

# Appendix 5-5: Annual Permit Compliance Monitoring Report for Mercury in the Stormwater Treatment Areas

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## KEY FINDINGS AND OVERALL ASSESSMENT

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This report summarizes data from compliance monitoring of mercury (Hg) storage, release, and biomagnification in Stormwater Treatment Areas (STAs) during the 2005 calendar year.

Key findings are as follows:

1. **All STAs:** There were no violations of the Florida Class III numerical water quality standard (WQS) of 12 nanograms (ng) of total mercury per liter (THg/L) during the reporting year at any of the STAs. As such, the project has met the requirements of Section 6.i of the mercury monitoring program of the referenced permits.
2. **STA-1W:** Stormwater Treatment Area 1 West (STA-1W) subsumed the Everglades Nutrient Removal (ENR) Project in April 1999; the ENR Project had served as the prototype STA and had been in operation since 1994. After 10 years of operation, this STA continued to have only low concentrations of both total mercury (THg) and methylmercury (MeHg) in surface water, and consistently exhibited a negative percent change in both THg and MeHg (i.e., concentrations in the outflows were consistently lower than in the inflow). Furthermore, MeHg biomagnification in resident large-bodied fishes (e.g., sunfish and largemouth bass) has remained relatively constant over the monitoring period at levels almost an order of magnitude lower than observed in fishes from the downstream Everglades. Mercury levels in fish at this STA do not appear to pose a threat to fish-eating wildlife based on the U.S. Fish and Wildlife Service (USFWS) and the U.S. Environmental Protection Agency (USEPA) predator protection criteria.
3. **STA-1E:** Both the central flow-way (Cells 3, 4N, and 4S) and the westernmost flow-way (Cells 5 through 7) met the startup criteria, as specified in the Everglades Forever Act (EFA) Permit No. 0195030-001-GL, in August 2005. During the remaining portion of 2005, both THg and MeHg remained at relatively low concentrations in the outflow, as compared to the multiple inflows. Mercury levels in mosquitofish from the interior marshes were comparable to other STAs and did not increase markedly over the final two quarters in 2005. By

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comparison, the mosquitofish from the near-field downstream site in Water Conservation Area 1 (WCA-1) contained levels generally higher than fish collected from other STAs and, more importantly, levels in mosquitofish from this site increased markedly in the fourth quarter of 2005. Background mercury levels were also elevated in STA-1E sunfish and bass, particularly those fish from the downstream site, as compared to the other STAs. Mercury levels in fish from the near-field downstream site (ST1ELX) were also elevated compared to levels recently observed at a more southerly downstream site in WCA-1. Fish at the near-field downstream site show mercury levels in excess of the predator protection criteria.

4. **STA-2:** During 2005, both THg and MeHg remained at a low concentration in the outflow from the STA compared to previous years. Outflow loads of both constituents from this STA have also greatly reduced from previous years. Levels of mercury in tissue (tissue-Hg) also remained low in mosquitofish, including fish from Cell 1, as compared to other STAs and downstream marshes. Although sunfish from Cell 1 continued to exhibit significant among-cell differences, the fish showed declines in mercury levels. However, resident fish in Cell 1 continued to have mercury levels in excess of the predator protection criteria, unlike fish from other cells.
5. **STA-3/4:** Water-column THg concentration spiked in the two inflows during the second quarter of 2005 and exceeded levels in the outflows. By the third quarter, THg declined in the inflows and remained at levels comparable to the outflows. Concentrations of MeHg were more highly variable among structures and occasionally concentrations in one or more of the outflows exceeded inflow concentrations; however, there were not consistent differences in MeHg outflow concentration among the three flow-ways. In general, MeHg concentrations remained relatively low as compared to levels observed during start-up. Tissue-Hg levels were only slightly elevated in mosquitofish from this STA as compared to mosquitofish from other STAs. Similarly, resident sunfish from the interior marshes of STA-3/4 contained slightly elevated mercury levels compared to fish from other STAs, but not compared to downstream sites. Only Cell 3 of westernmost flow-way produced largemouth bass in 2005. An age-standardized three-year-old fish from this cell was estimated to contain  $485 \pm 94$  mg Hg/kg, which is elevated compared to that of fish in other STAs. Nonetheless, based on USFWS and USEPA predator protection criteria, fish-eating wildlife foraging preferentially at STA-3/4 appear to have a relatively low risk from mercury exposure.
6. **STA-5:** With the exception of a couple of minor spikes in THg in the inflows during the third quarter, water-column concentrations of both THg and MeHg remained low at STA-5 during the year. Outflow loads of both THg and MeHg were similar to or smaller than inflow loads. Mosquitofish collected in 2005 contained relatively low mercury levels compared to fish previously collected at this STA, fish collected at other STAs, and fish collected from downstream marshes. Although sample quotas for sunfish and bass were again unmet in 2005, sunfish from the interior marshes had lower mercury levels than fish either from the supply or discharge canal. Analysis of sunfish from these interior marshes indicates that fish-eating wildlife foraging preferentially at STA-5 were not at elevated risk from mercury exposure.
7. **STA-6:** Both Cell 3 and 5 dried down during the year, yet neither THg nor MeHg spiked in outflows. While it is possible that methylation rate did not spike, past STA performance following the rewetting of the marsh indicates the likelihood that quarterly surface water sampling missed the transient spike. Mosquitofish continued to contain relatively low Mercury levels compared to fish collected previously from this area; it is possible that semi-annually collected mosquitofish also missed any transient spike in MeHg production. Sunfish and bass collected from the interior marsh did show increases in mercury levels over last year; however, it is uncertain whether these fish, which likely reinvaded the marsh from the

canal, did not contain higher levels prior to the immigration. Even with the increased levels, based on USFWS and USEPA predator protection criteria, fish-eating wildlife foraging preferentially at STA-6 would appear to have a relatively low risk from mercury exposure.

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## INTRODUCTION

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This is the annual permit compliance monitoring report for mercury (Hg) in Stormwater Treatment Areas (STAs). This report summarizes the mercury-related reporting requirements of the Florida Department of Environmental Protection (FDEP) Everglades Forever Act (EFA) permits [Chapter 373.4592, Florida Statutes (F.S.)], including permits for STA-1W, STA-1E, STA-2, STA-3/4, STA-5, and STA-6. This report summarizes the results of monitoring in the 2005 calendar year. The results of mercury monitoring at far-field sites downstream of the STAs in accordance with these permits, as well as non-Everglades Construction Project (non-ECP) discharge structures (Permit No. 06.502590709) is reported separately, in Appendix 3B-1 of the *2007 South Florida Environmental Report – Volume I*.

This report consists of key findings and overall assessment, an introduction and background, a summary of the Mercury Monitoring and Reporting Program, and monitoring results. The background section briefly summarizes previously identified and published concerns regarding possible impact of STA operation on South Florida's mercury problem. The following section summarizes sampling and reporting requirements of the Mercury Monitoring Program within the STAs. Monitoring results are summarized and discussed in two subsections: results from pre-operational monitoring, and results from STA operational monitoring during the reporting year (i.e., bulk of new discussion).

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## BACKGROUND

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The STAs are constructed wetlands designed to remove phosphorus from stormwater runoff originating from upstream agricultural areas and Lake Okeechobee releases. The STAs are being built as part of the Everglades Construction Project (ECP) authorized under the EFA [Chapter 373.4592, Florida Statutes (F.S.)]. When completed, the ECP will include six large treatment marshes totaling about 47,000 acres.

Even prior to passage of the EFA, concerns were being raised that, in attempting to reduce downstream eutrophication, the restoration effort could inadvertently worsen the mercury problem known to be present in the Everglades (Ware et al., 1990; Mercury Technical Committee, 1991). These concerns stemmed from studies in other areas that showed flooded soils in new impoundments to be a source of inorganic mercury (Cox et al., 1979). Of greater concern, studies had shown wetlands to be an important site of mercury methylation; methylmercury (MeHg) is more bioaccumulative and toxic than the inorganic or elemental form of mercury (St. Louis et al., 1994; Rudd, 1995). Decomposition of flooded terrestrial vegetation and soil carbon in new reservoirs had been reported to stimulate the sulfate-reducing bacteria that methylate inorganic mercury (Kelly et al., 1997; Paterson et al., 1998). Environments that favor methylation drive bioaccumulation. For example, Paterson et al. (1998) found that annual fluxes of MeHg increased 10 to 100 times through a zooplankton community after impoundment. Newly created reservoirs have also been found to contain fish with elevated mercury burdens (Abernathy and Cumbie, 1977; Bodaly et al., 1984; Bodaly and Fudge, 1999). This so-called "reservoir effect" can occasionally persist for several decades after initial flooding (Bodaly et al., 1984; Verdon et al., 1991; Fink et al., 1999). For instance, Verdon et al. (1991) reported that mercury levels in northern pike (*Esox lucius*) increased from 0.61 to 2.99 parts per million and continued to increase nine years after the initial flooding. Given these observations, Kelly et al. (1997) recently recommended that in siting a new reservoir (1) total land area flooded should be minimized and

(2) flooding the wetlands, which contain more organic carbon than the uplands, should be avoided.

However, applying these observations directly to the Everglades was problematic because most of these observations were made in deepwater lakes or reservoirs in temperate regions. In a report to the South Florida Water Management District (SFWMD or District), Watras (1993) stated that “the boreal and temperate watersheds, wetlands and reservoirs studied to date are very different geologically, hydrologically, meteorologically and ecologically from the subtropical systems in the Everglades.” Waters recommended monitoring and integrating mass balance and process-oriented studies to understand how the system would behave. Such studies were initiated in 1994 with the start-up of the prototype STA, the Everglades Nutrient Removal (ENR) Project. Baseline collections at the ENR Project (funded by the SFWMD and others) found no evidence of MeHg spikes in either surface water (PTI, 1994 attributed to KBN, 1994a; Watras, 1993 and 1994) or resident fishes (mosquitofish and largemouth bass; PTI, 1994 attributed to KBN, 1994b). During the first two years of operation, median concentrations of total mercury (THg) and MeHg in unfiltered surface water were reported to be 0.81 and 0.074 nanograms per liter (ng/L), respectively (Miles and Fink, 1998). These low levels persisted in later years; from January 1998 through April 1999, median water-column concentrations in the interior marsh (i.e., excluding inflows and outflows) were 0.81 ng THg/L and 0.04 ng MeHg/L (Rumbold and Fink, 2002b). Resident fishes also continued to have only low mercury levels: 8 to 75 nanograms per gram (ng/g) in mosquitofish, and 100 to 172 ng/g in three-year-old bass (Miles and Fink, 1998; SFWMD, 1999a; Lange et al., 1999). Finally, a mass balance assessment found the ENR Project to be a net sink for both THg and MeHg, removing approximately 70 percent of the inflow mass (Miles and Fink, 1998). Nonetheless, to provide continuing assurance that the ECP does not exacerbate the mercury problem, FDEP-issued construction and operating permits for the STAs require the SFWMD to monitor levels of THg and MeHg in various abiotic (e.g., water and sediment) and biotic (e.g., fish and bird tissues) media, both within the STA and the downstream receiving waters.

Results from monitoring programs at STAs constructed and operated after the ENR Project since 1999 have revealed transitory spikes in MeHg production (see previous reports published by the SFWMD, including Rumbold and Fink, 2002b). These monitoring results combined with the results of a 1999 field study on the effect that drought and muck fires had on mercury cycling in the Everglades (Krabbenhoft and Fink, 2001) have demonstrated that spikes can sometimes occur following drydowns and rewetting. Accumulating evidence suggests that oxidation of sulfide pools in the sediments (e.g., organic sulfide, disulfides, and acid volatile sulfides) during the drydown can lead to increased methylation upon rewetting of the marsh either by providing free sulfate, which stimulates the sulfate-reducing bacteria or, in highly sulfidic areas, by reducing porewater sulfide, which can inhibit methylation (Benoit et al., 1999a and b).

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## **SUMMARY OF THE MERCURY MONITORING AND REPORTING PROGRAM**

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The monitoring and reporting program summarized below is described in detail in the Mercury Monitoring and Reporting Plan for the Everglades Construction Project, the Central and Southern Florida Project, and the Everglades Protection Area. The SFWMD submitted this plan to the FDEP, the U.S. Environmental Protection Agency (USEPA), and the U.S. Army Corps of Engineers (USACE) in compliance with the requirements of the aforementioned permits (SFWMD, 1999b). Details on the procedures for ensuring the quality of and accountability for data generated in this monitoring program are set forth in the SFWMD's Quality Assurance Project Plan (QAPP) for the Mercury Monitoring and Reporting Program, which was approved

on issuance of the permit by the FDEP. QAPP revisions were approved by the FDEP on June 7, 1999 (SFWMD, 1999c).

## **EVERGLADES MERCURY BASELINE MONITORING AND REPORTING REQUIREMENTS**

Levels of THg and MeHg in the pre-operational soils of each of the STAs and various abiotic and biotic media of the downstream receiving waters define the baseline condition from which to evaluate mercury-related changes, if any, brought about by the operation of the STAs. An Everglades Mercury Background Report, prepared prior to the operation of the first STA, defines pre-ECP mercury baseline conditions (FTN Associates, 1999).

## **PRE-OPERATIONAL MONITORING AND REPORTING REQUIREMENTS**

Prior to completion of construction and flooding of the soils of each STA, the District is required to collect 10-centimeter (cm) core samples of soil at six representative interior sites for THg and MeHg analyses. Prior to initiation of discharge, the District is also required to collect biweekly samples of supply canal and interior unfiltered water for THg and MeHg analyses. If concentrations at the interior sites are not significantly greater than that of the supply canal, this information is reported to the permit-issuing authority, and the biweekly sampling can be discontinued. Discharge begins after all the start-up criteria are met.

## **OPERATIONAL MONITORING**

Following approval for initiation of routine operation of an STA and thereafter, the permits require that the following samples be collected at the specified frequencies and analyzed for specified analytes:

### **Water**

On a quarterly basis, 500-milliliter unfiltered grab samples of water are collected in pre-cleaned bottles using the ultraclean technique at the supply canals and outflows of each STA. They are analyzed for MeHg and THg (this includes the sum of all mercury species in sample, e.g.,  $\text{Hg}^0$ ,  $\text{Hg}^{\text{I}}$ , and  $\text{Hg}^{\text{II}}$ , as well as organic mercury). THg results are analyzed for compliance with the Florida Class III water quality standard of 12 ng/L. Outflow concentrations of both THg and MeHg are compared to concentrations at the supply canal.

### **Sediment**

Triennially, sediment cores are collected at depth from zero to 10 cm at six representative interior sites. Each depth-homogenized core is then analyzed for THg and MeHg.

### **Prey Fish**

Semiannually, grab samples of between 100 and 250 mosquitofish (*Gambusia* sp.) are collected using a dip net at the supply canal sites, interior sites, and outflow sites of each STA. Individual fish are composited from each size, the homogenate is subsampled in quintuplicate, and each subsample is then analyzed for THg. On March 5, 2002, the FDEP approved a reduction in the number of replicate analyses of the homogenate from five to three (correspondence from F. Nearhoof, FDEP).

## Top Predator Fish

Annually, 20 largemouth bass (*Micropterus salmoides*) are collected primarily through electroshocking methods at representative supply and discharge canal sites and representative interior sites in each STA. The fish muscle (fillet) samples are analyzed for THg as an indicator of potential human exposure to mercury.

In 2000, the District began routine collection of sunfish (*Lepomis* spp.) at the same frequency, intensity (i.e.,  $n = 20$ ), and locations as for largemouth bass collection. This permit revision fulfilled a USFWS recommendation (USFWS recommendation 9b in USACE Permit No. 199404532; correspondence to Bob Barron, USACE, July 13, 2000). Sunfish, analyzed as whole fish, also serve as a surrogate for attempts to monitor mercury in wading birds that do not nest in the STAs. (For details on the monitoring program tracking mercury in wading birds in downstream areas, see Appendix 3B-1 of this volume.) The addition of sunfish to the compliance monitoring program was approved by the FDEP on March 5, 2002 (correspondence from F. Nearhoof, FDEP).

Tissue concentrations in each of the three monitored fishes will reflect ambient MeHg levels, i.e., their exposure is a function of a combination of factors including body size, age, rate of population turnover, and trophic position. Mosquitofish should respond rapidly to changing ambient MeHg concentrations due to their small size, lower trophic status, short life span, and rapid population turnover. Mosquitofish become sexually mature in approximately three weeks and have an average lifespan of only four to five months; the lifespan of males is shorter than females (Haake and Dean, 1983; Haynes and Cashner, 1995; Cabral and Marques, 1999). Conversely, sunfish (thought to have an average lifespan of four to seven years in the wild) and bass should take a longer to respond, in terms of tissue concentrations, to changes in ambient MeHg availability. Most importantly, sunfish and bass represent exposure at higher trophic levels (TL) with a requisite time lag for trophic exchange. While this focus on a three-year old bass is appropriate to evaluate exposure to fishermen, it complicates the data results by only interpreting tissue concentration will reflect integrated over a three-year period. The key is to use these species-related differences to better assess MeHg availability within the system.

It is important to also recognize that virtually all (more than 85 percent) of the Mercury in fish muscle tissues is in the methylated form (Grieb et al., 1990; Bloom, 1992). Therefore, the analysis of fish tissue for THg, which is a more straightforward and less costly procedure than for MeHg, can be interpreted as being equivalent to the analysis of MeHg. Further details regarding rationales for sampling scheme, procedures, and data reporting requirements are set forth in the Everglades Mercury Monitoring Plan revised in March 1999 (Appendix 1 of QAPP, June 7, 1999).

## QUALITY ASSURANCE MEASURES

For a quality assurance/quality control (QA/QC) assessment of the District's Mercury Monitoring Program during 2005, see Appendix 3B-1 of this volume.

## STATISTICAL METHODS

The proper interpretation of residue levels in tissues can sometimes prove problematic due to the confounding influences of age or species of collected animals. For comparison, special procedures are used to normalize the data (Wren and MacCrimmon, 1986; Hakanson, 1980). To be consistent with the reporting protocol used by the Florida Fish and Wildlife Conservation Commission (FWC) (Lange et al., 1998 and 1999), mercury concentrations in largemouth bass were standardized to an expected mean concentration in three-year-old fish at a given site by regressing mercury against age (hereafter symbolized as EHg3). To adjust for the month of

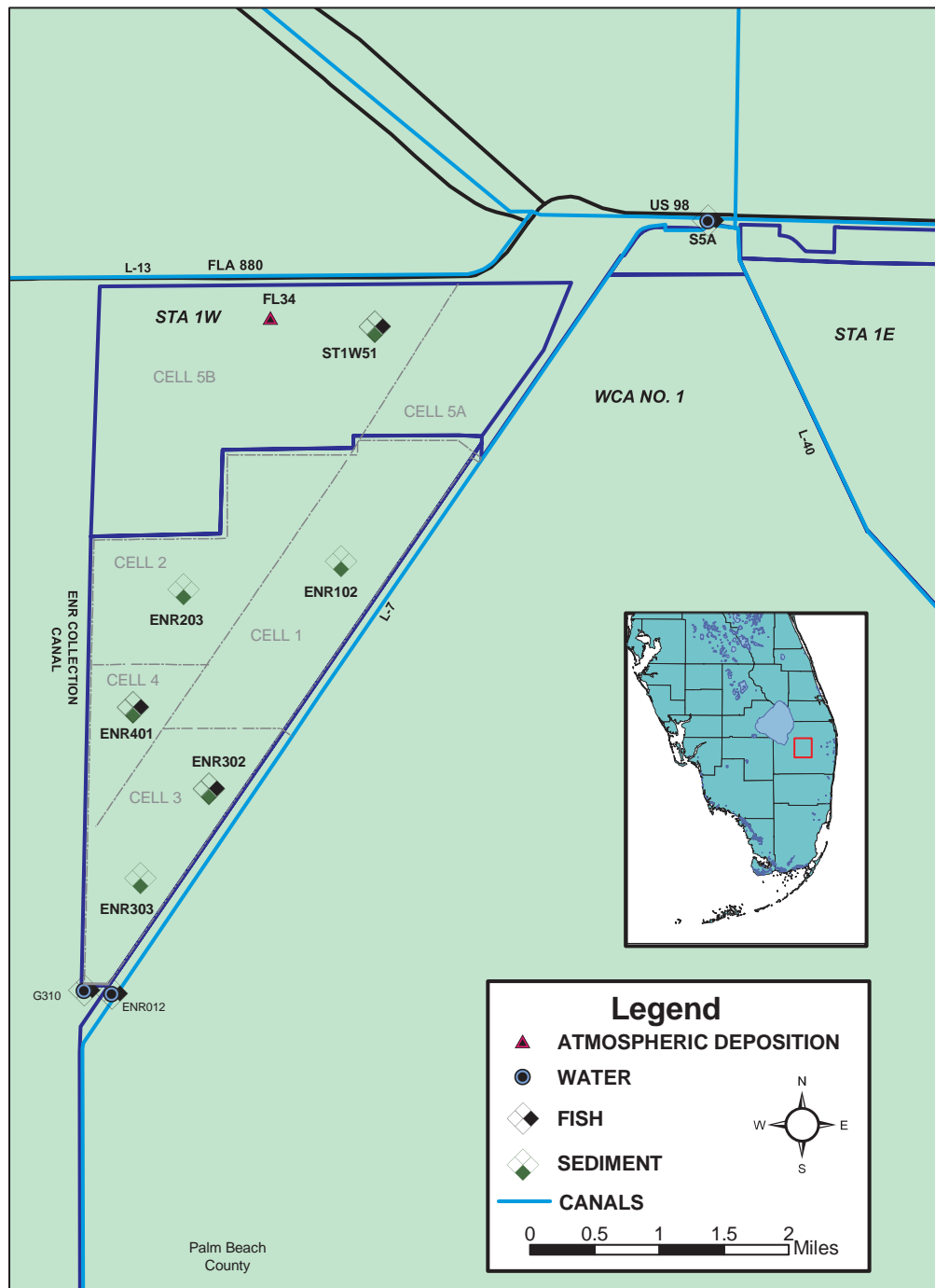
collection, otolith ages were first converted to decimal ages using protocols developed by Lange et al. (1999). Sunfish were not aged. Instead, arithmetic means were reported. However, efforts were made to estimate a least square mean mercury concentration based on the weight of the fish. Additionally, the distribution of the different species of *Lepomis* (warmouth, *L. gulosus*; spotted sunfish, *L. punctatus*; bluegill, *L. macrochirus*; and redear sunfish, *L. microlophus*) that were collected during electroshocking was also qualitatively considered as a potential confounding influence on mercury concentrations prior to each comparison.

