Enhanced Water Quality Program Parameter Reduction Rationale

Report No. LOXA05-004

Prepared by:
Donatto Surratt, Ph.D.
A.R.M. Loxahatchee National Wildlife Refuge
December 2005

BACKGROUND

In 2004 Congress authorized funding for an Enhanced Water Quality Monitoring Program, which would aid in improving the scientific understanding of water quality issues in the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge). The 1991 Federal Consent Decree established a set of analytical parameters based on previous work carried out across the greater Everglades and 14 sampling location across the Refuge. These stations are also part of a larger effort conducted by the South Florida Water Management District to sample water quality in the Everglades Protection Area (EVPA). The Enhanced Water Quality Monitoring Program (LOXA), initiated in June 2004, consists of an additional 39 sampling locations that are monitored for 23 of the water quality parameters monitored at the 14-station Consent Decree network (Table 1).

The LOXA Work Plan (Brandt et al. 2004) states that, "data will be reviewed… and the list of parameters reduced as appropriate" (p. 12) with the objective to optimize the marsh monitoring network. Further, the reduction of parameters has the potential to reduce analytical cost and these reclaimed funds can be applied to extending the duration of the LOXA monitoring effort. This document highlights the procedures and rationale applied in selecting the analytical parameters for reduction in the Refuge's Enhanced Water Quality Monitoring Program. The analysis presented here are specific to the Refuge and the objectives of our study. Parameter elimination recommendations presented here may not be appropriate for other studies in the Everglades (e.g., EVPA).

PARAMETER REDUCTION PROCEDURES

In the effort to review and determine whether analytical parameters could be eliminated from the LOXA program several approaches were involved: (1) collaboration with members of the South Florida Water Management District (District) and experts in the Department of Interior, (2) times-series characterization and correlation analysis, and (3) consideration of rationale for parameter reduction by the District for the Storm Water Treatment Areas (STA) in the non-ECP EFA Permit Modification Request of February 2005. Resource requirements for analyzing a particular constituent (e.g., field or laboratory effort, cost to process) were not considered in this exercise, however the recovered cost resulting from elimination of the selected parameters is presented in Table 2.

(1) Collaboration between the Refuge (Michael Waldon, Ph.D.; Matthew Harwell, Ph.D.; Laura Brandt, Ph.D.; and Donatto Surratt, Ph.D.), the District (Sue Newman, Ph.D. and Scot Hagerthey, Ph.D.) and the United States Geological Survey (Paul McCormick, Ph.D.) involved discussions of expert opinions on parameters that may be less important from a management and scientific perspective, including those that generally do not lead to increased understanding of water quality within the Refuge.

Eleven parameters identified as worth initial consideration for elimination were: alkaline phosphatase (APA), color, dissolved organic carbon (DOC), hardness (HARD), magnesium (Mg), sodium (Na), ammonium (NH_4), nitrite (NO_3), silica (SiO_2), total dissolved solids (TDS), and turbidity (TURB).

(2) The next approach involved time-series characterization, spatial characterization, and simple correlation analysis for all the parameters over the entire sampling period (June 2004 – May 2005). Time-series characterization of the data was applied to explore, and validate where possible, some of the expert opinions when selecting parameters to eliminate. Time-series characterization was an observation of change in a parameter over the year that data was collected. The approach for characterization was two fold in some cases including (1) an all marsh site analysis and where necessary (particularly when observation of quantitative variability in the form of a coefficient of variation was necessary) (2) an individual site analysis. If the parameter had low variability over the year it generally did not yield quantitative information about localized changes to the ecosystem, thus the parameter could be consider for elimination. If the parameter demonstrated high variability then further analysis was necessary to determine if it could be eliminated. There was no consistent pattern in variability for the

parameters in the marsh or in the canal. Another characterization approach was the spatial analysis approach which was performed from canal to the interior of the marsh on several parameters. In most cases this analysis was performed to determine if there was an observable pattern for the parameter demonstrating some dependence on canal water penetration into the interior of the Refuge. Simple correlation analysis was applied to determine if there were parameters that produced redundant information. The analysis included both canal and interior sites, which allowed the spectrum of rain-driven soft water and hard canal water to be analyzed collectively. Correlation values, reported as r, were used to assess how well parameters associated. Parameters with r greater than or equal to 0.95 (Table 3) were considered well correlated and in some cases resulted in one or more parameters being added to the list of parameters for elimination.

(3) The PRO ECP Non-ECP EFA Permit Modification Request of February 2005 drafted by the District and sent to the Florida Department of Environmental Protection (FDEP) was reviewed for rationales for parameter reduction used by the District. This letter provided rationale for eliminating seven parameters also monitored in LOXA: ammonia, chloride, turbidity, total dissolved phosphorus, ortho-phosphate, total dissolved nitrogen, and total dissolved solids. FDEP approved elimination from Non-ECP EFA sampling of all except turbidity.

Personal emails between Dr. Surratt and David Struve, Ph.D. provided further insight on the procedures for parameter reduction by the District. Dr. Struve was on the review panel for parameter reduction for the PRO ECP Non-ECP EFA Permit Modification Request of February 2005. Dr. Struve related some of the considerations used to generate the modification request and some of these considerations were used to address the parameter elimination issues in the present report. Two considerations applied for our purposes were: (1) is there any significant variability in the given parameters over time and (2) are there related parameters being measured that give the same information (example: plot chloride vs. conductance and see if the data are a good fit. If so, conductance values may be good enough to infer the chloride values). A final consideration was the comparison of the parameter time-series data with the Class III criteria defined in F.A.C. 62-302.530 and applied in the 2004 Everglades Consolidated Report (SFWMD, 2004). If the data were observed to extend beyond the Class III criteria over the monitored period then it was determined that the parameter should continue to be monitored. Some parameters only had narrative criteria associated with them and the narrative criteria were not assessed in this study. Because of this limitation, Class III criteria comparison was performed on only a portion of the analytes, particularly alkalinity, dissolved oxygen, potassium, pH, and turbidity. Further, because of the short time-series (12 months), less weight was given to the time-series – Class III criteria comparison when determining whether or not to eliminate the parameter.

PARAMETER REDUCTION RATIONALE

There are 29 parameters used in the initial sample design. All the parameters were reviewed for potential to eliminate them from the water quality analytical suite. The following is a breakdown of all the parameters with rationales for elimination based on the three approaches presented above. Correlation analysis with coefficients greater than or equal to 0.95 is presented in Table 3. Because, in some case, we are eliminating parameters based on the ability to reproduce that parameter from another analytical parameter, it was necessary to choose an r cut-off limit that was high enough to show exceptionally strong proportional relationships between the two parameters. Appendix A presents the full correlation table for all parameters. Appendix B provides time-series (June 2004 – May 2005) graphs of the parameters for elimination and cross-plots of correlated parameters identified in Table 3.

<u>ALKA</u>: Alkalinity correlated well with four parameters – calcium (r = 0.98), hardness (r = 0.98), specific conductance (r = 0.96), and total dissolved solids (r = 0.95). The high correlation between ALKA, calcium, and hardness is most likely an artifact of their dependence on the concentration of $CaCO_3$. Although each of these parameters share this dependency they are still determined through unique analytical procedures and explain different conditions of the analyzed water parcels and as such yield different values and patterns through time, which is why they are not 100% correlated. Further, these correlations allow the observer to quickly qualify data points as outliers (prior to a rigorous quantitative assessment) with respect to specific conductance, which is

exceptionally important for tracking water movement from the canal to the interior marsh.

Alkalinity has a Class III criterion of = 20 mg L^{-1}. In October and November 2004 five sampled sites had values below the criteria. This criterion is inappropriate for rainwater dominated wetlands where alkalinity is naturally below 20 mg L^{-1} (Weaver, 2005). A water quality goal of the Refuge is to maintain this low alkalinity condition. Because ALKA provides the ability to quickly determine specific conductance outliers; because there is an established numeric criterion pursuant to Section 62-302.530 F.A.C.; and because ALKA is important to the ecology of softwater marshes, ALKA will not be eliminated from the analytical suite. *Alkalinity remains a monitored parameter*.

APA: There were no strong correlations associated with alkaline phosphatase activity (APA). APA can indicate phosphorus limitation in wetland ecosystems, as inducible phosphatase enzymes are produced when the system becomes deplete in phosphorus (Newman, et al., 2002). Spatial observation of APA for the marsh indicates that APA values increase towards the interior of the marsh (>1.5 km interior of the canals), which coincides with the reported phosphorus limitation for the Refuge (Vymazal, and Richardson, 1995). APA has also been applied as an early warning indicator of wetland eutrophication. The technique applied for analyzing APA for LOXA is not suitable for using APA as an ecological warning indicator. We only measure standing water APA, while the protocol requires the direct measurement of periphyton APA and the subtraction of standing water APA to determine periphyton response to nutrient enrichment (Newman et al., 2002). Because the only other applicable use of APA for the marsh found in this research effort is the determination of phosphorus limitation, which can be assessed with phosphorus and other parameters on the analytical list, APA can be removed from the list of analytical parameters. *APA is on the list of parameters to be eliminated*.

Ca: Calcium correlated well with hardness (r = 0.99), specific conductance (r = 0.95), and total dissolved solids (r = 0.95). Temporal observation of Ca can indicate shifts between minerotrophic (flow [stream, canal, groundwater] driven) and ombortrophic (precipitation driven) wetland systems (Kadlec and Knight, 1996). Further, alterations to Ca levels impacts plant growth rates, which can alter community structures and reduce biodiversity. *Calcium remains a monitored parameter.*

Cl: Chloride had strong correlations with sodium (r = 0.99) and specific conductance (r = 0.95). Elevated Cl has been associated with fertilizers and other contaminants that may reach the Refuge from Everglades Agricultural Area (EAA) operations during by-passes of untreated water (McPherson and Halley, 1996; Orem, 2004). Chloride concentrations can be used as a tracer of flow rates in wetland systems because of it low biological demand. *Chloride remains a monitored parameter.*

COLOR: There were no strong correlations associated with color. Color was initially considered for elimination because it was expected to have a small range of values over time, ultimately providing little information about water quality. Based on a station by station time-series characterization the coefficient of variation for color was ~ 24%. Color is often used in assessing raw drinking water sources for treatability. It is often found to be correlated with the presence of organic materials including lignin and tanic acids. Color is a semi-qualitative parameter and did peak strongly when there were heavy precipitation events (i.e., hurricanes) in September and October 2004. Regardless of this observation color is being eliminated as a monitored parameter, because of its qualitative nature and the fact that there are other parameters that provide more quantitative information about hurricane and other events (i.e., SO_4, TPO_4, $TDPO_4$, SiO_2, etc.). *Color is on the list of parameters to be eliminated.*

DO: There were no strong correlations observed between dissolved oxygen and other analytes. Dissolved oxygen (DO) has an alternative Class III criterion called the site-specific alternative criteria (SSAC). The SSAC is a sinusoidal diel cycling algorithm (Weaver et al., 2001). The algorithm was adjusted, finalized, and presented in the Everglades Marsh Dissolved Oxygen Site Specific Alternative Criterion Technical Support Document (Weaver, 2004). Between June 2004 and May 2005 approximately 79% of the marsh samples were below the modeled criterion, 42% of the canal samples were below the criterion, and 72% of all the samples from the Refuge were below the determined criterion. DO in marsh systems gives a measure of oxidation potentials in the water column. When DO drops below 2 mg L^{-1} plant mortality significantly increases (Kadlec and Knight, 1996). None of the calculated SSAC values were below the 2 mg L^{-1}, 43% of marsh samples, 18% of canal samples, and 39% of all the Refuge samples were below the 2 mg L^{-1}. *DO remains a monitored parameter.*

<u>DOC</u>: Dissolved organic carbon has been linked to microbial respiration and fulvic acid regulated mercury methylation in the southern Everglades (Reddy and Aiken, 2001). One of the experts in preliminary lab experiments revealed microbial respiration to be strongly carbon limited instead of phosphorus or nitrogen limited as for most system. Additional influxes of labile carbon can affect marsh soil processes. Reddy and Aiken (2001) demonstrate strong correlations between Hg bioaccumulation and DOC concentrations. Correlation analysis for DOC did not reveal significant correlation with other parameters. Because neither Hg nor microbial respiration are monitored in the Refuge; because of the potential of DOC concentration changes to cause Hg bioaccumulation rates to change; and because no other parameters can serve as surrogates of DOC, monitoring DOC is recommended. *DOC remains a monitored parameter.*

<u>HARD</u>: Hardness is measured as an equivalent concentration of calcium carbonate ($CaCO_3$) and was expected to correlate well with alkalinity (which is also measured as an equivalent concentration of $CaCO_3$). Hardness correlated well with ALKA ($r = 0.98$), Ca ($r = 0.99$), magnesium ($r = 0.97$), specific conductance ($r = 0.97$), and TDS ($r = 0.97$). Although these strong correlations are observed the Florida Class III water quality criteria for various metals (Cd, Cr, Cu, Pb, Ni, Zn) require hardness in order to calculate the metal criterion (Bechtel, 2000). These metals have never been measured as a part of the LOXA project and where discontinued from the EVPA project in 2000. From the perspective of tracking softwater movement interior of the canals ALKA and specific conductance appears to provide the necessary information, thus the elimination of the hardness appears to be warranted. *Hardness is on the list of parameters to eliminate.*

K: Potassium did not correlate well with any other parameters and does not have a specific Class III criterion. Although there were no strong correlations associated with K, a station by station time-series characterization (not including August and September of 2004) showed low variability with a coefficient of variation of 19% and the pattern for the entire data set matched well with the TDS pattern. K in the interior of the Refuge did not drop below 0.64 mg L-1 and averaged 4.2±2.8 mg L-1, which is above the reported 2 mg L-1 K water column limitation value (Demaneche et al., 2001; Spijkerman and Coesel, 1998; Palmen et al., 1994). Based on the low variability in the K data set, the matching patterns between K and TDS, and because the K concentration was above the limitation concentration, K will be eliminated as a monitored water quality parameter. *Potassium is on the list of parameters to be eliminated.*

Mg: Magnesium is expected to contribute to hardness. Mg had a strong correlation with hardness (r = 0.97), specific conductance (r = 0.97), and TDS (r = 0.97), thus specific conductance and TDS can serve as a proxy for Mg in future analysis. Because hardness was dropped and there was no other indication that Mg contributed to an increased understanding of water quality magnesium was added to the elimination list. *Magnesium is on the list of parameters to be eliminated.*

Na: Sodium is expected to contribute to observed alkalinity values. Na had a strong correlation with specific conductance (r = 0.96) and TDS (r = 0.95), thus specific conductance and TDS can serve as a proxy for Na in future analysis. Na can serve as a conservative tracer for calculating dilution and concentration and for tracking groundwater discharges from wetlands (Kadlec and Knight, 1996). Based on the analysis Na provides redundant information with respect to water quality and SPCOND or TDS may be applied to replace sodium as a tracer. *Sodium is on the list of parameters to be eliminated.*

NH_4: There were no strong correlations associated with ammonia-nitrogen. Ammonium is on the list of parameters to be dropped although it may provide useful information about the seasonal processes of plant growth and decomposition in marsh systems

(Kadlec and Knight, 1996). NH_4 is a plant nutrient contributing to total Kjeldahl nitrogen. It may impact dissolved oxygen through oxidation to nitrate and may also cause aquatic toxicity. NH_4 is generally quite low in Everglades Protection Area (EPA) waters and generally constitutes only a small fraction of EPA total nitrogen. The rationale for eliminating NH_4 is that total nitrogen encompasses NH_4 and because nitrogen is not considered a limiting nutrient in Refuge wetlands (Vymazal, and Richardson, 1995), the specific details of alteration to NH_4 are of little consequence. *Ammonium is on the list of parameters to be eliminated.*

$\underline{NO_3}$: There were no strong correlations associated with nitrate. Nitrate is generally a significant portion of nitrate-nitrite (NO_X) measurement and in combination with the other components of total nitrogen provides information about nutrient lability. Because NO_2 is generally only a small fraction of the NO_X, it was expected that NO_X values can be used to estimate the NO_3 concentration. This rationale holds true for station LZ40 in Lake Okeechobee such that NO_2 was ~11% and NO_3 was ~90% of the NO_X concentration. However, this pattern was not observed in the Refuge marsh. Observation of the data showed NO_2 at ~43% and NO_3 at ~58% of the NO_X concentrations. Thirty-one percent of the NO_3 values for the Refuge was below detection limits, which may have complicated this assessment and potentially confound any trend analysis attempted for the Refuge. Independently, NO_3 is not particularly useful and the value is maintained in NO_X. *Nitrate is on the list of parameters to be eliminated.*

$\underline{NO_2}$: There were no strong correlations associated with nitrite. Nitrite is on the elimination list because it was thought to be short lived and represent only a small fraction of the nitrogen pool due to its rapid conversion to nitrate. Generally, NO_2 found in wetlands above detection limits is indicative of an anthropogenic source of nitrogen (Kadlec and Knight, 1996). Inspection of Refuge data demonstrates that NO_2 can contribute up to 43% of the inorganic nitrogen pool, which does not support the assumption that NO_2 is a small portion of NO_X. Again this assessment may be skewed as ~25% of the NO_2 values were below detectable limits (0.004 mg L^{-1}). Conversely, the observed imbalance between NO_2 and NO_3 with respect to NO_X may reflect loading of anthropogenically generated nutrients in the Refuge. Regardless, nitrite will be incorporated in the analysis of nitrate-nitrite. *Nitrite is on the list of parameters to be eliminated.*

<u>NO_X</u>: There were no strong correlations associated with nitrate-nitrite. NOx is the sum of NO_2 and NO_3. NO_X is a fraction of the inorganic nitrogen pool and in a balanced wetland can serve as a proxy for the essential plant nutrient, NO_3. The sum of NO_X and total Kjeldahl nitrogen approximates total nitrogen. Total nitrogen can be employed to determine the lability of food sources for marsh plant communities (Thomann, 1972). Total nitrogen is also a concern for water downstream of the Refuge. *NO_x remains a monitored parameter.*

<u>OPO_4</u>: Ortho-phosphate had a strong correlation ($r = 0.99$) with total dissolved phosphate and appears to provide redundant information, thus OPO_4 is on the list for parameter elimination. Although OPO_4 is on the parameter elimination list it was argued that the presence of OPO_4 was a good indicator of phosphorus enrichment in Water Conservation Area 2 (WCA2), and may play a similar role within the Refuge. Also, eleven percent of the reported OPO_4 values were below detection limits (0.004 mg L^{-1}). At greater than 1 km interior of the canals surrounding the Refuge, OPO_4 values do not exceed 0.03 mg L^{-1}, which suggest that OPO_4 does not provide useful information about Refuge water quality dynamics. *Ortho-phosphate is on the list of parameters to be eliminated.*

<u>pH</u>: There were no strong correlations associated with pH. pH has a Class III criterion that suggests the pH should remain between 6 and 8.5. The maximum limit of this criterion was not exceeded during the study period. In November 2004 the sample values fail below a pH of 6 in the northeastern region of the Refuge. *pH remains a monitored parameter.*

<u>SiO_2</u>: There were no strong correlations associated with silica. Silica shows a seasonal pattern for the interior sites of the Refuge. Silica is higher in the wet-warm season (late

