

# Appendix 5-5: Annual Permit Compliance Monitoring Report for Mercury in the STAs

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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). Fish data in this report are summarized for calendar year 2009 (CY2009) while surface water data are summarized for Water Year 2010 (WY2010) (May 1, 2009–April 30, 2010).

Key findings are as follows:

1. **All STAs:** There were no violations of the Florida Class III numerical water quality standard of 12 nanograms (ng) of total mercury per liter (THg/L) during the reporting year at any of the STAs and the project has met all action level requirements listed in the Protocol for Monitoring Mercury and Other Toxicants (SFWMD, 2006). Overall, the fish catch for CY2009 had lowest quantity of individuals since sampling began for these STAs, particularly for large-bodied fish, and fish THg concentrations were at one of the lowest levels since monitoring began.
2. **STA-1W:** Stormwater Treatment Area 1 West (STA-1W) subsumed the Everglades Nutrient Removal (ENR) project in April 1999. The ENR project served as the prototype STA and started up in 1994. Methylmercury (MeHg) biomagnification in resident large-bodied fish such as sunfish (*Lepomis* spp.) and largemouth bass (*Micropterus salmoides*) has remained relatively constant over the monitoring period at levels almost an order of magnitude lower than those observed in fish from downstream Everglades sites and is the lowest compared with other STAs. Mercury levels in STA-1W in fish across trophic levels did not pose a threat to fish-eating wildlife based on U.S. Fish and Wildlife Service (USFWS) and U.S. Environmental Protection Agency (USEPA) predator protection criteria. Consistent with the Protocol for Monitoring Mercury and Other Toxicants

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(SFWMD, 2006), all mercury monitoring was terminated in STA-1W in 2009 (see the *Phase 3: Operational Monitoring* section of this Appendix).

3. **STA-1E:** During WY2010, surface water total mercury (THg) and MeHg inflow concentrations were greater than all other STAs and outflow concentrations were comparatively moderate in Stormwater Treatment Area 1 East (STA-1E). Total mercury and MeHg loads in outflow were less than inflow, and the difference in loading rates was the greatest in STA-1E compared with all other STAs. Mercury levels in mosquitofish (*Gambusia holbrooki*) from the interior marshes were the second lowest out of all STAs and did not change appreciably from the first to the fourth quarter of 2009. Sunfish also showed low to moderate mercury levels. Levels in largemouth bass were the highest compared to STA-2 and STA-5, the only other STAs where bass collections were made. Regarding risks to fish-eating wildlife, mosquitofish (trophic level 2 or 3) from the interior locations did not exceed the USEPA's 77 nanograms per gram (ng/g) predator protection criterion; however, mosquitofish from the downstream locations did exceed the criterion in the third and fourth quarters. Most sunfish from the interior marsh of STA-1E had mercury concentrations below both USFWS (100 ng/g) and USEPA (77 ng/g) criteria for trophic level (TL) 3 fish. However, all downstream sunfish assayed had concentrations greater than 77 ng/g. After whole-fish standardization, there was no exceedance of the USEPA criterion (346 ng/g) for TL 4 fish species (largemouth bass).
4. **STA-2:** During WY2010 in Stormwater Treatment Area 2 (STA-2), both THg and MeHg remained at low concentrations in the outflow relative to previous years and outflow loading of MeHg and THg was lower than inflow. However, out of all the STAs, STA-2 demonstrated the least difference between inflow and outflow load of both MeHg and THg. Average levels of mercury in mosquitofish began to increase in 2007 (tissue Hg; measured as ng Hg/g). This increase, including that for largemouth bass, resulted in a parabolic trend which was likely related to the startup of Cell 4 in 2007. This trend has since decreased to pre-startup conditions at both the interior and downstream locations. Sunfish THg concentrations from interior cells show no major change since 2007, but doubled at the downstream sampling location. All mosquitofish within and downstream of STA-2 contained mercury levels less than both the USFWS and USEPA predator protection criteria for TL 3 species. Several sunfish from the interior and downstream locations exceeded the USFWS criterion of 100 ng/g for TL 2 or TL 3 species. After whole-fish standardization, there was no exceedance of the USEPA criterion of 346 ng/g for TL 4 fish species in largemouth bass.
5. **STA-3/4:** In 2009, tissue Hg levels in mosquitofish from Stormwater Treatment Area 3/4 (SAT-3/4) were less than the USEPA criterion (77 ng/g) and less than concentrations in mosquitofish from other STAs. There is no data to report for sunfish and largemouth bass for 2009 since large-bodied fish in STA-3/4 are collected on a triennial basis. The next large-bodied fish collection is scheduled for 2011. Consistent with SFWMD (2006) THg and MeHg surface water sampling is no longer conducted in STA-3/4.
6. **STA-5:** Water-column concentrations of both THg and MeHg were comparatively moderate at the inflows and outflows of Stormwater Treatment Area 5 (STA-5) during WY2010 while the outflow loadings of each were less than inflow for WY2010. Mosquitofish collected in 2009 contained higher mercury levels compared with other STAs. For approximately five months, water levels were below mean cell bottom elevations in Cells 1A and 2A. This drop in water level likely contributed to substantial increases in surface water sulfate (up to five times background) that lasted for approximately one month following dryout. Contrasting previous years, sunfish had comparatively low mercury levels for both the interior and downstream site. Despite a concerted collection effort, no largemouth bass were caught. All resident mosquitofish

and sunfish, except two samples, within and downstream from STA-5 contained mercury levels below the USEPA criterion of 77 ng/g for TL 3 fish species and all fish were below the USFWS criterion of 100 ng/g.

7. **STA-6:** In Stormwater Treatment Area 6 (STA-6), Section 2, THg and MeHg concentrations at the inflow and outflow locations were relatively high compared with all other STAs in WY2010. All cells dried down once during WY2010 for approximately two months. During and following dryouts, neither THg nor MeHg spiked, yet surface water sulfate did spike on one occasion. Although the quarterly surface water mercury sampling results for 2009 did not show a jump in MeHg, previous evaluations of STA performance following a drydown-rewetting event have shown a positive correlation between sulfate concentration increases and methylation. For WY2010, THg and MeHg outflow loading were less than inflow. Overall, this STA continues to have some of the highest THg levels in all fish species. Even though MeHg spikes or constant elevations of MeHg have not been observed, it is likely that the seasonal dryout/rewetting process within STA-6 is playing a major role in the elevated THg levels in fish. The cycle of dryout and rewetting has been historically greatest in STA-5 and STA-6. Mosquitofish from the interior and downstream locations did not exceed the 77 ng/g TL 2-3 USEPA criterion for 2009. For sunfish, 80 percent of the catch from the interior marsh exceeded the USEPA TL 3 criterion and 40 percent exceeded the USFWS 100 ng/g criterion. All sunfish from the downstream site exceeded the TL 3 criterion and all but one sunfish sample exceeded the USFWS criterion. Fifty percent of all largemouth bass (whole-body concentration estimated from fillet concentration) from the interior marsh of STA-6 were above the USFWS criterion (100 ng/g), but none were above the USEPA criterion (346 ng/g) for TL 4 species.

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## INTRODUCTION

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This appendix contains the annual permit compliance monitoring report for mercury (Hg) in the Everglades Stormwater Treatment Areas (STAs) by the South Florida Water Management District (SFWMD or District) and 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.)]. This report summarizes the results of monitoring in the calendar year 2009 (CY2009) for fish and Water Year 2010 (WY2010) (May 1, 2009–April 30, 2010) for surface water in Stormwater Treatment Areas 1 East (STA-1E), 1 West (STA-1W), STA-2), 3 (STA-3), 4/5 (STA-4/5), and 6 (STA-6). 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), are reported separately in Appendix 3B-1 of this volume.

This report consists of key findings and overall assessment, an introduction and background, a summary of the Mercury Monitoring and Reporting Program (MMAP) and monitoring results. The background section briefly summarizes previously identified and published concerns regarding possible impact of STA operations on South Florida's mercury problem. The following sections summarize MMAP, quality assurance/quality control (QA/QC), and statistical applications, followed by a summary and discussion of monitoring results. The monitoring results section comprises the bulk of new discussion. The last section of this appendix provides updates on mercury monitoring network optimization in each STA.

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## BACKGROUND

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Stormwater Treatment Areas are constructed wetlands designed to remove phosphorus from stormwater runoff originating from upstream agricultural areas and other areas, including Lake Okeechobee releases. The original six STAs, totaling over 65,000 acres, equating to approximately 45,000 acres of effective treatment area, were built as part of the Everglades Construction Project (ECP) authorized under the EFA (Chapter 373.4592, F.S.).

Even before passage of the EFA in 1994, concerns were being raised that attempts to reduce downstream eutrophication could inadvertently aggravate 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 also showed wetlands to be a significant 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 was reported to stimulate the sulfate-reducing bacteria that methylate inorganic mercury (Kelly et al., 1997; Paterson et al., 1998). Environments that favor methylation also 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 were also found to contain fish with elevated mercury levels (Abernathy and Cumbie, 1977; Bodaly et al., 1984; Bodaly et al., 1999). This so-called "reservoir effect" can occasionally persist for several decades after initial soil flooding (Bodaly et al., 1984; Verdon et al., 1991; Fink et al., 1999). For instance, Verdon et al. (1991) reported that total mercury levels in northern pike (*Esox lucius*) increased from 0.61 to 2.99 parts per million (ppm or milligrams per liter) and continued to increase nine years after the initial soil flooding. Given these observations, Kelly et al. (1997) recently recommended that in siting a new reservoir total

land area flooded should be minimized and flooding the wetlands, which contain more organic carbon than uplands, should be avoided.

However, applying these recommendations directly to the Everglades is problematic because most of the observations were made in deepwater lakes or reservoirs in temperate regions. In a report to the SFWMD on the potential impact of nutrient removal on the Everglades mercury problem (Watras, 1993), the author 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.” Watras recommended monitoring and integrating mass balance and process-oriented studies to understand how this subtropical system would behave. Such studies were initiated in 1994 with the start-up of the prototype STA, the Everglades Nutrient Removal (ENR) Project (later incorporated within Stormwater Treatment Area 1 West). 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 fish [mosquitofish (*Gambusia holbrooki*) and largemouth bass (*Micropterus salmoides*); 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 fish also continued to have only low mercury levels: 8–75 nanograms per gram (ng/g) in mosquitofish, and 100–172 ng/g largemouth bass age-standardized to three years (age-3) (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 EFA implementation does not exacerbate the mercury problem, the FDEP construction and operating permits issued for the STAs require the SFWMD to monitor levels of THg and MeHg in various abiotic (e.g., surface water and sediment) and biotic (e.g., fish and bird tissues) media, both within STAs and the downstream receiving waters (see also Appendix 3B-1 of this volume).

Results from monitoring programs at STAs constructed and operated since 1999 (after the ENR Project) have revealed transitory spikes in MeHg production (see previous reports published by the SFWMD, including Rumbold and Fink, 2002b). 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), these monitoring results demonstrated that spikes can sometimes occur following dryout and rewetting. Accumulating evidence suggests that oxidation of sulfide pools in the sediments (e.g., organic sulfide, disulfides, and acid volatile sulfides) during dryout can lead to increased methylation upon rewetting of the marsh either by providing free sulfate, which stimulates 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 ASSESSMENT PROGRAM

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The following section provides information on current monitoring and reporting activities used for the District's Mercury Monitoring and Assessment Program (MMAP) (SFWMD, 1999c). Mercury monitoring for the MMAP was initially developed for the Everglades Construction Project, the Central and Southern Florida Project, and the Everglades Protection Area (EPA). The SFWMD developed and submitted a plan to the FDEP, the U.S. Environmental Protection Agency (USEPA), and the U.S. Army Corps of Engineers (USACE) in compliance with the permit requirements (SFWMD, 1999b) and was later approved. Details on the procedures for ensuring the quality of and accountability for data generated under this monitoring program were set forth in the SFWMD's Quality Assurance Project Plan (QAPP) for the Mercury Monitoring and Assessment Program (SFWMD, 1999c), which was also approved on issuance of the FDEP permit. QAPP revisions were approved by the FDEP on June 7, 1999.

On February 13, 2006, a revised sampling protocol was approved by the FDEP and the District which was entitled A Protocol for Monitoring Mercury and Other Toxicants (Protocol) (SFWMD, 2006). Adapted from Rumbold and Pfeuffer (2005), this new plan was developed to replace the initial plan developed under the MMAP. The primary drivers of the Protocol are to (1) streamline sampling procedures, (2) eliminate the need for extended, open-ended sampling activities, and (3) phase out surface water sampling. The Protocol continues to use the QAPP modified in 1999. As of May 16, 2008, all mercury monitoring within each STA follows the Protocol. On September 29, 2009, additional modifications to the Protocol were approved by FDEP that involved altering the fish collection length for largemouth bass to the current range of 307–385 millimeters (mm).

### PROTOCOL FOR MONITORING MERCURY AND OTHER TOXICANTS

#### Phase 1: Baseline Collection and Assessment

Phase 1 baseline collection and assessment is meant to provide information regarding the likelihood that a constructed facility under an EFA project may exacerbate or create a mercury (or other toxicant) problem. Identifying problematic areas will allow managers to avoid sites or areas that may present risk.

Phase 1 is operated under three tier levels: Tier 1 (Compilation and Review of Available Data), Tier 2 (Field Sampling), and Tier 3 (Bioaccumulation Tests and Dynamic Modeling).

Under Tier 1, the Environmental Site Assessment (ESA) is evaluated to determine (1) if any corrective actions were taken during the ESA, (2) there was potential for contamination, and/or (3) the time interval between the ESA and project construction. If information data gaps exist, or where the preponderance of baseline data demonstrates a potential problem, then Phase 1, Tier 2 or Tier 3 is initiated.

Under Phase 1, Tier 2, five representative soil/sediment cores are collected and analyzed for several constituents that help evaluate MeHg production and mercury bioaccumulation. **Figure 1** summarizes sediment collection under Phase 1 to date. Along with sediment, mosquitofish and large-bodied fish are collected and analyzed for THg within the same operating unit (OU). The methods used for fish and sediment collection are described in the sections below.

Phase 1, Tier 3 is initiated if at least one of the following occurs: (1) absolute concentrations of MeHg or average percent MeHg in sediments/soils from an OU exceeds the 90 percent upper confidence level of the basin average or, if not available, the 75<sup>th</sup> percentile concentration

(percent MeHg) for all basins; or (2) ambient fish collected with the project boundary demonstrate excessive bioaccumulation that exceeds the 90 percent upper confidence level of the basin-wide average or, if that value is not available, the 75<sup>th</sup> percentile concentration for all basins. Phase 1, Tier 3 is used to evaluate extending uncertainties surrounding mercury bioaccumulation. This is accomplished through the use of bioaccumulation testing and modeling.

### **Phase 2: Monitoring During Three-Year Stabilization Period**

If Phase 1 monitoring is not necessary, then Phase 2, Tier 2 monitoring can occur following OU flow-through. Under Phase 2, Tier 1, one surface water sample is collected and analyzed for THg and MeHg on a quarterly basis at inflow and outflow structures. Additionally, at least 100 mosquitofish are collected from multiple locations within each OU on a quarterly basis, to be composited and analyzed for THg. Sunfish (*Lepomis* spp.) and largemouth bass (LMB) ( $n \geq 5$ ) are collected and analyzed for THg on an annual basis.

Six criteria are used to evaluate the performance of an OU with respect to mercury bioaccumulation and enhancement (SFWMD, 2006). These criteria are related to long-term trends in fish tissue concentrations, surface water THg/MeHg loading and water quality standards.

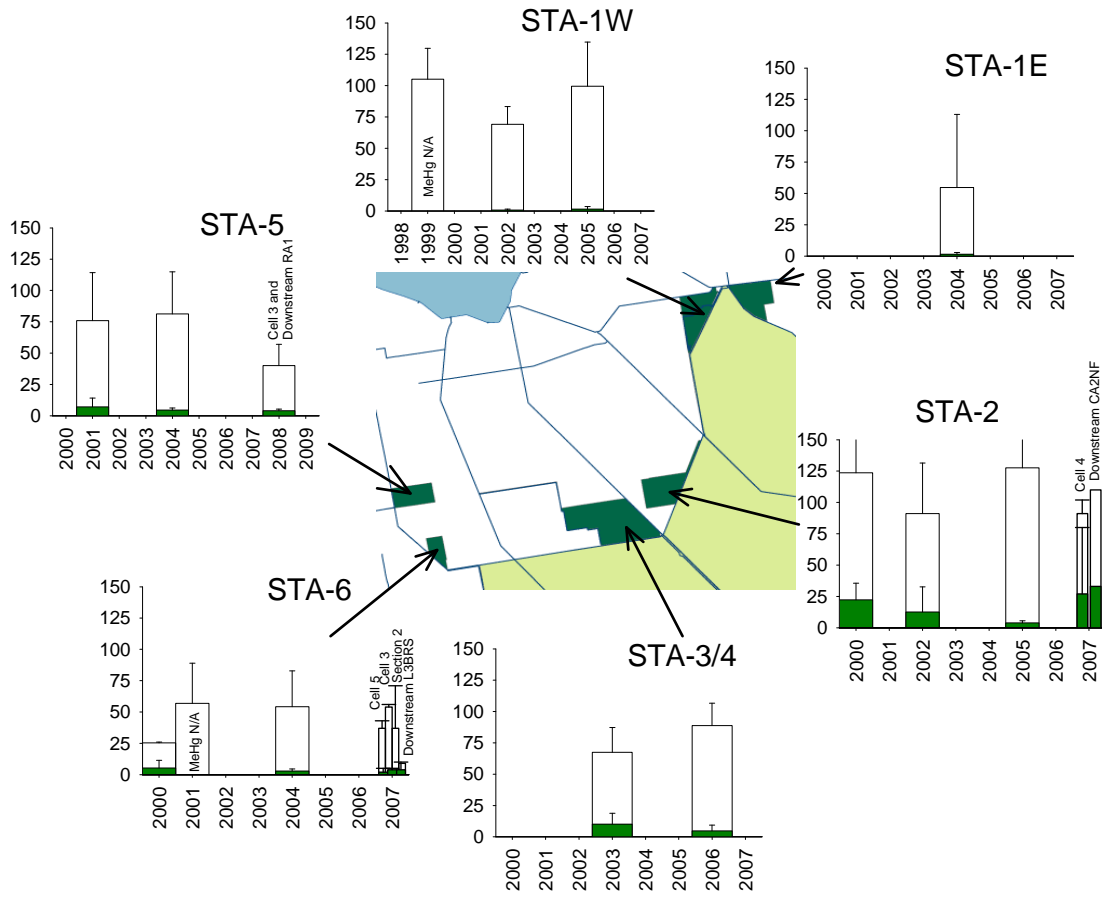
If any of the action criteria is exceeded, then Phase 2, Tier 2 is triggered. Tier 2 sequentially involves (1) notifying the permitting authority, (2) resampling the media that triggered Tier 2 Monitoring, (3) evaluating the spatial and temporal extent of the mercury bioaccumulation/enhancement accompanied with bioaccumulation modeling, and (4) developing an adaptive management plan.

### **Phase 3: Operational Monitoring**

If after the first three years of monitoring, neither downstream loading nor residue levels in fish have exceeded action levels in the two years prior, then the project can move into Phase 3, Tier 1. Under Phase 3, Tier 1, (1) surface water sampling is discontinued, (2) the frequency of mosquitofish collection is reduced to semiannually, and (3) the frequency of large-bodied fish collection is reduced to one collection every three years. If the conditions are not met within the first three years, then criteria can be reevaluated annually based on the preceding two-year period.

Phase 3, Tier 2 is triggered if (1) the annual average THg levels in mosquitofish progressively increase over time; (2) any semiannual mosquitofish composite exceeds the 90 percent upper confidence level of the basin-wide annual average (or, if basin-specific data are lacking, exceeds the 75<sup>th</sup> percentile concentration for the period of record for all basins); or (3) if triennial monitoring of large-bodied fish (i.e., in years 6–9) reveal tissue mercury levels have statistically increased over time (i.e., over two or more years) or have become elevated to the point of exceeding the 90 percent upper confidence level of the basin-wide annual average (or if basin-specific data are lacking, exceeds the 75<sup>th</sup> percentile for the period of record for all basins).

If fish under Phase 3 operational monitoring have not exceeded action levels by the ninth year, project-specific mercury monitoring can be moved into Phase 3, Tier 3. Under Phase 3, Tier 3, all of the project's mercury-related monitoring is discontinued; however, project managers are cautioned that action levels may be revised in the future.



**Figure 1.** Mean concentration [+1 standard deviation (SD); dry-weight basis] of total mercury (THg) in nanograms per gram (ng/g) and methylmercury (MeHg) (10x ng/g) in sediment cores (n = 5 per cell/section; 0–10 cm deep) collected from each Stormwater Treatment Area (STA) to start-up. Crossed-hatched columns indicate collections following the mercury monitoring program (SFWMD, 2006). These are the most recent datasets on THg and MeHg for sediment collections in the STAs.



## QUALITY ASSURANCE MEASURES

This section is a quality assessment of the District's mercury monitoring program during WY2010 and an evaluation of the accuracy, precision, and completeness of the data quality where appropriate. This assessment is based on data quality objectives contained in the QAPP.

Quality assurance and quality control (QA/QC) are integral parts of all monitoring programs. A stringent QA/QC program is especially critical when dealing with ultra-trace concentrations of analytes in natural and human-impacted environments. Quality assurance includes design, planning, and management activities conducted prior to implementing the project to ensure that the appropriate types and quantities of data will be collected with the required representativeness, accuracy, precision, reliability, and completeness. The goals of QA are to ensure the following: (1) standard collection, processing, and analysis techniques will be applied consistently and correctly; (2) the number of lost, damaged, and uncollected samples will be minimized; (3) the integrity of the data will be maintained and documented from sample collection to entry into the data record; and (4) data are usable based on project objectives.

Quality assurance measures are incorporated during the sample collection and laboratory analysis to evaluate the quality of the data. These measures give an indication of measurement error and bias (or accuracy and precision). Aside from using these results as an indication of data quality, an effective QA program must utilize QC results to determine areas of improvement and implement corrective measures. QC measures include both internal and external checks. Typical internal QC checks include replicate measurements, internal test samples, method validation, blanks, and the use of standard reference materials. Typical external QC checks include split and blind studies, independent performance audits, and periodic proficiency examinations. Data comparability is a primary concern because mercury-related degradation of water quality is defined here as relative to baseline data generated by one or more laboratories. It is important to establish and maintain comparability of the performance and results among participating laboratories assessing the reporting units and calculations, database management processes, and interpretative procedures. Comparability of laboratory performance must be ensured if the overall goals of the monitoring program are to be realized.

### Laboratory Quality Control

Data for this program was generated by the District and the FDEP, both of which are certified by the Florida Department of Health under the National Environmental Laboratory Accreditation Program. The following methods were utilized when analyzing samples for THg and MeHg during WY2010: FDEP-USEPA Method 1631E (Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry); USEPA Draft Method 1630 (Methylmercury in Water and Tissues by Distillation, Extraction, Aqueous Phase Ethylation, Purge and Trap, Isothermal GC Separation, Cold Vapor Atomic Fluorescence Spectrometry); USEPA Method 245.6 [Mercury in Tissues by Cold Vapor AAS (uses liquid digestion)]; EPA 7471A [Mercury in Solids by Cold Vapor AAS (uses liquid digestion)]; District-EPA 7473 [Mercury in Solids and Tissues by Direct Thermal Decomposition, Amalgamation and AA (does not incorporate liquid digestion)]. All of the above methods use performance-based standards employing the appropriate levels of QA/QC required by the National Environmental Laboratory Accreditation Conference, the specific reference method, and the Protocol.

### Field Quality Control Samples

For WY2010, a total of 78 field QC samples, including field kit prep blanks (FKPB), equipment blanks [both laboratory-cleaned equipment blanks (EB) and field-cleaned equipment blanks (FCEB)], replicate samples (RS) and trip blanks (TB) were collected for both THg and MeHg surface water samples at STA-1W, STA-1E, STA-2, STA-3/4, STA-5, and STA-6. These

field QC check samples represented approximately 48 percent of the 162 water samples collected during this reporting period. The results of the field QC blanks are summarized in **Table 1**. An FKPB is a sample of the deionized distilled water (DDW) for field QC that remains at the lab to monitor low-level background inorganic mercury contamination of the laboratory DDW system, which can vary over time. An EB is collected at the beginning of every sampling event, and an FCEB is collected at the end of the event. A TB is a blank sample (DDW) that is used to identify potential contamination during field transport. For this field collection blank, DDW is carried through the field collection trip, remains sealed in a container, and is then analyzed with all other samples at the FDEP laboratory.

For WY2010, there were no flagged QA/QC samples for THg in contrast to WY2009, when the percent flagged for THg was between 10 and 33 percent; MeHg samples also showed a reversal, with flagged samples this water year (none were flagged in WY2009). Trip blanks were temporally implemented into MMAP to assess contamination associated with MeHg. The TBs indicated that some element of contamination was occurring between the points of preparation and shipment back to the laboratory. Measures are currently being taken to determine the source of contamination.

The sample corrective action criterion for FCEB and EBs is currently 10x the FCEB/EB level. All routine samples associated with an FCEB or EB are flagged if its value is less than 10x the method detection limit of 0.1 ng/L for THg or 0.022 ng/L for MeHg.

**Table 1.** Frequency of field quality control (QC) blanks from STAs 1 West, 1 East, 2, 3/4, 5, and 6 for Water Year 2010 (May 1, 2009–April 30, 2010) (WY2010). Method detection limits are 0.1 nanograms per liter (ng/L) for total mercury (THg) and 0.022 ng/L for methylmercury (MeHg).

FieldQC <sup>1</sup>	n <sup>2</sup>	THg					MeHg					
		Collection <sup>4</sup> Frequency %	n > MDL <sup>5</sup>	Mean ng/L <sup>3</sup>	n Flagged	% Flagged <sup>4</sup>	Collection <sup>4</sup> Frequency %	n > MDL <sup>5</sup>	Mean ng/L <sup>3</sup>	n Flagged	% Flagged <sup>4</sup>	
<b>FKPB</b>	1	1.20	0	-0.10	0	0	1	1.20	0	-0.022	0	0
<b>EB</b>	12	14.8	0	-0.10	0	0	12	14.8	5	0.006	5	6.10
<b>FCEB</b>	8	9.80	0	-0.10	0	0	8	9.80	4	0.009	4	4.93
<b>TB</b>	6	7.40	0	-0.10	0	0	6	7.40	2	0.004	2	2.40

<sup>1</sup>FKPB-Field kit preparation blank; EB-Lab-cleaned equipment blank; FCEB-Field-cleaned equipment blank; TB-trip blank

<sup>2</sup>Total number (n) of respective QA/QC samples

<sup>3</sup>Mean concentration of quality control (QC) samples

<sup>4</sup>Percentage of all (QA/QC+ monitoring) samples collected for WY2010 (n = 81 for THg and n = 81 for MeHg)

<sup>5</sup>MDL-Method detection limit

## Analytical and Field Sampling Precision

Field replicates samples (RS) are samples that have been collected in rapid succession from the same site. Laboratory replicates are aliquots of the same sample that are prepared and analyzed within the same run.

### *Water Samples*

To assess the precision of field collection and analysis, 48 replicate, unfiltered surface water samples (24 THg and 24 MeHg) collected at STA-1W, STA-1E, STA-2, STA-3/4, STA-5, and STA-6 were processed during the course of WY2010. **Table 2** reflects the results of sample analyses. Two replicate samples (RS) were matched with one surface water sample. For WY2010, all of the THg and MeHg relative standard deviations were below the required 20 percent QA/QC precision level which is an improvement for THg from WY2009.

### *Mosquitofish Composite Samples*

To monitor spatial and temporal patterns in mercury residues in small-bodied fish, mosquitofish (at least 100 individuals) are collected at various locations in the STAs, ECP, and non-ECP marshes. These individuals are then composited for each site. Composite sampling can increase sensitivity by increasing the amount of material available for analysis, reduce inter-sample variance effects, and dramatically reduce analytical costs. However, there are disadvantages to composite sampling. Subsampling from a composite introduces uncertainty if homogenization is incomplete. Since 1999, the District has used a Polytron<sup>®</sup> homogenizer to homogenate composited mosquitofish. Until late 2001, the homogenate was subsampled in quintuplicate and each subsample analyzed for THg. Based on the apparent degree of homogenization as evidenced by the low relative standard deviation (RSD) among aliquots reported in the 2002 Everglades Consolidated Report, the District revised its Standard Operation Procedure after consultation with and approval by the FDEP, reducing subsampling of the homogenate from five to three. In 2007, replicates were further reduced from three to one homogenate. Laboratory replicates of mosquitofish were processed by the SFWMD and analyzed for THg. For CY2009, the mean percent RSD between replicate and routine samples for the 42 aliquots was 11.7 percent (**Table 2**) which is greater than CY2008 (mean of 9 percent). Three of the RSDs were greater than the required 20 percent QA/QC precision level.

**Table 2.** Relative standard deviations for media collected within STAs 1 West, 1 East, 2, 3/4, 5, and 6 during WY2010 (surface water) and calendar year 2009 (CY2009) (fish).

Analyte	n	% Relative Standard Deviation (RSD)*		
		Minimum	Maximum	Mean
Surface Water THg	10	0.60	13.9	5.1
Surface Water MeHg	10	2.38	10.5	6.6
Mosquitofish THg	14	2.93	28.4	11.7

### *Sediment Composite Samples*

For WY2010, no sediment samples were collected for THg/MeHg analysis for any of the STAs because no new cells came online and/or no extended sediment monitoring was needed.

## Inter-laboratory Comparability Studies

To ensure further reproducibility between ongoing mercury sampling initiatives and to evaluate the performance of contract laboratories used for mercury analysis, round-robin studies for water, fish, and sediment are routinely initiated. These studies are performed by the District and contracted laboratories.

### *Surface Water and Fish*

As in previous years, inter-laboratory studies were initiated by the FDEP for the purpose of assessing the comparability of total and MeHg analysis in water for several laboratories. Participating laboratories receive nine unknown samples of ambient water from the Everglades for analysis of THg and/or MeHg. The most recent report summarizing the inter-laboratory investigation can be found at: [www.dep.state.fl.us/labs/bars/sas/everglades/index.htm](http://www.dep.state.fl.us/labs/bars/sas/everglades/index.htm). In CY2009, the District participated in a QUASIMEME study to assess their performance in quantifying mercury in fish. The results of this study are presented in Attachment A.

### *Sediment*

In CY2009, the District participated in two performance testing (PT) studies to assess the ability of the District's laboratory to generate acceptable analytical data for THg in sediment/soil. NELAC certification requires participation in PT studies every six months. Further details on these evaluations are presented in Attachments B and C.

## 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 LMB were standardized to an expected mean concentration in three-year-old fish at a given site by regressing mercury against age (EHg3). Currently, the FWC targets LMB between lengths of 307–385 millimeters (mm) which includes age-3 fish. This length range is targeted to eliminate the need for fish ageing. Sunfish were not aged. Instead, arithmetic means were reported. Additionally, the distribution of the different species of sunfish (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. The target sunfish species is bluegill.

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 (LMB) 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 ( $n > 2$  groups)] or Student's t-tests ( $n \leq 2$  groups) 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 multi-group null hypotheses were rejected under ANOVA, then the group was compared using either Tukey HSD (Honestly Significant Difference; for equal-sized datasets) test, the Tukey-Kramer (for unequal-sized datasets), or the Holm-Sidak test.

If the group did not meet any of these assumptions, then raw datasets were evaluated using nonparametric tests such as the Kruskal-Wallis ANOVA on ranks ( $n > 2$  groups) or the Mann-Whitney Rank sum test ( $n \leq 2$  groups). If the multi-group null hypothesis was rejected, then the groups were compared using either the Nemenyi test (for equal-sized datasets) or Dunn's Method (for unequal-sized datasets). The Pearson Product moment (or the non-parametric equivalent Spearman Rank Order) was used to evaluate the relationship between two parameters. Linear regression was used to develop a line of best fit (linear model) between parameters.

## **SITE DESCRIPTIONS**

Site descriptions and operational plans for STA-1W, STA-1E, STA-2, STA-3/4, STA-5, and STA-6 are published elsewhere (SFWMD, 2007a-d; 2009). Maps of selected monitoring locations are given with the data for each STA in the *Monitoring Results* section of this Appendix.

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## MONITORING RESULTS

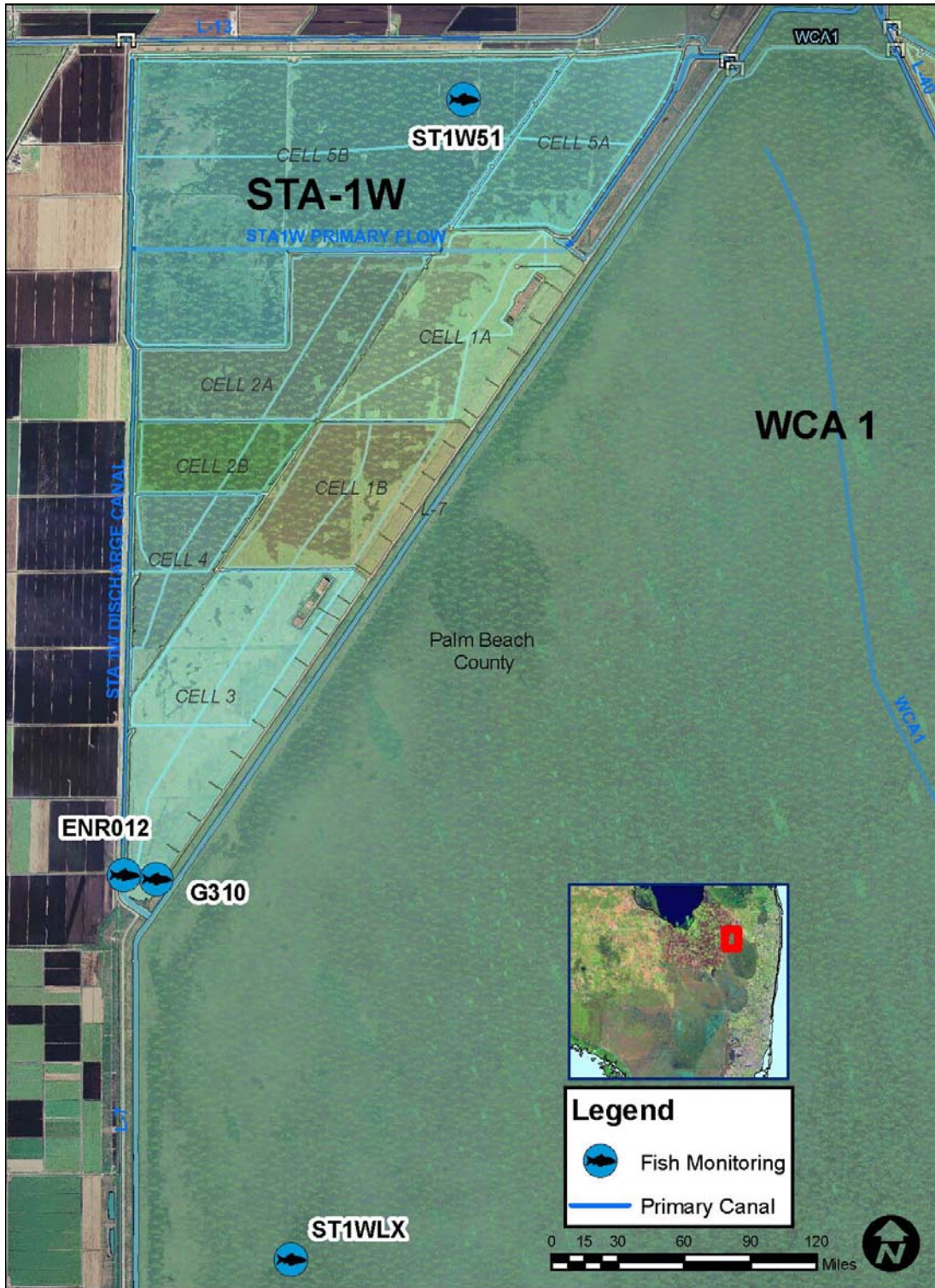
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### STA-1W

In 2000, STA-1W subsumed the ENR Project (Cells 1 through 4, **Figure 2**), 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 WY2009, see Rumbold and Rawlik, 2000; Rumbold et al., 2001, 2006; Rumbold and Fink, 2002a, 2003a; Rumbold, 2004, 2005a, Gabriel et al., 2007). In 2007, Phase 3, Tier 1 (SFWMD, 2006) conditions were approved and implemented and therefore surface water monitoring for THg and MeHg was terminated. After the first quarterly mosquitofish collection in 2009, Phase 3, Tier 3 monitoring was implemented and all remaining monitoring under the Protocol was discontinued.

