

**Analysis of Water Quality Monitoring Data
from A.R.M. Loxahatchee National Wildlife Refuge**

prepared for

U.S. Department of the Interior

by

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Introduction

This report summarizes water quality data collected by the U.S. Fish & Wildlife Service (USFWS) in and around Arthur R. Marshall Loxahatchee National Wildlife Refuge over the past several years. Data have been collected under three programs:

- Marsh Stations
- Refuge Inflows
- Atmospheric Deposition Stations

Monitoring station locations are shown in Figure 1. In each case, samples and field measurements have been collected by Refuge staff. Phosphorus analyses have been performed by the Southeast Environmental Research Laboratory at Florida International University (FIU). The data sets were provided by Refuge staff in June 1999 and generally reflect data collected through January 1999.

Marsh and inflow results are compared with data collected at similar locations and dates by South Florida Water Management District (SFWMD). For simplicity, the two data sets are identified by laboratory ('FIU' vs. 'SFWMD'), although the FIU data actually reflect a joint effort by Refuge staff and the FIU lab. Atmospheric deposition rates are compared with results of other studies conducted in South Florida.

Recommendations for future monitoring will be developed after review and discussion of these results with Refuge staff. Recommendations will be based upon redundancy with SFWMD programs, consistency with SFWMD results, relative costs, and the potential value of the data in supporting future management decisions.

Marsh Stations

Monitoring Program

Since 1994, the 14 interior marsh stations in the Refuge used for tracking compliance with the Settlement Agreement have been monitored simultaneously by the SFWMD and by USFWS/FIU. Samples have also been collected at two marsh stations downstream of the S5A and S6 inflow pump stations. Station locations are shown in Figure 1. Stations are reached by helicopter and sampled monthly.

Sampling Variability Study

In 1997-1998, a special study was conducted to evaluate potential impacts of water depth on the reproducibility of marsh phosphorus measurements. The study was undertaken because of concerns about potential contamination of samples collected when water depths are low (<10-20 cm). The study involved collection of triplicate samples by each lab at each station.

A previous analysis of SFWMD results (Walker, 1999) indicated that variability among replicates was independent of water depth in the 10-120 cm range. It was recommended that samples be collected routinely at depths down to 10 cm. A variance component analysis indicated that continued collection of triplicate samples would not significantly improve the precision of marsh geometric means computed on a monthly or annual basis. It was therefore recommended that routine monitoring involve single samples at each station, with replicates collected only as required under normal QA/QC protocol.

USFWS/FIU results from the same period are summarized below. Conclusions and recommendations regarding replicate variability and sampling protocol are identical to those based upon SFWMD data. Results are summarized in the following:

Table 1	Marsh Total P Concentration Data
Table 2	Marsh Water Depths
Table 3	Data from Replicate Sampling Period
Table 4	Variance Components of Marsh Phosphorus Data
Figure 3	Variability among Replicates vs. Water Depth
Figure 4	Variability among Replicates vs. Stage

Tables 1-3 are in the same format used to summarize SFWMD data (Walker, 1999). The entire USFWS/FIU data set extends from December 1992 through December 1998. Water depths were recorded in the database starting in October 1995.

Triplicate samples were collected between April 1998 and December 1998 (vs. August 1997 - December 1998 by SFWMD). For other periods, it is believed that phosphorus analytical results reported to the Refuge by FIU typically represented the average of duplicate analyses performed on the same sample. Prior to April 1998, the individual

duplicate results were not recorded in the database (averages only), so that stations and dates with duplicate analyses cannot be specifically identified and variability among replicates can be assessed for April-December 1998 samples only.

The lower detection limit in the SFWMD data set is 4 ppb. The FIU lab does not specify a detection limit and reports concentrations below 1 ppb. To provide a valid comparison with SFWMD results, FIU results have been adjusted to a minimum concentration of 4 ppb (i.e. FIU values less than 4 ppb have been set equal to 4 ppb). This is the protocol used in computing marsh geometric means for testing compliance with Settlement Agreement limits.

Table 4 lists variance components estimated from each data set for the August 1997-December 1998. The temporal, spatial, and replicate variance components are remarkably similar between the SFWMD and USFWS/FIU data sets. In fact, the variability among replicates was identical (0.18 expressed as a ln-scale standard deviation). This approximately corresponds to a relative standard deviation of 18% among replicate samples collected at the same station and date, when analyzed by the same laboratory.

Variability among replicates for each lab is plotted against water depth in Figure 2 and against stage in Figure 3. Significant correlations between replicate variability and depth/elevation are not evident in either data set. Therefore, conclusions reached previously based upon the SFWMD data are supported by the USFWS/FIU data. Routine sampling of marsh stations at water depths down to 10-cm is possible without introducing significant variability, provided that samples are collected under the same protocol used in the 1997-1998 study.

Between-Lab Variations

Conclusions of the sampling variability study are based upon analysis of each data set independently. This section combines the data sets and examines between-lab variations. Figure 4 plots the differences between FIU and SFWMD results with observations paired by station and month. The differences are expressed on linear and logarithmic scales. To reflect the standard sampling protocol, each pairing is based upon a single observation from each lab (i.e., replicate samples are not used). The comparisons are made for the 1994-1998 period, when data from both agencies were available. In any given month, the difference between the data sets represents the combined effect of sampling variations and analytical variations. In the 1997-1998 period, the between-lab variability is 40% (root mean square deviation of $\ln(TP_{FIU}/TP_{SFWMD}) = 0.40$). This is larger than expected based upon the 18% replicate variability estimated separately for each lab. If sampling and analytical variations were truly random, the expected standard deviation would be computed from the replicate variances $[0.18^2 + 0.18^2]^{1/2} = 25\%$.

It is hypothesized that the discrepancy reflects random variance between labs associated with sampling date. This would reflect random date-to-date variations in factors associated with collecting and processing a given batch of samples, possibly related to

sample bottle preparation, person collecting samples, sample preservation, holding times, reagents, standards, and/or instrument calibration. When the variance components are estimated separately for each lab, this factor represents a portion of the total variance among dates.

The variance component model previously calibrated to each lab separately was of the following form (Walker, 1999):

$$V_T = V_D + V_{DS} + V_{DSR}$$

where,

- V variance component (squared natural logarithm of total P concentration, ppb)
- T total variance
- D variance among dates
- DS variance among stations for a given date
- DSR variance among replicates for a given station and date

Parameter estimates for SFWMD data are ($V_D \sim 0.041$, $V_{DS} \sim 0.048$, $V_{DSR} \sim 0.033$). as compared with ($V_D \sim 0.063$, $V_{DS} \sim 0.052$, $V_{DSR} \sim 0.033$) for FIU data (Table 4). A revised model accounting for random variance between labs on a given date would be of the following form:

$$V_T = V_D + V_{DL} + V_{DLS} + V_{DLSR}$$

where,

- V variance component
- T total variance
- D variance among dates
- DL variance among laboratories on a given date
- DLS variance among stations for a given laboratory and date
- RSLD variance among replicates for a given station, laboratory, and date

Parameter estimates for the revised model (Table 4) indicate that most of the variance among dates is attributed to factors associated with lab and date, as opposed to true temporal variations in the marsh (i.e., $V_D \sim 0.007$, $V_{DL} \sim 0.059$, $V_{DLS} \sim 0.050$, $V_{DLSR} \sim 0.033$).

The lab-related variance ($V_{LD} = 0.059$) corresponds to a standard deviation of 24%. This represents a pooled estimate for both labs; it is possible that it could be higher for one lab than for the other. With a geometric mean of 10 ppb, the standard deviation would be 2.4 ppb on a linear scale. This value is below the SFWMD detection limit of 4 ppb. The importance of random lab-related variance is not unexpected, given the difficulties associated with sample collection and phosphorus analysis in low concentration ranges.

With these coefficients, the expected variance between labs in samples paired by station and date would be:

$$\text{Var} (Y_{DS1} - Y_{DS2}) = 2 (V_{DL} + V_{DLSR}) = 2 (0.059 + 0.033) = 0.184$$

where Y_{DS1} = natural logarithm of lab 1 concentration for date D and station S. This corresponds to a paired-sample standard deviation of 43% ($\sim[0.184]^{1/2}$), compared with the observed standard deviation of 40% (Figure 3).

Figure 5 plots differences between marsh geometric means paired by date. To provide a true pairing of the two data sets, geometric means are computed for each month using only data from stations sampled by both agencies. In the August 1997 - December 1998 period, the between-lab variability in marsh geometric means was 37%. With an average of 11.3 stations sampled on each date and 1 sample at each station, the expected variance between labs in the marsh geometric means across dates would be:

$$\text{Var} (Y_{DM1} - Y_{DM2}) = 2 (V_{DL} + V_{DLSR}/11.3) = 2 (0.059 + 0.033/11.5) = 0.124$$

where Y_{DM1} = natural logarithm of lab 1 concentration for date D averaged over all stations. This corresponds to a standard deviation of 35% ($\sim[0.124]^{1/2}$), as compared with the observed value of 37%. In the absence of a lab/date variance component ($V_{LD}=0$), the expected standard deviation in the paired marsh geometric means would be only 8% (Table 4).

Figure 6 plots the FIU marsh geometric means against the SFWMD geometric means for the 1994-1998 period. The weak correlation ($r = 0.18$) is consistent with the variance components estimated above (Table 4). Only ~9% of the total variance in the measured geometric means across dates reflects true temporal variations in the marsh (i.e., a true signal). The remainder reflects random variations associated with the laboratory, spatial, and replicate variance components. Implications for tracking compliance are discussed below.

A similar variance component analysis has been conducted for the two marsh stations located downstream of the S5A and S6 pump stations (Table 4). Figure 7 plots concentrations and between-lab differences as a function of time and station. In the August 1997 - December 1998 period, the observed standard deviation of the paired differences between lab results for each station and date was 0.22 for the inflow stations, as compared with 0.40 for the marsh stations (Figure 4). The estimated inter-lab variance component is $V_{DL} = 0.018$ (14%), as compared with 0.059 (24%) for the interior marsh stations. The estimated replicate variance component is $V_{DLSR} = 0.004$ (6.4%) as compared with 0.033 (18%) for the interior marsh stations. Lower values for the inflow stations may reflect the higher concentration ranges, which would be associated with greater analytical precision (on a percentage basis), less inter-lab variability, and less risk of contamination during the sampling process. The relatively high spatial variance component ($V_{DLS} = 0.289$ vs. 0.05 for marsh stations) reflects significant differences between the S5AD vs. S6 concentrations.

The following table compares laboratory and replicate variance components for Refuge marsh stations with values derived from the Everglades Round Robin (ERR) dataset compiled by the Florida Department of Environmental Protection :

Data Set	Laboratory	Replicate	Total
Refuge Interior Marsh	24%	18%	30%
Refuge S5A/S6D	14%	6%	15%
ERR - All Samples	27%	16%	31%
ERR - Low Conc.	30%	18%	35%
ERR - High Conc.	16%	5%	17%

The ERR data are from Rounds 2-8 and from the following laboratories: Duke School of the Environment, US Sugar Research, FDEP, SFWMD, & FIU. Triplicate or quadruplicate analyses were conducted by each lab on total of 38 samples. Variance components are similar to those derived from the Refuge datasets. For both datasets, the laboratory and replicate variance components are larger in samples in the low concentration range (<20 ppb). The slightly higher lab components for the ERR dataset may reflect the fact that a wider array of labs is considered.

The ERR replicates were derived from split samples, whereas the Refuge replicates were derived from separate samples taken at the same location. Theoretically, the ERR results do not include sampling variations. Given that the replicate variance components are similar between the two datasets, most of the variance among replicates at marsh stations is apparently due to analytical variations, as opposed to sampling variations. This further indicates that variability associated with sample collection is not a major factor influencing the tracking of marsh phosphorus levels.

The variance components estimated above are potentially useful for designing marsh monitoring networks to track monthly, annual, or long-term geometric means to within a specified level of precision. These may have future application in testing compliance with the numeric phosphorus criterion being developed by FDEP.

Implications for Tracking Compliance with Settlement Agreement

The monthly geometric means across the interior marsh stations are used for tracking compliance with the Settlement Agreement. Figure 8 plots marsh geometric means from each data set along with interim and long-term limits computed from stage. The observed values do not correspond exactly to those used for tracking compliance because they are computed using data from stations sampled by both labs on each date. This is a minor distinction that would influence results only on dates when one or more sample was not collected or lost by either lab.

As discussed above, random sampling and analytical variations account for most of the month-to-month variance in the measured marsh geometric means. These variations do not pose a problem in tracking compliance because they are implicit in the derivation of the marsh limits. The total variance in the observed geometric means attributed to analytical and sampling variations ($V_{DL} + V_{DLR}/11.3$) is 0.062. This corresponds to a

standard error of ~25% in the measured geometric mean for any month. The residual standard error in the ln(TP) vs. stage regression used to derive the interim and long-term limits is ~31% (SFWMD, 1992). It is likely that measurement error in the marsh geometric mean accounts for most of the residual variance.

Although the determination of compliance on any given date may be strongly dependent on sampling/analytical variations, this risk is built into the compliance test. The test was designed with a maximum Type I error of 10% (i.e., a 10% probability that the measured geometric mean will exceed the limit when the true geometric mean equals that which would have occurred during the 1978-1979 based period at the current stage). In the 1994-1998 period, the interim limit was exceeded in 9% and 12% of the months based upon the SFWMD and FIU data, respectively. The long-term limit was exceeded in 17% and 22%, respectively. Using a binary paired t-test (exceedence in a given month = 0 or 1), the difference in average exceedence frequencies between labs is not significantly different from zero ($p = 0.54$ for interim limits, $p = 0.49$ for long-term limits, 58 months). Similar conclusions are reached using the binomial distribution (Snedecor & Cochran, 1989) to estimate the standard errors of the observed exceedence frequencies.

Periods of systematic differences reflecting possible bias in the results from one or both labs are evident in Figure 8 (e.g., FIU results generally lower than SFWMD results in early 1998). The nature of these differences cannot be determined from this data set. As compared with the random variations evaluated above, these are of greater concern in tracking compliance. Strict adherence to QA/QC procedures is necessary to reduce risk of bias.

Refuge Inflow Monitoring

Table 5 lists phosphorus measurements at 10 stations located in the vicinity of the Everglades Nutrient Removal Project and other Refuge inflow points. A variety of codes were used to identify stations in the database. These codes have been translated into a set that is consistent with SFWMD station codes, as indicated in Table 6. Station locations are shown in Figure 1. Sampling frequencies are biweekly for the USFWS/FIU data and weekly or biweekly for the corresponding SFWMD data.

Comparisons with SFWMD results are shown in the following Figures:

- Figure 9 ENR Project Inflow
- Figure 10 ENR Project Outflow
- Figure 11 L7 Canal at Junction of ENRP Cells 1 & 3
- Figure 12 Upstream of S5A Pump Station

In general, sampling dates for the USFWS/FIU data did not correspond with sampling dates for the SFWMD data. Comparisons in Figures 9-12 are based upon monthly averages. At the ENR Project inflow and outflow stations, the SFWMD data consist of both grab and composite samples. All SFWMD data have been used in the comparisons. Comparison results are similar when only grab samples are used.

Sufficient samples are not yet available for comparing results at the ACME pump stations.

With the possible exception of the ENRP outflow station, there is reasonable agreement between the FIU & SFWMD results at these stations. At the ENRP outflow (Figure 10), the FIU results were generally higher than the SFWMD results in the early portion of the record (1994 thru early 1996, geometric means = 34 vs. 25 ppb) and generally lower than the SFWMD results in the later portion of the record (1997 thru early 1999, 16 vs. 20 ppb). The reason for these differences is unknown. They may be related to differences in the locations of sample collection (from middle of channel vs. bank), although the precise locations are not documented in the database. More recently, both agencies have been collecting samples from a platform that was installed at mid-channel upstream of the G251 pump station, so any effect of sample location would be factored out.

Figure 13 compares USFWS/FIU samples collected upstream and downstream of the ENR project outflow pump station (G251). SFWMD does not sample downstream of G251. The downstream values are slightly higher (geometric mean = 23.5 vs. 21.2 ppb). Based upon a paired t-test, the 13% difference is significantly different from zero ($p = 0.017$). The data plots indicate, however, that difference is attributed largely to high concentrations measured at the downstream station on 6 sampling dates. Agreement is better for the bulk of the data points. The median paired difference is only 5%.

It is possible that the upstream/downstream difference is related to difficulties in collecting a representative sample downstream of the pump station, given the turbulence, potential scouring of bottom sediments, potential entrainment of particulate matter from adjacent marsh areas, and spatial variations in the flow velocities related to the particular set of pumps that were running during the sampling event. When more than one pump is running, for example, it is not clear how a single grab sample can be collected to represent the entire cross-section. From a mass-balance perspective, there is no reason to expect that the phosphorus concentrations would actually increase as the water moves through the pumps. If the upstream and downstream samples could be collected in precisely the same way and with the same risk of contamination, no significant difference would be expected.

Atmospheric Deposition Monitoring

Monitoring Program

Measurements of atmospheric phosphorus deposition are potentially important for defining background phosphorus loads to Everglades marshes, evaluating anthropogenic impacts on atmospheric loads, and providing data for designing wetland treatment areas. Atmospheric deposition has been measured at 4 locations in the Refuge since February 1993 (Figure 1). Integrated samples have been collected at a weekly frequency using Aerochem[®] automated wet and dry deposition collectors. Corresponding rainfall volume estimates are derived from water volumes collected in the wet deposition collectors. Walker & Jewell (1997) presented a summary of the data

collected through July 1997. The following section discusses data collected through September 1998.

Atmospheric deposition rates provide one measure of background phosphorus loads to the marsh. Ideally, the measurements would reflect the net deposition from atmospheric sources outside of the marsh. Sources would be natural and anthropogenic in origin. The observed frequent contamination of samples with bird droppings, insects, and vegetation suggests that some portion of the measured phosphorus deposition reflects local recycling of phosphorus from surrounding marsh areas. Contamination problems reflect continuous exposure of the wet or dry collectors and their function as a convenient roosting site for birds. Measurement of dry deposition in general is fraught with a variety of problems related to particle dynamics (Redfield, 1998; McDowell et al., 1997).

To provide a partial basis for evaluating contamination effects, samples have been visually inspected and a database has been developed on the presence or absence of contaminants in various categories (bird droppings, other material of animal origin, insects, spider webs, vegetation, unidentified organic material, & ash). Table 7 summarizes contamination frequencies at each station. Samples were discarded in situations where gross contamination of the wet or dry collectors were evident (usually with bird or animal droppings). Depending upon quantity and type, contamination of some samples may go undetected. In addition, materials in the above categories may partially reflect sources outside of the marsh (e.g., ash). Specific identification of contaminant types can be difficult. Unidentified organic material identified in some samples may have actually reflected bird droppings. For the above reasons, a complete separation or removal of contaminant effects is not possible, but the sensitivity of deposition rates to contaminants in various categories can be explored.

Effects of contamination on dry deposition rates may have been reduced by removing gross particles from the collector surface before extracting the sample. This process would be less effective in the wet collectors where particle decomposition and/or leaching would be likely to occur before the sample is collected.

Wet and dry deposition rates have been computed from the volume of water (rainfall + dilution water), surface area of the collectors (0.0651 m^2), and measured phosphorus concentration. For each sampling interval, deposition rates have been expressed on an annual basis ($\text{mg}/\text{m}^2\text{-yr}$). The nominal sample collection interval was 7 days. Based upon examination of scatter plots (deposition rate vs. collection interval), samples collected over intervals exceeding 14 days had relatively low deposition rates and have been excluded from the analysis described below. Dry deposition samples containing more than 100 ml of rainwater (reflecting failure of the device to close during rainfall periods) have been excluded. Samples with droppings and other animal matter (frogs, feathers, etc.) have been excluded because they were most likely to reflect contamination from internal marsh sources.

As shown in Figure 1, stations are generally located in the central to southern portion of the Refuge and consist of two perimeter stations (West, L-1) and two interior stations (1-

7, 1-9). Stations L-1, 1-7, and 1-9 are located in sloughs/wet prairies interspersed with tree islands. The West station is located in a sawgrass marsh without tree islands. Refuge staff report a greater frequency of bird roosting and contamination at the West station, possibly because of the absence of tree islands as alternative roosting sites. As discussed below, deposition rates were significantly higher at this location, although the reported sample frequencies were similar to the other sites. The significantly higher deposition rates measured at this site may reflect frequent contamination and/or phosphorus transport from adjacent agricultural areas.

Wet Deposition Rates

Wet deposition data are plotted in Figures 14-17 (West, 1-7, 1-9, L-1, respectively). Scatter plots include:

- Rainfall P Concentration vs. Time
- Rainfall Volume vs. Time
- Wet Deposition Rate vs. Time
- Rainfall P Concentration vs. Rainfall Volume
- Wet Deposition Rate vs. Julian Day
- Rainfall P Concentration vs. Julian Day

In wet samples that were diluted with de-ionized water to provide a sufficient volume for phosphorus analysis, measured concentrations have been adjusted to reflect the true rainfall concentration. Concentrations and weekly deposition rates generally vary over 3-4 orders of magnitude. Generally, concentrations tend to be higher during the dry season, but deposition rates (concentration x volume) are not strongly dependent on season.

A negative correlation between rainfall concentration and rainfall volume is evident at each station. Figure 18 summarizes this relationship using different symbols to differentiate stations. For rainfall amounts < 1 cm, concentrations generally range from 10 to 1000 ppb. For rainfall amounts > 10 cm, concentrations range from .1 to 1 ppb. These patterns may reflect "washout" or scouring of atmospheric particles/aerosols, which would generate higher concentrations in small storms or in the earlier portions of large storms. It is also possible that these patterns reflect dilution of contamination effects. If the risk or rate of contamination (mg/m²-week) were independent of rainfall volume, then contaminants would have less effect on sample concentration in periods with greater rainfall. Thirdly, the pattern may reflect evaporation from the wet collector, which would tend to increase sample concentration and have a larger effect during drier periods. The strong dependence of sample concentration on rainfall volume demonstrates the importance of volume-weighting the samples in computing average rainfall concentrations. Dividing the average deposition rate by the average rainfall rate has approximately the same effect as volume weighting.

Wet deposition rates are summarized in Table 8 and plotted in Figure 19. Samples with various classes of contaminants are deleted in a cumulative fashion, with the order of contaminants selected to reflect increasing likelihood that contaminant class originated

outside of the marsh (i.e. reflected true atmospheric deposition), ranging from droppings/animal material to ash. The screening process started with a total of 835 samples and ended with 116 samples (containing no observed contaminants). Overall, wet deposition rates decreased from 47 to 3.1 mg/m²-yr and volume-weighted-mean concentrations decreased from 29 to 4.6 ppb. This is only one of a variety of methods that might be used to evaluate the impacts of contaminants on the measured deposition rates (Walker & Jewell, 1997). Additional analysis would be required to test alternative methods and develop "best" estimates of deposition rates and contaminant effects.

Wet deposition rates generally decreased with successive deletion of contaminant classes at stations L-1, 1-9, and West. At station 1-7, excluding insects/spider webs and vegetation had the apparent effect of increasing deposition rates. This pattern may be a statistical artifact because of the relatively high standard errors of deposition rates at this station (40% to 46%), which reflect high variability and limited number of samples. Deleting samples with ash (the last category) had the largest effect at stations 1-7, 1-9, and West. Wet deposition rates are relatively low at the interior 1-9 station and eastern L-1 station. At these stations, volume-weighted-mean concentrations are generally less than 10 ppb, regardless of data subset.

Dry Deposition Rates

Dry deposition rates are plotted against year and season in Figures 20-23 (West, 1-7, 1-9, L-1, respectively). Slight downward trends in dry and (to a lesser extent) wet deposition rates at L-1 are suggested. The tendency for dry deposition rates at all stations to be lower during the wet season may reflect souring of atmospheric particles during periods of frequent rainfall and the fact that the dry deposition samplers are open more often during the dry season. The pattern may also reflect seasonal variations in regional phosphorus sources (e.g., fall/winter burning of cane fields).

Dry deposition rates are summarized in Table 9 and plotted in Figure 24. Contaminant effects are explored using the same procedure applied above to the wet deposition data. With successive data screening, the total number of samples decreased from 556 to 5. Deleting samples with insects or spider webs had the largest effect on sample size (493 to 53 samples). Given the high frequency of contaminants in the dry collectors, reliable estimation of "contaminant-free" deposition rates is not feasible. Generally, compared with wet deposition rates, dry deposition rates appear to be less sensitive to contaminants. This possibly reflects attempts to remove large particles from the dry collectors prior to sample extraction. When samples with droppings, animal material, insects, or spider webs are excluded, the dry deposition rates range from 9 to 54 mg/m²-yr, with the highest rate observed at the West station and lowest rate, at the 1-9 station.

Total Deposition Rates

Table 10 lists total deposition rates at each station based upon two data subsets: (1) excluding samples with droppings or animal material; (2) excluding samples with droppings, animal material, insects or spider webs. Screening down to the ash category is not feasible because of the low number dry deposition samples. The second category

provides one estimate of true phosphorus deposition on the marsh. Because effects of vegetation and unidentified contaminants are still reflected in these samples, results probably over-estimate the true deposition rates. Results for the second category are summarized below:

Station	Total Deposition mg/m ² -yr	Bulk Conc. ppb	Rel. Std. Error %
West	118	86	32%
1-7	100	75	35%
1-9	16	11	14%
L-1	23	20	18%

The 16 - 118 mg/m²-yr range in deposition rates is similar to the 17 - 96 mg/m²-yr range by Hendry et al. (1981) for 9 South Florida Stations. Deposition rates in this region tend to be lowest in coastal areas and highest in agricultural areas (Hendry et al., 1981; Redfield, 1998). Higher values at the West & 1-7 stations may reflect anthropogenic impacts. Interpretation of spatial pattern is complicated by the fact that birds are more frequently observed at the West station. The higher relative standard errors for these stations reflects greater variability in the data, possibly caused by intermittent loading events driven by meteorology and/or by intermittent contamination events that were not visually detected.

Analysis of deposition rates in relation to dominant wind speeds and directions might help to identify causal mechanisms. If the program continues, additional efforts to discourage birds from roosting on the sample collectors may be helpful. If the spatial variations are real and of sufficient duration, they would be expected to result in elevated soil phosphorus levels. Analysis of soil phosphorus data may be useful in this regard, but complicated by gradients in water column concentration reflecting the unique loading patterns and hydrology of the Refuge.

The ecological significance of elevated P deposition rates is unknown. If the ~100 mg/m²-yr range (16 to 118) reflects anthropogenic loads, this rate would be equivalent to the expected rate of phosphorus deposition from the water column at a concentration of 10 ppb (assuming a settling rate of 10 m/yr). Elevated atmospheric deposition would have approximately the same effect on soil P deposition rates as increasing the water-column concentration from ~7 ppb to ~17 ppb.

Values for the 1-9 and L-1 stations provide important estimates of background atmospheric phosphorus deposition to the Refuge. The deposition rates and bulk concentrations are similar to those calculated by Walker (1989), based upon data collected by the SFWMD at the ENP Research Center (23 mg/m²-yr and 14 ppb, respectively). The 16-23 mg/m²-yr range in deposition rates is lower than the 30-40 mg/m²-yr range estimated for remnant Everglades marshes by McDowell et al. (1997).

Estimates of atmospheric deposition rates are required in design calculations for Stormwater Treatment Areas (STA's). STA's to achieve 50 ppb effluent concentration have been designed with an assumed bulk rainfall concentration of 50 ppb and a total

deposition rate of 57 mg/m²-yr. These values are within the range of those estimated above for Refuge stations. With a target outflow concentration of 50 ppb, STA designs (required treatment areas) are relatively insensitive to the assumed atmospheric deposition rate. Since sensitivity increases with lower target outflow concentrations, deposition rate estimates would be of greater importance in designing Phase II treatment areas.