April – early November) and lower during the dry-cool season (November to early April). Independent research has demonstrated that silica concentrations decrease during the cooler season when algae populations (dominated by diatoms) are dying off and increase during the warmer season when these populations grow in again. Changes in these patterns can serve as a good indication of eutrophication and even biota shifts (Biggs, 1990). These assertions are generally for flowing waters (i.e., rivers) and historically appear to be of less import for the Refuge wetland ecosystem which has a low diatom abundance associated with the periphyton population dominating as the primary producer of the Refuge (Kadlec and Knight, 1996). However, with STA-1E becoming operational in September 2005, there will be larger volumes of higher mineral content water discharge into the L-40 Canal. Canal water penetration into the marsh has been documented (Harwell et al., 2005). The introduction of higher mineral content water into a soft-water ecosystem is expected to impact the biotic community. The combination of temperature, nitrogen to phosphorus, and silica to phosphorus ratios has been shown to relate to algae species distributions (Adamus et al., 2001). This suite of indicators can theoretically be applied as an indicator of changes in periphyton community dynamics as the high mineral content water impacts the Refuge. Presently, WCA-2 has a higher diatom abundance associated with the periphyton communities (relative to the Refuge) and the Refuge perimeter canals are major sources of water for WCA-2. Because of the potential of silica concentration change to cause biotic shifts, and because the canals of the Refuge provide water to other areas of the Everglades, silica is not on the elimination list. *Silica remains a monitored parameter.*

$\underline{SO_4}$: There were no strong correlations associated with sulfate. Sulfate mediates methyl mercury production (Axelrad et al., 2005). Mercury contamination has been a concern for areas of the Everglades. As sulfate increases sulfide formation increases, which increases the potential for methyl mercury formation. At toxic levels sulfate can induce plant mortality, because of the reduction of sulfate to hydrogen sulfide (Armstrong et al., 1996). Increasing sulfate loads to the marsh can alter biogeochemical cycling (e.g., Fe and P) and result in decreased biodiversity for the ecosystem. Because of the significant role sulfate plays in the biogeochemical cycling and the generation of toxic forms of mercury sulfate is not being considered for elimination from the monitoring program. *Sulfate remains a monitored parameter.*

<u>SPCOND</u>: Specific conductance is a conservative parameter that can be used to track canal water penetration into the marsh. SPCOND can also be employed to develop hydrological and chemical budgets for the Refuge. SPCOND had strong correlations with ALKA (r = 0.96), Ca (r = 0.95), Cl (r = 0.95), HARD (r = 0.97), Mg (r = 0.97), Na (r = 0.96), and TDS (r = 0.98). The Class III criterion of = 1250 µS/cm for SPCOND is well in excess of values experienced in the marsh and as such the criterion is meaningless when compared to values observed in the marsh. *Specific conductance remains a monitored parameter.*

<u>TDKN</u>: There were no strong correlations associated with total dissolved Kjeldahl nitrogen (TDKN). TDKN is the fraction of the total Kjeldahl nitrogen (TKN) that passes through a 0.45 micron filter. The sum of organic nitrogen (in the trinegative oxidation state) and ammonia make up Kjeldahl Nitrogen (Clesceri et al., 1998). Sources of Kjeldahl nitrogen include the decay of organic material and urban and industrial organic waste. Large amounts of ammonia and organic nitrogen are applied to cropland as fertilizer. Both ammonia and organic nitrogen are relatively immobile in soils and ground water because of adsorption on soil surfaces and particulate filtering. These nitrogen constituents are susceptible to nitrification under aerobic conditions (Kadlec and Knight, 1996). The coefficient of variations for TDKN in the Refuge interior and canals were ~21% and ~20%, respectively. TDKN had a range of 0.65 and 2.57 mg L^{-1}. At greater than 3 km interior of the canals impounding the Refuge (with the exception of 2 outliers in August and September 2004) TDKN values drop below 1.3 mg L^{-1}, which suggest marsh TDKN maybe pulse driven by canal water penetration. TKN shows a similar pattern with a range of 0.63 to 4.11 mg L^{-1} (not including outliers) and dropping below 2 mg L^{-1} at greater than 3 km interior of the marsh canals. SPCOND serves as a more sensitive tracer of canal water penetration as the variable shows a finer gradient than TDKN. Because of the relatively low variability and because TKN will continue to

be monitored TDKN can be removed from the suite of analytical water quality parameters. *TDKN is on the list of parameters to be eliminated.*

<u>$TDPO_4$</u>: Total dissolved phosphorus (not phosphate) had a strong correlation with OPO_4 (0.99). $TDPO_4$ provides a quick estimation of biologically available phosphorus. $TDPO_4$ is subtracted from total phosphorus to yield total particulate phosphorus. The total particulate phosphorus value provides a good estimate of total phosphorus that is unavailable for biological uptake at the time of the measurement as well how much may become biologically available in the future. *Total dissolve phosphate remains a monitored parameter.*

<u>TDS</u>: Total dissolved solids was suggested as a parameter to be eliminated. TDS and conductance are highly correlated (r = 0.98). TDS, as well as ALKA, are used to determine if outliers or invalid measurement values exist in SPCOND data. Further the ratio between Cl and TDS is expected to indicate sources of water (i.e., canal, marsh, rain, groundwater, etc.) for the Refuge (Waldon, 2005). Because of these applications, the conservative nature of TDS, and the observed variability in the time-series data for TDS it was suggested that the parameter not be dropped. *Total dissolved solids remains a monitored parameter.*

<u>TEMP</u>: There were no strong correlations associated with temperature. Temperature is an integral parameter that changes seasonally. It is used to adjust conductance, dissolved oxygen measurements, determine DO saturation, and the DO-SSAC. There were no strong correlations associated with temperature. *Temperature remains a monitored parameter.*

<u>TKN</u>: There were no strong correlations associated with total Kjeldahl nitrogen. TKN combined with NO_X provides a value for total nitrogen, which is important in understand water quality and is of particular concern downstream of the Refuge. There were no strong correlations associated with TKN. *TKN remains a monitored parameter.*

TOC: There were no strong correlations associated with TOC. From the time-series characterization TOC demonstrated a consistent range and did not appear to indicate any anthropogenic or natural events that may have impacted the marsh. One caveat for TOC was presented by a recent USGS study that demonstrated problems in obtaining consistent TOC results (Aiken et al. 2001). The difference between TOC and DOC yields particulate organic carbon (POC). POC has been linked to mercury methylation in WCA2 (Reddy and Aiken, 2001). Because TOC is necessary for determining POC and because there are no surrogates for TOC, TOC will remain a monitored parameter. *TOC remains a monitored parameter.*

TPO_4: Total phosphorus (not total phosphate). Phosphorus is a nutrient required for plant growth and in most freshwater systems phosphorus is considered a limiting nutrient. Historic phosphorus loads for the Everglades were generally low and derived from atmospheric deposition. Recent (last half century) increases in phosphorus loading are associated, in part, with run-off from agricultural sources upstream of the Everglades in the EAA. Regardless of this relatively new source of nutrients for the Everglades, total phosphorus has been identified as the key limiting nutrient (McCormick et al., 2002). With the development of agricultural in regions north of the Refuge, nutrient run-off towards the Refuge has been an increasing concern. The Consent Decree issued in 1991 mandates the monitoring of phosphorus in the Refuge. *Total phosphate remains a monitored parameter.*

TSS: There were no strong correlations associated with total suspended solids. Total suspended solids are generally a concern for potable waters. There are conditions when water is pumped out of the Refuge as water supply for neighboring residential areas (e.g., Lake Worth Drainage District) and TSS serves as an indicator water clarity and hence the suitability of using the water for drinking and hygienic purposes. Further, high TSS has been associated with marsh disturbance and can help indicate sample sites that may have been agitated during sample collection. *TSS remains a monitored parameter*

TURB: There were no strong correlations associated with turbidity. Turbidity has a Class III criteria of less than or equal to 29 NTU above natural background. Natural background was defined for the STAs and cannot be applied for the marshes. Regardless, turbidity was suggested as a parameter to be dropped because it was expected to be correlated to TSS. Inversely, the coefficient of determination (r = 0.55) was less than expected. A station by station time-series variation analysis shows that turbidity had a coefficient of variation of ~65% compared to the even higher TSS coefficient of variation of ~128%. The observed high variability in turbidity suggest that the parameter is sensitive to small scale changes to water conditions and further analysis of the parameter may lead to increased understanding of temporal and spatial hydrologic dynamics. Turbidity is a proxy for the condition and productivity of natural bodies of water as it relays information about the clarity of the water parcel. Turbidity is a measure of light scatter and absorbance and can reveal a level of detail about light penetration to the marsh peat and algal communities (Clesceri et al., 1998). Also, high turbidity has been associated with marsh disturbance and can help indicate sample sites that may have been agitated during sample collection. *Turbidity remains a monitored parameter.*

FINAL LIST OF PARAMETERS FOR ELIMINATION

As a result of this exercise 11 monitoring parameters are being proposed for elimination:

- Alkaline phosphatase,
- Ammonium,
- Color,
- Hardness,
- Magnesium,
- Nitrate,
- Nitrite,
- Ortho-phosphate.
- Potassium,
- Sodium,
- Total dissolved Kjeldahl nitrogen, and

The work presented in this document was an important exercise for the LOXA program. Part of the recognition that these parameters may be acceptable to eliminate is that they are presently monitored at EVPA sites. Therefore, parameter reduction recommendations for the LOXA program may not be appropriate for the EVPA program, or other water quality studies in the Everglades.

REFERENCES

Adamus, P., Danielson, T.J., Gonyaw, A., 2001. Indicators for Monitoring Biological Integrity of Inland, Freshwater Wetlands A Survey of North American Technical Literature (1990-2000). Environmental Protection Agency, EPA843-R-01.

Aiken, G., Kaplan, L.A., Weishaarc, J., 2001. Assessment of relative accuracy in the determination of organic matter concentrations in aquatic systems. Journal of Environmental Monitoring v4, p70–74.

Armstrong, J., F. Afreen-Zobayed, and W. Armstrong. 1996. Phragmites die-back: Sulphide and acetic acid-induced bud and root death, lignifications, and blockages within aeration and vascular systems. New Phytologist, v134, p601-614.

Axelrad, D., Atkeson, T., Pollman, C., Lange, T., 2005. Chapter 2B: Mercury monitoring research and environmental assessment in South Florida. G. Redfield, ed. In: *2005 South Florida Environmental Report*. West Palm Beach, FL.

Bechtel, T., Hill, S., Iricanin, N., Mo, C., Van Horn, S., 2000. Chapter 4: Status of water quality criteria compliance in the Everglades Protection Area and at Non-ECP Structures. G. Redfield, ed. In: *2000 Everglades Consolidated Report*. West Palm Beach, FL.

Biggs, B. J., 1990. Periphyton communities and their environments in New Zealand Rivers. New Zealand Journal of Marine and Freshwater Research, v24, p367-386.

Brandt, L.A., Harwell, M., Waldon, M. 2004. Work Plan: Water Quality Monitoring and Modeling for the A.R.M. Loxahatchee National Wildlife Refuge: 2004-2006. Prepared for the A.R.M. Loxahatchee National Wildlife Refuge. April, 2004. 33 pp. http://sofia.usgs.gov/lox_monitor_model/workplans/2004-2006_workplan.html

Clesceri, L.S., Greenberg, A.E., Eaton, A.D., 1998. Standard Methods for the Examination of Water and Wastewater, 20th edition. Published by: American Public Health Association, American Water Works Association, and Water Environment Federation.

Demaneche, S., Kay, E., Gourbiere, F., and Simonet, P., 2001. Natural transformation of Pseudomonas fluorescens and Agrobacterium tumefaciens in soil. Applied Environmental Microbiology, v67, i6, p2617-2621.

Harwell, M, Surratt, D, Waldon, M, Walker, B, Laura, B. 2005. A.R.M Loxahatchee National Wildlife Refuge Enhanced Water Quality Monitoring and Modeling Interim Report

Kadlec, R. H., Knight, R. L., 1996. *Treatment of Wetlands*. Lewis Publishers, CRC Press LLC.

McCormick, P.V., Newman, S., Miao, S., Gawlik, D.E., Marley, D., Reddy, K.R., Fontaine, T.D., 2002. Effects of anthropogenic phosphorus inputs on the Everglades. J.W. Porter and K.G. Porter, ed. In: The Everglades, Florida Bay, and Coral Reefs of the Florida Keys – An ecosystem sourcebook. CRC Press LLC.

McPherson, B., Halley, R., 1996. The South Florida Environment: a region under stress. USGS, Circular no.1134. United States Government Printing Office.

Newman, S., McCormick, P.V., Backus, J.G., 2002. Phosphatase activity as an early waring indicator of wetland eutrophication: problems and prospects. Journal of Applied Phycology v15,i1, p45-59.

Non-ECP PM, 2005. Non-ECP EFA Permit Modification Request, February 2005

Orem, W., 2004. Impacts of sulfate contamination on the Florida Everglades. USGS, Fact Sheet, FS 109-03.

Palmen, R., Buijsman, P., Hellingwerf, K.J., 1994. Physiological regulation of competence induction for natural transformation in *Acinetobacter calcoaceticus*. Archives of Microbiology, v162, p344–351.

Reddy, M.M., Aiken, G.R., 2001. Fulvic acid-sulfide ion competition for mercury ion binding in the Florida Everglades. Water, Air, and Soil Pollution, v132, p89-104.

SFWMD, 2004. Everglades Consolidated Report 2004. South Florida Water Management District, West Palm Beach, Florida.

Spijkerman, E., Coesel, P.F.M., 1998. Different response mechanisms of two planktonic desmid species (Chlorophyceae) to a single, saturating addition of phosphate. Journal of Phycology v34, p 438-445.

Thomann, RV, 1972. System analysis and water quality measurement. Environmental Research and Application, Inc., New York.

Vymazal, J., Richardson, C.J., 1995. Species composition, biomass, and nutrient content of periphyton in the Florida Everglades. Journal of Phycology v31, p343-354.

Waldon, M., 2005. Verbal communication on September 19. Environmental Program Team, ARM Loxahatchee Wildlife Refuge..

Weaver, K., Bennett, T., Payne, G., Germain, G., Hill, S., Iricanin, N., 2001. Chapter 4: Status of Water Quality Criteria Compliance in the Everglades Protection Area. G. Redfield ed. In: *2001 Everglades Consolidate Report*. South Florida Water Management District.

Weaver, K., 2004. Everglades Marsh Dissolved Oxygen Site Specific Alternative Criterion Technical Support Document. Water Quality Standards and Special Projects Program Division of Water Resource Management Florida Department of Environmental Protection Tallahassee, FL. http://www.dep.state.fl.us/water/wqssp/everglades/dossac.htm

Weaver, K., Payne, G., 2005. Chapter 2A: Status of Water Quality in the Everglades Protection Area. G. Redfield, ed. In: *2005 South Florida Environmental Report*. South Florida Water Management District, West Palm Beach, FL.

EXPERTS CONSULTED

A.R.M. Loxahatchee National Wildlife Refuge
  Michael Waldon, Ph.D., Senior Hydrologist
  Matthew Harwell, Ph.D., Senior Ecologist
  Laura Brandt, Ph.D., Senior Wildlife Biologist
South Florida Water Management District
  Sue Newman, Ph.D., Senior Supervising Environmental Scientist
  Scot Hagerthey, Ph.D., Senior Environmental Scientist
  David Struve, Ph.D., Water Quality Division Director
United States Geological Survey
  Paul McCormick, Ph.D., Ecologist

Table 1. Analytical water quality monitoring parameters for the A.R.M. Loxahatchee National Wildlife Refuge - Enhanced Water Quality Project. Parameter descriptions and IDs are as listed in the SFWMD DBHYDRO database.

PARAMETER	**ID**	**UNITS**
ALKALINITY TOTAL as $CaCO_3$	ALKA	mg L^{-1}
ALKALINE PHOSPATASE	APA	nM/minmL
CALCIUM	Ca	mg L^{-1}
CHLORIDE	Cl	mg L^{-1}
COLOR	COLOR	PCU
DISSOLVED OXYGEN	DO	mg L^{-1}
DISSOLVED ORGANIC CARBON	DOC	mg L^{-1}
HARDNESS as $CaCO_3$	HARD	mg L^{-1}
POTASSIUM	K	mg L^{-1}
MAGNESIUM	Mg	mg L^{-1}
SODIUM	Na	mg L^{-1}
AMMONIUM	NH_4	mg L^{-1}
NITRATE	NO_3	mg L^{-1}
NITRITE	NO_2	mg L^{-1}
NITRATES and NITRITES as N	NOX	mg L^{-1}
PHOSPHATE, ORTHO as P	OPO_4	mg L^{-1}
pH	pH	mg L^{-1}
SILICA	SiO_2	mg L^{-1}
SULFATE	SO_4	mg L^{-1}
SP CONDUCTANCE	SpCOND	uS/cm
KJELDAHL NITROGEN, DISSOLVED	TDKN	mg L^{-1}
PHOSPHATE, DISSOLVED as P	$TDPO_4$	mg L^{-1}
TOTAL DISSOLVED SOLIDS	TDS	mg L^{-1}
TEMPERATURE	TEMP	Deg. C
KJELDAHL NITROGEN, TOTAL	TKN	mg L^{-1}
CARBON, TOTAL ORGANIC	TOC	mg L^{-1}
PHOSPHATE, TOTAL as P	TPO_4	mg L^{-1}
TOTAL SUSPENDED SOLIDS	TSS	mg L^{-1}
TURBIDITY	TURB	NTU

Table 2. Cost recovery resulting from parameter elimination. The reported cost of analysis from SFWMD for the second quarter of 2004 was projected over all four quarters of year 2 for the before parameter elimination cost assessment and only in the first quarter of year 2 for the after parameter elimination cost assessment.

		YR2 TOTAL ESTIMATED COST - BEFORE PARAMETER ELIMINATION		**YR2 TOTAL ESTIMATED COST - AFTER PARAMETER ELIMINATION**		**COST DIFFERENCE**
TEST CODE	**PRICE**	**COUNT**	**COST**	**COUNT**	**COST**	**COST**
ALKA	$6.53	488	$3,186.64	488	$3,186.64	$0.00
APA	$17.21	488	$8,398.48	122	$2,099.62	$6,298.86
CA	$8.13	488	$3,967.44	488	$3,967.44	$0.00
CL	$8.07	512	$4,131.84	512	$4,131.84	$0.00
COLOR	$6.30	488	$3,074.40	122	$768.60	$2,305.80
DOC	$12.20	488	$5,953.60	122	$5,953.60	$0.00
K	$8.13	488	$3,967.44	122	$991.86	$2,975.58
MG	$8.13	488	$3,967.44	122	$991.86	$2,975.58
NA	$8.13	488	$3,967.44	122	$991.86	$2,975.58
NH4	$6.53	492	$3,212.76	123	$803.19	$2,409.57
NO2	$6.53	488	$3,186.64	122	$796.66	$2,389.98
NOX	$6.53	504	$3,291.12	504	$3,291.12	$0.00
OPO4	$6.53	492	$3,212.76	123	$803.19	$2,409.57
SIO2	$8.25	488	$4,026.00	488	$4,026.00	$0.00
SO4	$8.07	512	$4,131.84	512	$4,131.84	$0.00
TDKN	$12.26	496	$6,080.96	124	$1,520.24	$4,560.72
TDPO4	$11.42	496	$5,664.32	496	$5,664.32	$0.00
TDS	$12.20	488	$5,953.60	488	$5,953.60	$0.00
TKN	$12.26	492	$6,031.92	492	$6,031.92	$0.00
TOC	$12.20	492	$6,002.40	123	$6,002.40	$0.00
TPO4	$9.14	520	$4,752.80	520	$4,752.80	$0.00
TSS	$7.77	488	$3,791.76	488	$3,791.76	$0.00
TURB	$6.53	488	$3,186.64	488	$3,186.64	$0.00
TOTAL		11352	$103,140.24	7311	$64,872.00	$38,268.24

Table 3. Correlation parameter with correlation coefficient (r) greater than or equal to 0.95.

