Final Report:

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Report of Activities during the period 1/1/96 - 12/31/97

Executive Summary

This report summarizes the research we conducted over the past two years under the support of a Special Projects award from the Water Quality Protection Program for the Florida Keys National Marine Sanctuary. During the funding period we 1) characterized the chemistry of the groundwater system surrounding a low-volume Class V wastewater injection facility at the Keys Marine Laboratory on Long Key Florida; and 2) performed non-reactive tracer and nutrient injection experiments to determine the reactivity of wastewater-derived nutrients in the subsurface.

We are unable to detect the effects of wastewater injection at depth within the groundwater system immediately surrounding the injection well (within 5m). Apparently, the groundwater flow and dispersion is sufficient to dilute the small amount (about 3000 L/day) of wastewater produced by this facility. Current research at Key Colony Beach will clarify whether this conclusion is applicable to much larger facilities (in this case, about 10^6 L/day). The results suggest that the shallow groundwater system (at 4m depth) *is* contaminated with wastewater nutrients, but it is not clear whether these nutrients were derived from the wastewater being injected at 60' subsurface depth. Rather, it is possible that they represent residual contamination from previous, inefficient wastewater disposal methods.

The tracer tests indicate that phosphate is preferentially removed from the tracer patch, likely the result of adsorption (followed by precipi-

tation) on the surfaces of the interstices within the carbonate bedrock. On the other hand, there is only weak evidence for nitrate conversion or uptake at depth. The flowpaths indicated by the non-reactive tracers are discussed in the Florida State final report. Manuscripts are in preparation that describe the results of our research, and will be submitted to peer-reviewed journals this summer.

INTRODUCTION

There were four extensive sampling campaigns that took place at the Keys Marine Laboratory (Long Key, Florida; Figure 1) in September 1995, February 1996, May 1996, October, 1996, and these were followed by a final check in January, 1998 (performed under separate funding). The objectives were slightly different for each one. The September campaign was designed to study the effect of the tidal cycle on the wastewater plume, and to characterize the plume over a short time period. We collected groundwater samples and made well water height measurements every 3 hours for 36 hours. At that time, only Wells 1-4 had been completed, and Well 5 had two shallow wells (2 and 5 m) available for sampling. The February campaign was organized and conducted under EPA guidelines. There was only one collection period, and Wells 1-7 were all available for sampling. The May campaign was also conducted under EPA guidelines and followed February's format in sample collection, however, this time, all eight wells were available for sampling. The October, 1996 sampling was identical in design to that in May, whereas the sampling in January, 1998 was restricted to the shallow (15') wells.

In addition, two tracer tests were conducted with our colleagues from Florida State. The first was in October, 1996, and involved the injection of a phosphate-rich solution with SF_6 as a non-reactive tracer. The second was in February of 1997. It was similar in design to the first, but in this case nitrate was the conservative tracer.

Some of the material presented here has appeared in past quarterly reports. These reports provide more detail on those experiments, analyses, and quality assurance. An overall quality assurance assessment is provided at the end of this report.

RESULTS

Hydrology

Well water levels were measured periodically on various sampling campaign. Their heights relative to MSL were converted to fresh-water head values according to the equations of Fetter (1994).

Hydraulic Head over Time. Example head values for each sampling depth of each well over time are presented for the May (Figures 2 and 3) sampling campaign. Other results were presented in past quarterly reports. In all cases, the head values of each sampling depth are the same, indicating that there is no vertical hydraulic gradient. In addition, the well head values follow the tidal cycles without any lag. The Florida bay tidal amplitude at KML for the May campaign is ~75% of the well amplitude (and 50% in other campaigns). This suggests that the aquifer is responding to both the Florida Bay and larger-amplitude, Atlantic-side tides, a finding supported by our observations at Fiesta Key (Machusak and Kump, 1997).

Head Contour Plots. All of the calculated fresh-water head values for one particular sampling depth have been compared and contoured to illustrate the direction and magnitude of horizontal hydraulic gradient. Head values from the shallow and deep wells have been contoured. Contours of the intermediate wells closely follow the deep wells, and therefore are excluded to avoid redundancy. Data from high tide points are used for the contour map of each campaign, although the patterns depicted here are mostly consistent throughout the tidal cycle with very minor changes.