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Water Depths (cm), December 1992 - December 1998

FIU Data

	LOX3	LOX4	LOX5	LOX6	LOX7	LOX8	LOX9	LOX10	LOX11	LOX12	LOX13	LOX14	LOX15	LOX16	Mean
9212															
9301															
9302															
9303															
9304															
9305															
9306															
9307															
9308															
9309															
9310															
9311															
9312															
9401															
9402															
9403															
9404															
9405															
9406															
9407															
9408															
9409															
9410															
9411															
9412															
9501															
9502															
9503															
9504															
9505															
9506															
9507															
9508															
9509															
9510	47	80	90	89	90	72	62	70							74
9511	42	55	40	70	60	55	60	50							54
9512	28	55	37	65	60	52	50	45							49
9601	32	52	38	65	52	54	40	46							47
9602	33	48	60	75	71	52	48	47							54
9603	15	35	21	48	42	48	29	32							34
9604	15	32	21	47	41	40	23	20							30
9605		20	18	32	35	30	18	18							24
9606	20	41	47	42	52	45	30	28							38
9607	30	48	40	48	65	48	33	32							43
9608	22	23	28	28	31	48	23								29
9609	30	48	37	60	60	53	55	42							48
9610	31	62	57	69	59	54	65	54							56
9611	45	51	34	65	60	53	37	47	73	105	51	85	120	100	66
9612	23	40	28	52	45	50	35	30							38
9701			21	47	38	42	30	28							34
9702				48	38	35	24	29							35
9703				53	37	38		32							40
9704				38	30	32									33
9705				25						63		54	83	62	57
9706				40	33	37									37
9707				42	43	41	24								38
9708	25	47	31	54	46	45	33	37							40
9709	26	51	39	78	52	52	43	45							48
9710	30	53	36	58	62	63	43	52							50
9711	35	58	52	74	64	62	48	58	90	108	45	89	121	102	72
9712	45	68	57	92	75	72	62	72							68
9801	31	61	60	70	65	67	54	49	65	90	75	90	125	103	72
9802	25	51	35	72	58	57	46	45							49
9803	43	44	43	53	60	62	42	38							48
9804	26		32	40	40	45	24	14							32
9805			10	10	8	27	10								13
9806															
9807						15									15
9808				20	16	12									16
9809									10	32		20	45	15	24
9810			22	20	30	40	26								28
9811	50	45	50	70	40	70	45	70							55
9812	20	45	50	75	62	60	32	45							49
Mean	31	49	39	54	49	48	39	42	60	80	57	68	99	76	43

Variance Components of Log-Transformed Marsh Phosphorus Data

Factor	Variances				Standard Deviations		
	SFWMD	FIU	Both	Both%	SFWMD	FIU	Both
Variance Components of Marsh Stations (LOX 3 - LOX 16)							
Dates	0.041	0.063	0.007	4.4%	0.202	0.251	0.081
Date/Lab			0.059	39.8%			0.243
Date/Lab/Station	0.048	0.052	0.050	33.5%	0.219	0.228	0.223
Date/Lab/Station/Rep	0.033	0.033	0.033	22.2%	0.181	0.182	0.182
Total	0.121	0.148	0.148	100.0%	0.348	0.385	0.385
Variance Components of Inflow Stations (S5AD + S6)							
Dates	0.000	0.051	0.005	1.5%	0.000	0.225	0.068
Date/Lab			0.018	5.8%			0.136
Date/Lab/Station	0.261	0.312	0.289	91.4%	0.511	0.558	0.538
Date/Lab/Station/Rep	0.007	0.003	0.004	1.3%	0.084	0.051	0.064
Total	0.268	0.365	0.317	100.0%	0.518	0.604	0.563
Variance of Concentration at a Given Station on a Given Date, Single Rep.							
Date/Lab	0.000	0.000	0.059	64%			
Date/Lab/Station/Rep	0.033	0.033	0.033	36%			
Total	0.033	0.033	0.092	100%	0.181	0.182	0.303
Difference between Labs (Paired Samples)							
Expected	0.066	0.067	0.184		0.256	0.258	0.429
Observed	0.156	0.156	0.156		0.395	0.395	0.395
Variance of Marsh Geometric Mean on a Given Date; Average of 11.3 Stations Per Date							
Date/Lab	0.000	0.000	0.059	95.3%	0.000	0.000	0.243
Date/Lab/Station/Rep	0.003	0.003	0.003	4.7%	0.054	0.054	0.054
Total	0.003	0.003	0.062	100.0%	0.054	0.054	0.249
Difference between Labs (Paired Geometric Means by Date)							
Expected	0.006	0.006	0.124		0.076	0.077	0.352
Observed	0.139	0.139	0.139		0.373	0.373	0.373
Total Variance of Marsh Geometric Mean; Average of 11.3 Stations Per Date							
Dates	0.041	0.063	0.007	9.0%	0.202	0.251	0.081
Date/Lab	0.000	0.000	0.059	81.0%	0.000	0.000	0.243
Date/Lab/Station	0.004	0.005	0.004	6.0%	0.065	0.068	0.066
Date/Lab/Station/Rep	0.003	0.003	0.003	4.0%	0.054	0.054	0.054
Total	0.048	0.070	0.073	100.0%	0.219	0.265	0.270
Variance of Inflow Concentration at a Given Station on a Given Date, Single Rep							
Date/Lab	0.000	0.000	0.018	81.7%	0.000	0.000	0.136
Date/Lab/Station/Rep	0.007	0.003	0.004	18.3%	0.084	0.051	0.064
Total	0.007	0.003	0.023	100.0%	0.084	0.051	0.150
Difference between Labs (Paired Samples)							
Expected	0.014	0.005	0.045		0.119	0.072	0.213
Observed	0.048	0.048	0.048		0.220	0.220	0.220

Values estimated from nested analysis of variance (Snedecor & Cochran, 1989). Aug 97-Dec 98 Data

Phosphorus Data from Refuge Inflow Stations

Date	ACME 1	ACME 2	ENR002	ENR004	ENR005	ENR012_D	ENR012_U	L-40	SSA_D	SSA_U
08/18/94			53			77	78	232		
08/25/94			237			153	62			
09/01/94			173			24	24			
09/08/94			132			33	23			
09/15/94			154		107	28	20			
09/29/94			195		133	87	79			
10/13/94			226		132	48	41			
10/26/94			106		55	46	47			
11/10/94			122		66	40	30			
11/18/94			42			42	37			
12/01/94			208		134	40	33			
12/14/94			161		112	28	34			
12/28/94			160		118	35	30			
01/11/95			145		52	27	31			
01/25/95			135		61	50	30			
02/08/95			54		65	59	61			
02/10/95									320	207
02/22/95			92			70	50		222	174
03/09/95			128		118	57	55		195	167
03/23/95			185		131	28	27			176
04/06/95			84		61	56	55			76
04/21/95			73		60	64	57			72
05/05/95			93		79	71	72			101
05/17/95			39		49	44	42			33
05/31/95			19		17	17	16			34
06/15/95			48		46	39	40			73
06/28/95			109		86	44	39			145
07/14/95			114		74	69	73			179
07/26/95			154		59	20	27			144
08/11/95			188		97	24	26		86	
08/25/95			129		78	17	15		146	
09/12/95			136		93	18	17		96	
09/28/95			48		29	19	17		60	
10/12/95			83	74		20	20		76	
10/26/95			183	112		39	31		125	
11/09/95			83	102		34	32		235	
11/21/95			160	101		13	14		180	
12/07/95			87	34		16	17		163	
01/11/96			42	5		5	5		8	
01/23/96			30	8		11	11		50	
02/09/96			192	43		50	47		174	
02/23/96			118	41		52	52		155	
03/05/96			76	69		61	58		103	
03/19/96			88	72		58	63		71	
04/02/96			133	164		205	63		60	
04/16/96			131	110		152	84		78	
04/30/96			84	36		55	27		28	
05/14/96			104	42		91	33		35	
05/31/96			100	112		15	14		140	
06/11/96			88	96		45	17		143	
06/25/96			108	105		12	13		70	
07/12/96			91	75		16	15		106	
07/26/96			66	55		20	21		64	
08/06/96			163	39		22	22		85	
08/20/96			106	68		24	25		87	
09/17/96			105	66		25	24		119	
10/01/96			62	70		23	23		61	
10/15/96			118	90		23	23		133	
10/28/96			74	46		20	20		72	
11/05/96			78	33		19	19		61	
11/21/96			89	37		17	17		67	
12/03/96			27	69		30	26		87	

Phosphorus Data from Refuge Inflow Stations

Date	ACME 1	ACME 2	ENR002	ENR004	ENR005	ENR012_D	ENR012_U	L-40	SSA_D	SSA_U
12/17/96			88	33		16	15		79	
01/02/97			41	38		36	43		65	
01/14/97			36	68		19	20		47	
01/30/97			69	37		29	28		45	
02/11/97			59	55		20	23		79	
02/27/97			94	48		27	31		83	
03/13/97			80	42		48	22		78	
03/24/97			89	38		17	15		48	
04/08/97			54	23		26	20		51	
04/24/97			62	54		8	7		49	
05/05/97			38	33		16	13		62	
05/20/97			59	64		14	14		70	
06/16/97			63	82		82	13		12	
07/01/97			58	43		10	11		61	
07/18/97			64	80		31	28		70	
07/28/97			130	74		11	12		87	
08/07/97			147			12	11			
08/12/97				98					158	
08/22/97			95	92		25	27		98	
09/05/97			172	76		21	16		116	
09/18/97			115	89		15	14		104	
10/03/97			166	91		21	20		135	
10/17/97			81	59		21	17		68	
10/31/97			74	50		17	13		73	
11/14/97			83	65		18	16			
11/28/97			119	70		16	13			
12/11/97			198	26		17	15		123	
12/30/97			152	136		27	17		167	
01/23/98			114	97		20	22		67	
02/13/98			93	30		18	17		54	
02/25/98			87	83		24	24		95	
03/12/98			51	61		23	22			86
04/02/98			93	30		37	31			39
04/27/98			121	23		19	18			40
05/14/98			129	36		16	16			38
06/01/98			90	16		10	10			27
06/15/98			75	43		27	26			35
07/13/98			86	21		13	12			27
07/31/98			46	36		15	13			121
08/13/98			63	24		19	14			39
08/27/98			130	56		20	15			75
09/18/98			102	107		16	15			
10/05/98			162	128		26	19			103
10/19/98	69	78	162	128		26	19			103
11/09/98	182	153	221	212		20	20			220
11/20/98	137	180	316	123		21	19			209
12/04/98	130	112	117	59		21	14			139
12/28/98	28	43	36	25		12	13			41
01/08/99	33	34	150	33		8	8			104
01/26/99	22	34	84	34		13	14			116
02/09/99	23	31	51	22		14	13			106
02/23/99	18	23	54	17		10	9			109
Count	9	9	112	80	26	112	112	1	64	33
Mean	71	77	107	63	81	33	27	232	97	102
Median	33	43	93	57	76	23	21	232	79	103
Geo.Mean	50	59	94	53	74	26	23	232	83	84

Summary of Phosphorus Data from Refuge Inflow Stations

<u>Station</u>	<u>Description</u>	<u>Station Codes Use in Database</u>
ENR002	ENR Inflow - Upstream of G250 Pump	002
ENR004	L7 Canal at Jct of ENR Cell 1 & 3	004
ENR005	L7 Canal Near G251 ENR Outflow	005
ENR012_U	ENR Outflow - Upstream of G251 Pump	012, 012 bottom H2O, 012 top H2O
ENR012_D	ENR Outflow - Downstream of G251 Pump	G251 DN, G251 DS, G251... at pump
ACME 1	ACME 1	ACME 1
ACME 2	ACME 2	ACME 2
S5A_U	S5A - Upstream of Pump	S5A, S5A UP
S5A_D	S5A - Downstream of Pump	S5A DN, S5A DS
L-40	L-40 Canal	L-40

<u>Station</u>	<u>Count</u>	<u>Mean</u>	<u>Std Dev</u>	<u>GeoMean</u>	<u>CV</u>	<u>Min</u>	<u>Max</u>	<u>First</u>	<u>Last</u>
ENR002	112	106.5	52.3	94.2	0.52	18.8	316.1	08/18/94	02/23/99
ENR004	80	63.5	37.3	52.9	0.65	5.0	212.1	10/12/95	02/23/99
ENR005	26	81.3	33.6	73.6	0.49	17.2	134.4	09/15/94	09/28/95
ENR012_U	119	28.4	18.7	23.7	0.59	4.9	84.0	08/18/94	02/23/99
ENR012_D	117	34.4	29.9	26.9	0.66	5.2	205.3	08/18/94	02/23/99
ACME 1	9	71.2	62.2	49.7	0.91	17.6	181.8	10/19/98	02/23/99
ACME 2	9	76.6	58.6	59.1	0.76	23.2	179.8	10/19/98	02/23/99
S5A_U	33	101.8	58.9	84.0	0.66	26.7	220.0	02/10/95	02/23/99
S5A_D	64	97.0	55.4	82.5	0.62	7.8	319.5	02/10/95	02/25/98
L-40	1	232.0		232.0		232.0	232.0	08/18/94	08/18/94

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Contamination Frequencies

<u>Station</u>	<u>Samples</u>	<u>Duration</u> <u>Days</u>	<u>Droppings</u>	<u>Animal</u> <u>Material</u>	<u>Insects</u>	<u>Spider</u> <u>Webs</u>	<u>Veget.</u>	<u>Unident.</u> <u>Organics</u>	<u>Ash</u>	<u>Any</u>
Wet Deposition										
All	835	6142	1.6%	1.4%	47.1%	6.2%	20.8%	8.9%	20.8%	86.1%
L-1	189	1378	2.6%	0.0%	62.4%	8.5%	33.3%	4.2%	33.3%	91.5%
1-7	220	1622	0.9%	1.4%	38.2%	4.5%	20.9%	10.9%	20.9%	84.1%
1-9	218	1602	0.9%	2.3%	35.8%	5.0%	13.3%	10.6%	13.3%	79.4%
West	208	1540	1.9%	1.9%	54.3%	7.2%	17.3%	9.1%	17.3%	90.4%
Dry Deposition										
All	556	4037	6.7%	5.6%	88.5%	10.4%	18.0%	10.6%	62.9%	99.1%
L-1	82	600	6.1%	1.2%	86.6%	18.3%	41.5%	7.3%	82.9%	100.0%
1-7	172	1264	4.7%	4.1%	86.0%	8.1%	14.0%	14.5%	62.2%	99.4%
1-9	193	1394	5.2%	6.7%	89.1%	7.8%	14.5%	10.4%	58.5%	99.5%
West	109	779	12.8%	9.2%	92.7%	12.8%	12.8%	7.3%	56.9%	97.2%

	<u>Total</u> <u>Dates</u>	<u>Wet Deposition</u>			<u>Dry Deposition</u>		
		<u>Analyzed</u>	<u>Not*</u> <u>Analyzed</u>	<u>% Not</u> <u>Analyzed</u>	<u>Analyzed</u>	<u>Not*</u> <u>Analyzed</u>	<u>% Not</u> <u>Analyzed</u>
All	1160	835	325	28%	556	604	52%
L-1	290	189	101	35%	82	208	72%
1-7	290	220	70	24%	172	118	41%
1-9	290	218	72	25%	193	97	33%
West	290	208	82	28%	109	181	62%

*Samples not analyzed due to gross contamination and/or equipment failure

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Summary of Wet Deposition Data

Station	Count	Sample Duration Days	Total Rainfall cm	Total P Mass mg/m ²	Mean Conc ppb	Vol-Wtd Conc ppb	Depo. Rate mg/m ² -yr	Rel. Std. Error	Geometric Means			Rel. Std. Error	First	Last	
									Conc ppb	Depo. Rate mg/m ² -yr	Depo. Rate CV				
All Samples															
All	835	6142	2700	793.4	53.7	29.4	47.2	21%	7.2	5.11	1.68	6%	02/10/93	09/29/98	
L-1	189	1378	588	60.2	27.8	10.2	16.0	36%	5.4	3.60	1.38	10%	02/10/93	09/29/98	
1-7	220	1622	711	277.9	58.1	39.1	62.6	33%	8.0	5.61	1.81	12%	03/09/93	09/29/98	
1-9	218	1602	710	58.9	14.7	8.3	13.4	25%	4.5	3.25	1.38	9%	03/09/93	09/29/98	
West	208	1540	691	396.4	113.6	57.4	94.0	34%	13.7	10.24	1.82	13%	03/23/93	09/29/98	
Excluding Samples with Droppings or Animal Material															
All	810	5940	2552	641.4	49.1	25.1	39.4	18%	7.1	4.92	1.64	6%	02/10/93	09/29/98	
L-1	184	1335	555	48.7	26.6	8.8	13.3	41%	5.2	3.42	1.32	10%	02/10/93	09/29/98	
1-7	215	1580	680	277.3	59.2	40.8	64.1	33%	8.1	5.64	1.83	12%	03/09/93	09/29/98	
1-9	211	1547	668	52.0	14.9	7.8	12.3	28%	4.6	3.21	1.37	9%	03/09/93	09/29/98	
West	200	1478	648	263.6	95.1	40.7	65.1	26%	13.0	9.36	1.74	12%	03/23/93	09/29/98	
Excluding Samples with Droppings, Animal Material, Insects, or Spider Webs															
All	402	2910	1064	359.3	52.1	33.8	45.1	28%	7.9	4.19	1.67	8%	02/10/93	09/29/98	
L-1	60	430	135	9.4	11.7	7.0	8.0	34%	5.9	2.86	1.25	16%	02/10/93	09/29/98	
1-7	127	916	333	222.7	82.1	66.9	88.8	40%	10.7	5.69	1.91	17%	03/09/93	09/29/98	
1-9	130	938	361	17.1	10.5	4.7	6.7	23%	4.3	2.53	1.27	11%	03/09/93	09/29/98	
West	85	626	235	110.0	99.3	46.8	64.2	44%	15.8	7.47	1.82	20%	04/06/93	09/29/98	
Excluding Samples with Droppings, Animal Material, Insects, Spider Webs, or Vegetation															
All	318	2302	764	301.6	44.7	39.5	47.9	33%	8.0	3.52	1.63	9%	02/10/93	09/29/98	
L-1	42	297	66	2.7	11.1	4.1	3.4	16%	6.4	2.07	1.02	16%	02/10/93	09/29/98	
1-7	98	703	231	191.4	52.1	82.8	99.5	46%	10.2	4.54	1.86	19%	03/29/93	09/29/98	
1-9	112	813	319	15.2	10.6	4.8	6.8	26%	4.2	2.45	1.29	12%	03/09/93	09/29/98	
West	66	489	148	92.2	113.2	62.4	68.9	52%	18.3	6.26	1.85	23%	05/04/93	09/02/98	
Excluding Samples with Droppings, Animal Material, Insects, Spider Webs, Vegetation, or Organic Material															
All	287	2045	640	191.2	36.7	29.9	34.1	41%	7.9	3.21	1.49	9%	02/10/93	08/19/98	
L-1	39	276	52	2.3	11.7	4.4	3.1	16%	6.7	1.97	0.95	15%	02/10/93	11/19/97	
1-7	89	634	198	144.4	49.8	73.1	83.2	53%	9.8	4.09	1.74	18%	03/29/93	02/25/98	
1-9	97	681	258	13.5	11.1	5.2	7.2	28%	4.5	2.42	1.30	13%	03/09/93	08/19/98	
West	62	454	132	31.0	73.7	23.4	24.9	41%	15.5	4.80	1.52	19%	05/04/93	10/29/97	
Excluding Samples with Droppings, Animal Material, Insects, Spider Webs, Vegetation, Organic Material, or Ash															
All	116	808	151	6.9	17.1	4.6	3.1	13%	7.6	1.75	1.12	10%	02/10/93	08/19/98	
L-1	16	114	8	0.9	16.8	11.3	2.7	30%	11.3	1.74	0.99	25%	02/10/93	02/14/96	
1-7	35	249	49	2.5	19.7	5.2	3.7	29%	8.4	1.87	1.16	20%	03/29/93	02/25/98	
1-9	45	307	74	2.2	11.4	3.0	2.7	21%	4.6	1.43	1.20	18%	03/09/93	08/19/98	
West	20	138	21	1.3	25.5	6.0	3.4	19%	15.1	2.45	0.91	20%	05/04/93	10/29/97	

Summary of Dry Deposition Data

Station	Samples	Duration Days	Mass mg/m ²	Deposition Rate				CV %	Rel Std Error	First	Last
				Mean mg/m ² -yr	Rel Std Error	G. Mean mg/m ² -yr	Rel Std Error				
All Samples											
All	556	4037	631.7	57.2	15%	17.6	133%	6%	02/16/93	09/29/98	
L-1	82	600	89.1	54.3	44%	19.3	96%	11%	02/16/93	11/19/97	
1-7	172	1264	188.4	54.4	21%	17.0	132%	10%	03/09/93	09/29/98	
1-9	193	1394	74.4	19.5	19%	10.6	99%	7%	03/29/93	09/29/98	
West	109	779	279.8	131.2	26%	42.7	163%	16%	03/23/93	09/29/98	
Excluding Samples with Droppings or Animal Material											
All	493	3586	378.1	38.5	13%	15.6	120%	5%	02/16/93	09/29/98	
L-1	76	557	83.3	54.6	47%	18.8	94%	11%	02/16/93	11/19/97	
1-7	158	1160	108.6	34.2	17%	15.4	124%	10%	05/18/93	09/29/98	
1-9	172	1249	52.3	15.3	12%	9.8	92%	7%	04/06/93	09/29/98	
West	87	620	133.9	78.9	19%	34.9	135%	14%	04/06/93	09/29/98	
Excluding Samples with Droppings, Animal Material, Insects, or Spider Webs											
All	53	379	17.9	17.3	22%	9.5	95%	13%	04/06/93	08/05/98	
L-1	10	68	2.8	15.1	20%	12.9	61%	19%	12/13/93	05/07/97	
1-7	22	161	5.0	11.3	28%	8.0	75%	16%	06/29/93	08/05/98	
1-9	14	98	2.4	9.1	16%	7.9	54%	14%	04/06/93	03/04/98	
West	7	52	7.7	54.0	46%	14.8	200%	76%	06/08/93	05/14/97	
Excluding Samples with Droppings, Animal Material, Insects, Spider Webs, or Vegetation											
All	37	269	13.7	18.6	28%	9.4	89%	15%	04/06/93	08/05/98	
L-1	4	28	1.0	13.2	41%	10.7	71%	36%	03/07/94	11/13/96	
1-7	19	140	4.5	11.9	31%	8.3	77%	18%	05/23/95	08/05/98	
1-9	10	70	1.7	8.7	21%	7.5	56%	18%	04/06/93	03/04/98	
West	4	31	6.5	76.3	56%	25.2	172%	86%	06/08/93	01/16/97	
Excluding Samples with Droppings, Animal Material, Insects, Spider Webs, Vegetation, or Organic Material											
All	30	220	12.6	20.9	31%	9.7	97%	18%	04/06/93	05/13/98	
L-1	4	28	1.0	13.2	41%	10.7	71%	36%	03/07/94	11/13/96	
1-7	14	105	3.7	12.8	39%	8.2	88%	24%	05/23/95	05/13/98	
1-9	8	56	1.4	9.1	24%	7.8	61%	22%	04/06/93	03/04/98	
West	4	31	6.5	76.3	56%	25.2	172%	86%	06/08/93	01/16/97	
Excluding Samples with Droppings, Animal Material, Insects, Spider Webs, Vegetation, Organic Material, or Ash											
All	5	37	5.8	56.9	63%	14.2	154%	69%	06/08/93	03/04/98	
L-1	0	0	0.0								
1-7	1	6	0.1	4.6		4.6			02/25/98	02/25/98	
1-9	1	7	0.3	18.0		18.0			03/04/98	03/04/98	
West	3	24	5.3	81.3	74%	18.9	198%	115%	06/08/93	01/16/97	

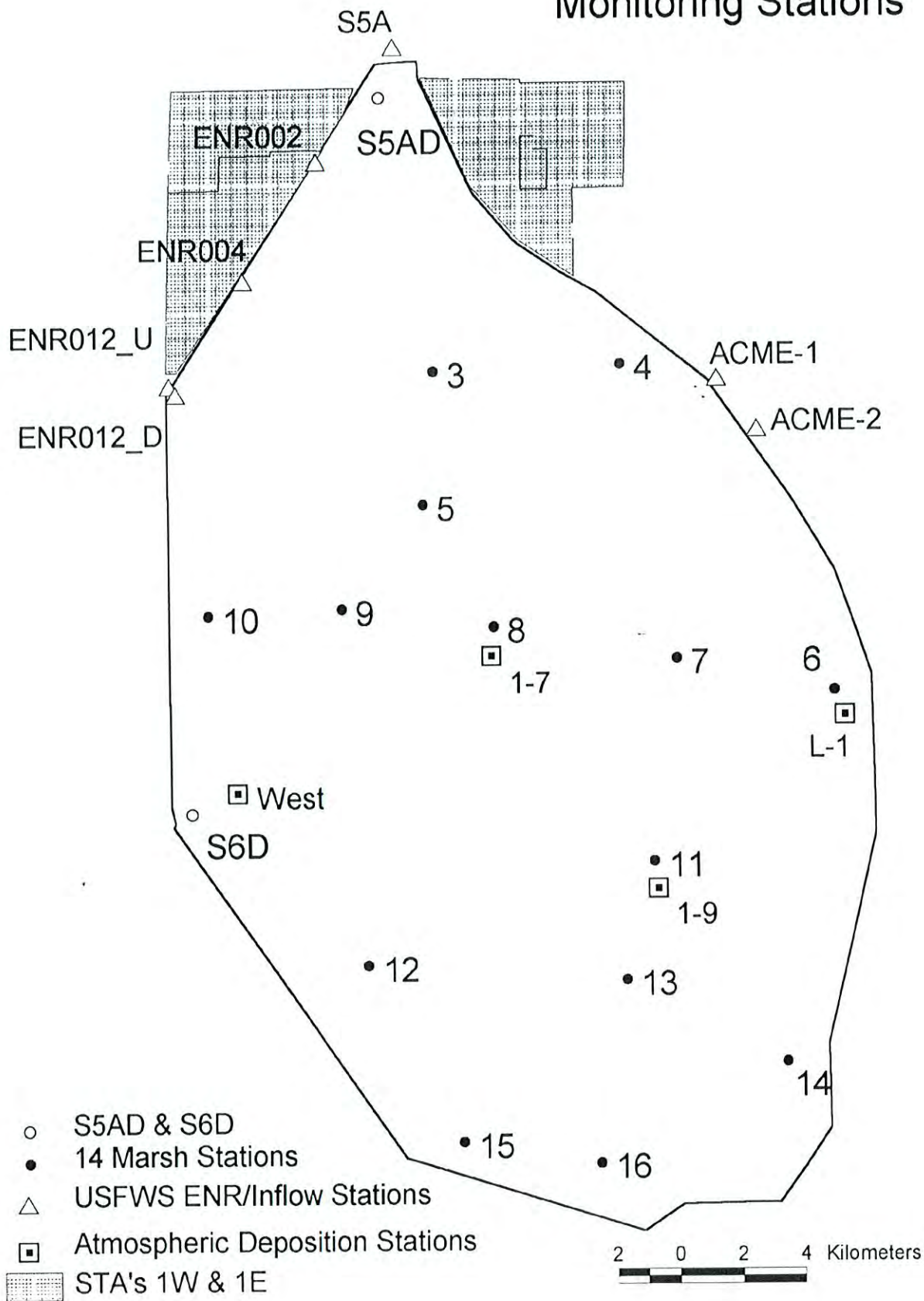
Summary of Total Deposition Rates

Station	Collected			Deposition Rates (mg/m ² -yr)								Geometric Means--->					
	Samples		Rain									Conc (ppb)		Deposition Rate (mg/m ² -yr)			
	Wet	Dry	cm/yr	Wet	RSE	Dry	RSE	Total	RSE	Dry%	Wet	Bulk	Wet	Dry	Total	Dry%	
Excluding Samples with Droppings or Animal Material																	
All	810	493	157	39	18%	39	13%	78	11%	49%	25	50	4.9	15.6	20.6	76%	
L-1	184	76	152	13	41%	55	47%	68	38%	80%	9	45	3.4	18.8	22.2	85%	
1-7	215	158	157	64	33%	34	17%	98	22%	35%	41	62	5.6	15.4	21.0	73%	
1-9	211	172	158	12	28%	15	12%	28	14%	55%	8	17	3.2	9.8	13.0	75%	
West	200	87	160	65	26%	79	19%	144	16%	55%	41	90	9.4	34.9	44.3	79%	
Excluding Samples with Droppings, Animal Material, Insects, or Spider Webs																	
All	402	53	134	45	28%	17	22%	62	21%	28%	34	47	4.2	9.5	13.7	69%	
L-1	60	10	115	8	34%	15	20%	23	18%	65%	7	20	2.9	12.9	15.7	82%	
1-7	127	22	133	89	40%	11	28%	100	35%	11%	67	75	5.7	8.0	13.7	59%	
1-9	130	14	141	7	23%	9	16%	16	14%	58%	5	11	2.5	7.9	10.4	76%	
West	85	7	137	64	44%	54	46%	118	32%	46%	47	86	7.5	14.8	22.3	66%	

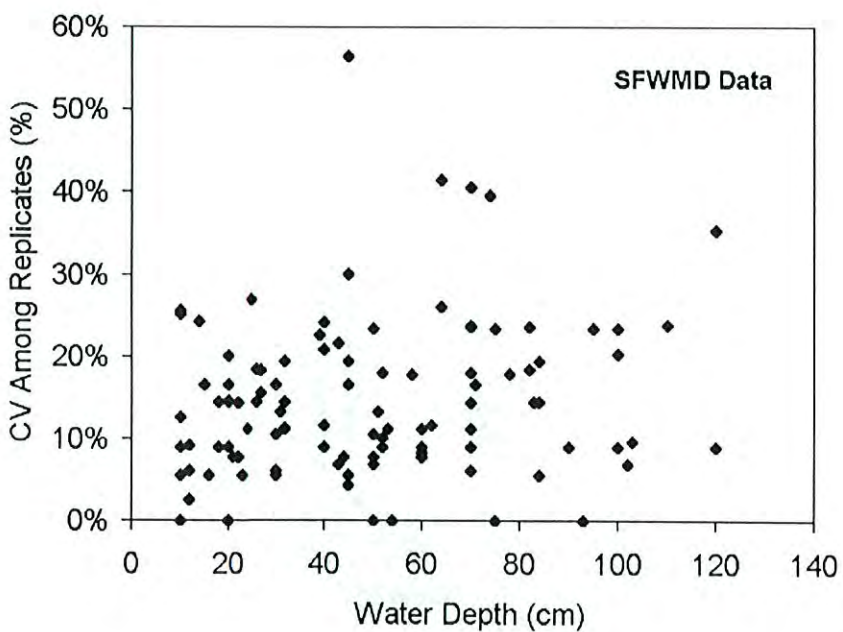
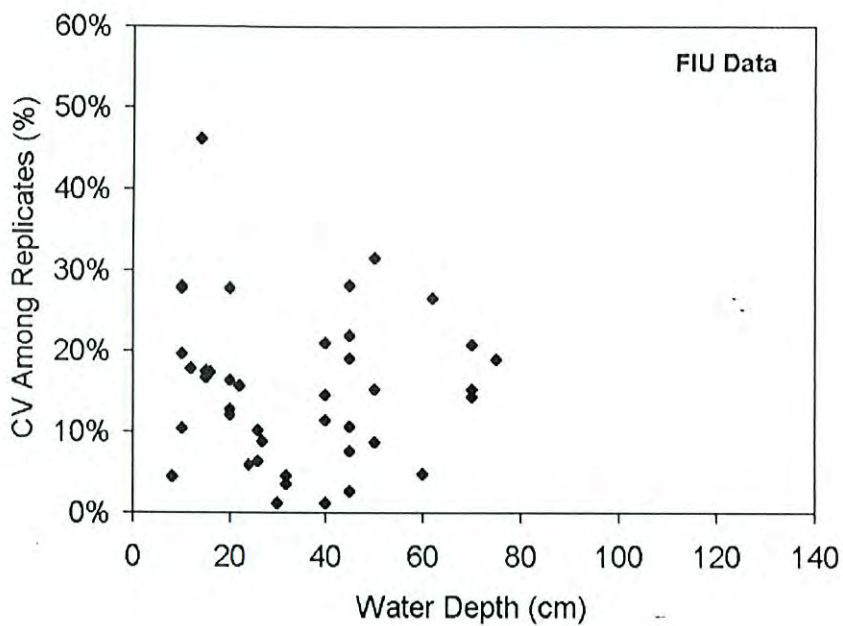
Bulk Concentration = total deposition rate / rainfall collection rate