Concentrations of THg in mosquitofish in CY2009 are summarized in **Table 3** and graphically presented in **Figure 3**. Mosquitofish from STA-1W continue to have very low mercury levels particularly from the interior sampling sites. These levels are similar to previous conditions 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 (see Appendix 3B-1 of this volume). Mosquitofish in STA-1W have consistently exhibited a negative percent change in tissue mercury levels since this STA was put into operation (**Table 3**). The slope of this decreasing trend has in recent years reached closer to zero, likely indicating that the internal mercury biogeochemical cycle has reached a minimum in fish THg concentration [see 2010 South Florida Environmental Report (SFER) – Volume I, Appendix 5-6]. This pattern was also observed in sunfish and largemouth bass for previous collections. In 2008, the outflow data for G310 and ENR012 were combined with downstream location ST1WLX, resulting in overall higher levels as downstream marsh locations typically contain higher fish mercury concentrations. In CY2009, only ST1WLX data was available. The average annual total mercury mosquitofish composite concentration for CY2009, including all individual mosquitofish composites within STA-1W, did not exceed the period of record (POR) 75<sup>th</sup> percentile for all Everglades downstream receiving water sampling locations (see Appendix 3B- of this volume).

Contrary to other areas of the Everglades, fish-eating wildlife foraging preferentially at STA-1W is not at risk from mercury exposure. STA-1W mosquitofish (see previous SFERs) continue have some of the lowest tissue-Hg levels in South Florida — well below both USEPA and USFWS guidance levels for predator protection (Eisler, 1987; USEPA, 1997). Historical data on mercury concentrations in fish from STA-1W are presented in previous SFERs.



**Figure 2.** Stormwater Treatment Area 1 West (STA-1W) showing CY2009 mercury monitoring sites. Atmospheric deposition locations are presented in Appendix 3B-1 of this volume.

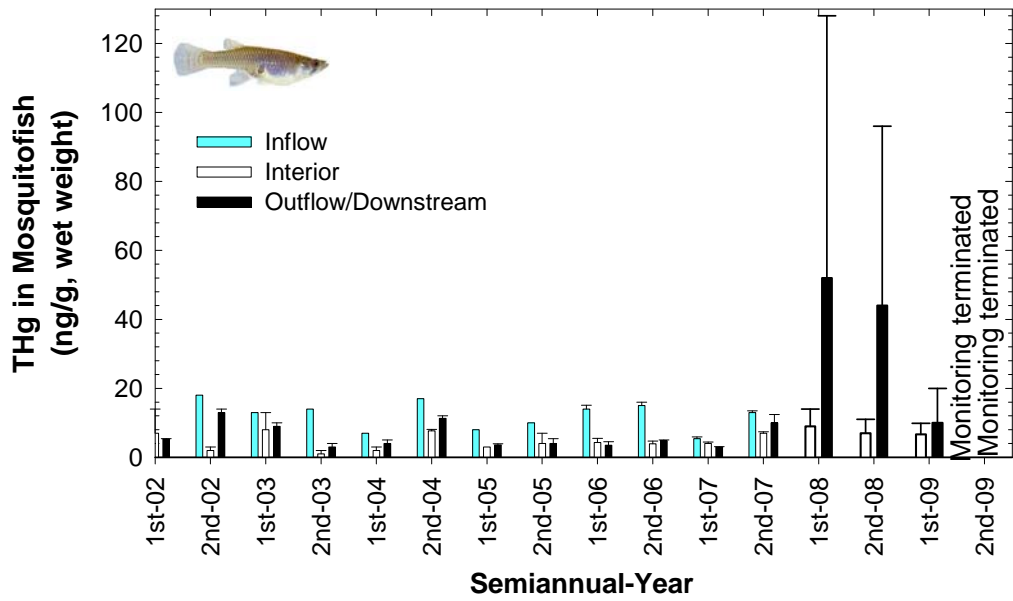
**Table 3.** Concentration of THg (ng/g, wet weight) in mosquitofish (*Gambusia holbrooki*) composites from STAs.

STA	Semiannual/ Quarterly Collection	Interior Fish	Outflow/Downstream Fish
STA-1W	2009-1	6.66	10.0
	2009-2	MT	MT
	Annual mean	Not Applicable	Not Applicable
	Cumulative mean	19.3	14.6
STA-1E	2009-1	6.66	65.0
	2009-2	15.6	56.0
	2009-3	16.0	77.0
	2009-4	9.30	128
	Annual mean	11.1	81.5
	Cumulative mean	18.6	74.5
STA-2	2009-1	9.25	21.0
	2009-2	16.2	11.0
	2009-3	7.75	26.0
	2009-4	4.25	11.0
	Annual mean	12.8	17.2
	Cumulative mean	70.0	68.0
STA-3/4	2009-1	15.6	13.0
	2009-2	6.66	7.00
	Annual mean	11.1	10.0
	Cumulative mean	14.7	27.7
STA-5	2009-1	15.0	28.0
	2009-2	35.5	NA
	2009-3	19.3	53.0
	2009-4	14.3	9.00
	Annual mean	21.0	30.0
	Cumulative mean	25.4	30.4
STA-6	2009-1	15.0	28.0
	2009-2	48.0	35.5
	2009-3	20.0	35.5
	2009-4	5.00	10.0
	Annual mean	22.0	27.2
	Cumulative mean	16.4	25.3

MT = Monitoring terminated

NA = Not available





**Figure 3.** Mercury concentrations (ng/g, wet weight) in mosquitofish composites (mean ± 1 SD) collected at STA-1W.

## STA-1E

Monitoring 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 5–7) met the start-up criteria, as specified in EFA Permit No. 0195030-001-GL, in August 2005 (correspondence from R. Bearzotti, SFWMD, dated September 9, 2005). The USACE constructed a Periphyton-Based Stormwater Treatment Area (PSTA) Demonstration Project in the easternmost flow-way (Cells 1 and 2) of STA-1E. The most recent eastern flow-way passed start-up in 2007. Currently, all of STA-1E is under Phase 2 monitoring (**Figure 4**).

In WY2010, STA-1E displayed moderate surface water THg and MeHg concentrations at inflow and outflow locations in comparison to all other STAs (**Figures 5 and 6**). All THg levels were less than the Florida Class III numerical water quality standard of 12 ng/L (**Figure 7**). Both THg and MeHg loads at the outflow were less than inflow [124 g THg (inflow), 28.3 g MeHg (inflow); 71.5 g THg (outflow), 8.68 g MeHg (outflow)] (**Table 4**). Out of all STAs, STA-1E shows the largest reduction in THg loading between the inflow and outflow for WY2010.

Quarterly collection of mosquitofish from STA-1E sites at interior marshes (in each cell) and the single downstream site (ST1ELX), began during the third quarter of 2005. As shown in **Table 3**, annual mean mercury levels in mosquitofish from the interior marsh in 2009 were the lowest, tied with STA-3/4. This is similar to 2008. Average annual mosquitofish composites for the interior of STA-1E, including all mosquitofish composites, did not exceed the POR 75<sup>th</sup> percentile for all Everglades downstream sampling locations during 2009 (see Appendix 3B-1 of this volume).

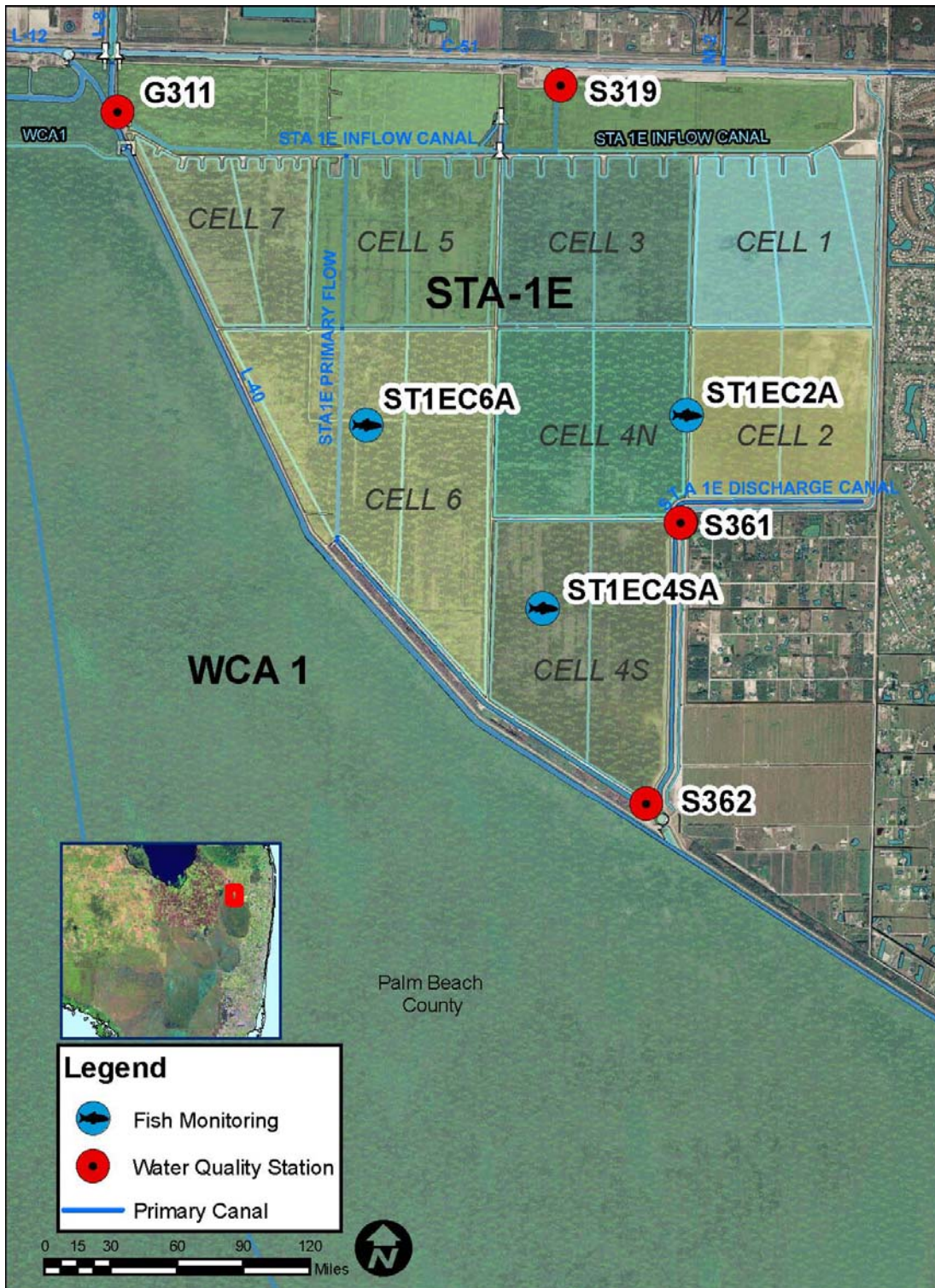
Surface water sulfate, water level, and rainfall for STA-1E are presented in **Figure 8**. Water levels within the cells of this STA typically do not fall below mean cell bottom elevation. Sulfate levels at the inflow and outflow locations are comparable to other STAs and there does not appear to be any seasonal trend in sulfate concentration.

Annual collection of sunfish occurred in October and November 2009. As evident from **Table 5**, mercury levels were on the lower end in STA-1E sunfish compared to the other STAs. Levels in sunfish from the near-field downstream site (ST1ELX) were three times the levels recently observed at one of the far-field downstream sites, LOXF4 (see Appendix 3B-1 of this volume). The weight-standardized concentration in bluegill from ST1ELX was 1.75 ng/g/mm, whereas bluegill from nearby LOXF4 averaged 0.86 ng/g/mm, which contrasts the previous two years where levels at both stations were similar. Site ST1ELX had the highest downstream concentration out of all other STAs. The average annual sunfish THg concentration for interior and downstream locations for STA-1E did not exceed the POR 75<sup>th</sup> percentile for all Everglades downstream receiving water sampling locations in CY2009 (see Appendix 3B-1 of this volume).

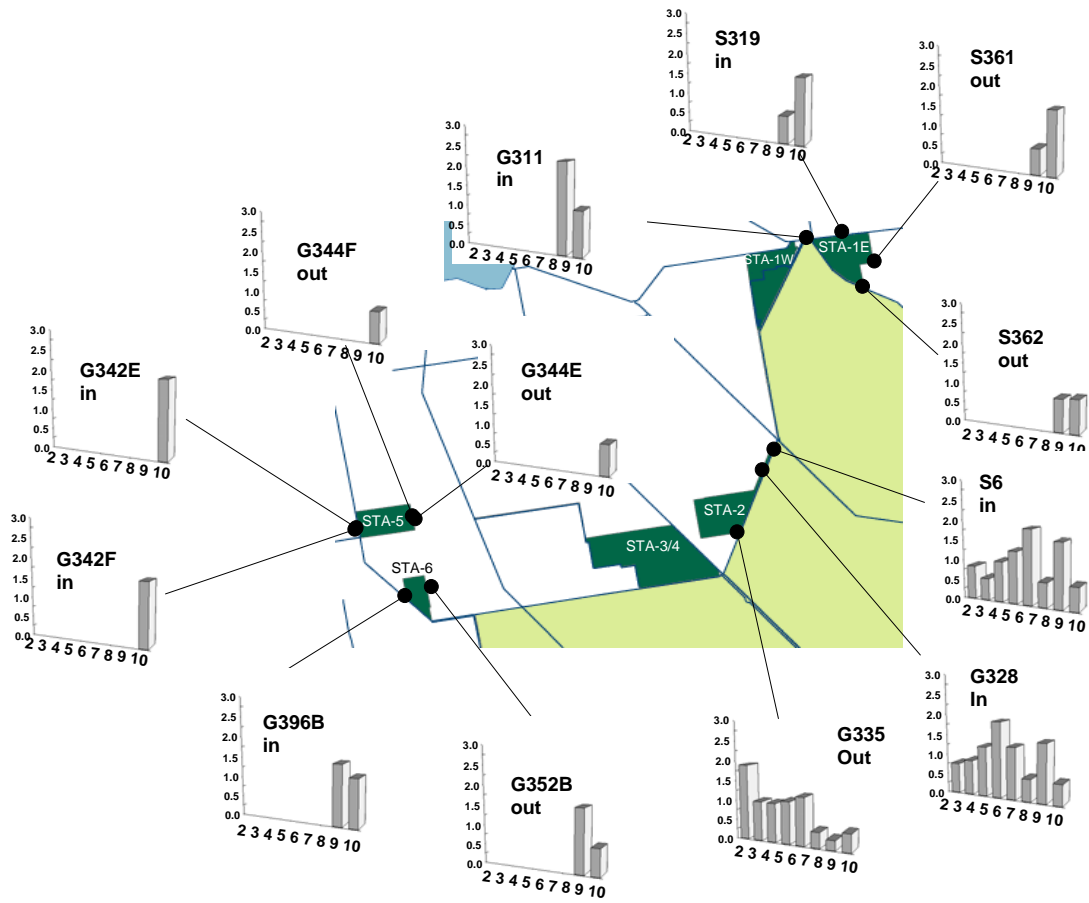
For 2009, largemouth bass were collected from the STA-1E interior site, but none were available at the downstream site (**Table 6 and Figure 9**). For the interior site nearly all LMB were within the 307–385 mm range. Largemouth bass THg concentrations, cumulative and within the 307–385 mm range, were the highest compared to all other STAs; however, this is only in comparison to two other STAs where LMB were available (STA-2 and STA-5). Interior LMB were not assayed for the remaining STAs either because there were no LMB available or because CY2009 was not a scheduled sampling year. The average annual LMB THg concentration for interior and downstream locations did not exceed the POR 75<sup>th</sup> percentile for all Everglades downstream receiving water sampling locations in CY2009 (see Appendix 3B-1 of this volume).

All fish species from the interior cells (ST1EC2A, ST1EC4SA, and ST1EC6A) and downstream of STA-1E show no visible temporal increase in THg levels for  $\geq$  three years to merit statistical investigation.

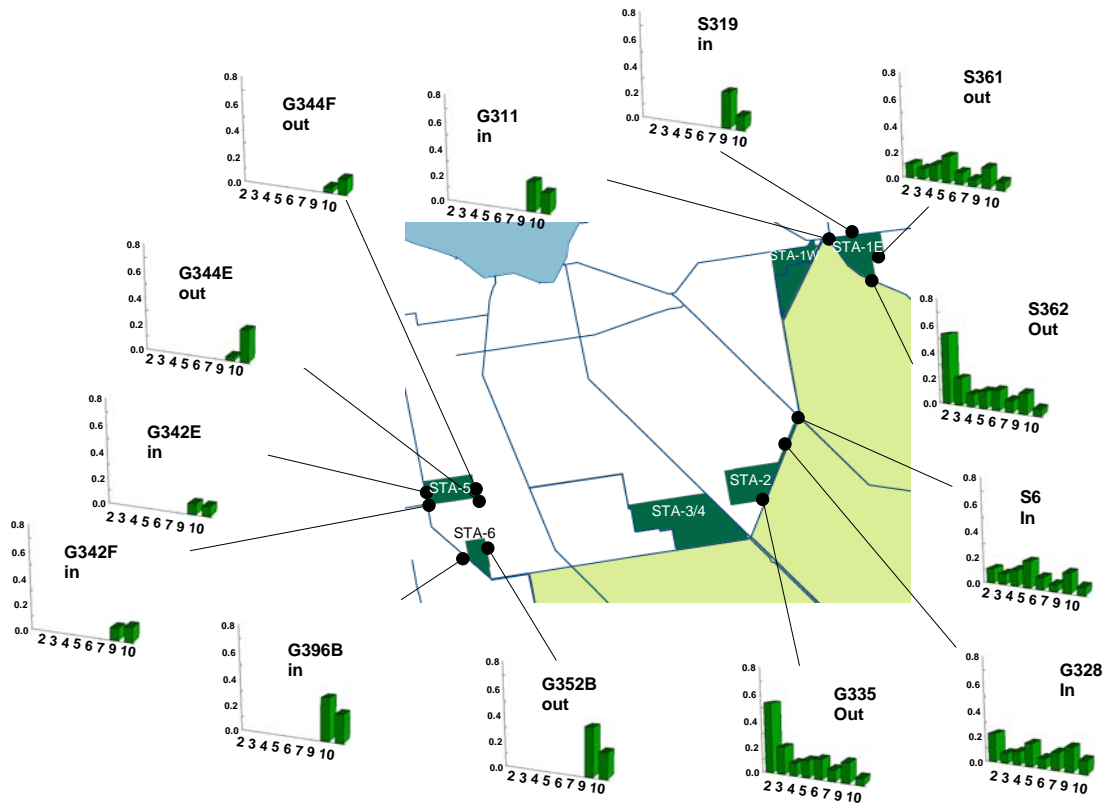
Regarding risks to fish-eating wildlife, interior mosquitofish [falling under trophic level (TL) 2 or 3] did not exceed the USEPA's 77 ng/g criterion; however, the mosquitofish from the downstream location did exceed this criterion for the third and fourth quarters. All resident interior sunfish within STA-1E were well below the USFWS criterion of 100 ng/g and nearly all were below the USEPA predator protection criterion of 77 ng/g for TL 2 or 3 fish. All downstream sunfish were above the USEPA's 77 ng/g and USFWS 100 ng/g criteria. After standardizing by whole fish length concentration [fillet concentration x 0.695 (Lange et al., 1998)], there was no exceedance of the USEPA criterion of 346 ng/g for TL 4 fish species for LMB. Therefore, fish-eating wildlife foraging preferentially with and downstream of STA-1E appears to have an overall low to moderate risk of mercury exposure.



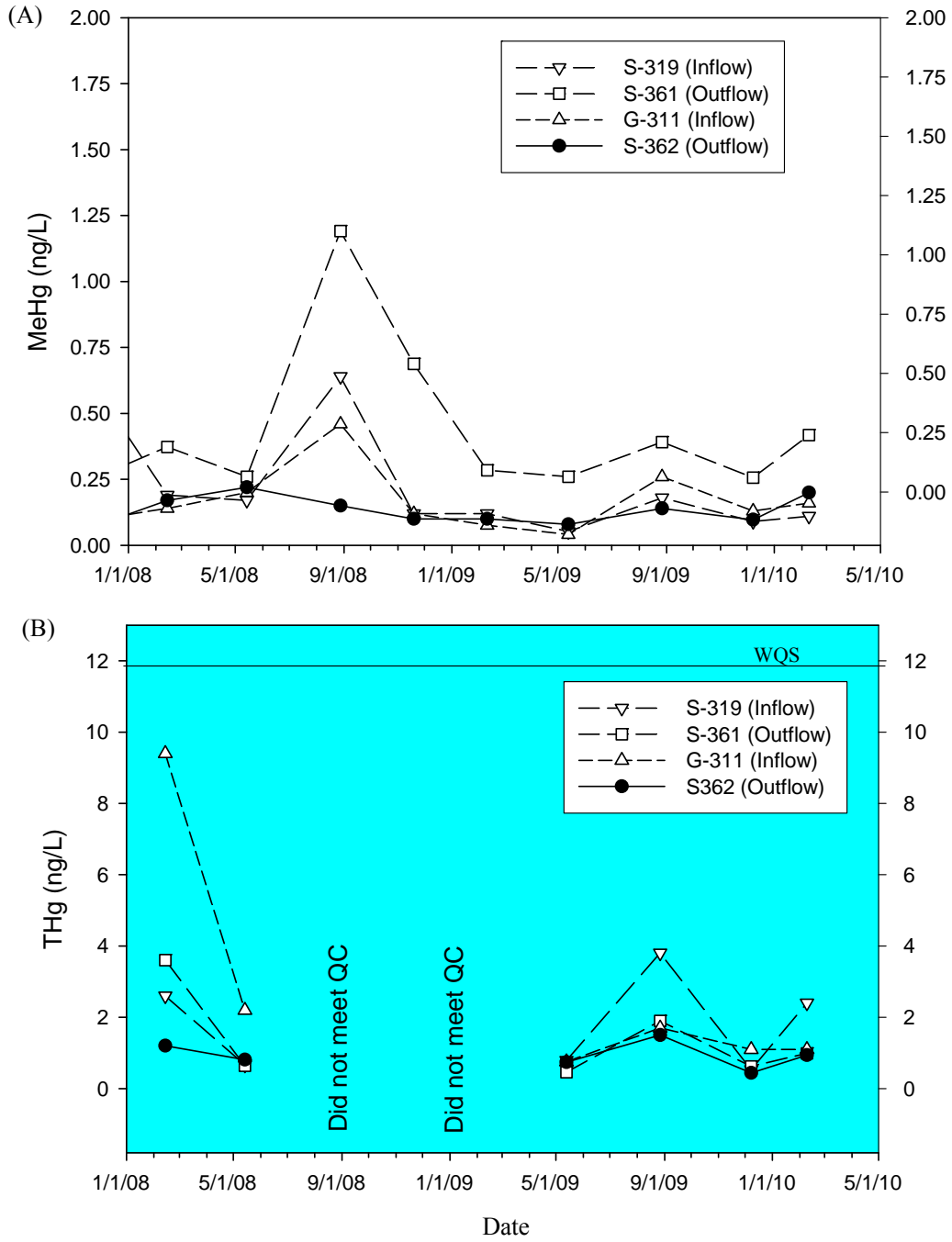
**Figure 4.** Map of Stormwater Treatment Area 1 East (STA-1E) showing selected mercury monitoring sites. Mosquitofish are collected downstream of STA-1E at ST1ELX and within each cell of the STA, and submitted as one composite sample per flow-way.



**Figure 5.** Annual median THg concentrations in monitored surface waters (ng/L) for the STAs from WY2002 through WY2010.



**Figure 6.** Annual median MeHg concentrations in monitored surface waters (ng/L) for the STAs through WY2010.



**Figure 7.** Concentrations of (A) MeHg and (B) THg (ng/L) in unfiltered surface water collected at STA-1E.

**Table 4.** THg and MeHg inflow and outflow loadings in grams (g) for WY2010.

	Inflow load		Outflow load		% Difference <sup>1</sup>	
	THg	MeHg	THg	MeHg	THg	MeHg
<b>STA-1E<sup>2</sup></b>	124	28.3	71.5	8.68	-42.3	-69.6
<b>STA-2<sup>3</sup></b>	356	75.2	286	66.0	-19.6	-12.2
<b>STA-5<sup>4</sup></b>	59.4	19.0	41.1	4.66	-30.8	-75.4
<b>STA-6<sup>5</sup></b>	35.1	27.3	27.3	14.7	-22.2	-46.1

<sup>1</sup> (outflow–inflow/inflow)\*100

<sup>2</sup> S-319 (inflow), S-361 (outflow), S-362 (outflow)

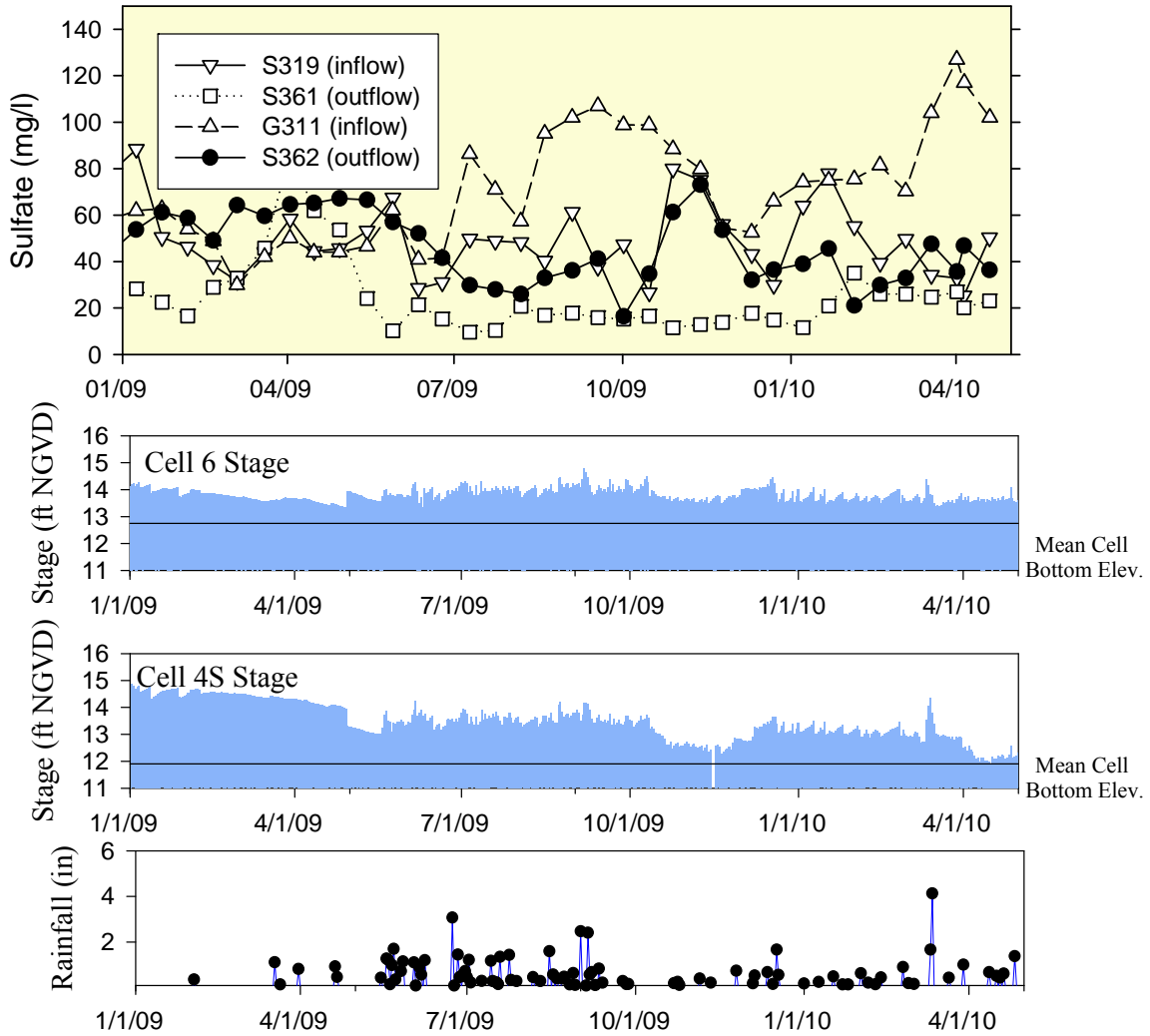
<sup>3</sup> Includes stations S6, G328 (inflow) and G335(outflow)

<sup>4</sup> Includes stations G342E, G342F (inflow, Flow-way 3) and G344E, G344F (outflow, Flow-way 3)

<sup>5</sup> Includes stations G600, G396B (inflow) and stations G354, G393, G354C, G393B, and G352B (outflow)

Note: surface water THg/MeHg monitoring was terminated in STA-3/4 and STA-1W





**Figure 8.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell), and rainfall at STA-1E.

**Table 5.** Concentration of THg (ng/g, wet weight) in sunfish collected from STAs in CY2009 (sample size in parentheses).

STA	Interior Fish	Outflow/Downstream Fish
STA-1E	51.2 ± 33.0 (15 <sup>a</sup> )	198 ± 15.8 (3)
Cumulative mean	66.1	174
STA-2	63.4 ± 62.3 (5)	137 ± 96.0 (20 <sup>a</sup> )
Cumulative mean	97.0	114
STA-3/4	TRI	TRI
Cumulative mean	75.6 <sup>b</sup>	70.0 <sup>b</sup>
STA-5	40.3 ± 7.20 (8 <sup>a</sup> )	56.0 ± 20.0 (5)
Cumulative mean	93.0	91.0
STA-6	80.4 ± 34.0 (5)	111 ± 16.0 (5)
Cumulative mean	56.0	94.2

a Where n > 5, multiple sites were sampled and pooled, i.e., multiple interior or outflows (see the *Protocol for Monitoring Mercury and Other Toxicants* section of this appendix).

b Cumulative through CY2008 data

TRI = Triennial fish collection

**Table 6.** Largemouth bass THg concentrations (ng/g, wet weight) collected in the STAs between lengths 307–385 mm for 2009. In parentheses all data is presented, which includes data within and outside of the 307–385 mm range. Cumulative mean includes all fish within and outside the 307–385 mm range for the period of record. All data show arithmetic mean  $\pm$  1 SD.

STA	Interior Fish	Outflow/Downstream Fish
STA-1E	152 $\pm$ 119, 12 <sup>a</sup> (135 $\pm$ 112, 15 <sup>a</sup> )	NA
Cumulative mean	178	322 <sup>d</sup>
STA-2	110 $\pm$ 23, 5 <sup>c</sup>	257 $\pm$ 79, 5 (328 $\pm$ 158, 20 <sup>a</sup> )
Cumulative mean	246	505
STA-3/4	TRI	TRI
Cumulative mean	313 <sup>d</sup>	423 <sup>d</sup>
STA-5	NA	NA
Cumulative mean	327 <sup>d</sup>	362 <sup>d</sup>
STA-6	155, 1 <sup>c</sup> (109 $\pm$ 37, 4 <sup>b</sup> )	NA
Cumulative mean	197	471 <sup>d</sup>

<sup>a</sup> Where  $n > 5$ ; multiple sites were sampled and pooled, i.e., multiple interior or downstream/outflows (see the *Protocol for Monitoring Mercury and Other Toxicants* section of this appendix)

<sup>b</sup> Where  $n < 5$ , not enough fish in sample area

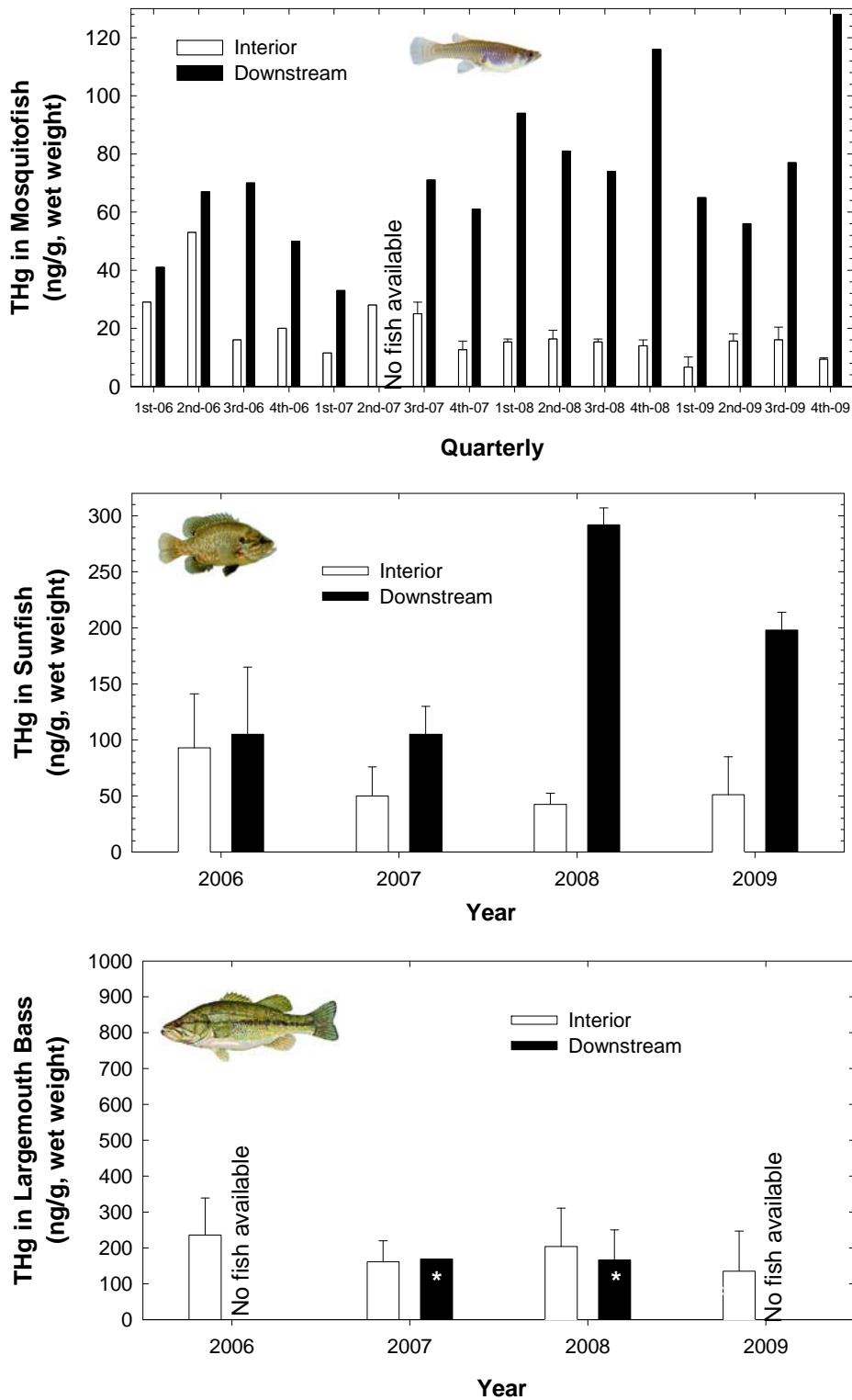
<sup>c</sup> Where  $n < 5$ , not enough fish with the 307–385 millimeter (mm) length range

<sup>d</sup> Cumulative through CY2008 data

NA – Not available; no fish in sample area

NA\* – Not available; no fish within the sample length range (307–385 mm)

TRI – Triennial fish collection



**Figure 9.** Total mercury concentrations (ng/g, wet weight) in (top) mosquitofish composites ( $\pm$  SD), (middle) whole sunfish ( $\pm$  SD), and (bottom) fillets of largemouth bass (arithmetic mean,  $\pm$  SD) collected at STA-1E. An asterisk indicates an arithmetic mean of all available largemouth bass.

## 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 for mercury at STA-2 began during the third quarter of 2001 after completion of the S-6 connection (Rumbold and Fink, 2002b, 2003b; Rumbold 2004, 2005a; Rumbold et al., 2006). The most recently developed area, Cell 4, passed mercury start-up criteria and flow-through began in 2007. Currently, all of STA-2 is under Phase 2 monitoring (**Figure 10**).

