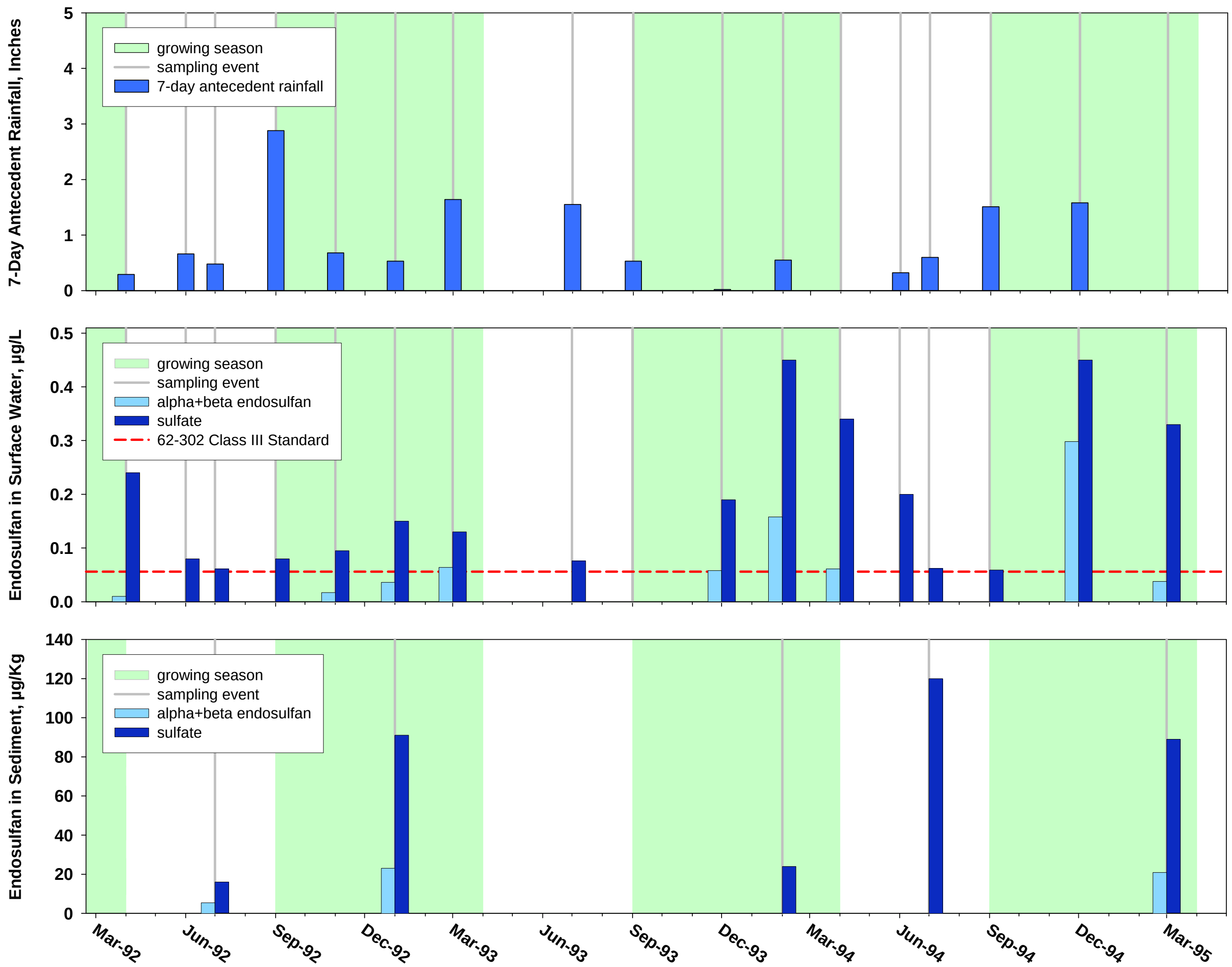

Figure 18b. Endosulfan detections at S178 from June 1995 to July 1998.