RSE = relative standard error

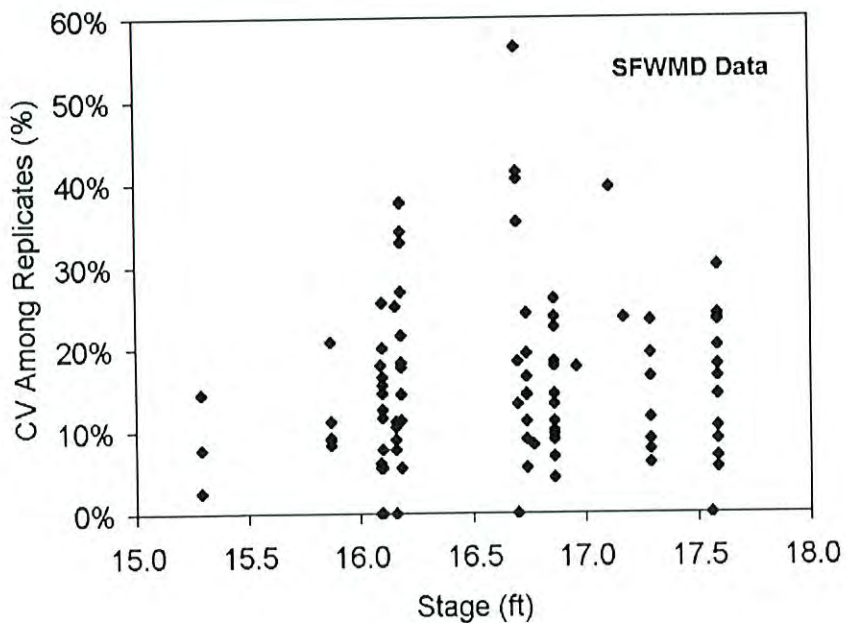
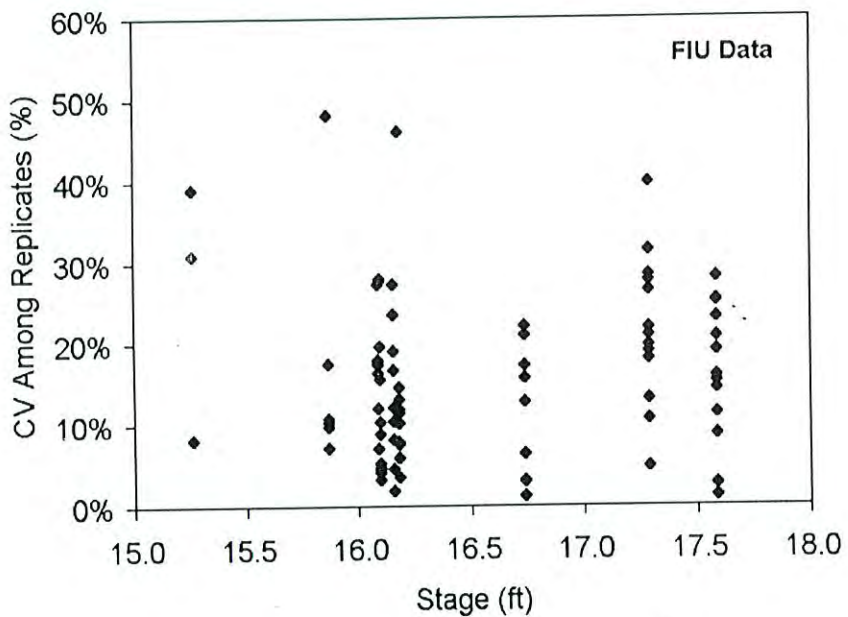
Monitoring Stations



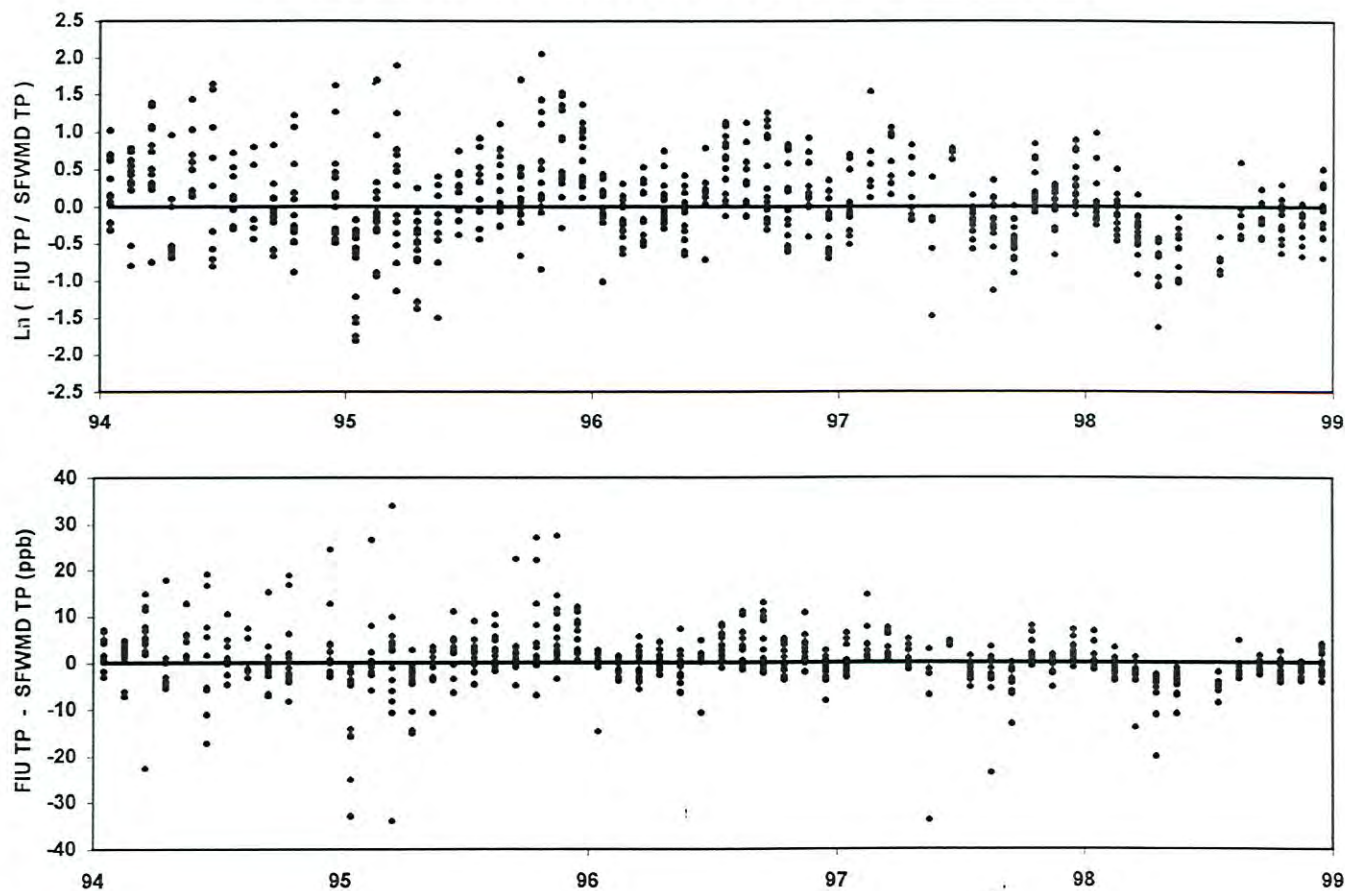
Variability Among Replicates vs. Depth
August 1997-December 1998



Variability Among Replicates vs. Stage
 August 1997-December 1998



Comparison of SFWMD & FIU Samples Paired by Station & Date

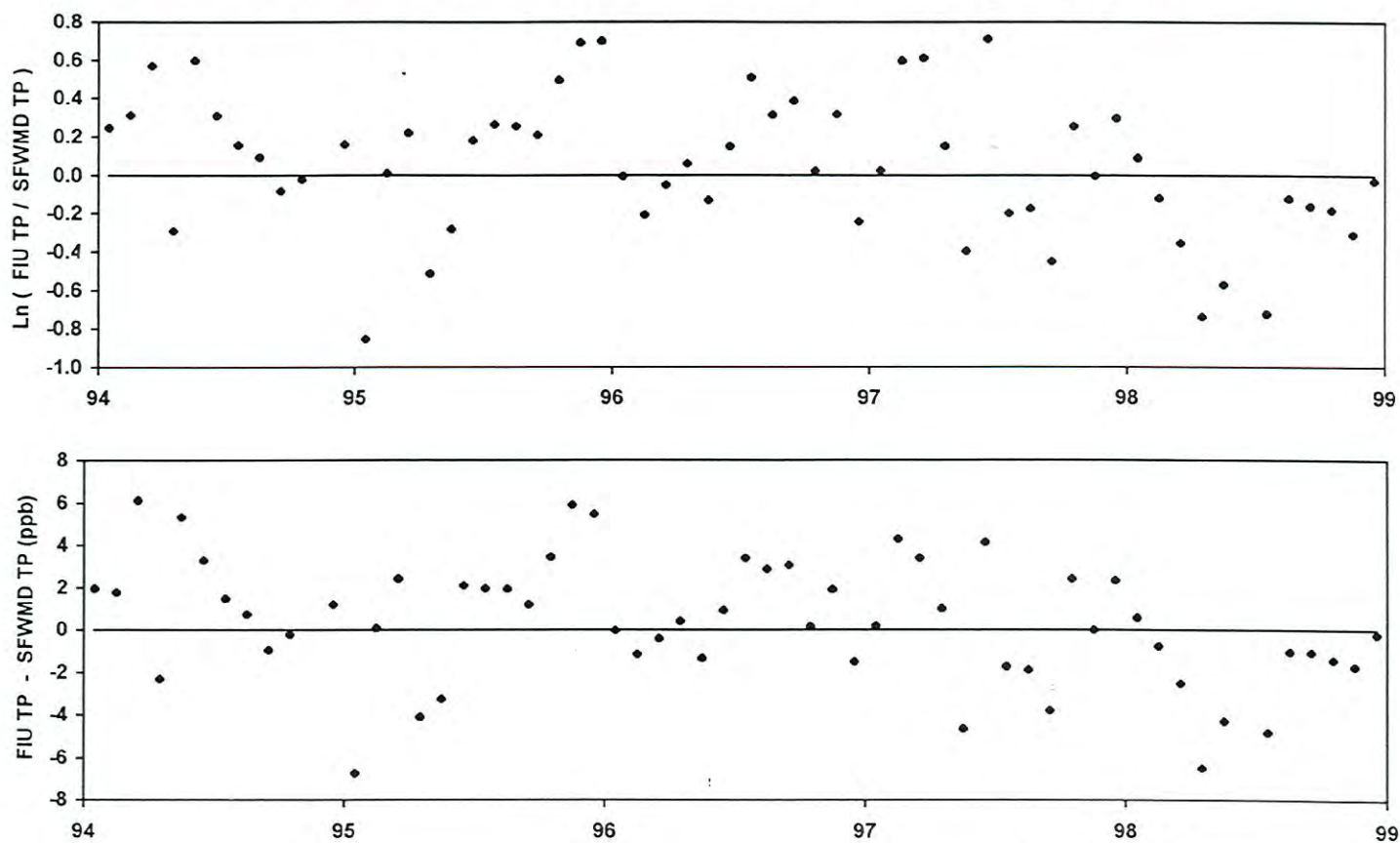


Period	Jan 94 - Dec 98		Aug 97 - Dec 98	
	Linear	Ln	Linear	Ln
Scale				
Count	679	679	59	59
Median	0.030	0.005	-1.420	-0.227
Mean	0.236	0.049	-1.343	-0.220
Std Dev	6.840	0.561	2.457	0.327
Root Mean Sq	6.844	0.563	2.801	0.395
Correl	0.239	0.221	0.679	0.443
t (Mean = 0)	0.897	2.292	-4.199	-5.160
Prob(>t)	0.370	0.022	0.000	0.000

Linear = FIU TP - SFWMD TP (ppb)

Ln = Natural Log (FIU TP / SFWMD TP)

Comparison of SFWMD & FIU Marsh Geometric Means Paired by Date

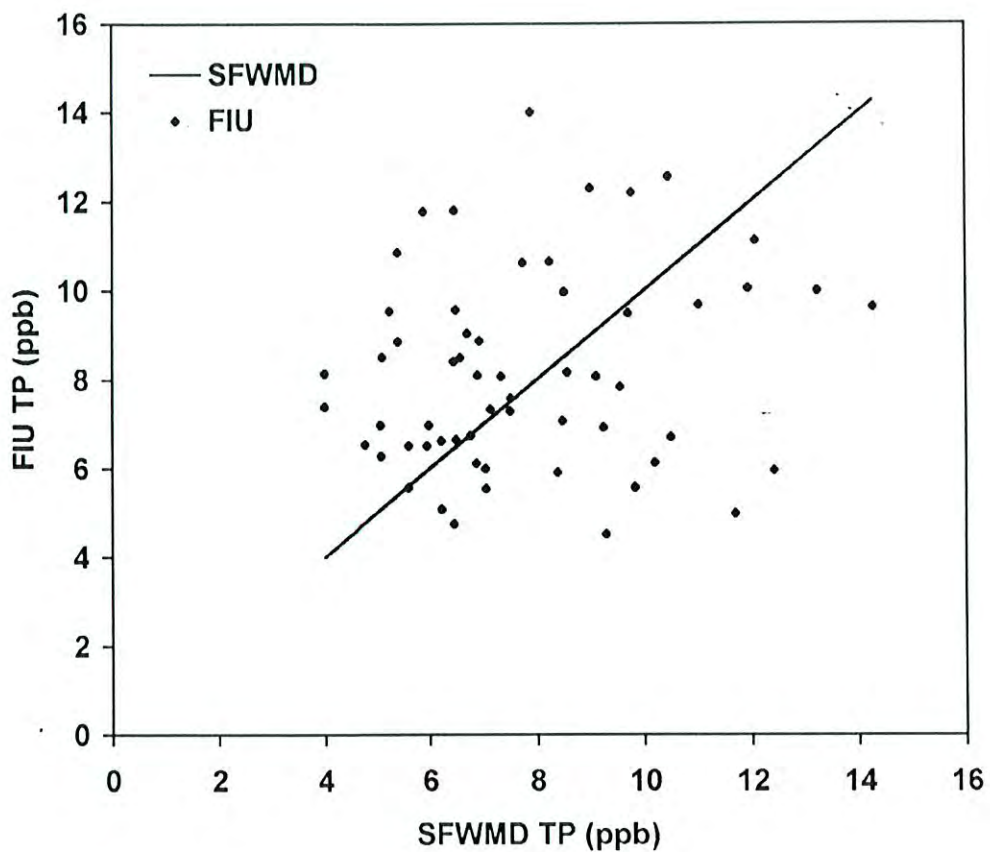


Period	<u>Jan 94-Dec 98</u>		<u>Aug 97-Dec 98</u>		Linear = FIU TP - SFWMD TP (ppb)
	Linear	Ln	Linear	Ln	
Scale					
Count	58	58	16	16	
Median	0.301	0.045	-1.229	-0.167	
Mean	0.333	0.049	-1.535	-0.204	
Std Dev	2.945	0.370	2.432	0.307	
Root Mean Sq	2.964	0.373	2.876	0.369	
Correl	0.176	0.144	0.136	0.119	
t (Mean = 0)	0.860	1.013	-2.524	-2.658	
Prob (>t)	0.393	0.315	0.023	0.017	

Ln = Natural Log (FIU TP / SFWMD TP)

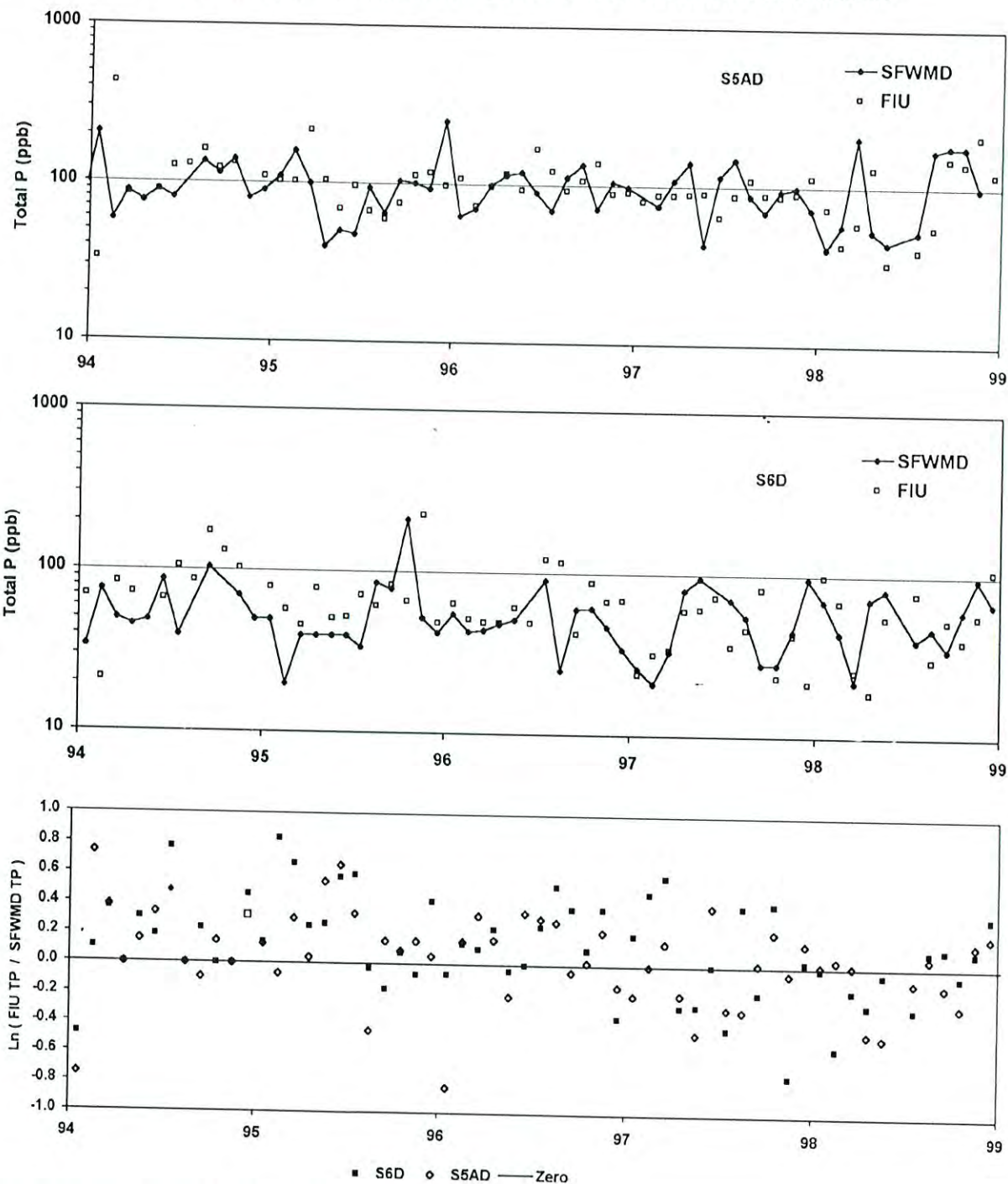
Figure 5

Correlation between FIU & SFWMD Marsh Geometric Means



Correlation Coef = 0.176

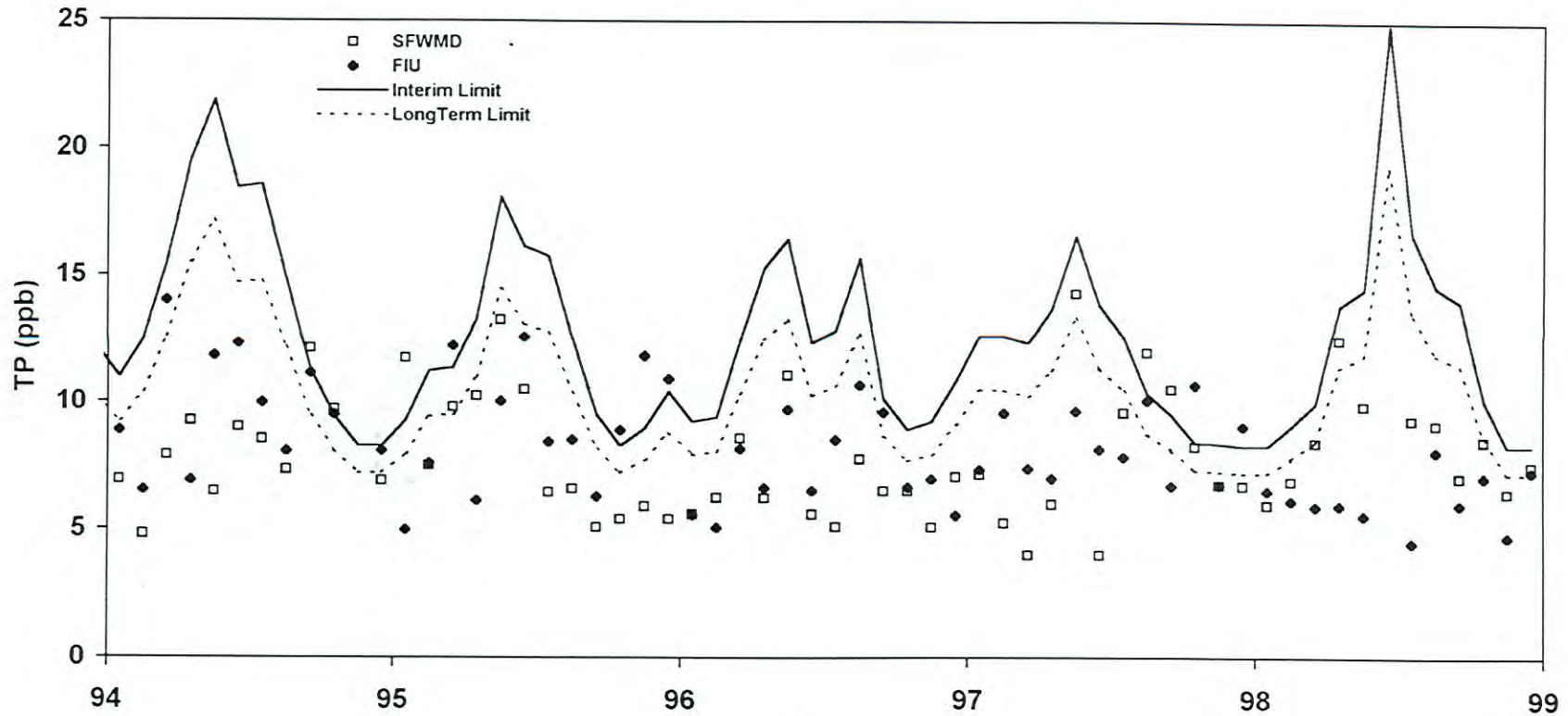
Paired Phosphorus Data from Stations Downstream of S5A and S6



Statistical Summary: $\ln (\text{FIU TP} / \text{SFWMD TP})$

Period	Jan 94 - Dec 98	Aug 97 - Dec 98
Count	55	16
Mean	0.052	-0.054
Std Dev	0.316	0.217
Root Mean Sq	0.320	0.224
Correlation Coef	0.736	0.916
t	1.211	-0.990
Prob(>t)	0.115	0.169

Marsh Geometric Means & Compliance Limits



Geometric Mean TP Concentrations across 14 Marsh Stations in ARM Loxahatchee National Wildlife Refuge
 Paired Observations - Each Station Sampled by Each Lab on Each Date
 Settlement Agreement Interim & Longterm Compliance Limits Computed from Stage

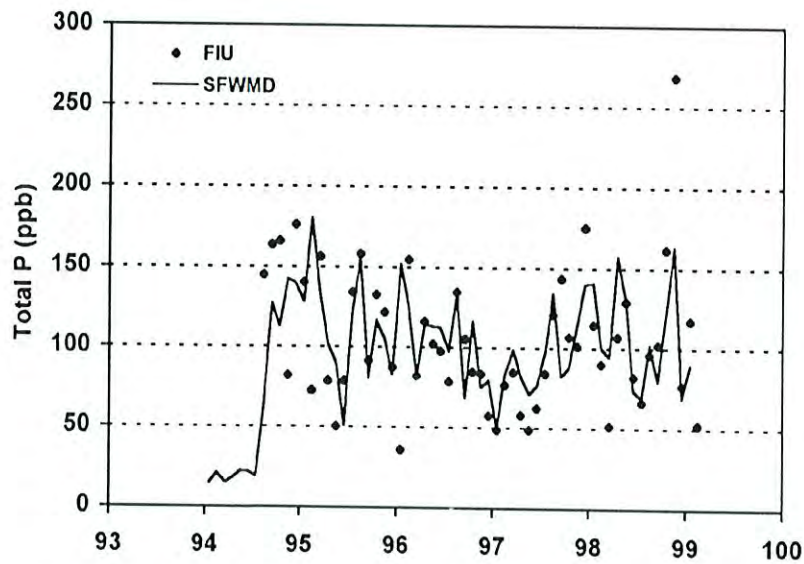
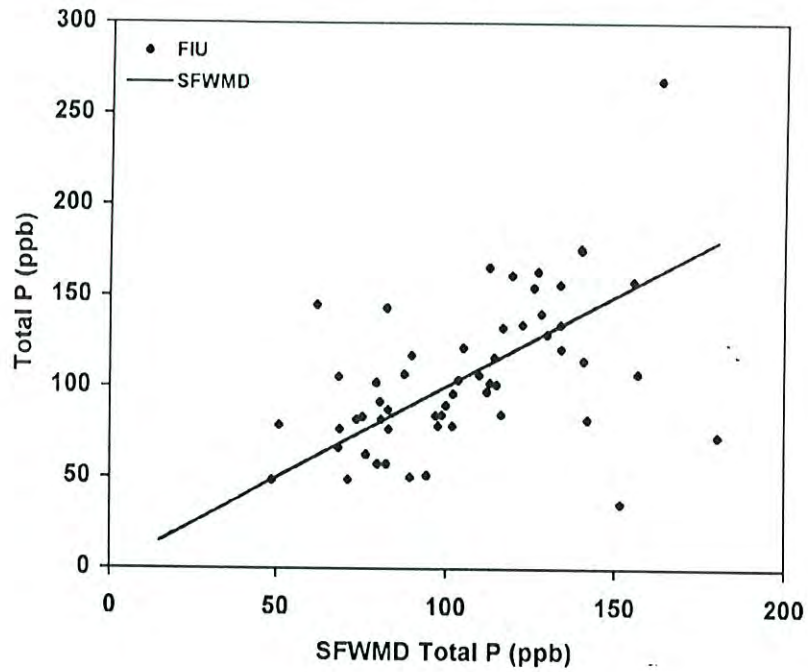
Exceedence Frequencies Number of Dates = 58

	Interim Limits		Longterm Limits	
	Mean	Std Error	Mean	Std Error
SFWMD	9%	3.7%	17%	5.0%
FIU	12%	4.3%	22%	5.5%
p	0.53		0.37	

<--- Test for Significant Difference in Exceedence Frequencies Based upon SFWMD vs. FIU Data

Figure 8

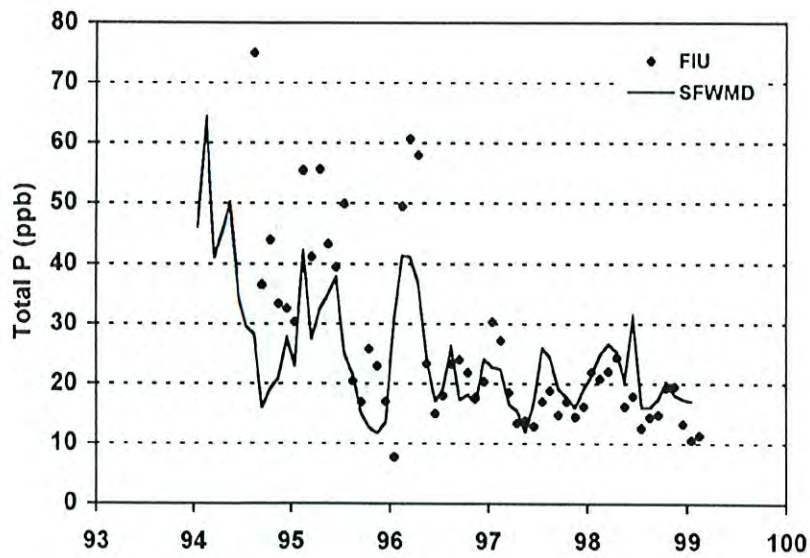
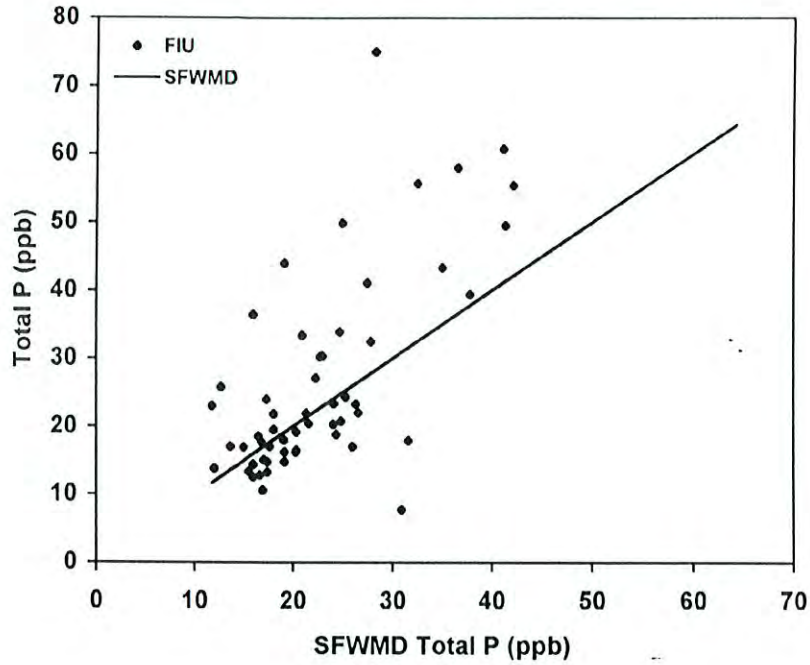
Paired Phosphorus Data
Station: ENR002 - ENR Inflow - Upstream of G250 Pump



Values Averaged by Month

Paired Phosphorus Data

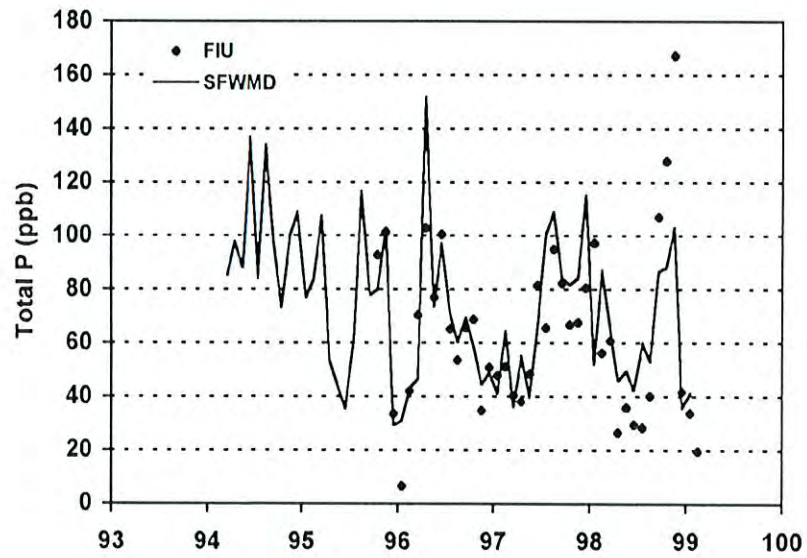
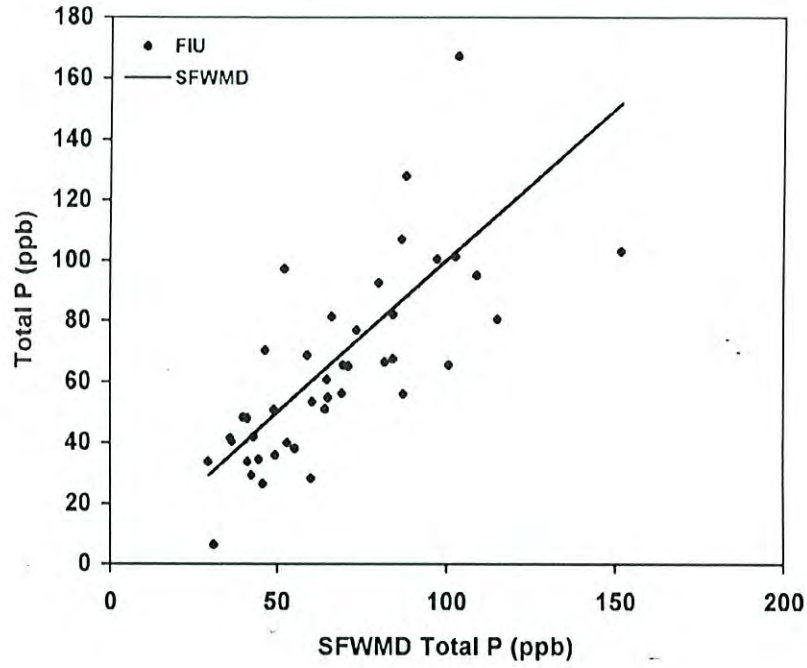
Station: ENR012_U - ENR Outflow - Upstream of G251 Pump