CORRELATED PARAMETERS		r VALUE
ALKA	Ca	0.98
ALKA	HARD	0.98
ALKA	SPCOND	0.96
ALKA	TDS	0.95
Ca	HARD	0.99
Ca	SPCOND	0.95
Ca	TDS	0.95
Cl	Na	0.997
Cl	SPCOND	0.95
HARD	Mg	0.97
HARD	SPCOND	0.97
HARD	TDS	0.97
Mg	Na	0.95
Mg	SPCOND	0.97
Mg	TDS	0.97
Na	SPCOND	0.96
Na	TDS	0.95
OPO_4	$TDPO_4$	0.997
SPCOND	TDS	0.98

Table 4. Finalized list of water quality parameters to be eliminated from the Enhanced Water Quality Monitoring Program.

Parameter	Primary Justification for Elimination
APA	Non-stand alone parameter requiring further data to be useful
COLOR	Low value with respect to water quality in the marsh
HARD	Redundant to alkalinity
K	Redundant to TDS; low value as WQ indicator for the marsh
Mg	Redundant to hardness and thus alkalinity
Na	Redundant to alkalinity
NH_4	Encompassed in total nitrogen measurement
NO_3	Captured in NO_X measurement
NO_2	Short lived and captured in NO_X measurement
OPO_4	Redundant to $TDPO_4$
TDKN	Captured in total nitrogen measurement

Appendix A

Table A.1. Pearson product moment correlation analysis for the suite of 29 parameters considered for elimination from the A.R.M. Loxahatchee National Wildlife Refuge - Enhanced Water Quality Monitoring Program.

	ALKA	APA	CA	CL	COLOR	DEPTH	DISS_O2	DOC	HARD	K	MG	NA	NH4	NO2	NOX	OPO4	PH_FIELD	SIO2	SO4	SpCond	TDKN	TDPO4	TDS	TEMP	TKN	TOC	TPO4	TSS	TURB	TN	TPP
ALKA	1.000																														
APA	-0.622	1.000																													
CA	0.981	-0.615	1.000																												
CL	0.883	-0.528	0.857	1.000																											
COLOR	0.385	-0.292	0.419	0.199	1.000																										
DEPTH	0.536	-0.359	0.561	0.556	-0.072	1.000																									
DISS_O2	-0.022	0.095	-0.030	0.131	-0.463	0.331	1.000																								
DOC	0.705	-0.391	0.683	0.772	0.594	0.137	-0.106	1.000																							
HARD	0.984	-0.610	0.993	0.897	0.395	0.553	-0.012	0.720	1.000																						
K	0.916	-0.597	0.916	0.860	0.515	0.473	-0.081	0.776	0.929	1.000																					
MG	0.943	-0.570	0.931	0.937	0.324	0.511	0.027	0.762	0.968	0.911	1.000																				
NA	0.894	-0.539	0.868	0.997	0.217	0.553	0.110	0.770	0.909	0.867	0.950	1.000																			
NH4	0.387	-0.224	0.414	0.320	0.251	0.505	-0.087	0.249	0.389	0.393	0.320	0.326	1.000																		
NO2	0.429	-0.242	0.450	0.392	0.264	0.498	0.089	0.318	0.445	0.434	0.415	0.396	0.491	1.000																	
NOX	0.382	-0.202	0.386	0.365	-0.024	0.536	0.297	0.158	0.390	0.341	0.381	0.367	0.339	0.775	1.000																
OPO4	0.258	-0.219	0.322	0.100	0.370	0.323	-0.164	0.062	0.264	0.362	0.131	0.103	0.514	0.286	0.161	1.000															
PH_FIELD	0.774	-0.556	0.770	0.797	0.061	0.683	0.327	0.484	0.786	0.743	0.783	0.793	0.320	0.415	0.431	0.209	1.000														
SIO2	0.641	-0.403	0.620	0.613	0.521	0.191	-0.295	0.609	0.659	0.690	0.709	0.632	0.114	0.215	0.065	0.033	0.354	1.000													
SO4	0.842	-0.482	0.865	0.835	0.344	0.524	-0.003	0.656	0.902	0.847	0.937	0.854	0.343	0.427	0.368	0.217	0.731	0.676	1.000												
SpCond	0.958	-0.590	0.950	0.954	0.330	0.552	0.022	0.759	0.972	0.917	0.972	0.962	0.403	0.429	0.381	0.199	0.796	0.659	0.895	1.000											
TDKN	0.741	-0.371	0.752	0.753	0.602	0.283	-0.098	0.907	0.769	0.815	0.769	0.752	0.432	0.420	0.255	0.269	0.560	0.548	0.728	0.782	1.000										
TDPO4	0.294	-0.241	0.358	0.136	0.365	0.361	-0.145	0.078	0.301	0.395	0.165	0.138	0.526	0.301	0.182	0.997	0.249	0.040	0.248	0.236	0.290	1.000									
TDS	0.953	-0.574	0.950	0.941	0.415	0.525	-0.020	0.794	0.972	0.938	0.974	0.949	0.377	0.430	0.342	0.214	0.765	0.721	0.910	0.979	0.816	0.247	1.000								
TEMP	0.218	-0.119	0.233	0.203	0.218	0.215	-0.170	0.090	0.244	0.293	0.255	0.215	0.189	0.134	-0.039	0.222	0.236	0.412	0.381	0.260	0.189	0.226	0.289	1.000							
TKN	-0.021	0.138	-0.015	0.032	0.285	-0.073	-0.054	0.227	-0.011	0.045	-0.001	0.021	0.018	0.048	-0.014	0.002	-0.050	0.089	-0.006	0.010	0.232	-0.003	0.037	-0.332	1.000						
TOC	0.675	-0.425	0.666	0.673	0.491	0.144	-0.134	0.811	0.690	0.727	0.708	0.679	0.287	0.258	0.117	0.117	0.463	0.557	0.635	0.700	0.769	0.137	0.730	0.305	-0.280	1.000					
TPO4	0.023	0.157	0.049	0.008	0.254	0.042	-0.081	0.109	0.033	0.087	-0.002	0.002	0.138	0.106	0.038	0.275	-0.015	0.020	0.029	0.024	0.133	0.274	0.044	-0.276	0.728	-0.227	1.000				
TSS	0.021	0.010	0.027	0.059	-0.211	0.038	0.157	-0.001	0.030	-0.023	0.035	0.047	0.114	0.024	0.054	0.002	0.127	-0.124	0.017	0.035	0.078	0.009	0.015	0.024	0.139	0.017	0.056	1.000			
TURB	0.431	-0.218	0.445	0.490	-0.188	0.587	0.341	0.149	0.452	0.363	0.446	0.478	0.321	0.384	0.489	0.150	0.584	0.076	0.443	0.467	0.268	0.184	0.427	0.130	0.053	0.124	0.107	0.547	1.000		
TN	-0.015	0.135	-0.009	0.038	0.284	-0.065	-0.050	0.230	-0.005	0.050	0.005	0.027	0.023	0.060	0.002	0.004	-0.043	0.090	0.000	0.016	0.236	0.000	0.042	-0.333	1.000	-0.279	0.729	0.140	0.061	1.000	
TPP	-0.061	0.232	-0.053	-0.034	0.163	-0.062	-0.045	0.091	-0.053	-0.021	-0.051	-0.040	-0.007	0.028	-0.012	0.004	-0.090	0.010	-0.041	-0.045	0.053	0.003	-0.026	-0.354	0.751	-0.274	0.962	0.017	0.044	0.751	1.000

Appendix B

Temporal graphs of parameters considered for elimination by the expert scientists. Graphs with stars (*) in the upper left corner are also on the final list of parameters to be dropped.

Figure 1. *Alkaline Phosphatase for the period June 2004 to May 2004.
Figure 2. *Color for the period June 2004 to May 2004.
Figure 3. Dissolved organic carbon for the period June 2004 to May 2004.
Figure 4. *Hardness for the period June 2004 to May 2004.
Figure 5. *Potassium for the period June 2004 to May 2004.
Figure 6. *Magnesium for the period June 2004 to May 2004.
Figure 7. Total organic carbon for the period June 2004 to May 2004.
Figure 8. *Sodium for the period June 2004 to May 2004.
Figure 9. *Ammonium for the period June 2004 to May 2004.
Figure 10. *Nitrite for the period June 2004 to May 2004.
Figure 11. *Total dissolved Kjeldahl nitrogen for the period June 2004 to May 2004.
Figure 12. *Ortho-phosphate for the period June 2004 to May 2004.
Figure 13. Silica for the period June 2004 to May 2004.
Figure 14. Total dissolved solids for the period June 2004 to May 2004.
Figure 15. Turbidity for the period June 2004 to May 2004.
Figure 16. Total organic carbon for the period June 2004 to May 2004.

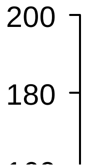
Correlation graphs for parameters with R values greater than or equal to 0.95.

Figure 17. Correlation graphs for (a) Alkalinity verses Calcium, (b) Alkalinity verses Hardness, (c) Alkalinity verses Specific conductance, and (d) Alkalinity verses Total dissolved solids.
Figure 18. Correlation graphs for (a) Calcium verses Hardness, (b) Calcium verses Specific conductance, (c) Calcium verses Total dissolved solids, and (d) Chloride verses Sodium.
Figure 19. Correlation graphs for (a) Chloride verses Specific Conductance, (b) Magnesium verses Specific Conductance, (c) Hardness verses Specific Conductance, and (d) Hardness verses Total dissolved solids.
Figure 20. Correlation graphs for (a) Alkalinity Magnesium verses Specific Conductance, (b) Magnesium verses Total Dissolved Solids, (c) Sodium verses Specific Conductance, and (d) Sodium verses Total Dissolved Solids.
Figure 21. Correlation graphs for (a) Ortho-phosphate verses Total Dissolved Phosphorus and (b) Specific Conductance verses Total Dissolved Solids.

Figure 1. Alkaline Phosphatase for the period June 2004 to May 2004.

*

*



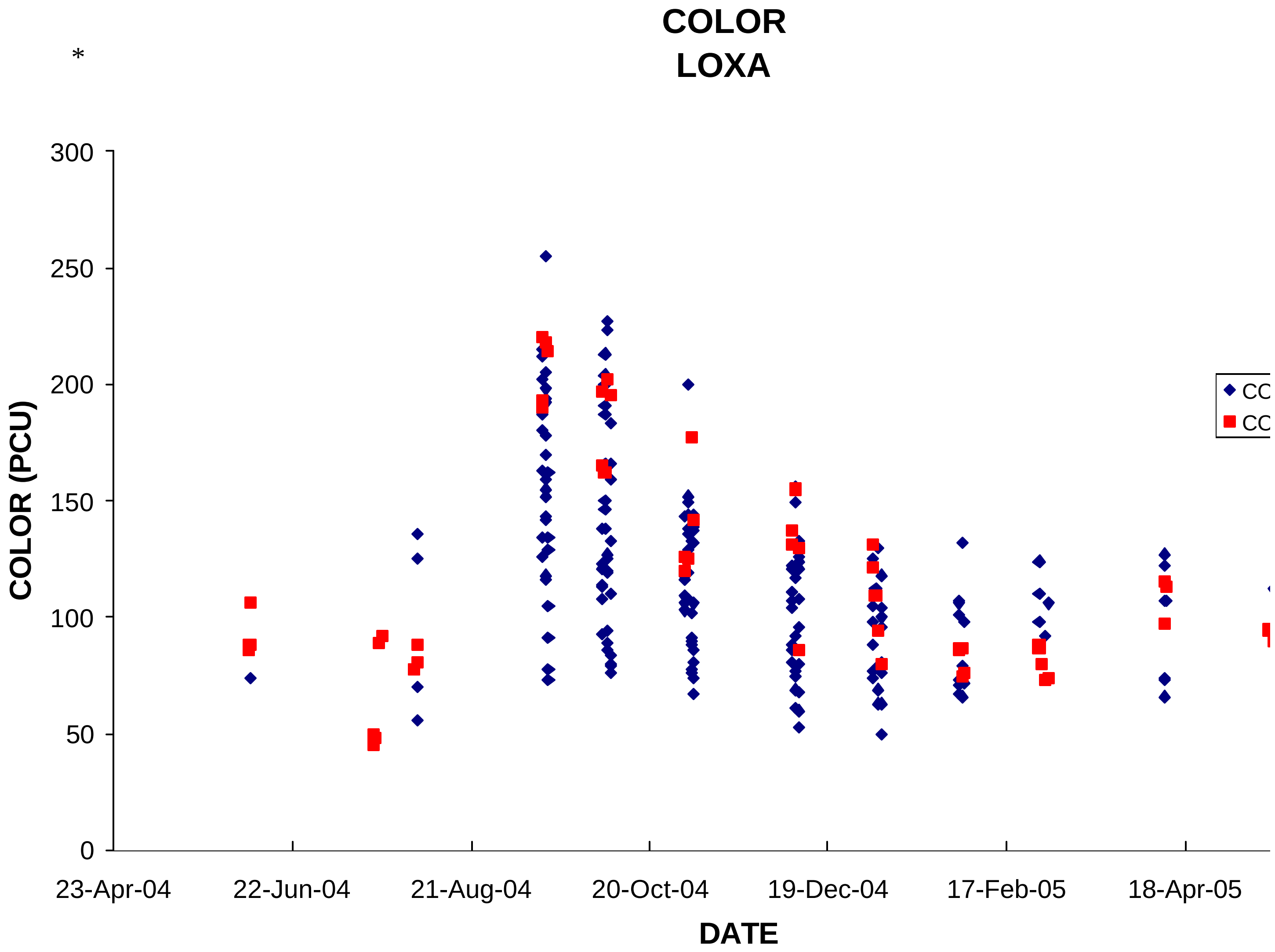


Figure 2. Color for the period June 2004 to May 2004.

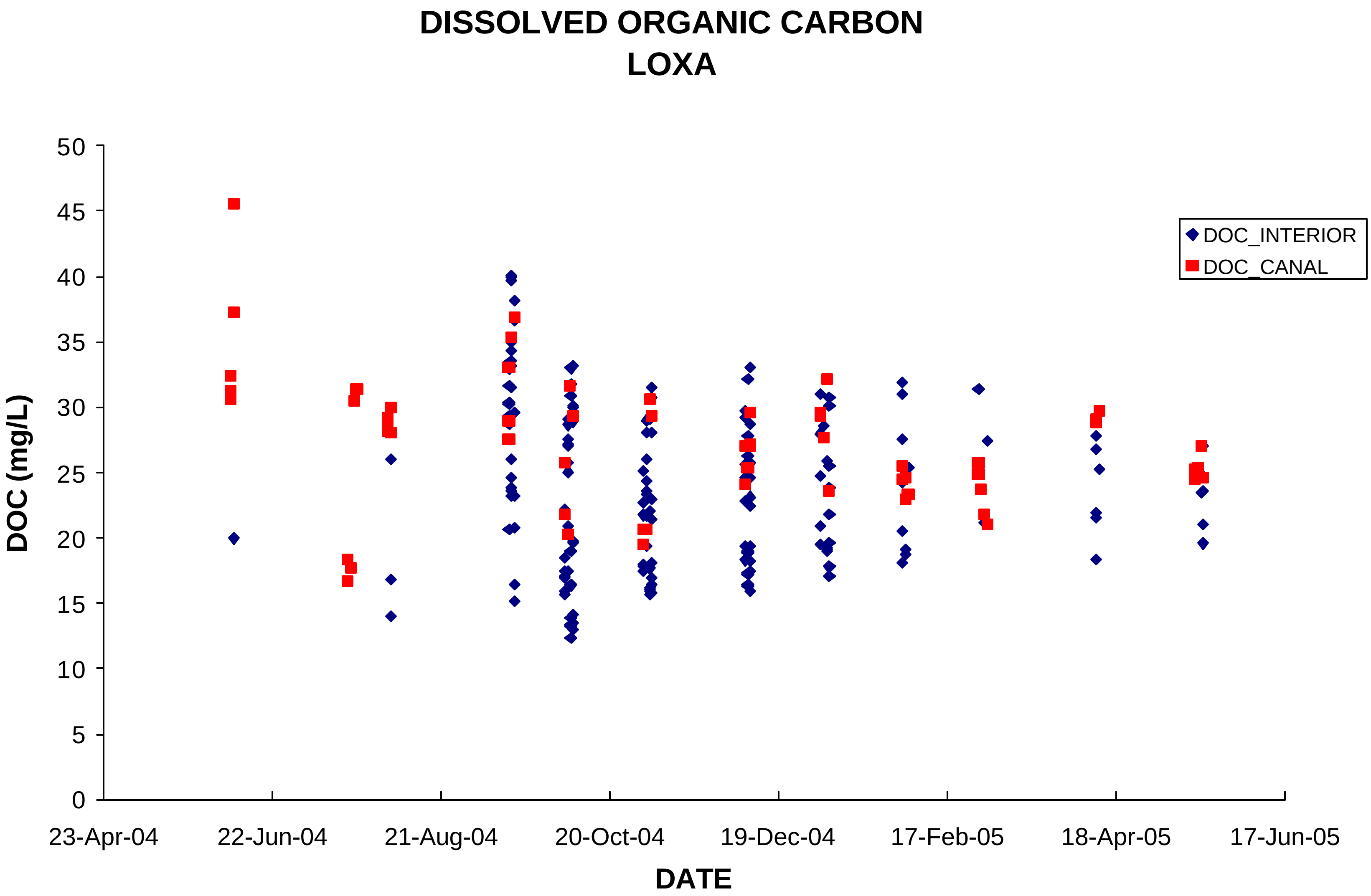


Figure 3. Dissolved organic carbon for the period June 2004 to May 2004.