Groundwater velocity (v) can be calculated from changes in head (δ_h) over distance (δ_l) according to:

$$v = (K/\phi) \times (\delta_h/\delta_l) \tag{4.6}$$

where K is the hydraulic conductivity, ϕ is the porosity, and δ_h/δ_l is the hydraulic gradient. By using the hydraulic conductivity of 1400 m/d for KML from Vacher et al. (1990), and an average porosity of 0.50 as a conservative value from our porosity results, the groundwater velocity can be determined for each contour map. The value is only an approximate one, however, since the values for hydraulic conductivity and porosity are estimates for this site.

Contour plots of the May measurements show that the general flow is southerly, from Well 6 to Well 7 with a plateau around the injection well. In the shallow wells (Figure 4), groundwater velocity is ~11 m/d across the site and ~ 21 m/d to the north of the injection well. In the deep

wells (Figure 5), cross-site flow ~12 m/d. These results are consistent with the tidal pumping hypothesis of Halley et al. (1994).

Groundwater Chemistry

To observe the chemical composition of the groundwaters over time, the results of the of the last five campaigns are presented together, for each individual species, with relative concentrations/results colored in at each depth. These results are displayed on a general site base map so that the data may be more easily related to their relative geographical location.

Salinity. The salinity results of the first four campaigns (Figure 6) identify the establishment of a shallow, low-salinity lens situated atop saline groundwaters. The depth of the low-salinity lens reaches to between the 5 and 9 m sampling depths, with high salinities (comparable to those found at 14 and 18 m) at the 9 m depth. The wastewater being injected is essentially fresh (0.5 psu) for each campaign, while the Bay waters' salinity has varied from 35 psu in September, to 33 psu in February, to 37 psu in May. The deep wells more-or-less maintain their salinity values from one campaign to the next.

Phosphate. Phosphate analyses have been performed since the first drilling expedition, when initial results showed a cross-island trend at shallow depth. This trend is still seen, with the highest concentrations for each campaign generally located at Wells 2, 5, and 6 (Figure 7). The highest concentration for each campaign is located at Well 2. It is interesting to note that while the higher concentrations are located at the shallow depth in Wells 2, 5 and 6, the shallow depths of the other wells have below-MDL phosphate concentrations. The rise in phosphate concentration at wells 1, 3, and 6 over the sampling interval is accompanied by a drop in pH. As we will argue below, these trends are consistent with the hypothesis that phosphate is adsorbed and/or precipitated during its interaction with the calcite/aragonite bedrock.

pH. The pH results over all three campaigns show the clearest and most consistent pattern (Figure 8). The pH of many of the shallow wells near the wastewater injection point began with high pH. Over the next year, and particularly by January, 1998, pH fell in these wells to values more typical of natural waters (pH 6.5-8.5). As of January, 1998, pH remains "elevated" in shallow wells 1 and 4.

Nitrate. The pattern of the nitrate results for each campaign is generally the same in that the highest concentrations are located at the same depth in the same wells (Figure 9). High concentrations are found in the shal-

low wells at site 2 and, especially, site 3, ~5m to the north and east of the injection. Other than the high concentrations observed at these two wells, the other wells and sampling depths have below-MDL concentrations. We also note that the high concentrations have persisted over the sampling interval, although the values have fluctuated somewhat.

A very surprising and dramatic change in nitrate concentration occurs in the wastewater. Its concentration plummets from 1921 mM in September to 8.7 mM in February, and then to 7.1 mM in May.

Ammonia. The highest ammonia concentration for each campaign is found at shallow Well 1, while the intermediate depths of Well 1 maintain some of the next-highest values (Figure 10). The other three wells surrounding the injection well (Wells 2, 3 and 4) garner most of the remaining higher ammonia concentrations at their shallow and intermediate depths. Deep groundwaters have ammonia concentrations in the 30-60 μM range, characteristic of groundwaters presumably unimpacted by wastewater contamination throughout the Florida Keys (Shinn et al., 1994).