Results from monitoring mercury concentrations in surface water at STA-2 (**Figure 11**) show THg concentration in inflow and outflow did not exceed the Florida Class III numerical water quality standard of 12 ng/L during WY2010. More importantly, both MeHg, which has no numerical water quality standard, and THg remained at low concentrations in the outflow. Outflow loads of THg and MeHg were both less than inflow (**Table 4**). The difference between inflow and outflow load for MeHg and THg was the least out of all STAs. A drop in water level below mean cell bottom elevation is a common occurrence in this STA. In WY2010, the drop in water level for Cell 1 may have triggered increased sulfate levels as concentrations show a steady increase from fall to winter 2009 (**Figure 12**).

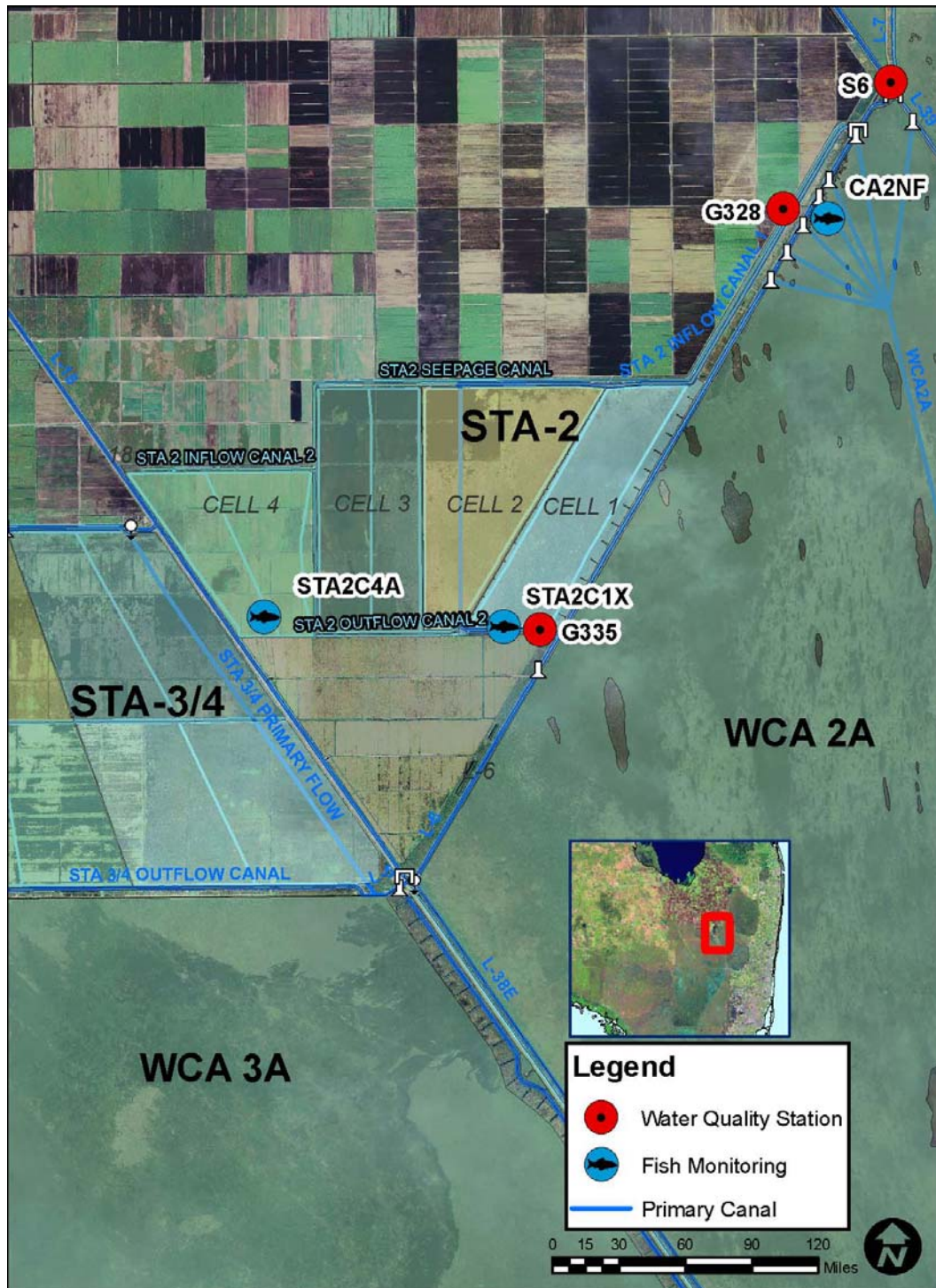
**Table 3** and **Figure 13** summarize results from operational monitoring of mercury concentrations in STA-2 mosquitofish for CY2009. Starting in mid-2007, interior mosquitofish levels steadily increased until the second quarterly collection in 2008 then mostly decreased thereafter into 2009. This spike and decline is likely related to the operational startup of Cell 4 in 2007. In 2009, the average mosquitofish composite and each individual mosquitofish composite for the interior and downstream locations did not exceed the POR 75<sup>th</sup> percentile for the downstream Everglades sampling locations (see Appendix 3B-1 of this volume).

Sunfish from STA-2 interior sampling locations (STA2C4A and STA2C1X) show no major change since 2007 (**Table 5** and **Figure 13**). There is a slight decrease at the downstream location (CA2NF). As is expected, the newly established downstream location shows considerably higher levels than the previously sampled outflow stations (see previous SFERs). Standardizing by species (bluegill) and length reveals the same general trend in concentration distribution between interior and downstream locations. Following standardization, average concentration was 0.40 ng/g/mm at interior locations and 0.75 ng/g/mm for the downstream location. In 2009, the average annual sunfish concentration for all STA-2 interior locations and downstream did not exceed the POR 75<sup>th</sup> percentile for all downstream Everglades sampling locations (see Appendix 3B-1 of this volume).

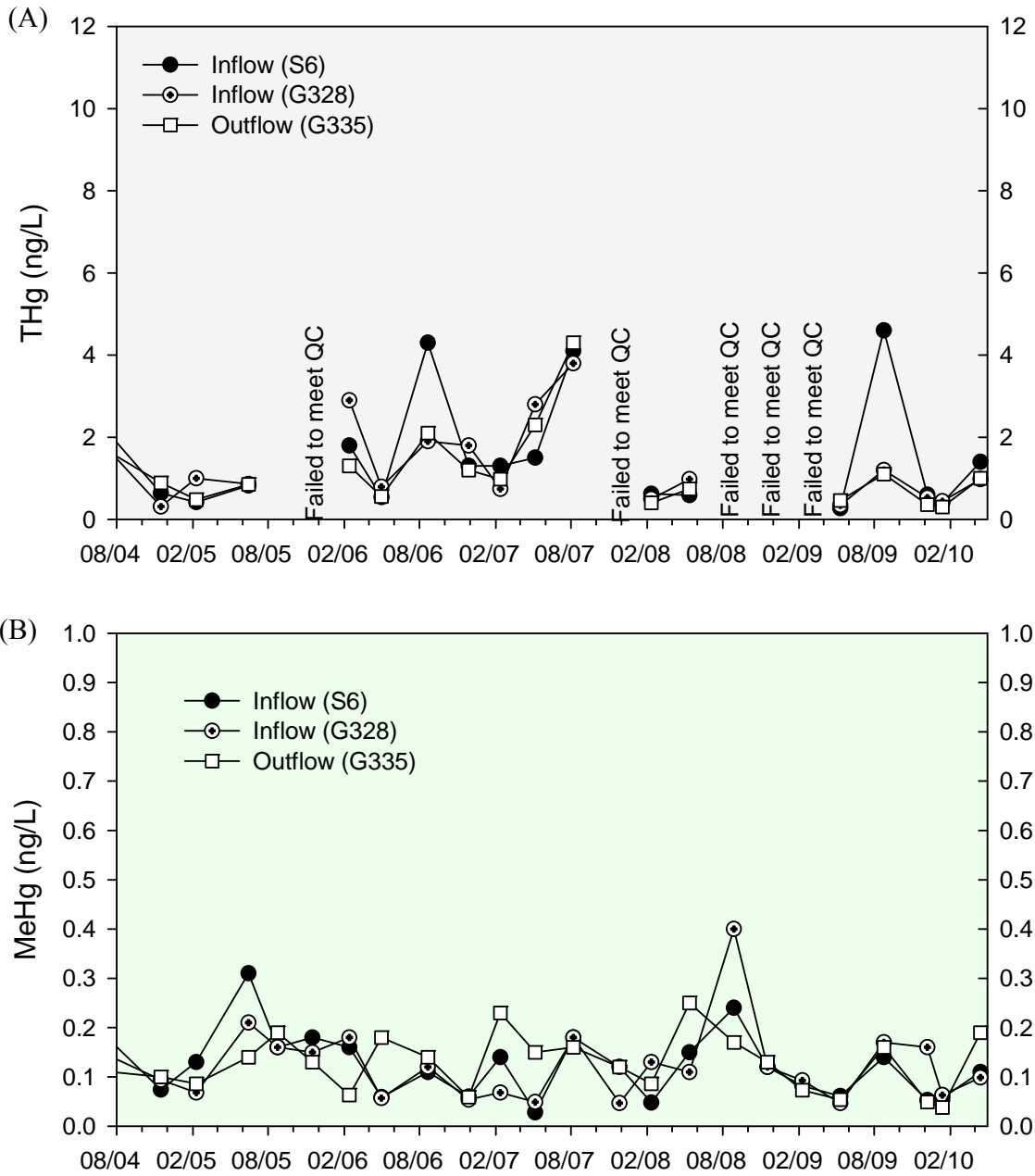
Concentrations of THg in fillets of resident largemouth bass from STA-2 (**Table 6** and **Figure 13**) in the length range of 307–385 mm reflect an overall average of  $110 \pm 23$  ng/g collected across Cell 4, which is the lowest of all interior STA sites. This is the opposite condition from 2008 where STA-2 LMB were the highest, however this in comparison to very few fish in 2009. Historically, fish THg levels within this STA have been high compared with the other STAs, which may be related to the previous land use within this area. Annual LMB concentration for all STA-2 locations did not exceed the POR 75<sup>th</sup> percentile for all Everglades downstream receiving water sampling locations (see Appendix 3B-1 of this volume).

Regarding risk to fish-eating wildlife, in CY2009 no mosquitofish composite within STA-2 contained mercury levels greater than the USEPA predator protector criteria of 77 ng/g for TL 2 or TL 3 species or the USFWS criteria of 100 ng/g. In contrast, several sunfish from the interior and downstream locations did exceed the USEPA or USFWS predator protector criteria for TL 2 or TL 3 species. After standardizing by whole fish length concentration [fillet concentration  $\times$  0.695 (Lange et al., 1998)], there was no exceedance of the USEPA criterion of 346 ng/g for TL 4

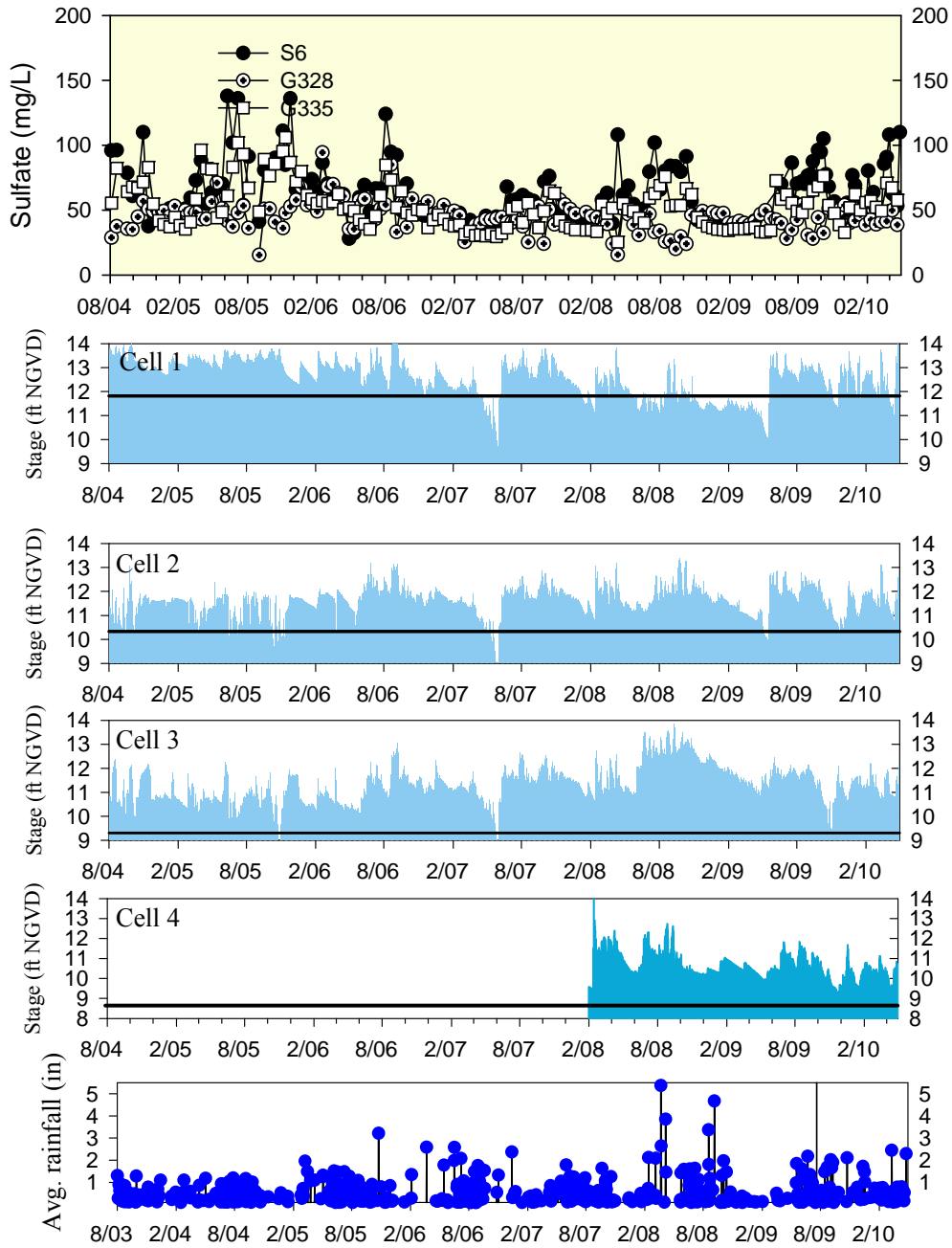
fish species in LMB within STA-2. Overall, fish-eating wildlife foraging preferentially within and downstream of STA-2 continue to appear to have an overall moderate risk of mercury exposure.



**Figure 10.** Map of Stormwater Treatment Area 2 (STA-2) showing current mercury monitoring sites. Mosquitofish samples are collected from downstream station CA2NF and in each cell, then submitted as a composite for each flow-way.

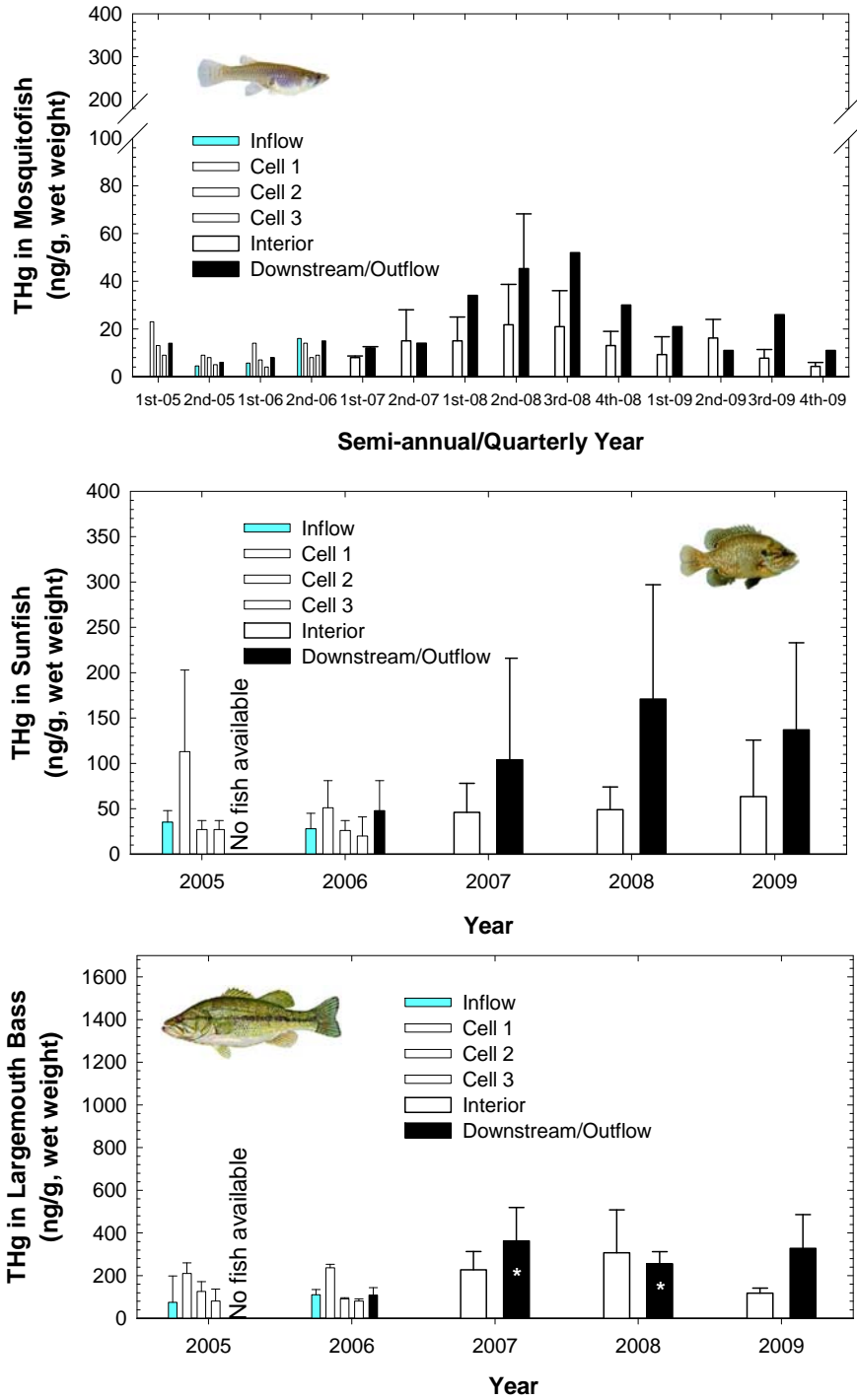


**Figure 11.** Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-2.



**Figure 12.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell), and rainfall totals at STA-2.





**Figure 13.** Mercury concentrations (ng/g, wet weight) in (top) mosquitofish composites ( $\pm$  SD) (STA2C4A and STA2C1X), (middle) whole sunfish ( $\pm$ SD), and (bottom) fillets of largemouth bass (arithmetic mean,  $\pm$  SD) collected at STA-2. An asterisk indicates an arithmetic mean of all available largemouth bass.

## STA-3/4

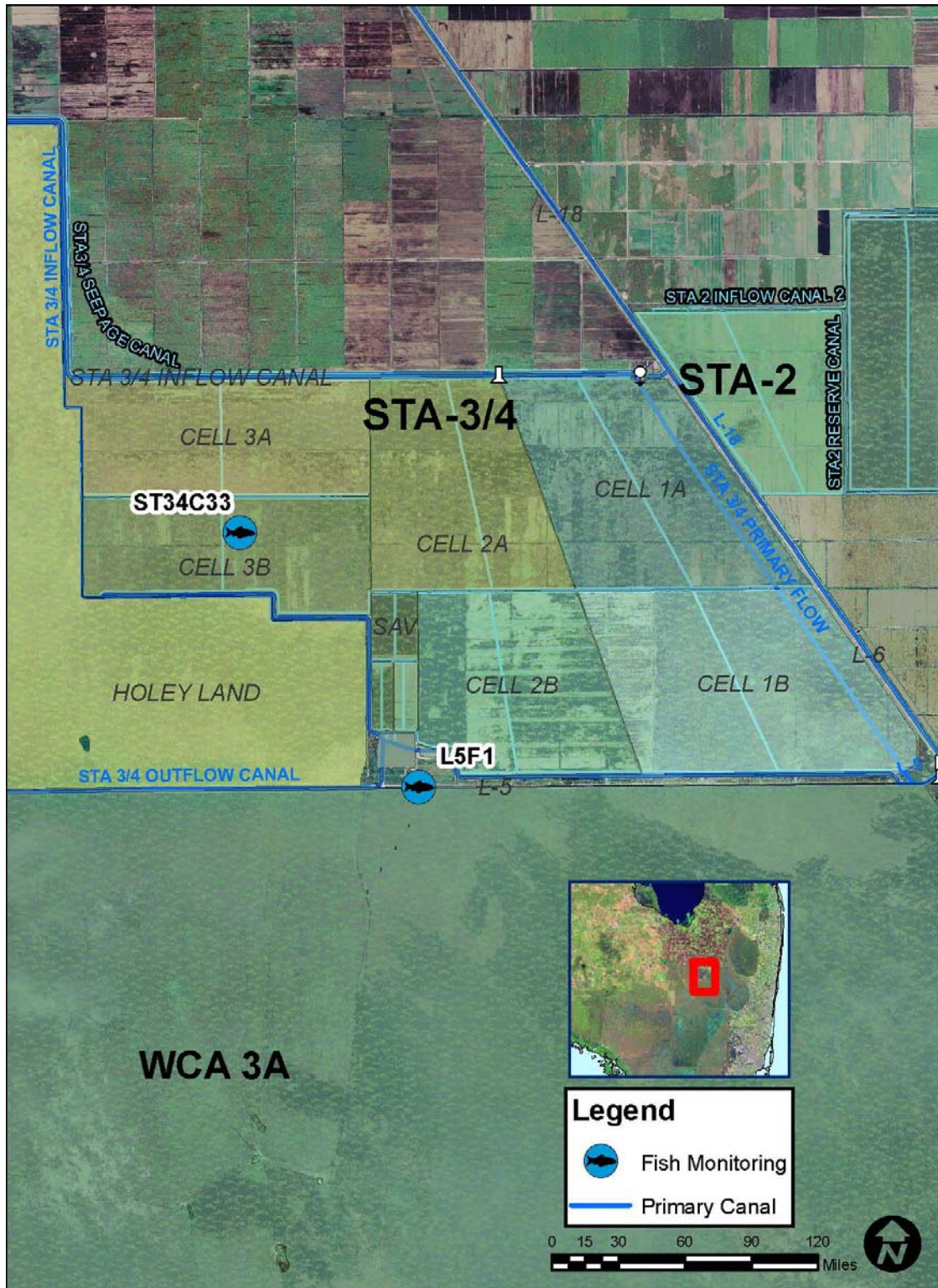
STA-3/4, Cell 1, satisfied start-up criteria for mercury in January 2004; the first discharges of treated water from this STA were in February 2004. Accordingly, routine operational monitoring of this flow-way began during the first quarter of 2004. STA-3/4, Cell 3, satisfied start-up criteria for mercury in June 2004 and Cell 2 passed in August 2004; with consensus from FDEP in September 2004, discharges began (for discussion of results observed prior to 2005, see Rumbold et al., 2006). In 2007, all mercury monitoring was moved into Phase 3, Tier 1 of the Protocol (SFWMD, 2006). Therefore, surface water monitoring for THg and MeHg was terminated and the last surface water dataset was collected in March 2008. Information on THg and MeHg for STA-3/4 is presented in previous SFERs. **Figure 14** shows current mercury monitoring locations for concentrations in resident fish at trophic levels 2 through 4.

Concentrations of THg in mosquitofish are summarized in **Table 3** and **Figure 15**. For CY2009, mosquitofish from STA-3/4 had low levels compared to all other STAs, which is consistent with past years. In the past, this STA, along with STA-5, demonstrated the largest difference between inflow and outflow mosquitofish THg levels, suggesting efficient MeHg bioaccumulation or food web exchange. The average annual composite for CY2009 and each individual mosquitofish composite within STA-3/4 did not exceed the POR 75<sup>th</sup> percentile for POR for all downstream receiving water sampling Everglades locations during the year (see Appendix 3B-1 of this volume).

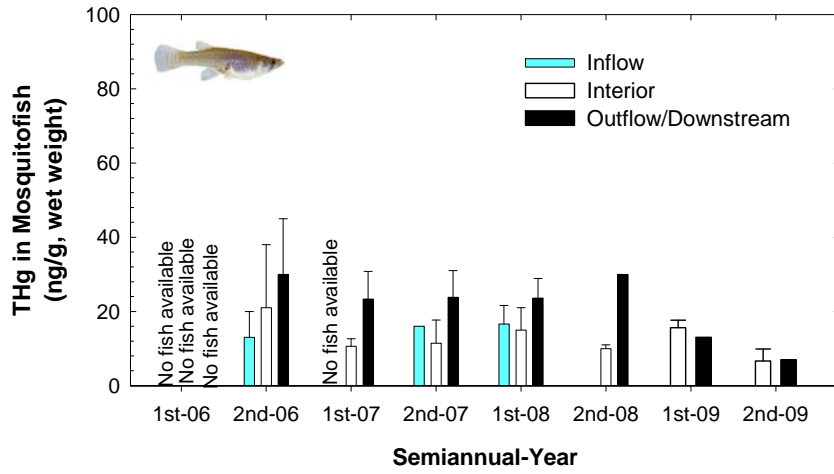
Surface water sulfate, water level and precipitation for STA-3/4 are presented in **Figure 16**. Water levels within the cells of this STA typically do not fall below mean cell bottom elevation. Sulfate levels at the inflow and outflow locations are comparable to other STAs and there does not appear to be any seasonal trend in sulfate concentration.

No sunfish or largemouth bass collections were made for CY2009 due to the triennial sampling schedule in effect under Phase 3 monitoring. The next collection will be in 2011. Data summaries and discussion for previous collections are available in the 2010 SFER – Volume I, Appendix 5-6.

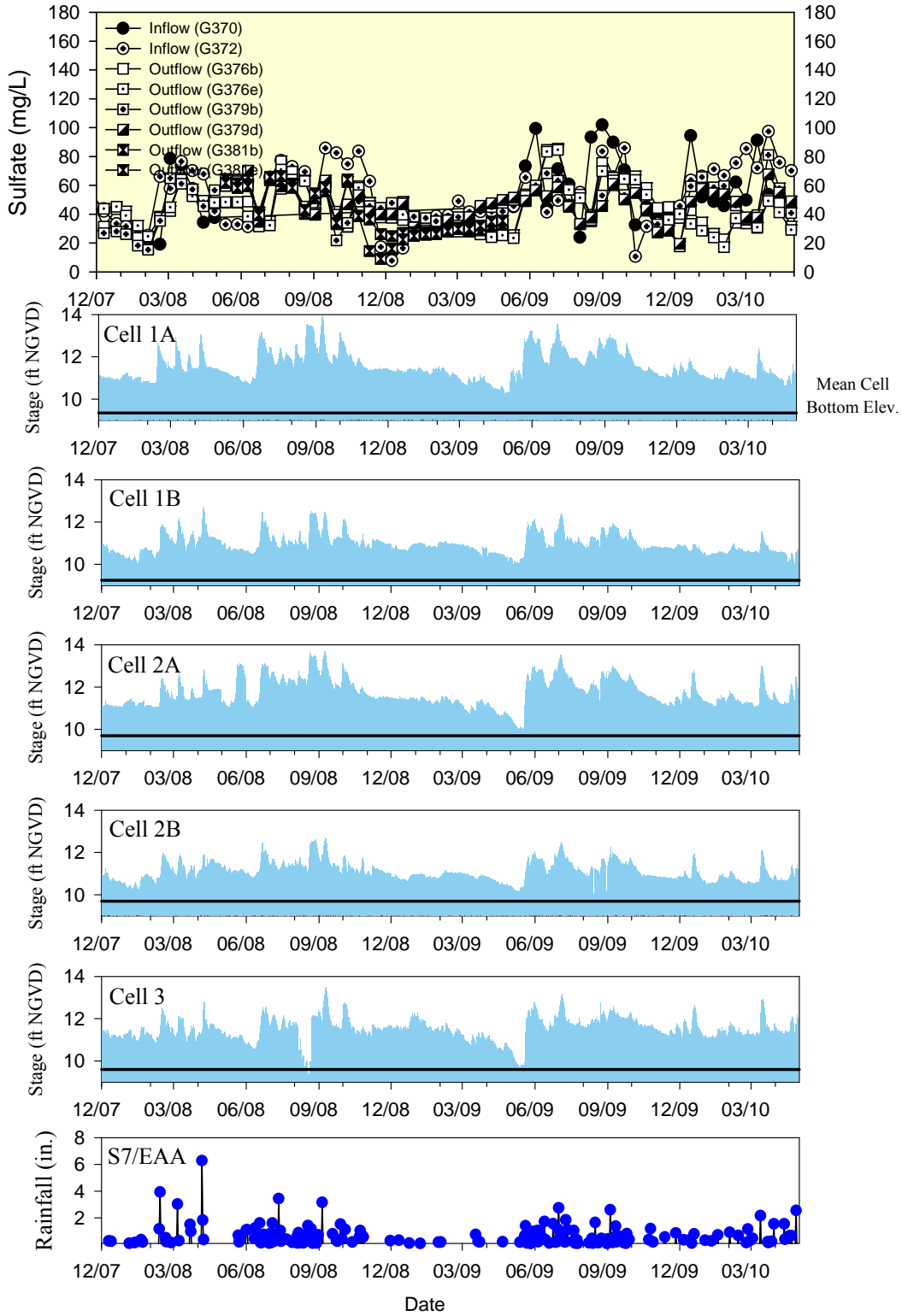
Regarding the risk to fish-eating wildlife, all resident mosquitofish within the marsh of STA-3/4 contain mercury levels below the USEPA criterion of 77 ng/g for TL 2-3 fish species. Based on the available mosquitofish data, fish-eating wildlife foraging preferentially within the interior marsh and downstream of STA-3/4 appear to be at low risk from mercury exposure.



**Figure 14.** Map of Stormwater Treatment Area 3/4 (STA-3/4) showing current mercury monitoring sites. Mosquitofish are collected at downstream site (L5F1) and within each cell, then submitted as a composite (ST34C33) for inflow/outflow comparison.



**Figure 15.** Mercury concentrations (ng/g, wet weight) in mosquitofish composites ( $\pm$  SD) collected at STA-3/4.



**Figure 16.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell), and rainfall at STA-3/4.

## 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 until July 2000 (for discussion of results observed prior to 2005, see Rumbold and Rawlik, 2000; Rumbold et al., 2001 and 2006; Rumbold and Fink, 2002a and 2003a; Rumbold, 2004 and 2005a). The new section, Flow-way 3, is under Phase 2 monitoring and Flow-ways 1 and 2 are under Phase 3 monitoring (**Figure 17**).

As shown in **Figure 18**, water-column concentrations of THg and MeHg in WY2010 remained low in STA-5. No THg sample was above the 12 ng/L WQS. On January 1, 2009, surface water sampling was temporally suspended due to dryout conditions. The consistent dryout and rewetting has likely created the elevated surface water sulfate concentrations (**Figure 19**). A clear increasing/decreasing trend in surface water sulfate is apparent, which, again, likely occurs from the frequent dryout and rewet processes (**Figure 19**). Outflow loading of THg and MeHg were both less than inflow for WY2010 (**Table 6**). STA-5 displayed the largest difference in MeHg inflow versus outflow loading compared to all other STAs.

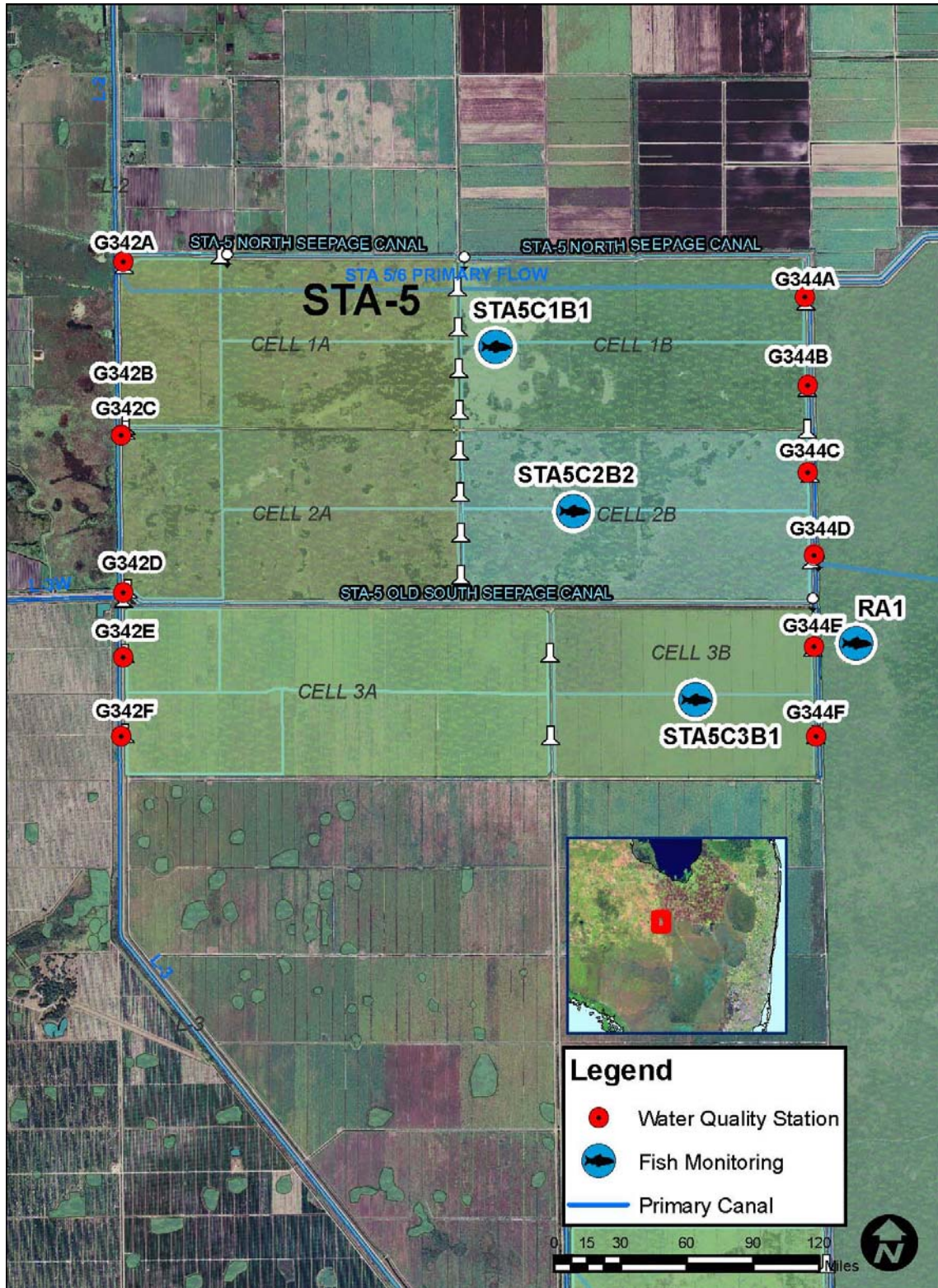
Mosquitofish collected from STA-5 in CY2009 contained moderate to high annual mean mercury levels (**Figure 20**), compared to the other STAs (**Table 3**) which is similar to previous years. Average levels for CY2009 in the interior marsh were down 25 percent from CY2009. Mosquitofish from the downstream location were lower than the interior marsh in the fourth quarter, which is a common finding in this STA, likely due to seasonal dryout and rewetting. The average annual mosquitofish composite for 2009 and each individual mosquitofish composite for all locations within STA-5 did not exceed the POR 75<sup>th</sup> percentile for all downstream Everglades sampling locations during 2009 (see Appendix 3B-1 of this volume).

Sunfish collected from the interior marsh and downstream contained the lowest levels of mercury compared to the other STAs (**Table 5**), which contrasts to previous years. All but three sunfish were bluegill; therefore, appropriate comparisons can be made to other STAs without standardizing by fish type. The average annual sunfish THg concentration for CY2009 within STA-5 did not exceed the POR 75<sup>th</sup> percentile for all downstream Everglades sampling locations (see Appendix 3B-1 of this volume).