Where appropriate, analysis of covariance (ANCOVA), using the SAS General Linear Model procedure, was used to evaluate spatial and temporal differences in mercury concentrations, with age (largemouth bass) or weight (sunfish) as a covariate. However, use of ANCOVA is predicated on several critical assumptions (Zar, 1996). These assumptions are that (1) regressions are simple linear functions; (2) regressions are statistically significant (i.e., nonzero slopes); (3) covariate is a random, fixed variable; (4) both the dependent variable and residuals are independent and normally distributed; and (5) slopes of regressions are homogeneous (parallel, i.e., no interactions).

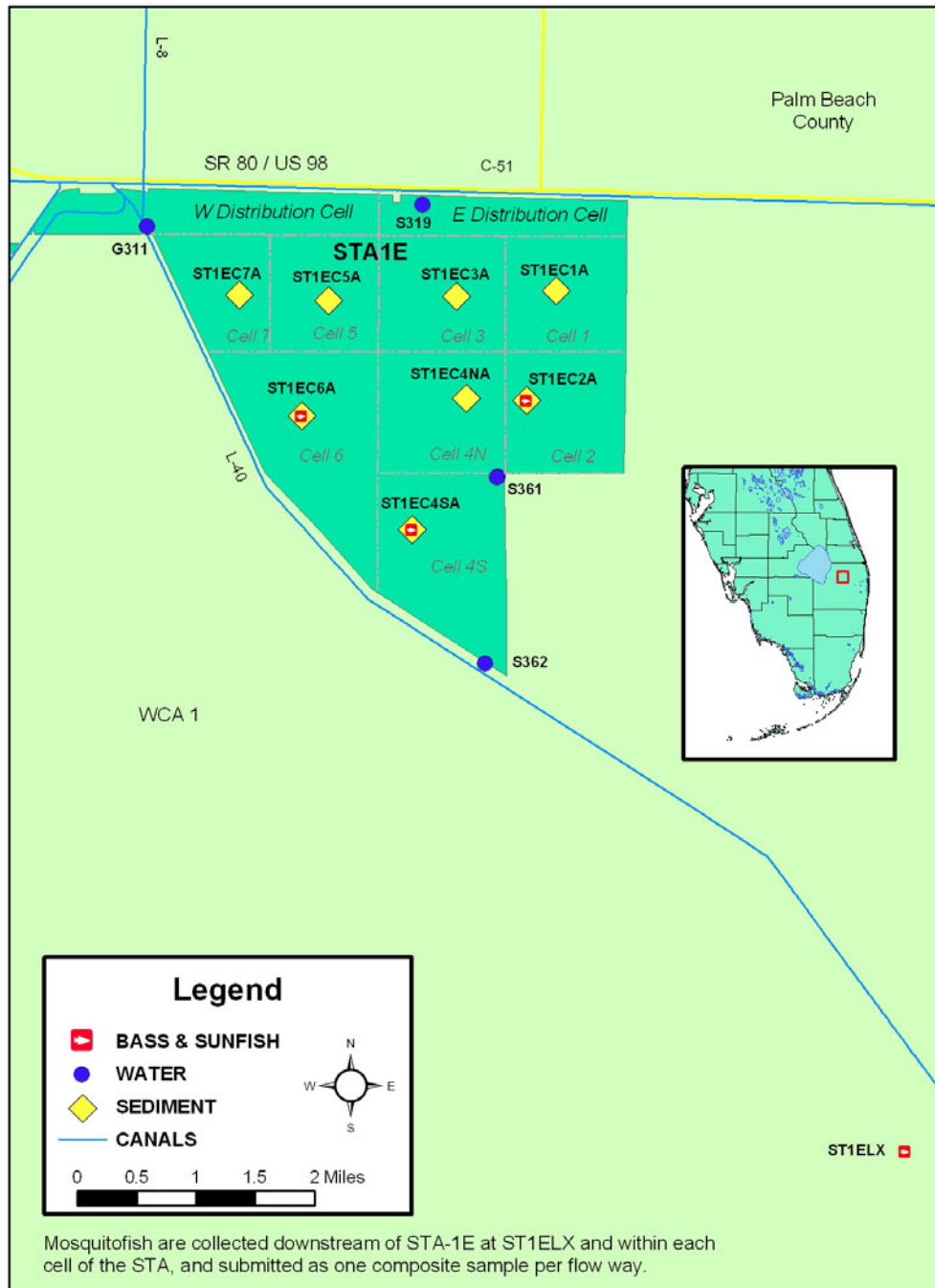
Regressions also require that collected samples exhibit a relatively wide range of covariate, that is, that fish from a given site are not all the same age or weight. Where these assumptions were not met, ANCOVA was inappropriate. Instead, standard analysis of variance (ANOVA) or Student's t-tests were used. Possible covariates were considered separately and often qualitatively. The assumptions of normality and equal variance were tested by the Kolmogorov-Smirnov and Levene Median tests, respectively. Datasets that either lacked homogeneity of variance or departed from normal distribution were natural-log transformed and reanalyzed. If transformed data met the assumptions, then they were used in ANOVA. If they did not meet the assumptions, then raw datasets were evaluated using nonparametric tests such as the Kruskal-Wallis ANOVA on ranks or the Mann-Whitney Rank sum test. If the multigroup null hypothesis was rejected, then groups were compared using either Tukey HSD (honestly significant difference) or Dunn's Method.

## SITE DESCRIPTIONS

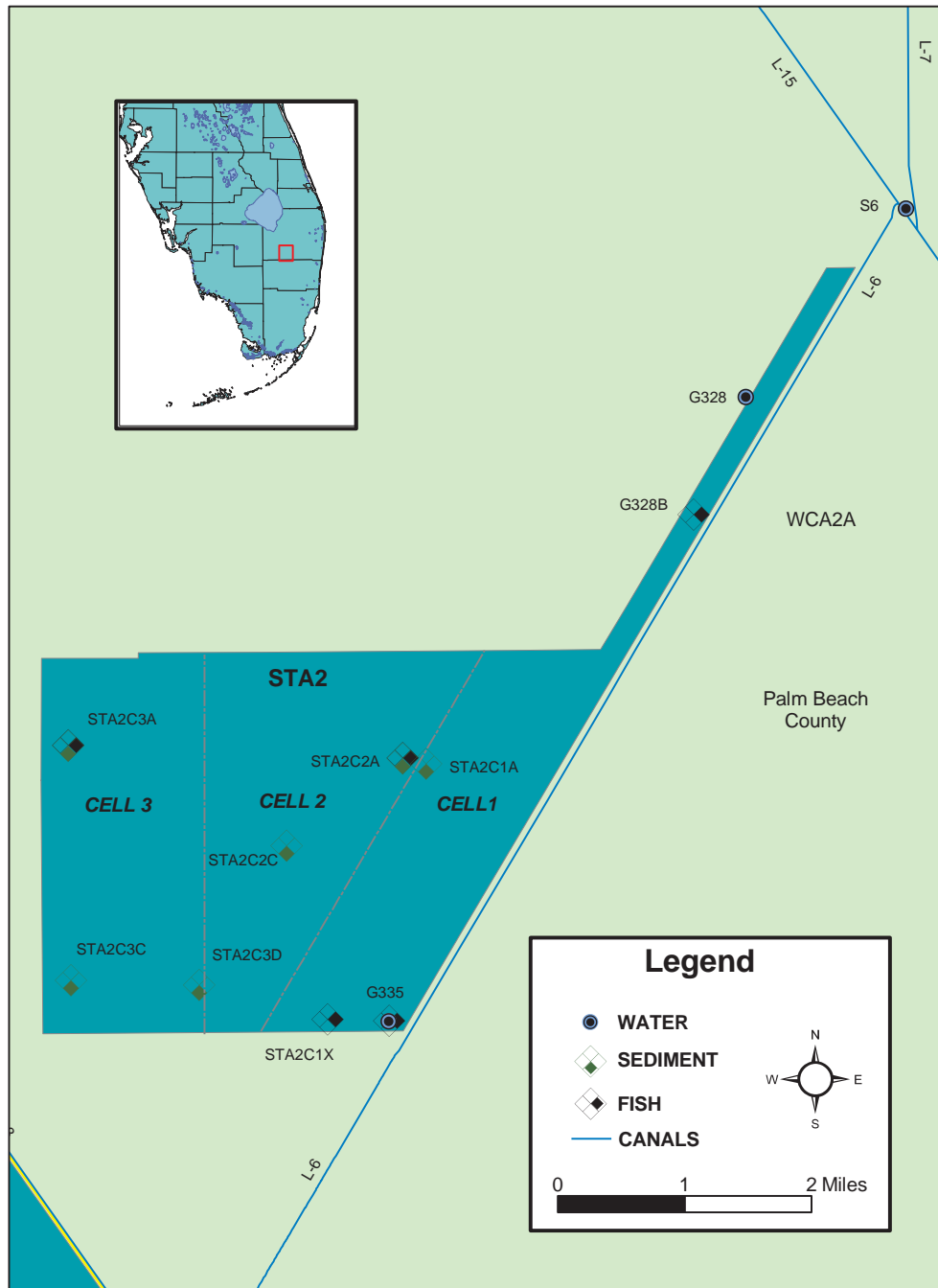
Site descriptions and operational plans for STAs 1W, 2, 3/4, 5, and 6 are published elsewhere (SFWMD, 1997; 1998a; 1998b; 1999d; 2004); similar information on STA-1E was not available as of the date of this report. For maps of monitoring locations, see **Figures 1** through **6**.



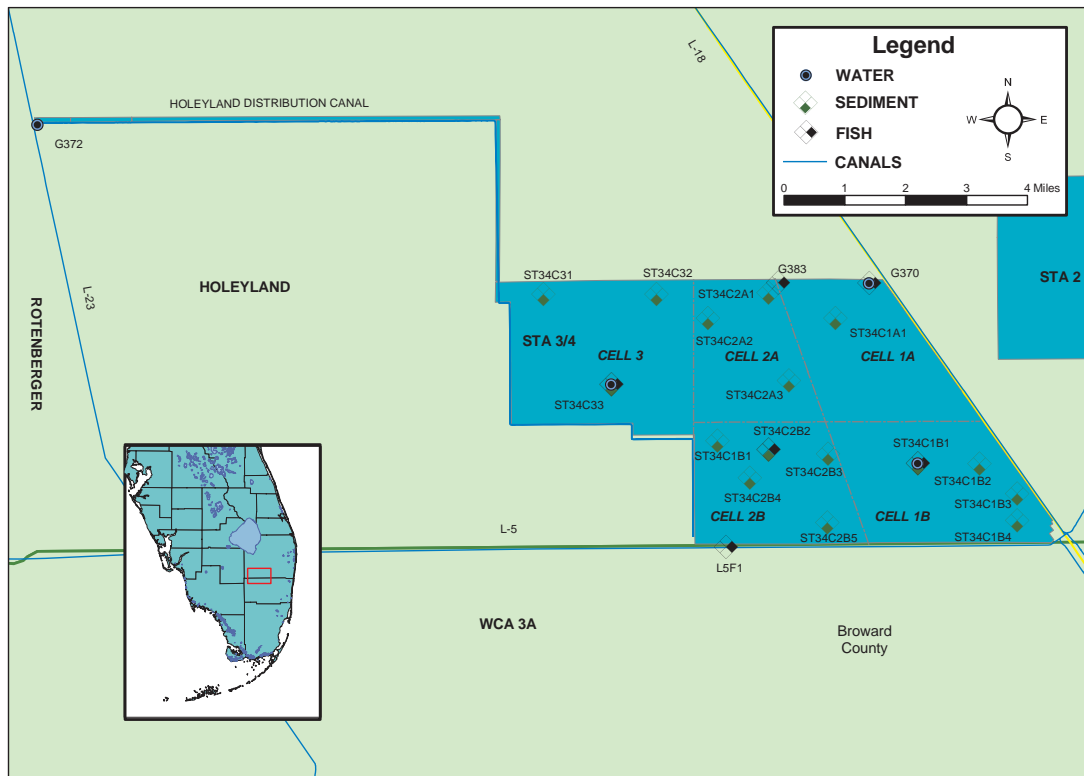
**Figure 1.** Mercury monitoring sites – Stormwater Treatment Area 1W.



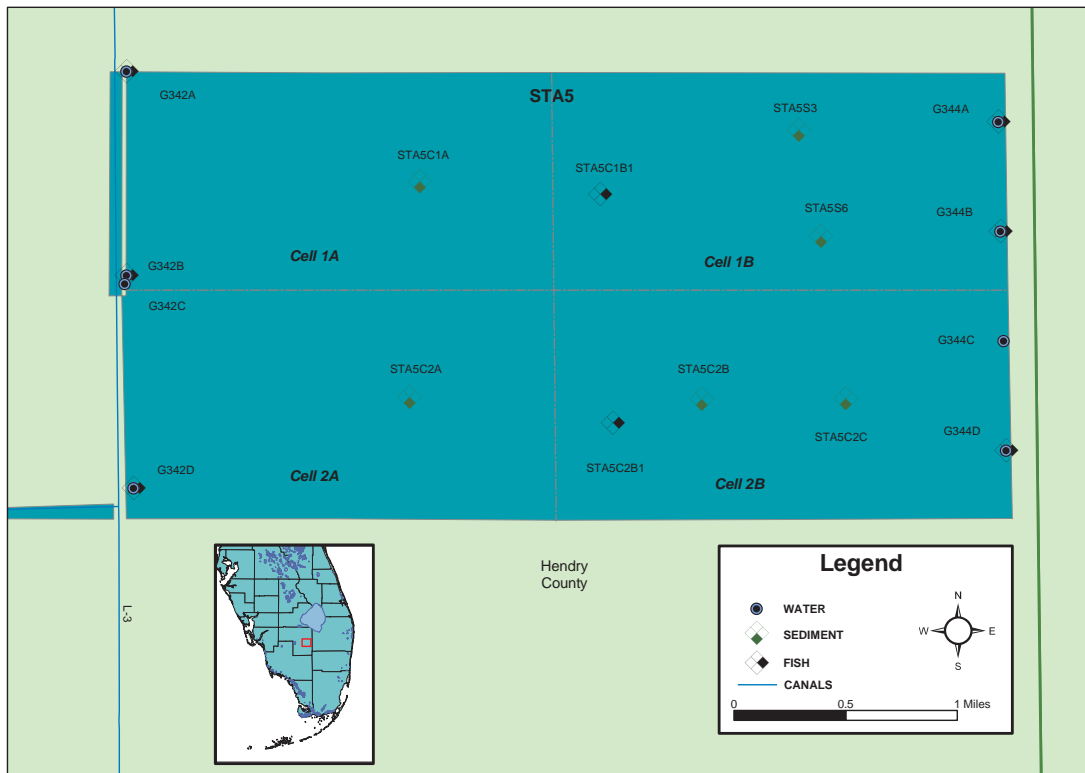
**Figure 2.** Mercury monitoring sites – Stormwater Treatment Area 1E.



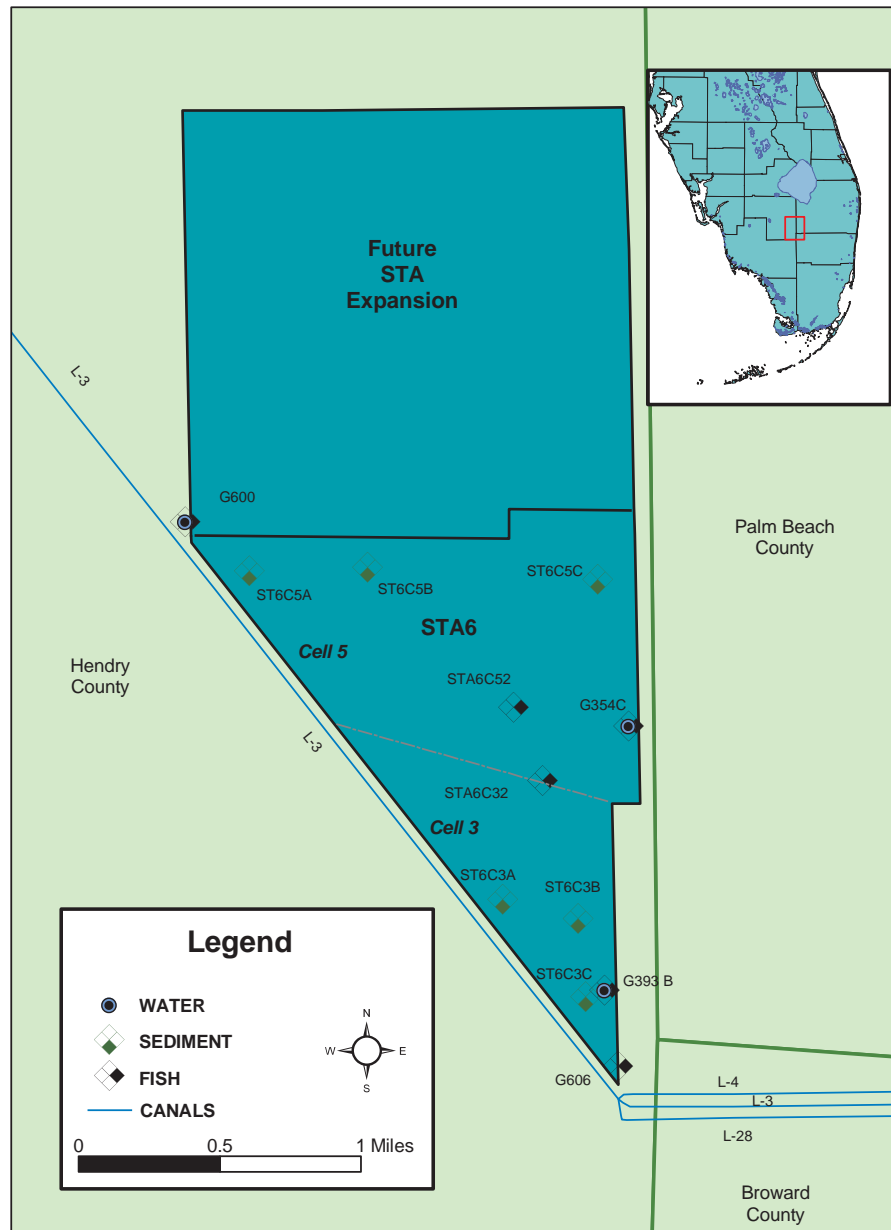
**Figure 3.** Mercury monitoring sites – Stormwater Treatment Area 2.