The ammonia concentration of wastewater undergoes as dramatic an increase as the decrease exhibited by nitrate over the sampling year. The ammonia concentration of wastewater starts at 11 μM in September, rises to 280 μM in February, and increases again to 1034 μM in May.

DISCUSSION

The chemical results identify elevated concentrations of phosphate, nitrate, and ammonia, and high pH values, in the low-salinity lens, roughly occupying the top 7 m of the groundwater. The source of these waters remains somewhat of an enigma, given that in none of our sampling did we detect low-salinity, undiluted wastewater in our deep wells close to the point of injection.

Sources of Low-Salinity Lens

Possible sources of the low-salinity groundwater located in the upper 7 m of our site are: 1) rainwater which has percolated through the ground, 2) wastewater which has undergone some degree of mixing with the underlying, saline groundwaters, and 3) a combination of the two sources. The second source, injected wastewater, would need high-porosity zones to facilitate flow to the low-salinity lens. The macroporosity results indicated that there are at least three high-porosity "layers" which appear to be site-wide (Monaghan, 1996; previous quarterly reports). One lies near the depth of wastewater injection at 18 m, the other at a mid-range of about 10 m, and the third is located at about 6 m, which

may be close to the bottom of the lens. Since the wastewater is essentially fresh (0.5 psu), its buoyancy could drive a direct flowpath towards the surface with a minimal degree of mixing. Head measurements plotted over time with the tidal cycle show that there is no tidal lag in any of the wells at any depth, indicating a strong connection between the shallow, low-salinity lens and the underlying saline groundwaters. However, contour plots do indicate some distinction between the two water bodies in terms of the direction of their flow.

However, we have no data to support the buoyant flow hypothesis, save for the observation of unusual waters at shallow depths in the wells near the point of injection. The persistence of these conditions suggests either that the effects of an earlier surface contamination are longer-lived than we would have expected, or that wastewaters do have a conduit to the surface, within 5m of the point of injection, that allow wastewaters to rise to the surface with little to no dilution. However, the distinction among the high nitrate waters at well 3, the high phosphate waters at well 4, and the high ammonia concentrations at well 1 are difficult to reconcile with a single source of contamination. The low phosphate concentrations at wells 1, 3 and 4 can be tied to the high pH of these wells. In support of this relationship, note that as pH fell at wells 1 and 3, phosphate concentrations increased. However, we have no explanation for the nitrate and ammonia data. Thus, at the moment, we favor the interpretation that these waters represent episodes of surface contamination that independently supplied large quantities of phosphate to well 2, nitrate to well 3, and ammonia to well 1. The persistence of these features is not inconsistent with the generally much smaller porosities (and presumably lower hydraulic conductivities) of the upper 5m or so of the Key Largo limestone.

Phosphate Removal

The absence of phosphate in the high pH waters of shallow Wells 1, 3, and 4 suggests phosphate removal by precipitation as a mineral. We employed a geochemical modeling program, SOLMINEQ.88 (Kharaka et al., 1988), to determine which minerals would be supersaturated under such conditions. The May results for seawater, wastewater, shallow Wells 1, 2, and 3, deep Well 3, and 14 m depth Well 7 were the input variables. The inclusion of our seawater sample was intended as a check on the completeness and accuracy of the program. The results stated that our seawater is supersaturated with respect to calcite and aragonite by factors of approximately 5 and 4 respectively. This is consistent with published values for seawater calcium carbonate saturation indices. The seawater is also supersaturated with respect to dolomite, chlorapatite and hydroxyapatite, and undersaturated with respect to brucite. The program determined

that the wastewater is undersaturated with respect to calcite, aragonite, brucite, and sepiolite, and at saturation with respect to dolomite.