Values Averaged by Month

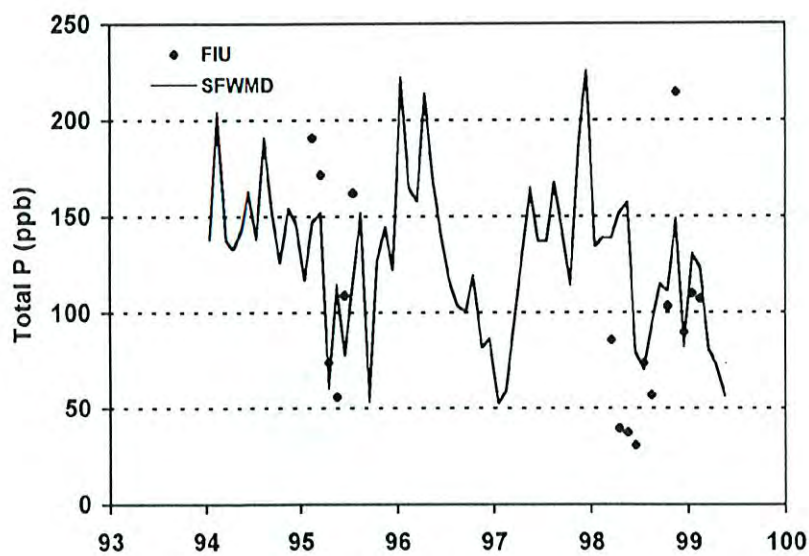
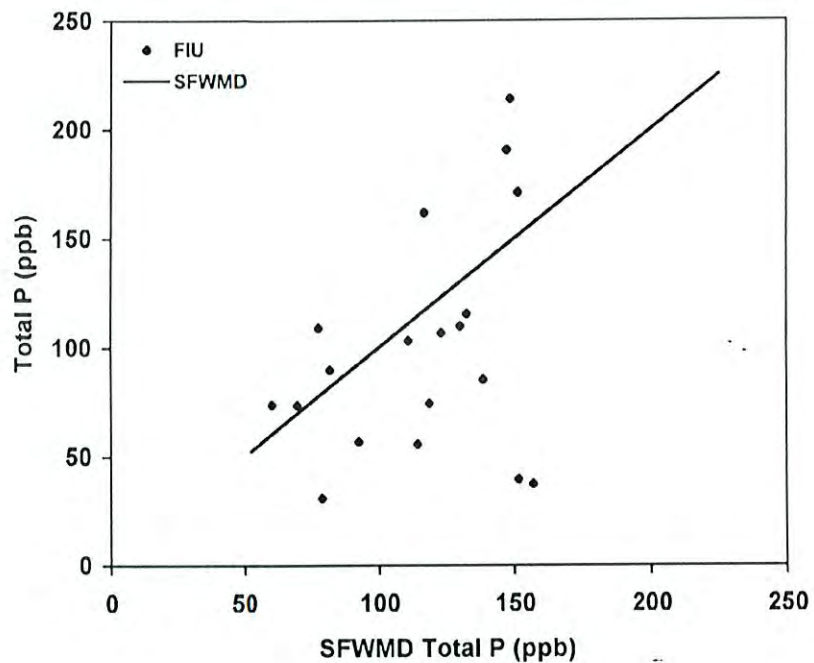
Paired Phosphorus Data

Station: ENR004 - L7 Canal at Jct of ENR Cell 1 & 3



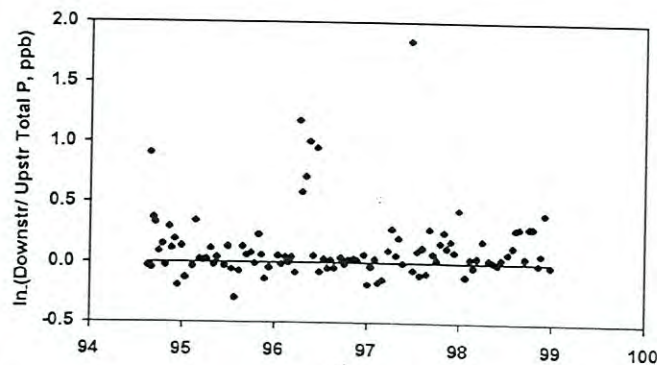
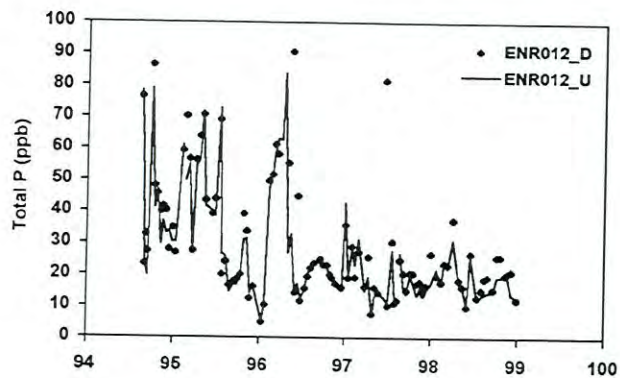
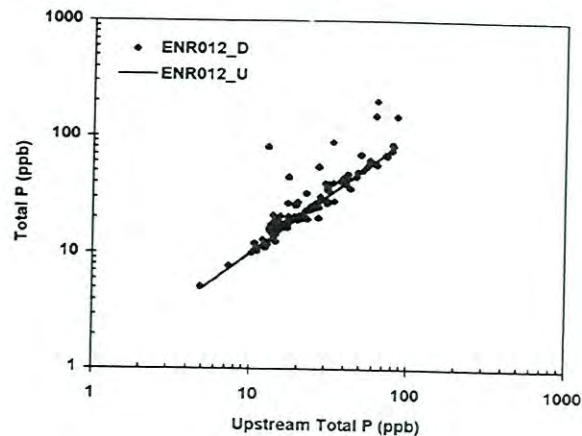
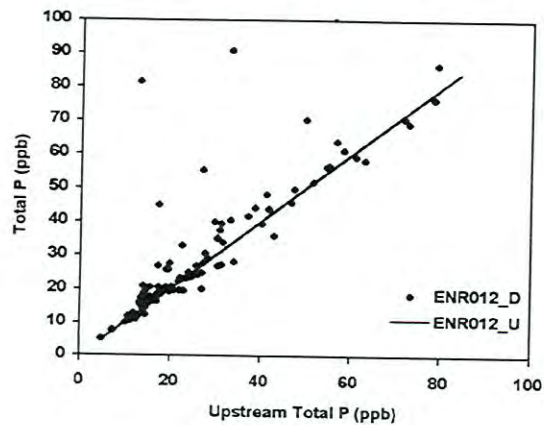
Values Averaged by Month

Paired Phosphorus Data
 Station: S5A_U - S5A - Upstream of Pump



Values Averaged by Month

Comparison of FIU Samples Upstream & Downstream of ENR Project Discharge



Paired Samples = 104

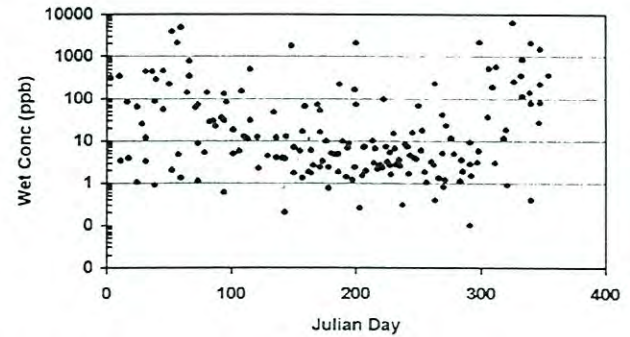
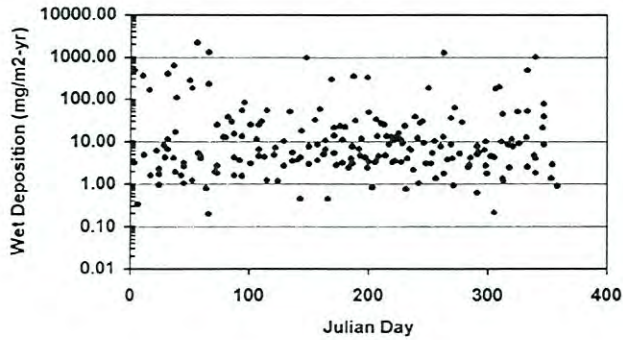
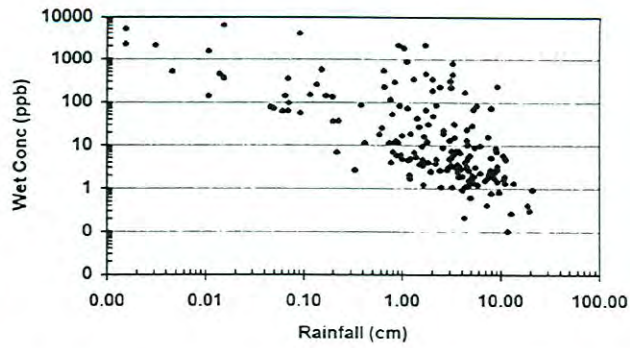
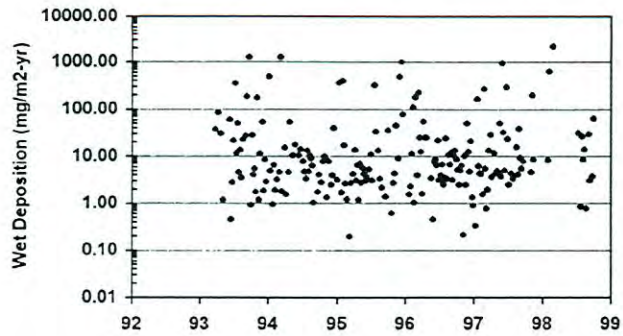
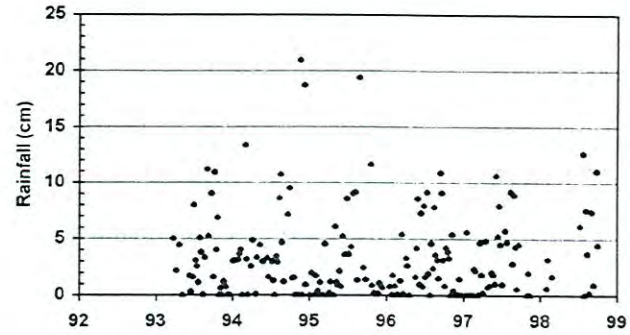
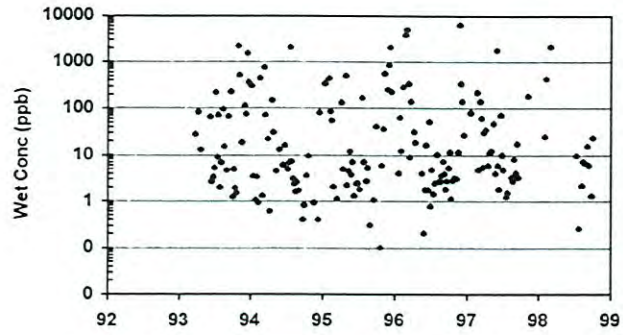
	<u>Geo. Mean</u>	<u>Median</u>	<u>CV</u>
Upstream	23.5	21.2	0.57
Downstream	26.7	23.4	0.65
% Difference	13%	10%	

ln (Downstream / Upstream)

Mean	0.13
Median	0.05
StdDev	0.29
t (Mean=0)	2.42
prob > t	0.017

Wet Deposition

Station: West

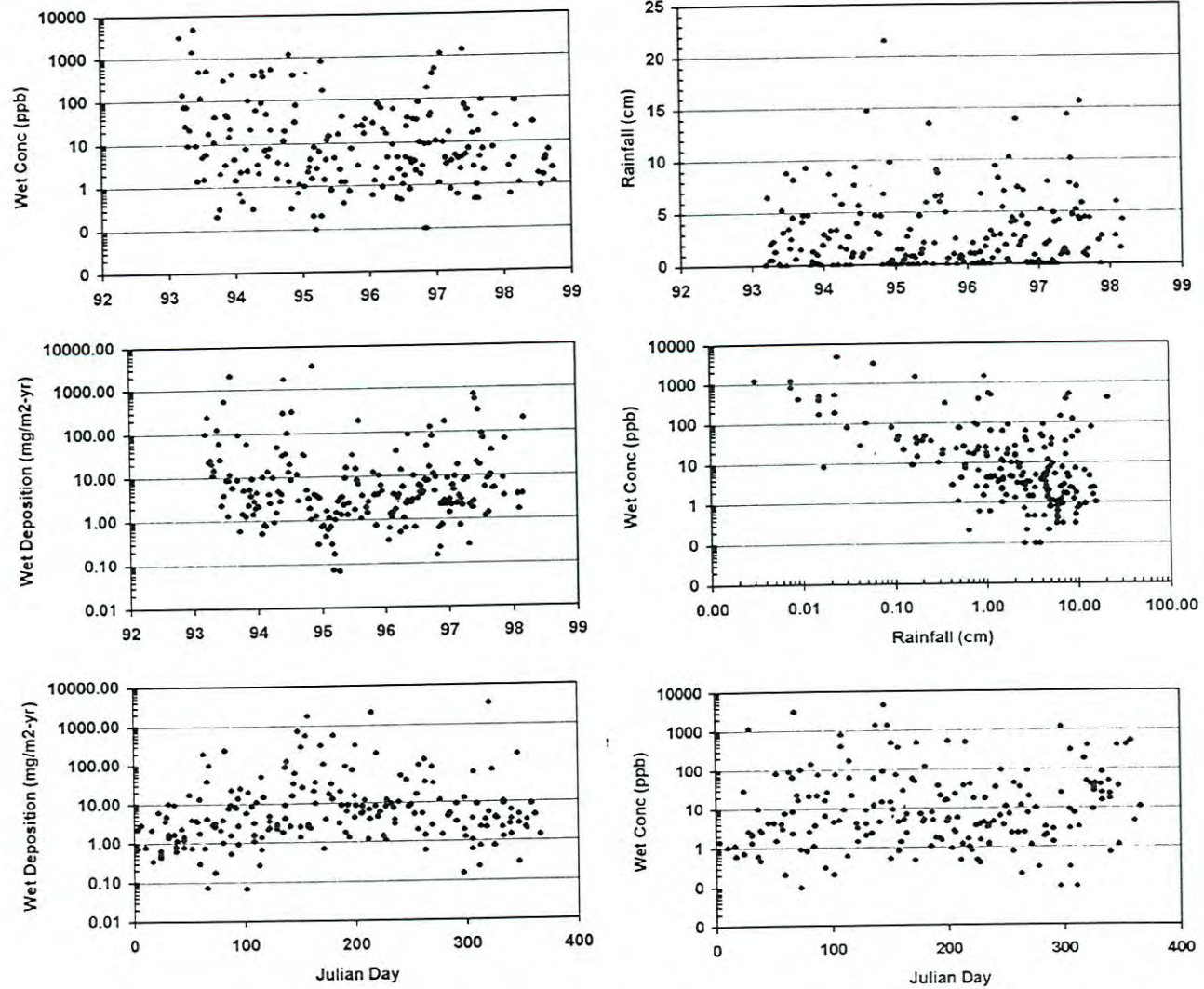


Sample Duration	1465 days			
Sample Count	199			
Volume Wtd Conc.	40.9 ppb	Medians	<u>Rainfall cm</u>	<u>Conc ppb</u>
		Means	1.84	10.1
			3.23	95.5
				<u>Depos. Rate mg/m2-yr</u>
				6.7
				69.7

Figure 14

Wet Deposition

Station: 1-7



Sample Duration 1580 days
 Sample Count 215
 Volume Wtd Conc. 40.8 ppb

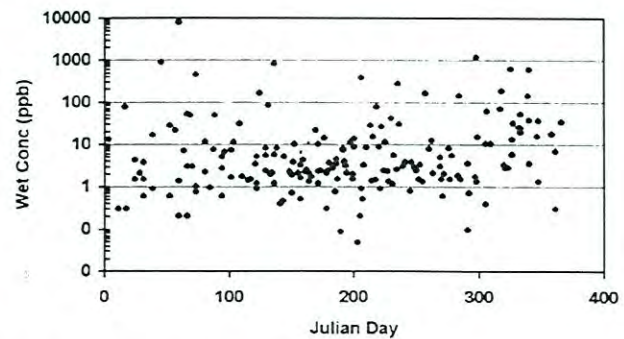
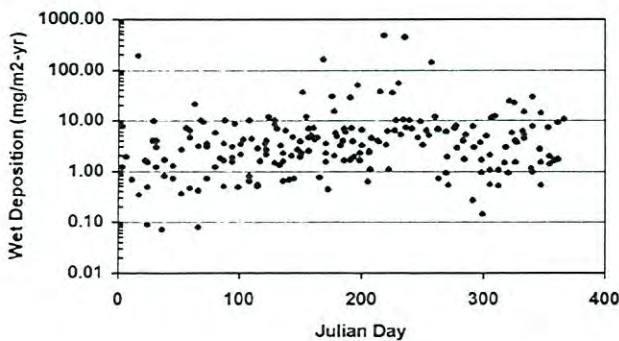
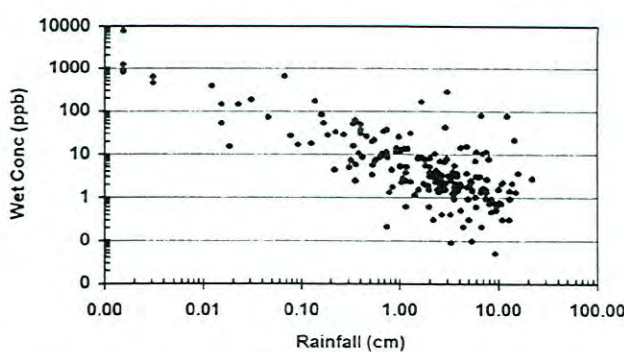
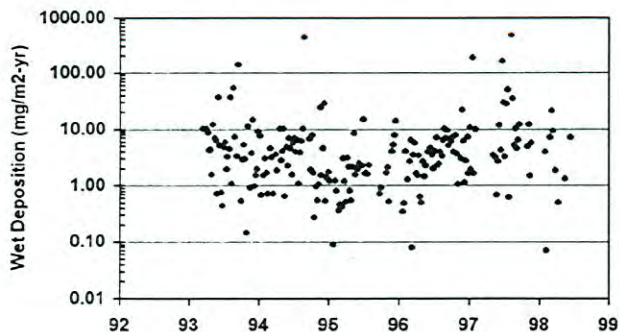
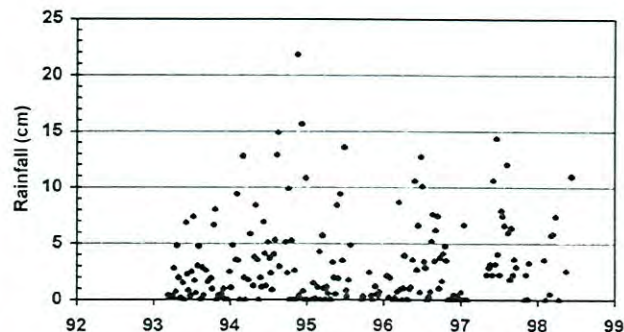
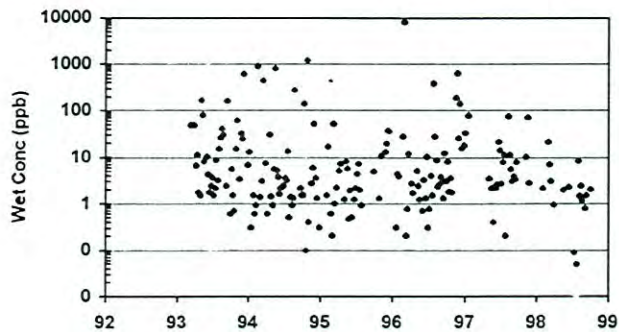
Medians
 Means

<u>Rainfall cm</u>	<u>Conc ppb</u>	<u>Depos. Rate mg/m²-yr</u>
1.76	7.5	4.0
3.16	59.2	62.3

Figure 15

Wet Deposition

Station: 1-9



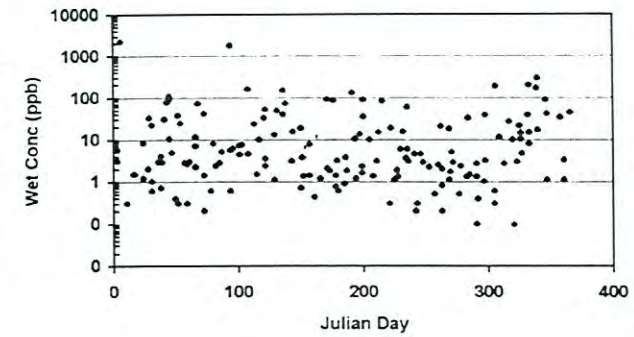
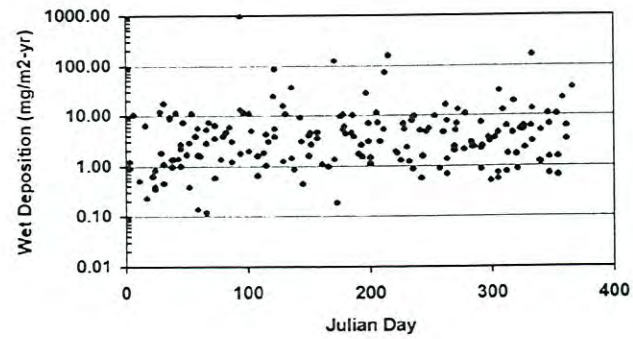
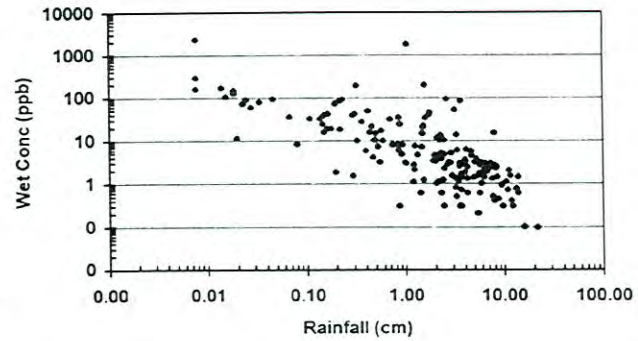
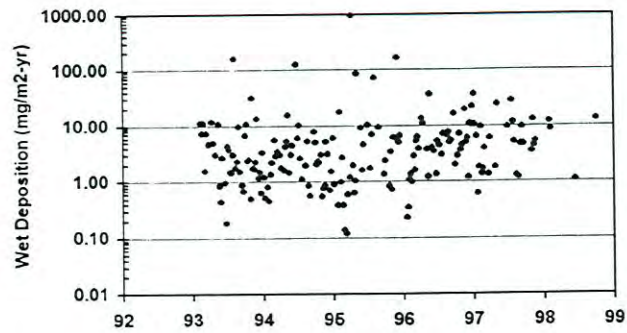
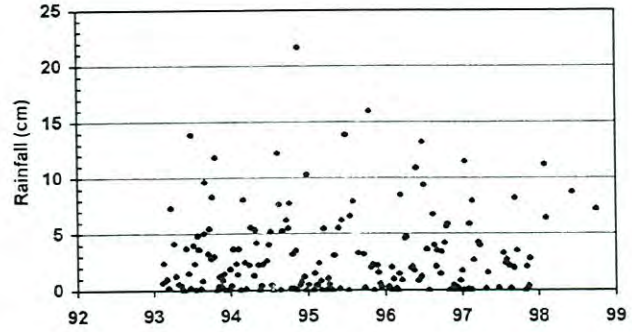
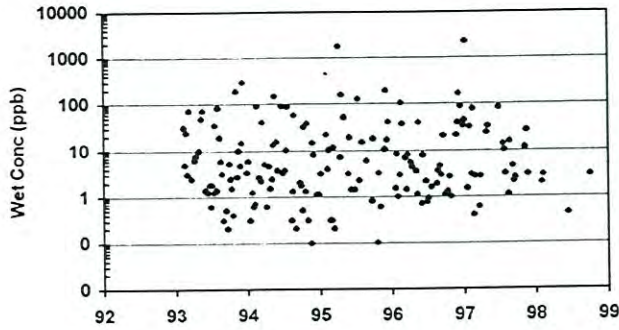
Sample Duration	1547 days			<u>Rainfall cm</u>	<u>Conc ppb</u>	<u>Depos. Rate mg/m2-yr</u>
Sample Count	211	Medians		2.00	3.9	3.3
Volume Wtd Conc.	7.8 ppb	Means		3.17	14.9	12.3

Figure 16

24

Wet Deposition

Station: L-1

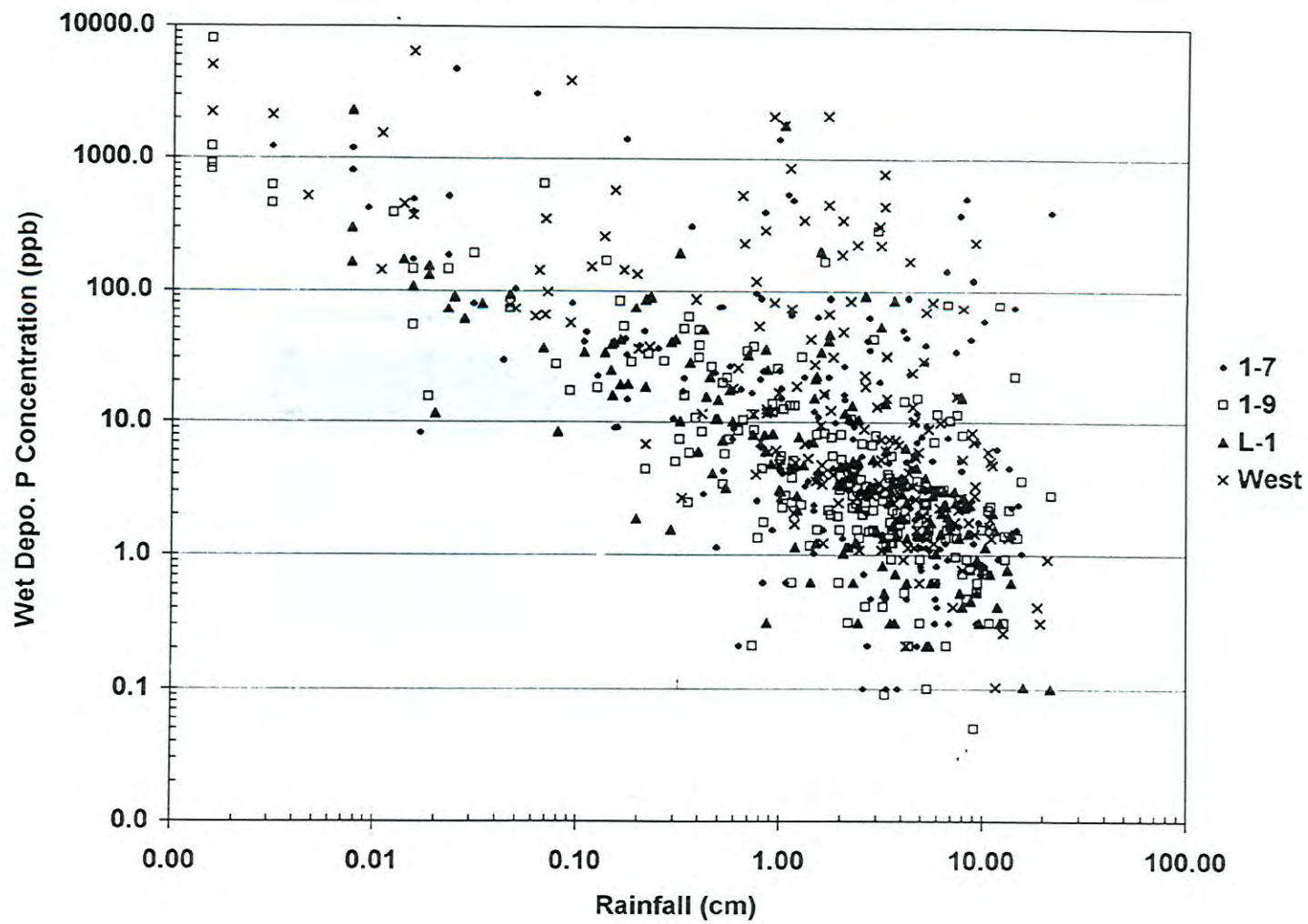


	Sample Duration	1335 days		Medians	Rainfall cm	Conc ppb	Depos. Rate mg/m2-yr
	Sample Count	184		Means	1.95	4.7	3.5
	Volume Wtd Conc.	8.8 ppb			3.02	26.6	13.7