As in previous years, the FWC (under contract to the District to electroshock and collect large-bodied fish for mercury monitoring) encountered difficulties in filling sample quotas for STA-5. As shown in **Table 6**, no LMB were available. For previous information on LMB within STA-5 refer to previous SFER appendices.

Annual average mercury levels in each fish species within the marsh sites (STA5C1B1, STA5C2B1, and STA5C3B1) of STA-5 show no visible temporal increase for  $\geq$  three years.

Regarding the risk to fish-eating wildlife, all resident mosquitofish and sunfish, except two samples, within and downstream from STA-5 contained mercury levels below the USEPA criterion of 77 ng/g for TL 2 or 3 fish species and all fish were below the USFWS criterion of 100 ng/g. Therefore, based on the available mosquitofish and sunfish data, fish-eating wildlife foraging preferentially from the interior marsh of STA-5 appears to be at low to moderate risk from mercury exposure and at a slightly elevated risk if feeding near outflow site RA1.



**Figure 17.** Map of Stormwater Treatment Area 5 (STA-5) showing current and historical mercury monitoring sites. Mosquitofish composite samples are collected for each flow-way and composited, and one mosquitofish sample is collected downstream (RA1).

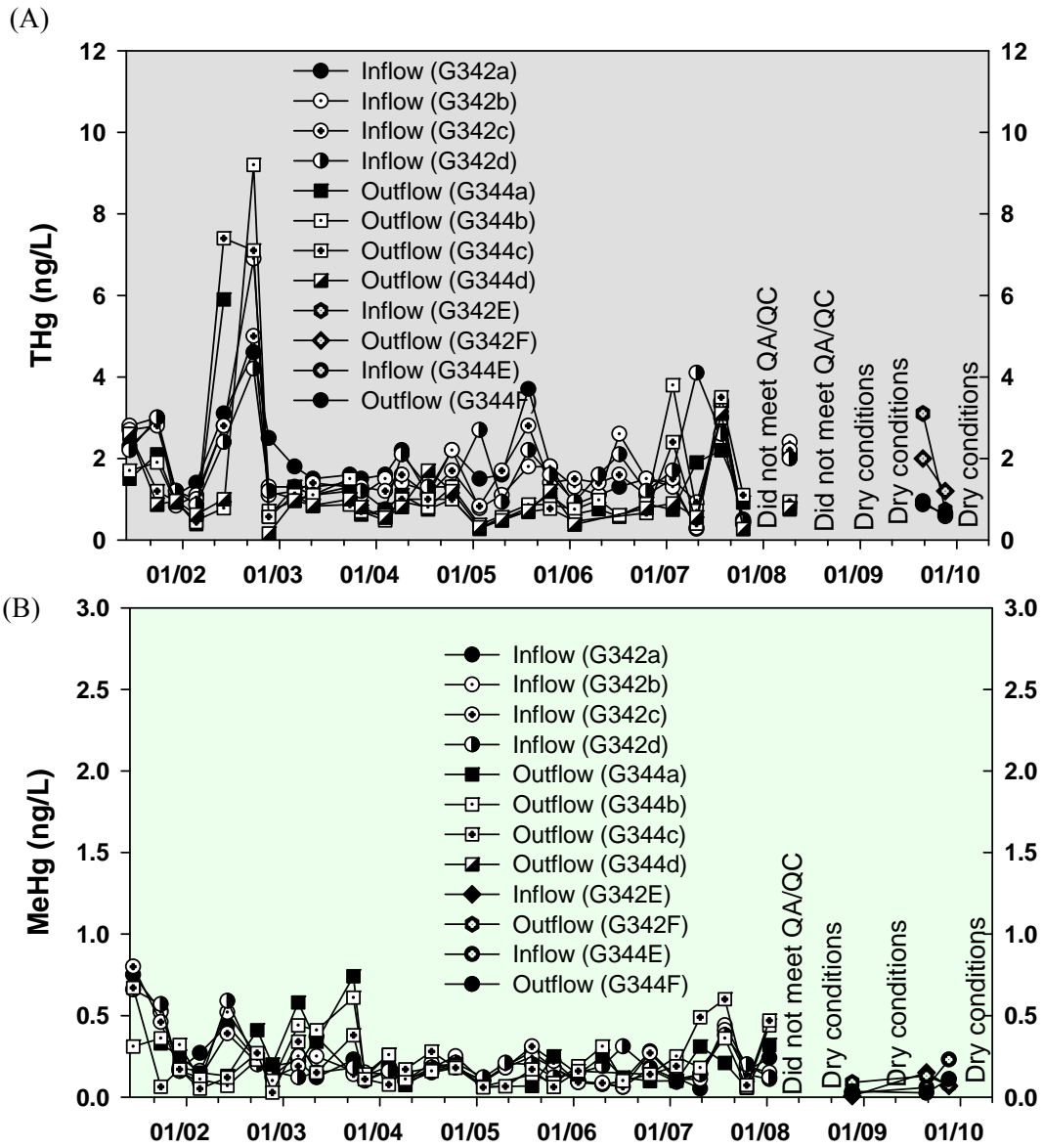
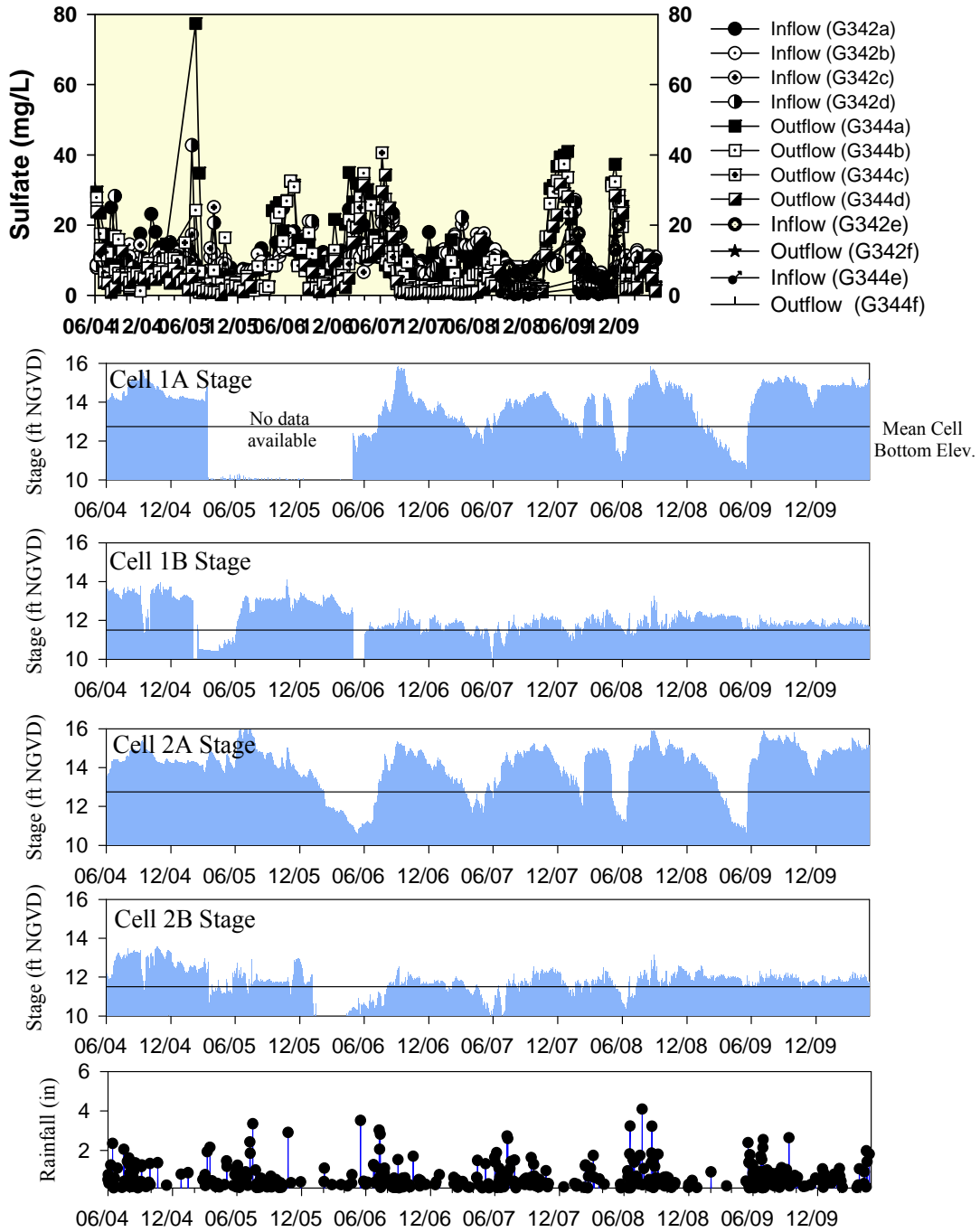
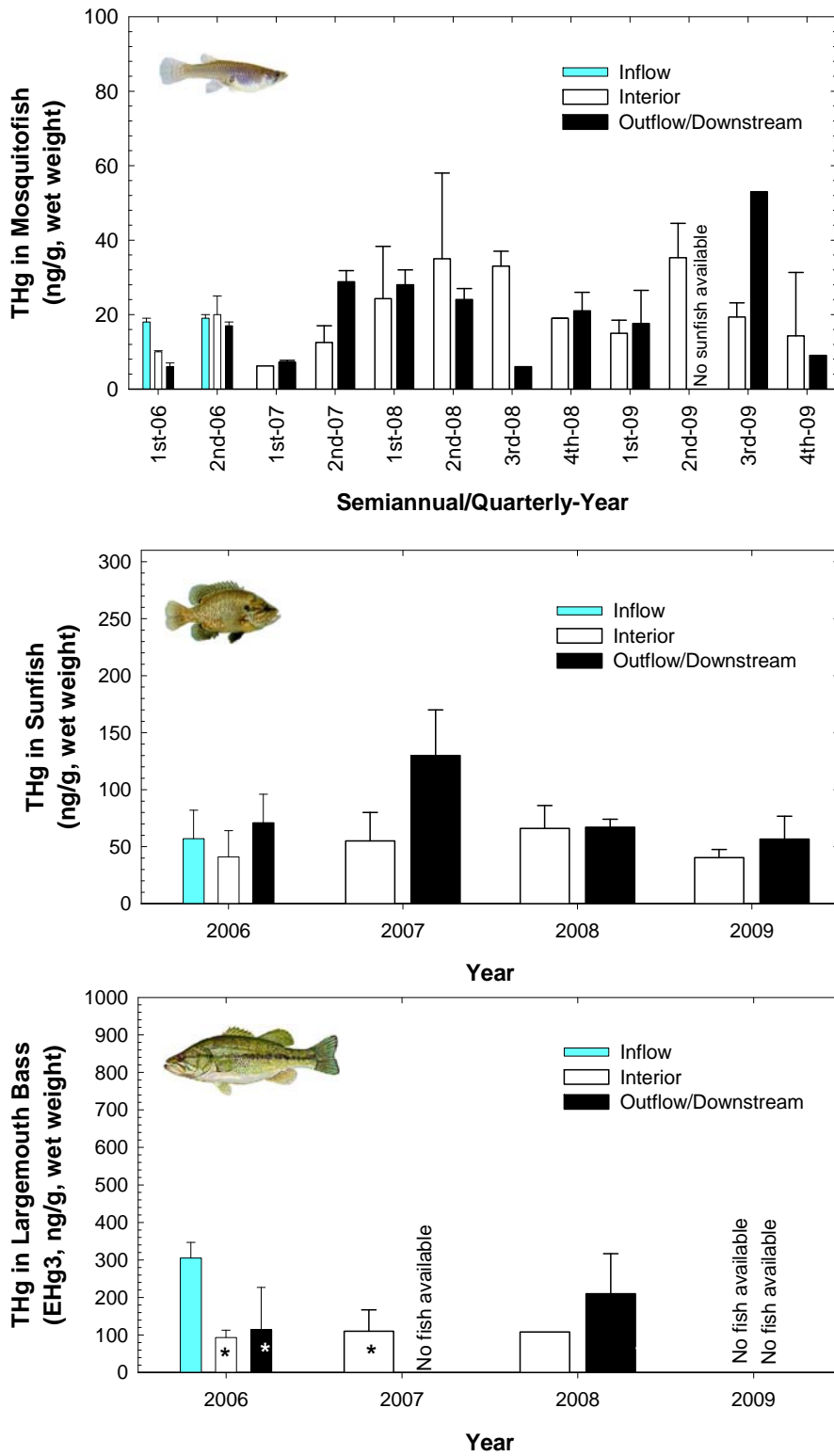


Figure 18. Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-5.





**Figure 19.** Concentrations of sulfate (*top*), stage in the two cells (recorded immediately upstream of the outflow culvert), and rainfall at STA-5.



**Figure 20.** Mercury concentrations (ng/g, wet weight) in (top) mosquitofish composites ( $\pm$  SD), (middle) whole sunfish ( $\pm$  SD), and (bottom) fillets of largemouth bass (arithmetic mean,  $\pm$  SD) collected at STA-5. An asterisk indicates an arithmetic mean of all available largemouth bass.

## STA-6

Start-up mercury monitoring occurred in the new section of STA-6, Section 2, on July 25, 2007. Currently, STA-6, Section 2, is under Phase 2 monitoring (**Figure 21**) as reported in this section. The remainder of STA-6 (Cells 3 and 5) is in Phase 3, so monitoring has been terminated. Monitoring results prior to May 2004 are reported elsewhere (SFWMD, 1998 and 1999d; Rumbold and Rawlik, 2000; Rumbold et al., 2001; Rumbold and Fink, 2002a; Rumbold and Fink, 2003a; Rumbold, 2004 and 2005a; Rumbold et al., 2006).

THg concentrations at the inflows and outflows of STA-6, Section 2, were fairly low throughout WY2010 (**Figure 22**) and remained relatively low compared to previous spikes. MeHg remained at very low concentrations throughout the year as well. No THg sample was above the Florida Class III numerical water quality standard of 12 ng/L. As shown in **Figure 23**, all cells dried down during WY2010 for a period lasting approximately three months each. These dryout periods could have created the high surface water sulfate level observed (**Figure 23**). A more pronounced dry/rewet impact in surface water sulfate level occurs in STA-5. The relatively low THg and MeHg concentrations in the outflows appear 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). Nonetheless, it is reasonable to assume that the dryout and rewetting of this rain-driven STA has some part in higher tissue-mercury levels in large-bodied fish. For WY2010, inflow loading of THg and MeHg were both greater than outflow (**Table 4**).

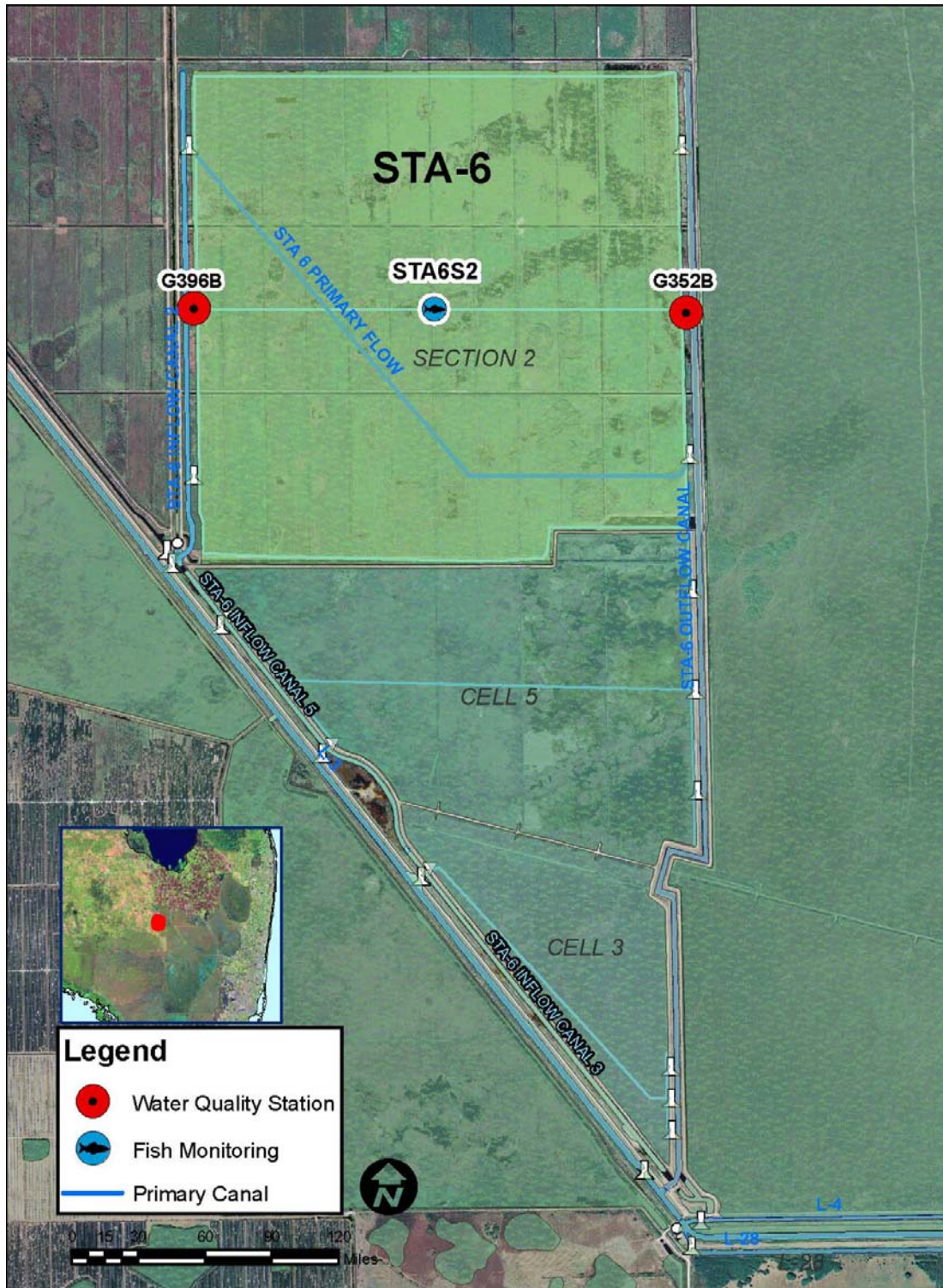
Concentrations of THg in mosquitofish are summarized in **Table 3** and graphically presented in **Figure 24**. Levels of mercury in mosquitofish from the interior of STA-6 for CY2009 were the highest out of all STAs; however, these levels were lower compared to previous years within STA-6. The persistent high levels in STA-6 are inconsistent with the historically low surface water percent MeHg levels, leading to the speculation that food chain dynamics enhance mercury bioaccumulation in STA-6. However, potential changes in porewater MeHg may also be a factor. The average annual composite for CY2009 and each individual mosquitofish composite for all locations within STA-6 did not exceed the POR 75<sup>th</sup> percentile for all downstream Everglades sampling locations (see Appendix 3B-1 of this volume).

As shown in **Table 5** and **Figure 24**, STA-6 sunfish from the interior marsh for CY2009 had mercury levels greater than those observed in sunfish at all other STAs, with the exception of locations within the Everglades and downstream monitoring locations. This has been the scenario since STA-6 was put into operation. The average annual sunfish Hg concentration for the interior marsh of STA-6 did not exceed the 75<sup>th</sup> percentile for POR for all receiving waters sampled in downstream Everglades locations during 2009 (see Appendix 3B-1 of this volume).

Similar to sunfish, largemouth bass (**Table 6**) at the interior site (STA6S2) had the highest THg concentration compared to all other STAs in 2009; however there was an approximate 50 percent decrease in concentration since 2008 (**Figure 24**). Although highly variable, the interior concentrations still show a decreasing trend since the start of the POR and 2009 levels are the lowest for the POR. Despite a concerted effort, no LMB were available at the downstream site (STA6DC). The average annual LMB collected for 2009 in STA-6 did not exceed the POR 75<sup>th</sup> percentile for all downstream Everglades sampling locations.

Regarding risks to fish-eating wildlife, mosquitofish from the interior and downstream locations did not exceed the 77 ng/g TL 2 or 3 USEPA criterion in 2009. For sunfish, 80 percent of the catch from the interior marsh exceeded the USEPA TL 3 criterion and 40 percent exceeded the USFWS 100 ng/g criterion. All sunfish from the downstream site exceeded the TL 3 criterion and all but one sunfish sample exceeded the USFWS criterion. Fifty percent of all largemouth bass (whole-body concentration estimated from fillet concentration) from the interior marsh of

STA-6 were above the USFWS criterion, (100 ng/g) but none were above the USEPA criterion of TL 4 species (346 ng/g). Therefore, the risk of mercury exposure to fish-eating wildlife foraging preferentially at interior and downstream locations within STA-6 remains moderate to high.



**Figure 21.** Map of Stormwater Treatment Area 6 (STA-6) showing current mercury monitoring sites. A mosquitofish composite sample is collected for STA-6, Section 2, and a single mosquitofish sample is collected downstream (STA6DC).

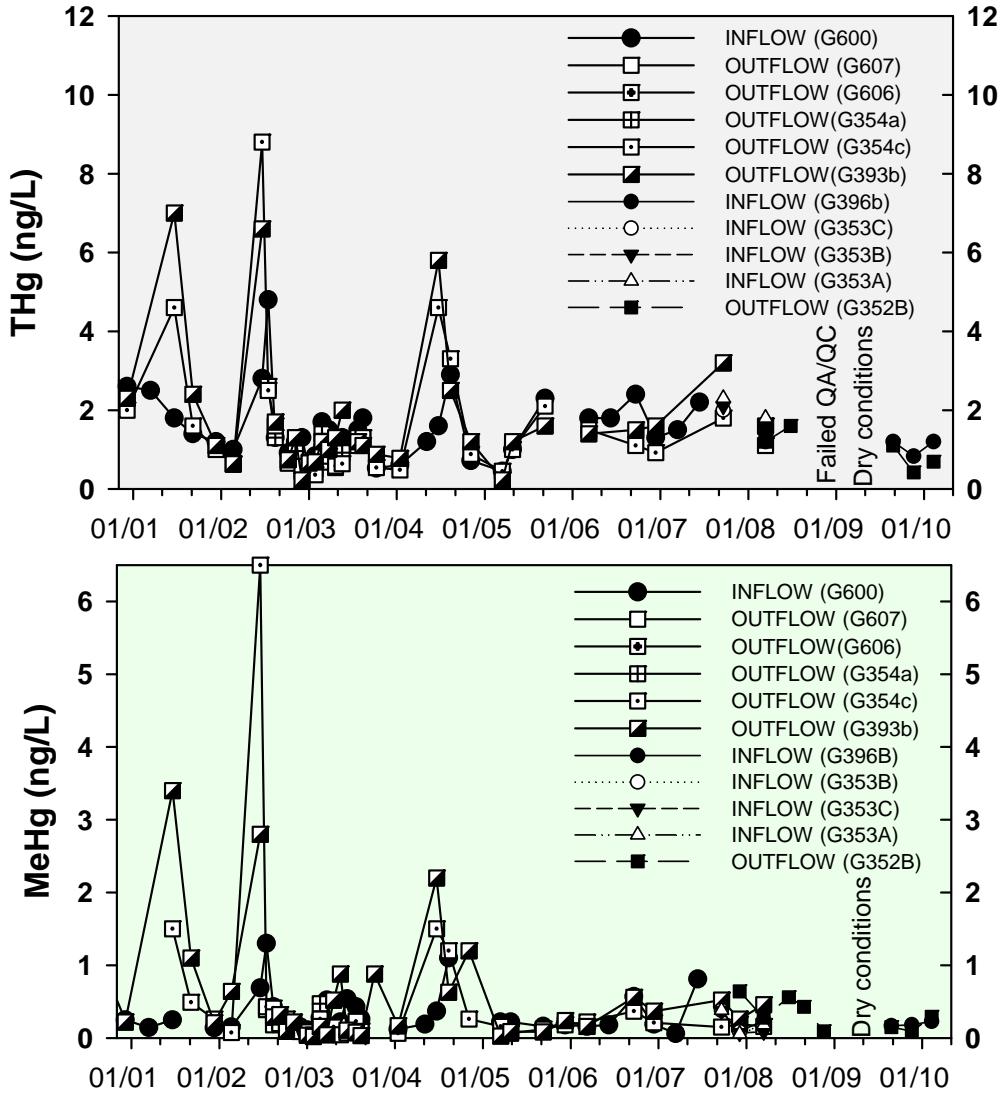
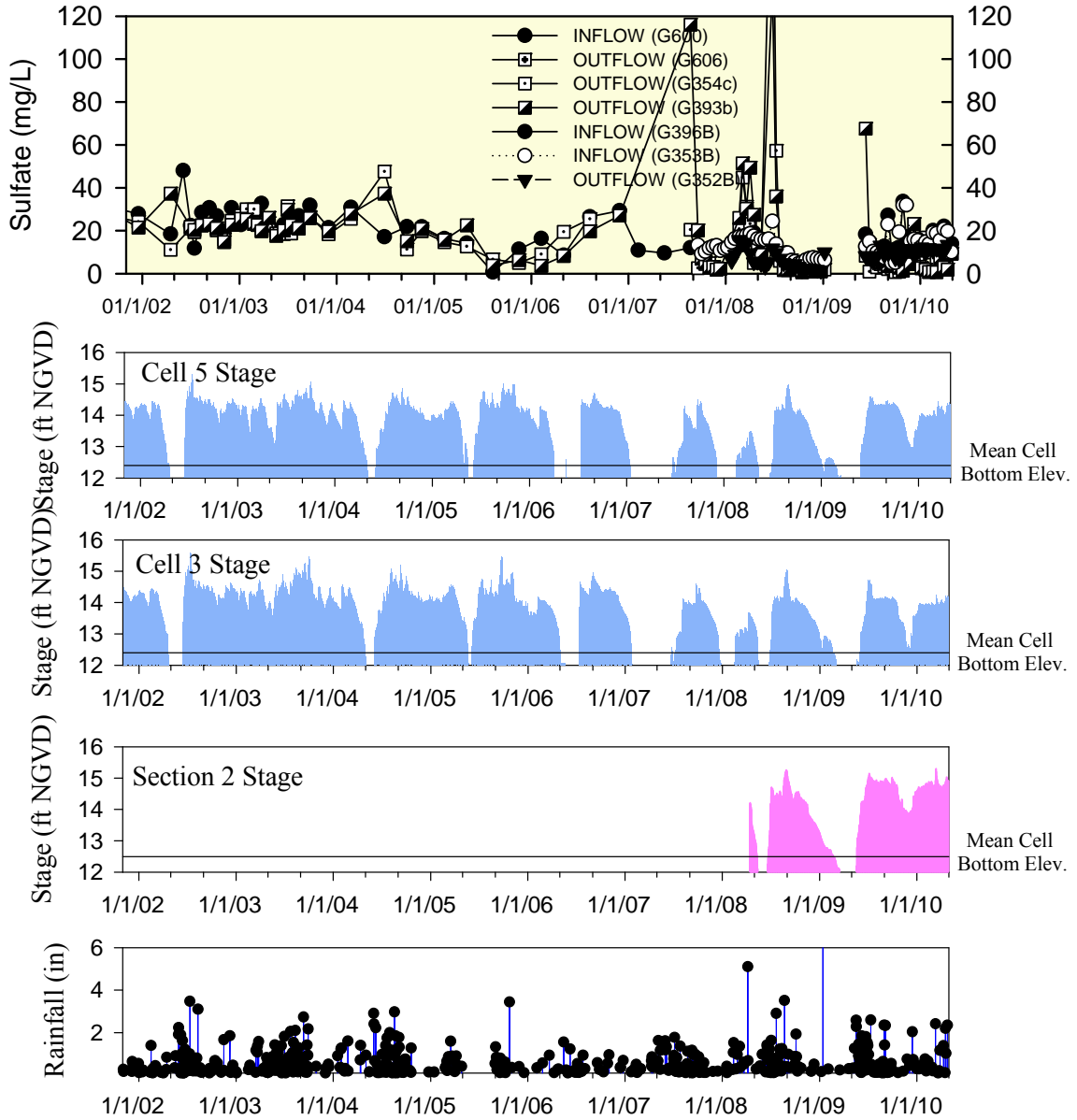
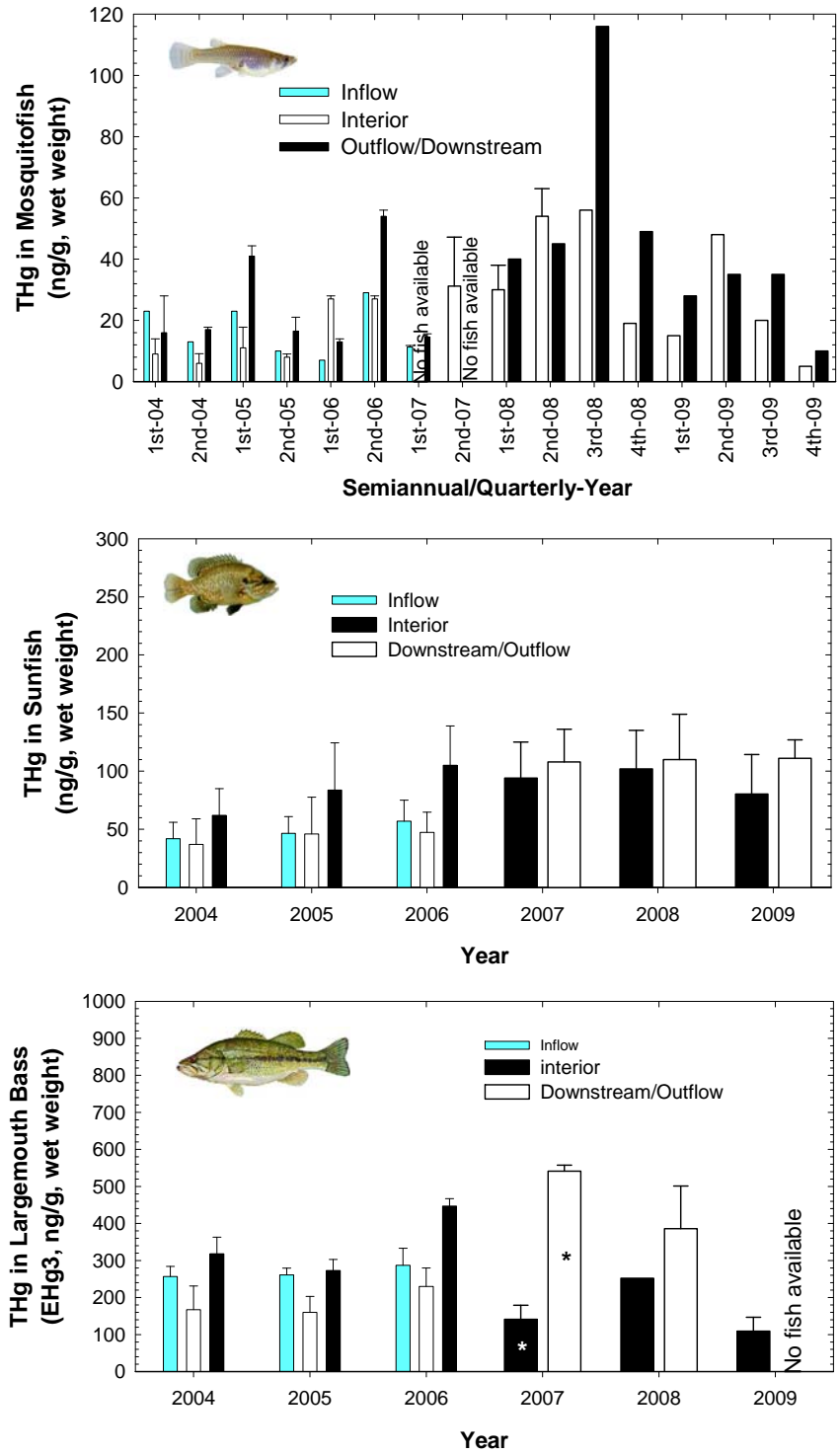


Figure 22. Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-6, Section 2.



**Figure 23.** Concentrations of sulfate (*top*), stage, and rainfall for STA-6.



**Figure 24.** Mercury concentrations (ng/g, wet weight) in (*top*) mosquitofish composites ( $\pm$  SD), (*middle*) whole sunfish ( $\pm$  SD), and (*bottom*) fillets of largemouth bass (arithmetic mean,  $\pm$  SD) collected at STA-6. An asterisk indicates an arithmetic mean of all available largemouth bass.



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## MERCURY MONITORING NETWORK OPTIMIZATIONS

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The summaries below provide information on the current mercury monitoring phase for each STA. These phases are concurrent with guidance contained in MMAP, SFWMD (2000).

### **STA-1W**

Mercury monitoring in STA-1W is currently in Phase 3, Tier 3. The Permit modification for moving from Phase 3, Tier 1 to Phase 3, Tier 3 was issued August 21, 2009. Phase 3 terminates all mercury monitoring in STA-1W (mosquitofish stations ST1W13COM, ST1W24COM, ST1WC5COM, ENR012, G310, ST1WLX; bass and sunfish stations ST1W51, ENR012, G310, ST1WLX).

### **STA-1E**

Mercury monitoring in STA-1E is currently in Phase 2, Tier 1. Evaluations to move from Phase 2 to Phase 3, Tier 1 are under way.

### **STA-2**

Mercury monitoring in STA-2 is currently in Phase 2, Tier 1. Evaluations to move from Phase 2 to Phase 3, Tier 3 are under way.

### **STA-3/4**

Mercury monitoring in STA-3/4 is currently in Phase 3, Tier 1. A permit modification was issued June 6, 2008, which moved Hg monitoring from Phase 2 to Phase 3. Under this modification, Hg monitoring terminated mosquitofish monitoring at G383, G370, ST34C1B1, ST34C2B4, G376B, G376E, G379B, G379D, G381B and G381E; largemouth bass and sunfish monitoring at G383, G370, ST34C1B1, and ST34C2B4. Mosquitofish monitoring continues semiannually at cell flow-ways and downstream station L5F1. Largemouth bass and sunfish collections are triennial, with the next collection and results anticipated to be reported in the 2012 SFER.

### **STA-5**

Mercury monitoring in STA-5, Flow-ways 1 and 2, is currently in Phase 3, Tier 3. The recently constructed Flow-way 3 is in Phase 2, Tier 1. The permit modification issued June 6, 2008 made these phase adjustments, terminating mosquitofish monitoring at G344B and G344D, largemouth bass and sunfish monitoring at G344D, and added mosquitofish station ST5C3COM and largemouth bass and sunfish collection station STA5C3B1.

### **STA-6**

STA-6 (Cells 3 and 5) is currently in Phase 3, Tier 3 and mercury monitoring has been terminated in these areas. The relatively new Section 2 of STA-6 is Phase 2, Tier 1 monitoring, which includes surface water and fish data for this region of the STA. The permit modification issued June 6, 2008, made these phase adjustments, terminated mosquitofish monitoring at STA6C3COM, STA6C5COM and terminated largemouth bass and sunfish monitoring at STA6C32.