**Figure 4.** Mercury monitoring sites – Stormwater Treatment Area 3/4.



**Figure 5.** Mercury monitoring sites – Stormwater Treatment Area 5.

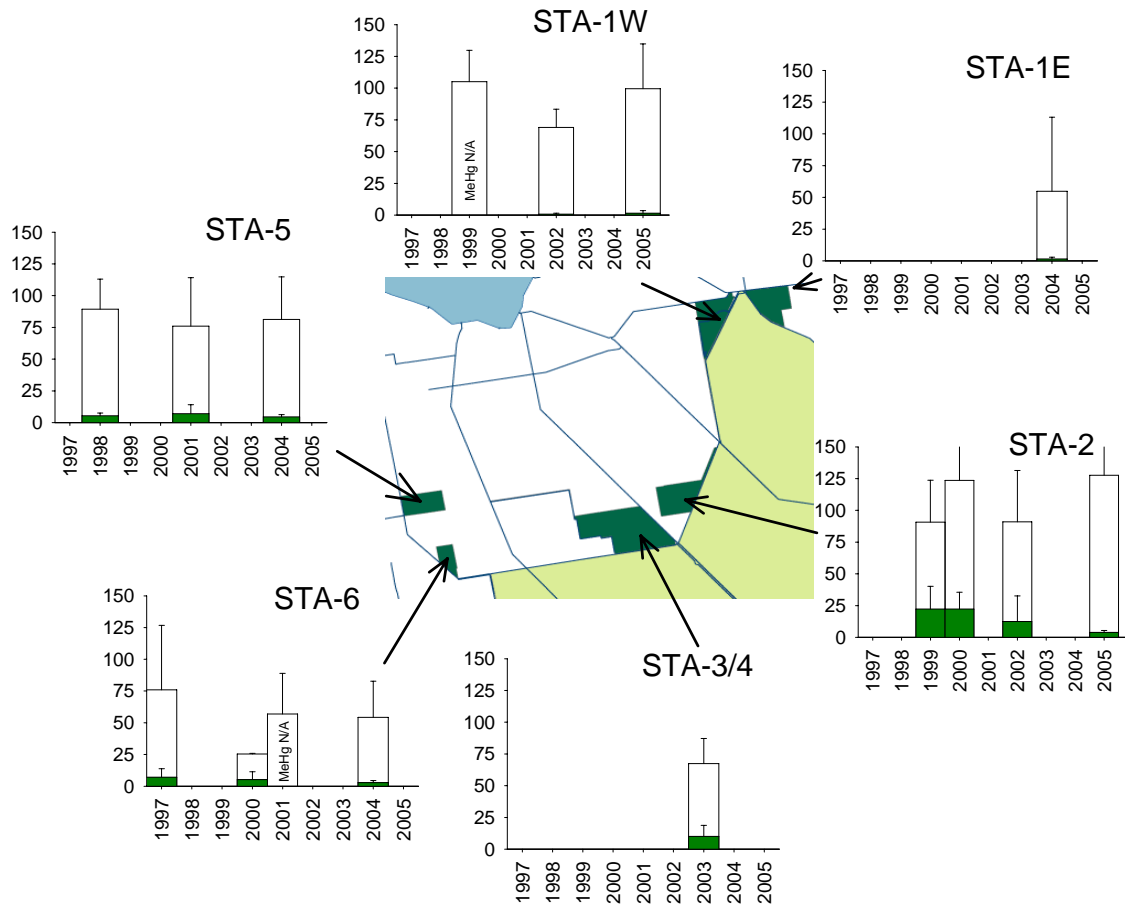


**Figure 6.** Mercury monitoring sites – Stormwater Treatment Area 6.

## MONITORING RESULTS

### PRE-OPERATIONAL MONITORING

Results from pre-operational monitoring of STAs 1W, 1E, 2, 3/4, 5, and 6 have been reported previously (SFWMD, 1998c, 1999d; Rumbold and Rawlik, 2000; Rumbold and Fink, 2002a, 2003a; Rumbold 2004a, 2005a; Rumbold et al., 2001a, 2006; **Figure 7** summarizes the results of pre-operational sediment collection).



**Figure 7.** Mean concentration (+1 Standard Deviation [SD]; dry weight basis) of THg (ng/g) and MeHg (10x ng/g) in sediment cores (n = 6; 0–10 cm) collected from each STA prior to start-up and once every three years thereafter.

### OPERATIONAL MONITORING

#### STA-1W

In 2000, STA-1W subsumed the ENR Project (Cells 1 through 4, **Figure 1**), which had been in operation since 1994. STA-1W surface water passed start-up criteria during the week of January 17, 2000; flow-through operations began in early February 2000. Formal monitoring of mercury levels in STA-1W surface water began on February 16, 2000 (for discussion of results

observed prior to 2005, see Rumbold and Rawlik, 2000; Rumbold et al., 2001a, 2006; Rumbold and Fink, 2002a, 2003a; Rumbold, 2004a, 2005a;).

As shown in **Figure 8**, concentrations of both THg and MeHg in surface water at the outflows of STA-1W remained low, as compared to the inflow and as compared to (inflows and outflows of) other STAs. As discussed in the 2006 report, after an period of inundation dating back to 1997 (Rumbold and Fink, 2002b), several of the cells were taken off-line during the calendar year and allowed to draw down to allow for construction activities (**Figure 9**). The drawdowns appeared to have no marked effect on water-column concentrations at the outflows during this calendar year (**Figure 8**). Further, the long-term trend of lower annual median concentrations in the outflows as compared to the inflow continued through the calendar year (**Figures 10 and 11**). These lower concentrations, combined with flows, resulted in smaller loads of THg and MeHg in the two outflows (e.g., G-251 and G-310) as compared to the estimated loads to the cells (**Figures 12 and 13**).

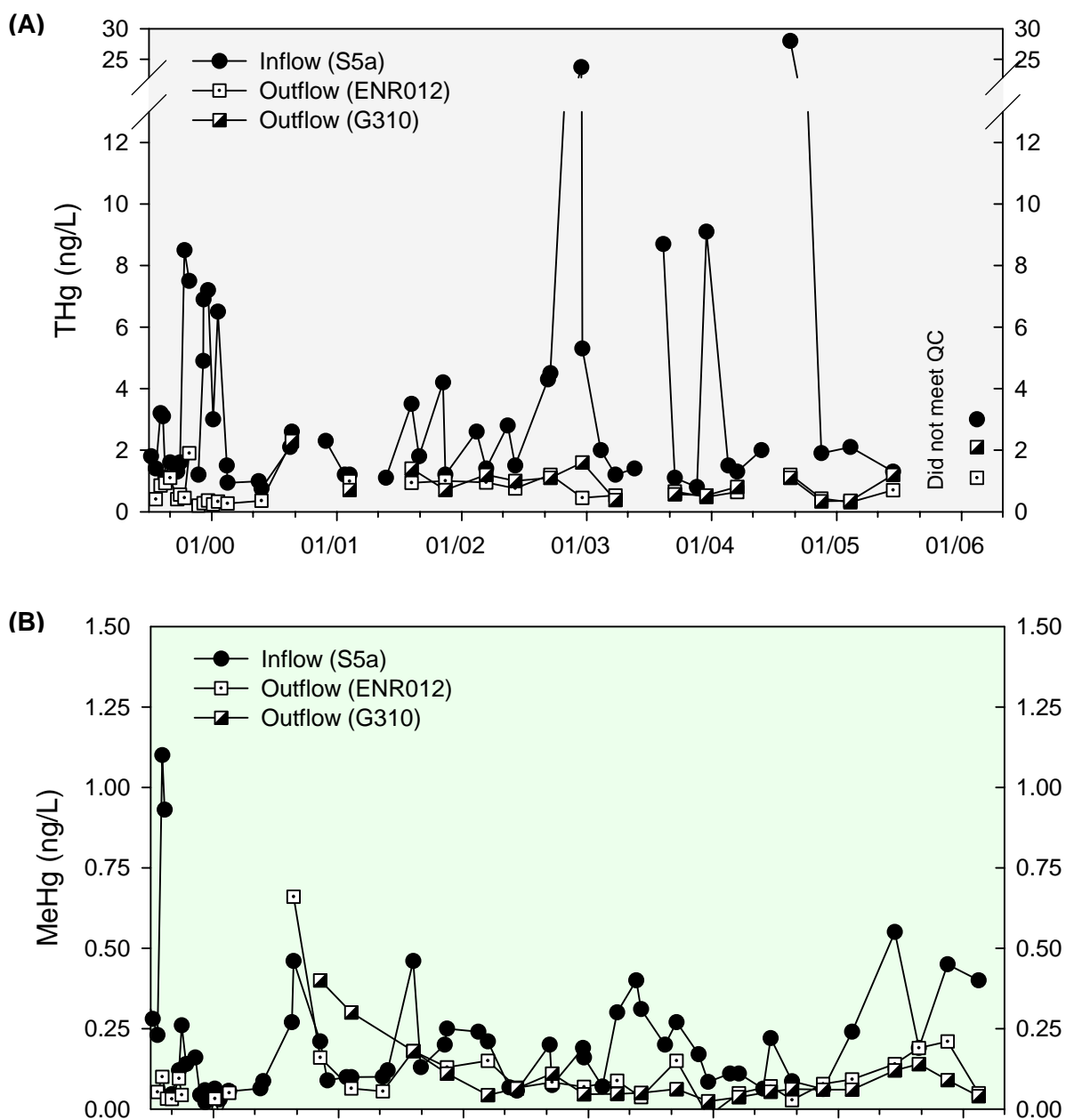
Concentrations of THg in mosquitofish summarized in **Table 1** are graphically presented in **Figure 14**. Mosquitofish from STA-1W continue to have very low mercury levels, similar to levels when the area was operated as the ENR project (Rumbold and Fink, 2002b). Furthermore, mercury levels in STA-1W mosquitofish continue to be lower than levels currently observed in fish from other areas of the Everglades (Appendix 3B-1 of this volume). As noted with water-column concentrations, mercury levels in mosquitofish from STA-1W did not increase markedly following the drawdowns and reflooding during the year; mosquitofish consistently exhibited a negative percent change in tissue-Hg levels across STA-1W (**Table 1**). This pattern was also observed in sunfish and largemouth bass.

As shown in **Table 2** and **Figures 14 and 15**, STA-1W sunfish continued to have mercury levels much lower than those observed in sunfish at the other STAs and locations within the Everglades (Appendix 3B-1 of this volume). When the dataset was censored to consider only bluegill, *L. macrochirus*, and normalized mercury levels based on fish length, it is even more evident that mercury levels have remained relatively low at STA-1W compared to other STAs (**Figure 15**) and downstream sites (Figure 13 in Appendix 3B-1 of this volume).

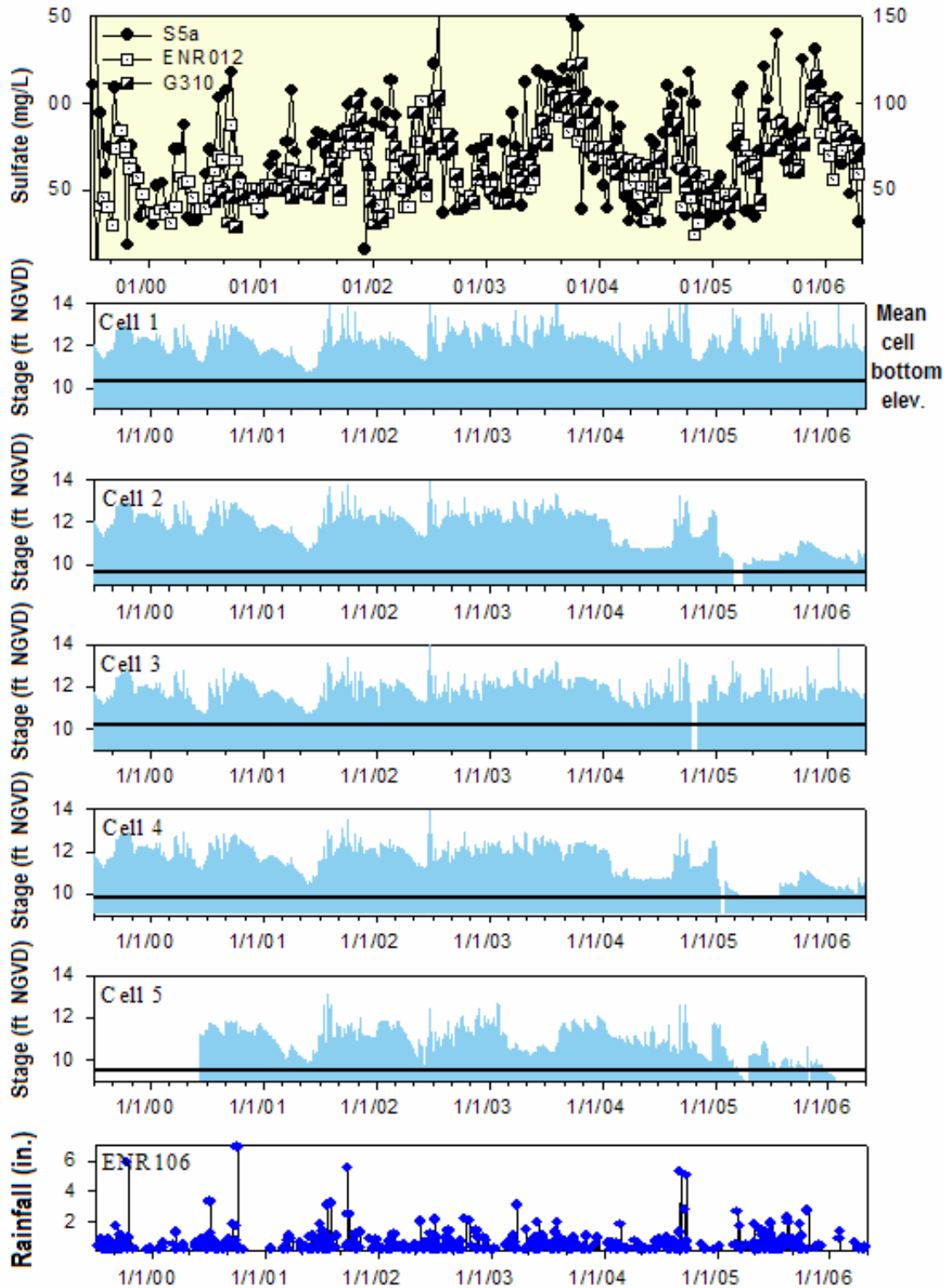
As with sunfish, largemouth bass from interior of STA-1W contained lower mercury levels than bass from the other STAs (**Table 3** and **Figure 14**). Moreover, STA-1W bass contained much lower mercury than fish from downstream sites in the WCAs (Appendix 3B-1 of this volume). As with mosquitofish and sunfish, the bass exhibited a negative percent change in mercury levels across the STA (**Table 3**); **Figure 14** shows that bass from the supply canal (upstream of S5A) contained substantially greater mercury levels than fish both from interior marshes and from the discharge canals.

Consistent with previous assessments, mercury–age regressions were not statistically significant for fish from the two outflow sites. In other words, mercury levels did not increase significantly as age of fish increased. Notably, a young 0.8-year-old bass from site ENR012 contained 0.29 milligram per gram (mg/g), which produced a negative slope in the mercury–age regression. Although this level is relatively high for STA-1W, it is not unprecedented; at least seven other bass captured at this site or the interior marshes contained similar or higher levels over the period of record. By comparison, fish from the inflow site often contain much higher mercury levels (**Figure 14**).

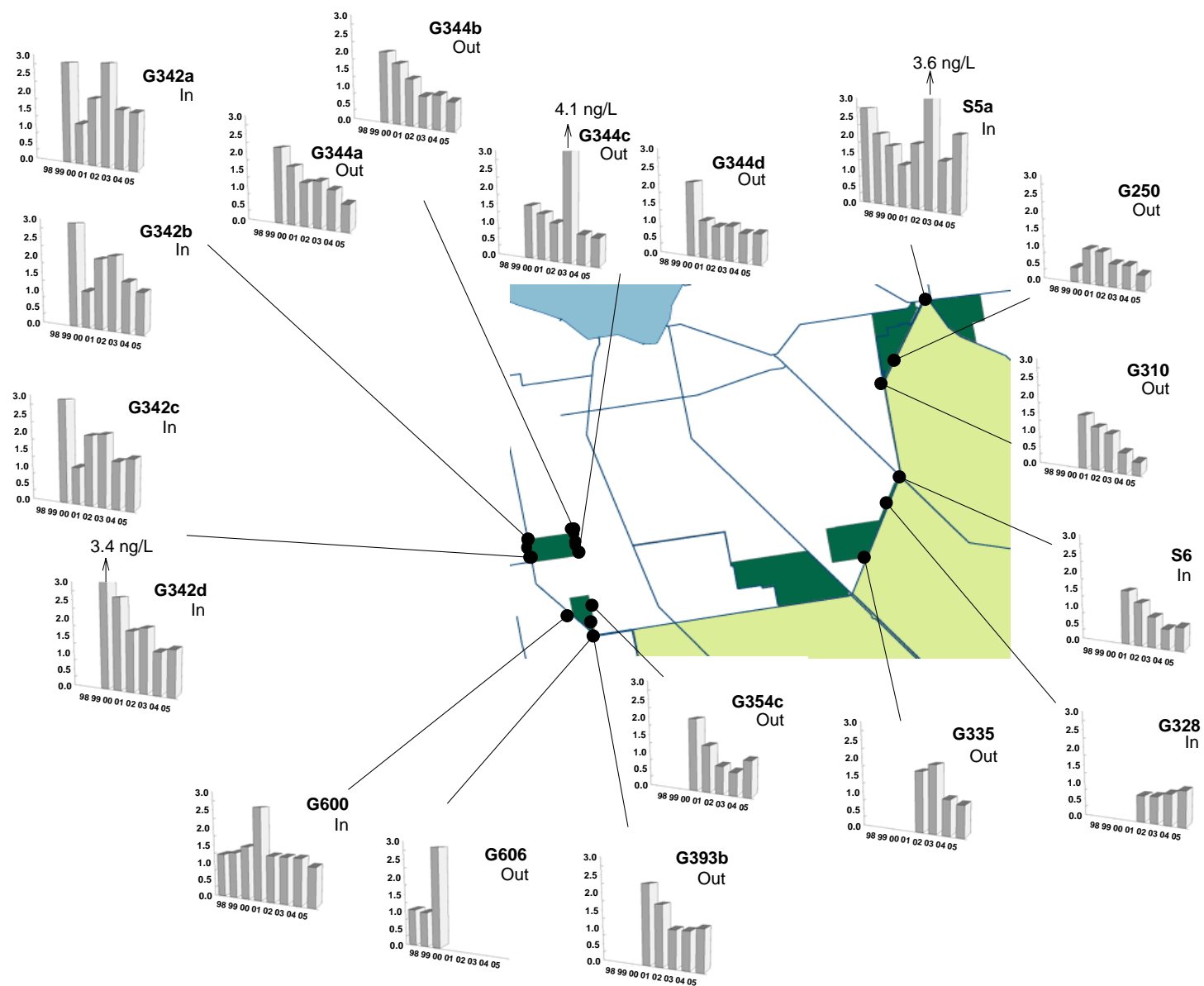
Mercury levels in fish tissues can also be evaluated for risk to fish-eating wildlife. Contrary to other areas of the Everglades, fish-eating wildlife foraging preferentially at STA-1W do not appear to be at risk from mercury exposure. STA-1W mosquitofish, sunfish, and largemouth bass continue to have some of the lowest tissue-Hg levels in South Florida — well below both the USEPA and USFWS guidance level for predator protection. (Eisler, 1987; USEPA, 1997).



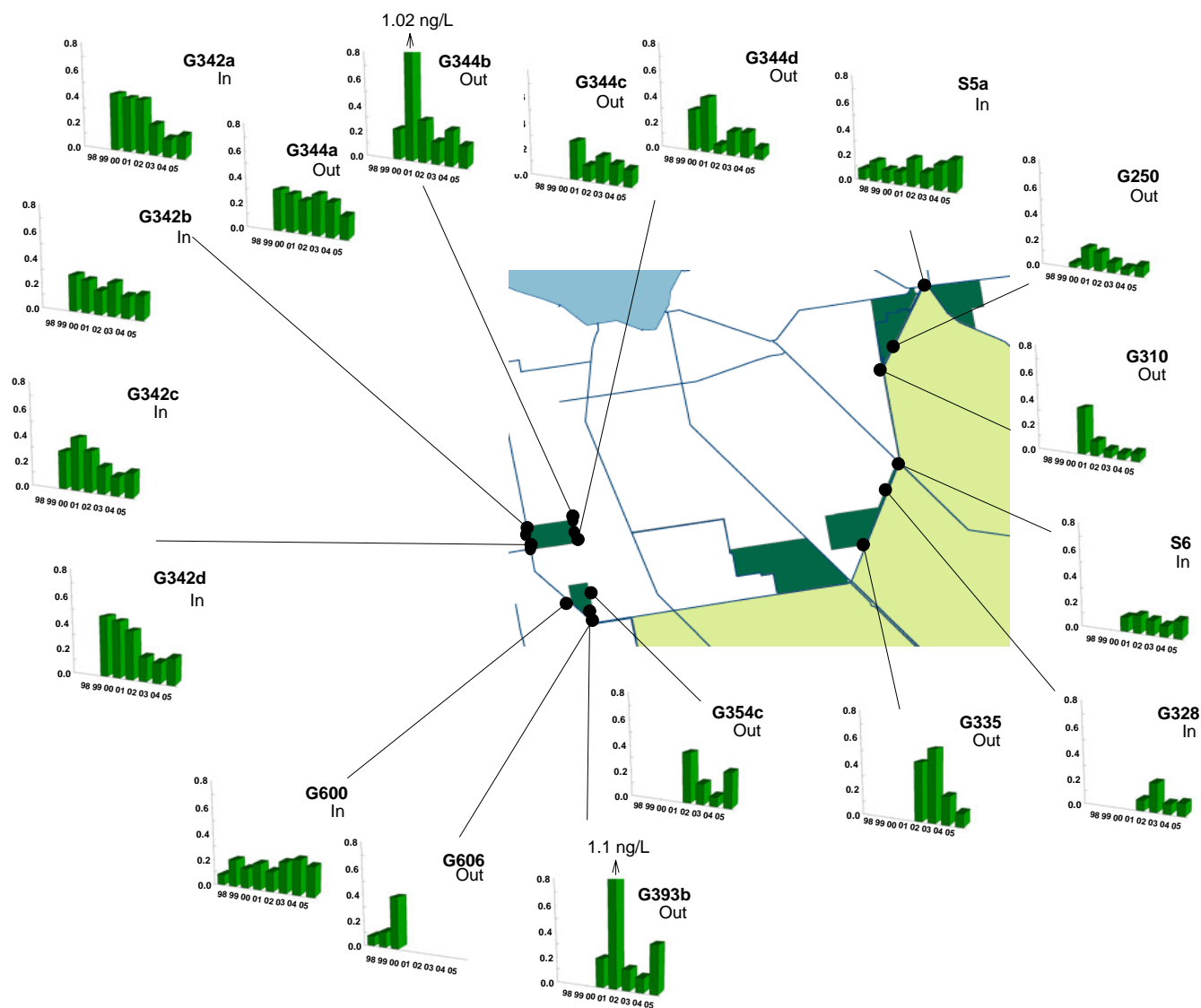
**Figure 8.** Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-1W.