SOLMINEQ.88 calculated that shallow Wells 1 and 3 are supersaturated with respect to calcite ($CaCO_3$), aragonite ($CaCO_3$), brucite ($Mg(OH)_2$), dolomite ($CaMg(CO3)_2$), and sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$) (Isphording, 1973). Shallow Well 2 is supersaturated with respect to calcite, aragonite, dolomite, chlorapatite and hydroxyapatite, but undersaturated with respect to brucite and sepiolite. These undersaturations are most likely due to the lower hydroxyl ion concentration in the well. Deep Well 3 and 14 m depth Well 7 were included in the modeling analysis in order to compare the geochemically anomalous shallow wells to some of the deeper groundwater samples. Both wells are supersaturated with respect to calcite, dolomite, chlorapatite, and hydroxyapatite, and undersaturated with respect to aragonite, brucite and sepiolite. These results are similar to those of our seawater sample, except that sepiolite is included and aragonite is undersaturated. The saturation index for sepiolite was not calculated for seawater because it has no detectable silica. And although the deeper well samples are undersaturated with respect to aragonite, this may reflect mineralogical stabilization from aragonite to calcite. Coniglio and Harrsion (1983) examined the mineralogy of cores taken from Big Pine Key and found that shallower sediments contain a significant amount of aragonite, while at depth calcite is the predominant mineral. The authors suggest meteoric water diagenesis of limestone as the driving force.

The apatite minerals included in the saturation index calculations by SOLMINEQ.88, chlorapatite and hydroxyapatite, are phosphate-bearing minerals related to the carbonate fluorapatite (CFAP) discussed previously. Since no fluoride results are available, saturation states with respect to CFAP were not determined. However, by using published fluoride concentrations for seawater, and the stoichiometry ($Ca_5(PO4)_{2.5}F(OH)_{0.5}(CO_3)_{0.5}$) and solubility constant ($K_{sp} = 3.2 \times 10^{-61}$) for CFAP determined by Nriagu (Gaudette and Lyons, 1980), the saturation index may be calculated for shallow Wells 1 and 3. The values used for the activity coefficients and concentrations are those calculated by SOLMINEQ.88.

Shallow Well 3 is highly supersaturated with respect to CFAP, having an SI of 15.3. For shallow Well 1, the seawater fluoride value and the phosphate MDL are used for the unknown quantities. The calculated SI is 25.4, again indicating supersaturation. The stoichiometry and solubility constant for CFAP are not well known, with reported K_{sp} values ranging from 10^{-106} (Gaudette and Lyons, 1980) to $10^{-99.7}$ (Jahnke, 1984). Therefore, these calculations are only intended to illustrate that CFAP could be

forming even though our analytical techniques are not able to quantify very small concentrations of some of its constituents.

Sources of High pHs

In past quarterly reports we have provided a variety of explanations for the high pH of several wells. The observation that those pH values seem to be falling over the last two years suggests that the high pH might be a consequence of well installation. In particular, we are concerned that the Portland cement used to seal off sampling intervals may not have set properly in the shallow, low salinity groundwater system and is now contributing hard alkalinity to the well waters. Similarly high pH values have been observed now at our new site at Key Colony Beach. There we are performing an experiment to see if acid addition neutralizes the source of alkalinity (presumably unset cement).

Adequacy of Disposal Method

Aside from the enigmatic observations of high nutrient concentrations in the shallow wells, all other well analyses reveal a groundwater system with no noticeable impact of wastewater injection. We have sampled the near-field wells on an hourly basis following wastewater injection, and over a two year interval of time, and have yet to detect the passage of anomalous nutrient concentrations through the subsurface. As we show below, dilutional effects are large: typical maximum tracer concentrations are 1/1000th of the initial concentrations 5m from the point of injection. The small quantities of wastewater injected at this site, approximately 3000 L per day, are insufficient to impact groundwater concentrations. High permeability of the limestone aquifer, together with rapid groundwater flow in response to tidal influences, provide significant dilution of wastewater. Current research at Key Colony Beach, where wastewater injection rates are approximately three orders of magnitude larger, will determine whether sufficient dilution occurs under substantially greater loadings.