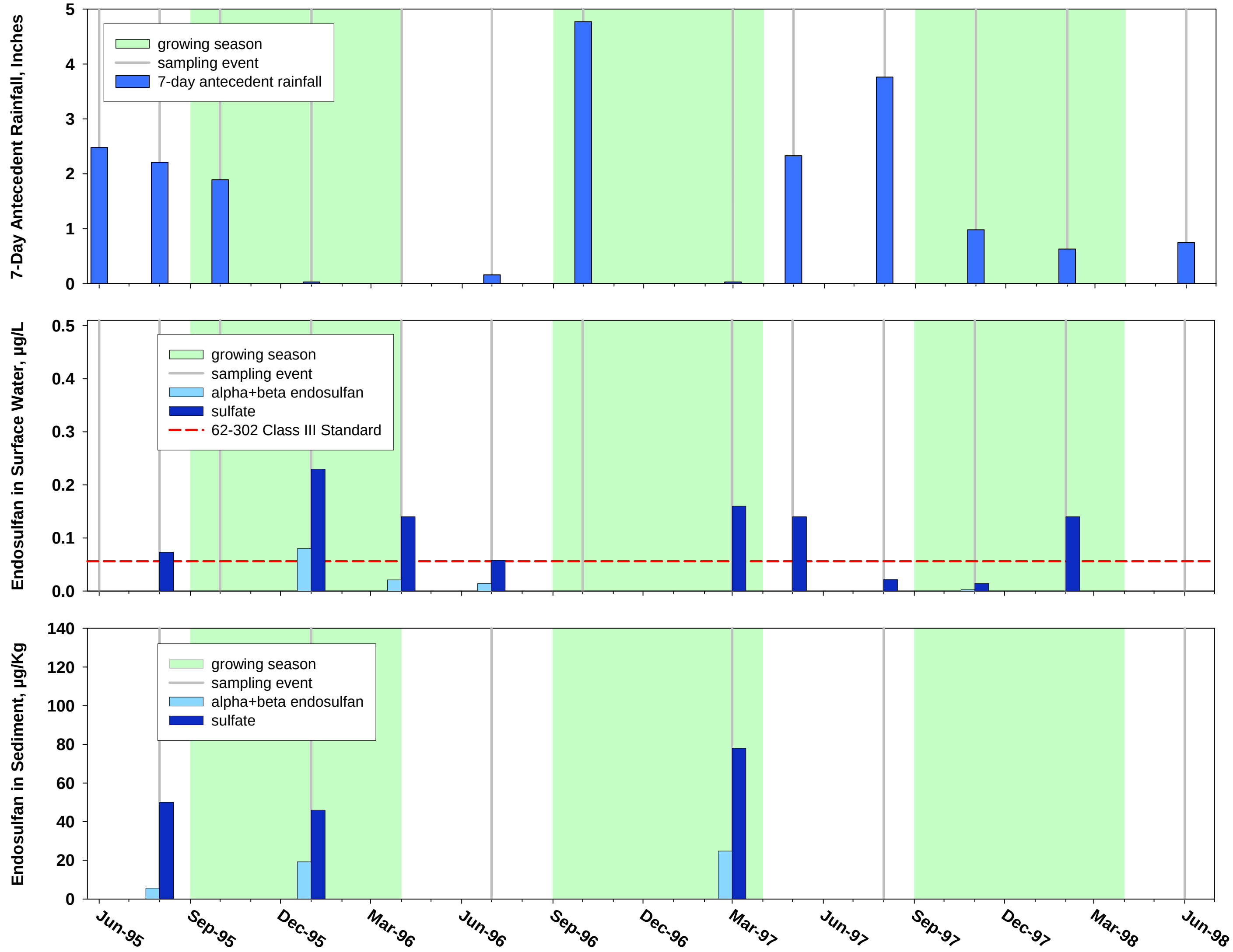

Figure 18c. Endosulfan detections at S178 from July 1998 to August 2001.