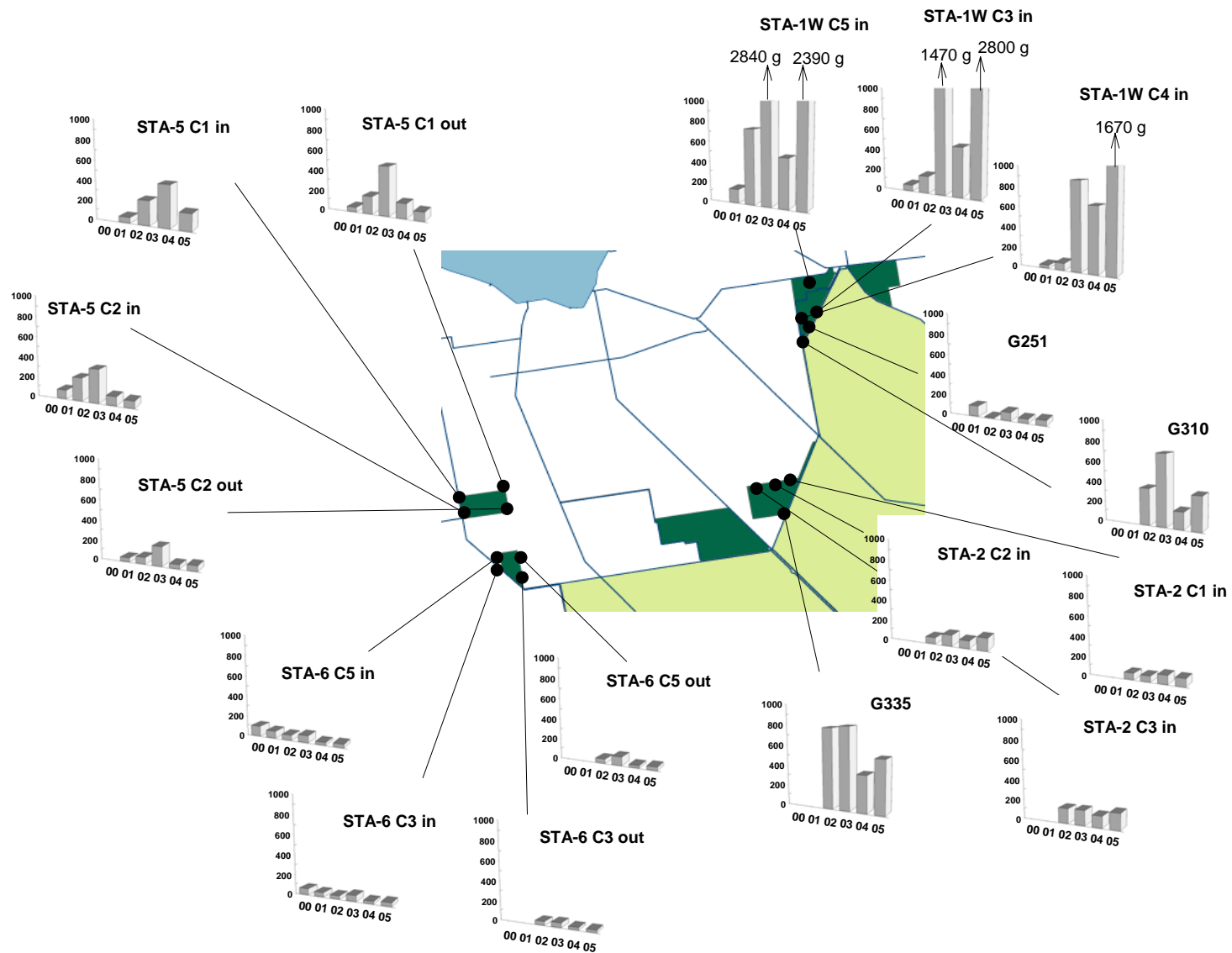
**Figure 9.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell) and rainfall at STA-1W.



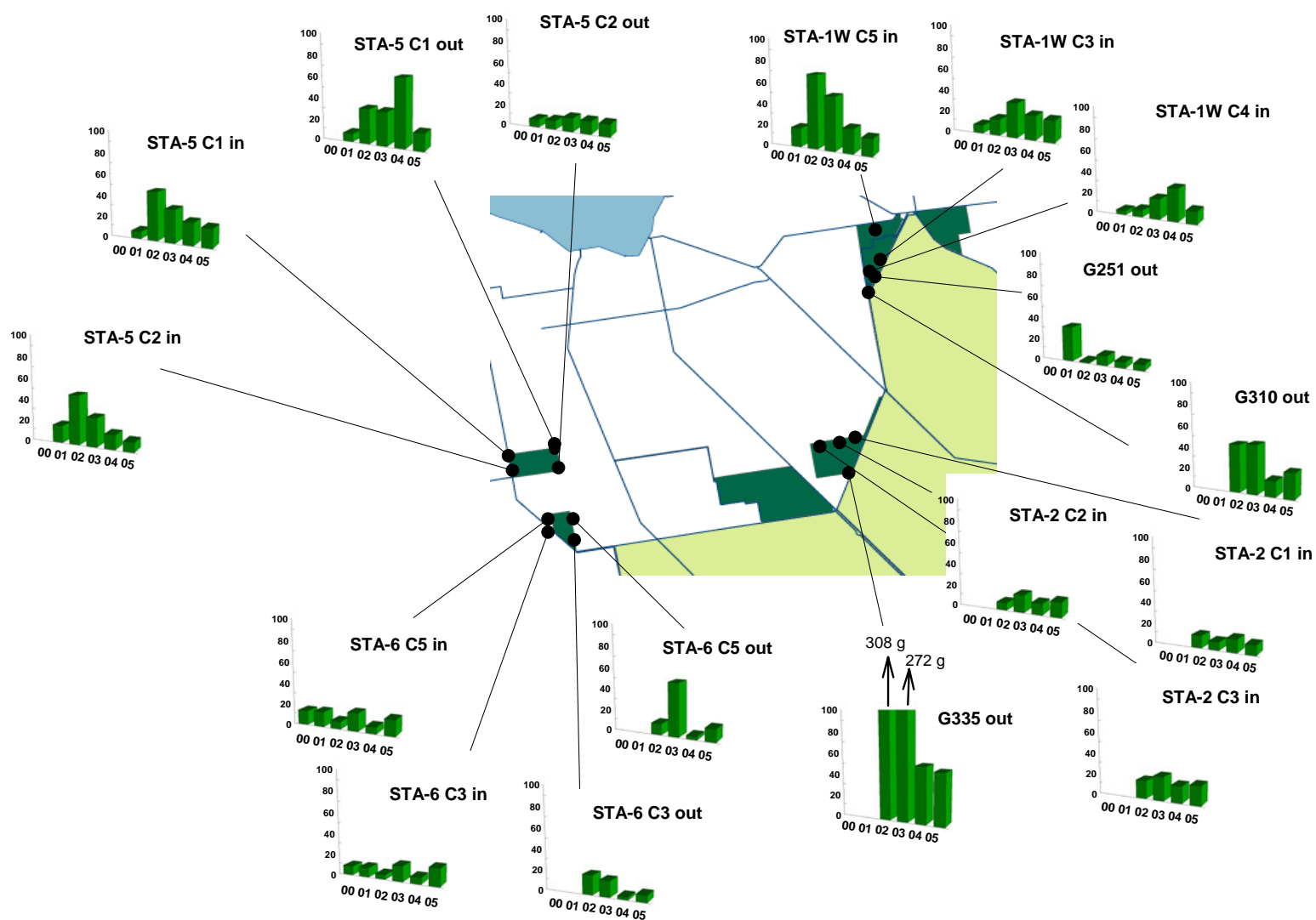
**Figure 10.** Annual median THg concentrations (ng/L) for period of record at inflows and outflows of STAs.



**Figure 11.** Annual median MeHg concentrations (ng/L) for period of record at inflows and outflows of STAs.



**Figure 12.** Estimated annual THg loads (in grams) for period of record at inflows and outflows of STAs.



**Figure 13.** Estimated annual MeHg loads (in grams) for period of record at inflows and outflows of STAs.

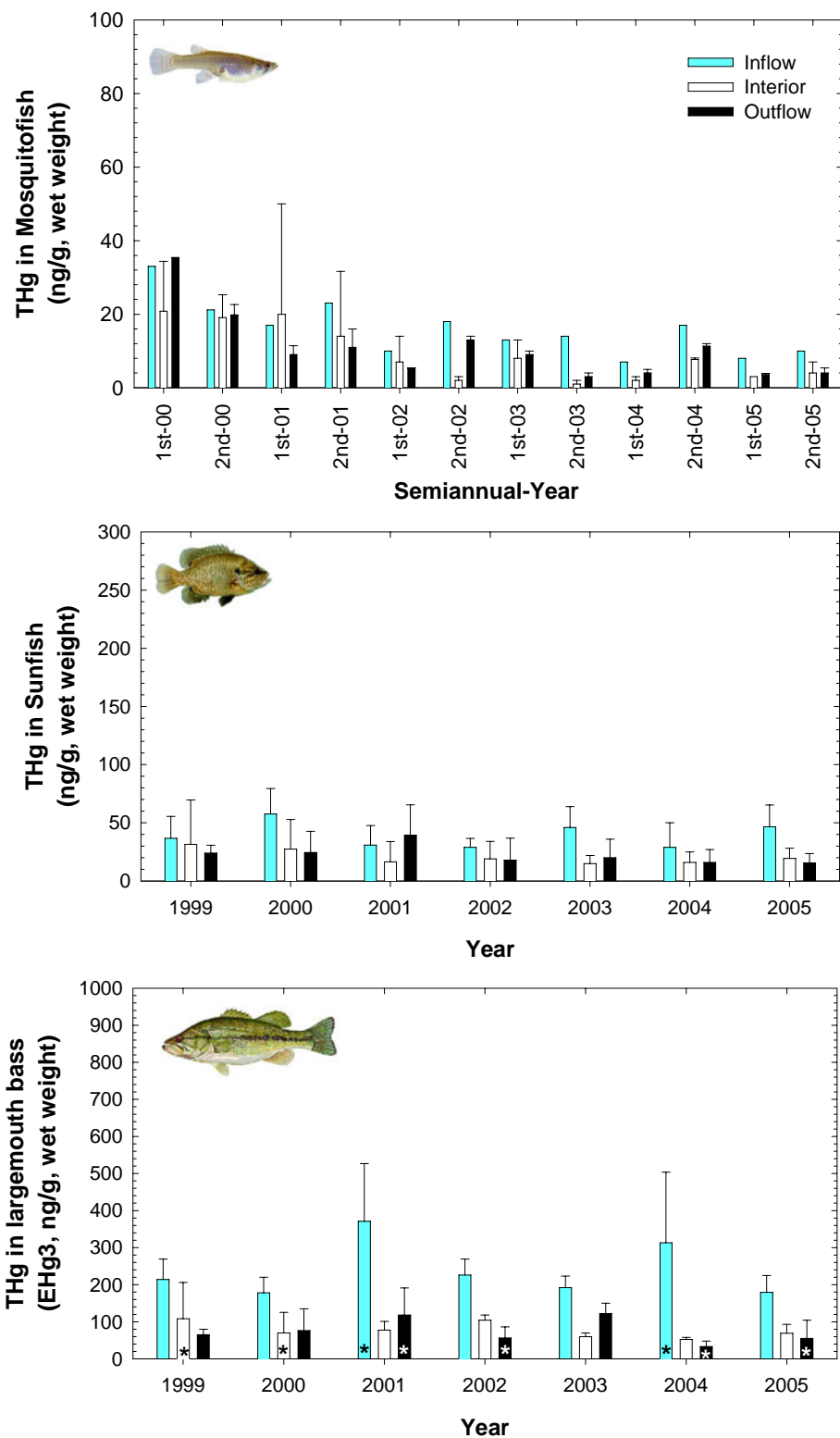
**Table 1.** Concentration of THg in mosquitofish\* composites collected semiannually from STAs (units ng/g wet weight).

STA	Half-year	Inflow Fish	Interior Fish	Outflow Fish	Percent Change <sup>a</sup>
STA-1W	2005 – 1	8	3	4	-50%
	2005 – 2	10	5	5	-50%
	Annual mean	9	4	4	-56%
	Cumulative mean	26	14	13	-50%
STA-1E <sup>b</sup>	2005 – 3	Not applicable	25	60	Not applicable
	2005 – 4	Not applicable	33	110	Not applicable
	Annual mean	Not applicable	29	85	Not applicable
	Cumulative mean	Not applicable	29	85	Not applicable
STA-2	2005 – 1	No fish	15	14	--
	2005 – 2	5	7	6	20%
	Annual mean	5	11	10	100%
	Cumulative mean	10	69	91	810%
STA-3/4	2005 – 1	16	31	31	94%
	2005 – 2	7	11	30	329%
	Annual mean	11	19	30	173%
	Cumulative mean	13	18	35	169%
STA-5	2005 – 1	13	10	13	0%
	2005 – 2	10	3	3	-70%
	Annual mean	11	7	8	-27%
	Cumulative mean	28	22	30	7%
STA-6	2005 – 1	23	11	41	78%
	2005 – 2	10	8	17	70%
	Annual mean	16	9	29	81%
	Cumulative mean	25	13	31	24%

\* Mosquitofish collected semiannually at inflow, interior, and outflow sites.

a Percent change = outflow-inflow/inflow

b STA-1E differs from other STAs in that mosquitofish are collected on a quarterly basis, are not collected from inflows, and outflow collection has been relocated to downstream marsh.



**Figure 14.** Mercury concentrations (ng/g, wet weight) in (*top*) mosquitofish composites (+range), (*middle*) whole sunfish ( $\pm$ SD), and (*bottom*) fillets of largemouth bass ( $\pm$ 95 percent Confidence Interval [C.I.] or, if arithmetic, SD) collected at STA-1W.

**Table 2.** Concentration of THg (ng/g, wet weight) in sunfish (*Lepomis* spp.) collected from STAs in 2005 (sample size in parentheses).

STA	Inflow Fish	Interior Fish	Outflow Fish	Percent Change <sup>a</sup>
STA-1W	47 ±19 (20)	19 ±9 (57 <sup>b</sup> )	16 ±8 (28)	-66%
Cumulative mean <sup>c</sup>	39	20	22	-44%
STA-1E <sup>d</sup>	Not applicable	120 ±56 (10)	138 ±34 (5)	--
Cumulative mean	--	120	138	--
STA-2	35 ±13 (20)	41 ±50 (48)	Not available	--
Cumulative mean	64	116	123	--
STA-3/4	50 ±38 (40)	70 ±56 (60 <sup>b</sup> )	104 ±46 (20 <sup>b</sup> )	108%
Cumulative mean	50	92	102	104%
STA-5	83 ±73 (20)	46 ±21 (8)	112 ±35 (20)	35%
Cumulative mean	72	88	90	25%
STA-6	46 ±14 (20)	46 ±32 (37 <sup>b</sup> )	84 ±41 (20)	83%
Cumulative mean	59	52	102	73%

a Percent change = outflow-inflow/inflow

b Where n > 20; multiple sites were sampled and pooled, i.e., multiple interior or outflows.

c Grand mean of annual means; sunfish collected in 1999 were included in the cumulative average prior to permit revision or STA operation (in the case of STA-5 and STA-1W).

d STA-1E differs from other STAs; sunfish were not collected from inflows, sample size is 5, and outflow collection has been relocated to downstream marsh.

**Table 3.** Standardized, EHg3  $\pm$  95%, and arithmetic mean concentration (mean  $\pm$  1 SD, n) of THg (ng/g, wet weight) in fillets from largemouth bass collected at STAs in 2005.

STA	Inflow Fish	Interior Fish	Outflow Fish	Percent Change <sup>a</sup>
STA-1W	179 $\pm$ 46 (230 $\pm$ 140, 18)	69 $\pm$ 24 (58 $\pm$ 55, 23 <sup>b</sup> )	Not calculated (1) (55 $\pm$ 49, 28)	-76%
Cumulative mean <sup>c</sup>	260	65	67	-74%
STA-1E <sup>d</sup>	Not applicable	Not calculated (2) (306 $\pm$ 15, 5)	Not calculated (2) (510 $\pm$ 169, 5)	67%
Cumulative mean <sup>c</sup>	--	306	510	67%
STA-2	75 $\pm$ 123 (334 $\pm$ 262, 20)	110 $\pm$ 35 (163 $\pm$ 129, 42)	Not available	--
Cumulative mean	260	279	753	190%
STA-3/4	292 $\pm$ 28 (217 $\pm$ 107, 36)	485 $\pm$ 94 (258 $\pm$ 79, 20)	Not calculated (1) (482 $\pm$ 120, 20)	122%
Cumulative mean	211	228	544	158%
STA-5	196 $\pm$ 57 (137 $\pm$ 73, 20)	Not available Not available	Not available Not available	-- --
Cumulative mean <sup>d</sup>	175	315	435	149%
STA-6	261 $\pm$ 18 (255 $\pm$ 69, 20)	160 $\pm$ 43 <sup>e</sup> (105 $\pm$ 59, 21)	273 $\pm$ 30 (290 $\pm$ 160, 20)	5%
Cumulative mean	265	295	470	77%

a Percent change = outflow-inflow/inflow based on EHg3 where available.

b Where n > 20; multiple sites were sampled and pooled, i.e., multiple interior or outflows.

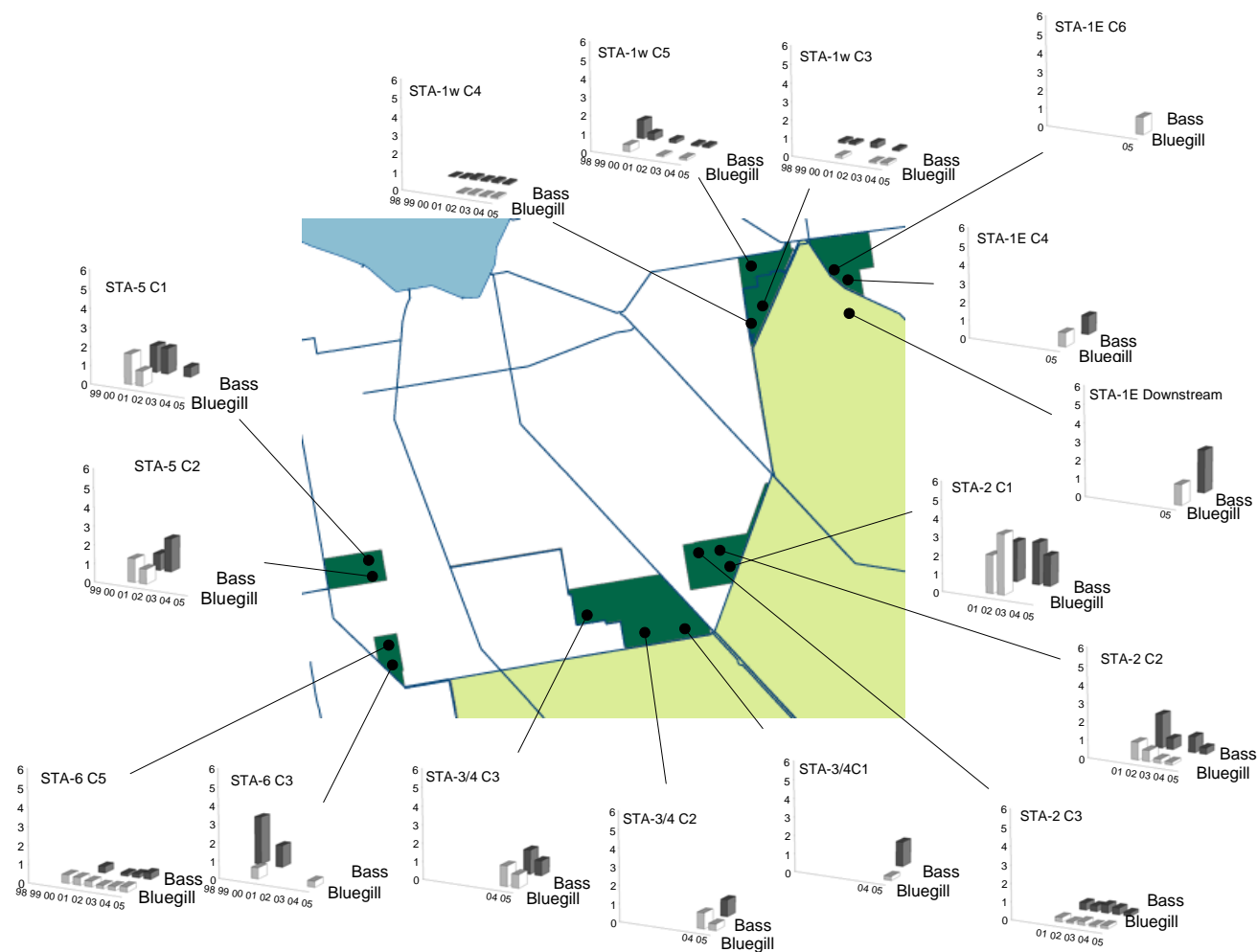
c Arithmetic grand mean of annual means; bass collected in 1999 prior to operation of STA-5 and STA-1W were included.

d STA-1E differs from other STAs in that sunfish are not collected from inflows, sample size is 5, and outflow collection has been relocated to downstream marsh.

e Cell 5 bass only; excludes single bass from Cell 3.