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## LITERATURE CITED

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- Abernathy, A.R. and P.M. Cumbie. 1977. Mercury Accumulation by Largemouth Bass (*Micropterus salmoides*) in Recently Impounded Reservoirs. *Bull. Environ. Contam. Toxicol.*, 17: 595-602.
- Benoit, J.M., C.C. Gilmour, R.P. Mason and A. Heyes. 1999a. Sulfide Controls on Mercury Speciation and Bioavailability to Methylating Bacteria in Sediment Pore Waters. *Env. Sci. Technol.*, 33(6): 951-957.
- Benoit, J.M., R.P. Mason and C.C. Gilmour. 1999b. Estimation of Mercury-Sulfide Speciation in Sediment Pore Waters Using Octanol-Water Partitioning and Its Implications for Availability to Methylating Bacteria. *J. Env. Toxicol. Chem.*, 8 (10): 2138-2141.
- Bodaly, R.A. and R.J.P. Fudge. 1999. Uptake of Mercury by Fish in an Experimental Boreal Reservoir. *Arch. Environ. Contam. Toxicol.*, 37: 103-109.
- Bodaly, R.A., R.E. Hecky and R.J.P. Fudge. 1984. Increases in Fish Mercury Levels in Lakes Flooded by the Churchill River Diversion, Northern Manitoba. *Can. J. Fish. Aquat. Sci.*, 41: 682-691.
- Cox, J.A., J. Carnahan, J. Dinunzio, J. McCoy and J. Meister. 1979. Source of Mercury in New Impoundments. *Bull. Environ. Contam. Toxicol.*, 23: 779.
- Eisler, R. 1987. Mercury Hazards to Fish, Wildlife and Invertebrates: A Synoptic Review. *U.S. Fish Wildl. Serv. Biol. Rep.*, 85 (1.10). U.S. Department of the Interior, U.S. Fish and Wildlife Services, Laurel, MD.
- Fink, L., D.G. Rumbold and P. Rawlik. 1999. Chapter 7: The Everglades Mercury Problem. G. Redfield, ed. In: *1999 Everglades Interim Report*, South Florida Water Management District, West Palm Beach, FL.
- Gabriel, M., N. Howard, F. Matson, S. Atkins and D. Rumbold. 2007. Appendix 5-6: Annual Permit Compliance Monitoring Report for Mercury in Stormwater Treatment Areas. In: *2008 South Florida Environmental Report – Volume I*, South Florida Water Management District, West Palm Beach, FL.
- Hakanson, L. 1980. The Quantification Impact of pH, Bioproduction and Hg-contamination on the Hg Content of Fish (Pike). *Environ. Pollut. (Series B)*, 1: 285-304.
- KBN. 1994a. Report of Water Sampling in the Holey Land, Water Conservation Area 2A, and the Everglades Nutrient Removal Project. Prepared for the Sugar Cane Growers Cooperative, Inc. by KBN Engineering and Applied Science, Inc., Gainesville, FL.
- KBN. 1994b. Biological Sampling and Tissue Analysis of Fish Collected in Palm Beach County, Florida. Prepared for the Sugar Cane Growers Cooperative, Inc., by KBN Engineering and Applied Science, Inc., Gainesville, FL.
- Kelly, C.A., J.W.M. Rudd, R.A. Bodaly, N.P. Roulet, V.L. St. Louis, A. Heyes, T.R. Moore, S. Schiff, A. Aravena, K.J. Scott, B. Dyck, R. Harris, B. Warner and G. Edwards. 1997. Increases in Fluxes of Greenhouse Gases and Methyl Mercury Following Flooding of Experimental Reservoir. *Environmental Science and Technology*, 31: 1334-1344.

- Krabbenhoft, D.P. and L.E. Fink. 2001. Appendix 7-8: The Effect of Dry Down and Natural Fires on Mercury Methylation in the Florida Everglades. In: *2001 Everglades Consolidated Report*, South Florida Water Management District, West Palm Beach, FL.
- Lange, T.R., D.A. Richard and H.E. Royals. 1998. Trophic Relationships of Mercury Bioaccumulation in Fish from the Florida Everglades. Annual Report. Florida Game and Freshwater Fish Commission, Fisheries Research Laboratory, Eustis, FL. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.
- Lange, T.R., D.A. Richard and H.E. Royals. 1999. Trophic Relationships of Mercury Bioaccumulation in Fish from the Florida Everglades. Annual Report. Florida Game and Freshwater Fish Commission, Fisheries Research Laboratory, Eustis, FL. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.
- Mercury Technical Committee. 1991. Interim Report to the Florida Governor's Mercury in Fish and Wildlife Task Force and Florida Department of Environmental Regulation. Center for Biomedical and Toxicological Research, Florida State University, Tallahassee, FL.
- Miles, C.J. and L.E. Fink. 1998. Monitoring and Mass Budget for Mercury in the Everglades Nutrient Removal Project. *Archives of Environ. Contam. and Toxicol.*, 35(4): 549-557.
- Paterson, M.J., J.W.M. Rudd and V. St. Louis. 1998. Increases in Total and Methylmercury in Zooplankton Following Flooding of a Peatland Reservoir. *Environ. Sci. Technol.*, 32: 3868-3874.
- PTI. 1994. The Influence of Phosphorus on Mercury Cycling and Bioaccumulation in the Everglades. Prepared for the Sugar Cane Growers Cooperative, Inc., by PTI Environmental Services, Inc., Waltham, MA.
- Rudd, J.W.M. 1995. Sources of Methyl Mercury to Freshwater Aquatic Ecosystems: A Review. *Water, Air, and Soil Pollut.*, 80: 697-713.
- Rumbold, D.G. 2004. Appendix 4A-4: Annual Permit Compliance Monitoring Report for Mercury in Stormwater Treatment Areas. In: *2004 Everglades Consolidated Report*, South Florida Water Management District, West Palm Beach, FL.
- Rumbold, D.G. 2005a. Appendix 4-4: Annual Permit Compliance Monitoring Report for Mercury in Stormwater Treatment Areas. In: *2005 South Florida Environmental Report – Volume 1* South Florida Water Management District, West Palm Beach, FL.
- Rumbold, D.G. and P. Rawlik. 2000. Appendix 7-2: Annual Permit Compliance Monitoring Report for Mercury in Stormwater Treatment Areas and Downstream Receiving Waters. In: *2000 Everglades Consolidated Report*, South Florida Water Management District, West Palm Beach, FL.
- Rumbold, D.G., L. Fink, K. Laine, F. Matson, S. Niemczyk and P. Rawlik. 2001. Appendix 7-9: Annual Permit Compliance Monitoring Report for Mercury in Stormwater Treatment Areas and Downstream Receiving Waters of the Everglades Protection Area. G. Redfield, ed. In: *2001 Everglades Consolidated Report*, South Florida Water Management District, West Palm Beach, FL.
- Rumbold, D.G. and L. Fink. 2002a. Appendix 4A-8: Annual Permit Compliance Monitoring Report for Mercury in Stormwater Treatment Areas. G. Redfield, ed. In: *2002 Everglades Consolidated Report*, South Florida Water Management District, West Palm Beach, FL.

- Rumbold, D.G. and L. Fink. 2002b. Appendix 4A-6: Report on Expanded Mercury Monitoring at Stormwater Treatment Area 2. In: *2002 Everglades Consolidated Report*, South Florida Water Management District, West Palm Beach, FL.
- Rumbold, D.G. and L. Fink. 2003a. Appendix 4A-4: Annual Permit Compliance Monitoring Report for Mercury in Stormwater Treatment Areas. In: *2003 Everglades Consolidated Report*, South Florida Water Management District, West Palm Beach, FL.
- Rumbold, D.G. and L. Fink. 2003b. Appendix 4A-7: Report on Expanded Mercury Monitoring at STA-2. In: *2003 Everglades Consolidated Report*, South Florida Water Management District, West Palm Beach, FL.
- Rumbold, D.G. and R. Pfeuffer. 2005. District Guidance in the Design of a Project-Level Monitoring and Assessment Plan for Mercury and Other Toxicants. Appendix A to CERP Guidance Memorandum 42.00. South Florida Water Management District, West Palm Beach, FL and U.S. Army Corps of Engineers, Jacksonville District, Jacksonville, FL.
- Rumbold, D., N. Niemeyer, F. Matson, S. Atkins, J. Jean-Jacques, K. Nicholas, C. Owens, K. Strayer and B. Warner. 2006. Appendix 4-4: Annual Permit Compliance Monitoring Report for Mercury in Stormwater Treatment Areas. In: *2006 South Florida Environmental Report – Volume 1*, South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 1998. Annual Permit Compliance Monitoring Report for Mercury in Stormwater Treatment Areas and Downstream Receiving Waters. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL, by the South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 1999a. Everglades Nutrient Removal Project: 1998 Monitoring Report. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL, by the South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 1999b. Mercury Monitoring and Reporting Plan for the Everglades Construction Project, the Central and Southern Florida Project, and the Everglades Protection Area. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 1999c. Quality Assurance Project Plan (QAPP) for the Mercury Monitoring and Reporting Program. Prepared by the South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 1999d. Stormwater Treatment Area 6, Section 1 Annual Monitoring Report. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL, by the South Florida Water Management, West Palm Beach, FL.
- SFWMD. 2006. A Protocol for Monitoring Mercury and Other Toxicants. Unpublished report, South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 2007a. Operation Plan, Stormwater Treatment Area 1 West. April 2007. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 2007b. Operation Plan, Stormwater Treatment Area 3/4. August 2007. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 2007c. Integrated Operation Plan, Stormwater Treatment Areas 5 and 6. August 2007. South Florida Water Management District, West Palm Beach, FL.

- SFWMD. 2007d. Operation Plan, Stormwater Treatment Area 2. December 2007. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 2009. Interim Operation Plan, Stormwater Treatment Area 1 East. May 2009. South Florida Water Management District, West Palm Beach, FL.
- St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, N.S. Bloom and R.J. Flett. 1994. Importance of Wetlands as Sources of Methyl Mercury to Boreal Forest Ecosystems. *Can. J. Fish. Aquat. Sci.*, 51: 1065-1076.
- USEPA. 1997. Mercury Study Report to Congress. Volume VI: An Ecological Assessment for Anthropogenic Mercury Emissions in the United States. U.S. Environmental Protection Agency. EPA-452/R-97-008.
- Verdon, R., D. Brouard, C. Demers, R. Lalumiere, M. Laperle and R. Schetagne. 1991. Mercury Evolution (1978–1988) in Fishes of the La Grande Hydroelectric Complex, Quebec, Canada. *Water, Air, Soil Pollut.*, 56: 405-417.
- Ware, F.J., H. Royals and T. Lange. 1990. Mercury Contamination in Florida Largemouth Bass. *Proc. Ann. Conf. Southeast Assoc. Fish Wildlife Agencies*, 44: 5-12.
- Watras, C. 1993. Potential Impact of the Everglades Nutrient Removal Project on the Everglades Mercury Problem. (EV 930034). Unpublished Report Prepared by the University of Wisconsin, Madison, WI, for the South Florida Management District, West Palm, Beach, FL.
- Watras, C. 1994. Mercury Field Training Exercise and Recommendations for Sampling Modification. Draft Letter Report dated February 19, 1994. Submitted to Larry Fink, South Florida Management District, West Palm Beach, FL.
- Wren, C.D. and H.R. MacCrimmon. 1986. Comparative Bioaccumulation of Mercury in Two Adjacent Freshwater Ecosystems. *Water Research*, 20: 763-769.
- Zar, J.H. 1996. *Biostatistical Analysis* (3rd edition). Prentice-Hall, Upper Saddle River, NJ.

# **Attachment A: Laboratory Performance Studies, BT-1 Metals in Biota**

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**QUASIMEME**  
**Laboratory Performance Studies**

**BT-1 Metals in Biota**

**Round 58 - Exercise 859**  
**July 2009 to October 2009**

**Report**

Issue 1: 271109

## QUASIMEME LABORATORY PERFORMANCE STUDIES

### BT-1 Metals in Biota Round 58 - Exercise 859

Data for exercise 859, BT-1, Metals in Biota, were returned by 39 of the 50 laboratories that participated in this study.

#### Test Materials

The test materials were supplied by Wageningen IMARES, Institute for Marine Resources and Ecosystem Studies, IJmuiden, The Netherlands and the Institute for Environmental Studies, Vrije Universiteit, Amsterdam, The Netherlands.

Test material QTM083BT was a haddock muscle homogenate. Test material QTM084BT was a Mussel homogenate from mussels from the Mediterranean Sea near Spain.

Each batch of material was prepared in bulk. The level of within and between sample homogeneity for the biota was determined. All materials have been shown to be homogeneous at or below the intake mass used by the participants, and stable for the purposes of the test.

#### Data Assessment

All data received from participants are entered into the QUASIMEME database and assessed using a standard procedure to allow direct comparison between participants in each round and between rounds. The approach to the assessment is based on the standard, ISO 13528<sup>1</sup>, the IUPAC International Harmonised Protocol for Proficiency Testing (Advanced Draft)<sup>2</sup>. Additions or differences in the assessment from these standards are given or referred to in this report.

The summary statistics provided in Table 1 are based on Robust Statistics following DIN 38402, the AMC method and the Cofino Model. However, the assigned value and the laboratory assessment using the z-score are based on the Cofino Model.

Comparison between the robust statistics and the Cofino model continues to be made, and where there are any significant discrepancies between the two methods then further investigative analysis is undertaken. Good agreement has been obtained (ca < 1% difference) for well-behaved measurements. The real differences occurred where there was an effect of methodology on the measurement, e.g. digestion of sediments for trace metal analysis. In these cases the Cofino model is generally able to separate the effects of the method on the results and provide a more reliable estimate of the measurement relating to the method. The standard, ISO 13528, includes statistics for proficiency testing schemes, and uses robust statistics as a basis for the assessment. However, it is generally acknowledged that robust statistics cannot cope with more than 10% extreme values, particularly with a skewed distribution. The Cofino model is able to routinely cope with these types of distribution and provide the best estimate of the consensus value, which may be used as the assigned value.

The Cofino model has been developed for the routine QUASIMEME assessments. From Round 45 the Cofino model uses a Normal Distribution Assumption (NDA). The assigned value is based on the Cofino NDA model without any trimming of the data. This approach includes all

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1 ISO 13528:2005. Statistical methods for use in proficiency testing by interlaboratory comparisons.

2 The International Harmonised Protocol for Proficiency Testing of Analytical Chemistry Laboratories. IUPAC Technical Report. Thompson, M., Ellison, S.L.R., Wood, R. Interdivisional Working Party for Harmonization of Quality Assurance Schemes.



data in the evaluation and no subjective truncation or trimming is made. This model has been further developed to include Left Censored Values (LCV)<sup>3</sup>. The development of these models has been fully documented and published.<sup>4, 5, 6</sup> An overview of the assessment with explanation and examples is given in the paper *Assessment Rules for the Evaluation of the QUASIMEME LP Studies Data*<sup>7</sup>.

The details of the Cofino Model are provided elsewhere,<sup>6, 7</sup> but in summary the approach is as follows:

- All data included in the assessment
- No data trimmed or downweighted
- Assigned values (AV) based on Cofino NDA model
- All LCV<sup>3</sup> are also included, provided certain criteria are met

## Tables and Plots

The assigned value, total allowable error and descriptive statistics for each determinand are shown in Table 1. Table 2 outlines the percentage of satisfactory data and the limit of determination values submitted for each determinand. Table 3 shows the ranked z-scores of the laboratories that participated in this study. Table 4 gives the constant and proportional errors for each determinand and an overview of indicative values. The performance of the laboratories in this study is illustrated in the z-score histograms. Where the assigned value for a determinand is indicative, the values are plotted as their original reported concentrations. The rules for confirming whether the consensus value should be an assigned value or an indicative value are given in *Assessment Rules for the Evaluation of the QUASIMEME LP Studies Data*<sup>7</sup> with appropriate examples.

Appendix I contains a page of graphical output from the Cofino Model for each determinand, describing the distribution of the data, which may be used in the interpretation and assessment.

Detailed descriptions of each of the plots in Appendix I, with examples are given in the Cofino Model handbook<sup>6</sup>. There are four plots for each determinand.

The upper left plot provides an impression of the probability density function for all data (black) and for the first mode (blue dotted) (PMF1) of the data. Superimposed on these pdf's is a histogram of the individual measurements given in grey color. This plot shows the distribution of the data as a whole, and of the data in the main mode (PMF1) on which the assigned value is based.

The Kilt Plot (Overlap Matrix) (upper right plot) provides an overview of the degree of overlap of each pair of data. It gives a clear indication of the homogeneity (or otherwise) of the data. As a key the white areas indicate maximum overlap of the pdf's and therefore highest agreement (an overlap of one implies that the two laboratories of the pair report exactly the same results), while the black area show the pairs in poor agreement.

The lower left plot is a ranked overview of all data with an error bar of  $\pm 2$  s.d. The numerical

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3 *Left Censored Values* is the correct nomenclature for "less than" values

4 Cofino, W.P., Wells, D.E., Ariese, F., van Stokkum, I, Wengener, J. W. and Peerboom, R., *J. Chemometrics and Intelligent Laboratory Systems*, **53**, (2000) 37-55

5 Cofino, W. P., van Stokkum, I.H.M., van Steenwijk, J., and Wells, D E. *Analytica Chimica Acta* **533**, (2005) 31–39.

6 Wells, D.E., Cofino, W.P. and Scurfield, J. A. *The Application of the Cofino Model to Evaluate Laboratory Performance Study Data using the BandWidth Estimator*. FRS Marine Laboratory, Aberdeen, Collaborative Report No. 04/04 (2004)

7 Wells, D.E., and Scurfield, J. A. (2004). *Assessment Rules for the evaluation of the QUASIMEME Laboratory Performance Studies Data – version 2, February 2004*. QUASIMEME Project, FRS Marine Laboratory, 375 Victoria Road, Aberdeen AB11 9DB

values are given in blue and the left censored values are given in red.

The ranked z-score plot (lower right) is NOT the FINAL ASSESSMENT. It is based on the Cofino mean of the data, which is normally also the assigned value. However, if there is any adjustment required to the assigned value as a result of the assessment, e.g. use of the nominal concentration or a trimmed value, then the final z-score given in the z-score histograms will reflect these changes. In most cases the two z-score plots will be the same. Any differences between this plot and the final assessment will be indicated in the report.

### **The Assigned Values**

The Assigned Value is obtained from the main mode of the data using the Cofino Model, and is centered around the highest density of values. Unless otherwise stated, the assigned value is based on this consensus value of *all* data.

Although *all* data are included in the assessment, those values that lie some distance from the Cofino mean (Assigned Value) contribute less to the mean than values which occur at or near the mean. The percentage of data in the main mode (blue area in the upper left Cofino Model plots) that contributes to the Cofino mean, and the Cofino standard deviation of this percentage of data are given in Table 1. The higher the percentage of data, the greater is the overall agreement of the measurements.

The Robust mean and between laboratory CV% are also given in Table 1 for comparison, but these values are not used as a basis for the assigned value or for the laboratory assessment.

### **The Indicative Values**

In some instances it is not possible to set an assigned value, and an indicative value is given. No assessment of laboratory performance is given where an indicative value is set. An overview of the assessment, with explanation, decision flowcharts and examples, is given in the paper *Assessment Rules for the evaluation of the QUASIMEME Laboratory Performance Studies Data*, available on the QUASIMEME website, [www.quasimeme.org](http://www.quasimeme.org). A summary of the categories is given below, and the decisions for each determinand in each matrix are listed in Table 4.

#### Category 1

For data with the number of numerical observations  $\geq 7$

An assigned value is based on the Cofino mean when  $\geq 33\%$  of values have a z-score of  $|Z| < 2$ . Where  $< 33\%$  of the data have  $|Z| < 2$  the value is indicative. i.e. at least 33% must be in good agreement.

#### Category 2

For data with the number of numerical observations  $> 3$  and  $< 7$

An assigned value is based on the Cofino mean when  $\geq 70\%$  of values have a z-score of  $|Z| < 3$  and a minimum of 4 observations have  $|Z| < 2$ . Otherwise the value is indicative. i.e. for small datasets,  $n > 3$  and  $n < 7$ , there needs to be very good agreement and a maximum of one extreme value before an assigned value can be given.

#### Category 3

For data with the number of numerical observations  $< 4$

No assigned value is given. Normally the median value is given as an indicative value.

#### Category 4

For data with the high Total Error%  $> 100\%$  in combination with bad performance, no assigned value is given.

The value given in table 1 is indicative.

### The Z-score Assessment

A z-score<sup>8</sup> is calculated for each participant's data for each matrix / determinand combination which is given an assigned value. The z-score is calculated as follows:

$$z - score = \frac{\text{Mean from Laboratory} - \text{Assigned Value}}{\text{Total Error}}$$

It is emphasized that in many interlaboratory studies the between-laboratory standard deviation obtained from the statistical evaluation of the study is used as 'total error' in the formula above. In Quasimeme the total error is estimated independently taking the needs of present-day international monitoring programs as starting point. For each determinand in a particular matrix, a proportional error (PE) and a constant error (CE) have been defined. The total error depends on the magnitudes of these errors and on the assigned value:

$$\text{Total Error} = \frac{\text{Assigned Value} \times \text{Proportional Error (\%)}}{100} + 0.5 \times \text{Constant Error}$$

The values for the PE and CE are set by the Scientific Assessment Group and are monitored annually. The values are based on the following criteria:

Consistency of the required standard of performance to enable participating laboratories to monitor their assessment over time.

Achievable targets in relation to the current state of the art and the level of performance needed for national and international monitoring programmes.

The assessment is based on ISO 43 as z-scores. The QUASIMEME model is designed to provide a consistent interpretation over the whole range of concentration of analytes provided, including an assessment where Left Censored Values (LCVs) are reported.

The proportional error is set at 6% for nutrients and for standard solutions, and 12.5% for all other matrices. This applies to all determinands. The constant error has been set for each determinand or determinand group (e.g. chlorinated biphenyls). This value was initially set to reflect the limit of determination, but is at present more closely related to the overall laboratory performance. The magnitude of the CE is set to provide a constant assessment in terms of z-score regardless of concentration. Therefore at low concentrations the level of accuracy required to obtain a satisfactory z-score is less stringent than at a high concentrations.

The performance of the laboratories is examined in detail when the total error exceeds 50% of the consensus concentration. If there is good agreement between the laboratories, i.e. the criteria to set an assigned value are met, the CE may be revised to a lower value reflecting the performance of laboratories for this measurement at lower concentrations. These revisions are undertaken at the time of the assessment and ratified by the Scientific Assessment Group. In making any adjustments to the CE an overall assessment of performance at these lower concentrations over a number of different rounds is reviewed. This provides evidence of a long-term trend of improved performance rather than a single set of data. When the agreement is judged to be insufficient, no assigned value is established. In such cases an indicative value is given.

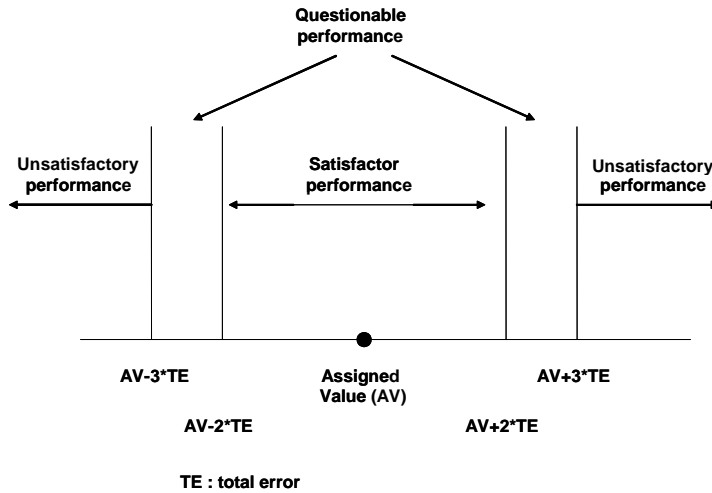
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<sup>8</sup> International Harmonised Protocol for Proficiency Testing of (Chemical) Analytical Laboratories. M Thompson, R Wood, Journal of AOAC International Vol. 76, No. 4, 1993

Following usual practices e.g. ISO 43, the z-scores can be interpreted as follows for laboratories which take part in Quasimeme to assure the quality of their data for use in international marine monitoring programmes:

- $|Z| < 2$  Satisfactory performance
- $2 < |Z| < 3$  Questionable performance
- $|Z| > 3$  Unsatisfactory performance

The following figure illustrates the interpretation of the z-scores:



$|z| > 6$  frequently points to gross errors (mistakes with units during reporting, calculation or dilution errors, and so on).

It is not possible to calculate a z-score for left censored values (LCV's). Quasimeme provides a simple quality criterion:

LCV/2 < (concentration corresponding to  $|z|=3$ ) : LCV consistent with assigned value  
 LCV/2 > (concentration corresponding to  $|z|=3$ ) : LCV inconsistent with assigned value, i.e. LCV reported by laboratory much higher than numerical values reported by other laboratories.

- Z score key: S – Satisfactory
- Q – Questionable
- U – Unsatisfactory
- LCV key: C – Consistent
- I – Inconsistent
- No data: B - Blanc

All details of publications relating to the QUASIMEME assessment are available on the website at [www.quasimeme.org](http://www.quasimeme.org).

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Table 1 Summary Statistics for QUASIMEME Participants

Exercise No. 859 Round 58  
 Group BT1 Year 2009  
 Total Number of laboratories 39

Matrix/ Determinand	Assigned Value	Units	Total Error%	NObs Numerical	NObs LCV	Median Value	Basis for	Skewness	Model mean	Model Between Lab CV%	Model percentage in PMF1	DIN38402 Mean	DIN38402 Between Lab CV%	FastS Mean	FastS Between Lab CV%
QTM083BT							AV								
Arsenic	10.3	mg/kg	12.6	32	0	10.3	NDA	5.22	10.3	9.81	74.8	10.4	12.2	10.2	10.2
<i>Cadmium</i>	<i>4.70</i>	<i>µg/kg</i>		<i>25</i>	<i>10</i>	<i>4.70</i>	<i>NDA</i>	<i>2.27</i>	<i>4.09</i>	<i>48.9</i>	<i>70.1</i>	<i>4.22</i>	<i>59.8</i>	<i>3.88</i>	<i>53.4</i>
Chromium	79.1	µg/kg	25.1	21	3	93.3	NDA	1.61	79.1	75.0	77.1	84.9	58.0	62.3	76.8
Copper	181	µg/kg	40.1	31	2	186	NDA	2.08	181	18.4	64.0	186	27.0	180	22.5
Lead	19.5	µg/kg	25.3	22	8	20.4	NDA	0.32	19.5	61.9	80.1	20.4	62.0	15.6	72.6
Mercury	47.7	µg/kg	33.5	30	3	48.2	NDA	4.10	47.7	13.7	74.6	47.8	15.9	48.0	13.1
Nickel	66.3	µg/kg	27.6	21	5	67.5	NDA	0.74	66.3	49.2	74.2	72.6	45.2	60.8	50.8
Selenium	316	µg/kg	14.1	18	2	329	NDA	3.69	316	21.7	78.7	314	21.9	340	20.2
<i>Silver</i>	<i>2.16</i>	<i>µg/kg</i>		<i>11</i>	<i>5</i>	<i>2.16</i>	<i>NDA</i>	<i>1.55</i>	<i>2.09</i>	<i>29.2</i>	<i>70.2</i>	<i>2.31</i>	<i>35.1</i>	<i>1.97</i>	<i>26.2</i>
Zinc	3.07	mg/kg	45.1	33	2	3.18	NDA	4.68	3.07	20.3	73.6	3.17	22.1	2.92	20.8
<i>Ash-Weight</i>	<i>1.30</i>	<i>%</i>		<i>5</i>	<i>0</i>	<i>1.30</i>	<i>NDA</i>	<i>1.39</i>	<i>1.31</i>	<i>2.78</i>	<i>57.7</i>	<i>1.08</i>	<i>92.5</i>	<i>1.31</i>	<i>2.81</i>
Dry-weight	21.3	%	12.7	25	0	21.3	NDA	-0.59	21.3	4.04	76.6	21.3	4.19	21.3	3.69
Total-Lipid	0.47	%	23.1	7	0	0.52	NDA	0.95	0.47	22.2	63.1	0.46	41.8	0.50	19.7
<i>Lipid-Extractable</i>		<i>%</i>		<i>2</i>	<i>0</i>										
QTM084BT															
Arsenic	2.45	mg/kg	12.9	34	0	2.44	NDA	4.06	2.45	11.3	73.0	2.42	12.9	2.52	11.0
Cadmium	160	µg/kg	18.7	37	0	160	NDA	5.25	160	13.0	72.5	157	14.9	164	12.3
Chromium	152	µg/kg	19.1	24	2	161	NDA	1.39	152	30.1	73.1	162	35.8	149	32.7
Copper	1174	µg/kg	16.8	34	0	1160	NDA	4.85	1174	11.8	74.6	1174	14.2	1180	11.7
Lead	146	µg/kg	14.2	31	3	145	NDA	5.16	146	15.0	72.0	147	17.4	141	15.1
<i>Mercury</i>	<i>11.1</i>	<i>µg/kg</i>		<i>28</i>	<i>5</i>	<i>11.1</i>	<i>NDA</i>	<i>1.93</i>	<i>11.1</i>	<i>10.5</i>	<i>59.9</i>	<i>11.2</i>	<i>16.2</i>	<i>11.1</i>	<i>12.2</i>
Nickel	126	µg/kg	20.5	27	2	130	NDA	-0.36	126	13.0	69.1	126	16.9	128	13.9
Selenium	491	µg/kg	13.5	19	1	500	NDA	3.39	491	24.2	76.7	502	26.2	463	23.5
Silver	3.22	µg/kg	90.2	12	6	3.49	NDA	1.32	3.22	23.2	62.2	3.54	27.3	3.29	22.9
Zinc	38.1	mg/kg	15.1	36	0	38.6	NDA	5.48	38.1	8.42	75.9	38.1	9.09	38.2	8.30
Ash-Weight	2.13	%	14.8	6	0	2.16	NDA	1.76	2.13	3.06	60.7	2.20	8.11	2.12	3.32
Dry-weight	25.3	%	12.7	26	0	25.2	NDA	3.85	25.3	2.99	70.6	25.3	4.10	25.3	3.29
Total-Lipid	2.45	%	14.5	7	0	2.60	NDA	0.95	2.45	12.6	67.4	2.45	20.8	2.44	11.1
<i>Lipid-Extractable</i>		<i>%</i>		<i>2</i>	<i>0</i>										

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Entries in italics are given as indicative values only  
 NObs = Total number of observations reported

Table 2 Summary of Z scores and Left Censored Values (LCVs)

Exercise No. 859 Round 58  
 Group BT1 Year 2009  
 Total Number of laboratories 39

Matrix/ Determinand	% of the data received	% of Zscores  Z <2 Satisfactory	% of Zscores 3> Z >2 Questionable	% of Zscores 6> Z >3 Unsatisfactory	% of Zscores  Z >6 Extreme	% Consistent LCV	% Inconsistent LCV	Minimum LCV	Maximum LCV
QTM083BT									
Arsenic	82	97			3				
Cadmium	90							4.10	100.00
Chromium	64	56	12	8	8	4	8	41.00	1000.00
Copper	90	77	6	6		6		200.00	2000.00
Lead	79	35	26	10		13	13	40.00	1000.00
Mercury	85	88		3		9		50.00	100.00
Nickel	72	64	4	7		11	7	41.00	2000.00
Selenium	54	81			5	10		400.00	1000.00
Silver	44							3.00	1000.00
Zinc	90	91			3	3	3	6.00	30.00
Ash-Weight	13								
Dry-weight	64	100							
Total-Lipid	18	71			29				
Lipid-Extractable	5								
QTM084BT									
Arsenic	87	91		3	6				
Cadmium	95	95	3		3				
Chromium	69	74	4	4	7	4	4	400.00	1000.00
Copper	92	86	6		3			2000.00	2000.00
Lead	87	79	6	3	3	6	3	200.00	500.00
Mercury	85							20.00	100.00
Nickel	79	81	3	3		3	3	300.00	2000.00
Selenium	54	67	14	5	5	5		600.00	1000.00
Silver	49	63				11	21	3.00	1000.00
Zinc	92	94	3		3				
Ash-Weight	15	83			17				
Dry-weight	67	96		4					
Total-Lipid	18	71			29				
Lipid-Extractable	5								

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Units of measurement for LCVs ('Less than') are given in Table 1

Table 3 Ranked Z scores for all determinands with assigned values

Exercise No. 859 Round 58  
 Group BT1 Year 2009  
 Total Number of laboratories 39

Labcode	NObs	Possible	Labcode	NObs	Actual %
	Z <2	%  Z <2		Submitted	% Z <2
AK069	19	86	AK031	1	100
AK127	19	86	AK052	12	100
AK130	19	86	AK058	7	100
AK122	17	77	AK061	14	100
AK133	17	77	AK080	10	100
AK154	17	77	AK091	13	100
AK053	16	73	AK108	16	100
AK054	16	73	AK125	15	100
AK062	16	73	AK126	1	100
AK092	16	73	AK127	19	100
AK098	16	73	AK128	1	100
AK108	16	73	AK130	19	100
AK151	16	73	AK134	9	100
AK002	15	68	AK154	17	100
AK124	15	68	AK092	17	94
AK125	15	68	AK002	16	94
AK061	14	64	AK124	16	94
AK097	14	64	AK097	15	93
AK105	14	64	AK070	13	92
AK085	13	59	AK189	13	92
AK091	13	59	AK123	11	91
AK052	12	55	AK152	11	91
AK068	12	55	AK069	21	90
AK070	12	55	AK133	19	89
AK189	12	55	AK054	18	89
AK291	11	50	AK062	18	89
AK011	10	45	AK151	18	89
AK080	10	45	AK079	7	86
AK123	10	45	AK291	13	85
AK152	10	45	AK098	19	84
AK134	9	41	AK011	12	83
AK190	9	41	AK105	17	82
AK058	7	32	AK085	16	81
AK079	6	27	AK053	20	80
AK096	5	23	AK068	15	80
AK059	2	9	AK122	22	77
AK031	1	5	AK190	12	75
AK126	1	5	AK096	7	71
AK128	1	5	AK059	13	15

NObs ( |Z| < 2 ) Total number of satisfactory observations ( |Z| < 2 ) from each laboratory.  
 % ( |Z| < 2 ) Possible Total number of satisfactory observations as a % of the total number of determinands with assigned values  
 NObs submitted Number of datasets submitted by each laboratory for each determinand with an assigned value.  
 % ( |Z| < 2 ) Actual % of observations submitted that were satisfactory ( |Z| < 2 )



Table 4 Constant and Proportional Errors and Criteria for Indicative Values

Exercise No. 859 Round 58  
 Group BT1 Year 2009  
 Total Number of laboratories 39

Matrix/ Determinand	Proportional Error	Constant Error	Indicative Category
<b>QTM083BT</b>			
Arsenic	12.5	0.02	
<i>Cadmium</i>	12.5	20	4
Chromium	12.5	20	
Copper	12.5	100	
Lead	12.5	5	
Mercury	12.5	20	
Nickel	12.5	20	
Selenium	12.5	10	
<i>Silver</i>	12.5	5	4
Zinc	12.5	2	
<i>Ash-Weight</i>	12.5	0.1	2
Dry-weight	12.5	0.1	
Total-Lipid	12.5	0.1	
<i>Lipid-Extractable</i>	12.5	0.1	3
<b>QTM084BT</b>			
Arsenic	12.5	0.02	
Cadmium	12.5	20	
Chromium	12.5	20	
Copper	12.5	100	
Lead	12.5	5	
<i>Mercury</i>	12.5	20	4
Nickel	12.5	20	
Selenium	12.5	10	
Silver	12.5	5	
Zinc	12.5	2	
Ash-Weight	12.5	0.1	
Dry-weight	12.5	0.1	
Total-Lipid	12.5	0.1	
<i>Lipid-Extractable</i>	12.5	0.1	3

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Indicative values are shaded grey

Category 1: NObs (num)  $\geq 7$ , AV requires more than 33%  $|Z| < 2$  and a minimum of 4 observations with  $|Z| < 2$

Category 2:  $3 < \text{NObs (num)} < 7$ , AV requires  $> 70\%$  of data have  $|Z| < 3$  and a minimum of 4 observations with  $|Z| < 2$

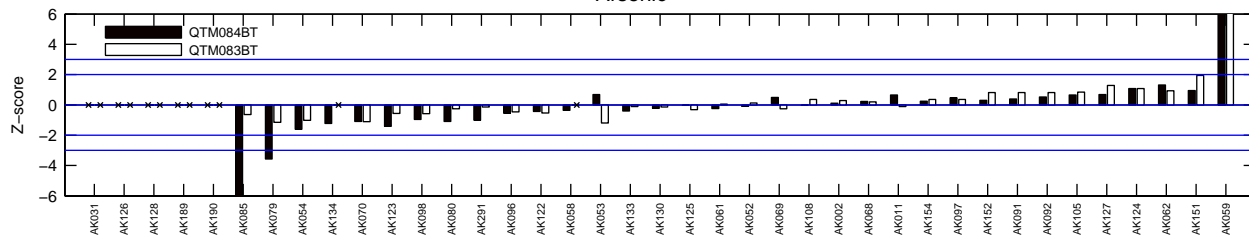
Category 3: NObs (num)  $< 4$ , No assigned value