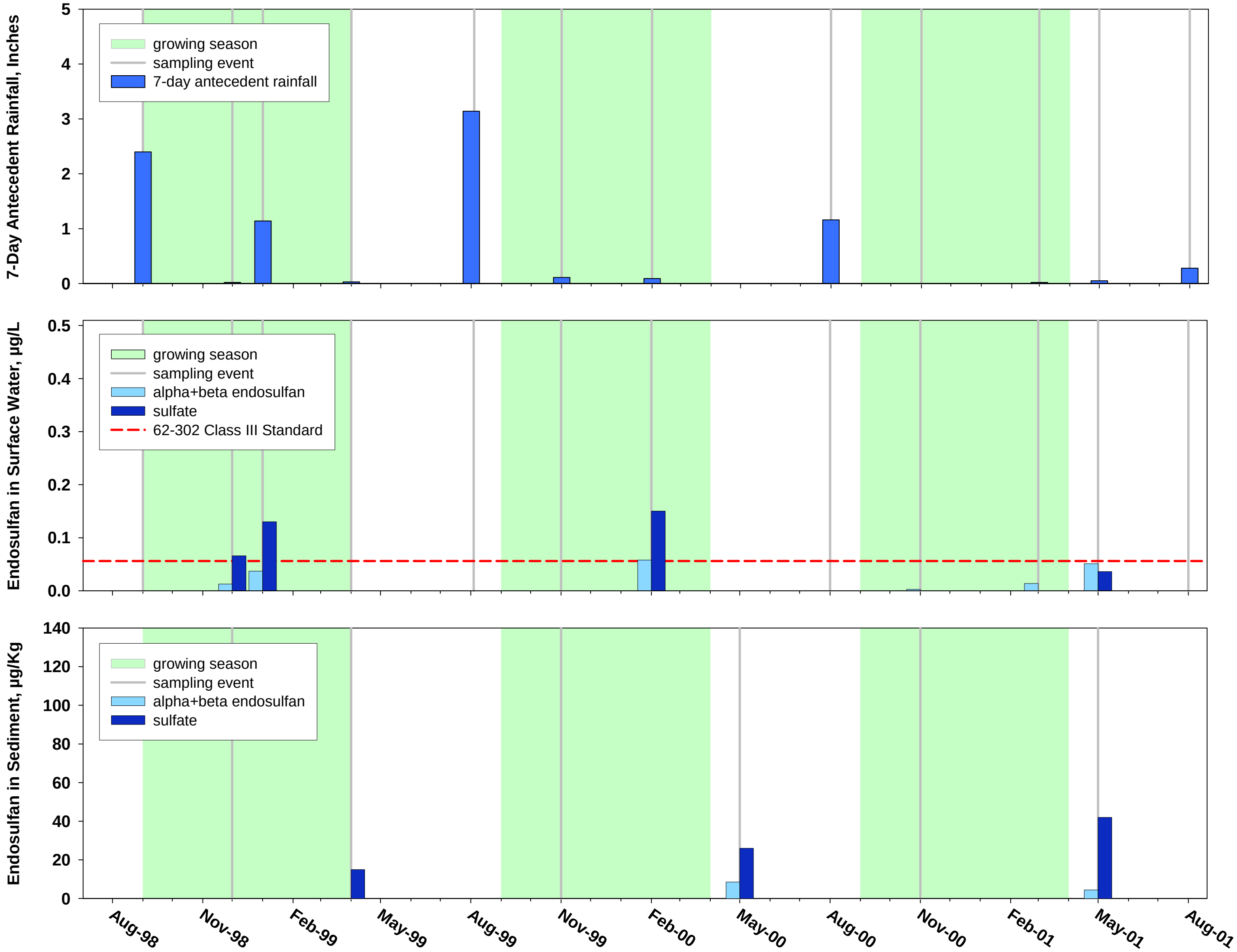

Figure 18d. Endosulfan detections at S178 from September 2001 to September 2004.