Not calculated Where (1) regression slope was not significantly different from 0 or (2) poor age distribution of collected fish.

Not available No bass in sample.



**Figure 15.** Spatial and temporal patterns in Mercury levels in young largemouth bass (less than 1.8 years old) and bluegill sunfish (4 to 7 inches in length).<sup>2</sup>

<sup>2</sup> Hg levels in fish were further normalized by dividing concentration in a fish by its total length, hence, y-axis units are in mg/kg/m (*cf.* Brumbaugh et al., 2001). The x-axis shows years in which fish were sampled; however, fish of appropriate species, size or age were not collected in all years.

## STA-1E

Monitoring of water-column concentrations of THg and MeHg began in January 2005 at STA-1E. Both the central flow-way (Cells 3, 4N, and 4S) and the westernmost flow-way (Cells 5 through 7) met the startup criteria, as specified in EFA Permit No. 0195030-001-GL, in August 2005 (correspondence from R. Bearzotti, SFWMD, dated September 9, 2005). As of the date of this report, the USACE is constructing and shall operate a Periphyton-Based Stormwater Treatment Area (PSTA) Demonstration Project in the easternmost flow-way (Cells 1 and 2) of STA-1E.

As shown in **Figure 16**, both THg and MeHg remained at relatively low concentrations in the outflow, as compared to the multiple inflows, following the operation of the central and western flow-ways. THg concentration in the outflow of STA-1E did not exceed the Class III Water Quality Standard (WQS) of 12 ng/L. Interestingly, **Figures 16** and **17** reveal unexpected if small differences in water quality between the two northern inflows (i.e., G-311 and S-319).

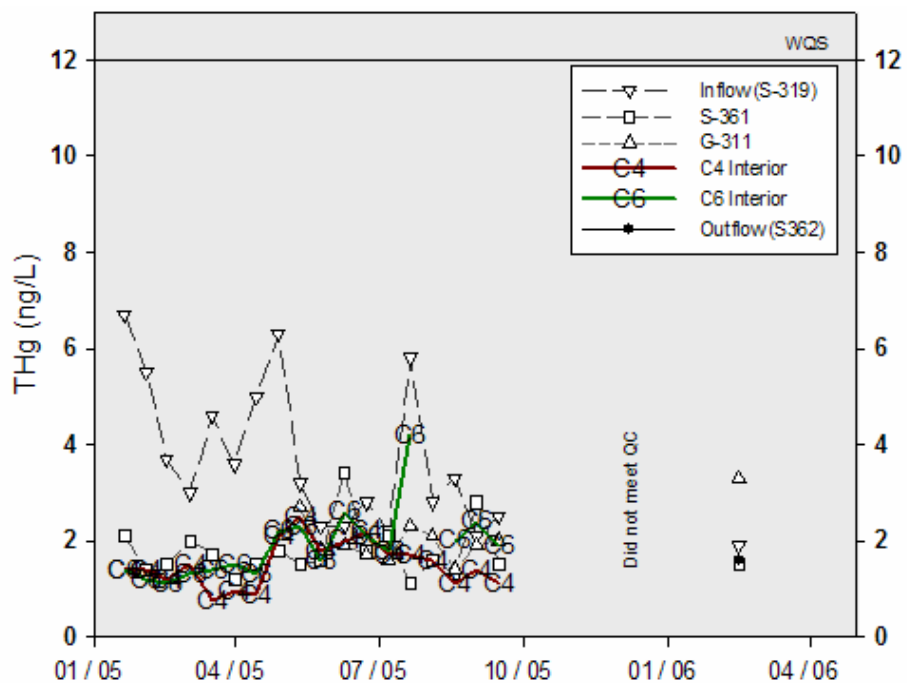
Before assessing the results from monitoring tissue concentrations in resident fish from STA-1E, several points should be emphasized. It should be noted that sampling locations, frequency of mosquitofish collections and numbers of sunfish and bass sampled at this STA differ from the older STAs (i.e., no inflow site and outflow site has been relocated to become a near-field downstream site within WCA-1 marsh, semi-annual collection to quarterly,  $n = 5$  each). It was felt that these changes in the monitoring plan would better capture and alert us to environmental impacts; it is the intent of the District to make similar changes to monitoring plans for the other STAs. It should also be noted that the first samples of mosquitofish were collected within a month of flooding. Although this may have been sufficient time for body burdens in mosquitofish to change in response to altered mercury cycling, results from the sunfish and bass collected in October 2005 should be considered baseline.

Quarterly collection of mosquitofish from STA-1E sites at interior marshes and the single downstream site (ST1ELX), began during the third quarter of 2005 (**Table 1**, **Figure 18**). As shown in **Figure 18**, mercury levels in mosquitofish from the interior marshes were comparable to other STAs and did not increase markedly over the final two quarters in 2005. By comparison, the mosquitofish from the near-field downstream site in WCA-1 contained levels generally higher than fish collected from other STAs (**Table 1**) and levels in these fish increased markedly in the fourth quarter. While the increase in mercury in the downstream mosquitofish warrant further scrutiny, it is premature to attribute the increases to STA-1E, given the mercury levels in interior mosquitofish and in discharges from this STA (**Figure 16**). On the other hand, this cannot be ruled out, particularly as the outflow sulfate concentration at S-362 averaged  $41.6 \pm 14.5$  mg/L from October through December 2005. (Mercury levels in downstream mosquitofish did decline to 41 ng/g by the first quarter of 2006, outside the reporting period.)

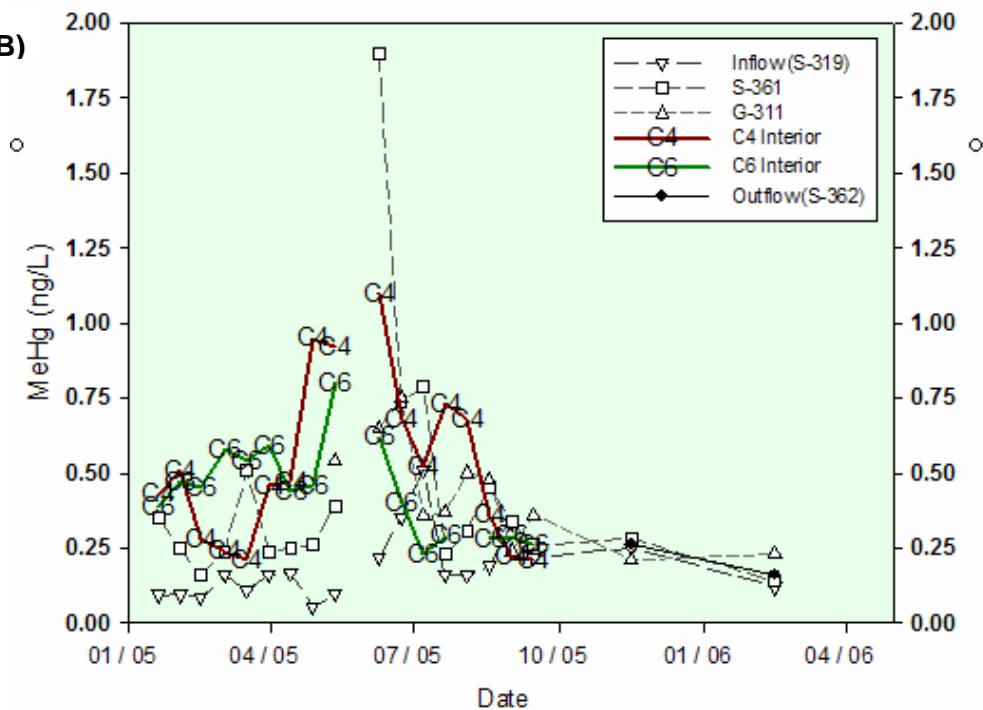
Annual collection of bluegill (*Lepomis macrochirus*) and largemouth bass occurred at these sites in October 2005 (five each from each site, except Cell 6 where no bass were found). As evident from **Tables 2** and **3**, mercury levels were elevated in STA-1E fish, particularly those from the downstream site, as compared to the other STAs. Levels in fish from the near-field downstream site (ST1ELX) were also elevated compared to levels recently observed at one on the far-field downstream sites, LOX4 (Appendix 3B-1). Standardized concentrations in bluegill from ST1ELX averaged 1.12 mg/kg/cm whereas bluegill from LOX4 averaged 0.88 mg/kg/cm (**Figure 15**; cf. Figure 13 in Appendix 3B-1). Bass from ST1ELX were all 0.8 years old and consequently a standardized EHg3 could not be estimated; however, these young fish averaged  $510 \pm 169$  mg/kg as compared to  $208 \pm 38$  mg/kg in similar aged bass from LOX4. Owing to the age and body mass of these fish, these levels should be interpreted as baseline levels. At this

point, the factor(s) responsible for this geographical difference in mercury levels between ST1EX and LOX4 are unknown.

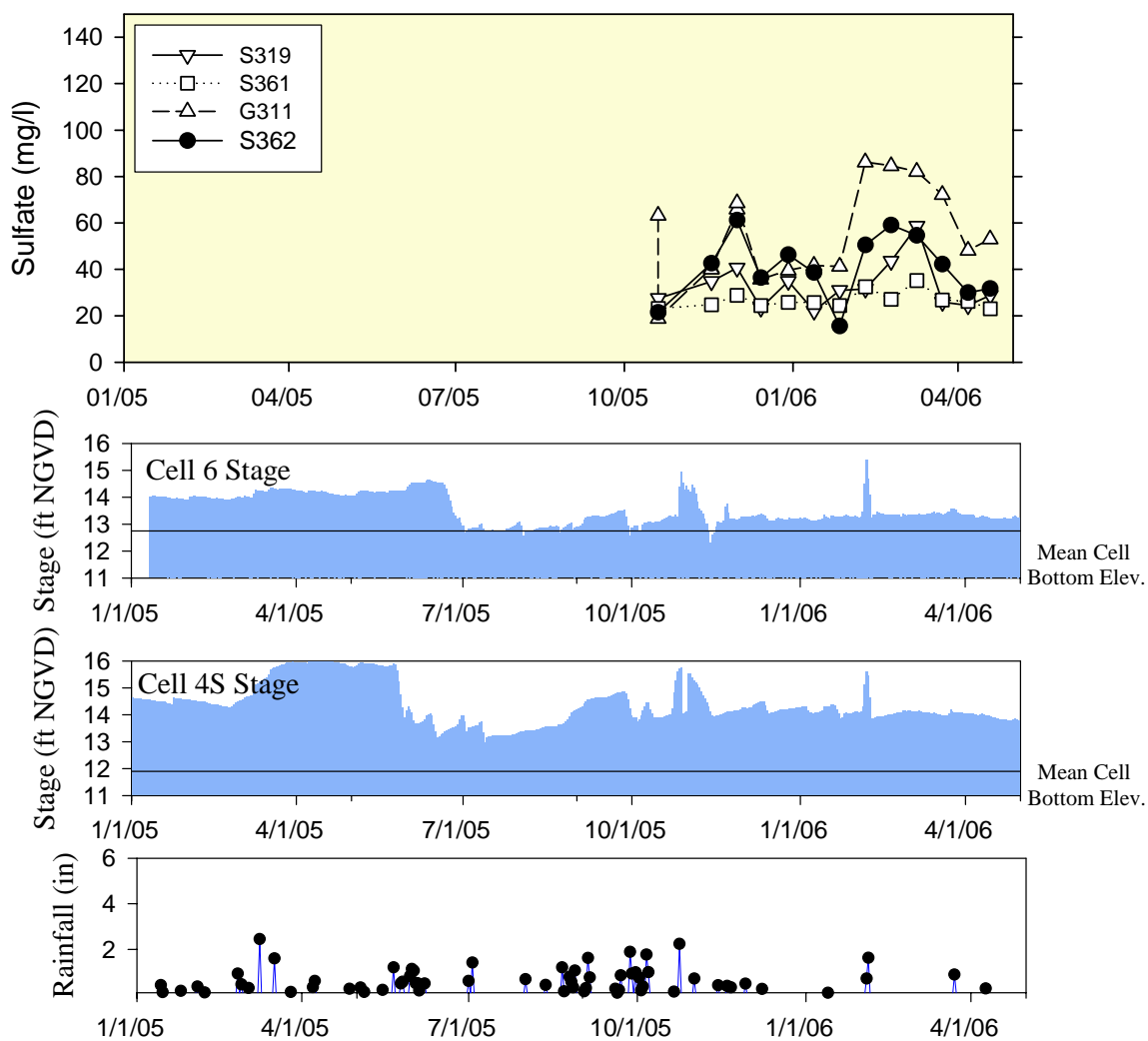
(A)



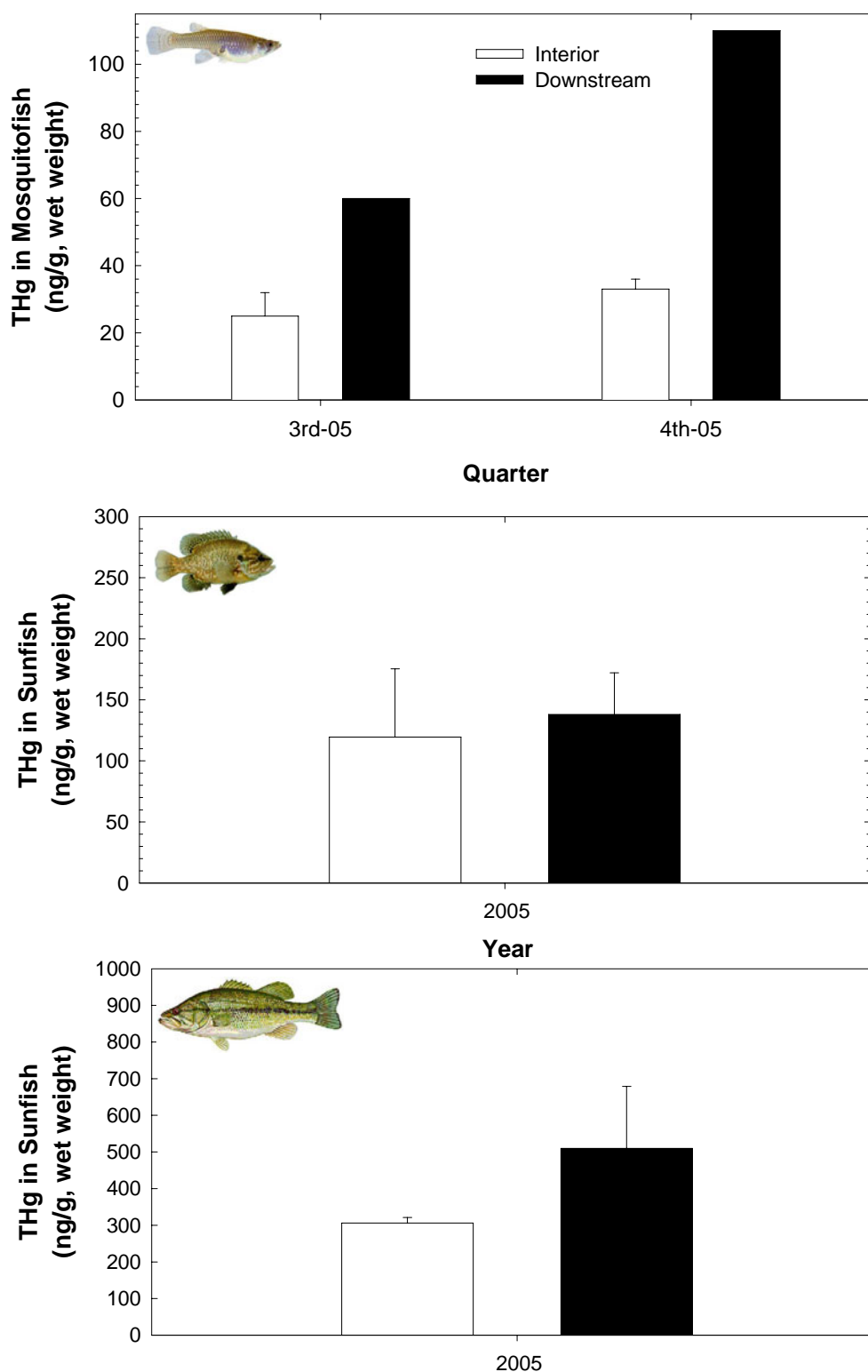
(B)



**Figure 16.** Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-1E.



**Figure 17.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell), and rainfall at STA-1E.



**Figure 18.** Mercury concentrations (ng/g, wet weight) in (*top*) mosquitofish composites (+range), (*middle*) whole sunfish ( $\pm$ SD), and (*bottom*) fillets of largemouth bass ( $\pm$ 95 percent C.I. or, if arithmetic, SD) collected at STA-1E.

Regarding risk to fish-eating wildlife, resident fish inside STA-1E generally contained mercury levels lower than both USFWS (100 ng/g) and USEPA predator protection criteria (77 ng/g and 346 ng/g for TL 3 and 4 fish, respectively). However, baseline data show that mercury levels exceeded protection criteria in fish at the near-field downstream site (ST1ELX).

## STA-2

STA-2 Cells 2 and 3 met mercury start-up criteria in September 2000 and November 2000, respectively. In August 2001, flow-through operation of Cell 1 was approved under a permit modification. Cell 1 met start-up criteria in November 26, 2002. Operational monitoring of mercury at STA-2 began during the third quarter of 2001 after completion of the S6 connection (for discussion of results observed prior to 2005, see Rumbold and Fink, 2002b, 2003b; Rumbold 2004a, 2005a; Rumbold et al., 2006).

The triennial collection of sediments cores (10 cm depth) from STA-2 occurred in May 2005. The average concentration of THg (**Table 4**) in the sediments was similar to levels previously observed at this STA and only slightly higher than at other STAs (**Figure 7**). More importantly, MeHg concentrations were relatively low compared to levels in previously collected sediment and as compared to the other STAs (**Figure 7**). It should be noted that samples collected from STA-2 in 2005 were analyzed by Battelle Marine Science Laboratory and not FGS, which had been the primary laboratory used by the District for MeHg determination. Statistically, there was no significant difference in MeHg levels in sediments collected among years (one-way ANOVA  $F=1.77$ ;  $df = 3.17$ ;  $p = 0.191$ ).

**Table 4.** THg and MeHg concentrations (ng/g, dry weight) in STA-2 soils (i.e., 10-cm depth composited) collected during 2005.

Station	n	THg	Qualifier <sup>a</sup>	MeHg	Qualifier <sup>b</sup>	% MeHg
Cell 1	1	217		0.429		0.2%
Cell 2	1	127		0.285		0.2%
Cell 2	1	96.2		0.306		0.3%
Cell 3	1	85.7		0.2	V	
Cell 3	1	121		0.284		0.2%
Cell 3	1	119		0.644		0.5%
Mean		127.6	± 46	0.390	± 0.15	0.33%

a For qualifier definitions, see FDEP Rule 62-160: J3 – estimated value, poor precision.

b V – analyte detected in both the sample and the associated method blank.

Results from monitoring mercury concentrations in surface water at STA-2 (**Figure 19**) show that THg concentration in outflow did not exceed the Class III WQS of 12 ng/L during 2005. More importantly, both MeHg, which has no numerical WQS, and THg remained at low concentration in the outflow of STA-2 as compared to previous monitoring results; annual outflow loads remained low as compared to 2002 and 2003 (**Figures 12 and 13**). Notably, although stage has fallen several times, Cell 1 has remained inundated since late 2002 (**Figure 20**), when the weir boxes in front of the outflow culverts were reconfigured, in part to prevent recurrence of steep gradients in stage that were thought to have influenced methylation rates.

Both **Table 1** and **Figure 21** summarize results from operational monitoring of mercury concentrations in STA-2 mosquitofish. **Figure 21** graphs results from different interior sites separately for this STA, because of the degree of spatial variability previously observed here. The figure indicates that mercury levels in mosquitofish from Cell 1 and the discharge canal have declined dramatically since 2001 and 2002 (in some cases, by an order of magnitude) and have remained low. Moreover, among-cell differences in mercury levels in mosquitofish decreased greatly in the second quarter of 2005.