*

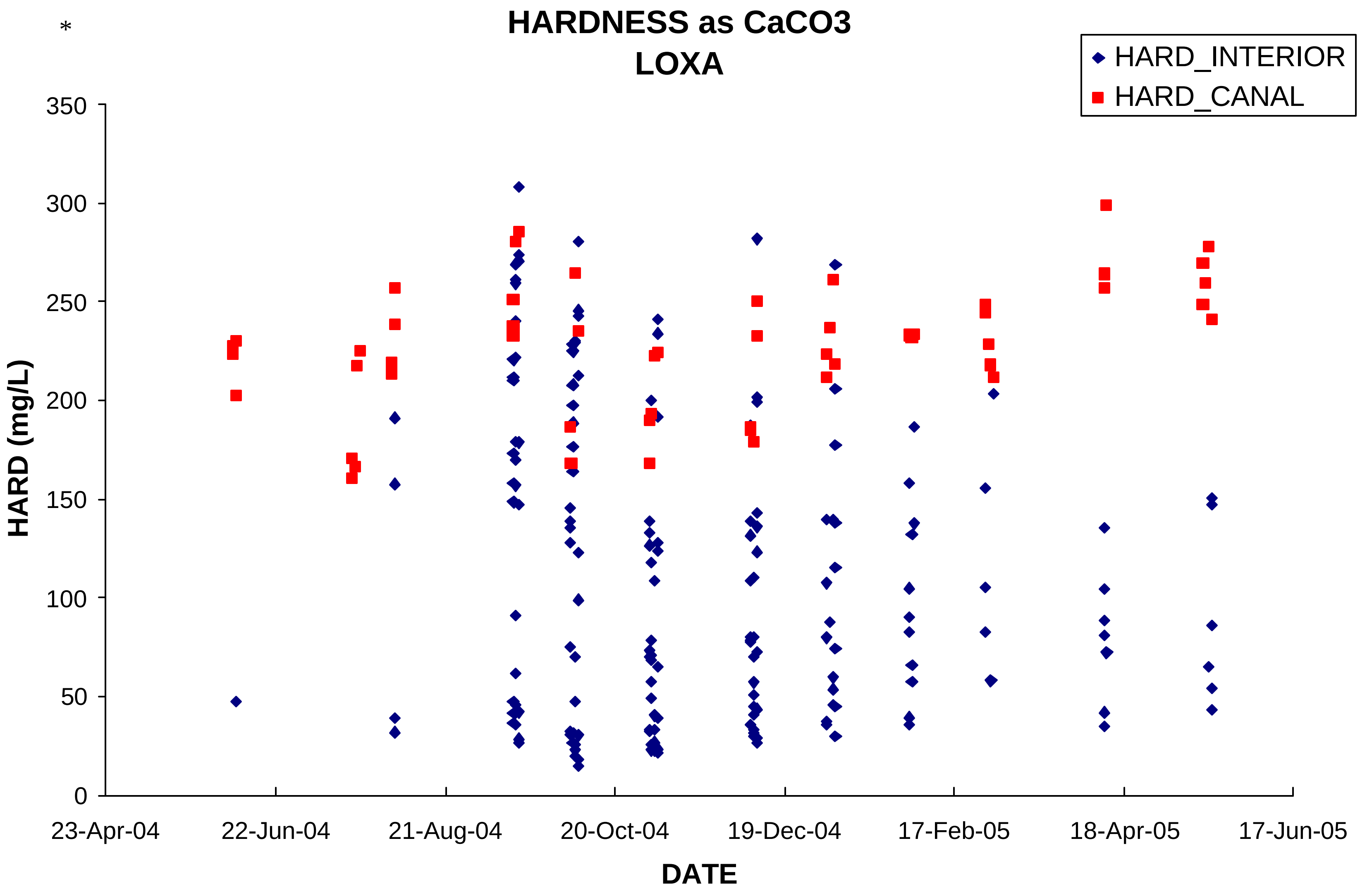


Figure 4. Hardness for the period June 2004 to May 2004.

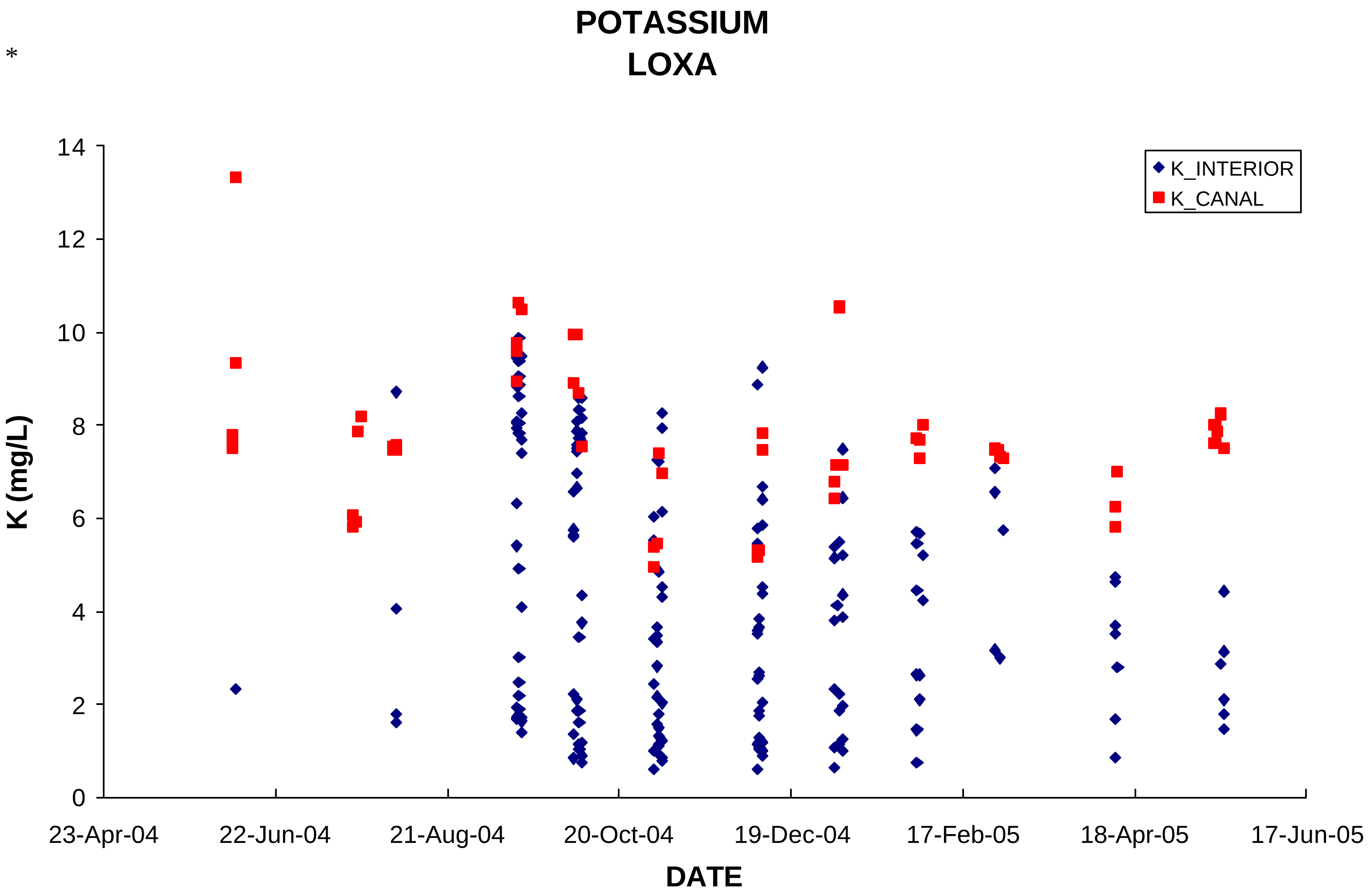


Figure 5. Potassium for the period June 2004 to May 2004.

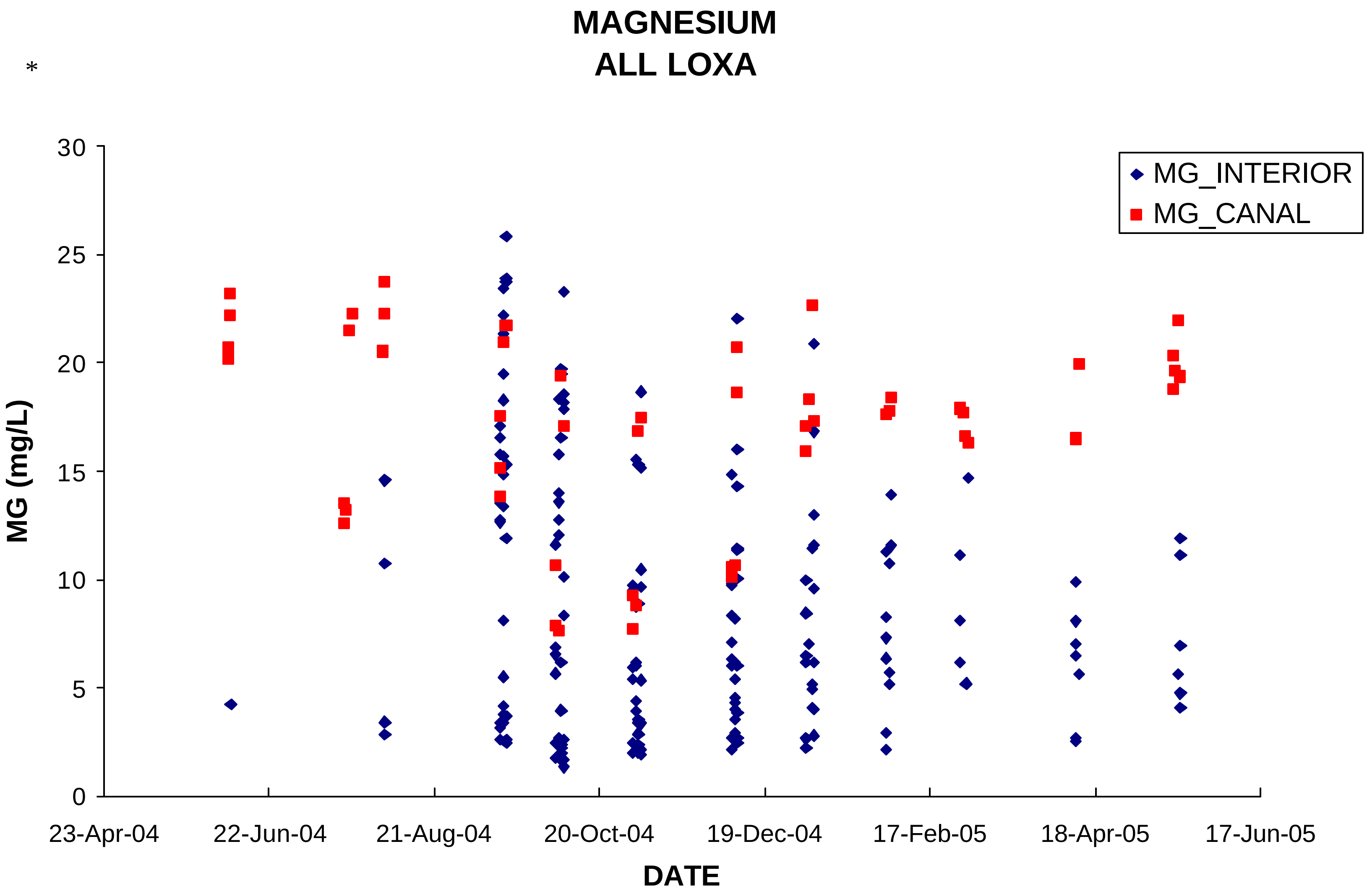


Figure 6. Magnesium for the period June 2004 to May 2004.

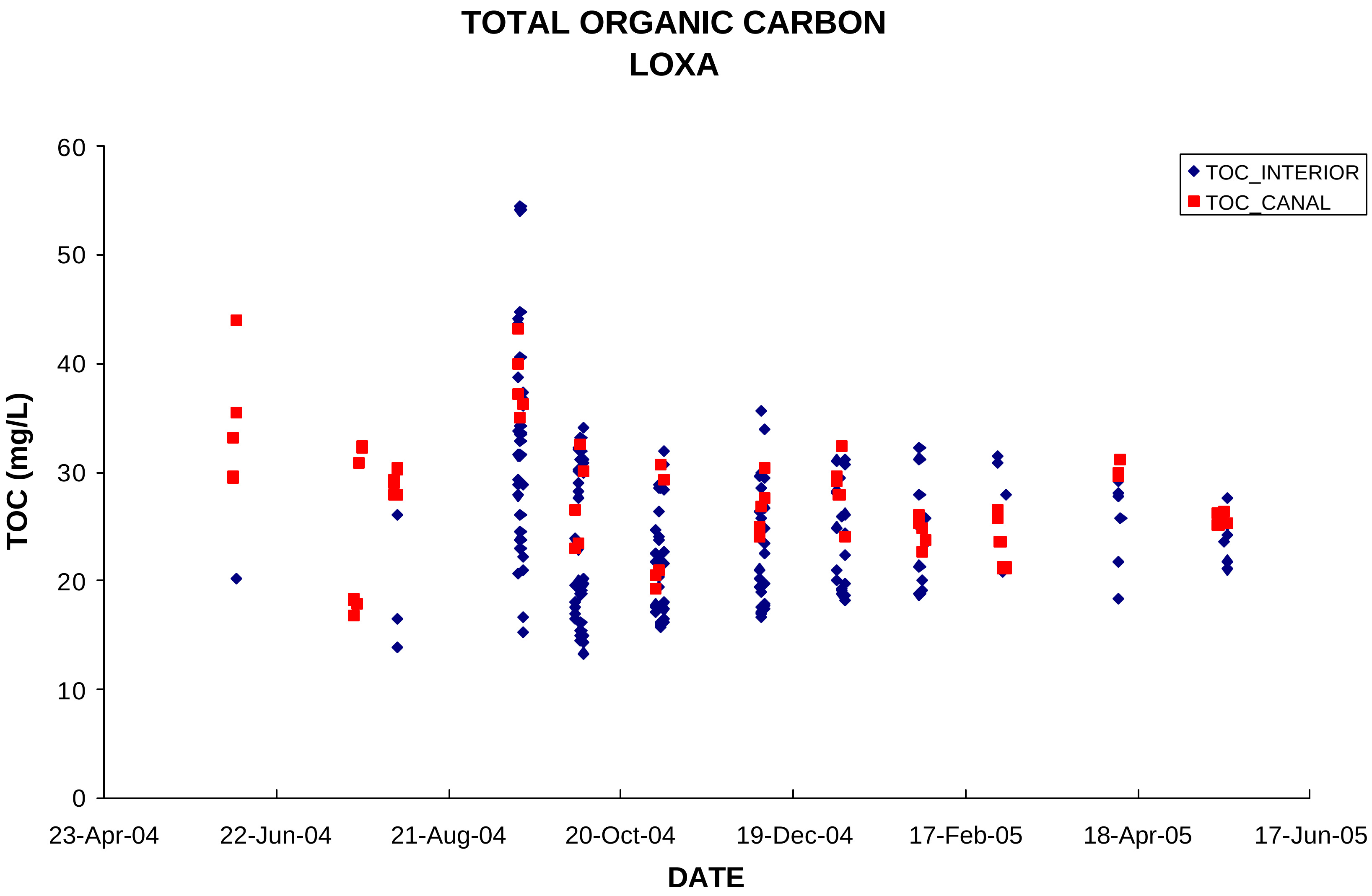


Figure 7. Total organic carbon for the period June 2004 to May 2004.

*

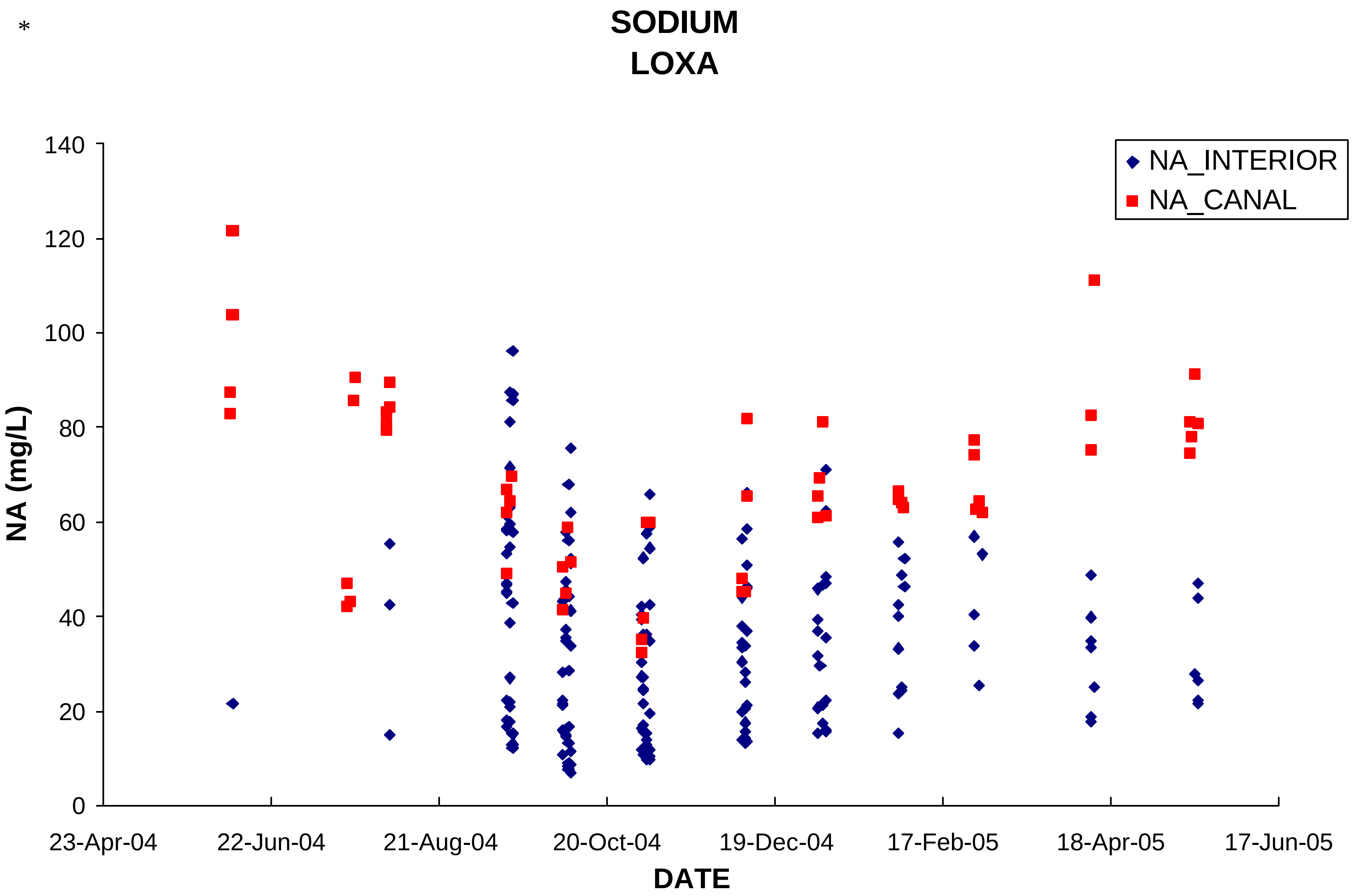


Figure 8. Sodium for the period June 2004 to May 2004.