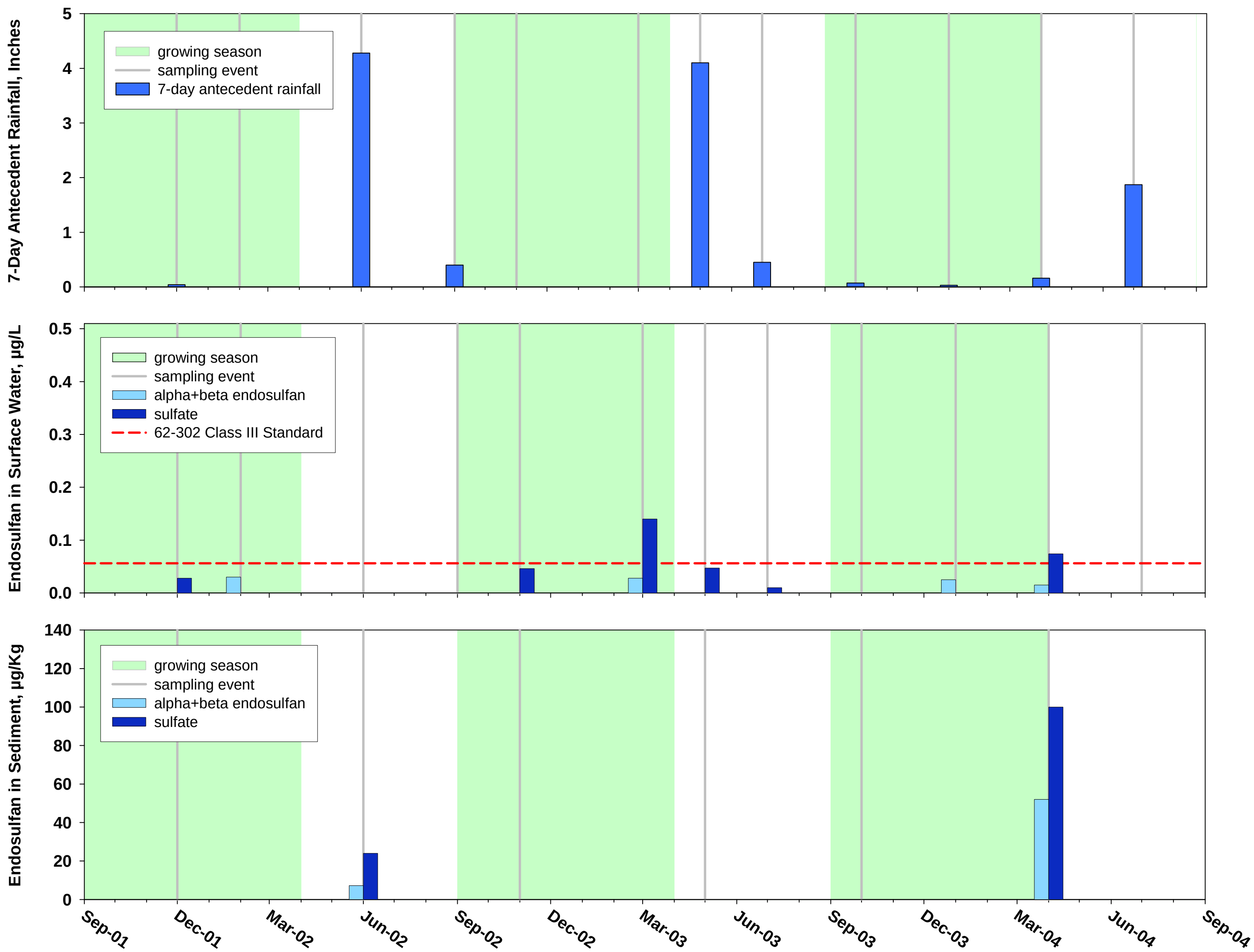

Figure 18e. Endosulfan detections at S178 from September 2004 to December 2007.