Figure 17

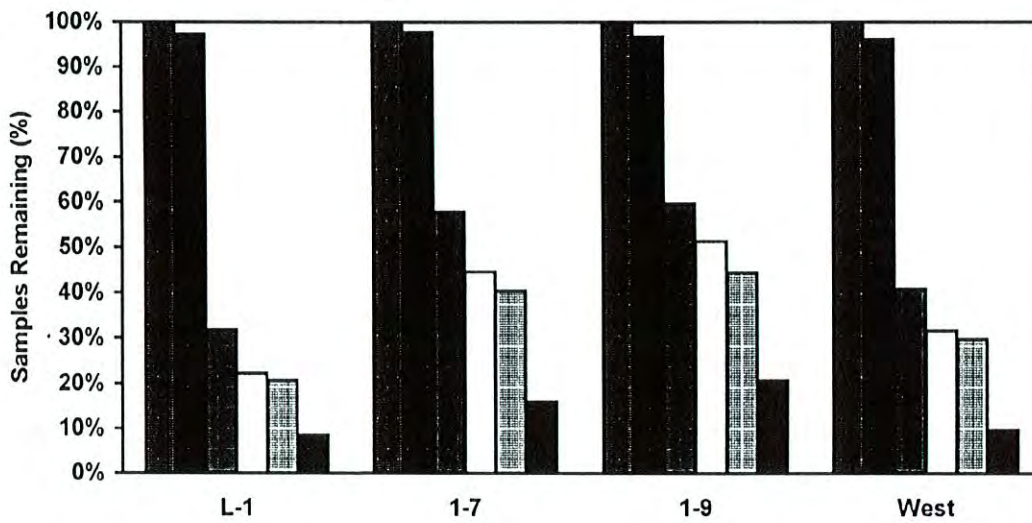
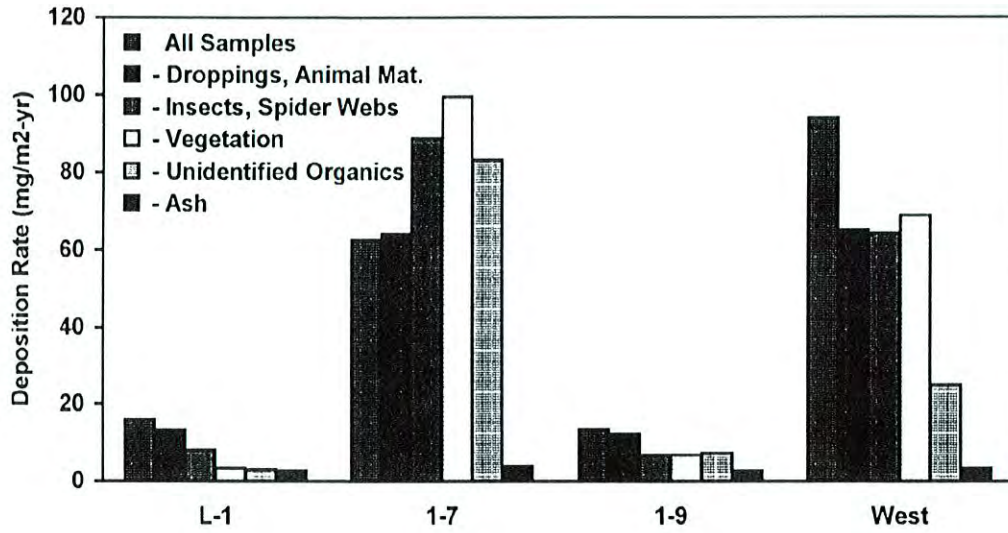
59

Rainfall P Concentration vs. Rainfall Volume



66

Sensitivity of Wet Deposition to Contaminants

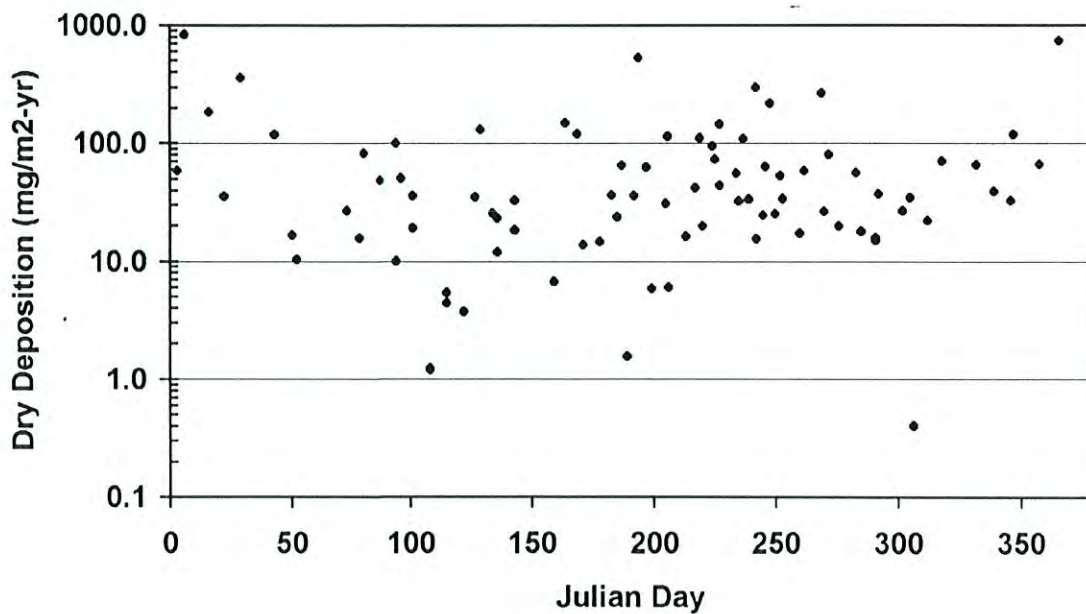
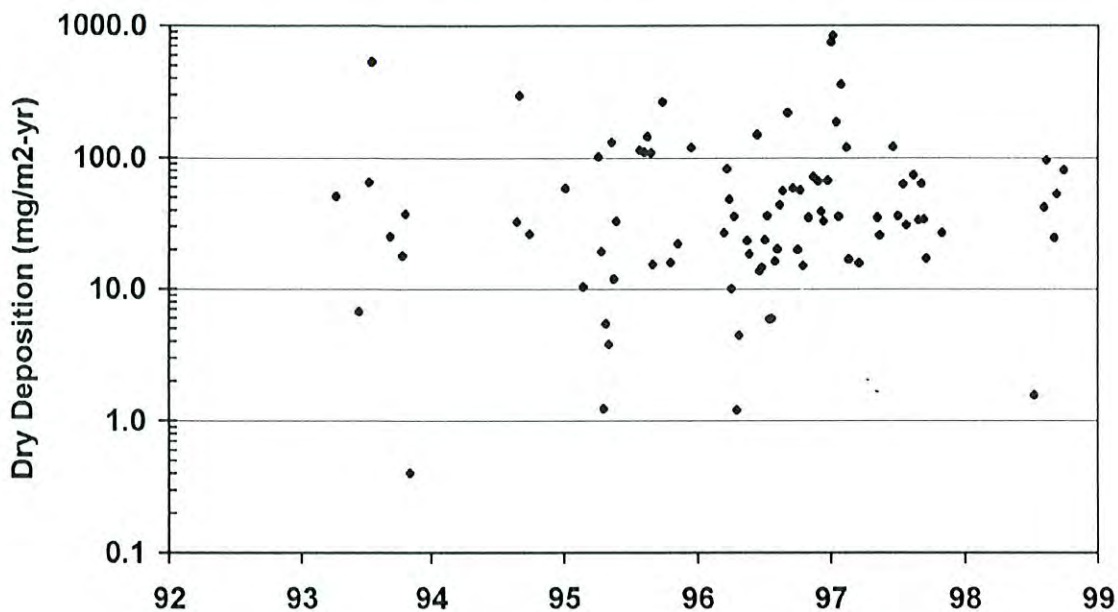


Sample Counts

Analyzed	189	220	218	208
Not Analyzed	85	54	56	66
% Not Analyzed	31%	20%	20%	24%

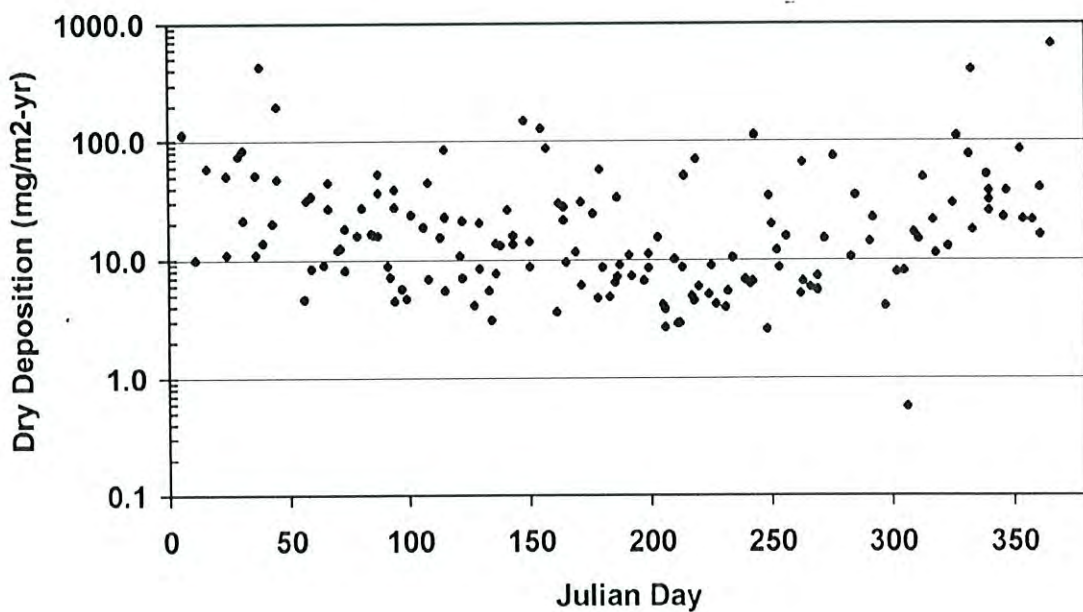
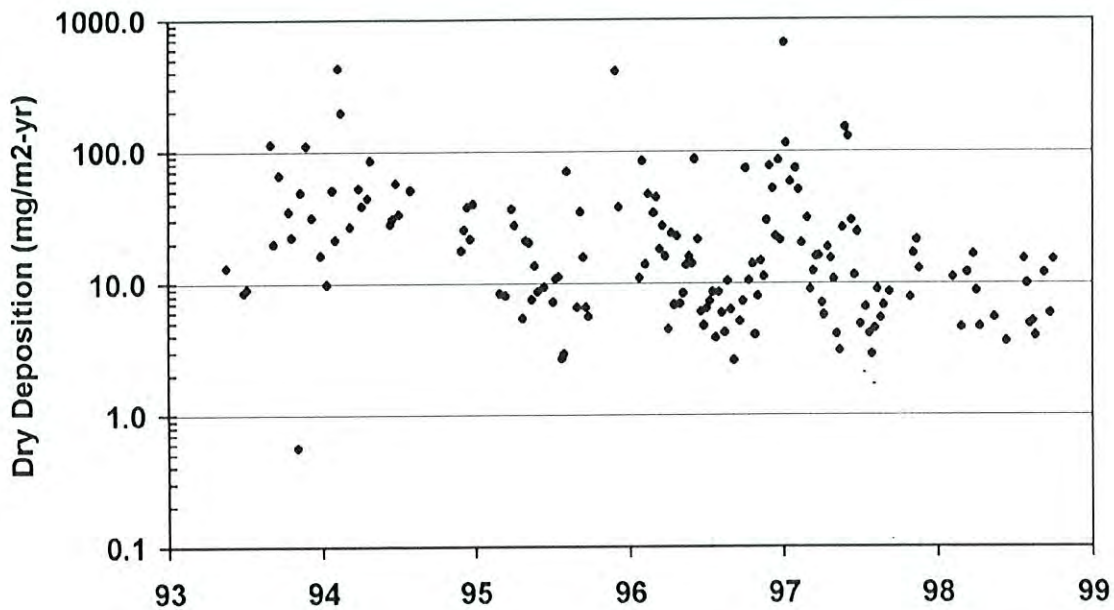
Cumulative Effects of Deleting Samples with Various Types of Contaminants

Dry Deposition Station: West



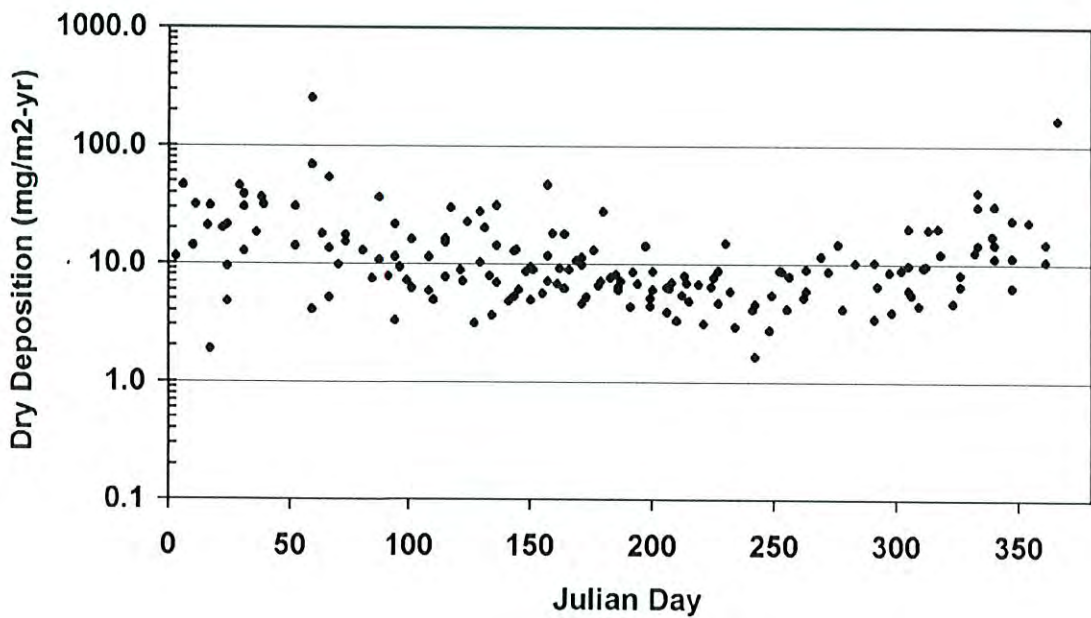
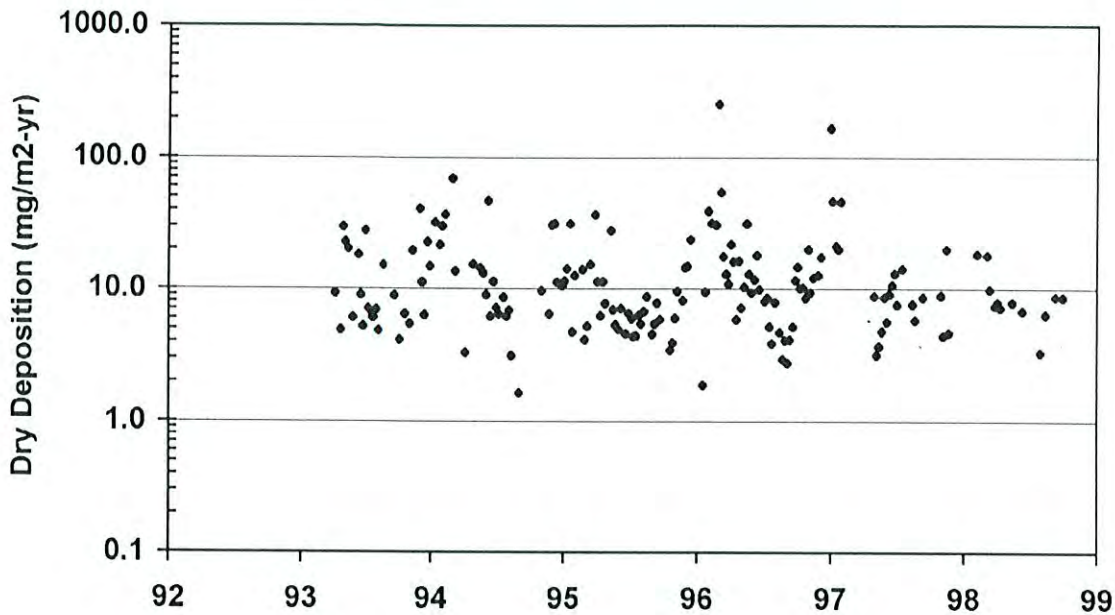
Samples	87	Mean	79.3 mg/m ² -yr
Duration	620 days	Median	35.3 mg/m ² -yr
		CV	1.74

Dry Deposition Station: 1-7

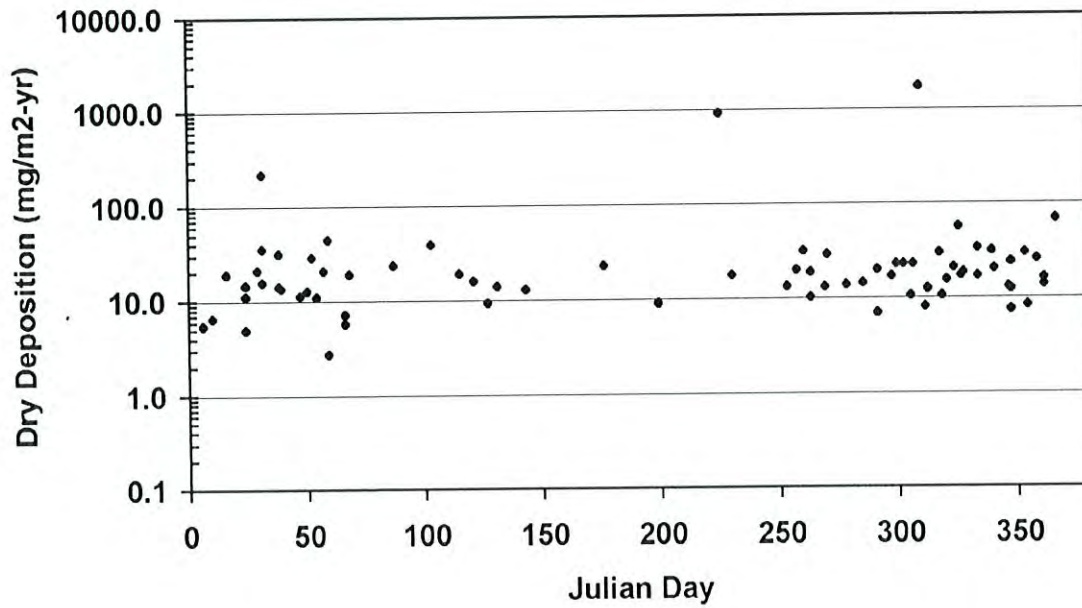
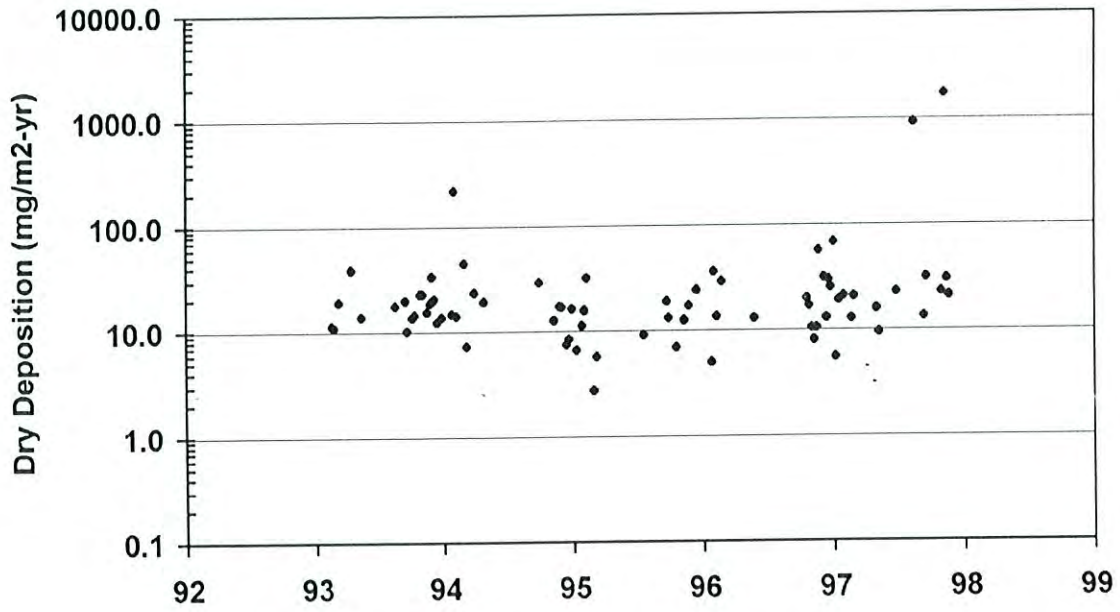


Samples	158	Mean	34.1 mg/m2-yr
Duration	1160 days	Median	14.1 mg/m2-yr
		CV	2.16

Dry Deposition Station: 1-9

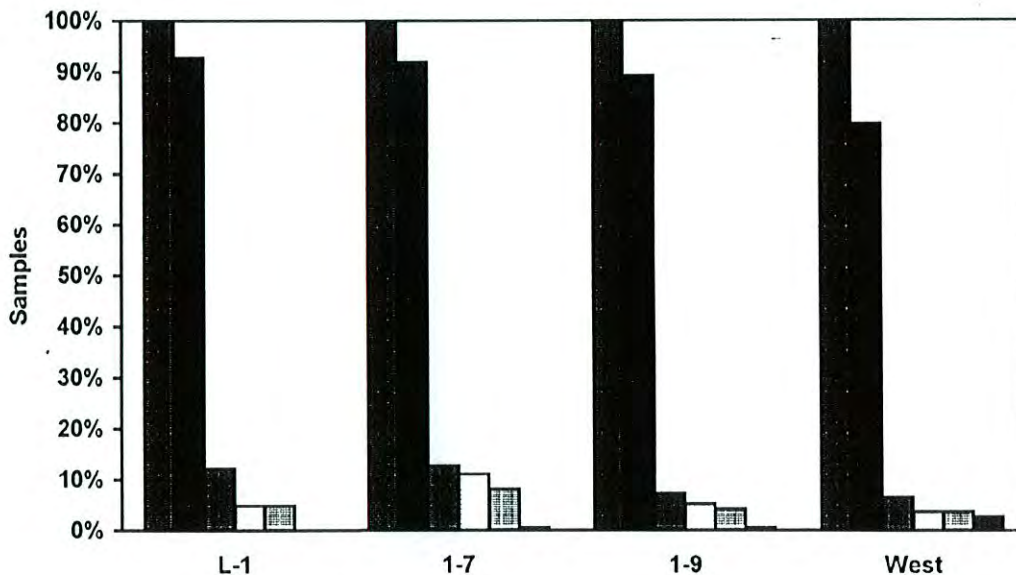
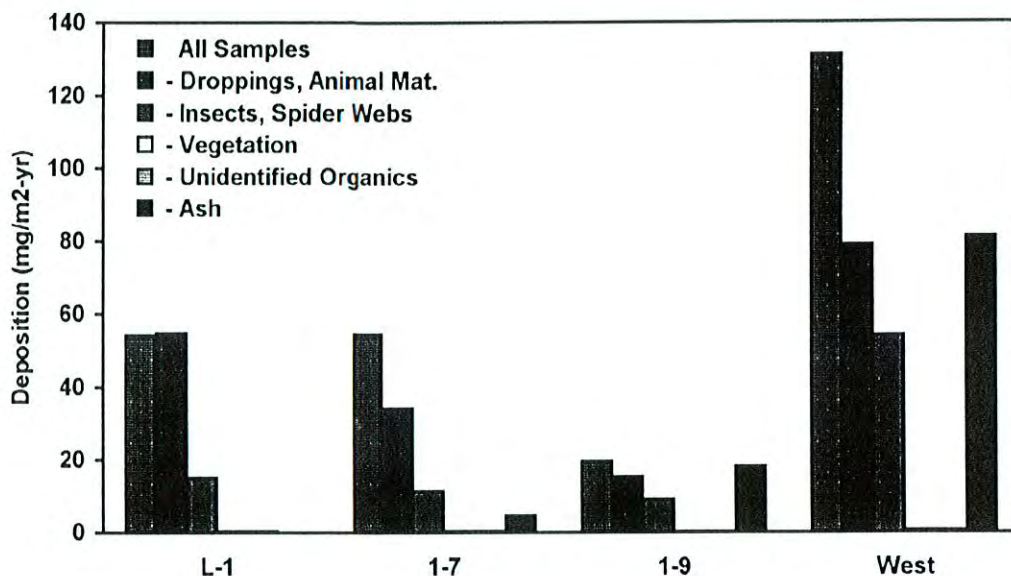


Dry Deposition Station: L-1



Samples	76	Mean	55.9 mg/m ² -yr
Duration	557 days	Median	17.2 mg/m ² -yr
		CV	3.97

Sensitivity of Dry Deposition to Contaminants



Sample Counts

Analyzed	82	172	193	109
Not Analyzed	192	102	81	165
% Not Analy.	70%	37%	30%	60%

Cumulative Effects of Deleting Samples with Various Types of Contaminants

Analysis of Everglades Round Robin Results

Rounds 2-8

W. Walker for U.S. Department of the Interior
wwwalker@shore.net

October 19, 1999

Procedure:

- 1 Compile data for Round Robins 2-8; Govt, Research, Contract Labs Used by SFWMD
- 2 Set observations ≤ 4 ppb to 4 ppb (~removes effects of differences in lab detection limits)
- 3 Take median of 3-4 replicates for each sample & lab
- 4 Compute reference value for each sample = median (DEP, FIU, Duke, SFWMD, USSC)
- 5 Compare lab result with reference value for each sample.
- 6 Summarize Accuracy (vs. Reference V) & Precision (Replicate Variance) for each lab (P1)
- 7 Plot lab results vs. reference values (P 2-4)
- 8 Plot Deviations from Reference vs. Sample for each lab (P 5-12)
- 9 Plot Correlations with Reference Value for each lab (P 13-20)

Results:

- 1 Statistical Summary
- 2 Lab Results vs. Reference Values - Linear Scales
- 3 Lab Results vs. Reference Values - Linear Scales, 0-20 ppb
- 4 Lab Results vs. Reference Values - Log Scales
- 5 Deviations from Reference Value DEP
- 6 Deviations from Reference Value Duke
- 7 Deviations from Reference Value FIU
- 8 Deviations from Reference Value PBB
- 9 Deviations from Reference Value PBS&J
- 10 Deviations from Reference Value SFWMD
- 11 Deviations from Reference Value USGS
- 12 Deviations from Reference Value US Sugar Research
- 13 Correlations with Reference Value DEP
- 14 Correlations with Reference Value Duke
- 15 Correlations with Reference Value FIU
- 16 Correlations with Reference Value PBB
- 17 Correlations with Reference Value PBS&J
- 18 Correlations with Reference Value SFWMD
- 19 Correlations with Reference Value USGS
- 20 Correlations with Reference Value US Sugar Research

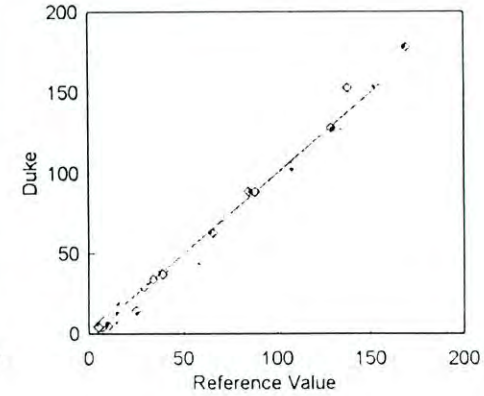
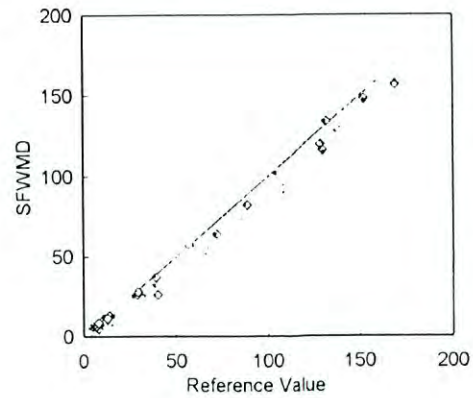
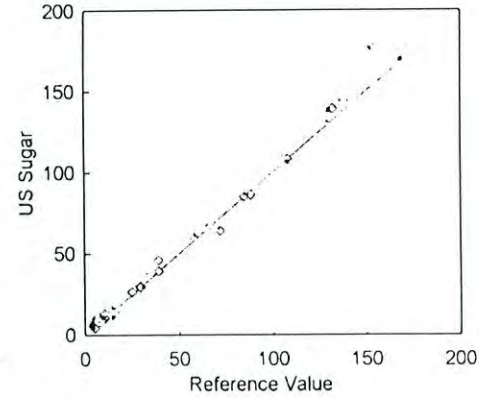
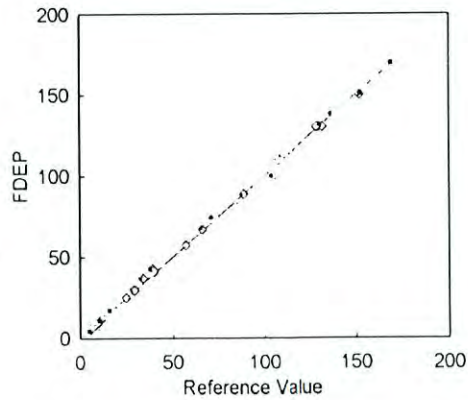
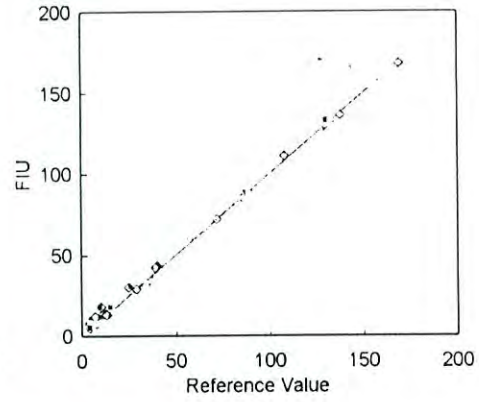
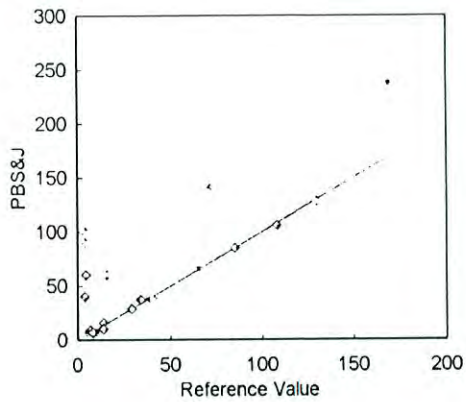
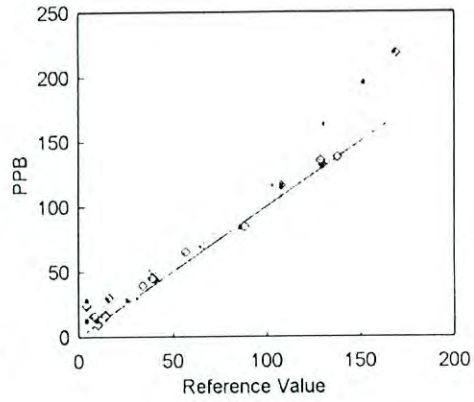
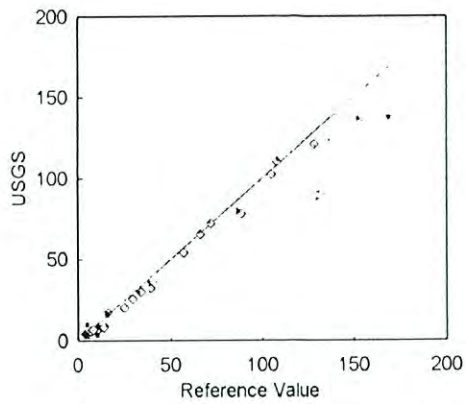
* dashed lines in Pages 5-12 show +/- 2 standard deviation control limits, with standard deviations computed from DEP results (= 7% or 1.7 ppb).