*

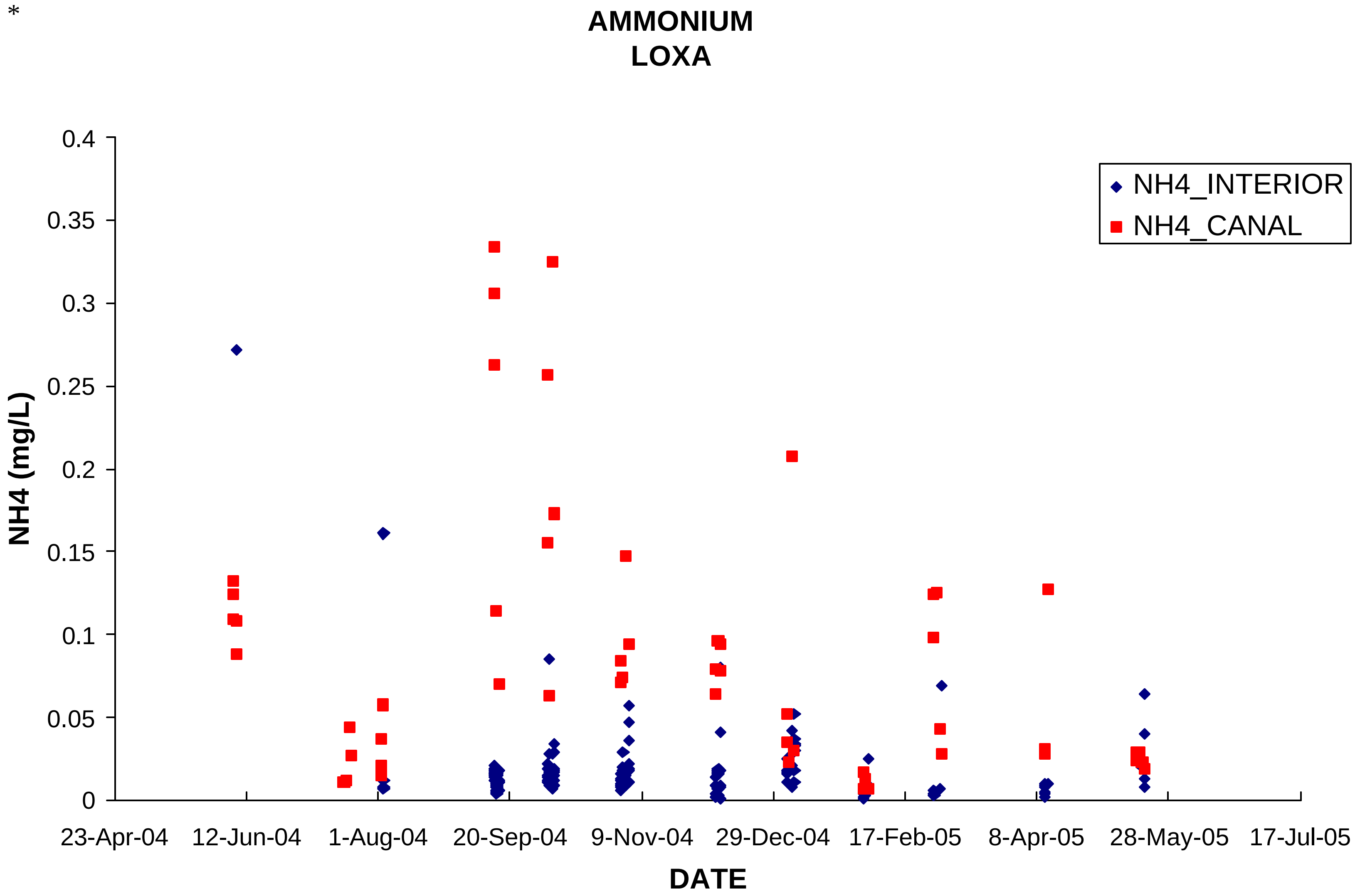


Figure 9. Ammonium for the period June 2004 to May 2004.

*

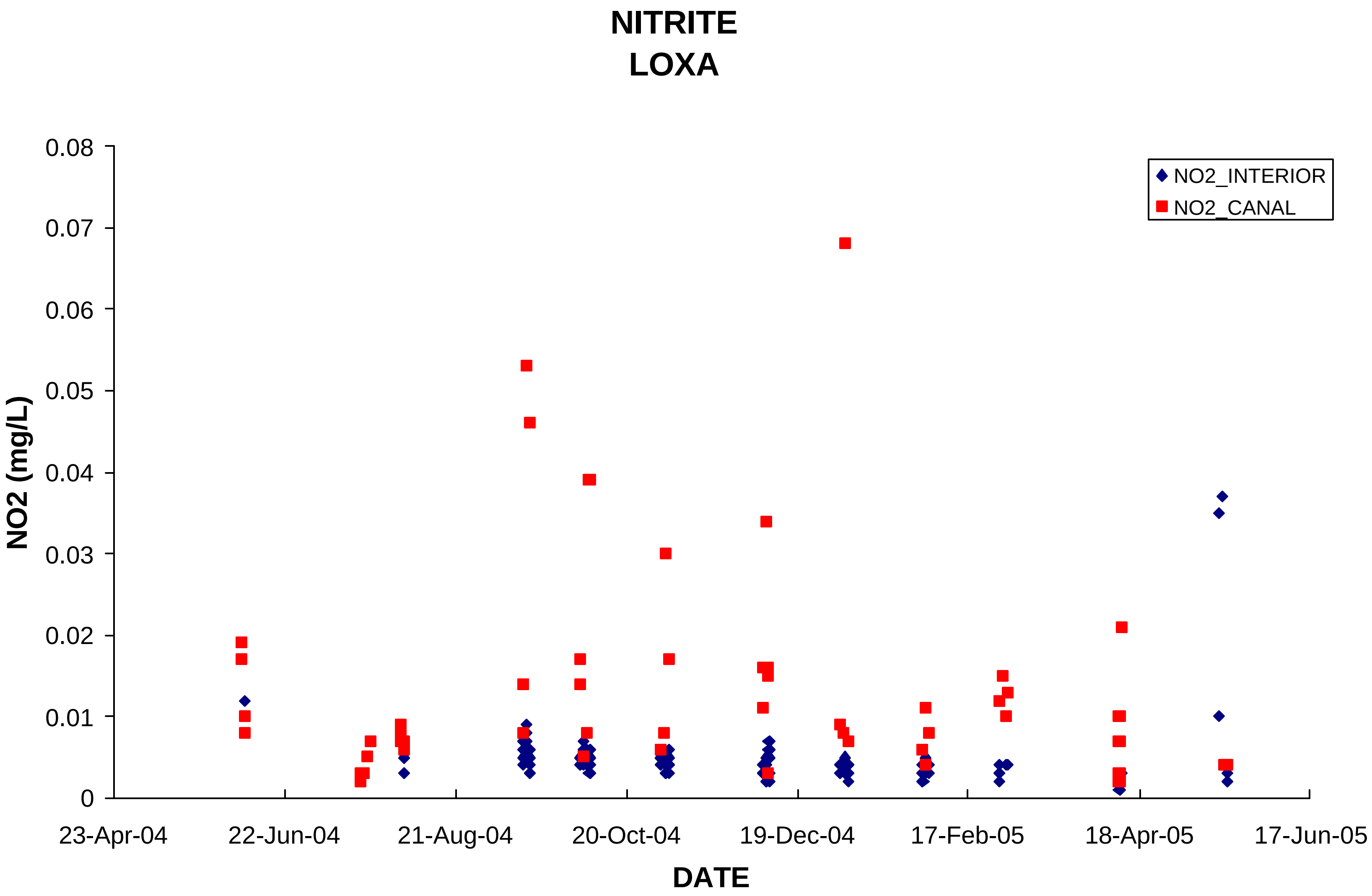


Figure 10. Nitrite for the period June 2004 to May 2004.

*

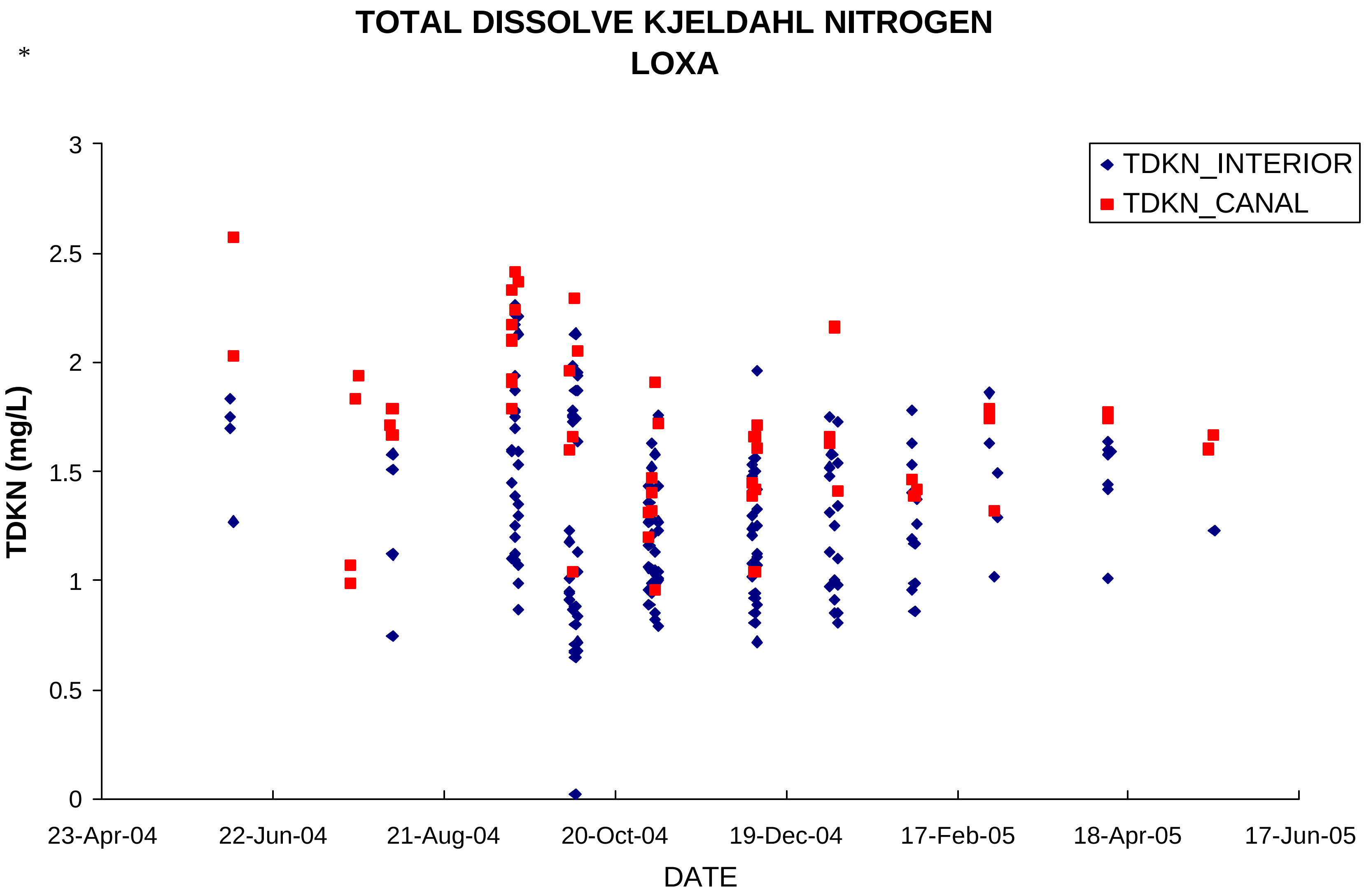


Figure 11. Total dissolved Kjeldahl nitrogen for the period June 2004 to May 2004.

*

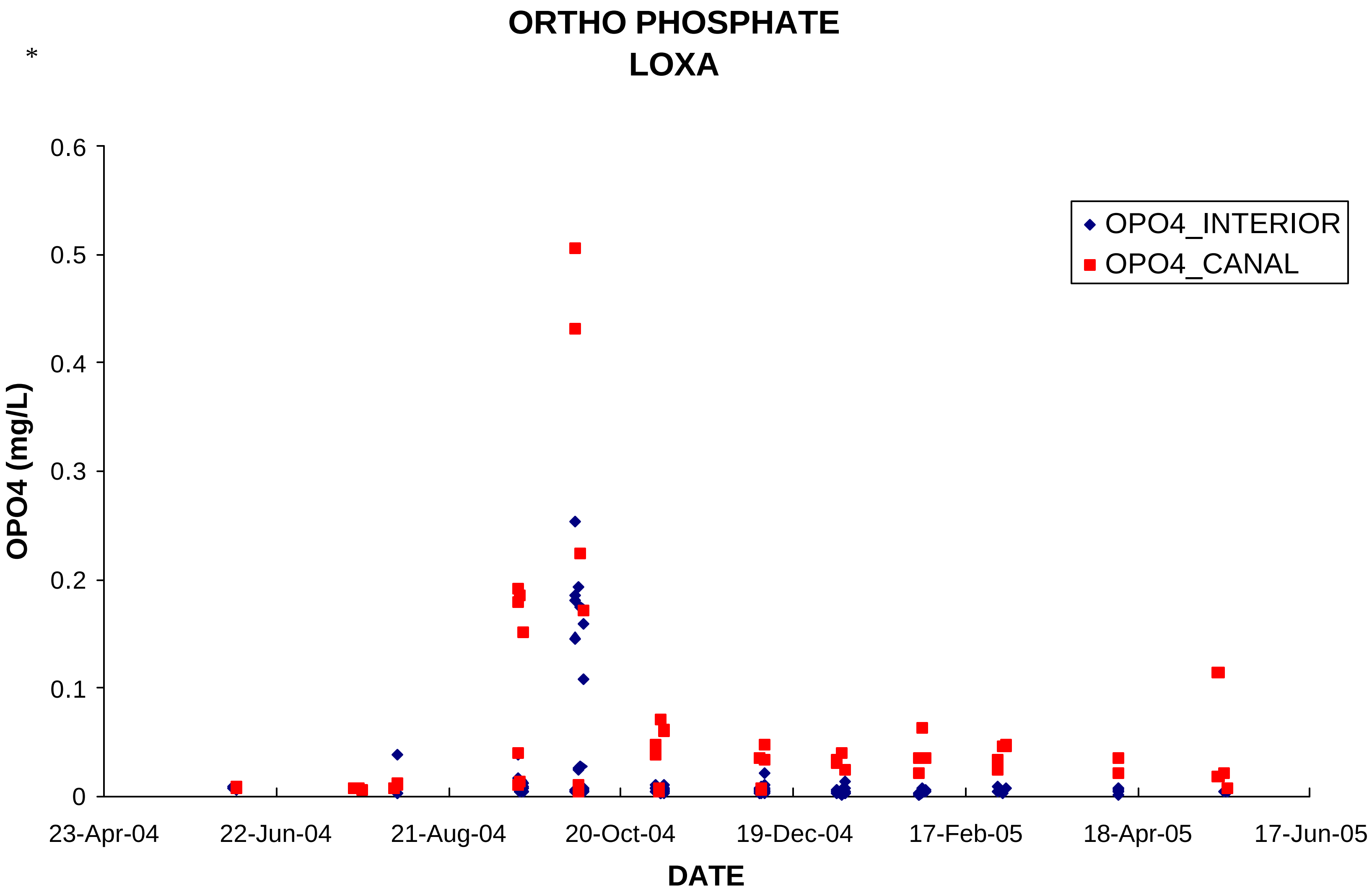


Figure 12. Ortho-phosphate for the period June 2004 to May 2004.

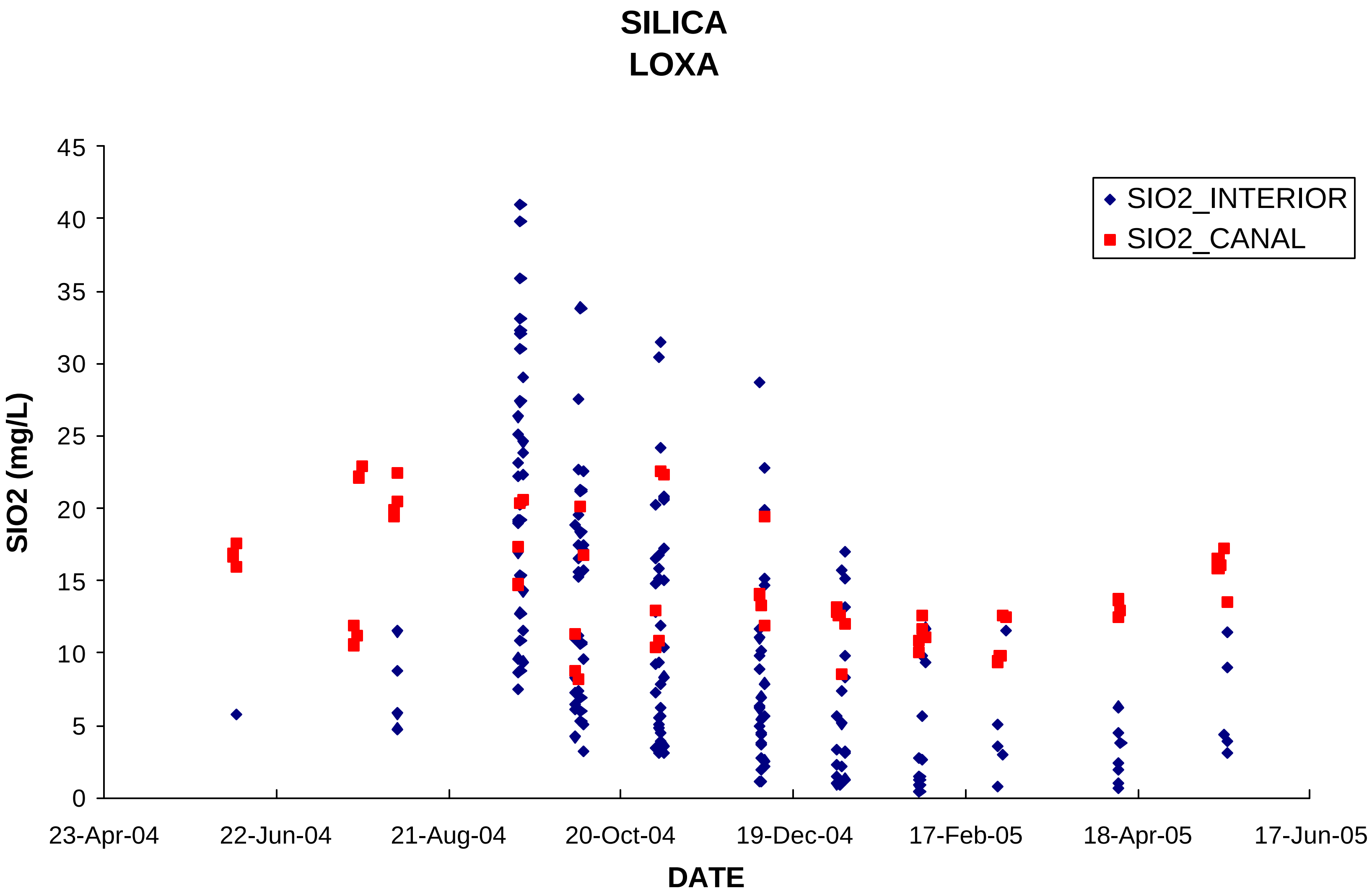


Figure 13. Silica for the period June 2004 to May 2004.