Category 4: Total Error greater than 100%

Category 5: Judgement of QPO

**Appendix I**  
**Summary Plots**

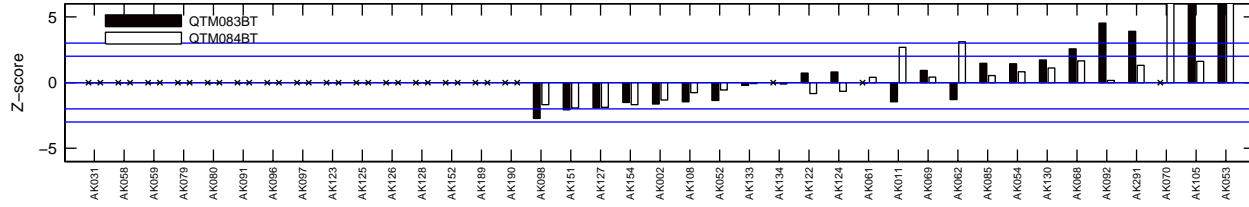
### Arsenic



Z = 3  
Z = 2

Z = -3  
Z = -2

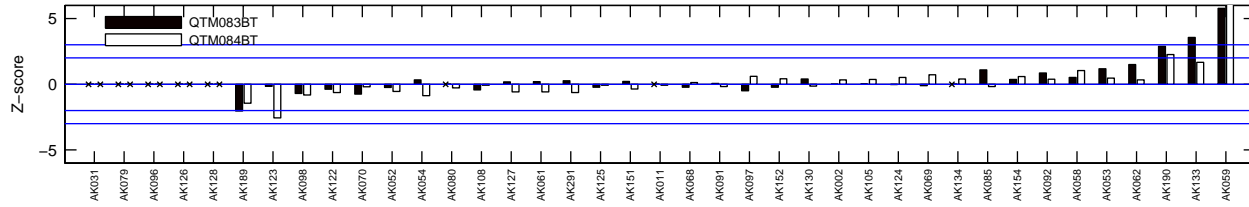
### Chromium



Z = 3  
Z = 2

Z = -3  
Z = -2

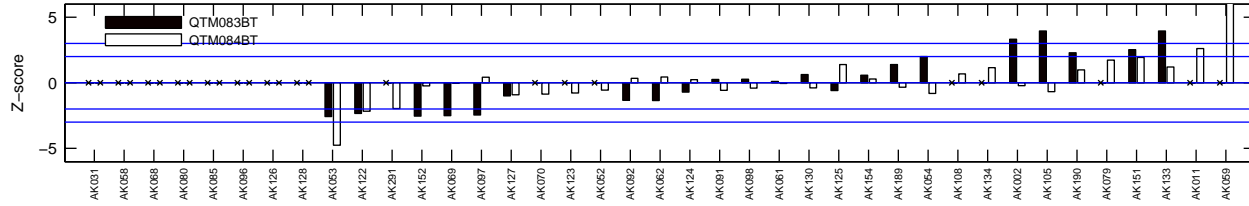
### Copper



Z = 3  
Z = 2

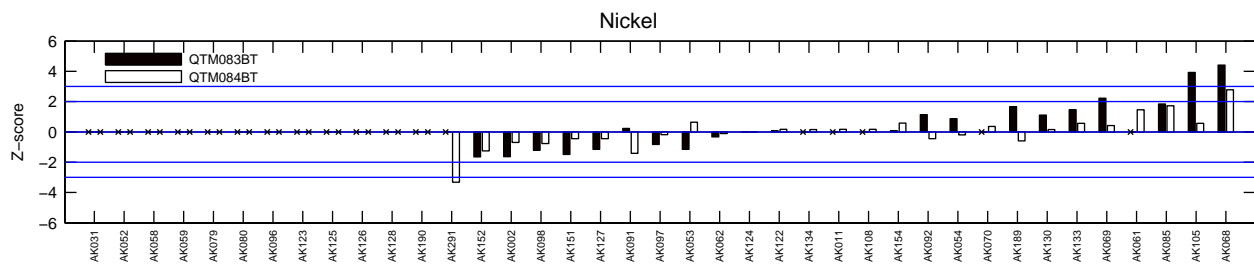
Z = -3  
Z = -2

### Lead



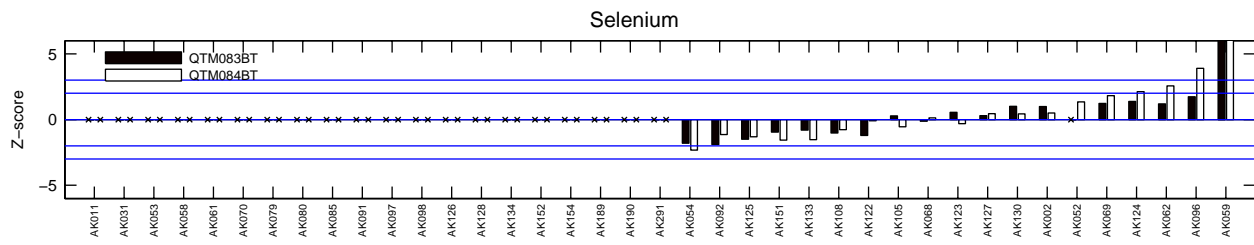
Z = 3  
Z = 2

Z = -3  
Z = -2



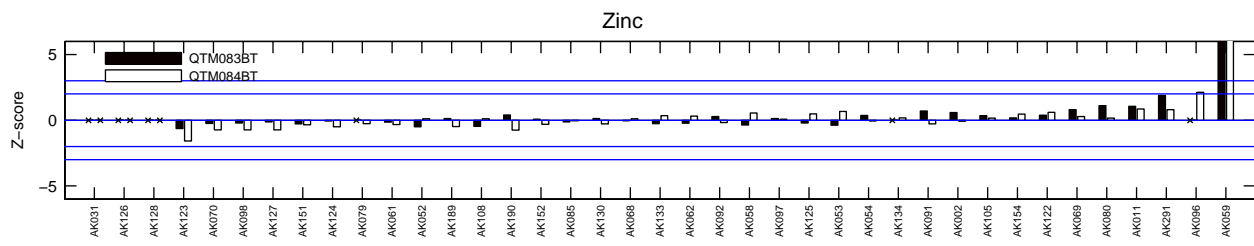
Z = 3  
Z = 2

Z = -3  
Z = -2



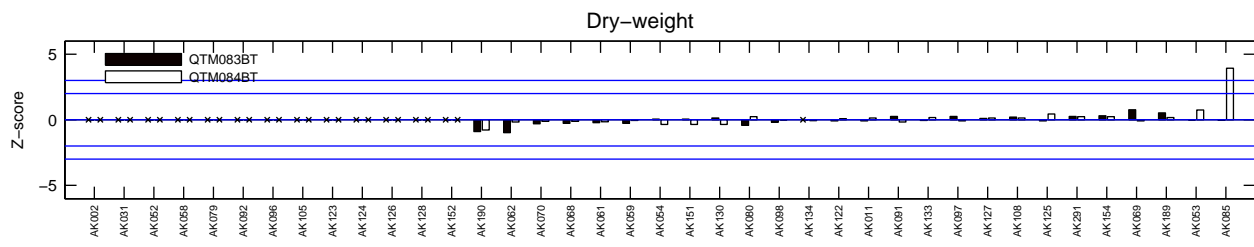
Z = 3  
Z = 2

Z = -3  
Z = -2



Z = 3  
Z = 2

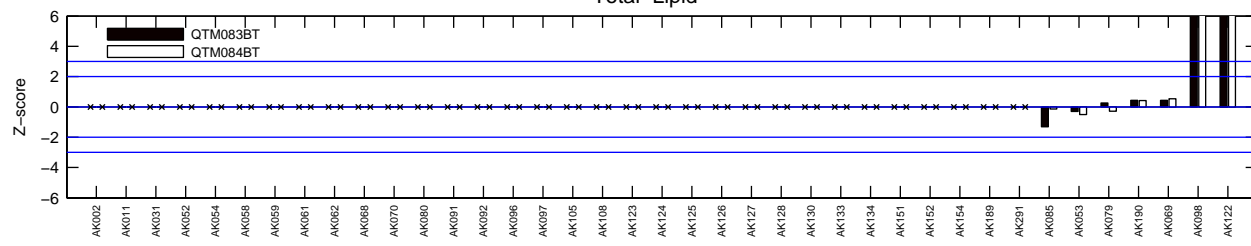
Z = -3  
Z = -2



Z = 3  
Z = 2

Z = -3  
Z = -2

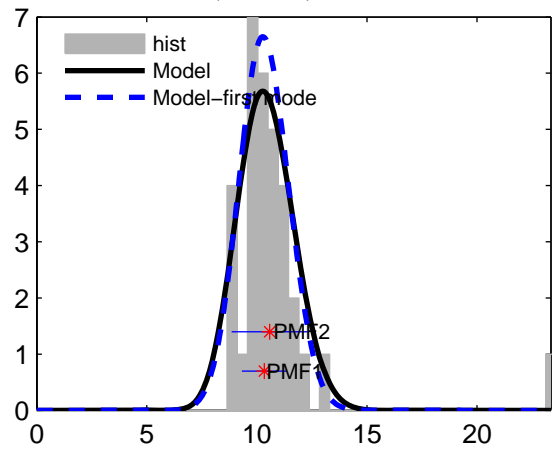
# Total-Lipid



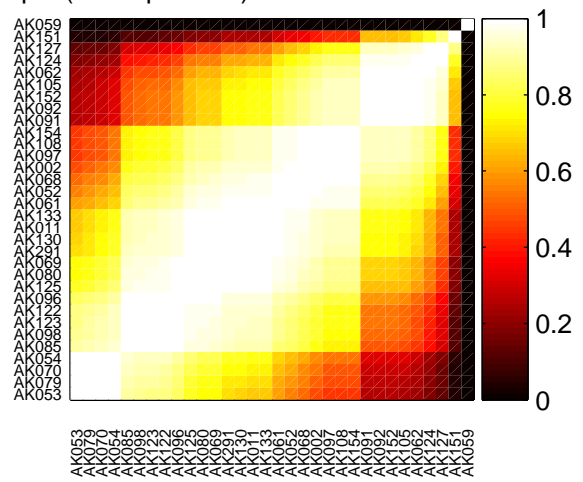
Z = 3  
Z = 2

Z = -3  
Z = -2

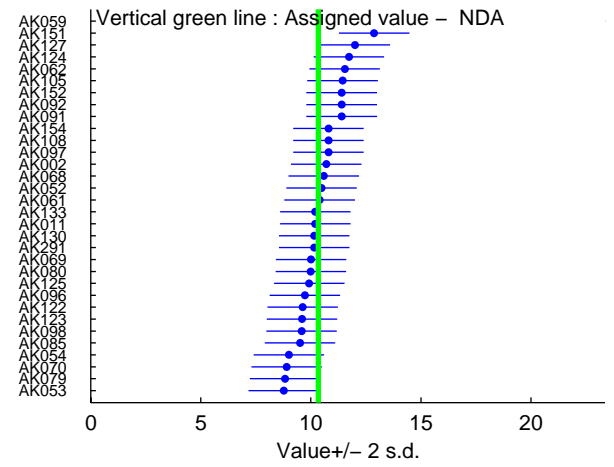
( $\Sigma OMF^2$ ) NDA



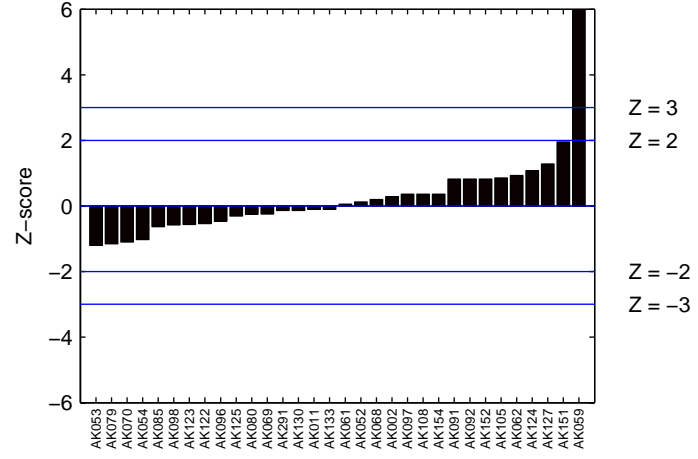
Kilt(overlap matrix) QTM083BT Arsenic



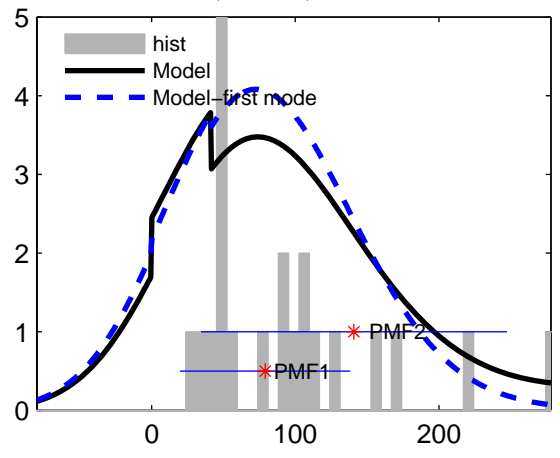
Ranked Overview – QTM083BT Arsenic



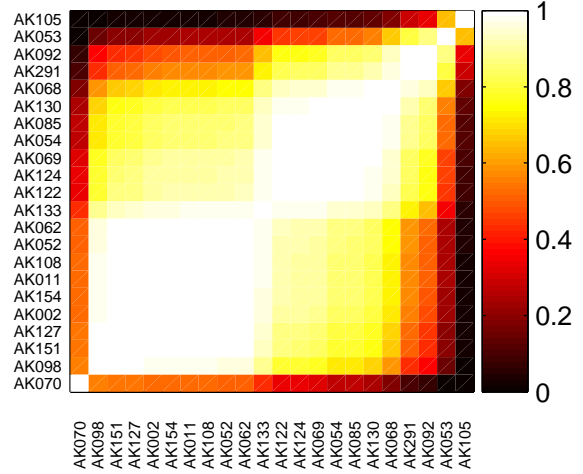
Ranked Z score – QTM083BT Arsenic



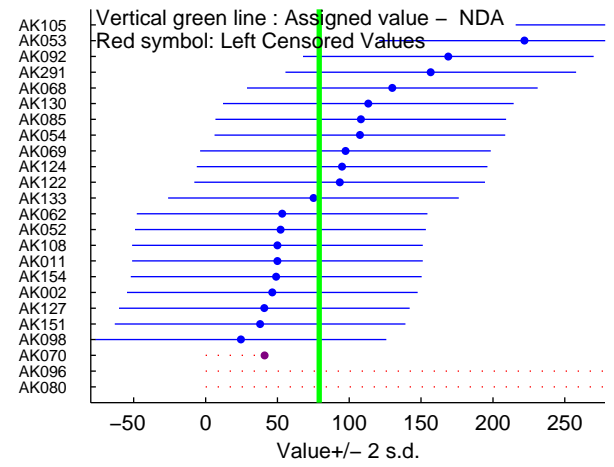
( $\Sigma OMF^2$ ) NDA



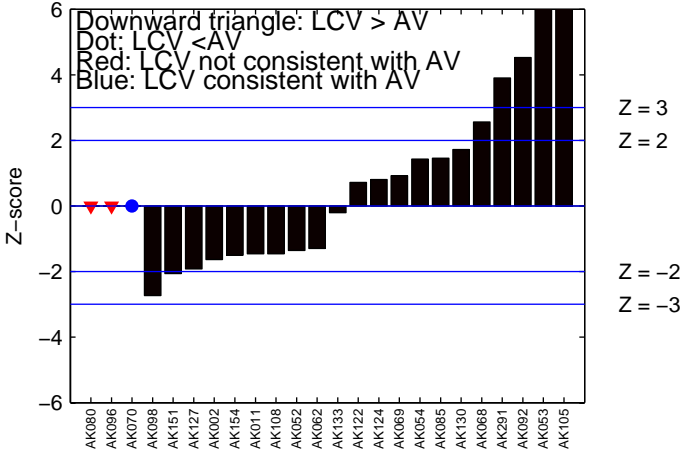
Kilt plot (overlap matrix) QTM083BT Chromium



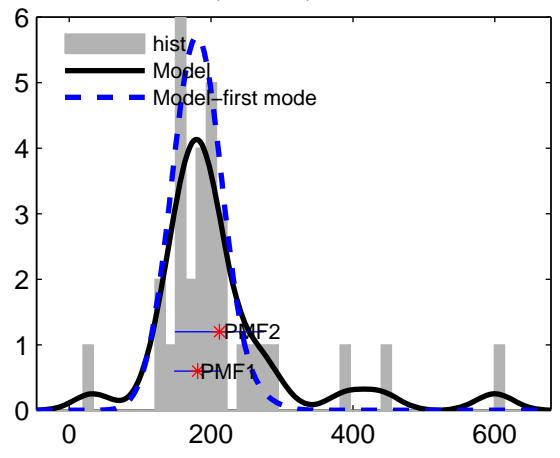
Ranked Overview – QTM083BT Chromium



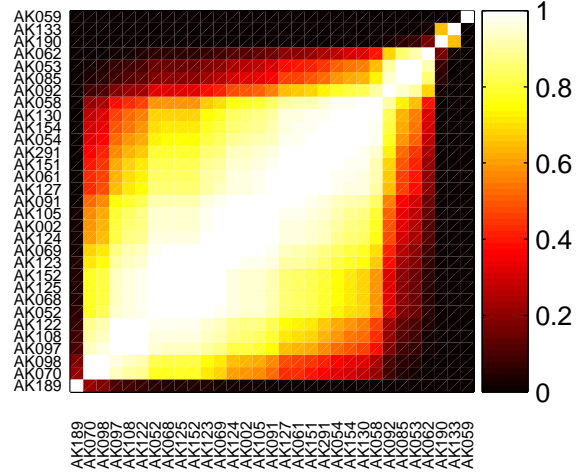
Ranked Z score – QTM083BT Chromium



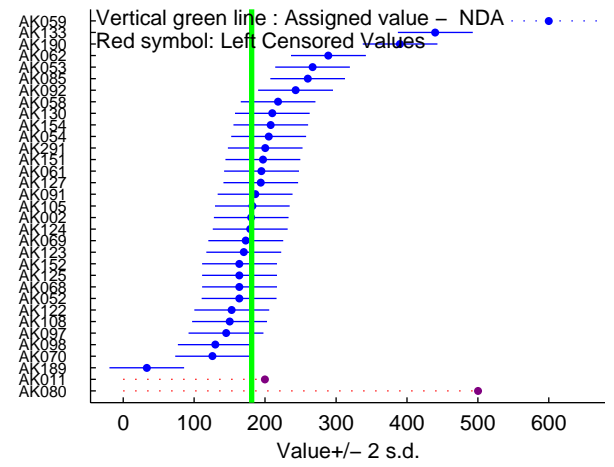
( $\Sigma$  OMF<sup>2</sup>) NDA



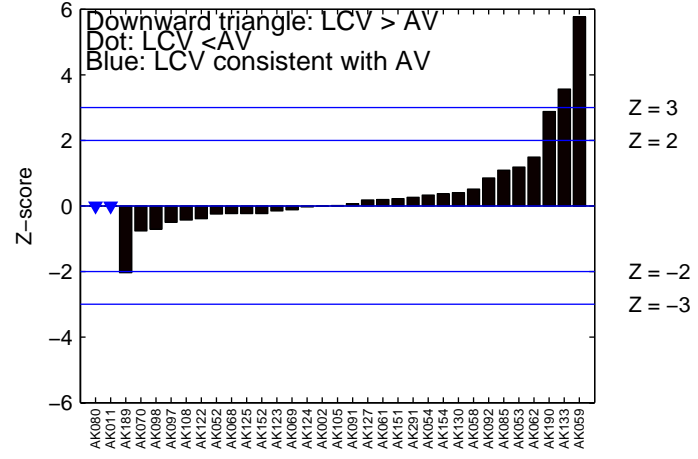
Kilt plot (overlap matrix) QTM083BT Copper



Ranked Overview – QTM083BT Copper

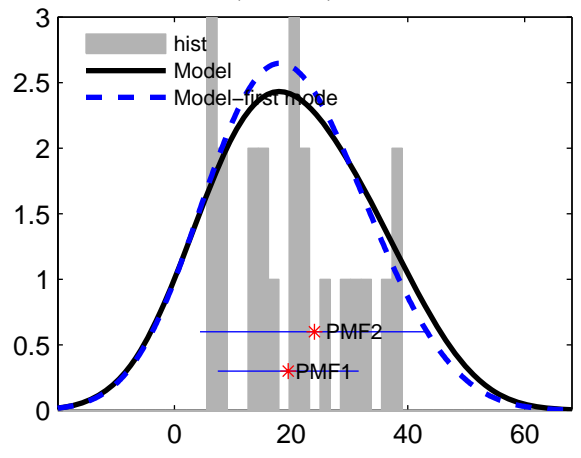


Ranked Z score – QTM083BT Copper

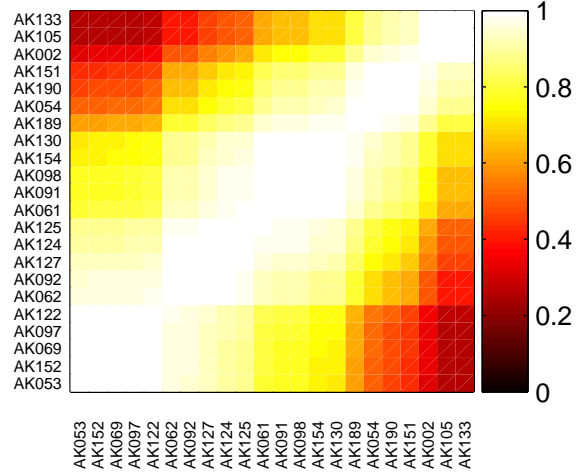




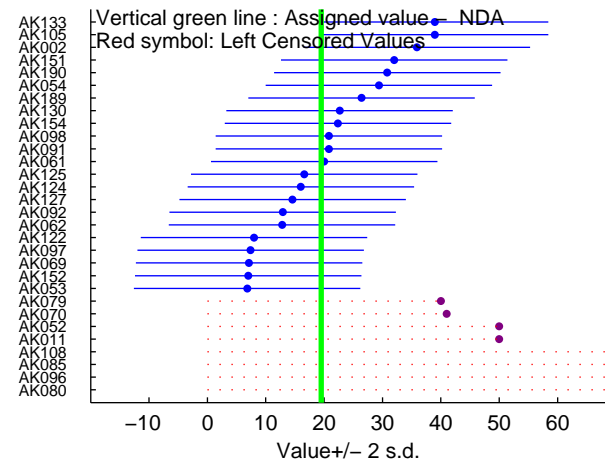
( $\Sigma OMF^2$ ) NDA



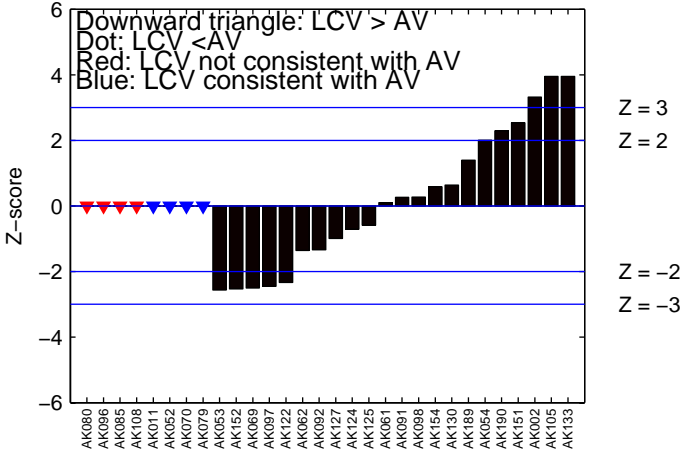
Kilt plot (overlap matrix) QTM083BT Lead



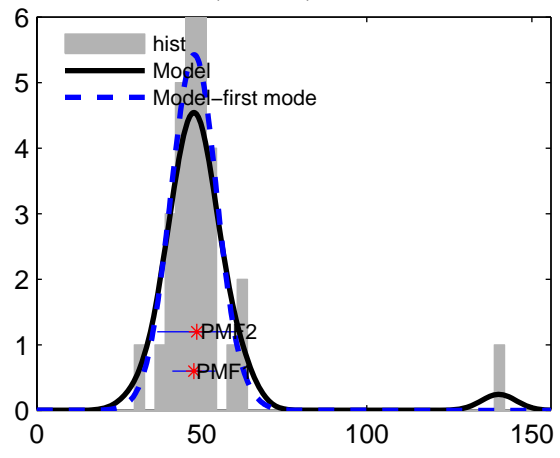
Ranked Overview – QTM083BT Lead



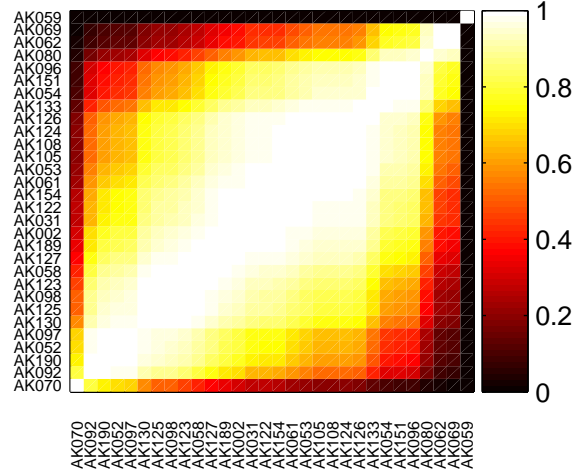
Ranked Z score – QTM083BT Lead



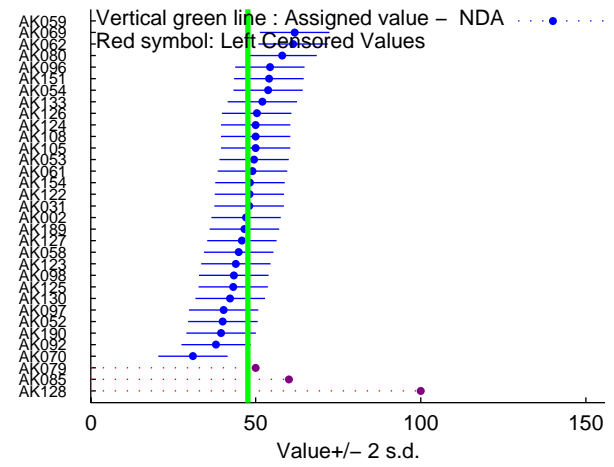
( $\Sigma OMF^2$ ) NDA



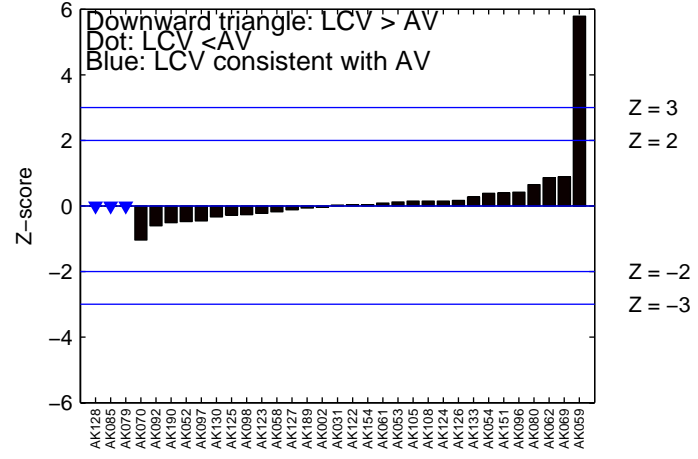
Kilt plot (overlap matrix) QTM083BT Mercury



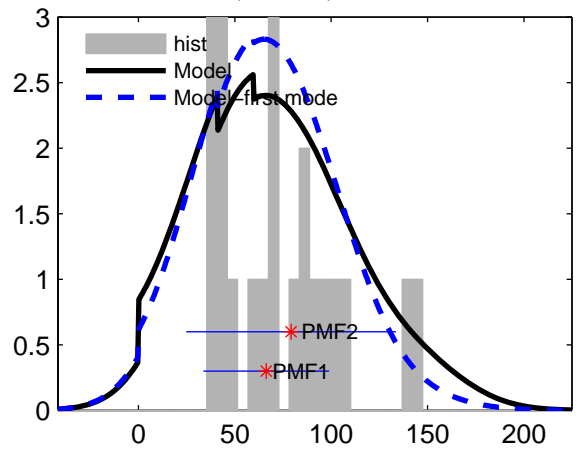
Ranked Overview – QTM083BT Mercury



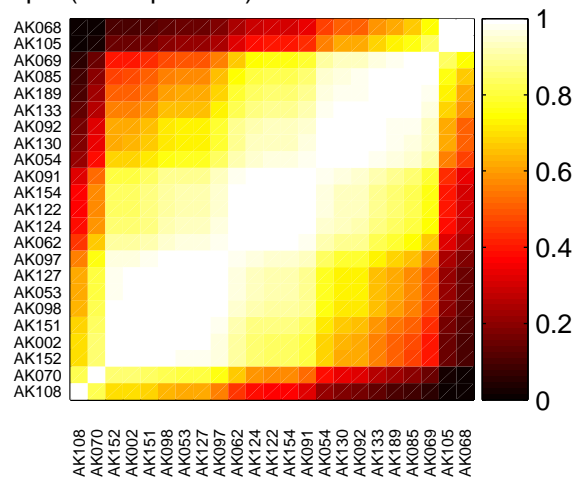
Ranked Z score – QTM083BT Mercury



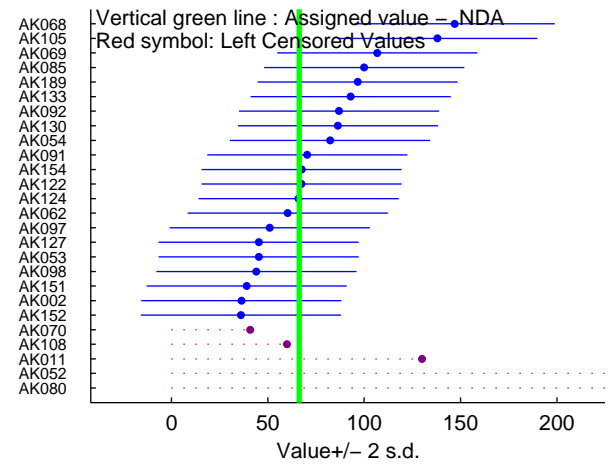
( $\Sigma$  OMF<sup>2</sup>) NDA



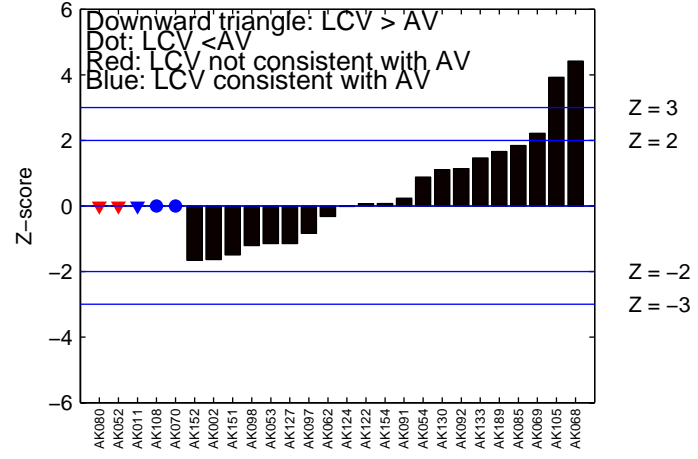
Kilt plot (overlap matrix) QTM083BT Nickel



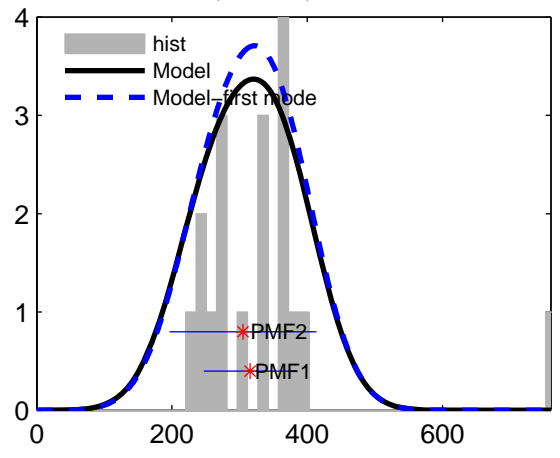
Ranked Overview – QTM083BT Nickel



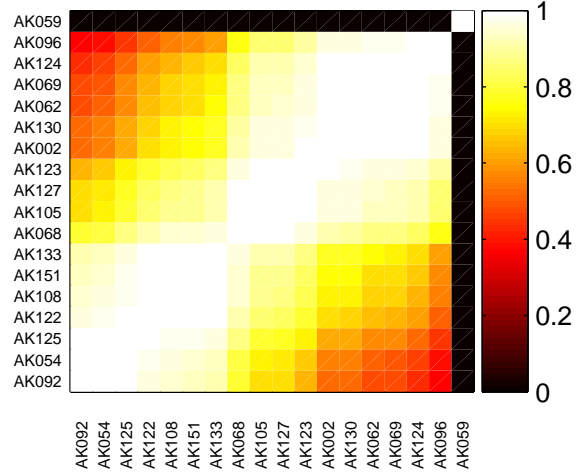
Ranked Z score – QTM083BT Nickel



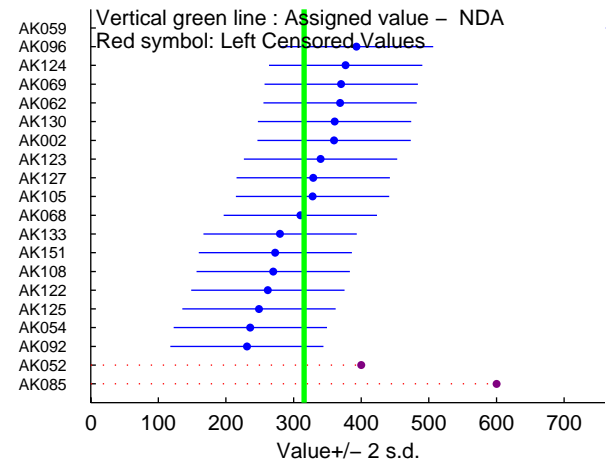
( $\Sigma OMF^2$ ) NDA



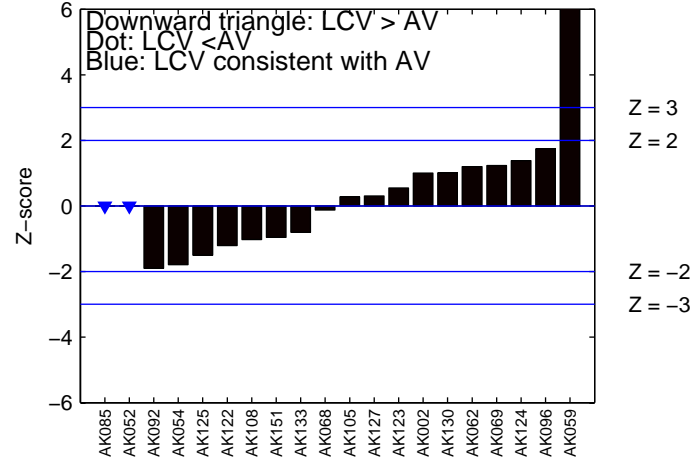
Kilt plot (overlap matrix) QTM083BT Selenium