Statistical Summary - Everglades Round Robins 2-8

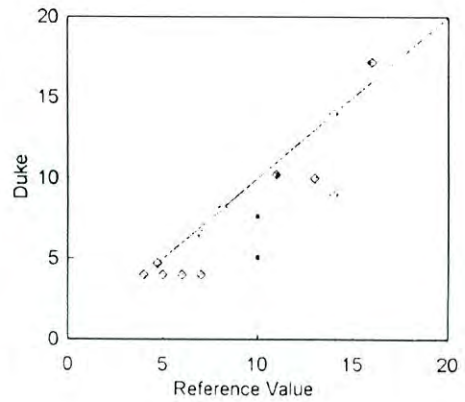
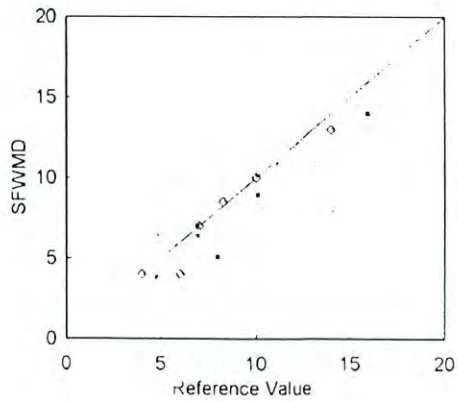
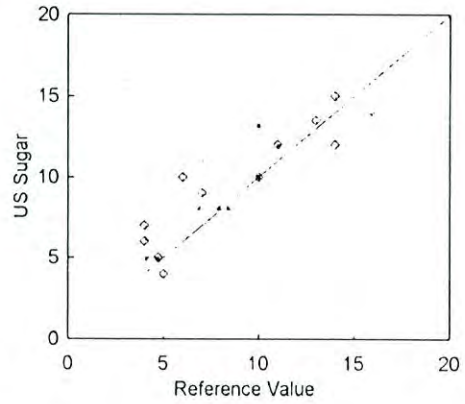
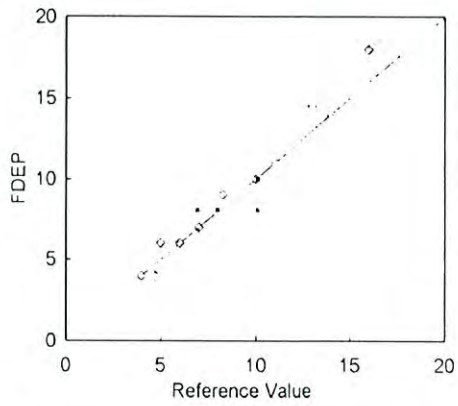
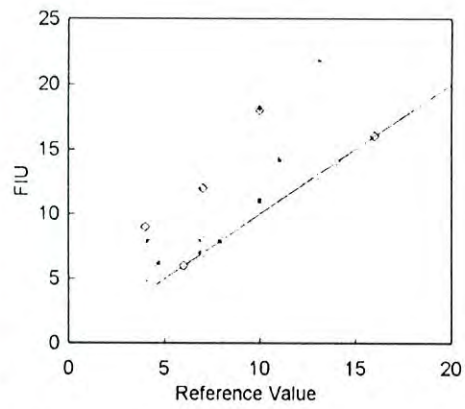
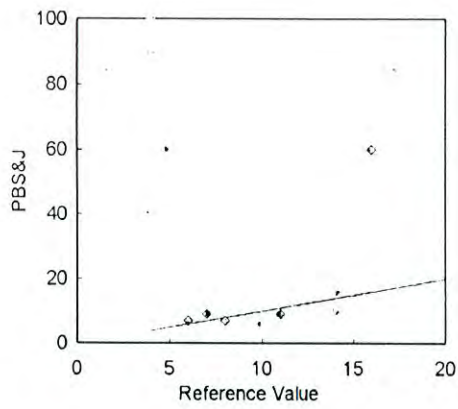
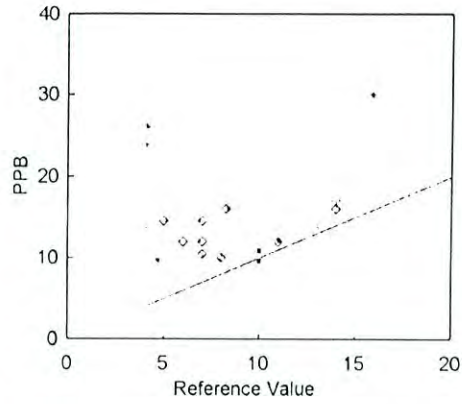
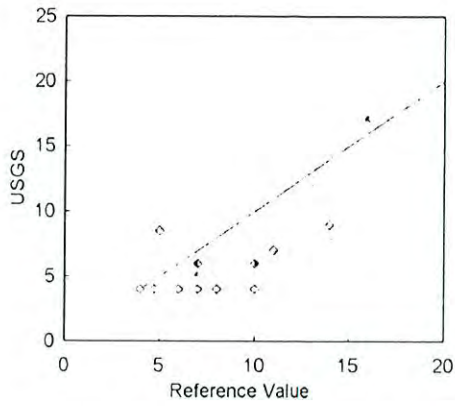
Reference Values: Median (Duke WC, US Sugar Research, SFWMD, FIU, DEP)

Lab	Duke WC	US Sugar	USGS	PBB	PBS&J	SFWMD	FIU	DEP
All Samples								
Samples	38	38	38	38	38	38	33	38
Relative Accuracy: Lab Result - Reference Result, %								
Median	-0%	4%	-13%	14%	10%	-7%	1%	0%
Mean	-9%	10%	-15%	63%	214%	-9%	16%	2%
Standard Deviation	16%	21%	21%	123%	553%	13%	32%	7%
t (Mean = 0)	-3.35	3.00	-4.42	3.17	2.39	-4.32	2.90	1.49
Signif	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.14
Relative Accuracy: Lab Result - Reference Result, ppb								
Median	-0.13	0.90	-4.00	5.15	2.00	-2.00	0.50	0.00
Mean	-0.77	1.92	-6.43	8.19	14.88	-4.08	1.32	0.31
Standard Deviation	4.62	4.87	10.29	11.18	26.92	4.97	2.44	1.56
t (Mean = 0)	-1.03	2.42	-3.85	4.52	3.41	-5.07	3.11	1.23
Signif	0.31	0.02	0.00	0.00	0.00	0.00	0.00	0.23
Relative Precision: Standard Deviations Among Replicates %								
Median	14%	11%	13%	20%	25%	21%	19%	13%
Mean	20%	19%	23%	41%	39%	28%	33%	19%
Low-Range Samples (Reference Value < 20 ppb)								
Samples	18	18	18	18	18	18	16	18
Relative Accuracy: Lab Result - Reference Result, %								
Median	-7%	8%	-25%	79%	42%	-4%	18%	0%
Mean	-16%	18%	-20%	122%	436%	-8%	31%	2%
Standard Deviation	19%	28%	30%	161%	752%	17%	40%	10%
t (Mean = 0)	-3.59	2.70	-2.80	3.20	2.46	-2.06	3.12	0.81
Signif	0.00	0.02	0.01	0.01	0.02	0.06	0.01	0.43
Relative Accuracy: Lab Result - Reference Result, ppb								
Median	-0.65	1.00	-1.88	5.15	3.75	-0.25	1.00	0.00
Mean	-1.38	0.98	-2.00	6.67	20.95	-0.91	2.02	0.20
Standard Deviation	1.82	1.79	2.53	6.45	31.29	1.66	2.42	0.86
t (Mean = 0)	-3.22	2.31	-3.35	4.39	2.84	-2.33	3.34	0.97
Signif	0.01	0.03	0.00	0.00	0.01	0.03	0.00	0.34
Relative Precision: Standard Deviations Among Replicates %								
Median	24%	24%	21%	41%	47%	34%	24%	26%
Mean	25%	26%	30%	55%	47%	36%	32%	25%

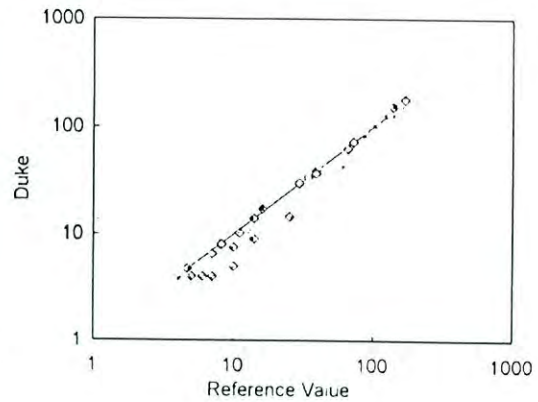
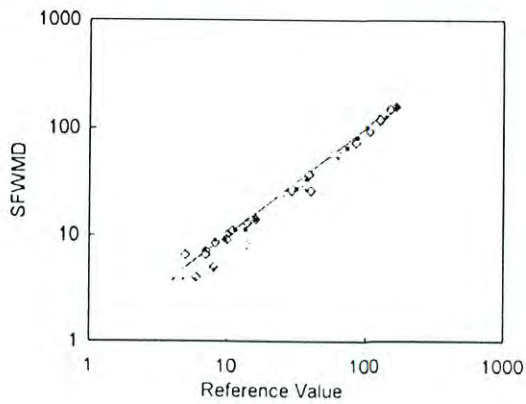
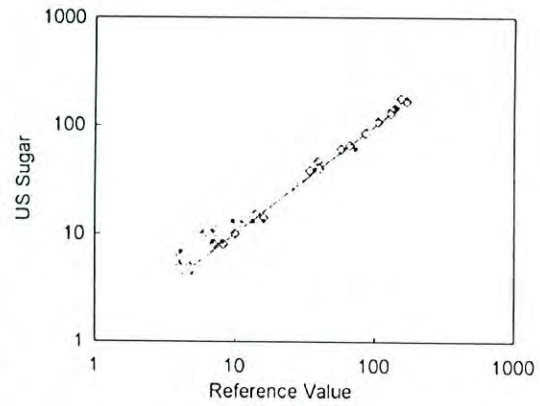
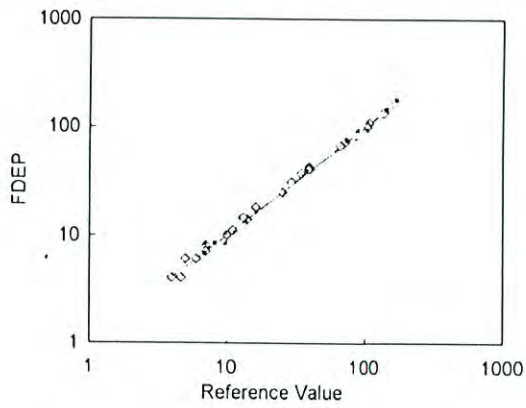
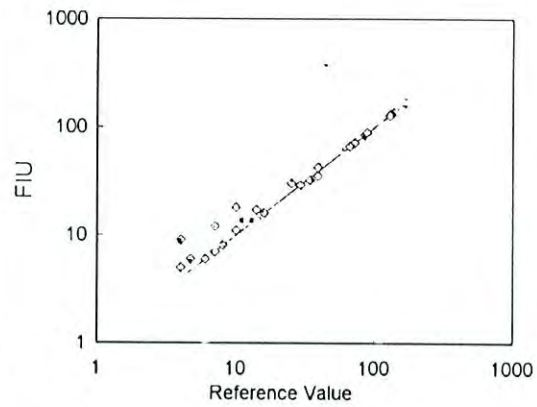
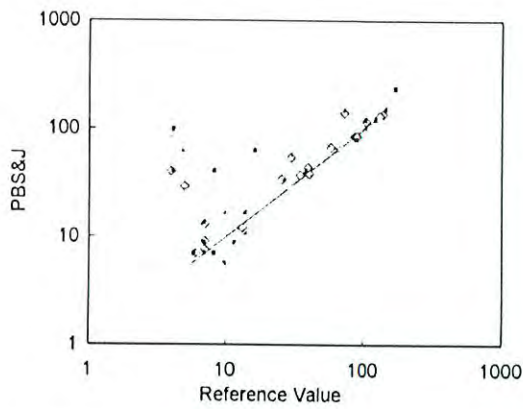
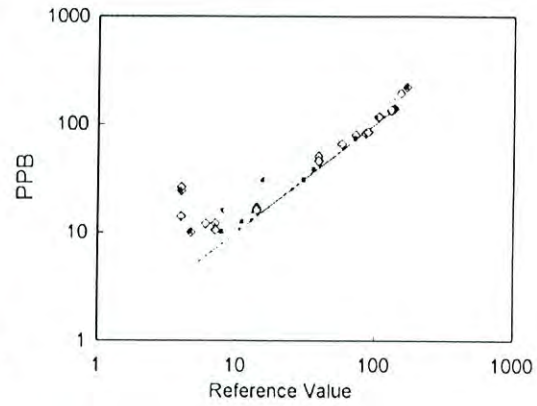
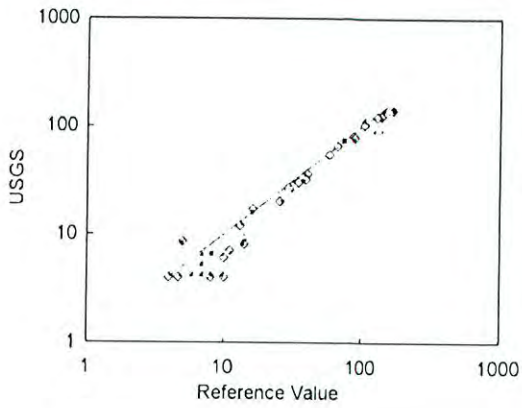
Comparison of Sample Medians - Linear Scales
 Reference Value = Median (Duke WC, US Sugar Research, SFWMD, FIU, DEP)



Comparison of Sample Medians - Linear Scales - 0-20 ppb
 Reference Value = Median (Duke WC, US Sugar Research, SFWMD, FIU, DEP)

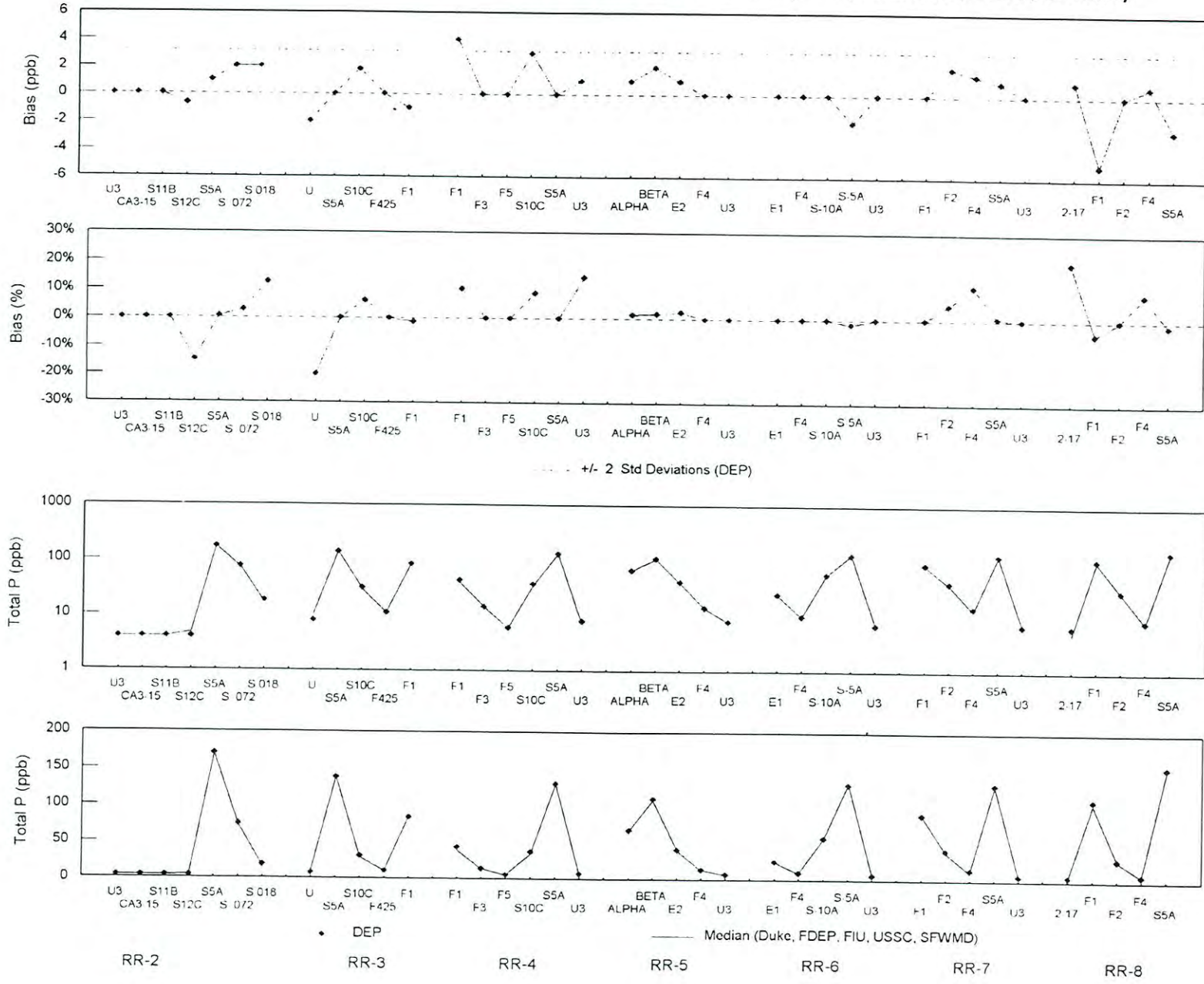


Comparison of Sample Medians -Logarithmic Scales
 Reference Value = Median (Duke WC, US Sugar Research, SFWMD, FIU, DEP)



Lab: DEP

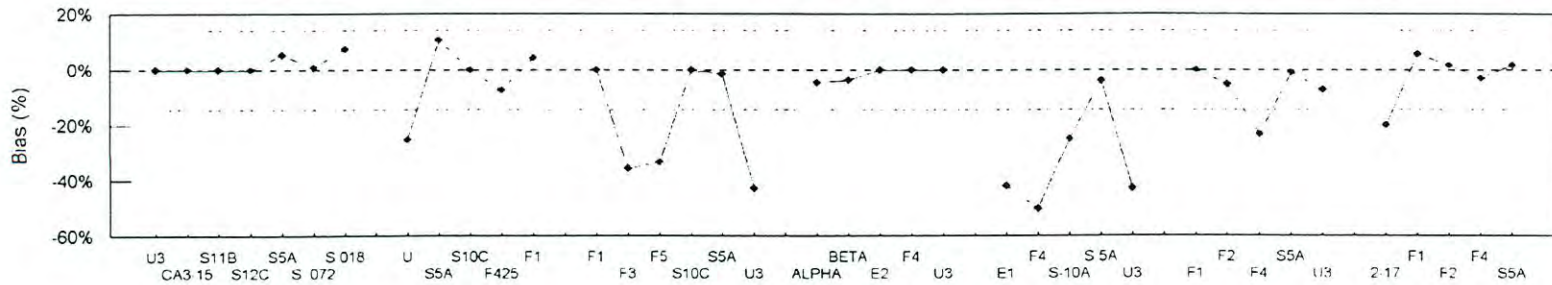
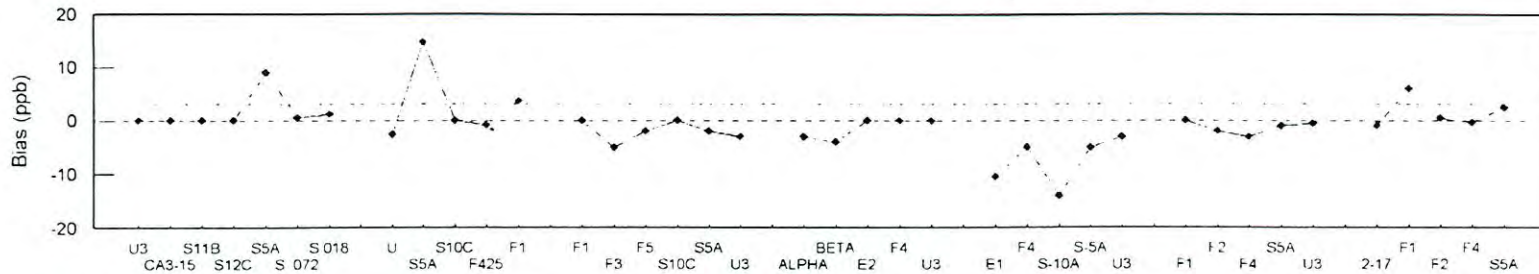
Bias = Lab Result - Median (Duke, FDEP, FIU, USSC, SFWMD)



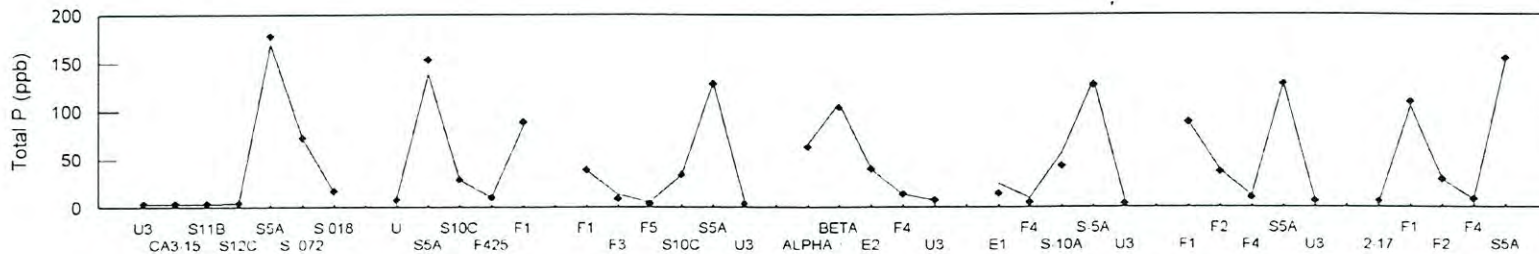
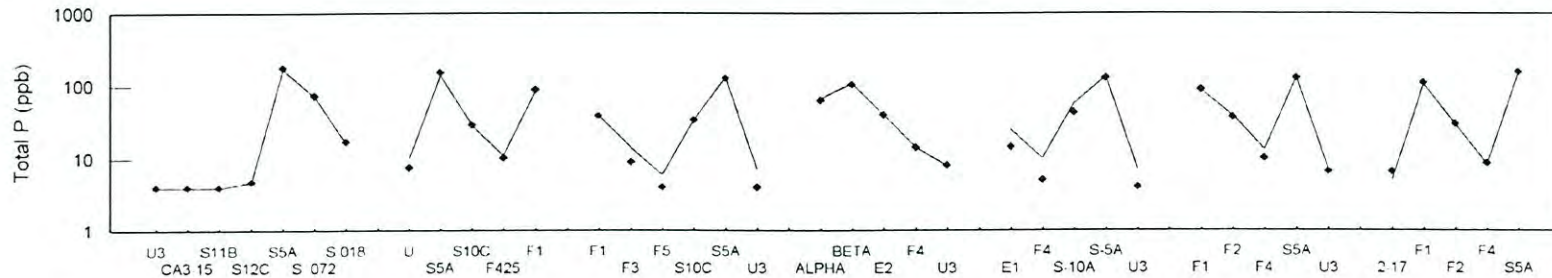
72

Lab: Duke

Bias = Lab Result - Median (Duke, FDEP, FIU, USSC, SFWMD)



--- +/- 2 Std Deviations (DEP)



• Duke

— Median (Duke, FDEP, FIU, USSC, SFWMD)

RR-2

RR-3

RR-4

RR-5

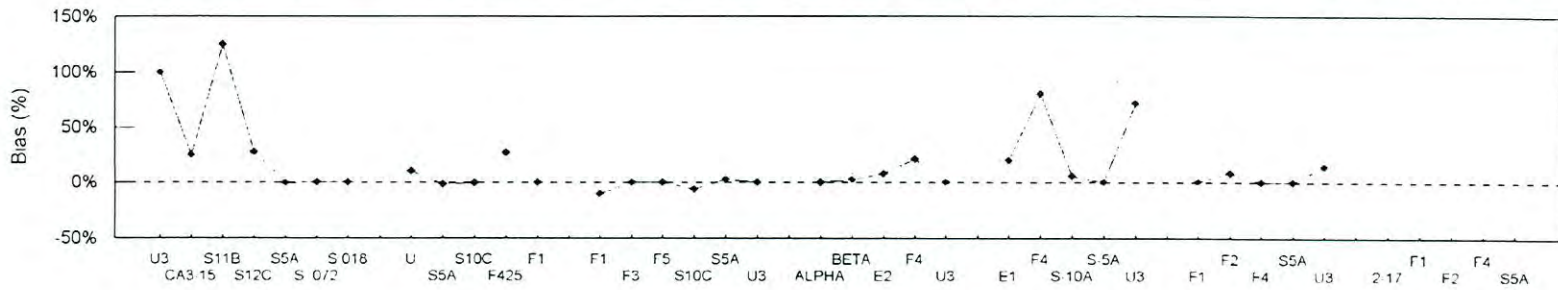
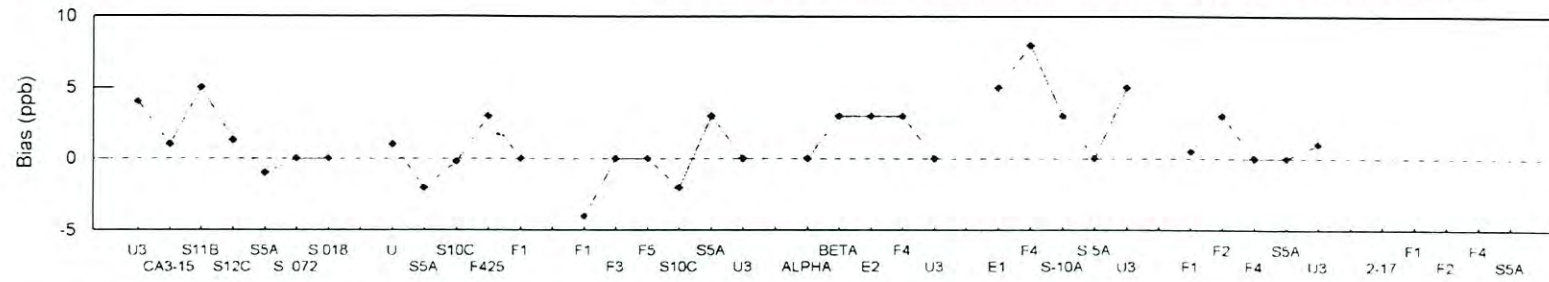
RR-6

RR-7

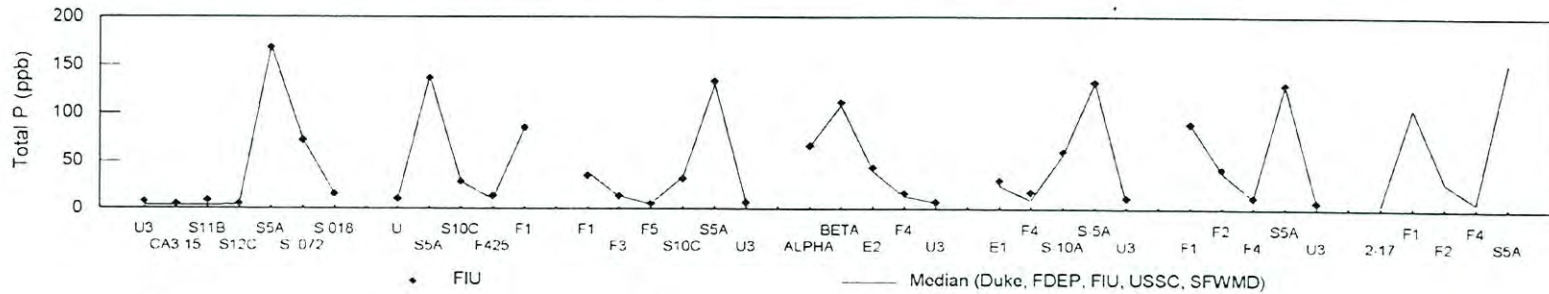
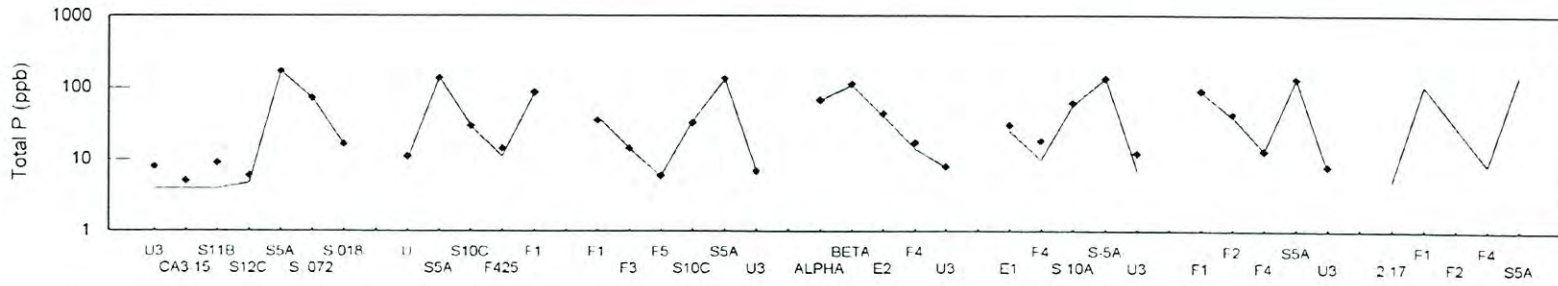
RR-8

Lab: FIU

Bias = Lab Result - Median (Duke, FDEP, FIU, USSC, SFWMD)



--- +/- 2 Std Deviations (DEP)