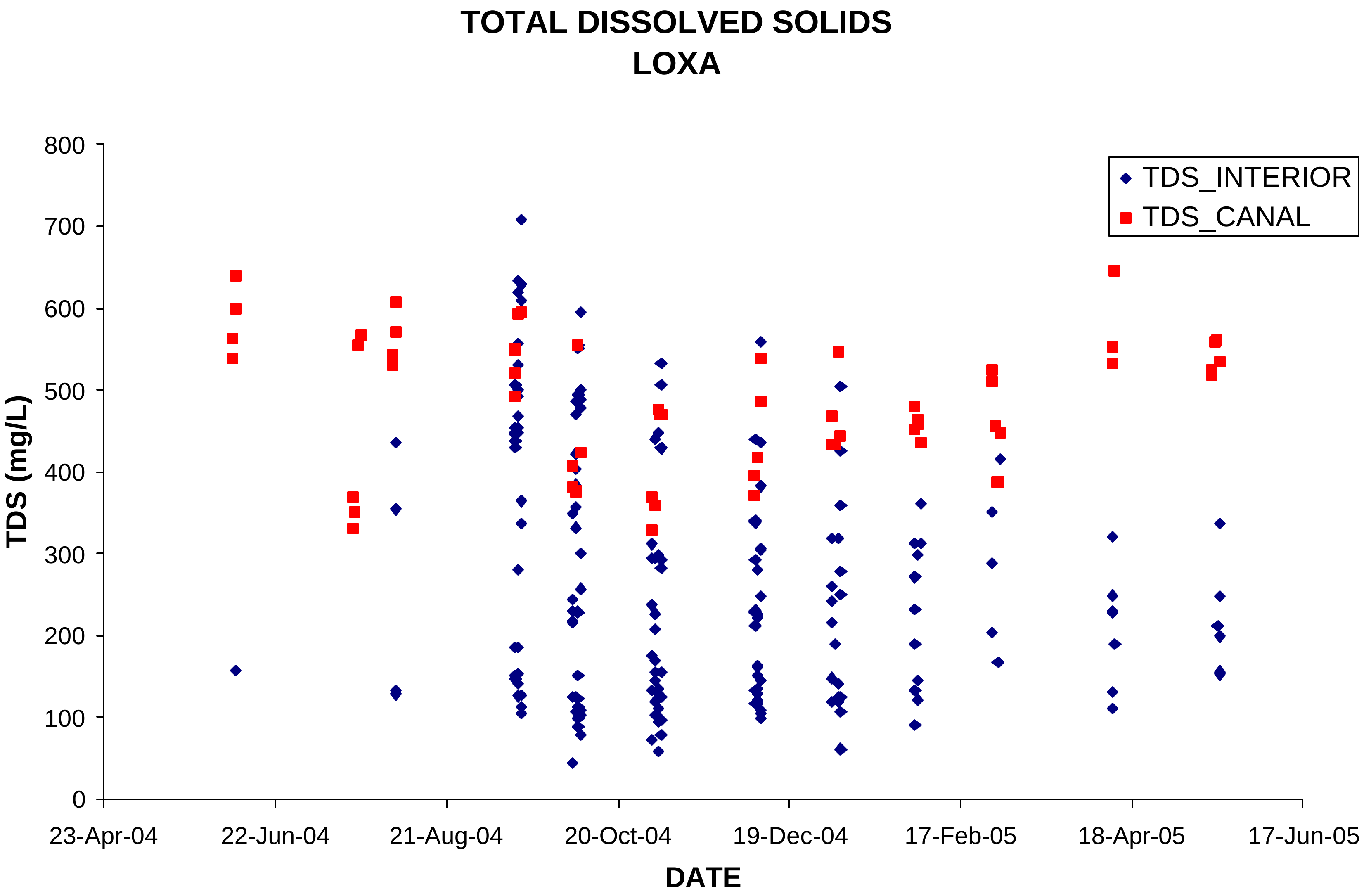


Figure 14. Total dissolved solids for the period June 2004 to May 2004.

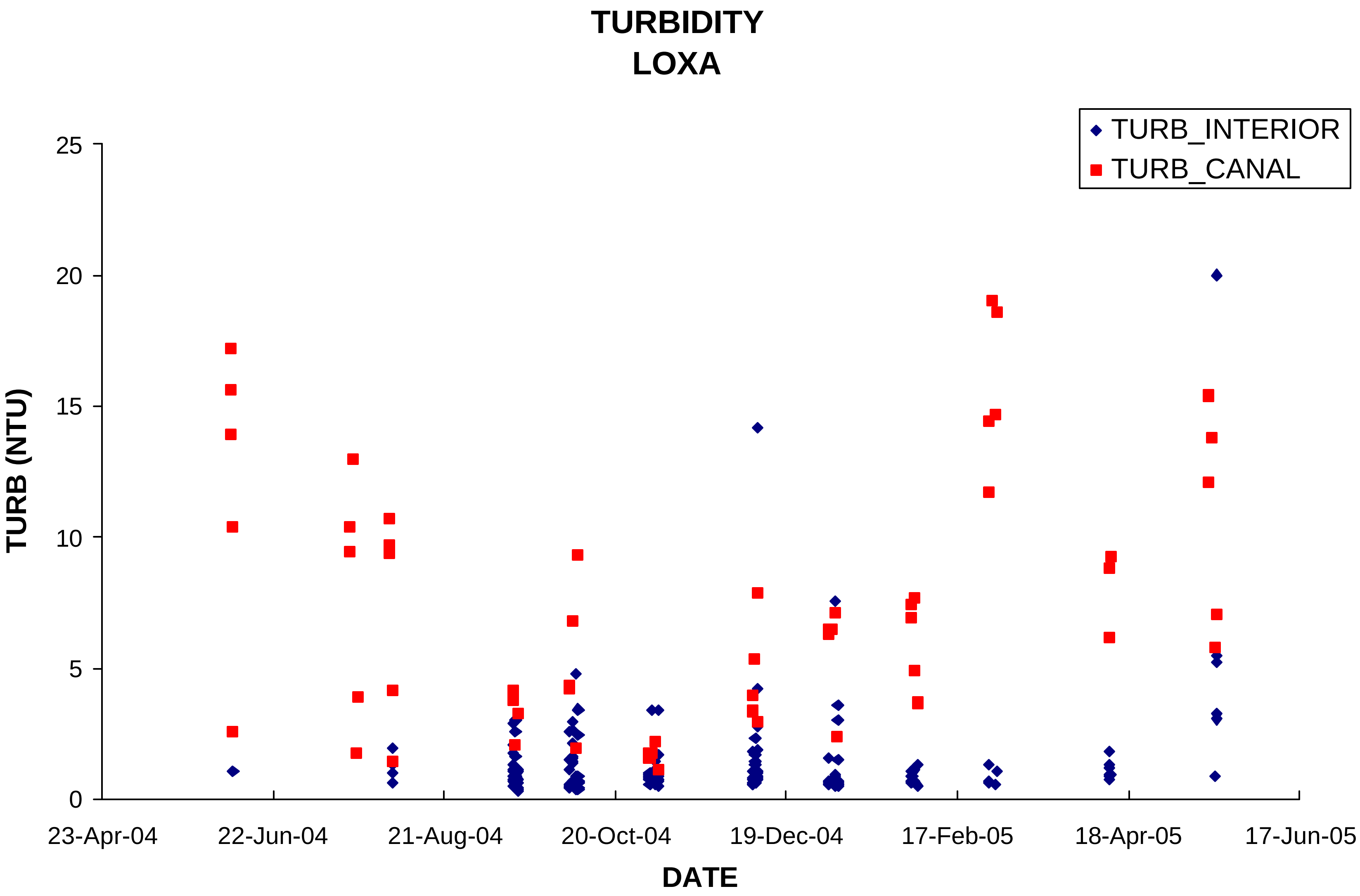


Figure 15. Turbidity for the period June 2004 to May 2004.

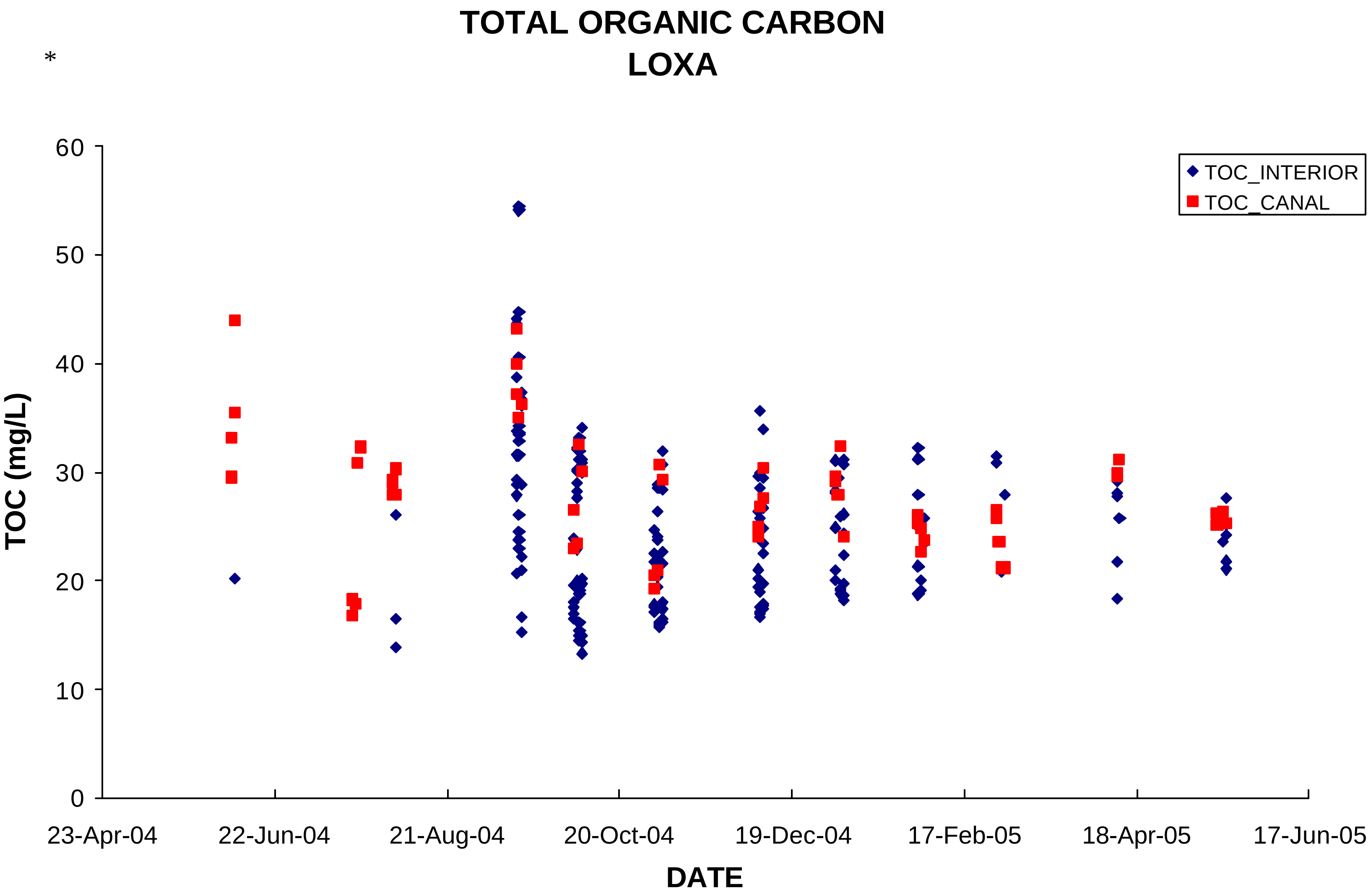


Figure 16. Total organic carbon for the period June 2004 to May 2004.

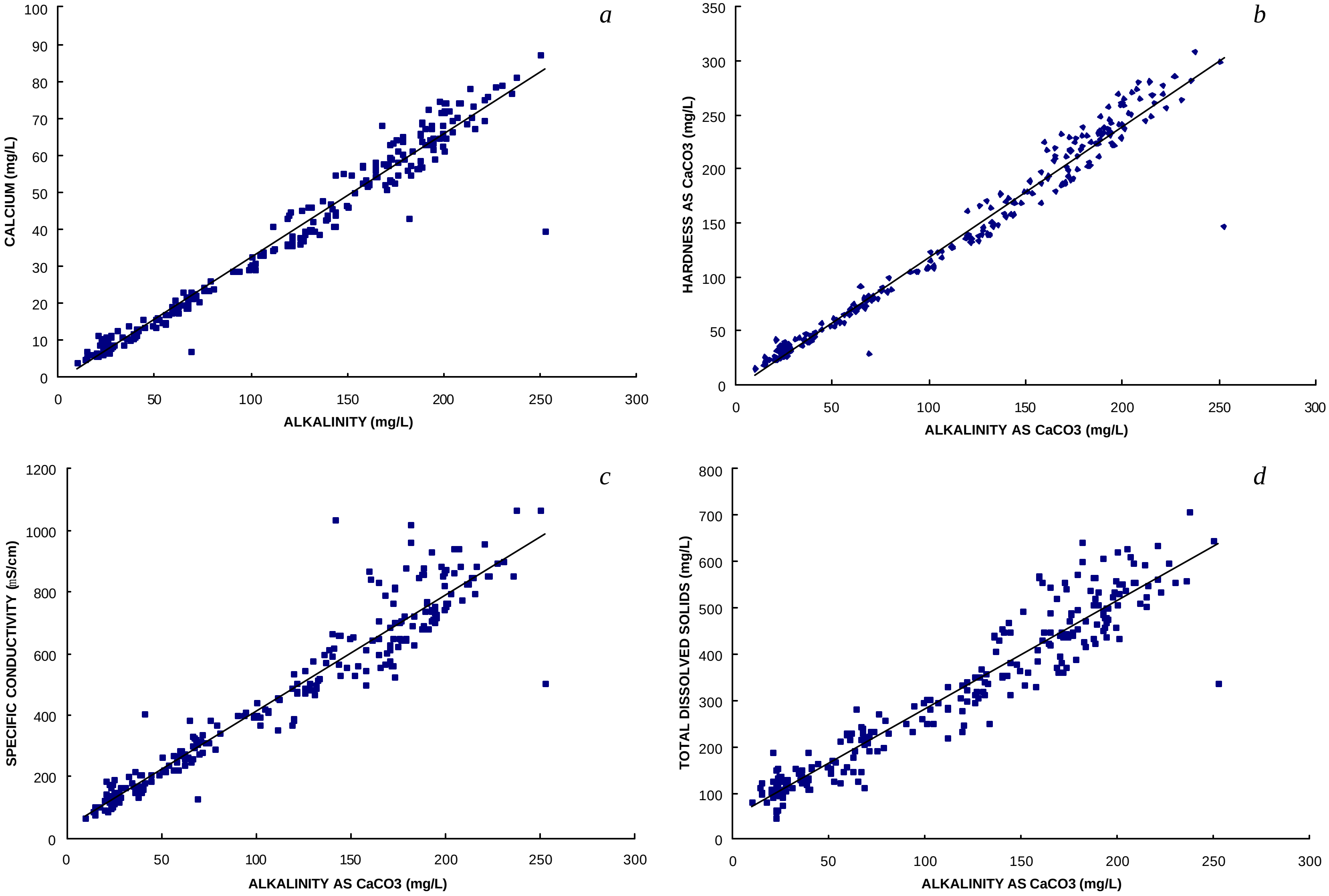


Figure 17. Correlation graphs for (a) Alkalinity verses Calcium, (b) Alkalinity verses Hardness, (c) Alkalinity verses Specific conductance, and (d) Alkalinity verses Total dissolved solids.

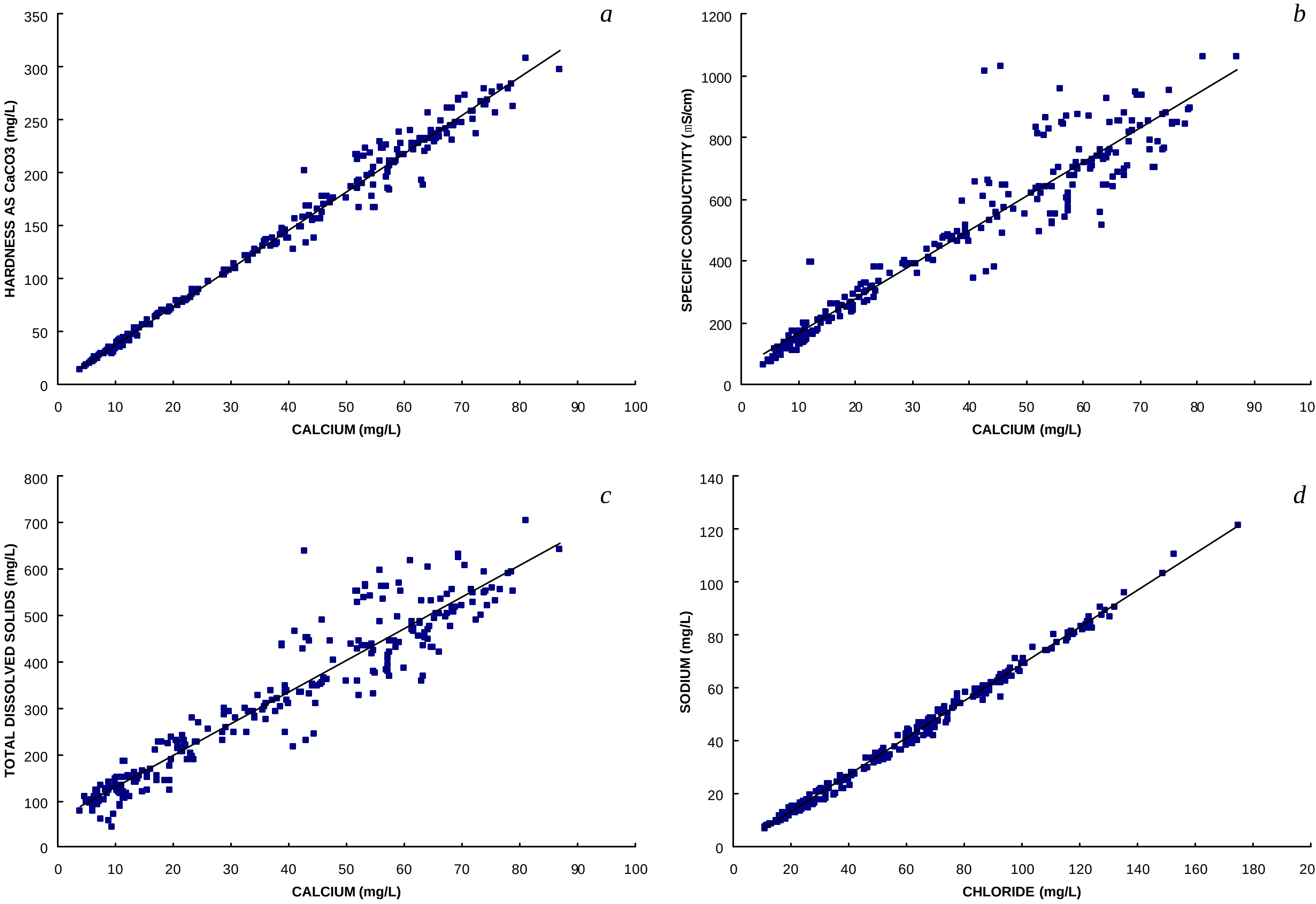


Figure 18. Correlation graphs for (a) Calcium verses Hardness, (b) Calcium verses Specific conductance, (c) Calcium verses Total dissolved solids, and (d) Chloride verses Sodium.