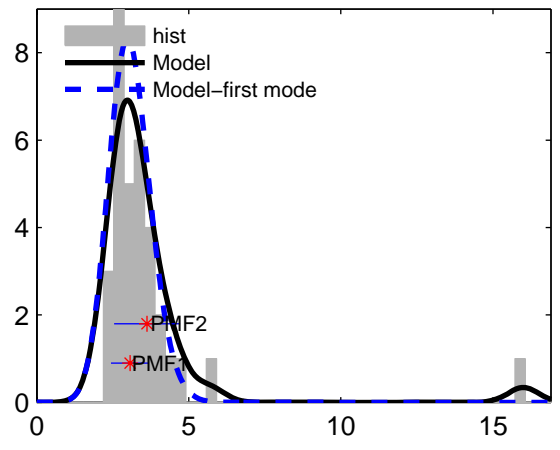
Ranked Overview – QTM083BT Selenium



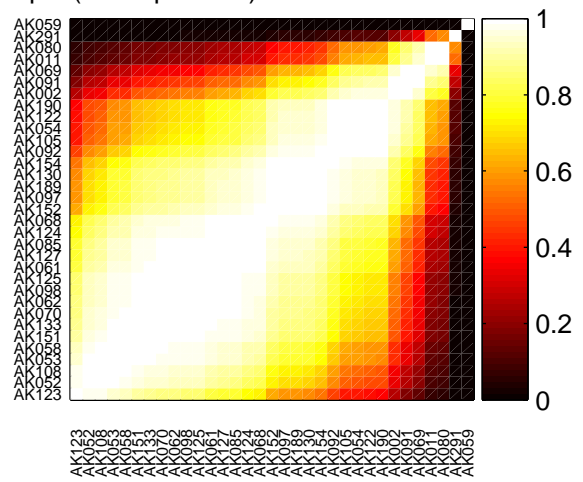
Ranked Z score – QTM083BT Selenium



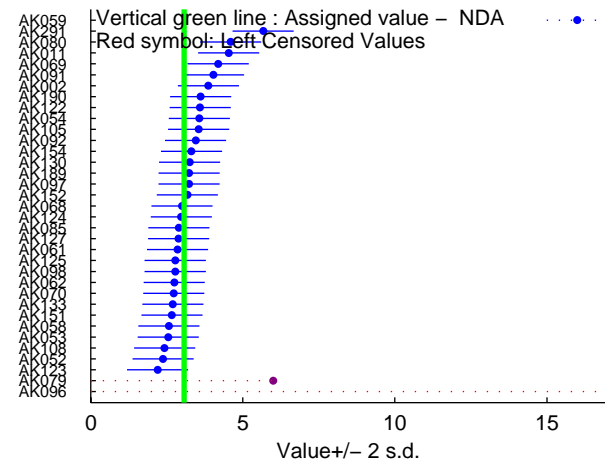
( $\Sigma$  OMF<sup>2</sup>) NDA



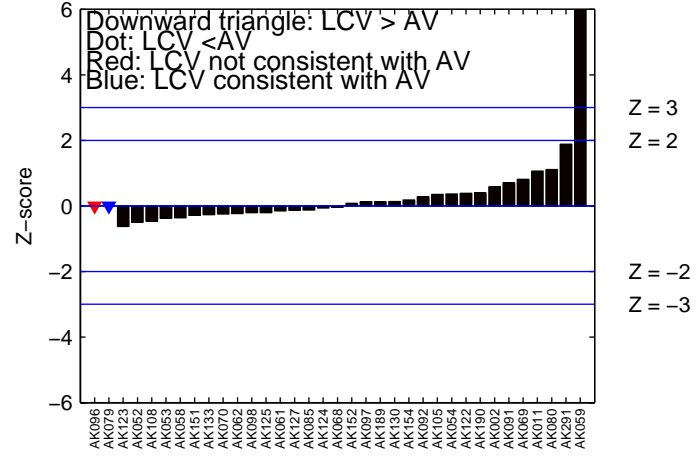
Kilt plot (overlap matrix) QTM083BT Zinc



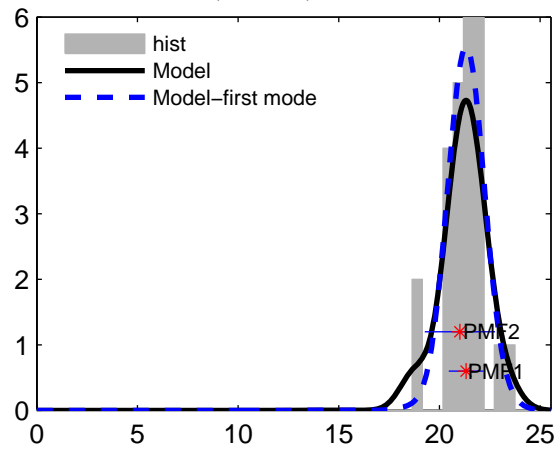
Ranked Overview – QTM083BT Zinc



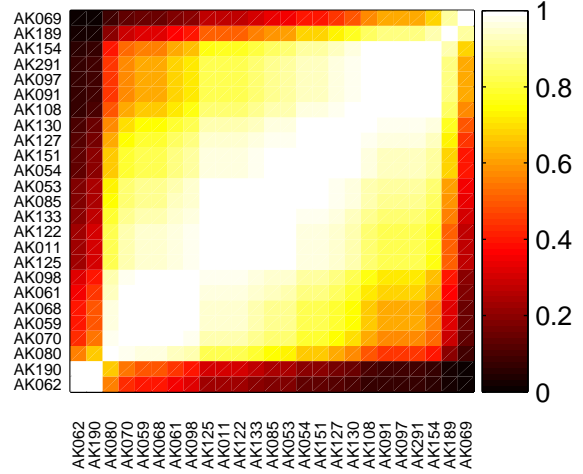
Ranked Z score – QTM083BT Zinc



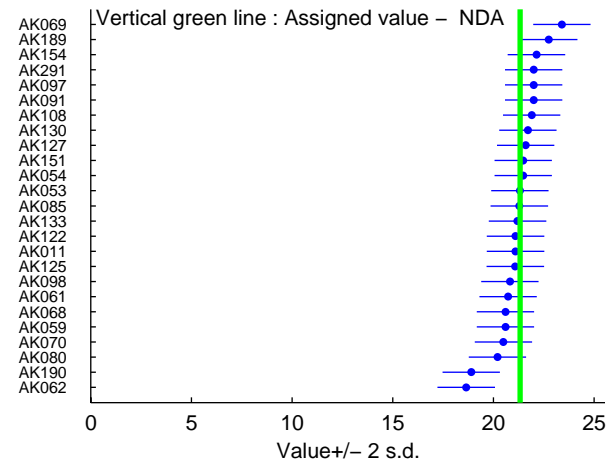
( $\Sigma OMF^2$ ) NDA



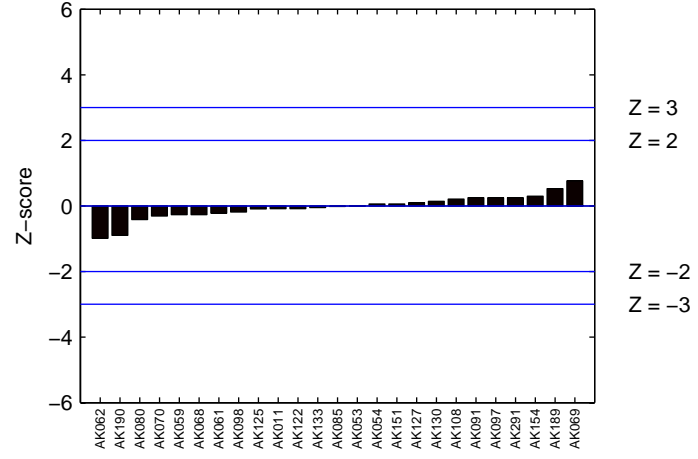
Kilt plot(overlap matrix) QTM083BT Dry-weight



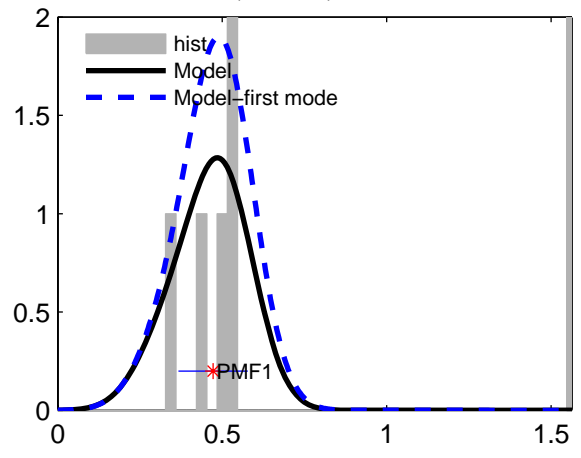
Ranked Overview – QTM083BT Dry-weight



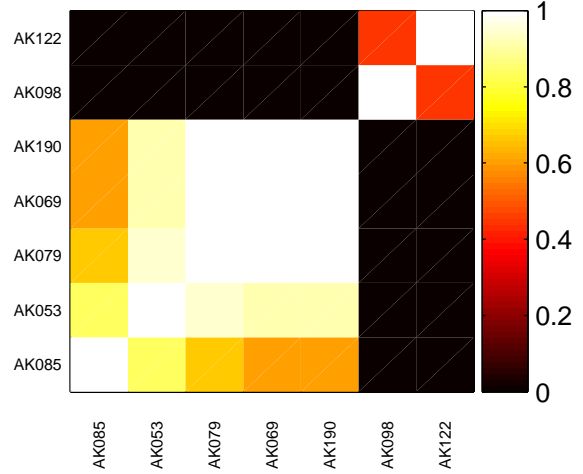
Ranked Z score – QTM083BT Dry-weight



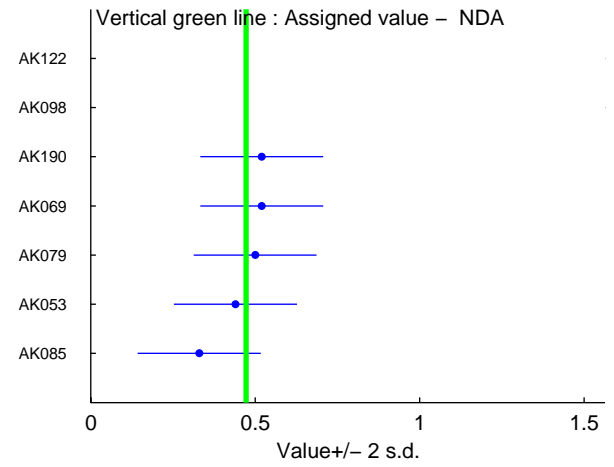
( $\Sigma$  OMF<sup>2</sup>) NDA



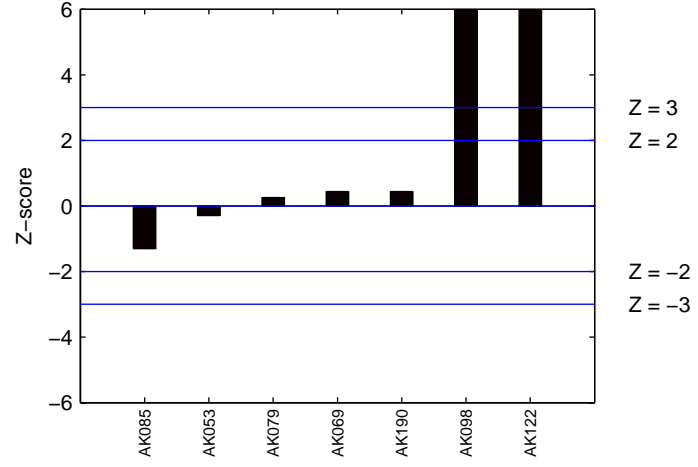
Kilt plot(overlap matrix) QTM083BT Total-Lipid



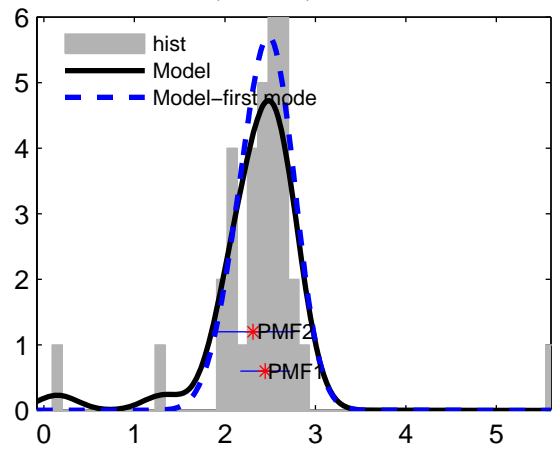
Ranked Overview – QTM083BT Total-Lipid



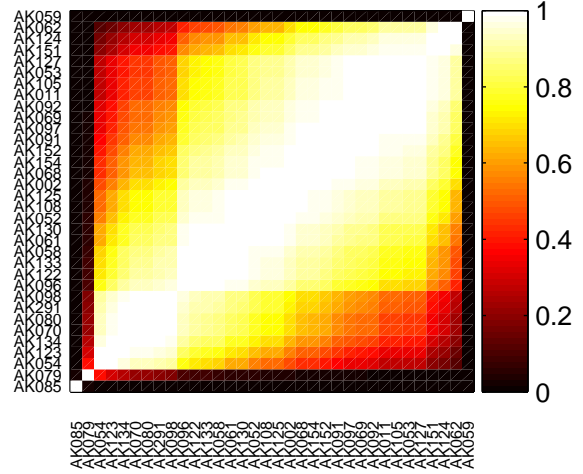
Ranked Z score – QTM083BT Total-Lipid



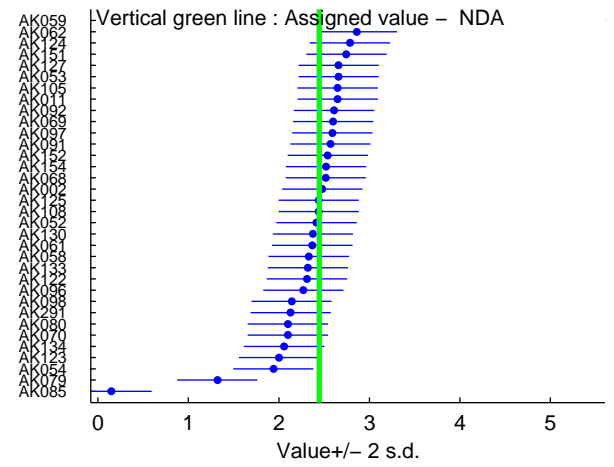
( $\Sigma$  OMF<sup>2</sup>) NDA



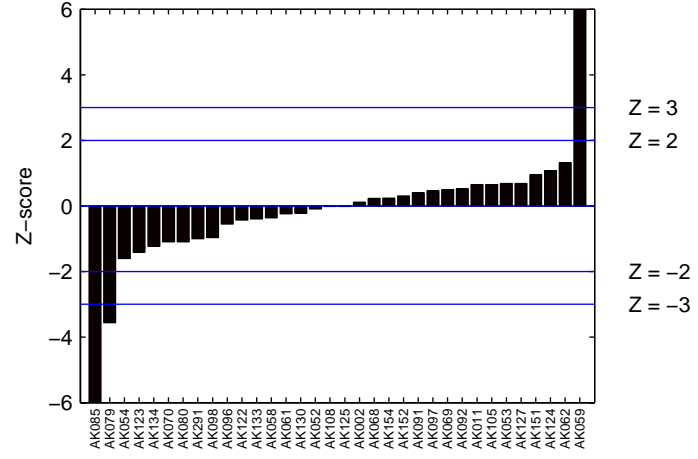
Kilt plot (overlap matrix) QTM084BT Arsenic



Ranked Overview – QTM084BT Arsenic

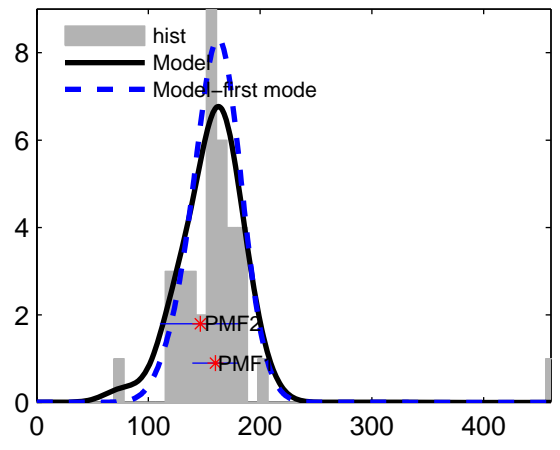


Ranked Z score – QTM084BT Arsenic

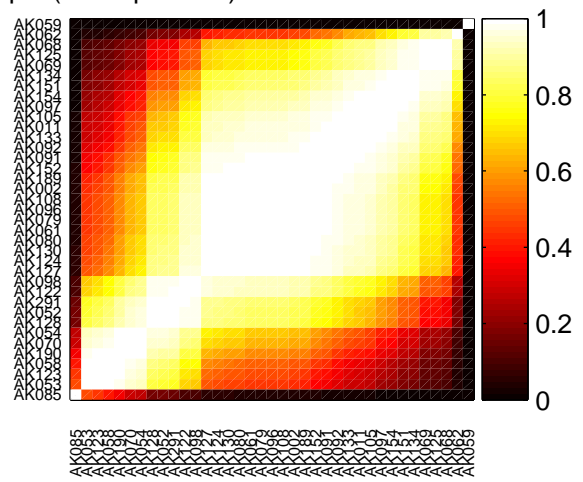




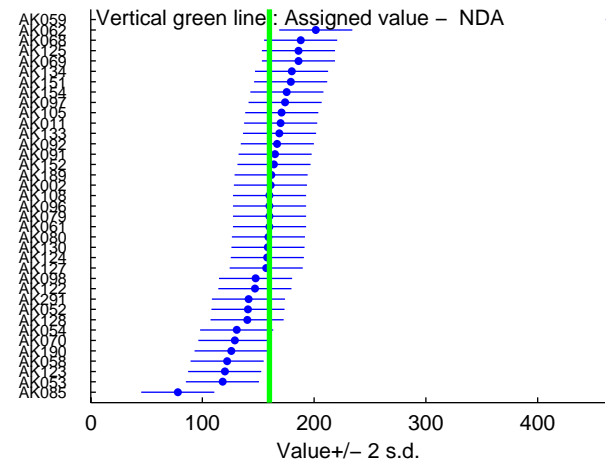
( $\Sigma$  OMF<sup>2</sup>) NDA



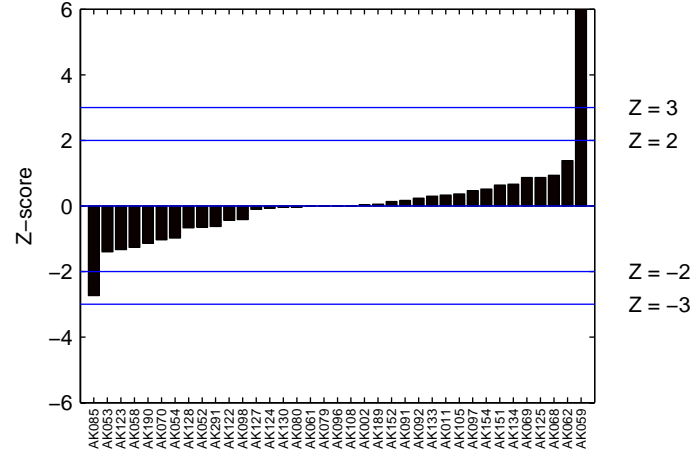
Kilt plot(overlap matrix) QTM084BT Cadmium



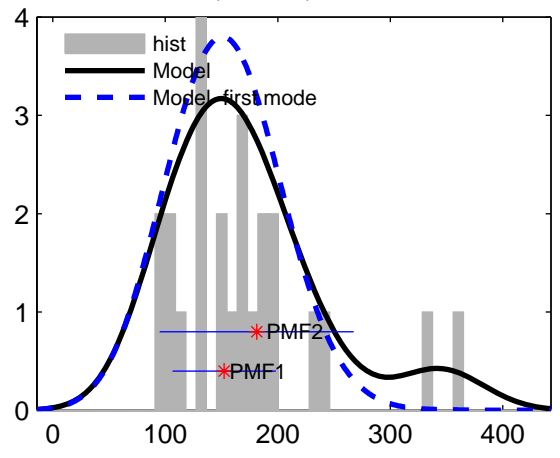
Ranked Overview – QTM084BT Cadmium



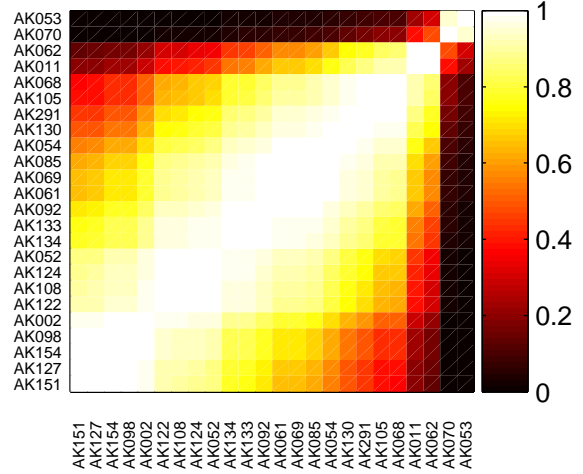
Ranked Z score – QTM084BT Cadmium



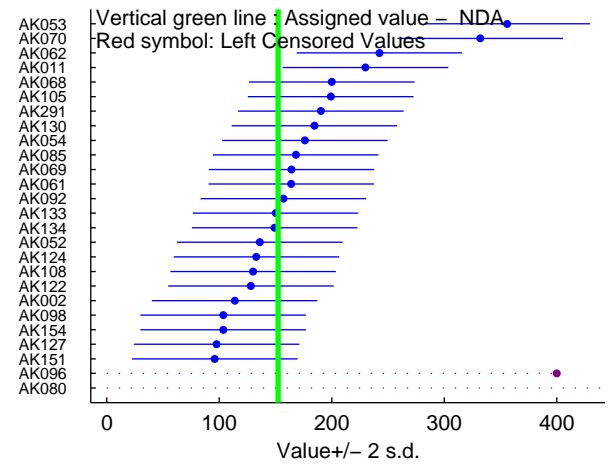
( $\Sigma$  OMF<sup>2</sup>) NDA



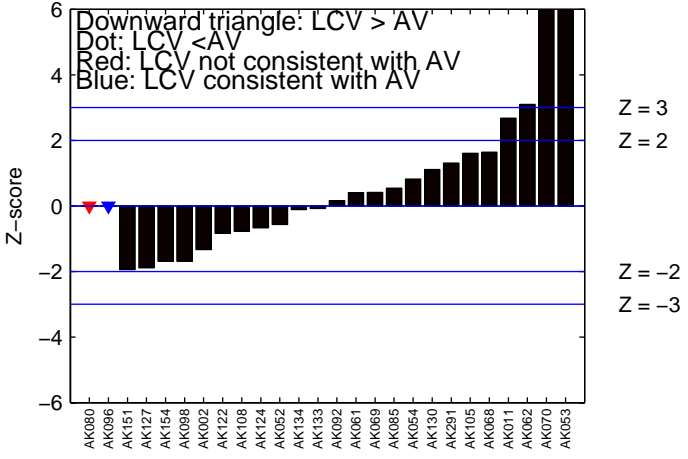
Kilt plot(overlap matrix) QTM084BT Chromium



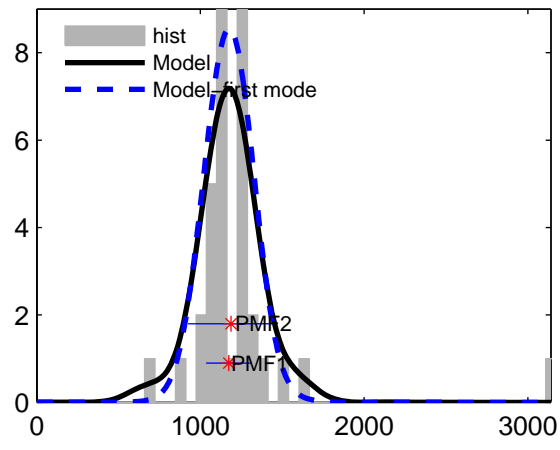
Ranked Overview – QTM084BT Chromium



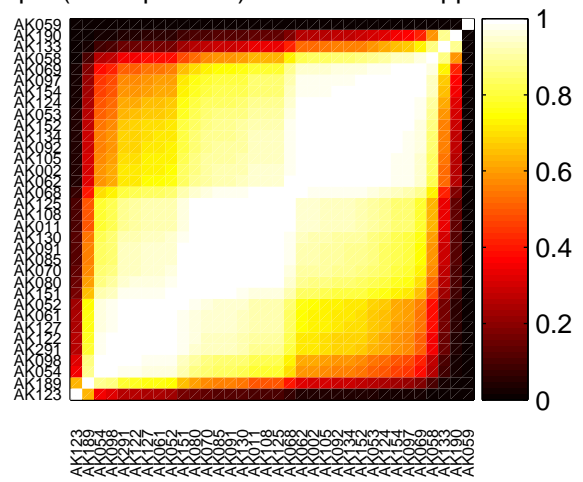
Ranked Z score – QTM084BT Chromium



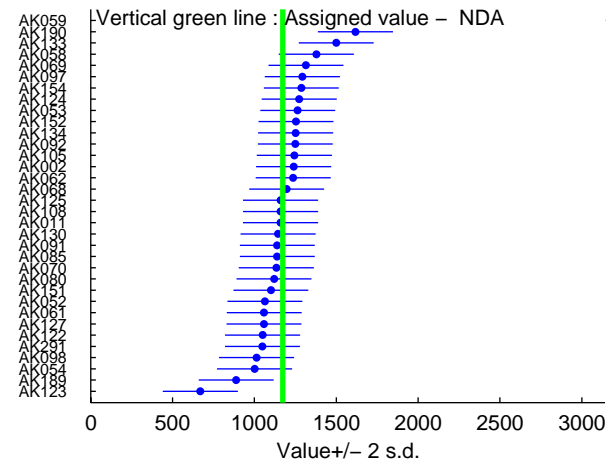
( $\Sigma$  OMF<sup>2</sup>) NDA



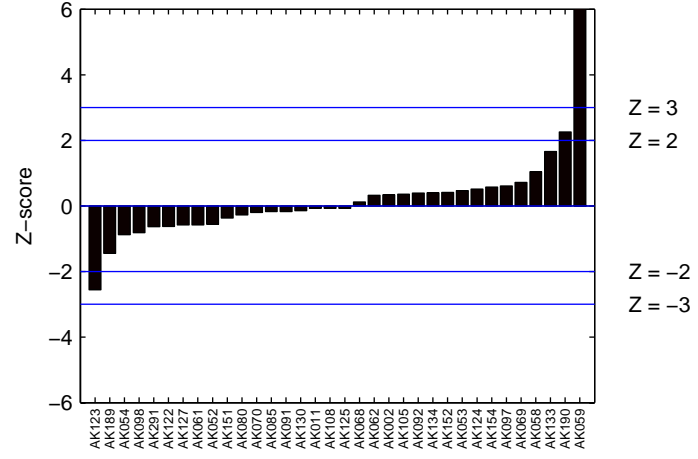
Kilt plot (overlap matrix) QTM084BT Copper



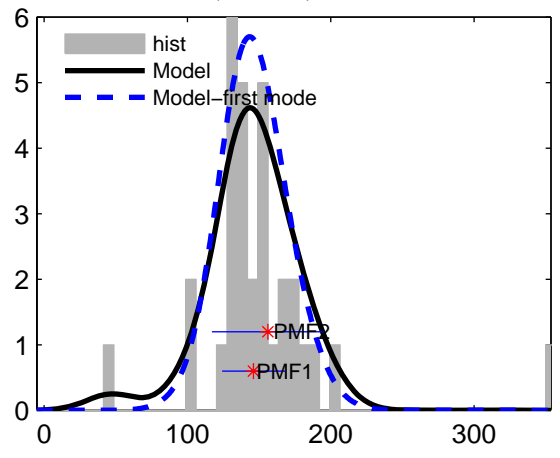
Ranked Overview – QTM084BT Copper



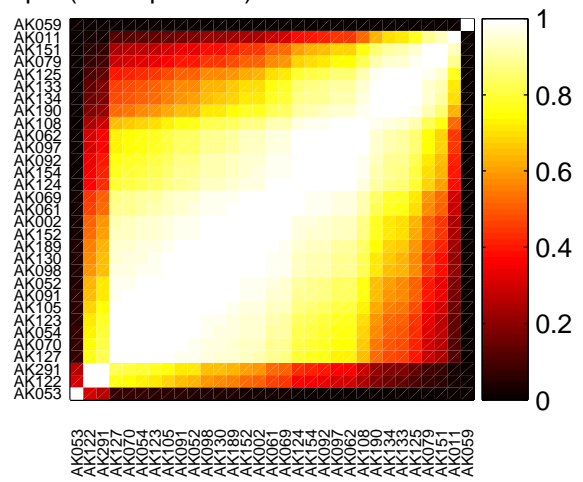
Ranked Z score – QTM084BT Copper



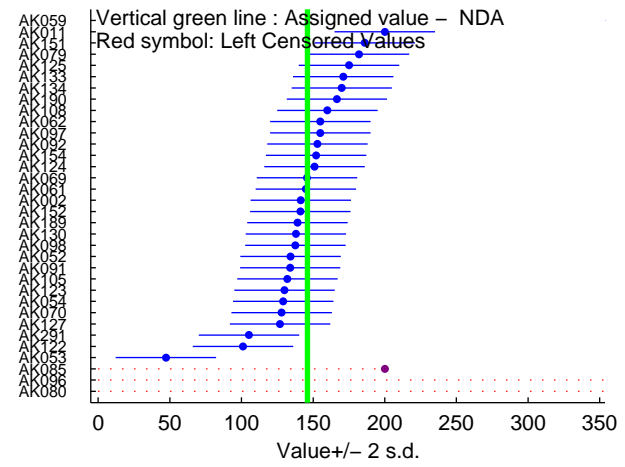
( $\Sigma$  OMF<sup>2</sup>) NDA



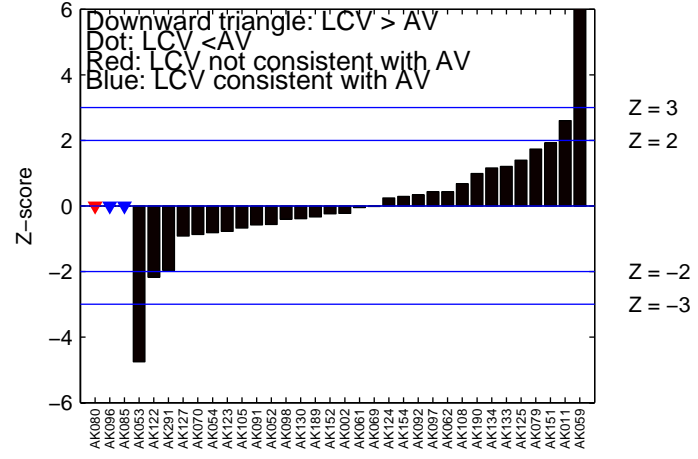
Kilt plot (overlap matrix) QTM084BT Lead



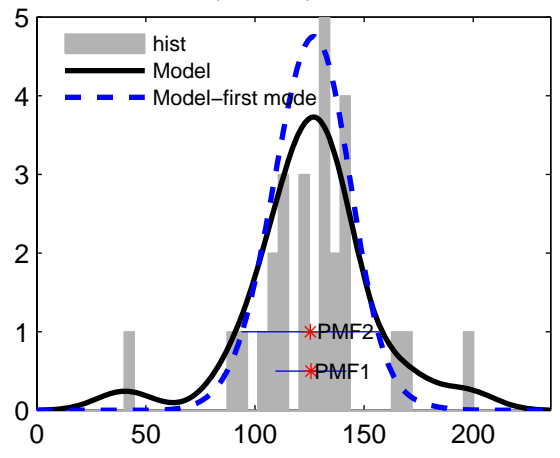
Ranked Overview – QTM084BT Lead



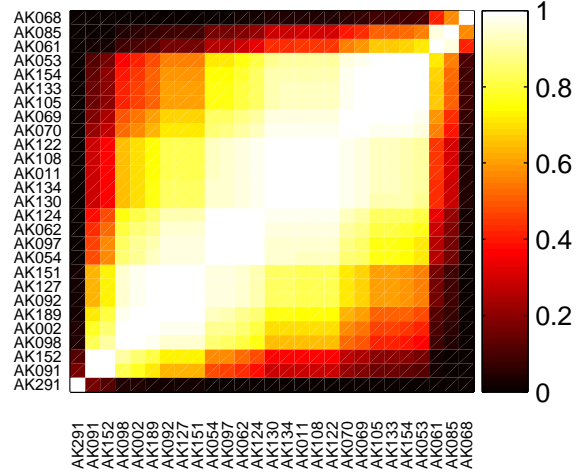
Ranked Z score – QTM084BT Lead



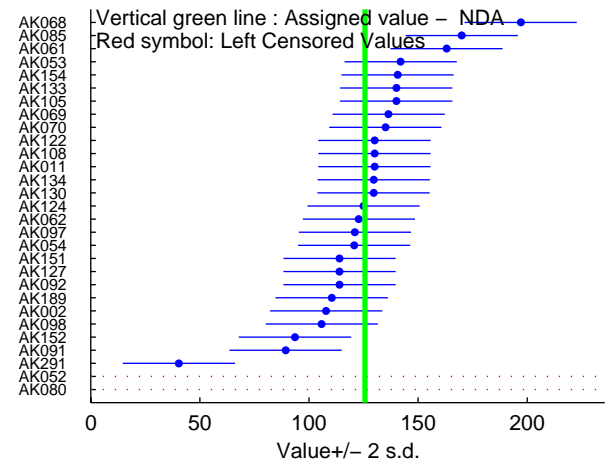
( $\Sigma$  OMF<sup>2</sup>) NDA



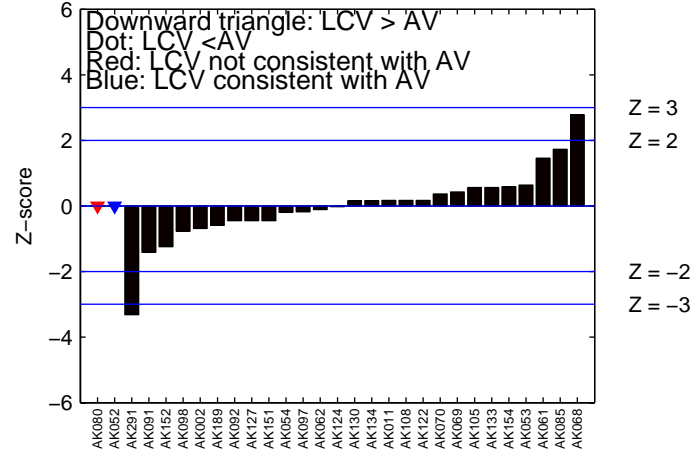
Kilt plot (overlap matrix) QTM084BT Nickel



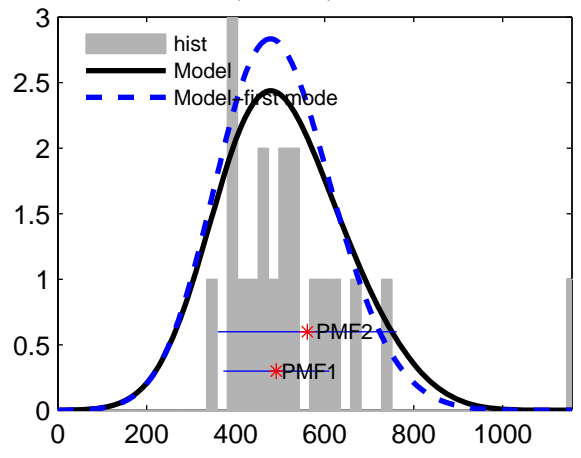
Ranked Overview – QTM084BT Nickel



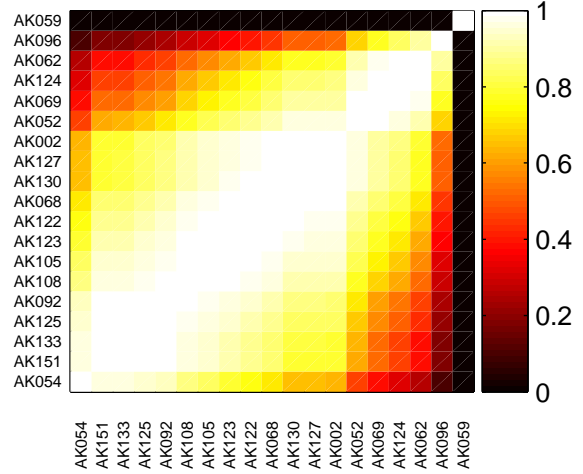
Ranked Z score – QTM084BT Nickel



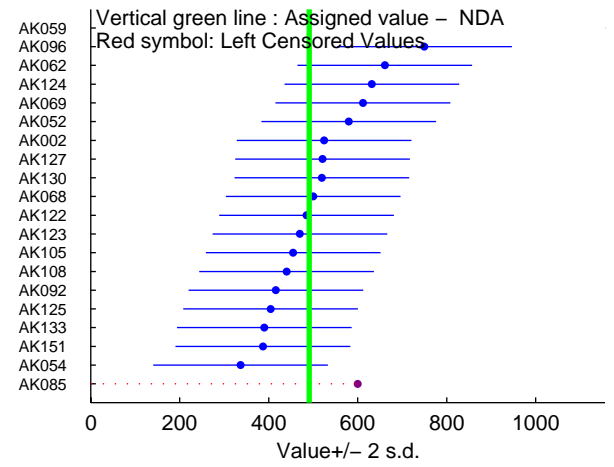
( $\Sigma OMF^2$ ) NDA



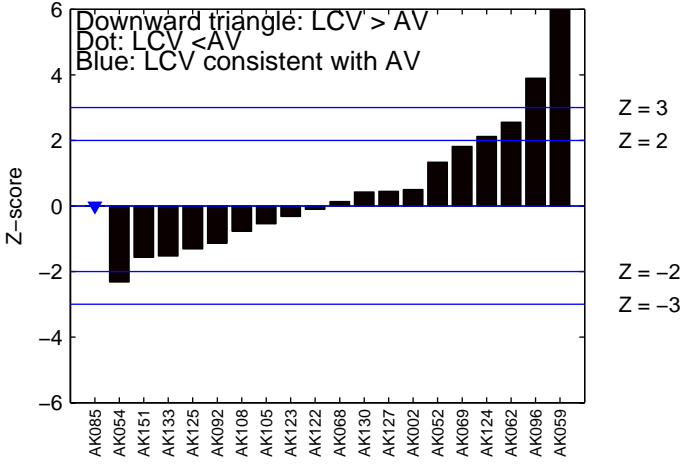
Kilt plot (overlap matrix) QTM084BT Selenium