Unlike the mosquitofish, sunfish from STA-2 continued to show substantial among-cell differences in mercury levels, with relatively higher levels occurring in resident fish from Cell 1 (**Figure 21**). Yet, mercury levels have declined in sunfish from Cell 1 (**Figure 21**) — though the magnitude of the decline is difficult to accurately assess due to common confounding factors, namely that (1) multiple lepomid species were collected and mercury levels have been found to vary among species, and (2) sunfish size (an indicator of age) varied, and mercury levels in fishes tend to increase with age. Regrettably, both sunfish and bass samples from the discharge canal were lost during shipment to the analytical lab. Although aliquots from archive samples from these fish were acquired, results of analyses will have to be reported at a later date.

Concentrations of THg in fillets of resident largemouth bass from STA-2 (**Table 3** and **Figure 21**) reflect an overall EHg3 of  $110 \pm 35$  mg/kg in bass collected across the three cells that is relatively low compared to previous estimates and as compared to downstream fish (Appendix 3B-1 of this volume). Only two bass were collected from site C1X from Cell 1 and thus an EHg3 could not be estimated; however, both bass were 2.8 years old; thus, the average concentration of 205 mg/kg is nearly equivalent to an EHg3, albeit based on a very small sample size.

Regarding risk to fish-eating wildlife, resident fish at STA-2 generally contained mercury levels lower than both USFWS (100 ng/g) and USEPA predator protection criteria (77 ng/g and 346 ng/g for TL 3 and 4 fish, respectively); sunfish from Cell 1 were the only notable exception.

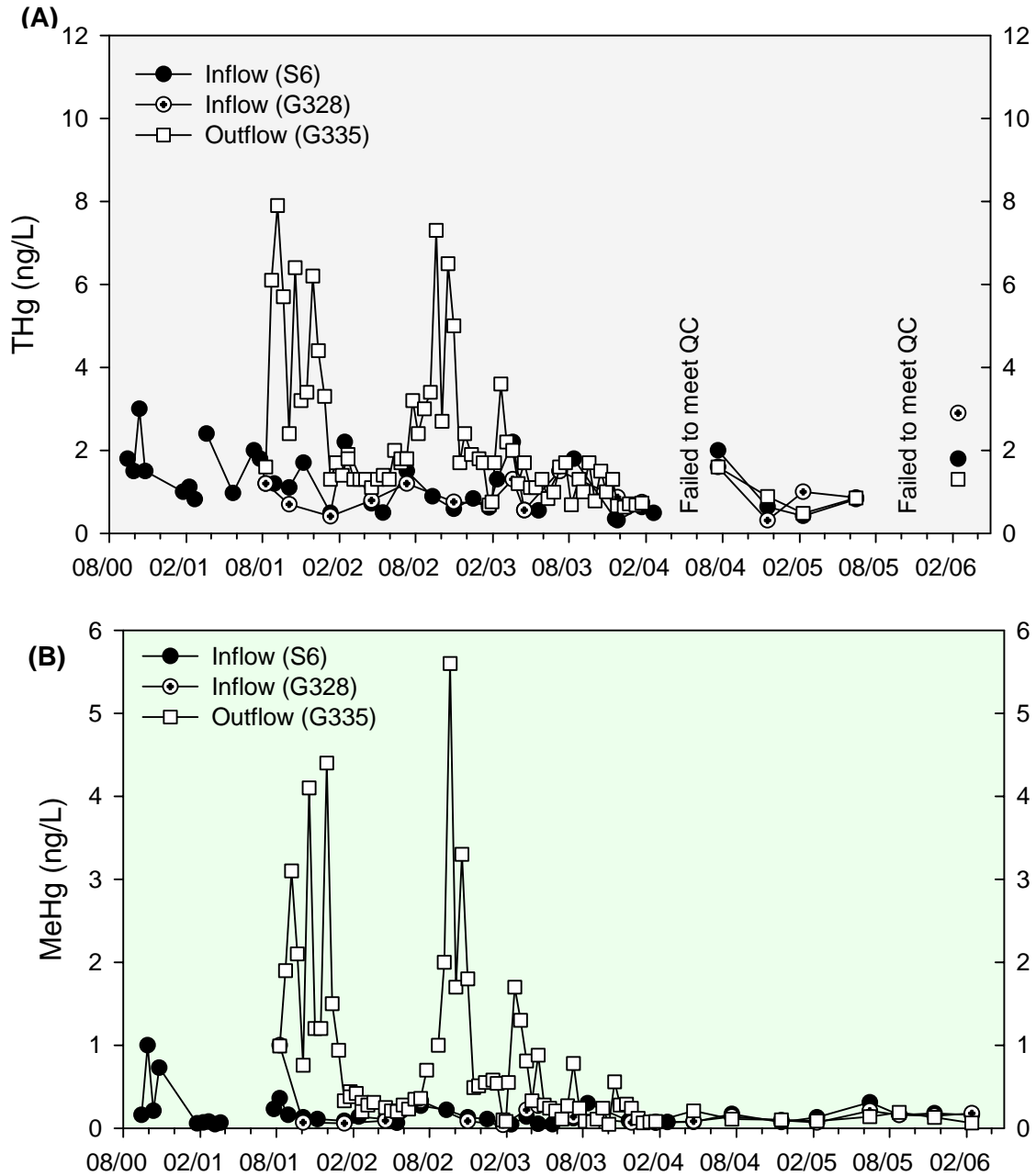
### STA-3/4

STA-3/4 Cell 1 satisfied start-up criteria for mercury in January 2004; the first discharges of treated water from this STA were in February 2004. Accordingly, routine operational monitoring of this flow-way began during the first quarter of 2004. STA-3/4 Cell 3 satisfied start-up criteria for mercury in June 2004; Cell 2 in August 2004, with consensus from FDEP in September 2004, at which time discharges began (for discussion of results observed prior to 2005, see Rumbold et al., 2006)

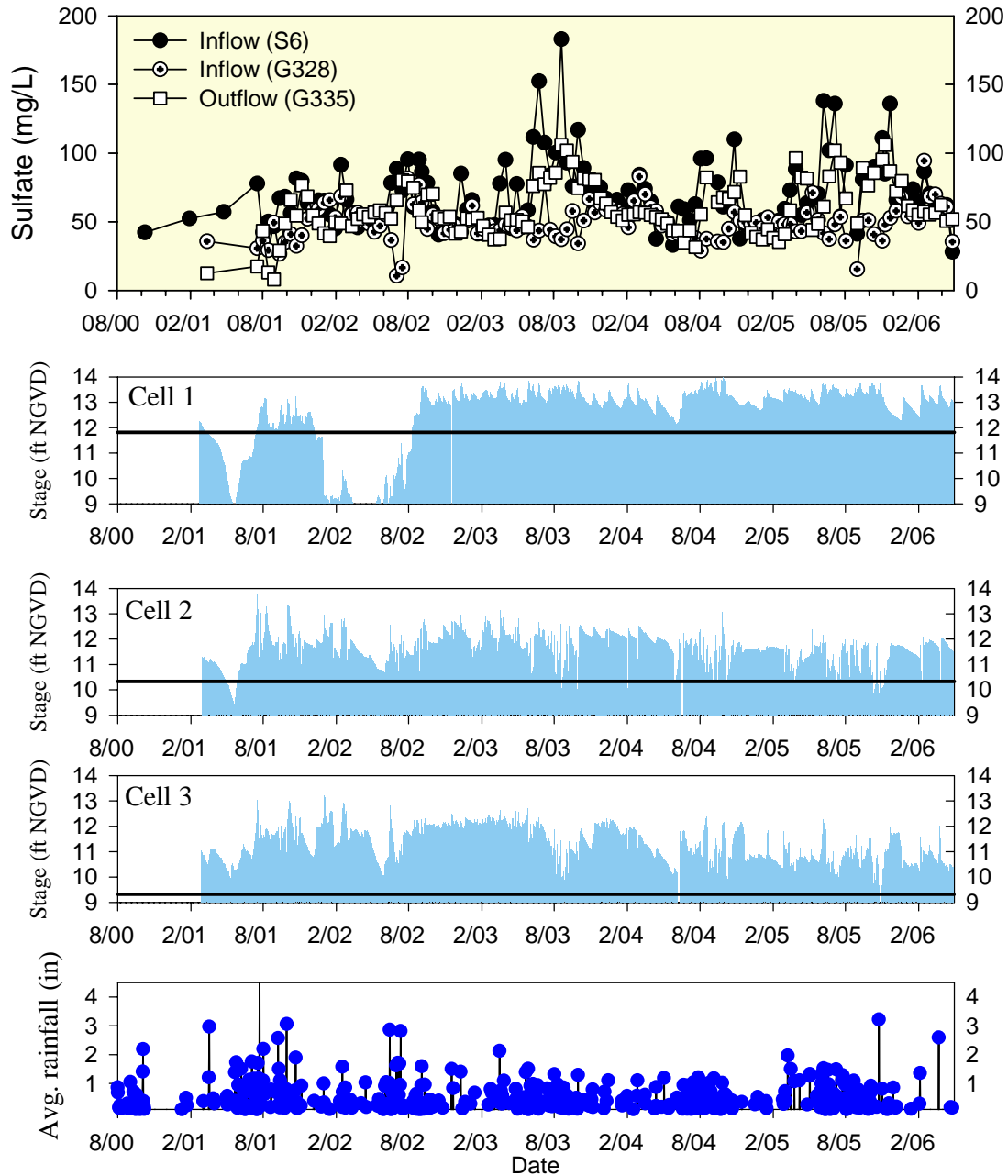
Results from monitoring mercury concentrations in surface water at STA-3/4 (**Figure 22**) show THg concentration spiking in the two inflows during the second quarter of 2005, and at much greater concentration compared to outflows. THg then declined at the inflows and was at similar concentration in both inflows and outflows. At no time during 2005 did THg concentration at any of the individual outflows of STA-3/4 exceed the Class III WQS of 12 ng/L. Concentrations of MeHg were more highly variable among structures and occasionally concentrations in one or more of the outflows exceeded inflow concentrations. This was most pronounced in comparisons to G372, where concentrations remained low throughout the reporting year. Inspection of **Figure 22** reveals consistent differences in MeHg outflow concentration among the three flow-ways. In general, MeHg concentrations remained relatively low as compared to levels observed during start-up. Sulfate concentrations in the inflows, (**Figure 23**) particularly G370, tended to be higher than outflows.

Results from operational monitoring of mercury concentrations in resident fish from STA-3/4 are summarized in **Tables 1, 2, and 3**, and in **Figure 24**. Although mercury levels in mosquitofish were similar to or lower than concentrations found in mosquitofish inhabiting downstream sites (Appendix 3B-1 of this volume), levels were slightly elevated as compared to mosquitofish from

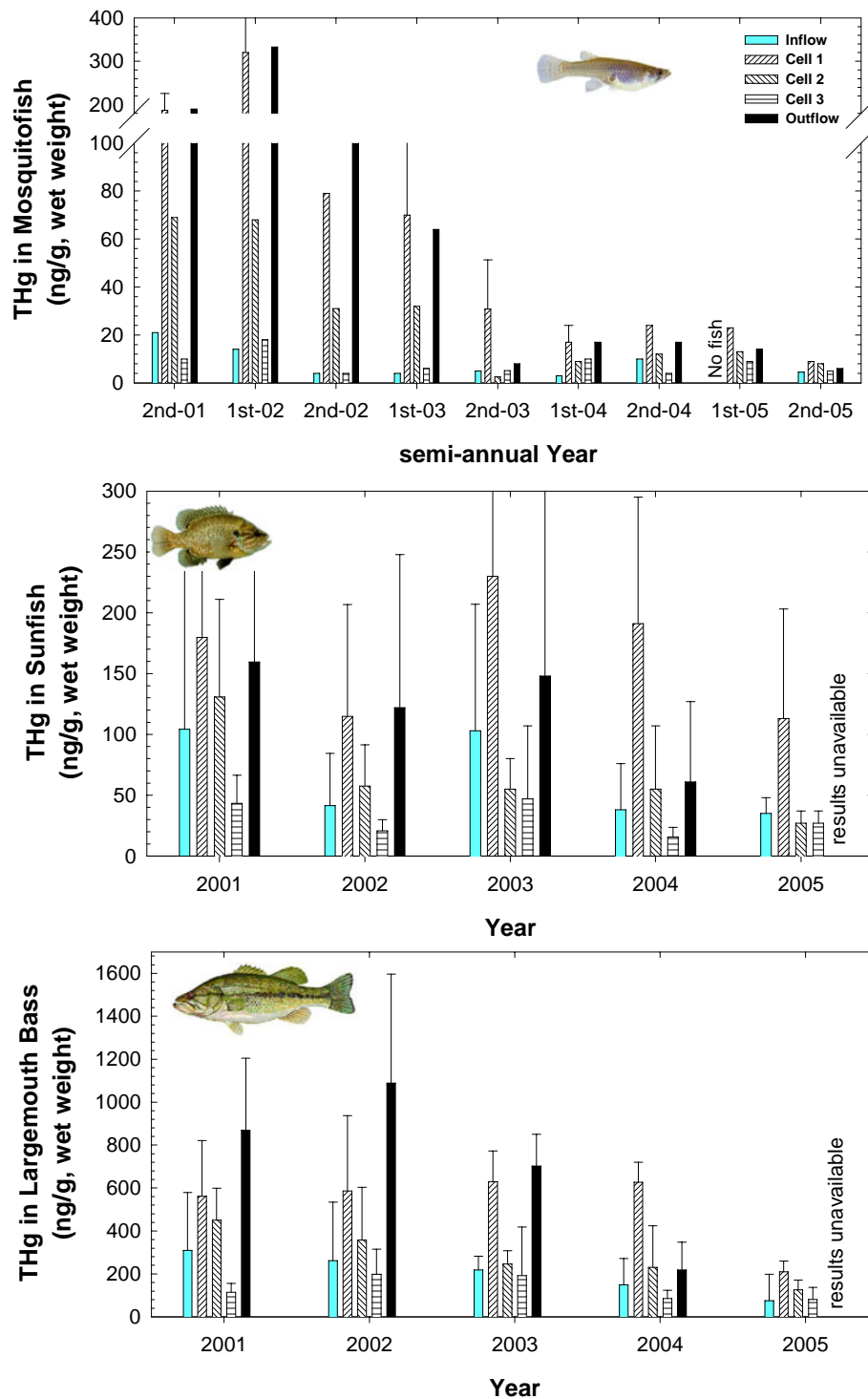
other STAs (**Table 1**). Mosquitofish from the discharge canal generally contained higher mercury levels than fish from the interior marshes or the supply canal (**Figure 24**). Currently, mosquitofish are collected at two outflow culverts from each flow-way.



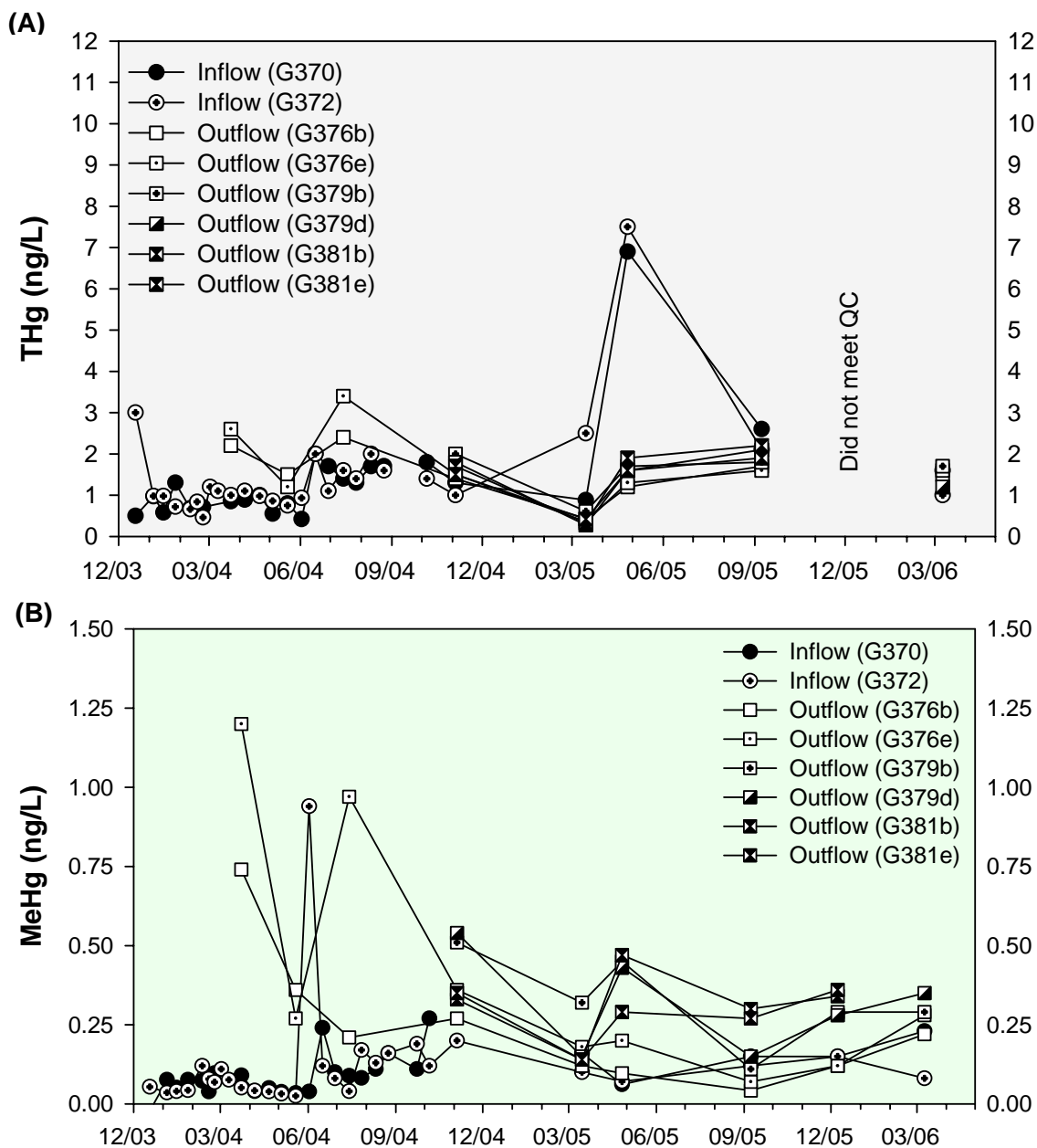
**Figure 19.** Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-2, including routine and expanded sampling.



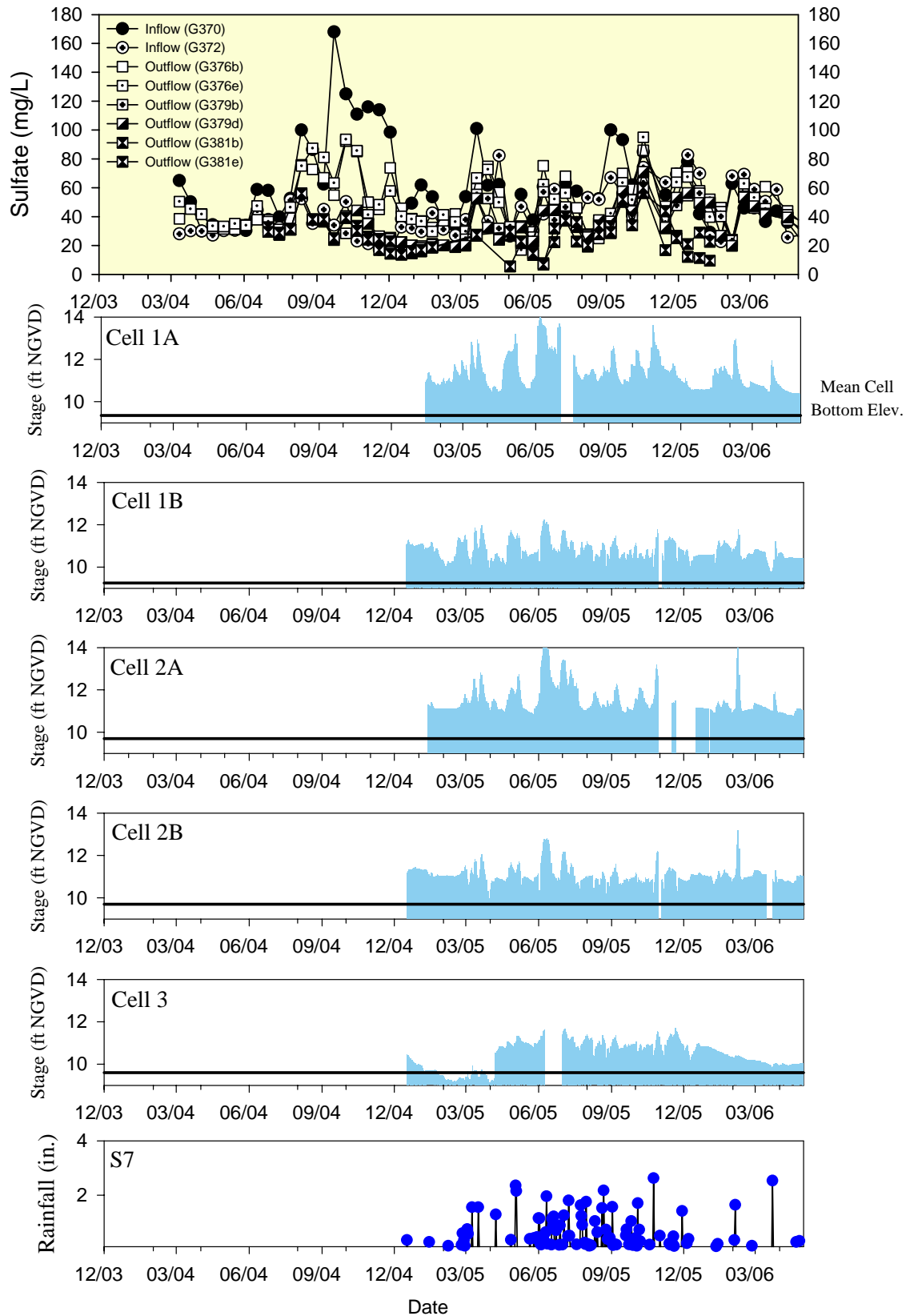
**Figure 20.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell), and rainfall totals at STA-2.