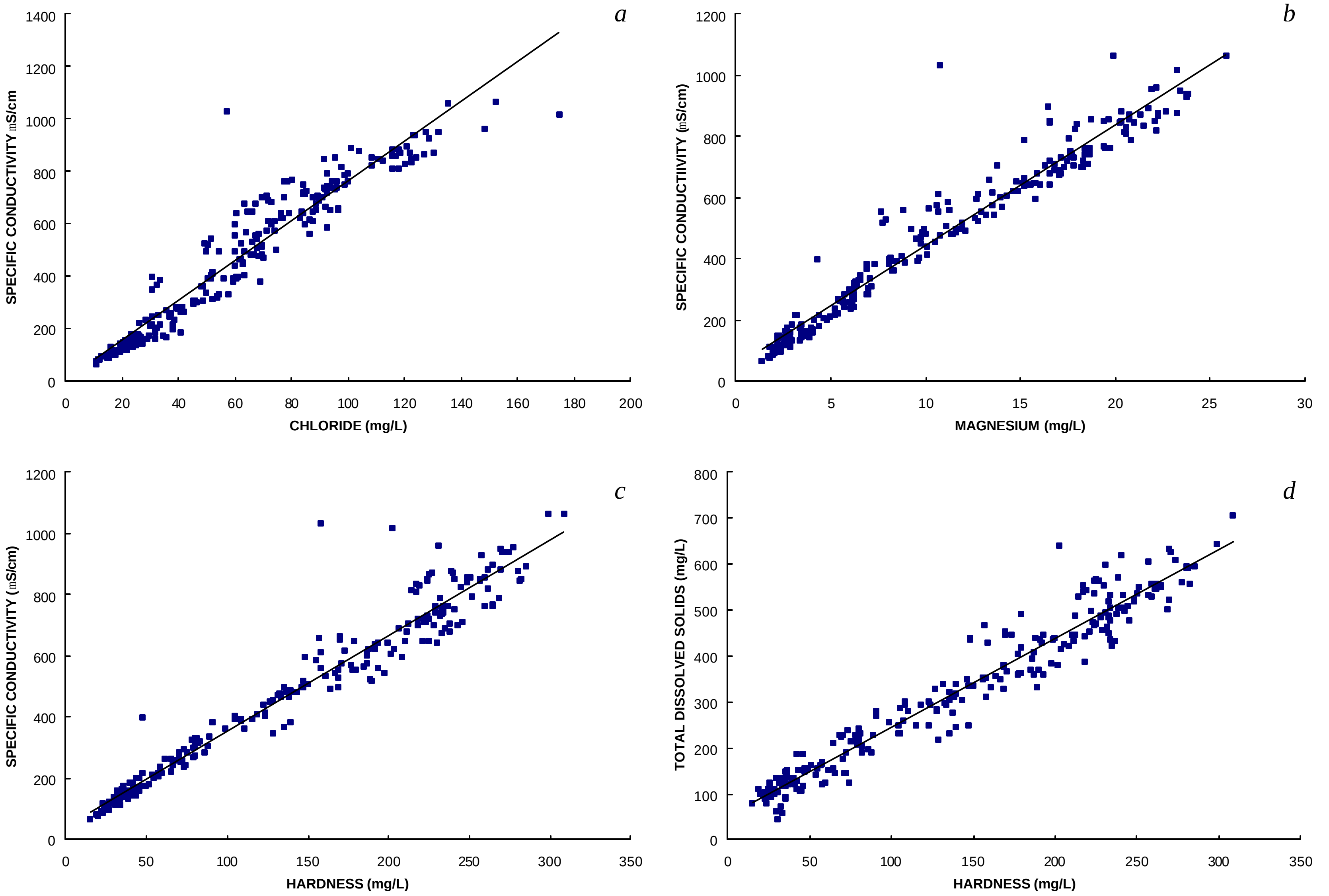


Figure 19. Correlation graphs for (a) Chloride verses Specific Conductance, (b) Magnesium verses Specific Conductance, (c) Hardness verses Specific Conductance, and (d) Hardness verses Total dissolved solids.

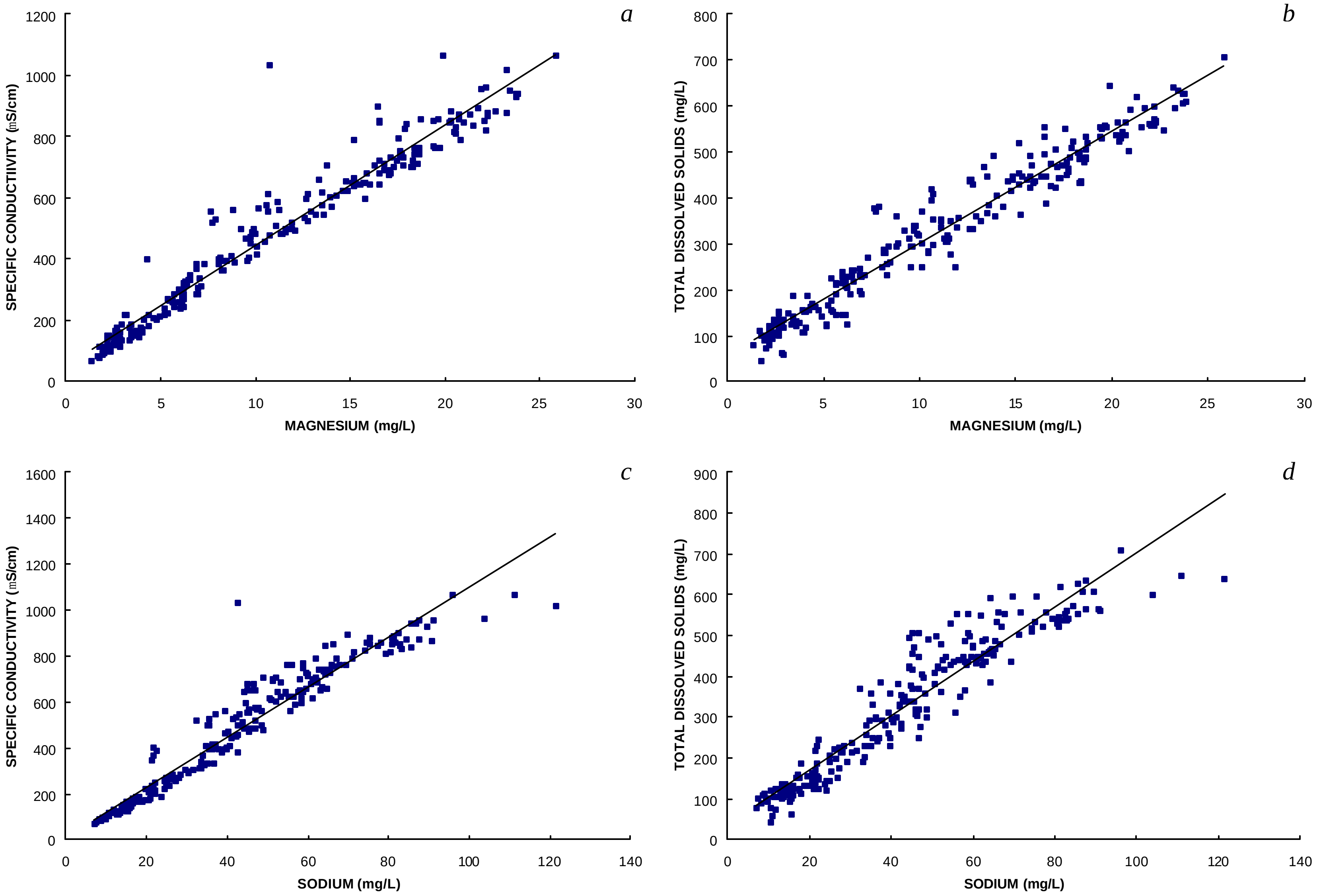


Figure 20. Correlation graphs for (a) Alkalinity Magnesium verses Specific Conductance, (b) Magnesium verses Total Dissolved Solids, (c) Sodium verses Specific Conductance, and (d) Sodium verses Total Dissolved Solids.

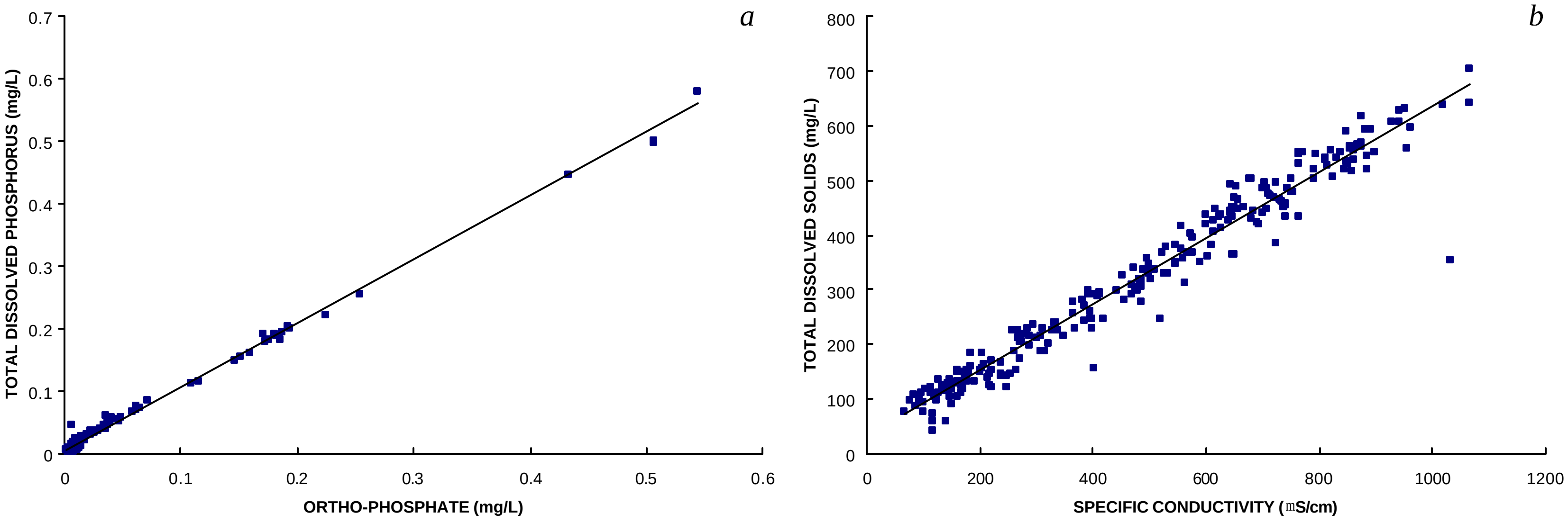


Figure 21. Correlation graphs for (a) Ortho-phosphate verses Total Dissolved Phosphorus and (b) Specific Conductance verses Total Dissolved Solids.

APPENDIX C

United States Department of the Interior
FISH AND WILDLIFE SERVICE
10216 Lee Road, Boynton Beach, Florida 33437-4796
Phone (561) 732-3684 Fax (561) 369-7190

January 17, 2006

To: TOC and interested parties

From: Donatto Surratt, Ph.D.
Matt Harwell, Ph.D.

Subject: **Response to written comments on the November 7, 2005 draft *A.R.M. Loxahatchee National Wildlife Refuge Enhanced Water Quality Program – Parameter Reduction Rationale***

We appreciate the continued interest in our water quality monitoring program and the careful and detailed review that outside interested parties gave our draft report, "Enhanced Water Quality Program Parameter Reduction Rationale. Report No. LOXA05-004" by Surratt, D. This exercise to reduce unnecessary parameters from our monitoring program benefited from the constructive technical comments we received. Below we provide a written response to the comments we received, as well as identify how the final version of the report (available at: http://www.sofia.usgs.gov/lox_monitor_model) was modified.

SFWMD Comments

First bullet: "*The objective for reducing parameters, as stated in the second paragraph on the first page, was to reduce analytical costs and reclaim funds to extend the duration of the LOXA monitoring effort. The rationale for selecting parameters to meet this objective did not appear to be consistently applied across parameters…*"

Response – As stated in the cover memo when the draft report was circulated for review and comment, the primary aim of the exercise was to eliminate redundant parameters and those not providing valuable information. Cost savings was intentionally not a driving factor in the analysis. To clarify this point we added, "The LOXA Work Plan (Brandt et al. 2004) states that, "data will be reviewed… and the list of parameters reduced as appropriate" (p. 12) with the objective to optimize the marsh monitoring network".

Second bullet: "*… It is important to undertake an initial data analysis to assess whether some sites can be eliminated for optimizing the expanded network.*"

Response – As stated in the cover memo when the draft report was circulated for review and comment, we are currently undertaking a site optimization exercise.

Responses to “more detailed technical comments” from SFWMD.

Page 3, Line 2 (missing text and need for editing?)
Response – The revised text now reads: “Another characterization approach was the spatial analysis approach which was performed from canal to the interior of the marsh on several parameters.”

Alkalinity: *“Calcium, alkalinity and hardness correlated well because two of the parameters are reported in units as $CaCO_3$. It seems that the correlation analysis of this parameter was unnecessary. The reason to keep ALKA is not because of its correlation with calcium or hardness. It was kept because it had a numeric criterion pursuant to Section 62-302.530 F.A.C. and is important to the basic ecology of a softwater marsh.”*

Response – The revised text now reads: “Alkalinity correlated well with four parameters – calcium (r = 0.98), hardness (r = 0.98), specific conductance (r = 0.96), and total dissolved solids (r = 0.95). The high correlation between ALKA, calcium, and hardness is most likely an artifact of their dependence on the concentration of $CaCO_3$. Although each of these parameters share this dependency, they are still determined through unique analytical procedures and explain different conditions of the analyzed water parcels and as such yield different values and patterns through time, which is why they are not 100% correlated. Further, these correlations allow the observer to quickly qualify data points as outliers (prior to a rigorous quantitative assessment) with respect to specific conductance, which is exceptionally important for tracking water movement from the canal to the interior marsh.

Alkalinity has a Class III criterion of = 20 mg L^{-1}. In October and November 2004, five sampled sites had values below the criterion. This criterion is inappropriate for rainwater-dominated wetlands where alkalinity is naturally below 20 mg L^{-1} (Weaver, 2005). A water quality goal of the Refuge is to maintain this low alkalinity condition. Because ALKA provides the ability to quickly determine specific conductance outliers; because there is an established numeric criterion pursuant to Section 62-302.530 F.A.C.; and because ALKA is important to the ecology of softwater marshes, ALKA will not be eliminated from the analytical suite. *Alkalinity remains a monitored parameter*.”

Chloride: *“Chloride is strongly correlated with sodium and specific conductance (and strongly correlated with TDS). If it has a strong correlation with specific conductivity and cost needs to be reduced, specific conductivity might be an acceptable surrogate and chloride could be reduced. If justification is needed, why isn’t mass balance modeling mentioned?”*

Response – We decided to keep chloride as it provides a check for specific conductance. We have found a number of occasions when specific conductance has been entered incorrectly in DBHYDRO. Further, these two parameters are the only parameters that act as true biologically and chemically conservative parameters out of the monitored suite of parameters and as such we are maintaining both of them to ensure we will be able to track canal water penetration in the future.

Dissolved Organic Carbon (DOC): *"DOC is very important to the biogeochemical cycling in the marsh. It may not be appropriate to eliminate DOC as a monitoring parameter."*

Response – We have revisited DOC and agree with the conclusion to continue monitoring DOC. The revised text now reads: "Dissolved organic carbon has been linked to microbial respiration and fulvic acid regulated mercury methylation in the southern Everglades (Reddy and Aiken, 2001). One of the experts in preliminary lab experiments revealed microbial respiration to be strongly carbon limited instead of phosphorus or nitrogen limited as for most system. Additional influxes of labile carbon can affect marsh soil processes. Reddy and Aiken (2001) demonstrate strong correlations between Hg bioaccumulation and DOC concentrations. Correlation analysis for DOC did not reveal significant correlation with other parameters. Because neither Hg nor microbial respiration are monitored in the Refuge, because of the potential of DOC concentration changes to cause Hg bioaccumulation rates to change, and because no other parameters can serve as surrogates of DOC, continued monitoring DOC is recommended. *DOC remains a monitored parameter.*"

Dissolved Oxygen (DO): *"Since DO follows a diel cycle influenced by light and temperature, the usefulness of DO grab samples is highly debatable. As described in the Refuge's draft paper current legal mandates were adjusted by a Site Specific Alternative Criteria (SSAC). The value of grab sample monitoring of DO at an expanded list of stations is questionable. A more practical approach would be deployments at selected stations for several days."*

Response – Along the central transect in the marsh we do monitor DO for several consecutive days during the wet season. However, this does not replace the entire monitoring network. Grab sample monitoring for DO will continue.

Hardness: *"Hardness is calculated from calcium and magnesium: Hardness=2.497 (Ca, mg/L) + 4.118 (Mg, mg/L). If magnesium is eliminated from the parameter list, hardness can not be calculated. The argument presented for keeping hardness stems from the fact that it is used to calculate criteria for a variety of trace metals. However, since trace metals are not monitored in the LOXA program, is there another reason for keeping this parameter? From the viewpoint of tracking the softwater aspects of the marsh, alkalinity should provide all necessary information. A reconsideration of the value of hardness appears worthwhile."*

Response – We have revisited hardness based on the above suggestion and concur with the recommendation to remove hardness from the monitored parameters. The revised text for hardness is:

"HARD: Hardness is measured as an equivalent concentration of calcium carbonate ($CaCO_3$) and was expected to correlate well with alkalinity (which is also measured as an equivalent concentration of $CaCO_3$). Hardness correlated well with ALKA (r = 0.98), Ca (r = 0.99), magnesium (r = 0.97), specific conductance (r = 0.97), and TDS (r = 0.97). Although these strong correlations are observed, the Florida Class III water quality criteria for various metals (Cd, Cr, Cu, Pb, Ni, Zn) require hardness in order to calculate the metal criterion (Bechtel, 2000). These metals have never been measured as a part of the LOXA project and were discontinued from the EVPA project in 2000. From the perspective of tracking softwater movement interior of the canals, ALKA and specific conductance appear to provide the necessary information, thus the elimination of the hardness appears to be warranted. *Hardness is on the list of parameters to eliminate.*"

NH4 (ammonium): *"The EPA in the context of south Florida refers to the Everglades Protection Area not the Environmental Protection Agency. It is worthwhile to note also that NH4 is rapidly recycled and instantaneous concentrations are not usually helpful in understanding N availability in a functioning marsh with relatively high levels of nitrogen. However, NH4 is the inorganic portion of the TKN value and it provides (through subtraction) an estimate of the organic nitrogen content. By dropping this parameter, it will not be known if that make-up shifts in the future."*

Response – We corrected the editorial mistake. NH4 is low in the Refuge marsh and TKN is comprised mostly of organic material. As such we do not find it necessary to continue the monitoring of this parameter.

Nitrate, nitrite, and NOx: *"The only reason that should be given for keeping NOx is that it is necessary to calculate total nitrogen. The rationales for eliminating NO3 and NO2 do not flow logically and some of the facts presented could argue to keeping them. It could be noted in these sections that NO2 and NO3 are not particularly useful as individual parameter and their value is maintained by measuring NOx."*

Response – The revised text now reads: "There were no strong correlations associated with nitrate. Nitrate is generally a significant portion of nitrate-nitrite (NO_X) measurement and in combination with the other components of total nitrogen provides information about nutrient lability. Because NO_2 is generally only a small fraction of the NO_X, it was expected that NO_X values can be used to estimate the NO_3 concentration. This rationale holds true for station LZ40 in Lake Okeechobee such that NO_2 was ~11% and NO_3 was ~90% of the NO_X concentration. However, this pattern was not observed in the Refuge marsh. Observation of the data showed NO_2 at ~43% and NO_3 at ~58% of the NO_X concentrations. Thirty-one percent of the NO_3 values for the Refuge were below detection limits, which may have complicated this assessment and potentially confound any trend analysis attempted for the Refuge. Independently, NO_3 is not particularly useful and the value of this nitrogen fraction is maintained in measurements of NO_X. *Nitrate is on the list of parameters to be eliminated.*"

OPO4 (Orthophosphate) and TDP: *"OPO4 is the bio-available fraction of P. It is the P fraction that can be compared to Si or inorganic N to look at nutrient availability and potential limitation. Since it may have a strong correlation to TDP and cost less to analyze, there is no compelling reason to eliminate it and keep TDP. TDP could be eliminated because it costs more and it does not provide a quick estimate of the biologically available P. Since OPO4 is extremely strongly correlated to TDP (r=0.99), then particulate P could be estimated by subtracting OPO4 from TP. Reconsideration of these parameters would seem appropriate."*

Response – The argument presented here is very strong, but the only issue is the number of times OPO4 is below the detection limit. TDP and OPO4 are already not analyzed when the water depth is below 20 cm. But even when OPO4 is below detection limit, TDP values generally are measurable. If we eliminate TDP to keep OPO4, we will have even larger data gaps. As such, we decided to estimate OPO4 from TDP and eliminate OPO4.