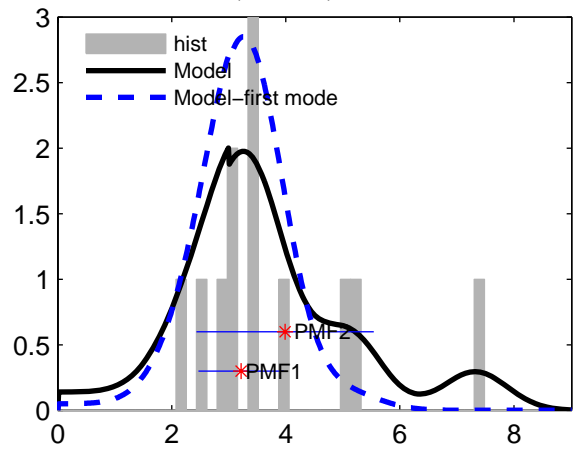
Ranked Overview – QTM084BT Selenium



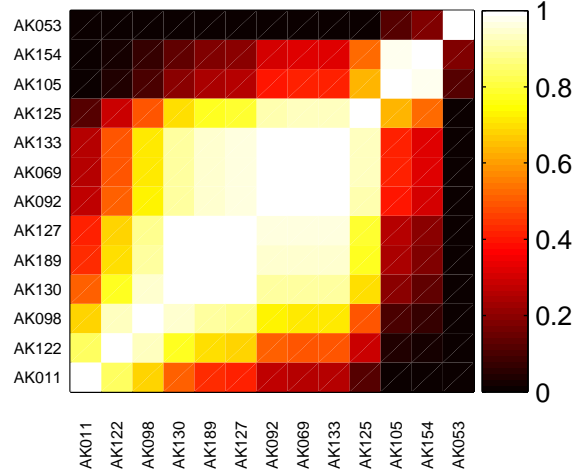
Ranked Z score – QTM084BT Selenium



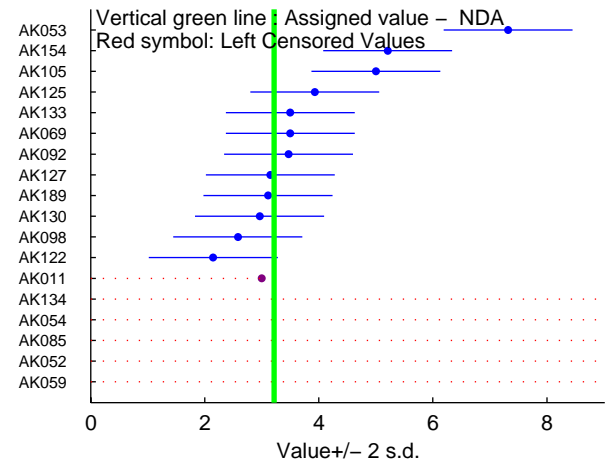
( $\Sigma$  OMF<sup>2</sup>) NDA



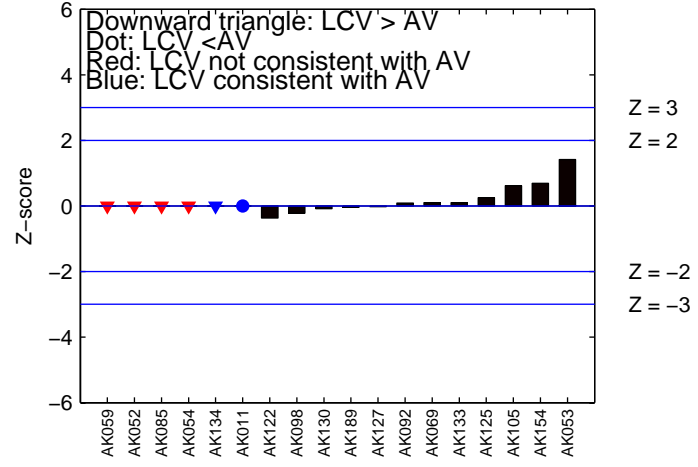
Kilt plot (overlap matrix) QTM084BT Silver



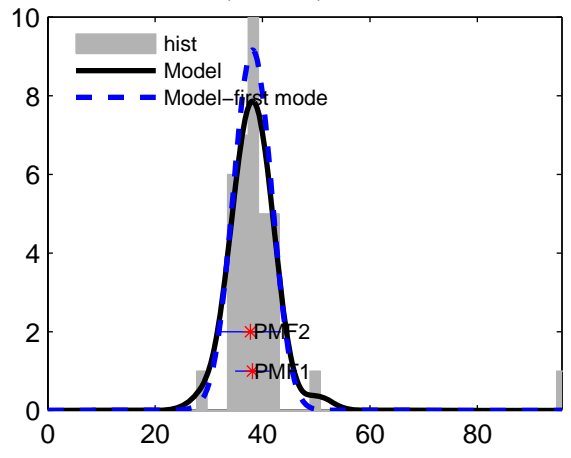
Ranked Overview – QTM084BT Silver



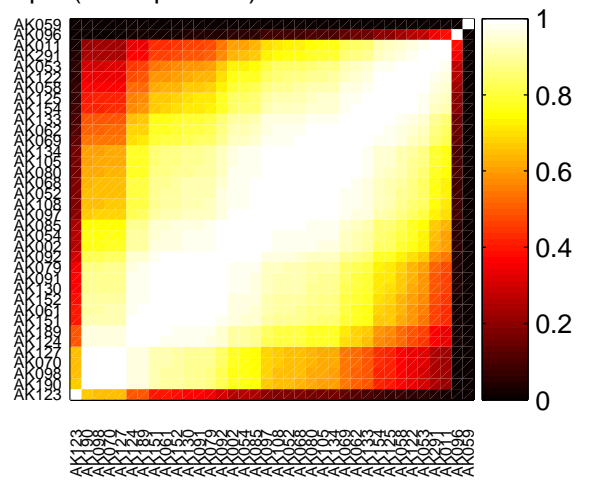
Ranked Z score – QTM084BT Silver



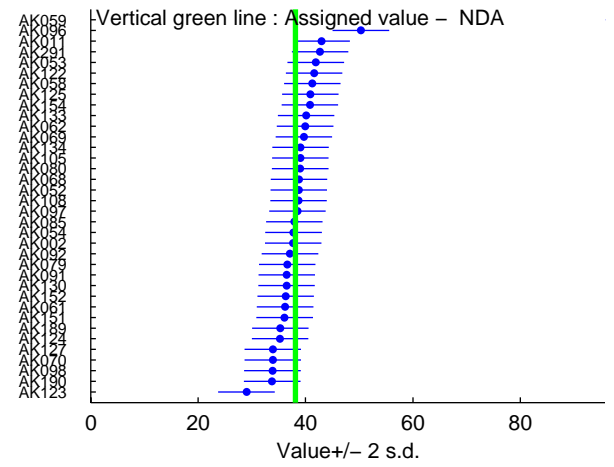
( $\sum OMF^2$ ) NDA



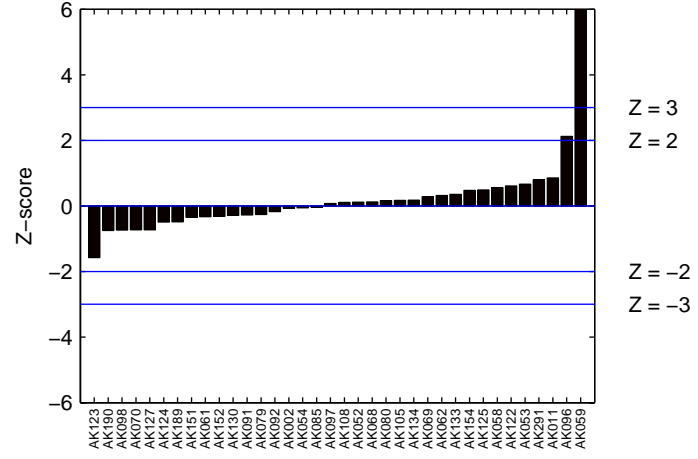
Kilt plot (overlap matrix) QTM084BT Zinc



Ranked Overview – QTM084BT Zinc

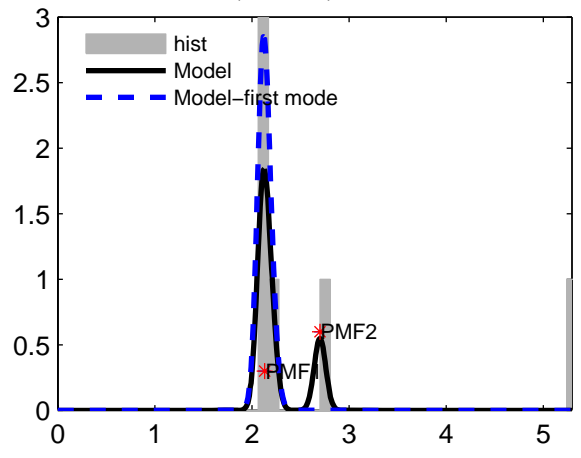


Ranked Z score – QTM084BT Zinc

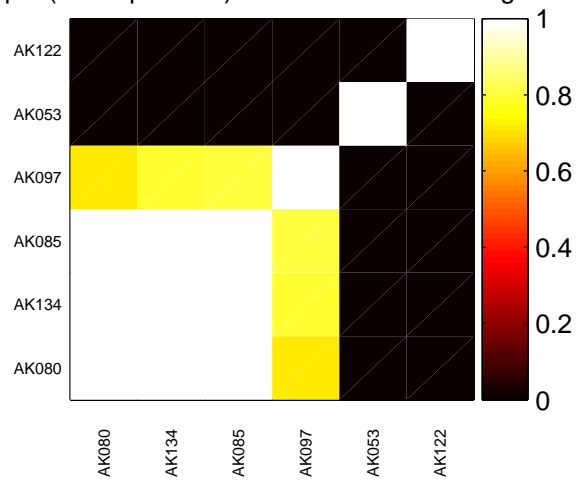




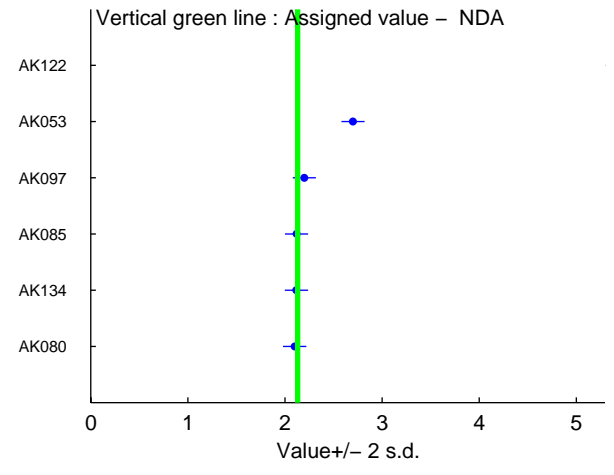
( $\Sigma$  OMF<sup>2</sup>) NDA



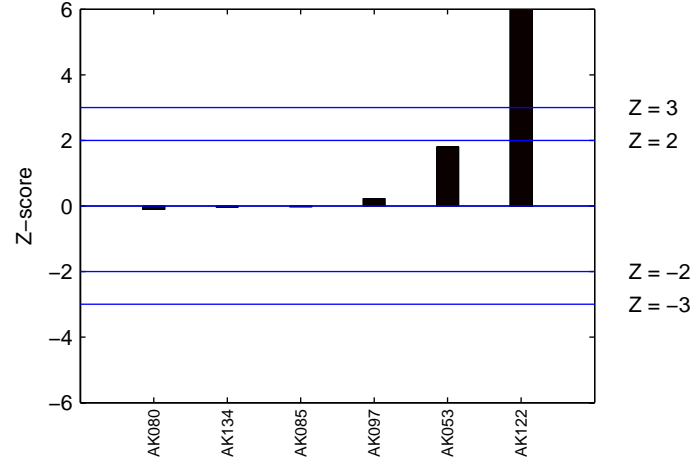
Kilt plot(overlap matrix) QTM084BT Ash-Weight



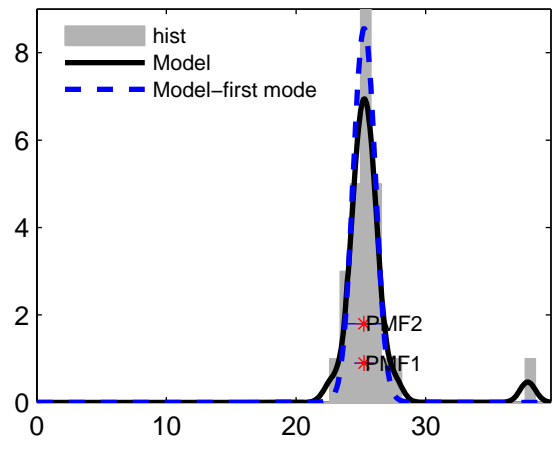
Ranked Overview – QTM084BT Ash-Weight



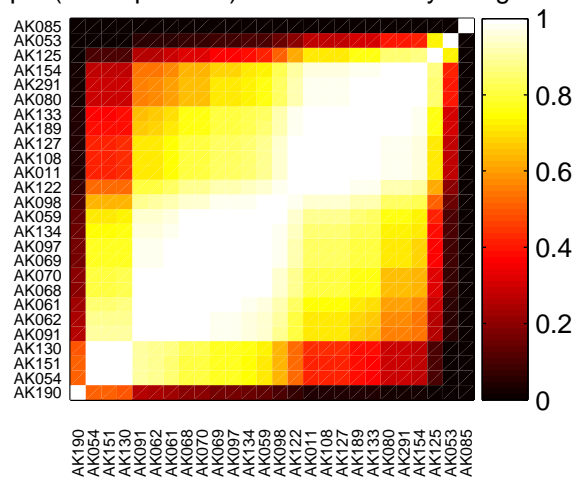
Ranked Z score – QTM084BT Ash-Weight



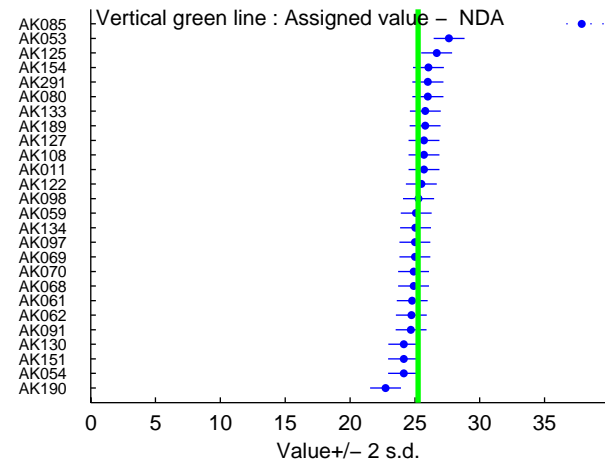
( $\Sigma OMF^2$ ) NDA



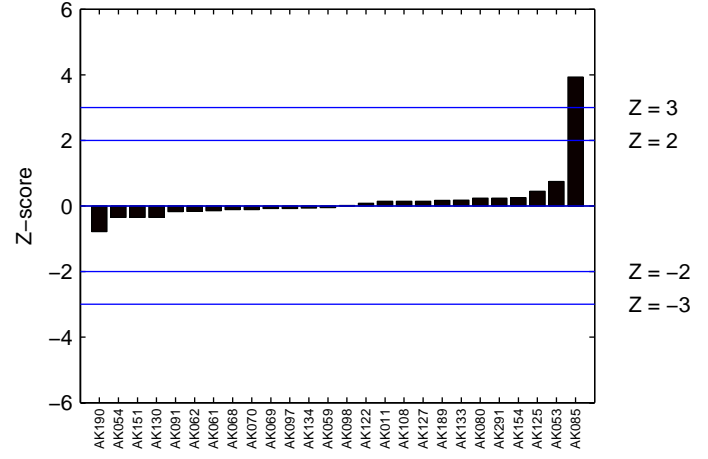
Kilt plot(overlap matrix) QTM084BT Dry-weight



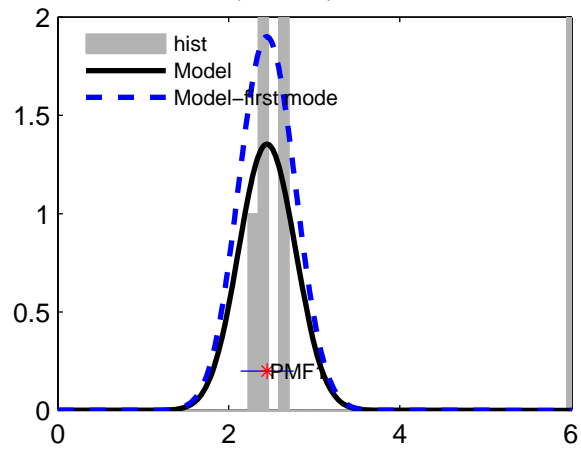
Ranked Overview – QTM084BT Dry-weight



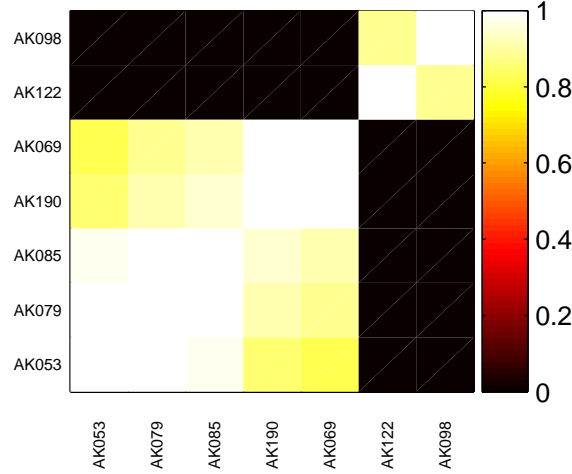
Ranked Z score – QTM084BT Dry-weight



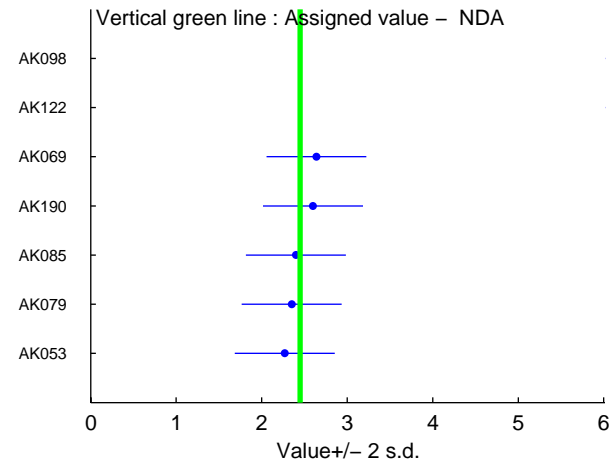
( $\sum OMF^2$ ) NDA



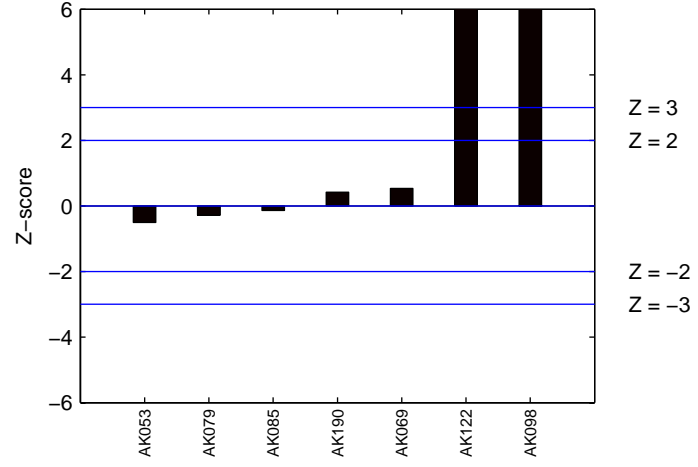
Kilt plot(overlap matrix) QTM084BT Total-Lipid



Ranked Overview – QTM084BT Total-Lipid



Ranked Z score – QTM084BT Total-Lipid



**Appendix II**  
**Method Codes - Exercise 859**



















# **Attachment B: SOIL-66 Final Report, Soil/Hazardous Waste Proficiency Testing**

Note: For reader convenience, this attachment is being reproduced verbatim and has not been revised through peer review or by the SFER production staff. This appendix was provided by Environmental Resource Associates, Arvada, CO, for the South Florida Water Management District.

Zdzislaw Kolasinski  
South Florida Water Mgt Dist  
Water Quality Analysis Div  
1480 Skees Rd Bldg #9  
West Palm Beach, FL 33411

**SOIL-66**



***Final Report***

# **Soil/Hazardous Waste Proficiency Testing**

**Soil Study**

**Open Date: 04/20/09**

**Close Date: 06/04/09**

**Report Issued Date: 06/25/09**

June 25, 2009

Zdzislaw Kolasinski  
South Florida Water Mgt Dist  
Water Quality Analysis Div  
1480 Skees Rd Bldg #9  
West Palm Beach, FL 33411

Enclosed is your final report for ERA's SOIL-66 Proficiency Testing (PT) study. Your final report includes an evaluation of all results submitted by your laboratory to ERA.

Data Evaluation Protocols: All analytes in ERA's SOIL-66 Proficiency Testing (PT) study have been evaluated using the following tiered approach. If the analyte is listed in the most current National Environmental Laboratory Accreditation Conference (NELAC) PT Field of Testing tables, the evaluation was completed by comparing the reported result to the acceptance limits generated using the criteria contained in the NELAC FoPT tables. If the analyte is not included in the NELAC FoPT tables, the reported result has been evaluated using the procedures outlined in ERA's Standard Operating Procedure for the Generation of Performance Acceptance Limits (SOP 0260).

Corrective Action Help: As part of your accreditation(s), you may be required to identify the root cause of any "Not Acceptable" results, implement the necessary corrective actions, and then satisfy your PT requirements by participating in a Supplemental (Quik™ Response) or future ERA PT study. ERA's technical staff is available to help your laboratory resolve any technical issues that may be impairing your PT performance and possibly affecting your routine data quality. Our laboratory and technical staff have well over three hundred years of collective experience in performing the full range of environmental analyses. As part of our technical support, ERA offers QC samples that can be helpful in helping you work through your technical issues.

Thank you for your participation in ERA's SOIL-66 Proficiency Testing study. If you have any questions, please contact Shawn Kassner, Proficiency Testing Manager, or Curtis Wood, Director of Regulatory Affairs and Business Development, at 1-800-372-0122.

Sincerely,



Shawn Kassner  
Proficiency Testing Manager



Jay R. McBurney  
Quality Program Manager

attachments  
smk

<b>Report Recipient</b>	<b>Contact/Phone Number</b>	<b>Reporting Type</b>
Florida	Steve Arms / 904-791-1502	All Analytes



# SOIL-66 Definitions & Study Discussion

Study Dates: 04/20/09 - 06/04/09

Report Issued: 06/25/09

## SOIL Study Definitions

The Reported Value is the value that the laboratory reported to ERA.

The ERA assigned value for the Organic Proficiency Testing Standards is equal to 100% of the parameter present in the standard as determined by gravimetric and/or volumetric measurements made during standard preparation as applicable. The ERA assigned value for the Inorganic Proficiency Testing Standards, with the exception of the TCLP Metals in Soil, is equal to the maximum amount of the parameter available in the standard by applicable EPA methodologies. The ERA assigned value for the TCLP metals is equal to the mean of ERA's internal analytical analyses. All NELAC parameters not added to a standard are given an assigned Value of "0", per the guidance issued by the NELAC Board of Directors, on December 14, 2000. Non-NELAC parameters not added to a standard may be given an assigned value of less than a minimum verified concentration as determined in the background soil for applicable EPA methodologies.

The Acceptance Limits are established per the NELAC PT program criteria or ERA's SOP for the Generation of Performance Acceptance Limits™ as applicable.

The Performance Evaluation:

- Acceptable = Reported Value falls within the Acceptance Limits.
- Not Acceptable = Reported Value falls outside the Acceptance Limits.
- No Evaluation = Reported Value cannot be evaluated.
- Not Reported = No Value reported.

The Method Description is the method the laboratory reported to ERA.

## SOIL Study Discussion

ERA's SOIL-66 Proficiency Testing (PT) study has been reviewed by ERA senior management and certified compliant with the requirements of the National Environmental Laboratory Accreditation Conference (NELAC), Proficiency Testing Program Standards, Chapter 2, July 2003.

Per the requirements of the NELAC Proficiency Testing Program, a full review of all homogeneity, stability, and accuracy verification data was completed. All analytical verification data for all analytes in the Soil study standards met the acceptance criteria contained in the NELAC Proficiency Testing Program Standards, Chapter 2, July 2003. If the analyte is included in the NELAC Fields of Testing list the acceptance limits were calculated based on the NELAC Proficiency Testing Program Standards, Chapter 2, July 2003. If the analyte is not included in the NELAC Fields of Testing list, the acceptance limits were calculated using the procedures outlined in ERA's Standard Operating Procedure for the Generation of Performance Acceptance Limits (SOP 0260, Rev. 2.0).

The data submitted by participating laboratories was also examined for study anomalies. There were no anomalies observed during the statistical review of the data.

ERA's SOIL-66 Proficiency Testing study reports shall not be reproduced except in its entirety and not without the permission of the participating laboratory. The report must not be used by the participating laboratories to claim product endorsement any agency of the U. S. government.

The data contained herein are confidential and intended for your use only.

If you have any questions or concerns regarding your assessment in ERA's SOIL Proficiency Testing program, please contact Shawn Kassner, Proficiency Testing Manager, or Curtis Wood, Director of Regulatory Affairs and Business Development, at 1-800-372-0122.



Study: **SOIL-66**

ERA Customer Number: **S421405**

Laboratory Name: **South Florida Water Mgt  
Dist**

## Inorganic Results



# SOIL-66 Final Complete Report

Zdzislaw Kolasinski  
 Sr Scientist  
 South Florida Water Mgt Dist  
 Water Quality Analysis Div  
 1480 Skees Rd Bldg #9  
 West Palm Beach, FL 33411  
 561-681-2500

EPA ID: FL00103  
 ERA Customer Number: S421405  
 Report Issued: 06/25/09  
 Study Dates: 04/20/09 - 06/04/09

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
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**SOIL Metals in Soil (cat# 620)**

1000	Aluminum	mg/kg		12100	4890 - 16300	Not Reported	
1005	Antimony	mg/kg		262	26.2 - 288	Not Reported	
1010	Arsenic	mg/kg		113	74.2 - 139	Not Reported	
1015	Barium	mg/kg		344	245 - 417	Not Reported	
1020	Beryllium	mg/kg		79.2	54.8 - 93.5	Not Reported	
1025	Boron	mg/kg		176	98.5 - 205	Not Reported	
1030	Cadmium	mg/kg		263	179 - 308	Not Reported	
1035	Calcium	mg/kg		9880	7310 - 12100	Not Reported	
1040	Chromium	mg/kg		87.2	55.5 - 106	Not Reported	
1050	Cobalt	mg/kg		93.6	63.8 - 108	Not Reported	
1055	Copper	mg/kg		68.8	47.7 - 82.9	Not Reported	
1070	Iron	mg/kg		18700	7820 - 29000	Not Reported	
1075	Lead	mg/kg		118	76.4 - 138	Not Reported	
1085	Magnesium	mg/kg		4220	2850 - 5340	Not Reported	
1090	Manganese	mg/kg		443	345 - 556	Not Reported	
1095	Mercury	mg/kg	2.81	2.82	1.50 - 4.41	Acceptable	EPA 7473
1100	Molybdenum	mg/kg		55.1	31.1 - 63.1	Not Reported	
1105	Nickel	mg/kg		108	69.9 - 124	Not Reported	
1125	Potassium	mg/kg		4970	2950 - 6040	Not Reported	
1140	Selenium	mg/kg		195	121 - 234	Not Reported	
1150	Silver	mg/kg		49.0	30.6 - 61.7	Not Reported	
1155	Sodium	mg/kg		1100	642 - 1480	Not Reported	
1160	Strontium	mg/kg		105	72.6 - 134	Not Reported	
1165	Thallium	mg/kg		303	190 - 355	Not Reported	
1175	Tin	mg/kg		202	111 - 254	Not Reported	
1180	Titanium	mg/kg		447	0.00 - 826	Not Reported	
1185	Vanadium	mg/kg		130	77.6 - 152	Not Reported	
1190	Zinc	mg/kg		396	274 - 483	Not Reported	



# **Attachment C: SOIL-68 Final Report, Soil/Hazardous Waste Proficiency Testing**

Note: For reader convenience, this attachment is being reproduced verbatim and has not been revised through peer review or by the SFER production staff. This appendix was provided by Environmental Resource Associates, Arvada, CO, for the South Florida Water Management District.

Zdzislaw Kolasinski  
South Florida Water Mgt Dist  
Water Quality Analysis Div  
1480 Skees Rd Bldg #9  
West Palm Beach, FL 33411

**SOIL-68**



***Final Report***

# **Soil/Hazardous Waste Proficiency Testing**

**Soil Study**

**Open Date: 10/19/09**

**Close Date: 12/03/09**

**Report Issued Date: 12/21/09**

December 21, 2009

Zdzislaw Kolasinski  
South Florida Water Mgt Dist  
Water Quality Analysis Div  
1480 Skees Rd Bldg #9  
West Palm Beach, FL 33411

Enclosed is your final report for ERA's SOIL-68 Proficiency Testing (PT) study. Your final report includes an evaluation of all results submitted by your laboratory to ERA.

Data Evaluation Protocols: All analytes in ERA's SOIL-68 Proficiency Testing (PT) study have been evaluated using the following tiered approach. If the analyte is listed in the most current National Environmental Laboratory Accreditation Conference (NELAC) PT Field of Testing tables, the evaluation was completed by comparing the reported result to the acceptance limits generated using the criteria contained in the NELAC FoPT tables. If the analyte is not included in the NELAC FoPT tables, the reported result has been evaluated using the procedures outlined in ERA's Standard Operating Procedure for the Generation of Performance Acceptance Limits (SOP 0260).


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Thank you for your participation in ERA's SOIL-68 Proficiency Testing study. If you have any questions, please contact Shawn Kassner, Proficiency Testing Manager, or Curtis Wood, Director of Regulatory Affairs and Business Development, at 1-800-372-0122.

Sincerely,



Shawn Kassner  
Proficiency Testing Manager



Jay R. McBurney  
Quality Program Manager

attachments  
smk

<b>Report Recipient</b>	<b>Contact/Phone Number</b>	<b>Reporting Type</b>
Florida	Steve Arms / 904-791-1502	All Analytes

# SOIL-68 Definitions & Study Discussion

**Study Dates: 10/19/09 - 12/03/09**

**Report Issued: 12/21/09**

## SOIL Study Definitions

The Reported Value is the value that the laboratory reported to ERA.

The ERA assigned value for the Organic Proficiency Testing Standards is equal to 100% of the parameter present in the standard as determined by gravimetric and/or volumetric measurements made during standard preparation as applicable. The ERA assigned value for the Inorganic Proficiency Testing Standards, with the exception of the TCLP Metals in Soil, is equal to the maximum amount of the parameter available in the standard by applicable EPA methodologies. The ERA assigned value for the TCLP metals is equal to the mean of ERA's internal analytical analyses. All NELAC parameters not added to a standard are given an assigned Value of "0", per the guidance issued by the NELAC Board of Directors, on December 14, 2000. Non-NELAC parameters not added to a standard may be given an assigned value of less than a minimum verified concentration as determined in the background soil for applicable EPA methodologies.

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The Method Description is the method the laboratory reported to ERA.

## SOIL Study Discussion

ERA's SOIL-68 Proficiency Testing (PT) study has been reviewed by ERA senior management and certified compliant with the requirements of the National Environmental Laboratory Accreditation Conference (NELAC), Proficiency Testing Program Standards, Chapter 2, July 2003.

Per the requirements of the NELAC Proficiency Testing Program, a full review of all homogeneity, stability, and accuracy verification data was completed. All analytical verification data for all analytes in the Soil study standards met the acceptance criteria contained in the NELAC Proficiency Testing Program Standards, Chapter 2, July 2003. If the analyte is included in the NELAC Fields of Testing list the acceptance limits were calculated based on the NELAC Proficiency Testing Program Standards, Chapter 2, July 2003. If the analyte is not included in the NELAC Fields of Testing list, the acceptance limits were calculated using the procedures outlined in ERA's Standard Operating Procedure for the Generation of Performance Acceptance Limits (SOP 0260, Rev. 2.0).

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Study: **SOIL-68**

ERA Customer Number: **S421405**

Laboratory Name: **South Florida Water Mgt  
Dist**

## Inorganic Results



# SOIL-68 Final Complete Report

Zdzislaw Kolasinski  
 Sr Scientist  
 South Florida Water Mgt Dist  
 Water Quality Analysis Div  
 1480 Skees Rd Bldg #9  
 West Palm Beach, FL 33411  
 561-681-2500

EPA ID: FL00103  
 ERA Customer Number: S421405  
 Report Issued: 12/21/09  
 Study Dates: 10/19/09 - 12/03/09

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
<b>SOIL Metals in Soil (cat# 620)</b>							
1000	Aluminum	mg/kg		14000	5030 - 16600	Not Reported	
1005	Antimony	mg/kg		252	25.2 - 277	Not Reported	
1010	Arsenic	mg/kg		102	66.6 - 126	Not Reported	
1015	Barium	mg/kg		204	141 - 245	Not Reported	
1020	Beryllium	mg/kg		114	80.1 - 134	Not Reported	
1025	Boron	mg/kg		129	66.4 - 156	Not Reported	
1030	Cadmium	mg/kg		200	136 - 234	Not Reported	
1035	Calcium	mg/kg		13000	8260 - 14300	Not Reported	
1040	Chromium	mg/kg		145	115 - 212	Not Reported	
1050	Cobalt	mg/kg		190	133 - 224	Not Reported	
1055	Copper	mg/kg		188	136 - 225	Not Reported	
1070	Iron	mg/kg		22900	8340 - 30000	Not Reported	
1075	Lead	mg/kg		139	95.2 - 167	Not Reported	
1085	Magnesium	mg/kg		3320	1900 - 3890	Not Reported	
1090	Manganese	mg/kg		384	286 - 468	Not Reported	
1095	Mercury	mg/kg	7.39	14.1	3.82 - 15.5	Acceptable	EPA 7473
1100	Molybdenum	mg/kg		86.0	51.8 - 99.0	Not Reported	
1105	Nickel	mg/kg		88.5	59.8 - 107	Not Reported	
1125	Potassium	mg/kg		2230	1270 - 3050	Not Reported	
1140	Selenium	mg/kg		126	74.1 - 151	Not Reported	
1150	Silver	mg/kg		44.1	27.3 - 55.3	Not Reported	
1155	Sodium	mg/kg		263	55.5 - 370	Not Reported	
1160	Strontium	mg/kg		170	114 - 210	Not Reported	
1165	Thallium	mg/kg		209	134 - 254	Not Reported	
1175	Tin	mg/kg		138	76.1 - 182	Not Reported	
1180	Titanium	mg/kg		488	0.00 - 816	Not Reported	
1185	Vanadium	mg/kg		109	69.9 - 141	Not Reported	
1190	Zinc	mg/kg		180	116 - 221	Not Reported	