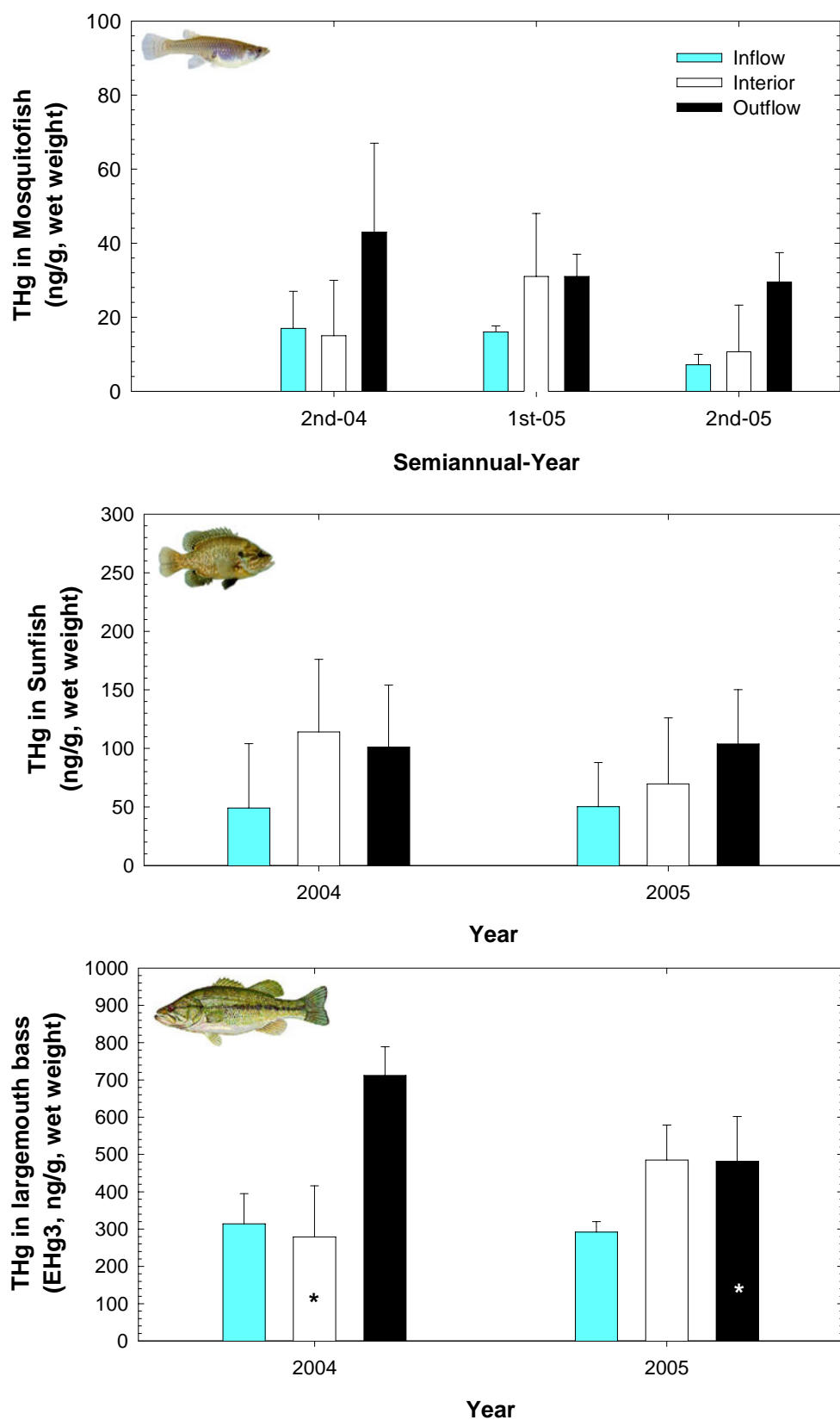
**Figure 21.** Mercury concentrations (ng/g, wet weight) in (*top*) mosquitofish composites ( $\pm$ range), (*middle*) whole sunfish ( $\pm$ SD), and (*bottom*) fillets of largemouth bass ( $\pm$ 95 percent C.I. or, if arithmetic, SD) collected at STA-2.



**Figure 22.** Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-3/4, including results of start-up monitoring at inflows (i.e., prior to flow-through operation of all cells).



**Figure 23.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell), and rainfall at STA-3/4.



**Figure 24.** Mercury concentrations (ng/g, wet weight) in (*top*) mosquitofish composites (+range), (*middle*) whole sunfish ( $\pm$ SD), and (*bottom*) fillets of largemouth bass ( $\pm$ 95 percent C.I. or, if arithmetic, SD) collected at STA-3/4.

Although occasionally mercury levels differed in mosquitofish collected at culverts from the same flow-way (with the largest relative percent difference [RPD] of 105 percent occurring between fish collected at G-381B and G-381E), one mosquitofish collection site could suffice for each flow-way, given the similarities. Specifically, the average RPD was 31 percent for the culverts' discharging flow-way 1, 24 percent for flow-way 2, and 56 percent for flow-way 3; and in October 2006, mosquitofish composites from G381B and G381E had an RPD of 7 percent. The RPD between Quality Control (QC) duplicate samples of mosquitofish (i.e., two composites of 100 fish each collected sequentially at the same site) ranged from 5.3 percent to 91 percent. (For Quality Assurance (QA) review of mercury monitoring, see Appendix 3B-1 of this volume.)

Similar to the mosquitofish, resident sunfish from the interior marshes of STA-3/4 contained mercury levels similar or lower than fish at downstream sites (Appendix 3B-1 of this volume) but slightly elevated compared to fish from other STAs (**Table 2**). The average tissue concentration in sunfish from the three southernmost cells of each of the flow-ways was  $70 \pm 56$  (n = 60; **Table 2**). However, among-cell differences were evident in bluegill; when normalized based on length, bluegill from Cell 3 had an average concentration of 0.73 mg/kg/cm as compared to 0.36 mg/kg/cm in Cell 2 and 0.22 mg/kg/cm in Cell 1. It should be noted that, following the removal of a plug from the discharge canal in 2005, sampling in the canal was confined to site L5F1 (as compared two stations, ST34DCW and ST34DCE sampled in 2004). Bluegill from this location had a mean, normalized tissue-Hg level of 1.16 mg/kg/cm in 2005. In 2003, prior to the start-up of this STA, this particular site had been sampled as a downstream site and those bluegill had a mean, normalized concentration of 0.95 mg/kg/cm.

Of the three flow-ways, only Cell 3 of the westernmost flow-way produced largemouth bass in 2005. An age-standardized three-year-old fish from this cell was estimated to contain  $485 \pm 94$  mg Hg/kg, which is elevated compared to the other STAs (**Table 3**). In 2004, bass from Cell 3 had been estimated to have an EHg3 of  $649 \pm 182$  ng/g. For a geographical comparison, bass from the discharge canal, which on average were 2.45 years old, contained  $483 \pm 120$  ng/g. (An EHg3 could not be estimated for bass from the discharge canal.)

Regarding risk to fish-eating wildlife, mosquitofish from STA-3/4 contained mercury at concentrations lower than either the USFWS (100 ng/g), or USEPA criteria (77 ng/g). While sunfish from interior marshes of STA-3/4 contained levels below the USFWS criteria, sunfish from the discharge canal exceeded it. After adjusting the arithmetic mean mercury concentrations in fillets to whole-body concentrations (whole-body THg concentration =  $0.69 \times$  fillet THg; Lange et al., 1998) mercury levels in largemouth bass from interior marshes of Cell 3 (mean was 178 ng/g) were less than the USEPA predator protection criteria based on TL 4 fish (i.e., 346 ng/g). Therefore, fish-eating wildlife foraging preferentially at STA-3/4 would appear to have a relatively low risk from mercury exposure.

## STA-5

STA-5 met start-up criteria for mercury in September 1999; however, because of drought conditions and the detection of high phosphorus concentrations at the outflows, STA-5 did not begin flow-through operation until July 2000 (for discussion of results observed prior to 2005, see Rumbold and Rawlik, 2000; Rumbold et al., 2001a, 2006; Rumbold and Fink, 2002a, 2003a; Rumbold, 2004a and 2005a).

As shown in **Figure 25**, water-column concentrations of both THg and MeHg in 2005 remained low at STA-5, with the exception of a couple of minor spikes in THg in the inflows during the third quarter. At no time during the reporting year did THg concentrations exceed the Class III WQS of 12 ng/L. Outflow loads of both THg and MeHg (**Figures 12 and 13**) were similar to or smaller than inflow loads. This is noteworthy given that cells within the STA were

drawn down during the year (**Figure 26**) for work on replacement of S-343A, S-343B, S-343C, and S-343D.

Mosquitofish collected from STA-5 in 2005 contained relatively low mercury levels compared to fish previously collected at this STA (**Figure 27**), fish collected at other STAs (**Table 1**) and fish from downstream marshes (Appendix 3B-1 of this volume). As seen previously, mosquitofish from the interior marshes contained less mercury than fish from both the supply canal and the discharge canal.

As in previous years, the FWC, which is under contract to the District to electroshock and collect large-bodied fishes for mercury monitoring, encountered difficulty in filling sample quotas for at STA-5. Only eight sunfish were collected from interior marshes (i.e., two from Cell 1B and six from Cell 2B); bass were collected only from the supply canal (**Table 2 and 3**). Sunfish from the interior marshes contained mercury levels similar to or lower than concentrations observed in the past (**Figure 27**). As observed in many of the STAs, fish from the interior marshes had lower mercury levels than fish either from the supply or discharge canal, possibly due to the tendency of greater piscivory of fish in canals. While data (**Figure 27**) suggest that sunfish inhabiting the discharge canal had increased mercury levels in 2005; the gap may owe to the 2005 sample composition (6 warmouth and 14 spotted sunfish); in previous years, sampled species included bluegill and redear, which often contain lower body burdens.

Regarding the risk to fish-eating wildlife, resident fish at STA-5, representing three different trophic levels, contained mercury levels below or just slightly higher than the USFWS (100 ng/g) and USEPA predator protection criteria (77 ng/g, 346 ng/g for TL 4 fish). Therefore, fish-eating wildlife foraging preferentially from interior marshes of STA-5 would not appear to be at elevated risk from mercury exposure.

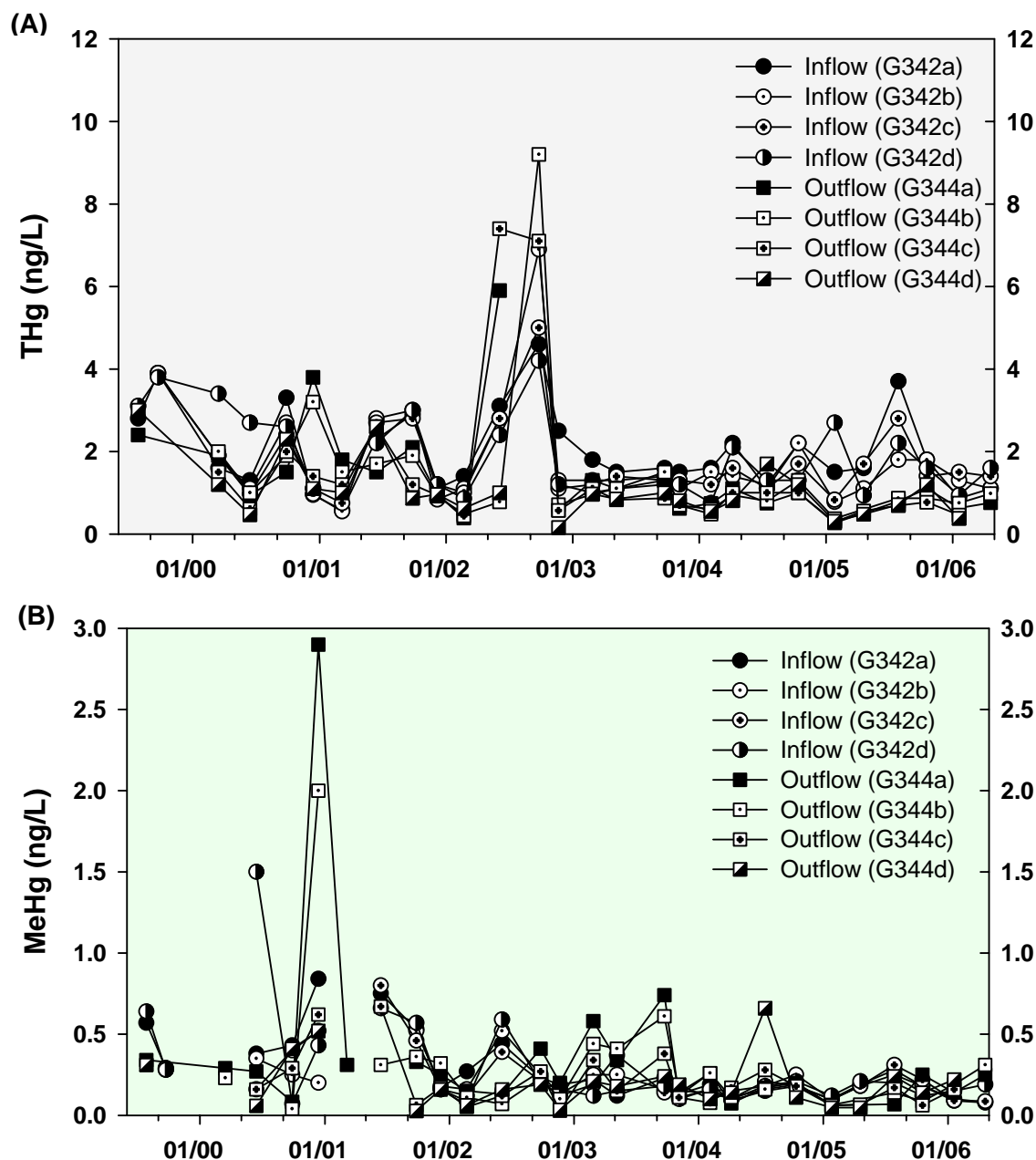
### STA-6, Section 1

STA-6, Section 1 (Cells 3 and 5) met start-up criteria for mercury in November 1997, and began operation in December 1997. Routine monitoring of mercury at STA-6 was initiated in the first calendar quarter of 1998. Monitoring results prior to May 2004 have been reported (SFWMD, 1998c and 1999d; Rumbold and Rawlik, 2000; Rumbold et al., 2001a; Rumbold and Fink, 2002a; Rumbold and Fink, 2003a; Rumbold, 2004a and 2005a; Rumbold et al., 2006).

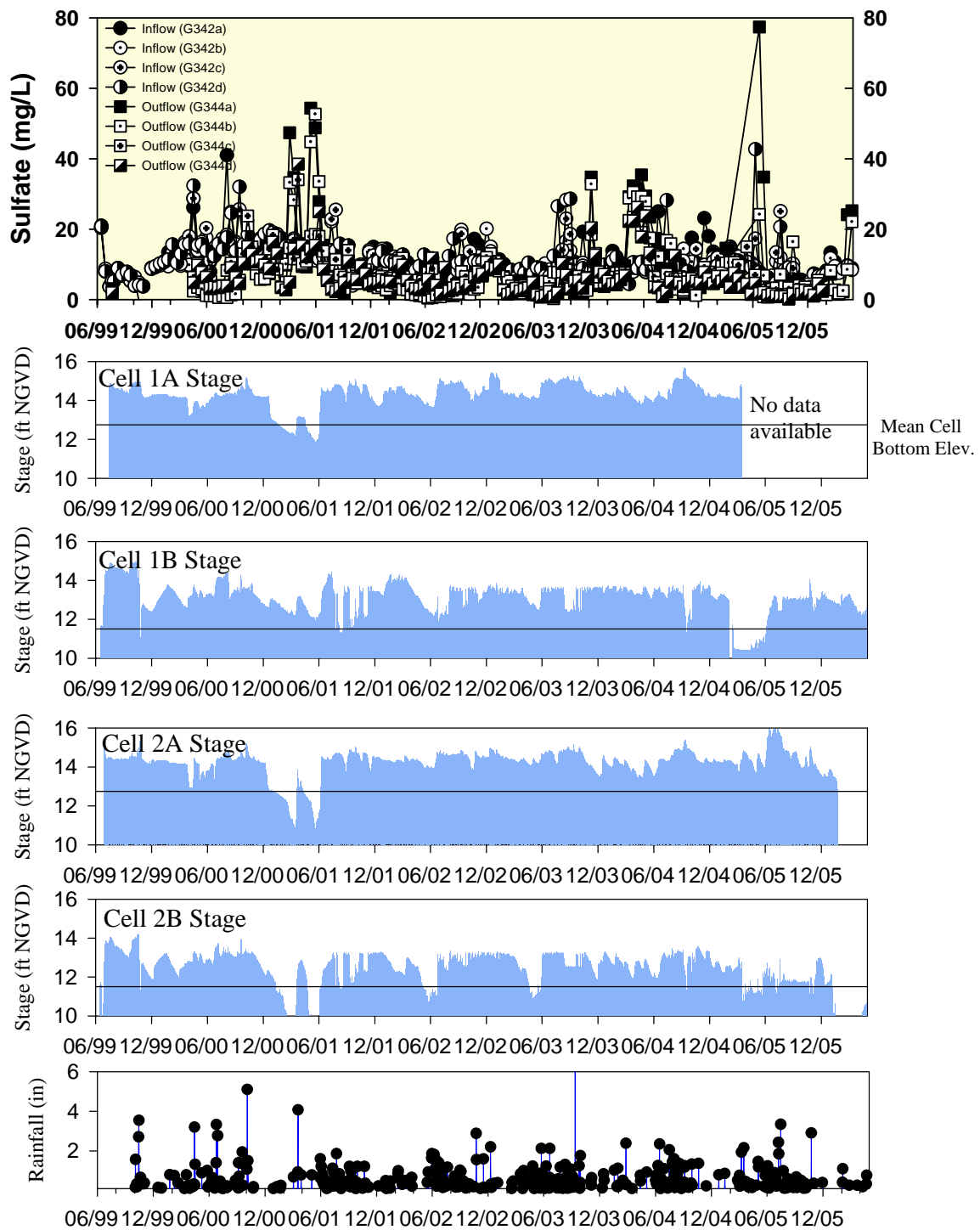
As shown in **Figure 28**, THg concentrations at both the inflows and outflows were very low in the first quarter and then increased slightly over the year; however, levels of THg remained relatively low as compared to previous spikes. By comparison, MeHg remained at very low concentration throughout the year. Yet, as shown in **Figure 29**, both cells dried down during the year. Hence, the relatively low concentrations of both THg and MeHg in the outflows may appear at first incongruous with hypotheses previously offered regarding dryout and rewetting effects on sediment oxidation, sulfur biogeochemistry and stimulation of methylation by sulfate-reducing bacteria (Rumbold et al., 2006). However, closer inspection of the data reveals that the drydown occurred between the second week of May and the first week of June, while monitoring for water column concentrations would have missed any transient spike in mercury species and sulfate due to the timing of quarterly sampling (April 26 and September 8 for mercury, and May 3 and August 9 for sulfate). Nonetheless, if a spike in MeHg production spike did occur as in the past following drydown and rewetting, and if it was environmentally significant, it would likely be evident in the levels of MeHg bioaccumulated in downstream fish and newly immigrated fish (see below).