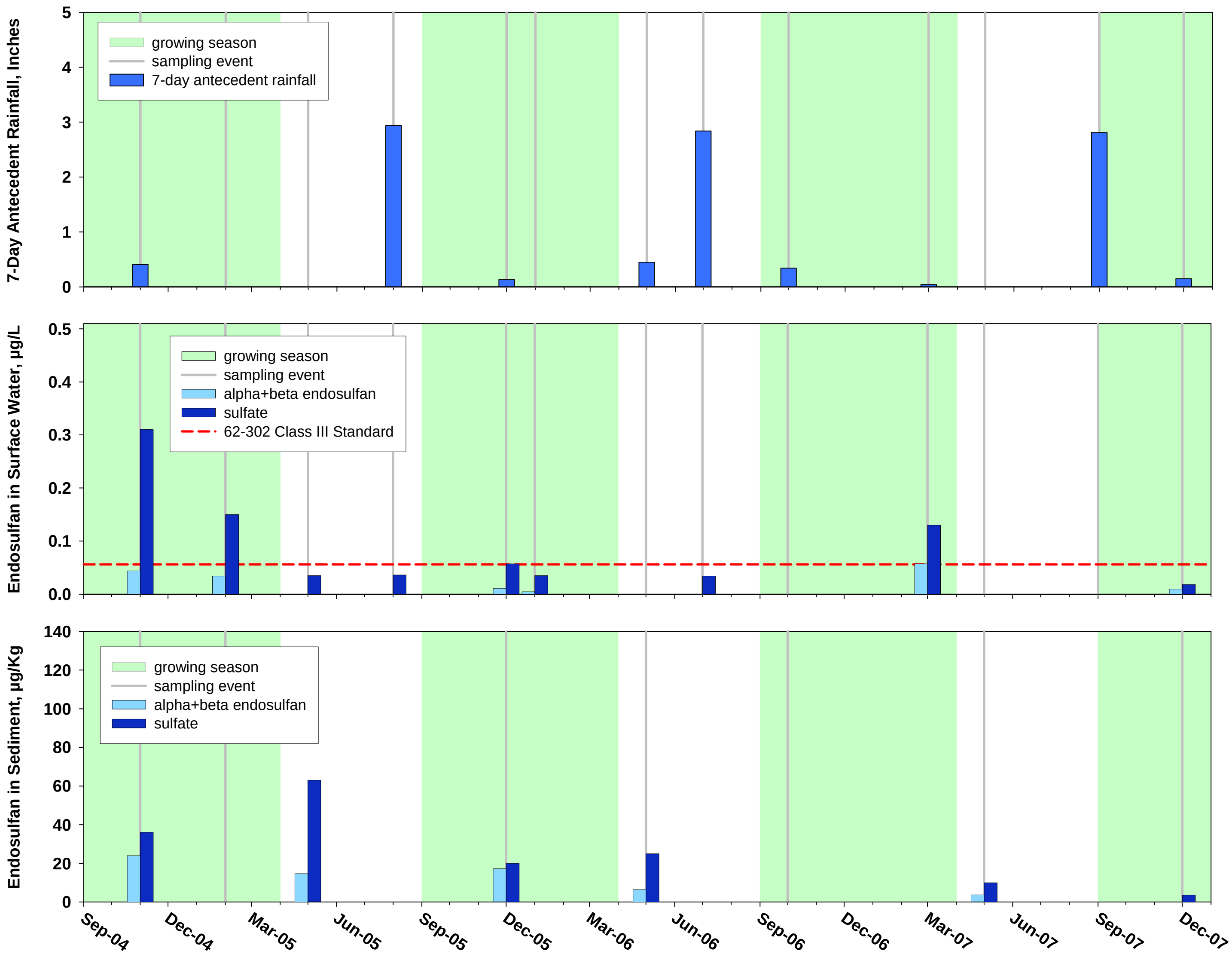

Table 22. Sediment pesticide detections for South Miami-Dade County agriculture sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/Kg)	Maximum Concentration (µg/Kg)	Threshold Effect Concentration (µg/Kg)	Probable Effect Concentration (µg/Kg)
p,p'-DDE	77	*15*	**89**	3.2	31
endosulfan sulfate	25	16	120	-	-
beta endosulfan	24	5	24	-	-
alpha endosulfan	17	6	30	-	-
p,p'-DDD	12	*7*	*15*	4.9	28
p,p'-DDT	5	2	3.2	4.2	63
bromacil	3	93	130	-	-
ethion	3	10	17	-	-

Italicized values exceed the Threshold Effect Concentration (TEC)
Bold values exceed the Probable Effect Concentration (PEC)
- No guideline available

Figure 19. Reference basin sampling locations.