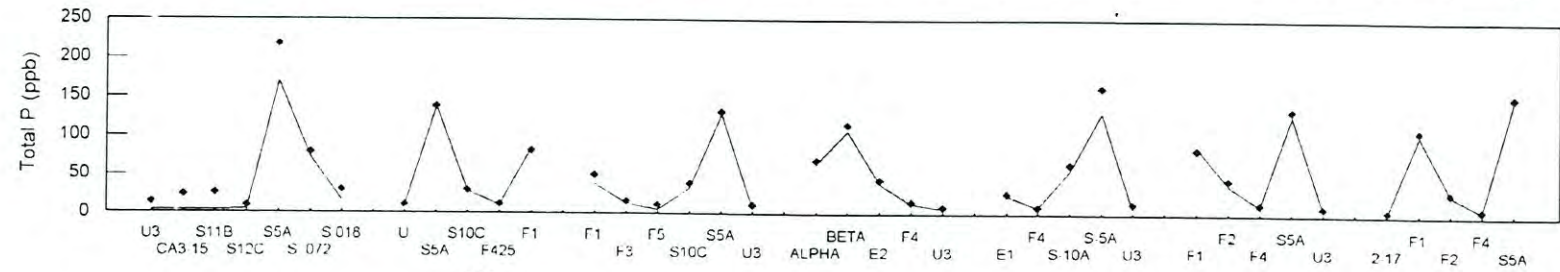
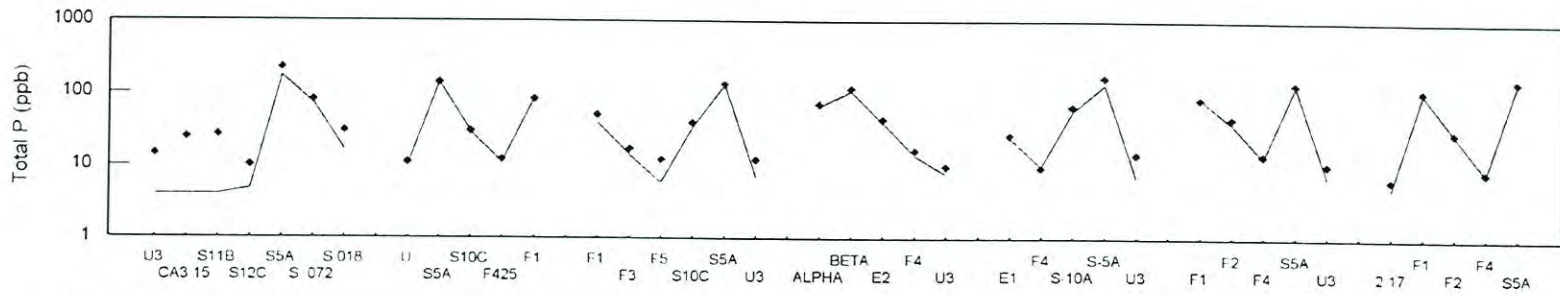
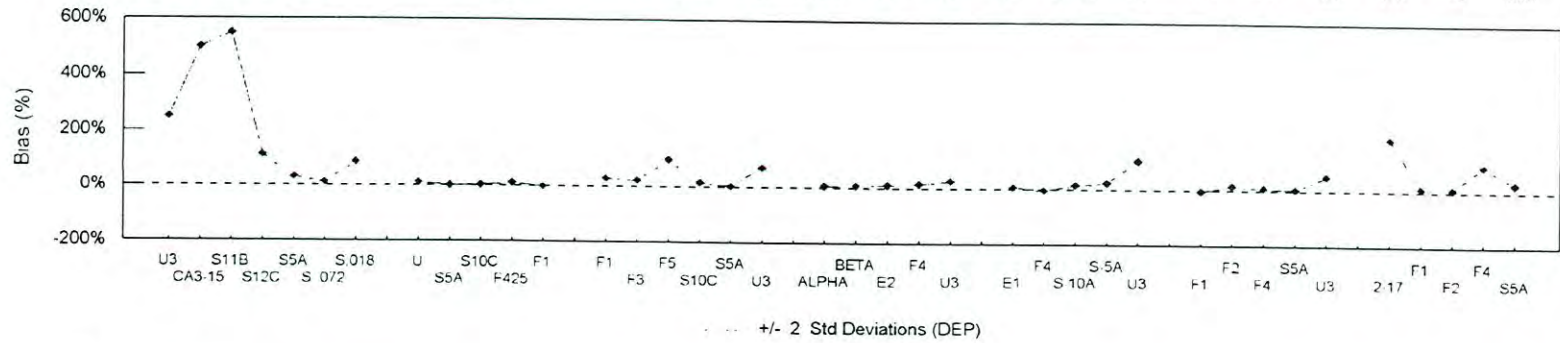
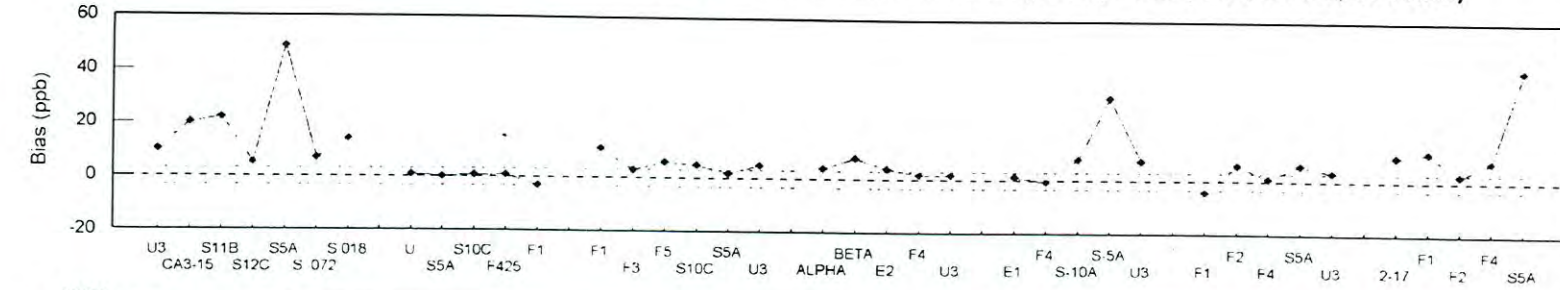


• FIU — Median (Duke, FDEP, FIU, USSC, SFWMD)

RR-2 RR-3 RR-4 RR-5 RR-6 RR-7 RR-8

Lab: PBB

Bias = Lab Result - Median (Duke, FDEP, FIU, USSC, SFWMD)



◆ PBB
 — Median (Duke, FDEP, FIU, USSC, SFWMD)

RR-2

RR-3

RR-4

RR-5

RR-6

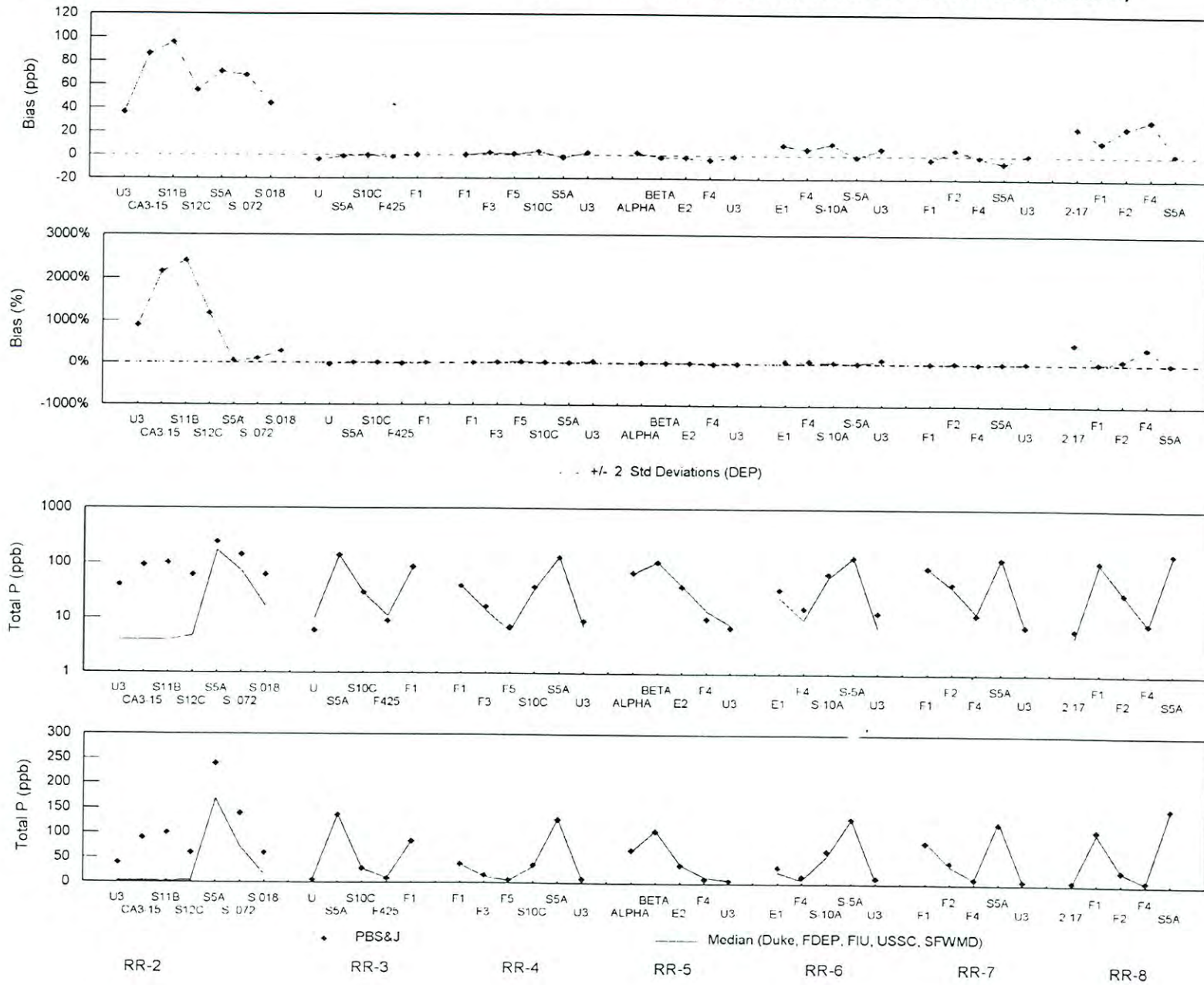
RR-7

RR-8

28

Lab: PBS&J

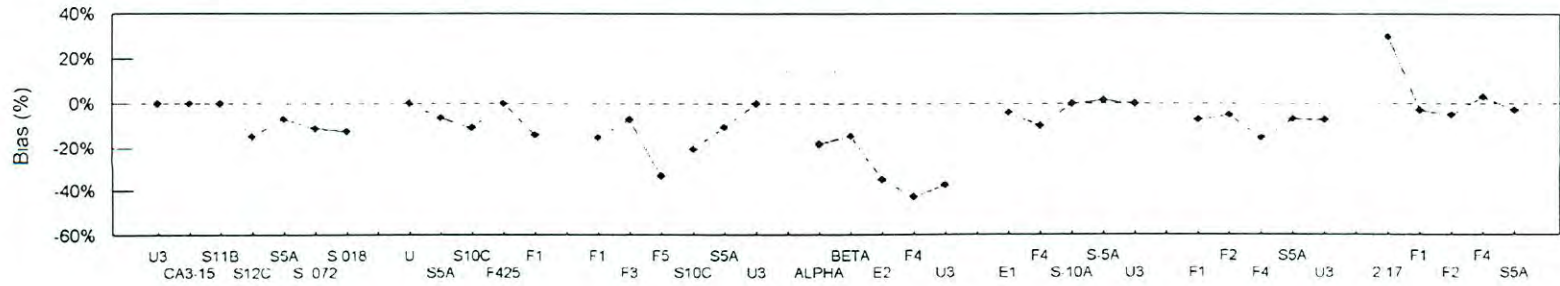
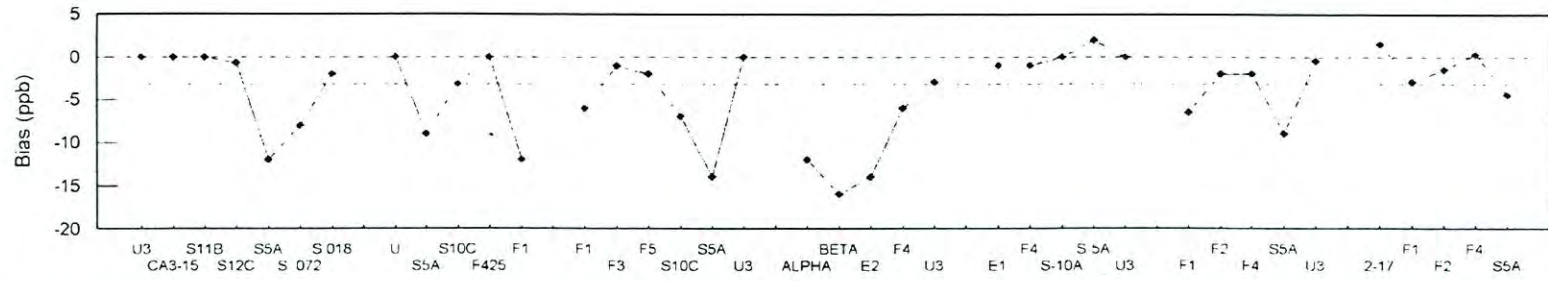
Bias = Lab Result - Median (Duke, FDEP, FIU, USSC, SFWMD)



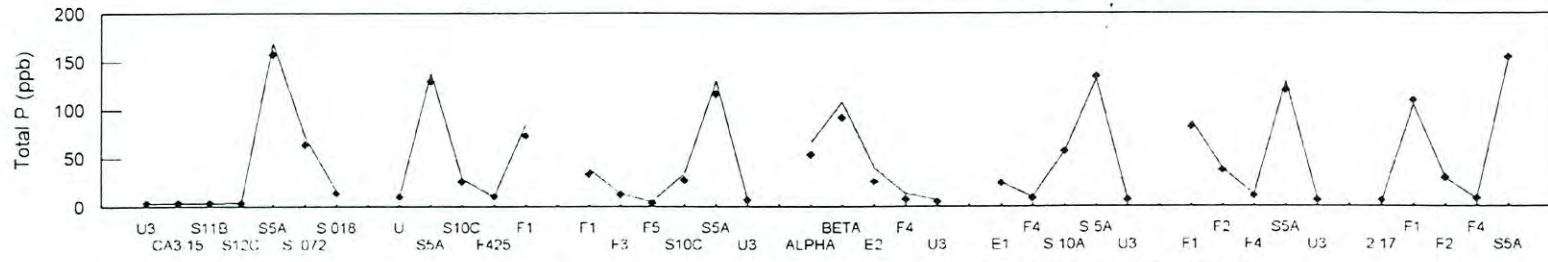
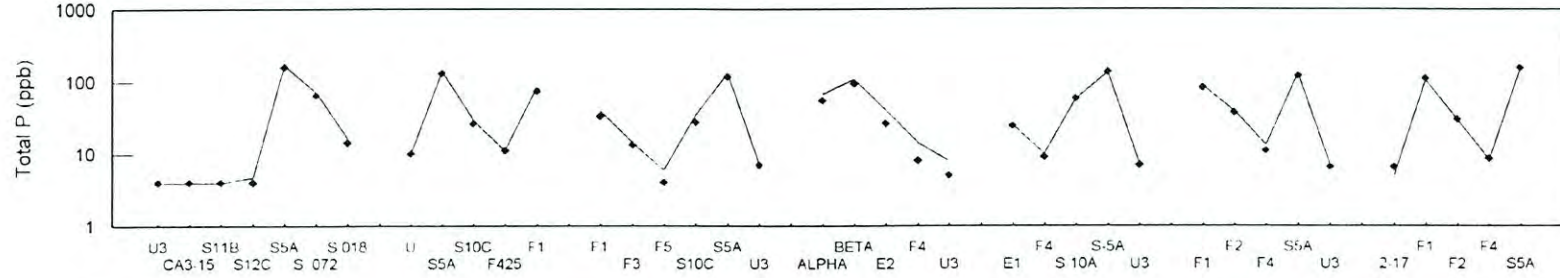
83

Lab: SFWMD

Bias = Lab Result - Median (Duke, FDEP, FIU, USSC, SFWMD)



--- +/- 2 Std Deviations (DEP)



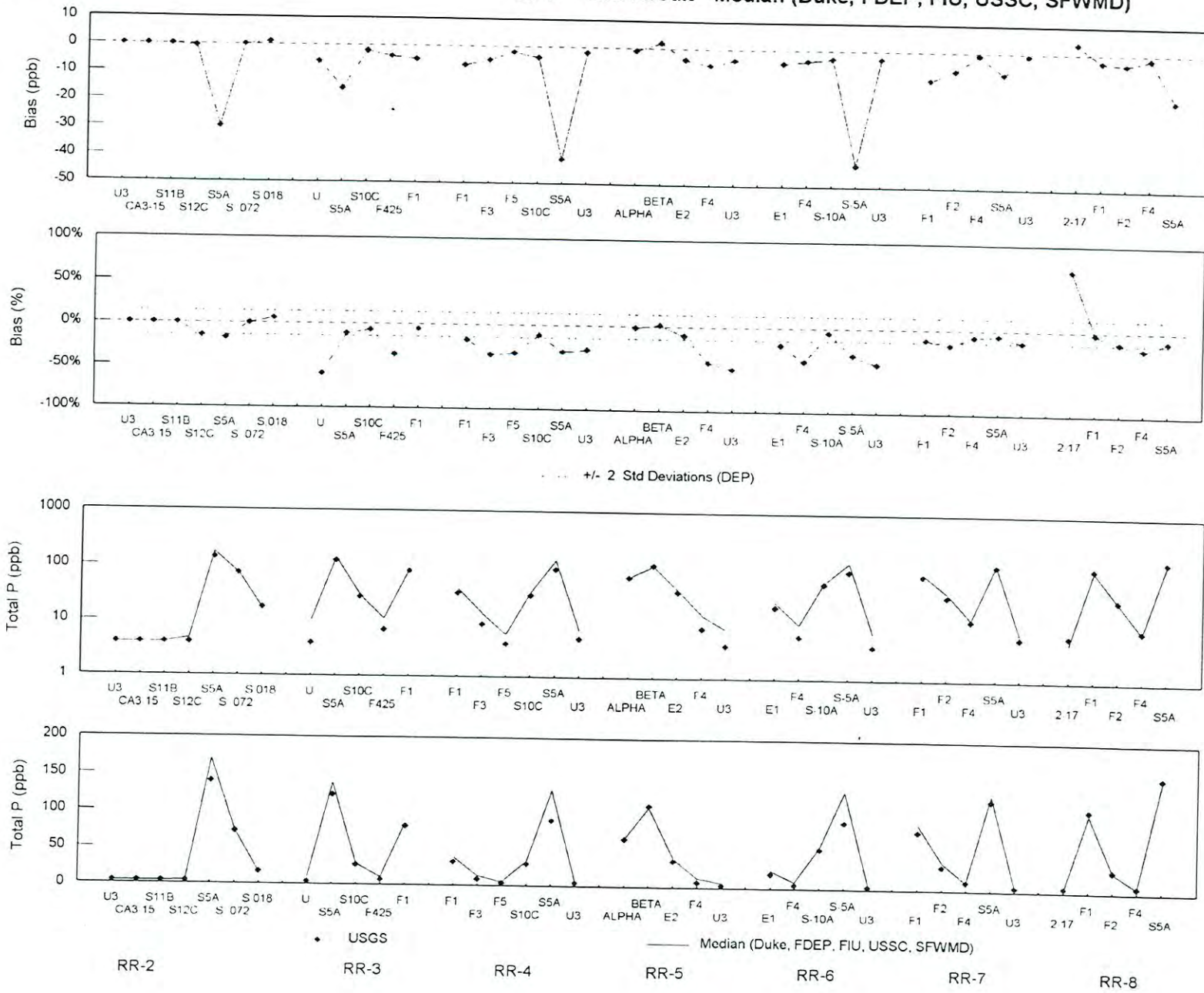
• SFWMD — Median (Duke, FDEP, FIU, USSC, SFWMD)

RR-2 RR-3 RR-4 RR-5 RR-6 RR-7 RR-8

48

Lab: USGS

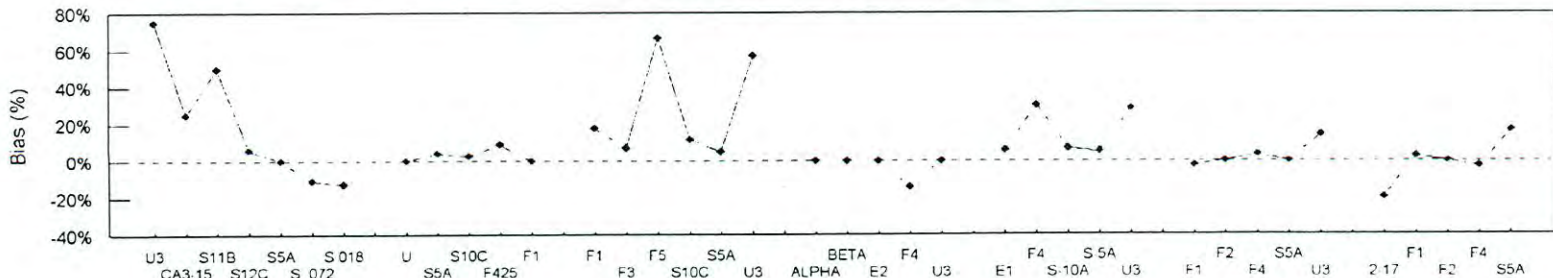
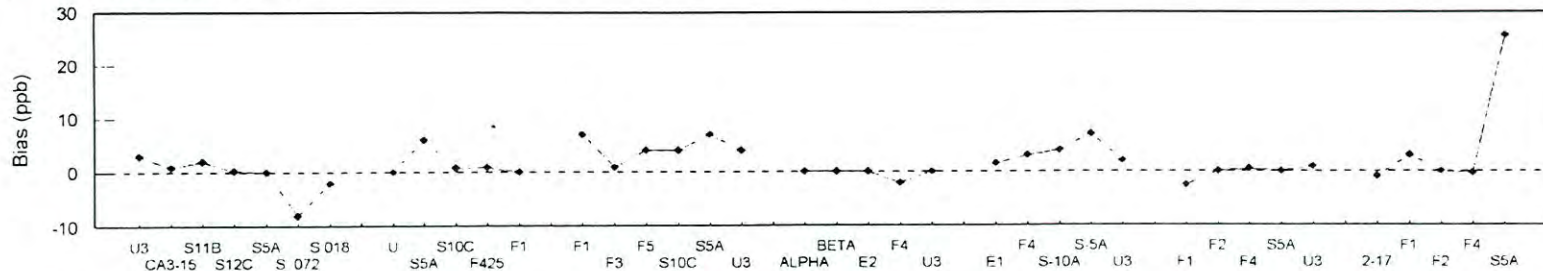
Bias = Lab Result - Median (Duke, FDEP, FIU, USSC, SFWMD)



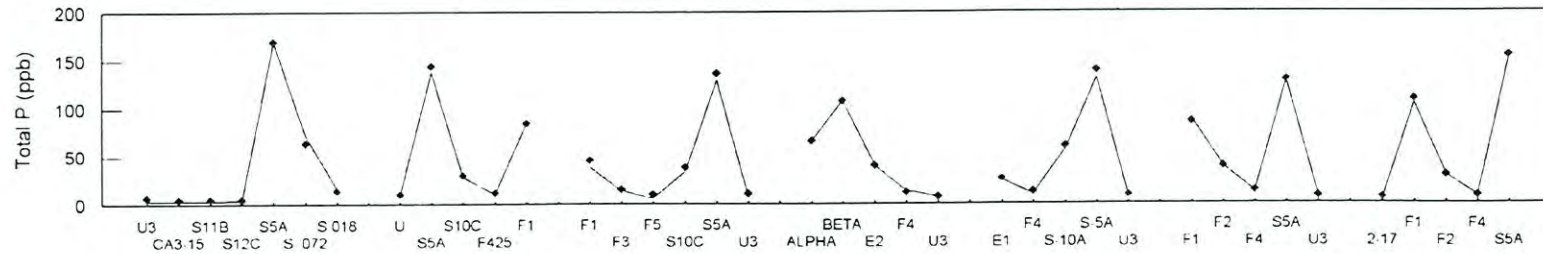
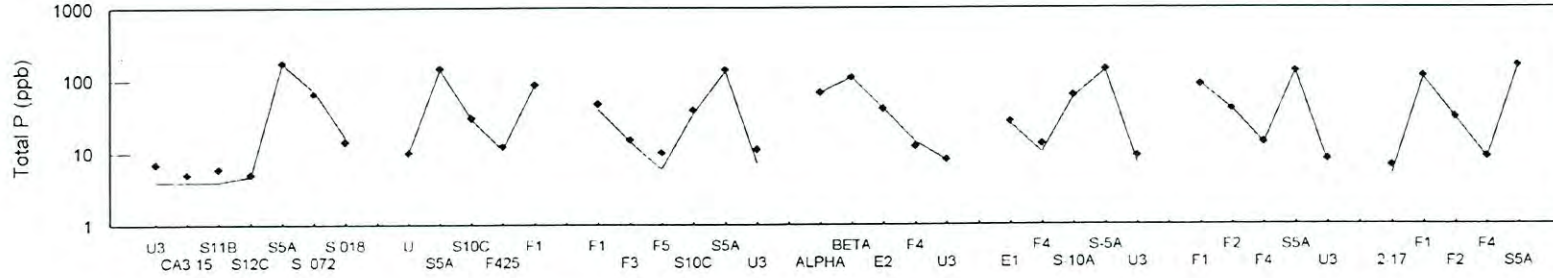
58

Lab: US Sugar Research

Bias = Lab Result - Median (Duke, FDEP, FIU, USSC, SFWMD)



--- +/- 2 Std Deviations (DEP)



• US Sugar Research — Median (Duke, FDEP, FIU, USSC, SFWMD)

RR-2

RR-3

RR-4

RR-5

RR-6

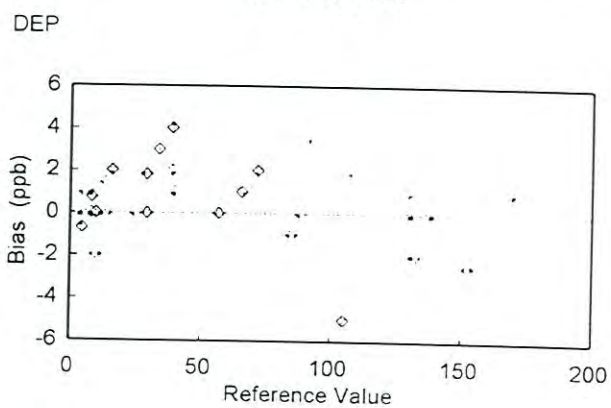
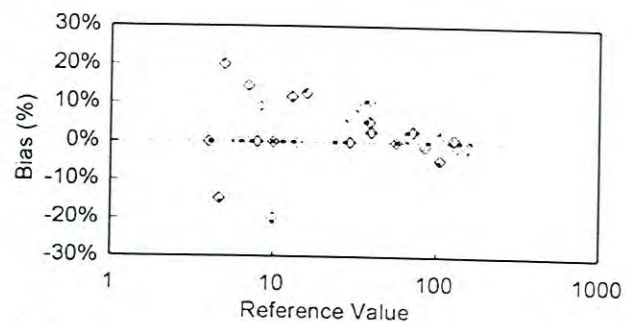
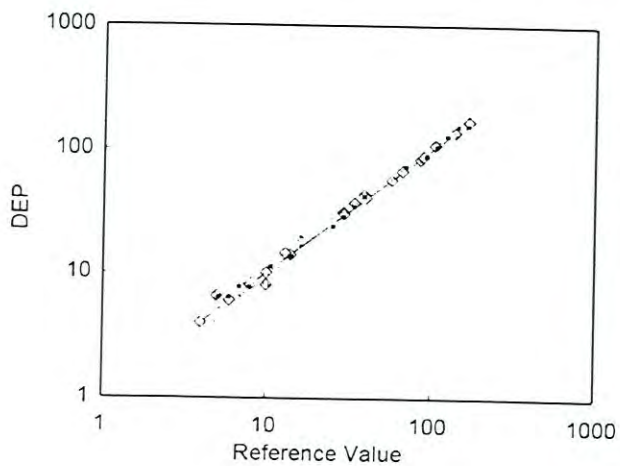
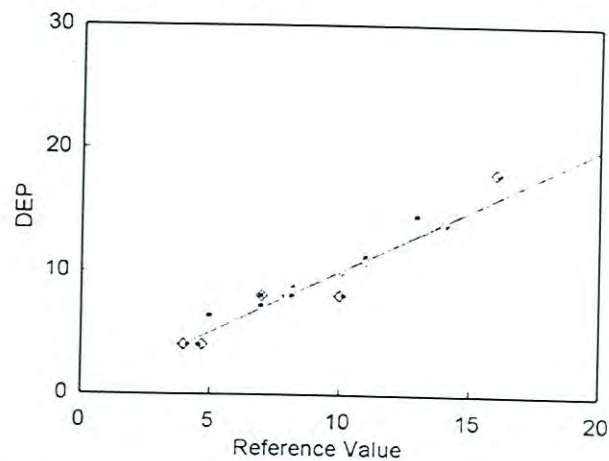
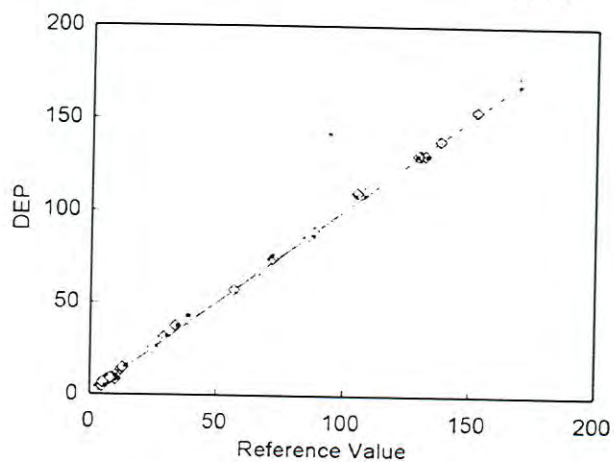
RR-7

RR-8

98

Lab: DEP

Comparisons with Reference Value

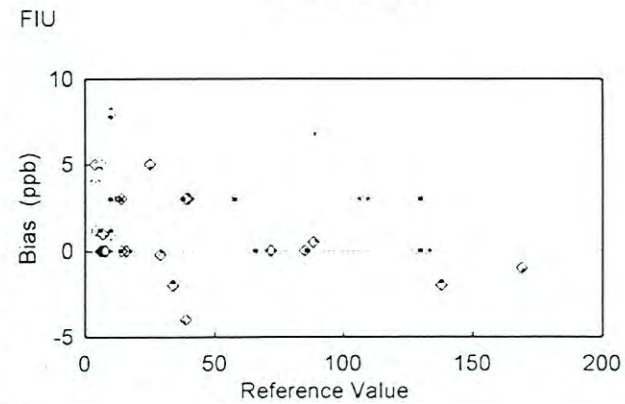
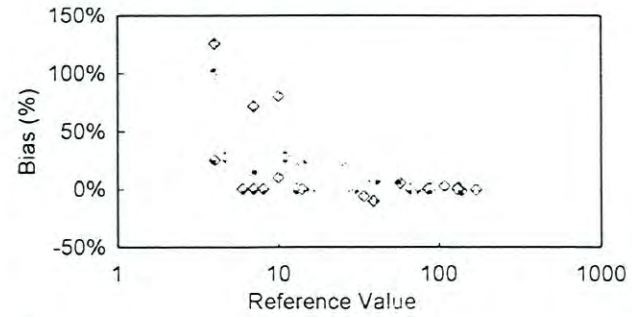
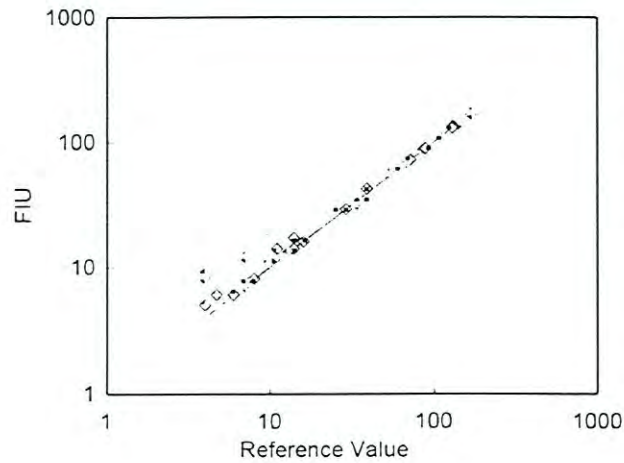
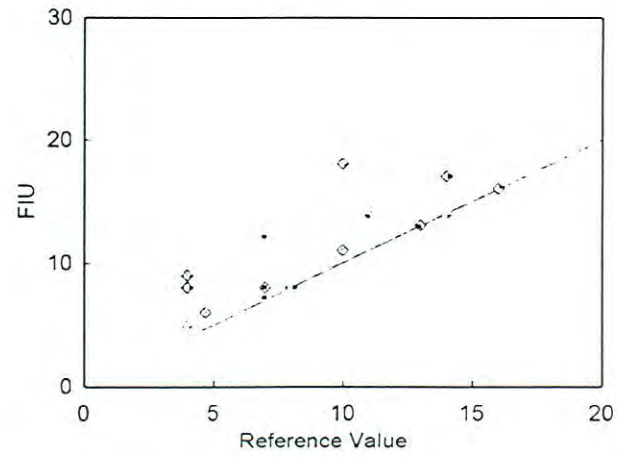
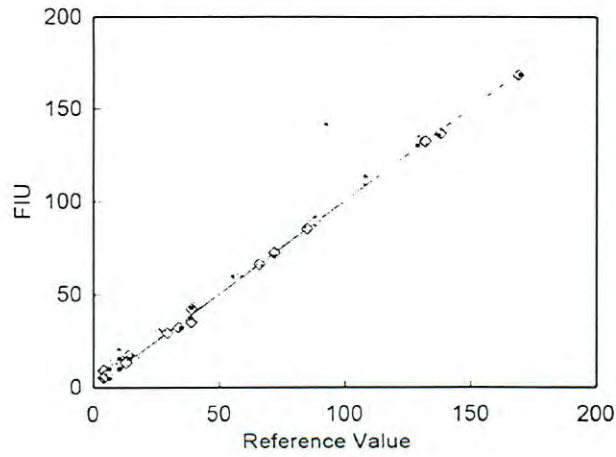