<u>pH</u>: *"Point measurements 'for' pH can hint at interesting processes but cannot resolve the actual issue. This parameter is better suited for diel deployments combined with research to understand the processes that drive pH below 6."*

Response – Presently, we monitor pH for several consecutive days during the wet season along the central transect through marsh. We do not have a research portion of this program dedicated to understanding what drives pH below 6. Our water is poorly buffered and even monthly snap shots help us understand the marsh and when conditions may be changing, particularly if pH deviates from the normal pH values we have observed.

<u>Silica (SiO2)</u>: *"The reference below is incorrect as written:*
… There is no mention of hard water altering ecosystem structure, only biotic communities. Has the author noticed the changes in Si:P ratios in the Refuge or are these changes associated with diatoms anticipated in the near future? The argument is not easily followed as written and not very compelling."

Response – The citation has been referenced appropriately in the revised text. "There were no strong correlations associated with silica. Silica shows a seasonal pattern for the interior sites of the Refuge. Silica is higher in the wet-warm season (late April – early November) and lower during the dry-cool season (November to early April). Independent research has demonstrated that silica concentrations decrease during the cooler season when algae populations (dominated by diatoms) are dying off and increase during the warmer season when these populations grow in again. Changes in these patterns can serve as a good indication of eutrophication and even biota shifts (Biggs, 1990). These assertions are generally for flowing waters (i.e., rivers) and historically appear to be of less importance for the Refuge wetland ecosystem which has a low diatom abundance associated with the periphyton population dominating as the primary producer of the Refuge (Kadlec and Knight, 1996). However, with STA-1E becoming operational in September 2005, there will be larger volumes of higher mineral content water discharge into the L-40 Canal. Canal water penetration into the marsh has been documented (Harwell et al., 2005). The introduction of higher mineral content water into a soft-water ecosystem is expected to impact the biotic community. The combination of temperature, nitrogen to phosphorus, and silica to phosphorus ratios has been shown to relate to algae species distributions (Adamus et al., 2001). This suite of indicators can theoretically be applied as an indicator of changes in periphyton community dynamics as the high mineral content water impact the Refuge. Presently, WCA-2 has a higher diatom abundance associated with the periphyton communities (relative to the Refuge) and the Refuge perimeter canals are major sources of water for WCA-2. Because of the potential of silica concentration change to cause biotic shifts, and because the canals of the Refuge provide water to other areas of the Everglades, silica is not on the elimination list. *Silica remains a monitored parameter.*"

Total Dissolve Solids (TDS): *"With the ability to measure specific conductivity, this parameter is unnecessary. Chloride (rather than TDS) could be used to verify that specific conductivity is measured correctly…"*

Response – As we have historically used TDS to identify outliers and erroneous data, we have decided to keep TDS.

Temperature: *"The reasoning for keeping TEMP is intriguing. All multi-parameter sonde units automatically correct specific conductance whether temperature is recorded or not. Just because it is used to adjust conductance is not a compelling reason to keep temperature. There are costs associated with data entry, data review, equipment calibration, etc., even if there are not analytical costs for temperature. If data are entered into the database, it should have value; point measurements for temperature have limited value."*

Response – There were no strong correlations associated with temperature. Temperature is an integral parameter that changes seasonally. It is used to adjust conductance, dissolved oxygen measurements, determine DO saturation, and the DO-SSAC. As noted above, cost savings was not the primary factor in this exercise, and the minor cost savings alone does not provide enough justification to eliminate this parameter. *Temperature remains a monitored parameter.*

Corps Comments

1. Most of the parameters that were eliminated, the logic is compelling. A few of them you may wish to reconsider. These are NH4 and DOC. You may wish to include these for the following reasons:
2. Relative to NH3- NH4, : certainly You can identify TN with TKN and
NOx but you may not fully understand any future transformations or changes to the Refuge due to ECP modifications and CERP. Consider the following:
a. NH3- NH4: Ammonium is a product of soil organic matter and NO-3 consumption per the simplified formula :
(CH2O) 106 (NH3) 16 (H3PO4) + 84.8NO3- ?106 CO2 + 16 NH3 + H3PO4+148.4 H2O
b. Increases in this may be increases in these patterns. (Davidson
2000)
c. This may contribute to substantial TN losses for poorly buffered waters in high photosynthetic areas (due to associated changes in pH),(DeBusk).
d. This is of particular interest to the down stream of the Refuge and will contribute to understanding the TN changes taking place in the refuge.
3. Relative to DOC:
a. Hg interaction with DOC may be important in regulating ecosystem mercury methylation patterns (Reddy and Aiken 2001).
b. Certainly, sulfate serves as the electron donor for bacteria
mediated methylation of mercury
c. but fulvic acid competes with the inorganic sulfide ion for mercury binding.
d. Fulvate is a substantial fraction of the DOC.
e. In my estimation, you really need both parameters to effectively track this.
f. I am attaching some the pictorial plates from REMAP as a file.

g. Note TOC (I couldn't find anything for DOC) corresponds to some of the methylation patterns.

Response to the NH4 comment– Though we recognize the potential value of the information lost when we eliminate NH4, NH4 is relatively low in the Refuge compared to most marsh systems. NH4 is also a very small component of TKN, which is mostly organic and is a parameter we continue to monitor. The rationale for eliminating NH4 is that total nitrogen encompasses the NH4 fraction and because nitrogen is not considered a limiting nutrient in the Refuge. The small NH4 fraction of total nitrogen provides limited ecologically meaningful information. As a result, NH4 is being eliminated from this monitoring network.

Response to the DOC comment – Please see comments for DOC above.

ENP Comments

"*Parameter reduction can also be achieved through application of "Principle Component or Factor Analysis" which are more robust statistical tools for such applications. Other rationale still can be applied to bring in or throw out parameters after that. Some links below can be referred to check whether these procedures would apply or not for your report.*"

Response – We agree that PCA techniques can be valuable for general data exploration and analysis. For the purposes of our exercise, we chose to stick with the presented degree of analysis which allowed us to look at variables from both individual and multivariate approaches. In our more robust analysis of the data sets (independent of the presented parameter reduction report) we do employ PCA and other similar techniques to include canonical correspondence analysis and multidimensional scaling approaches to assessing the datasets.

APPENDIX D

Comments from reviewers

SOUTH FLORIDA WATER MANAGEMENT DISTRICT
3301 Gun Club Road, West Palm Beach, Florida 33406 • (561) 686-8800 • FL WATS 1-800-432-2045 • TDD (561) 697-2574
Mailing Address: P.O. Box 24680, West Palm Beach, FL 33416-4680 • www.sfwmd.gov

November 21, 2005

Matthew C. Harwell, Ph.D.
Senior Ecologist, Everglades Program Team
A.R.M. Loxahatchee National Wildlife Refuge
10216 Lee Rd.
Boynton Beach, FL 33437

Dear ~~Dr. Harwell:~~ Matt

Thank you for giving the District the opportunity to review the draft paper prepared by the A.R.M. Loxahatchee National Wildlife Refuge (Refuge) on proposed parameter reductions to the LOXA monitoring program (Surratt, Donatto. November 2005. Enhanced Water Quality Program Parameter Reduction Rationale. Report No. LOXA05-004. A.R.M. Loxahatchee National Wildlife Refuge.). The report is a worthwhile contribution to the efficiency of expanded monitoring in the Refuge.

Overall, the District does not have any significant objections to the proposed monitoring reductions; however, we would like to offer the following general observations and comments:

- The objective for reducing parameters, as stated in the second paragraph on the first page, was to reduce analytical costs and reclaim funds to extend the duration of the LOXA monitoring effort. The rationale for selecting parameters to meet this objective did not appear to be consistently applied across parameters. Elimination of monitoring parameters should be based, in part, on an understanding of the chemistry of the system and the interaction of related parameters. In some cases where a strong correlation exists between multiple parameters, it might be preferable to eliminate the parameter with the higher analytical cost (e.g., eliminate total dissolved phosphorus [TDP] rather than orthophosphate). Regression analyses are potentially useful to determine which parameters could be eliminated to minimize the impact on the available data.

- The original monitoring plan anticipated a potential reduction in the number and spatial distribution of sites as well as the number of parameters analyzed in the laboratory. The Refuge's draft paper was focused only on parameters and did not address a reduction in monitoring sites. It is important to undertake an initial data analysis to assess whether some sites can be eliminated for optimizing the expanded network.

- As you are aware, the District laboratory analytical services for the LOXA water quality monitoring program have been provided through a 2-year cooperative agreement (No. IA050370) with the Refuge: however, this is due to expire on June 7, 2006. After this date, the District's limited laboratory resources will be committed to other critical programs and will not be available for this project. Therefore, if the Refuge intends to

> continue this monitoring beyond June 2006, it will need to pursue alternative laboratory arrangements. Recognizing that a general justification for parameter reductions is cost, changes laboratory service rates for samples after June 2006 must be considered in the analysis and weaved into the parameter analysis.

The following are some more detailed technical comments from District staff (specifically Nenad Iricanin, Cheol Mo, Garth Redfield, David Struve, Jana Newman, Peter Rawlik and Kristin Larson):

Page 3, Line 2 (missing text and need for editing?): "Another characterization approach was the spatial analysis approach which was performed from canal to the interior of the marsh a few parameters."

Alkalinity: Calcium, alkalinity and hardness correlated well because two of the parameters are reported in units as $CaCO_3$. It seems that the correlation analysis of this parameter was unnecessary. The reason to keep ALKA is not because of its correlation with calcium or hardness. It was kept because it had a numeric criterion pursuant to Section 62-302.530 F.A.C. and is important to the basic ecology of a softwater marsh.

Alkaline Phosphatase Activity (APA): It is interesting that there was no correlation between APA and any of the species of phosphorus in the marsh. We agree with the rationalization for discontinuing this parameter and encourage data analysis in other areas to determine if this parameter is either not useful or is redundant.

Chloride: Chloride is strongly correlated with sodium and specific conductance (and strongly correlated with TDS). If it has a strong correlation with specific conductivity and cost needs to be reduced, specific conductivity might be an acceptable surrogate and chloride could be reduced. If justification is needed, why isn't mass balance modeling mentioned?

Dissolved Organic Carbon (DOC): DOC is very important to the biogeochemical cycling in the marsh. It may not be appropriate to eliminate DOC as a monitoring parameter.

Dissolved Oxygen (DO): Since DO follows a diel cycle influenced by light and temperature, the usefulness of DO grab samples is highly debatable. As described in the Refuge's draft paper, current legal mandates were adjusted by a Site Specific Alternative Criteria (SSAC). The value of grab sample monitoring of DO at an expanded list of stations is questionable. A more practical approach would be deployments at selected stations for several days.

Hardness: Hardness is calculated from calcium and magnesium: Hardness= 2.497(Ca, mg/L) + 4.118(Mg, mg/L). If magnesium is eliminated from the parameter list, hardness can not be calculated. The argument presented for keeping hardness stems from the fact that it is used to calculate criteria for a variety of trace metals. However, since trace metals are not monitored in the LOXA program, is there another reason for keeping this parameter? From the viewpoint of tracking the softwater aspects of the marsh, alkalinity should provide all necessary information. A reconsideration of the value of hardness appears worthwhile.

Magnesium: Since magnesium is used to calculate hardness, the elimination of magnesium would also eliminate the ability to estimate hardness. However, as mentioned above, this should not be a problem unless calculated criteria for trace metals are required.

NH_4 (ammonium): The EPA in the context of south Florida refers to the Everglades Protection Area not the Environmental Protection Agency. It is worthwhile to note also that NH_4 is rapidly recycled and instantaneous concentrations are not usually helpful in understanding N availability in a functioning marsh with relatively high levels of nitrogen. However, NH_4 is the inorganic portion of the TKN value and it provides (through subtraction) an estimate of the organic nitrogen content. By dropping this parameter, it will not be known if that make-up shifts in the future.

Nitrate, nitrite, and NO_x: The only reason that should be given for keeping NO_x is that it is necessary to calculate total nitrogen. The rationales for eliminating NO_3 and NO_2 do not flow logically and some of the facts presented could argue to keeping them. It could be noted in these sections that NO_2 and NO_3 are not particularly useful as individual parameters and their value is maintained by measuring NO_x.

OPO_4 (Orthophosphate) and TDP: OPO_4 is the bio-available fraction of P. It is the P fraction that can be compared to Si or inorganic N to look at nutrient availability and potential limitation. Since it may have a strong correlation to TDP and costs less to analyze, there is no compelling reason to eliminate it and keep TDP. TDP could be eliminated because it costs more and it does not provide a quick estimation of the biologically available P. Since OPO_4 is extremely strongly correlated to TDP ($r=0.99$), then particulate P could be estimated by subtracting OPO_4 from TP. Reconsideration of these parameters would seem appropriate.

pH: Point measurements fro pH can hint at interesting processes but cannot resolve the actual issue. This parameter is better suited for diel deployments combined with research to understand the processes that drive pH below 6.

Silica (SiO_2): The reference below is incorrect as written:

"Silica to phosphorus ratios can be applied as an indicator of change in planktonic community dynamics as the hard-water alters the ecosystem structure of the Refuge (Adamus et al., 2001)"

However, the original reference from Adamus, Danielson and Gonyaw (2001) states:

"Nonetheless, some studies (Harper 1992) have reported that diatoms seem to dominate at lower temperatures and when phosphorus (P) but not silica (Si) is limiting, whereas green algae may dominate at higher temperatures with moderate or low N:P and Si:P ratios;"

There is no mention of hard water altering ecosystem structure, only biotic communities. Has the author noticed the changes in Si:P ratios in the Refuge or are these changes associated with diatoms anticipated in the near future? The argument is not easily followed as written and not very compelling.

Specific Conductance (SPCOND): SPCOND is a useful parameter as a grab sample/point measurement. The District concurs with the recommendation to retain SPCOND as a monitored parameter.

Total Dissolved Solids (TDS): With the ability to measure specific conductivity, this parameter is unnecessary. Chloride (rather than TDS) could be used to verify that the specific conductivity is measured correctly. TDS is more time consuming and not a quick measure. If possible, a more appropriate reference (other than a personal communication) should be used to justify keeping TDS as a monitoring parameter. What studies can you cite that used these ratios to indicate sources of water (i.e., canal, marsh, rain, and groundwater) correctly? Why not reference them? Also, using the argument that a parameter is necessary for verification of another can be counter-productive. If this argument is expanded over the entire parameter list, then all of the major ions and associated analyses should be kept to verify parameter results (i.e., check ionic balance, etc.)

Temperature: The reasoning for keeping TEMP is intriguing. All multi-parameter sonde units automatically correct specific conductance whether temperature is recorded or not. Just because it is used to adjust conductance is not a compelling reason to keep temperature. There are costs associated with data entry, data review, equipment calibration, etc., even if there are not analytical costs for temperature. If data are entered into the database, it should have value; point measurements for temperature have limited value.

We agree with the authors that this parameter reduction process is an important one and the LOXA data are useful for many purposes. The District appreciates the opportunity to contribute to this optimization process.

Sincerely,

Linda Lindstrom

Linda J. Lindstrom, P.G.
Department Director
Environmental Resource Assessment

Matt,

Thanks for the opportunity to review this.

1. Most of the parameters that were eliminated, the logic is compelling,.. A few of them you may wish to reconsider. These are NH_4 and DOC . you may wish to include these for the following reasons:
2. Relative to NH_3- NH_4, : certainly You can identify TN with TKN and
NOx but you may not fully understand any future transformations or changes to the Refuge due to ECP modifications and CERP. Consider the following:
a. NH_3- NH_4: Ammonium is a product of soil organic matter and NO^-_3 consumption. per the simplified formula :
$(CH_2O)\ 106\ (NH_3)\ 16\ (H_3PO_4) + 84.8NO_3^-\ ?106\ CO_2 + 16\ NH_3 + H_3PO_4+148.4\ H_2O$
b. Increases in this may be increases in these patterns. (Davidsson 2000)
c. This may contribute to substantial TN losses for poorly buffered waters in high photosynthetic areas (due to associated changes in pH), (DeBusk) .
d. This is of particular interest to the down stream of the Refuge.and
will contribute to understanding the TN changes taking place in the refuge.

3. Relative to DOC :
a. Hg interaction with DOC may be important in regulating ecosystem Mercury methylation patterns (Reddy and Aiken 2001)
b. Certainly , Sulfate serves as the electron donor for bacteria mediated methylation of mercury
c. But fulvic acid competes with the inorganic sulfide ion for mercury binding.
d. Fulvate is a substantial fraction of the DOC.
e. In my estimation, you really need both parameters to effectively tract this.
f. I am attaching some the pictorial plates from REMAP as a file.
g. Note TOC (I couldn't find anything for DOC) corresponds to some of
the methylation patterns.

References used :

1. Davidsson T.E. & Stahl M. " The influence of Organic Carbon and Nitrogen Transformations in Five Wetland Soils. In Soil Science Soc. Of America 64: 1129-1136 (2000)
2. DeBusk, W.F. "Nitrogen Cycling in Wetlands" IFAS circular http://edis.ifas.ufl.edu/SS303
3. REMAP plates attached.

-----Original Message-----
From: Matthew_Harwell@fws.gov [mailto:Matthew_Harwell@fws.gov]
Sent: Tuesday, November 08, 2005 11:32 AM
To: Brown, Edwin SAJ

Matthew Harwell/R4/FWS/DOI
11/16/2005 08:57 AM

To Donatto Surratt/R4/FWS/DOI@FWS
cc
bcc
Subject Fw: TOC FYI: Refuge WQ parameter reduction report draft - comments due 11/22

more comments
----- Forwarded by Matthew Harwell/R4/FWS/DOI on 11/16/2005 08:57 AM -----

Dilip_Shinde@partner.nps.gov
11/15/2005 01:17 PM

To Matthew_Harwell@fws.gov
cc Mike_Zimmerman@nps.gov, Joffre_Castro@nps.gov, Nick_Aumen@nps.gov
Subject Re: Fw: TOC FYI: Refuge WQ parameter reduction report draft - comments due 11/22

Hi Matthew,

Parameter reduction can also be achieved through application of "Priciple Component or Factor Analysis" which are more robust statistical tools for such applications . Other rationale still can be applied to bring in or throw out parameters after that. Some links below can be referred to check whether these procedures would apply or not for your report.

http://149.170.199.144/multivar/pca.htm
http://www.tc.umn.edu/~bakk0029/Klawiter_2000/princomp.html
http://www.statsoft.com/textbook/stfacan.html

Dilip Shinde, PhD
Water Quality Manager (Partner, UM)
Everglades & Dry Tortugas National Parks
South Florida Ecosystem Office
950 N Krome Ave 3rd Floor #31
Homestead, FL-33030-4443

305-224-4201 (phone)
305-224-4147 (fax)

Matthew_Harwell@fws.gov
11/08/2005 11:30 AM EST

To: mike_zimmerman@nps.gov, Dilip_Shinde@partner.nps.gov
cc:
Subject: Fw: TOC FYI: Refuge WQ parameter reduction report draft - comments due 11/22