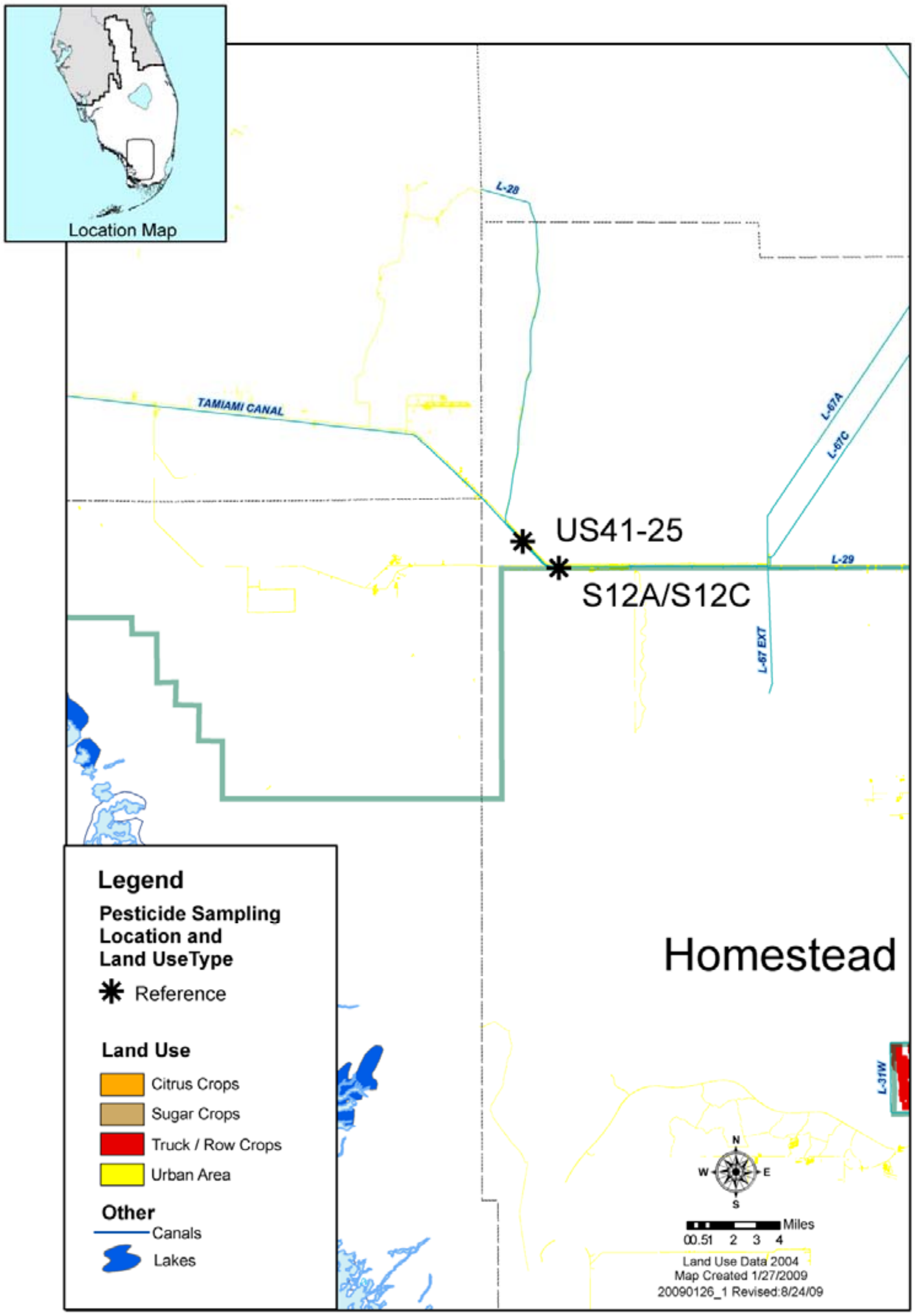

Table 23. Surface water pesticide detections for reference basin sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/L)	Maximum Concentration (µg/L)	Concentration Geometric Mean	Median Concentration
atrazine	49	0.052	0.93	0.027	0.019
ametryn	3	0.014	0.018	0.014	0.013

Table 24. Sediment pesticide detections for reference basin sampling locations from April 1992 to December 2007.

Chemical	Number of Detections	Average Concentration (µg/Kg)	Maximum Concentration (µg/Kg)	Threshold Effect Concentration (µg/Kg)	Probable Effect Concentration (µg/Kg)
p,p'-DDE	2	2.8	*6.2*	3.2	31
PCB-1260	2	21	26	60	680

Italicized values exceed the Threshold Effect Concentration (TEC)