Bias = Lab Result - Reference Value

Bias	Median	Mean	Std Dev	Signif
<u>All Samples</u>				
Percent	0.0%	1.7%	7.0%	0.145
ppb	0.00	0.31	1.56	0.226
<u>Low-Range Samples (< 20 ppb)</u>				
Percent	0.0%	1.8%	9.5%	0.432
ppb	0.00	0.20	0.86	0.345

Lab: FIU

Comparisons with Reference Value



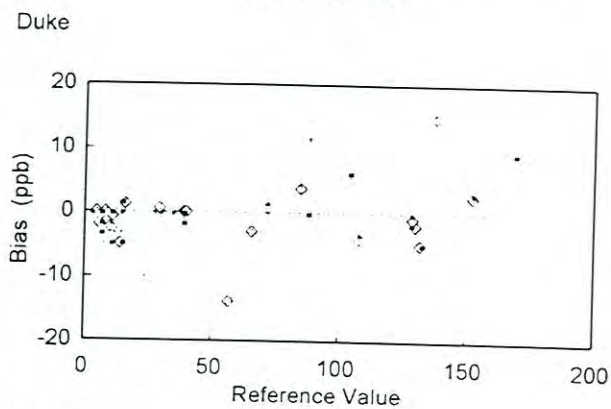
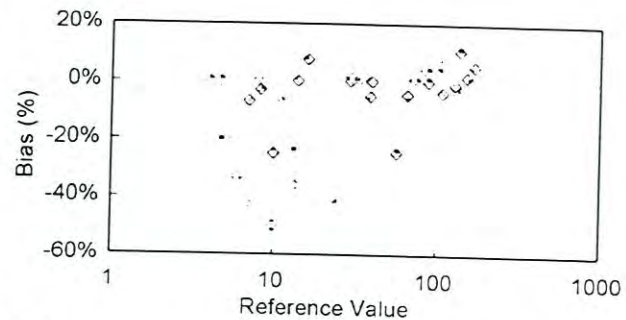
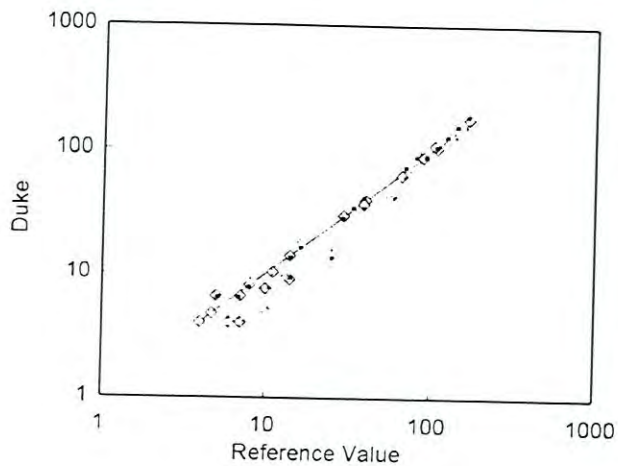
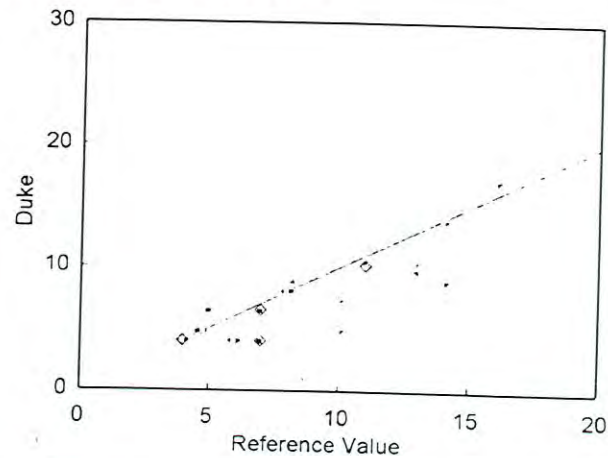
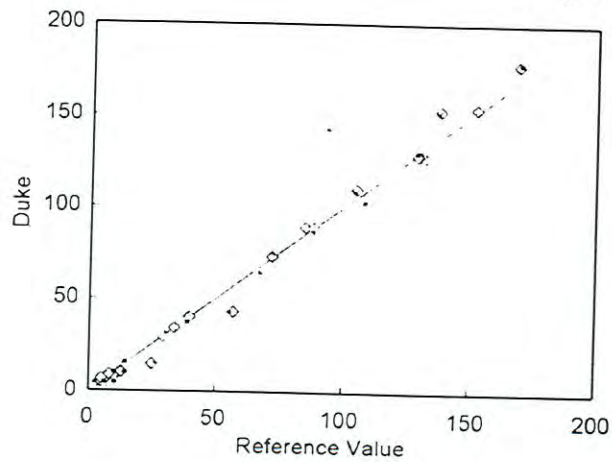
Bias = Lab Result - Reference Value

Bias	Median	Mean	Std Dev	Signif
<u>All Samples</u>				
Percent	0.6%	16.0%	31.7%	0.007
ppb	0.50	1.32	2.44	0.004
<u>Low-Range Samples (< 20 pbb)</u>				
Percent	17.9%	31.4%	40.2%	0.007
ppb	1.00	2.02	2.42	0.004

FIU

Lab: Duke

Comparisons with Reference Value



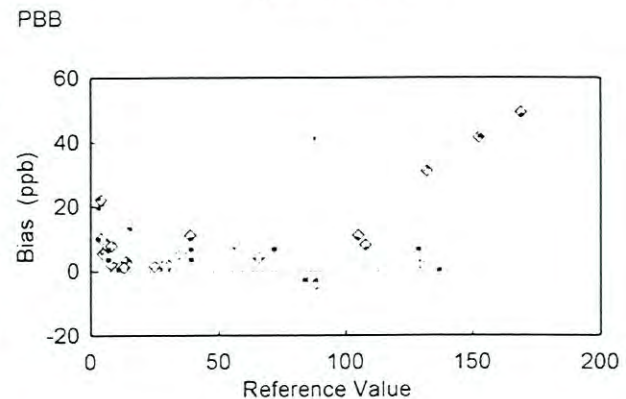
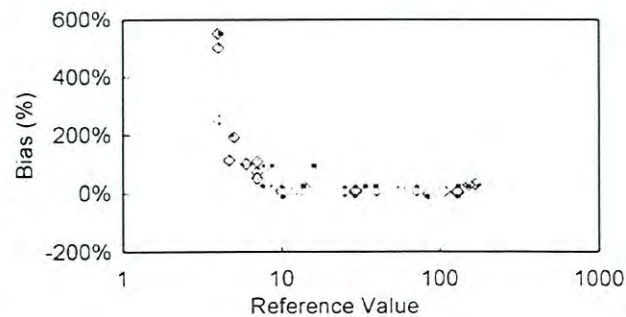
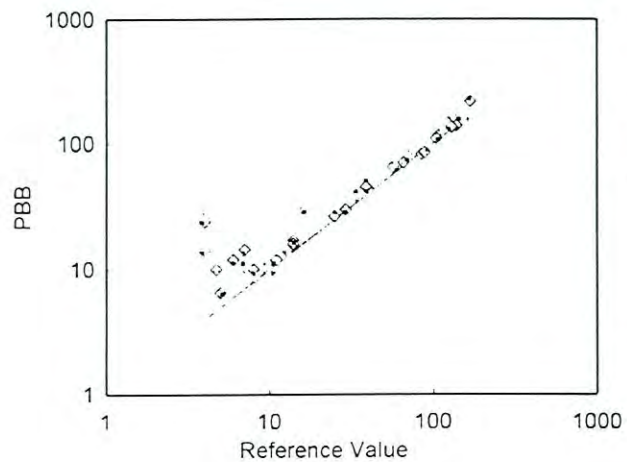
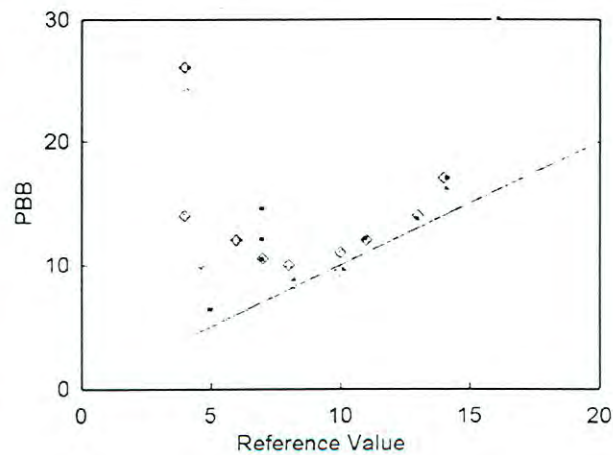
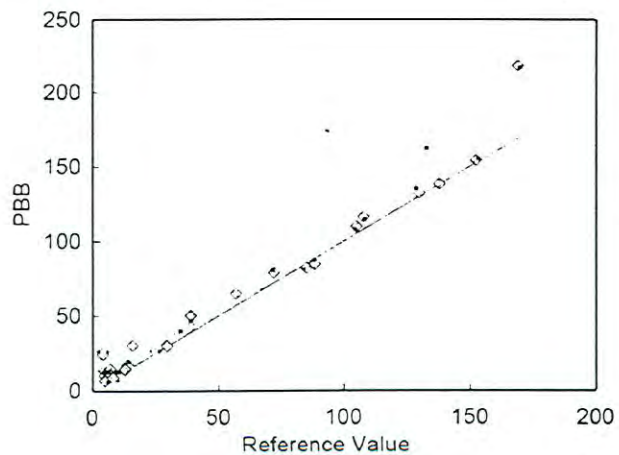
Bias = Lab Result - Reference Value

Bias	Median	Mean	Std Dev	Signif
<u>All Samples</u>				
Percent	-0.4%	-8.9%	16.4%	0.002
ppb	-0.13	-0.77	4.62	0.311
<u>Low-Range Samples (< 20 ppb)</u>				
Percent	-7.2%	-15.7%	18.5%	0.002
ppb	-0.65	-1.38	1.82	0.005

Duke

Lab: PBB

Comparisons with Reference Value

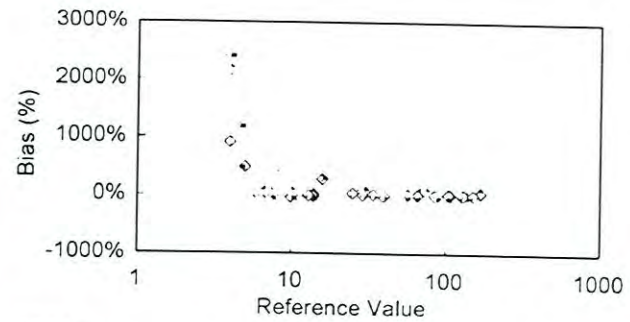
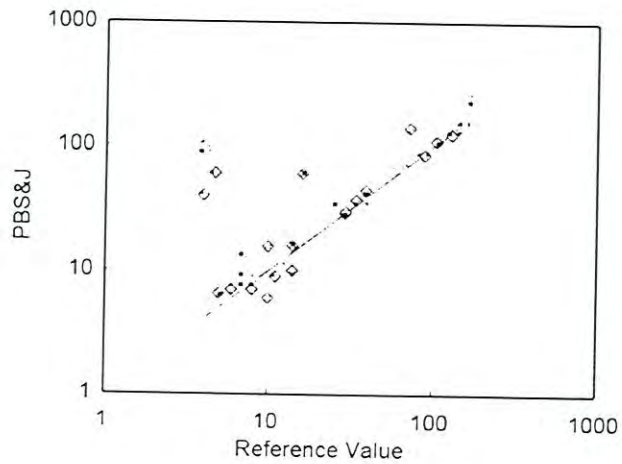
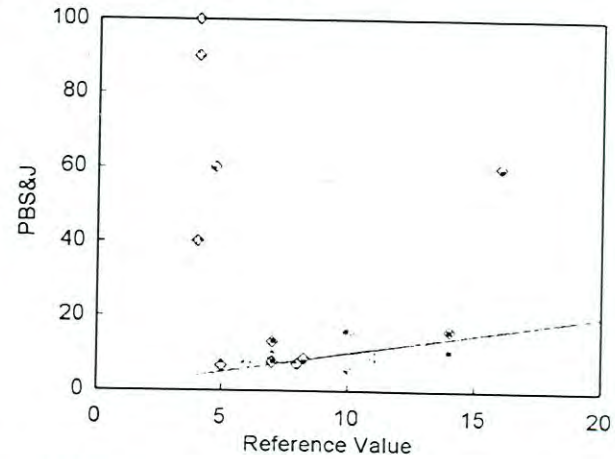
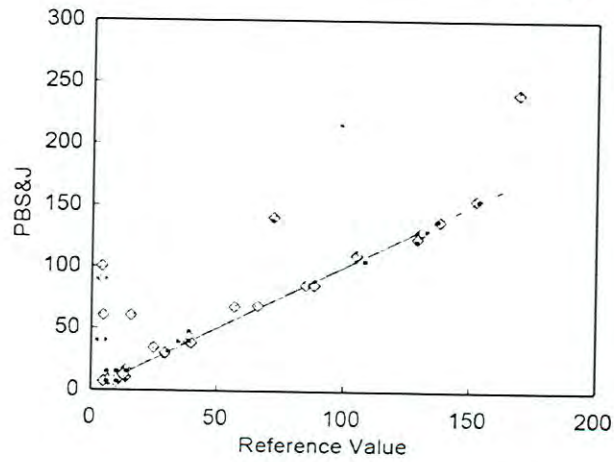


Bias = Lab Result - Reference Value

	Median	Mean	Std Dev	Signif
All Samples				
Percent	14.5%	63.3%	123.3%	0.003
ppb	-3.50	8.19	11.18	0.000
Low-Range Samples (< 20 pbb)				
Percent	79.5%	122.0%	161.5%	0.005
ppb	5.15	6.67	6.45	0.000

Lab: PBS&J

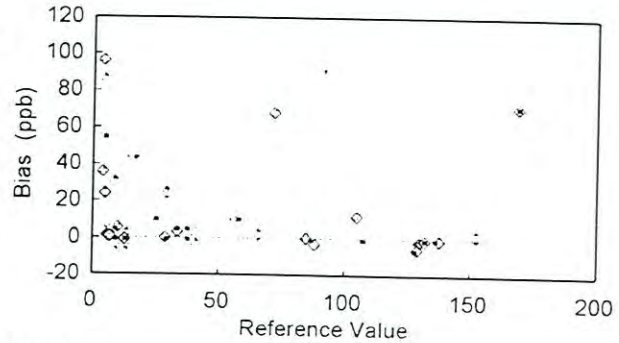
Comparisons with Reference Value



Bias = Lab Result - Reference Value

Bias	Median	Mean	Std Dev	Signif
<u>All Samples</u>				
Percent	10.1%	214.4%	552.9%	0.022
ppb	5.00	14.88	26.92	0.002
<u>Low-Range Samples (< 20 pbb)</u>				
Percent	41.8%	436.4%	751.8%	0.025
ppb	3.75	20.95	31.29	0.011

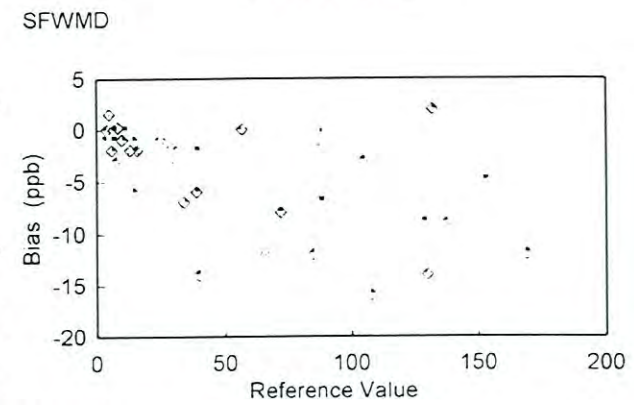
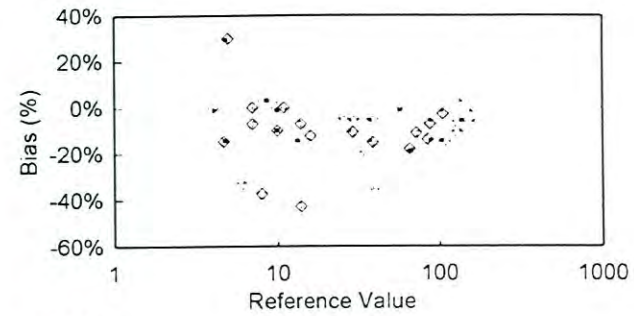
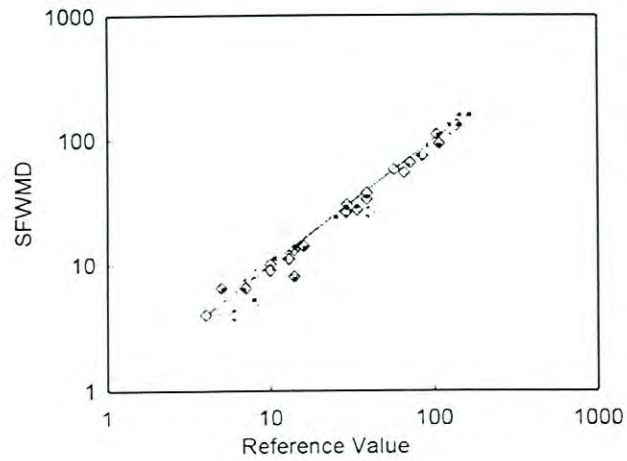
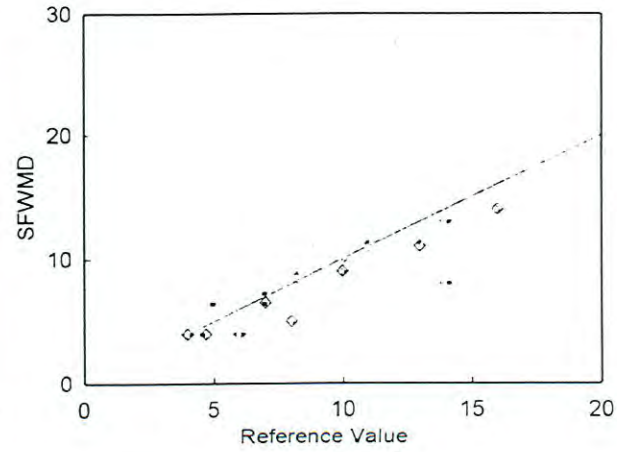
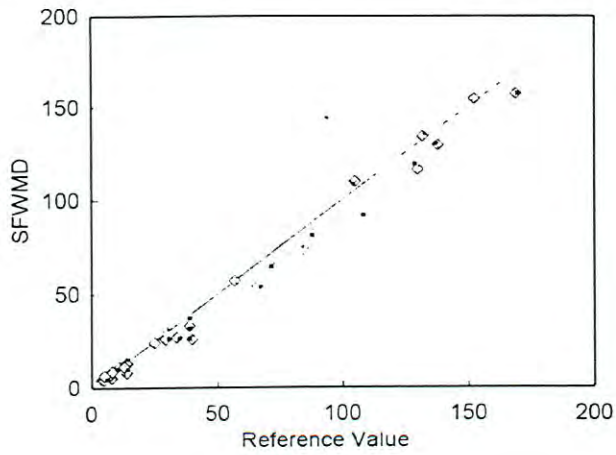
PBS&J



PBS&J

Lab: SFWMD

Comparisons with Reference Value

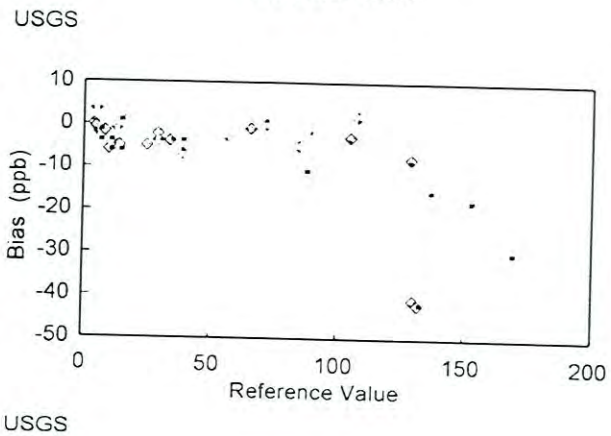
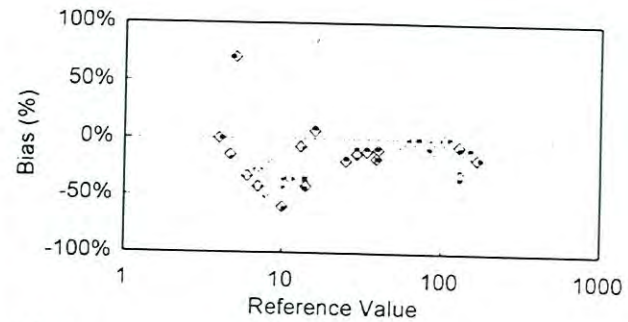
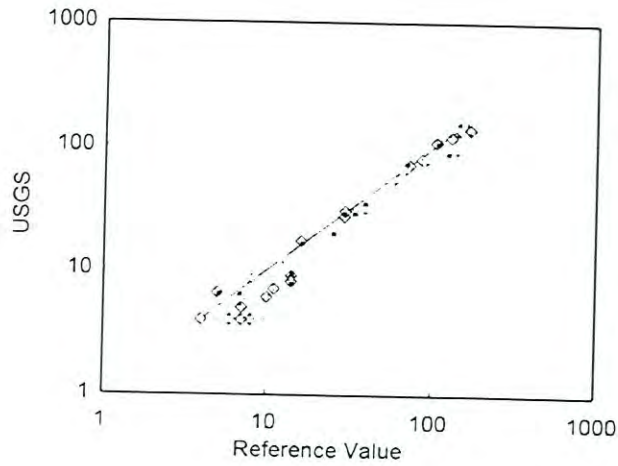
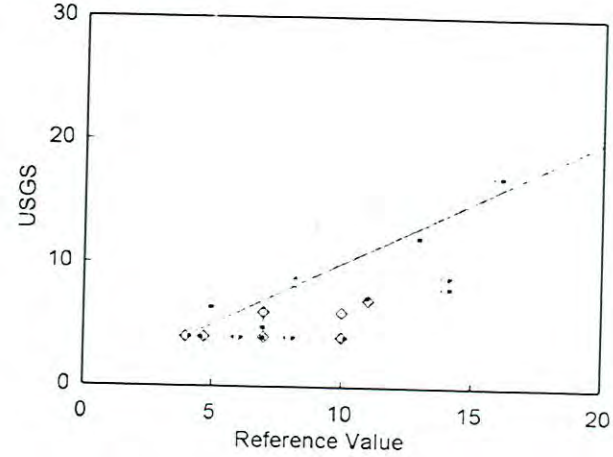
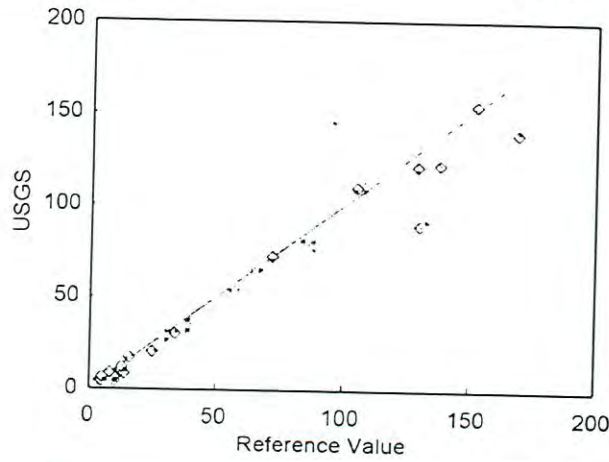


Bias = Lab Result - Reference Value

Bias	Median	Mean	Std Dev	Signif
All Samples				
Percent	-7.1%	-9.1%	13.0%	0.000
ppb	2.00	-4.08	4.97	0.000
Low-Range Samples (≤ 20 ppb)				
Percent	-3.6%	-8.2%	16.9%	0.055
ppb	-0.25	-0.91	1.66	0.032

Lab: USGS

Comparisons with Reference Value

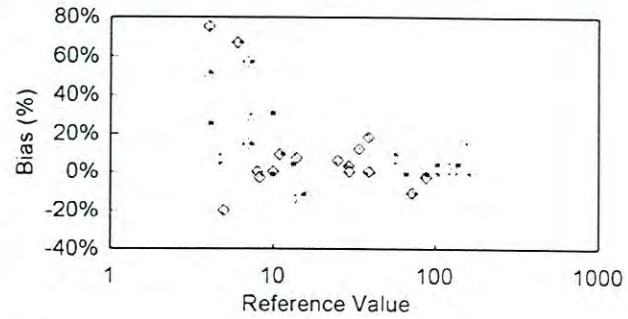
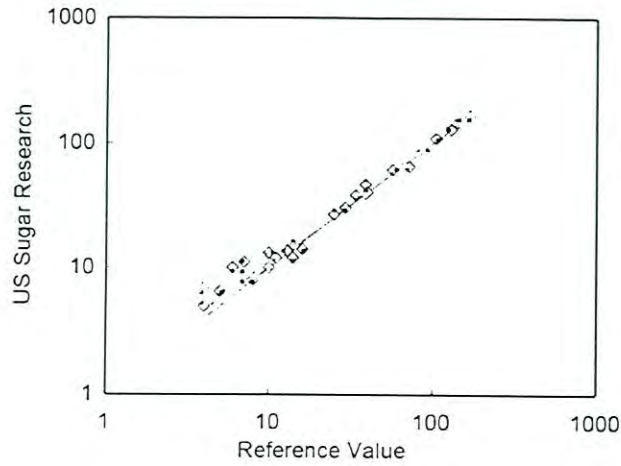
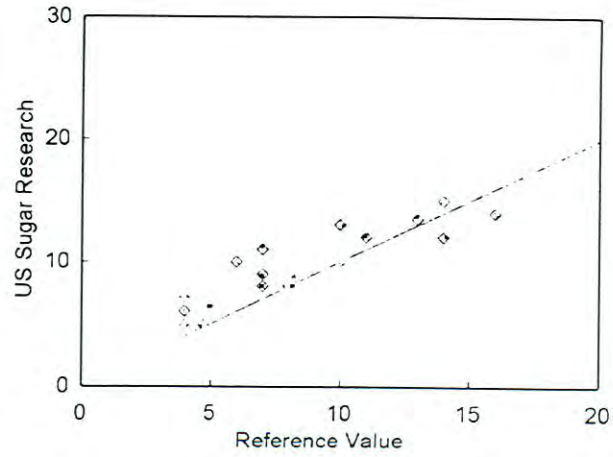
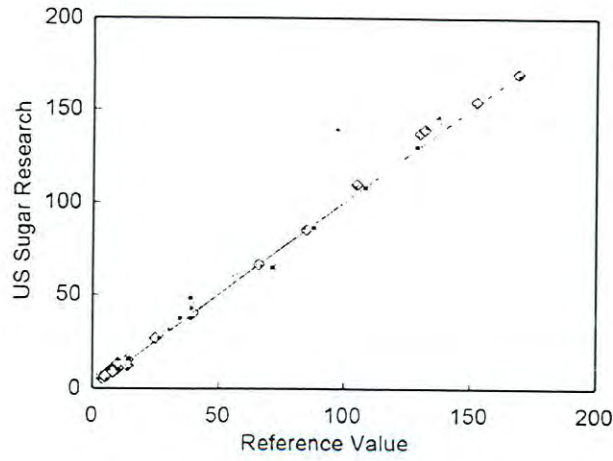


Bias = Lab Result - Reference Value

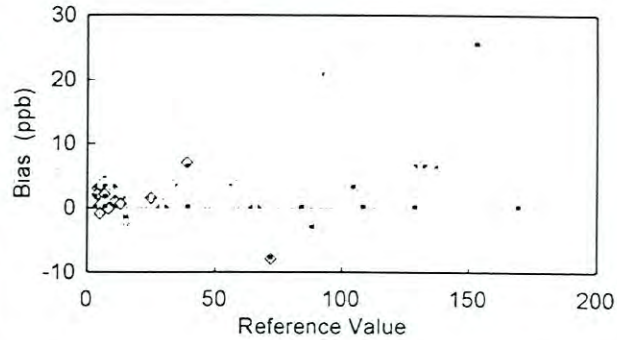
Bias	Median	Mean	Std Dev	Signif
<u>All Samples</u>				
Percent	-12.7%	-15.4%	21.5%	0.000
ppb	0.65	-6.43	10.29	0.000
<u>Low-Range Samples (< 20 ppb)</u>				
Percent	-24.9%	-19.5%	29.6%	0.012
ppb	-1.88	-2.00	2.53	0.004

Lab: US Sugar Research

Comparisons with Reference Value



US Sugar Research



US Sugar Research

Bias = Lab Result - Reference Value

Bias	Median	Mean	Std Dev	Signif
<u>All Samples</u>				
Percent	4.1%	10.2%	21.1%	0.005
ppb	-0.13	1.92	4.87	0.020
<u>Low-Range Samples (< 20 ppb)</u>				
Percent	8.1%	18.0%	28.2%	0.015
ppb	1.00	0.98	1.79	0.033