Concentrations of THg in mosquitofish are summarized in **Table 1** and are graphically presented in **Figure 30**. Levels of mercury in mosquitofish from STA-6 continue to be relatively low compared to fish collected previously from this area; levels spiked somewhat in fish from the

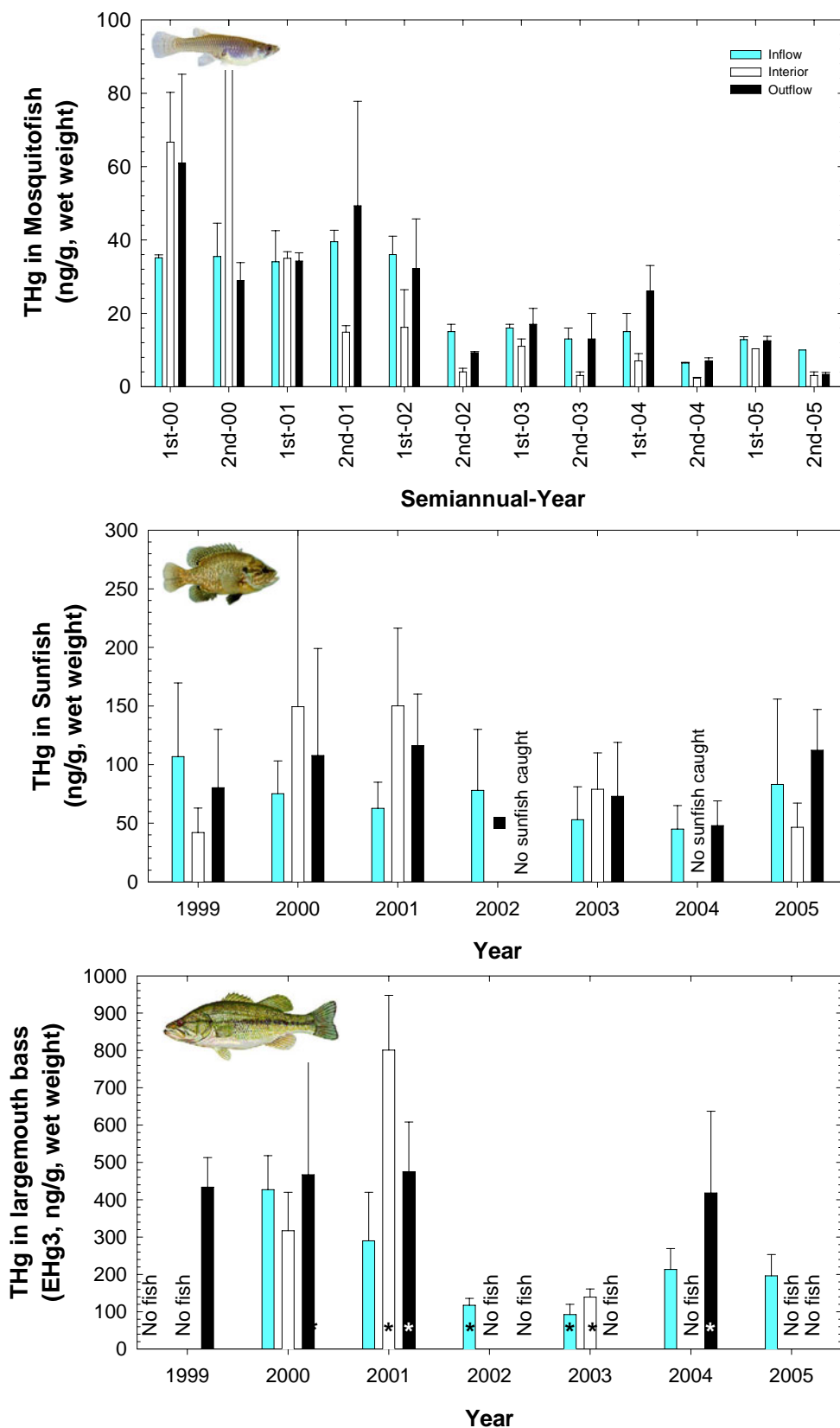
discharge canal in March but declined by November 2005. This small spike in outflow fish likely unrelated to the dryout. Because the semiannual (March and November) mosquitofish collection may have missed any transient spike related to dryout, moving to quarterly collection of mosquitofish is recommended (see also “STA-1E” in this operational monitoring discussion).



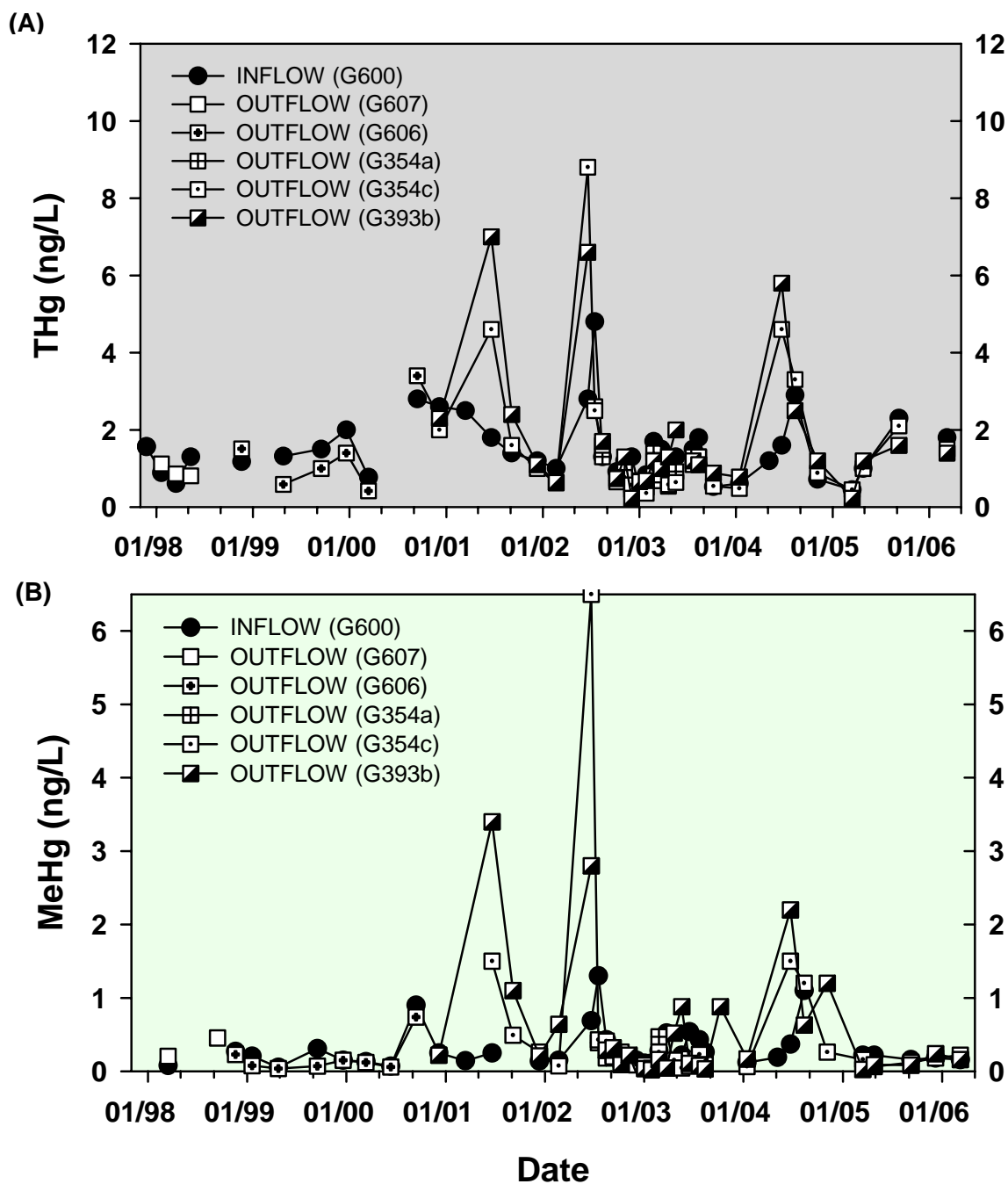
**Figure 25.** Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-5.



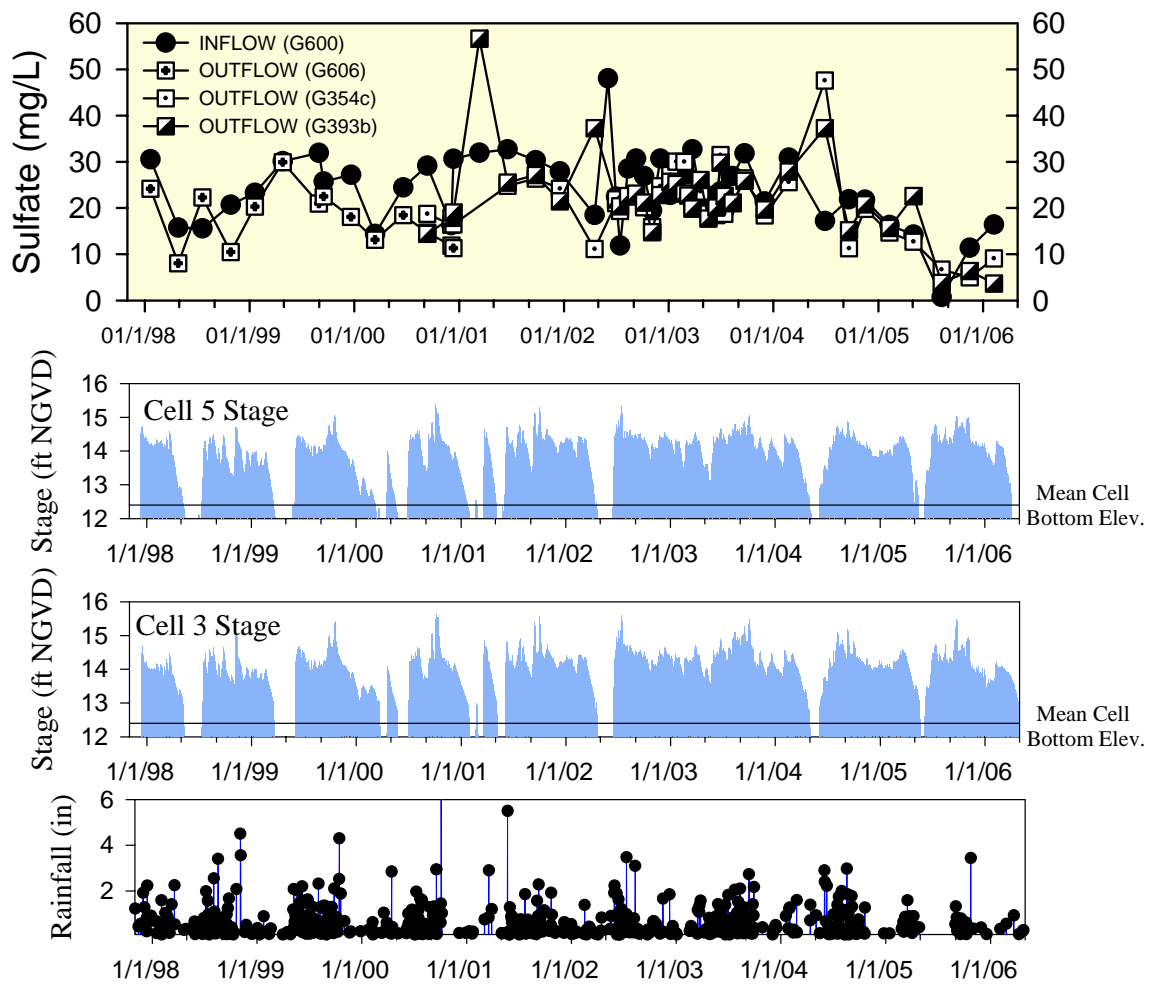
**Figure 26.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell), and rainfall at STA-5. In 2005, several structures were replaced with a long delay in instrumentation.



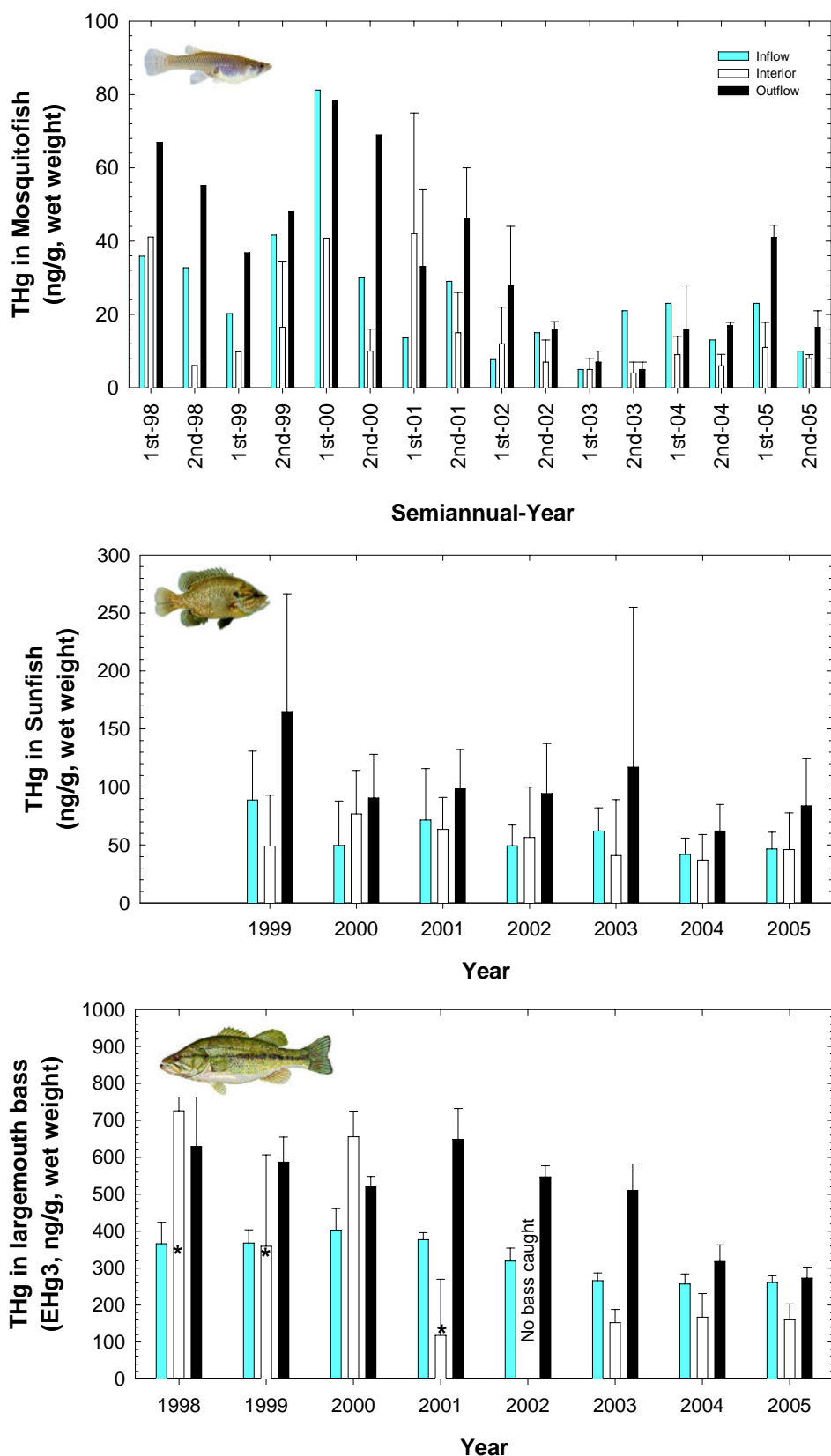
**Figure 27.** Mercury concentrations (ng/g, wet weight) in *(top)* mosquitofish composites (+range), *(middle)* whole sunfish ( $\pm$ SD), and *(bottom)* fillets of largemouth bass ( $\pm$ 95 percent C.I. or, if arithmetic, SD) collected at STA-5.



**Figure 28.** Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-6, including results from routine and expanded sampling.



**Figure 29.** Concentrations of sulfate (*top*), stage in the two cells (recorded immediately upstream of outflow culvert of cell), and rainfall at STA-6.



**Figure 30.** Mercury concentrations (ng/g, wet weight) in (*top*) mosquitofish composites (+range), (*middle*) whole sunfish ( $\pm$ SD), and (*bottom*) fillets of largemouth bass ( $\pm$ 95 percent C.I. or, if arithmetic, SD) collected at STA-6.

As **Table 2** and **Figures 30** and **15** indicate, STA-6 sunfish continued to have mercury levels comparable to those observed in sunfish at the other STAs (with the exception of STA-1W) and locations within the Everglades (Appendix 3B-1 of this volume). Visual inspection of **Figure 30** reveals no marked between-year difference in mercury levels from 2004 to 2005. However, closer examination of mercury levels in bass and bluegill normalized to fish length hints at the possibility that mercury levels increased from last year. Young bass (i.e.,  $\leq 1.8$  yrs old) in Cell 5 contained 0.21 mg/kg/cm in 2004 and 0.35 mg/kg/cm in 2005; bluegill in Cell 5 also contained 0.21 mg/kg/cm in 2004 and 0.28 mg/kg/cm in 2005 (**Figure 15**). Sunfish in the discharge canal also had higher levels in 2005 (**Figure 30**). Mercury levels in bluegill in the discharge canal increased from 0.49 mg/kg/cm in 2004 to 0.57 mg/kg/cm in 2005. It should be noted that this result is at odds with an analysis completed last year that indicated little impact in sunfish in the discharge canal from dryout of the STA (Rumbold et al., 2006). This inference was based largely on the observation that bluegill captured in the discharge canal in 2004 (a year in which both cells dried out) contained the lowest normalized mercury level observed over the period of record. Hence the small increase in 2005 sunfish from the discharge canal may simply be noise. Bass taken from the discharge canal in 2005 did not show an increase in mercury. However, sample size (n) of young bass was very small in both years (i.e., fewer than three fish). Consequently, it is not clear whether the dryout played a role in altering mercury levels in the large fish in the discharge canal. Furthermore, the inference regarding the increases in fish in the interior marsh is also not without uncertainty. The fish caught in Cell 5 in 2005 likely reinvaded the marsh following the dryout from either the supply or the discharge canal (more likely the former given the structures involved) and canal fish typically have higher mercury levels (**Figure 30**). Nonetheless, it is reasonable to assume that the dryout and rewetting in 2005 produced a spike in MeHg production similar to what has been observed in past. It is also reasonable to assume that annual pulses of MeHg maintain higher tissue-Hg levels in these fish.

Regarding risk to fish-eating wildlife, mercury levels in mosquitofish, sunfish, and bass (whole-body concentration estimated from fillet concentration) from STA-6 were at or below the USFWS (100 ng/g) and USEPA (77 ng/g, 346 ng/g for TL 4 fish) predator protection criteria. Therefore, the risk of mercury exposure to fish-eating wildlife foraging preferentially at STA-6 appears to represent a significant threat no longer.

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## OPPORTUNITIES FOR OPTIMIZING THE MONITORING NETWORK

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A key component of any monitoring program is regular reevaluation of objectives and methods to more sharply focus available finite resources. The monitoring plan should be revisited regularly to see if improvements, such as use of a different data collection method or a revised sampling regime can be implemented without compromising the quality of the data stream while continuing to meet the program's objectives. In early 2005, a strategic plan was drafted to optimize the District's mercury monitoring plan (Rumbold, 2005b). The recommendations below follow from that strategic plan and are based on guidance contained in "A Protocol for Monitoring Mercury and Other Toxicants" (adapted from Rumbold and Pfeuffer, 2005; signed by both the Department and District in February 2006; hereafter referred to as the Protocol).

### STA-1W

Data summarized above and elsewhere (in justification document written by D. Rumbold, SFWMD, and submitted to FDEP for support of revised monitoring plan, dated January 24, 2006)

for STA-1W demonstrate that it has met criteria contained in the Protocol that would allow monitoring of certain media to ramp down.

The Protocol states:

If after the first three years of monitoring neither downstream loading nor residue levels in fishes has exceeded action levels in the preceding two years, then (1) surface water sampling would be discontinued, (2) frequency of mosquitofish collection would be reduced to semiannually, and (3) frequency of large-bodied fish collection would be reduced to one collection event every three years. If not met within the first three years, criteria would be re-evaluated annually based on preceding two-year period.

For detail on the actions levels referenced above, refer to the Protocol document (Rumbold and Pfeuffer, 2005).

## **STA-1E**

Because STA-1E was only recently completed and because its monitoring plan was already consistent with guidance contained in the Protocol, only minor clarifications were recommended during the early permit renewal process (see plan dated April 27, 2006).

## **STA-2**

The District is constructing a new western flow-way, Cell 4, in STA-2. Based on the current status of the new western flow-way, initial performance of the other three flow-ways (summarized here) and the guidance contained in the Protocol, the District submitted a revised plan in May 2006 that continues to monitor inflows and outflows. This plan does revise the start-up protocols for the new cell and frequency of fish collections to be consistent with the Protocol.

## **STA-3/4**

Operation of STA-3/4 has been monitored for only two years and thus has not yet met the time requirement contained in the Protocol. Nonetheless, as part of the permit renewal process, the monitoring plan should be revised to reflect guidance on durations, sampling regime, action levels, and Tier 2 monitoring contained in the Protocol. Until the permit is renewed and those changes go into effect, the existing plan should be reviewed to determine whether mosquitofish collections at outflow culverts can be reduced to one site per flow-way.

## **STA-5 AND STA-6**

The District is constructing new flow-ways in both STA-5 and STA-6. Accordingly, continued monitoring of inflows and outflows likely will be required. However, during the permit renewal process, efforts should be made to revise each mercury monitoring plan consistent with guidance contained in the Protocol, especially as it relates to frequency of mosquitofish collection, numbers of large-bodied fish and re-location of current sampling site within the discharge canal to a near-field, downstream site.

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