Injection Experiments

Introduction

Two injection experiments have been conducted to compare the behaviors of phosphate and nitrate to non-reactive (conservative) tracers upon injection into the subsurface. In October of 1996 an injection experiment was performed to study the behavior of PO_4, in collaboration with the FSU Group (J. Chanton and W. Burnett). In February, the group performed a similar experiment using SF_6 and ^{131}I as non-reactive tracers, and nitrate as the (potentially) reactive tracer.

Objectives

The first injection experiment were designed to study the interaction of phosphate with the bedrock. In order to distinguish dilution and dispersion effects from selective adsorption or precipitation, we used a non-reactive tracer, SF_6. The ratio of PO_4/SF_6 should be constant unless reactions occur that remove or add either of the species. Therefore we were able to test the hypothesis that phosphate is being retarded in its transport through interaction (adsorption/precipitation) with the substrate. In the second experiment, we were interested not only in whether nitrate might also adsorb on the limestone surface, but whether microbial or inorganic reduction reactions might transform nitrate to other forms of nitrogen.

Methods

We dissolved 14-20 kg of nitrate and phosphate salts, respectively, in 200L of tap water. We then bubbled SF_6 for 30 minutes through the solution. Samples were taken from the solution before injection. These solutions were poured down the injection well and then "chased" by pumping the sewage holding tank dry (estimated volume of 1000 L of wastewater).

For the first day samples were taken frequently (every couple hours). Samples were then taken a few times a day for up to 2 weeks, and then infrequently for the following months. (Detailed discussion of the methods and results of the non-reactive tracer component is described in the FSU quarterly and final report.)

Results

Figure 11 shows the phosphate and SF_6 results for the first 10 days of the phosphate experiment at the 60' sampling depth of well 1. (We will refer to wells by their number and depth, in this case, 1-60.) The concentrations at this position are the highest we measured, yet the degree of dilution from the initial tracer concentrations are approximately 1/1000. Both phosphate and SF6 rise and then fall off rapidly after peaking just a few hours after injection, However, the phosphate concentration falls less rapidly than SF6, indicating preferential loss of phosphate. Note that in this and all subsequent figures, three lines are shown: the reactive tracer (here phosphate), the predicted reactive tracer concentration presuming no preferential loss or gain relative to the non-reactive tracer (calculated using the peak concentrations at well 1-60 in the first day due to analytical uncertainties at the very high concentrations of the initial injectant), and the non-reactive tracer itself. Here, the SF_6 curve is masked by the predicted phosphate curve.

Nitrate, in contrast, appears to behave conservatively at well 1-60 over the first 3-4 days (Figure 12). The predicted and observed nitrate curves are virtually indistinguishable after 1 day. In the first day, SF_6 peaks several hours before nitrate, implying some retardation of movement of the nitrate. Subsequent measurements, however, do not indicate further retarda-

tion.

Figures 13 and 14 show the predicted and observed concentrations of phosphate and nitrate in well 1-45, 15' shallower than the previous samples. Peak concentrations of phosphate, nitrate and SF_6 are achieved somewhat later than at 60', but still within the first 1-1.5 days. Peak concentrations of SF_6 were about 50% of those at well 1-60. Moreover, the observed phosphate concentrations were about a third of the concentrations expected from the SF_6 concentrations. The SF_6 peaks are also broader at this sampling depth, indicating a greater degree of dispersion of the injected patch by the time it has migrated from 60' to 45' at a position 5m (at the surface) from the site of injection. In contrast, the observed and predicted nitrate concentrations are effectively indistinguishable. These results corroborate are conclusion that phosphate is being preferentially stripped from the patch as it migrates, while nitrate is travelling essentiall conservatively.

We also determined ammonia concentrations on all samples for which nitrate was analyzed. In no case was the ammonia concentration perturbed from its pre-experiment concentration (an example is shown in Figure 15). This indicates that if any process other than dilution is affecting the nitrate concentration, it does not generate measurable quantities of ammonia (as would be expected, perhaps, if the thermodynamically favored reaction between nitrate and sulfide proceeded to any significant extent.

Peak concentrations of SF_6 were achieved at well 1-30 approximately 1.5 days after the phosphate injection (Figure 16), and were still rising when the nitrate experiment was terminated 3.5 days after injection (Figure 17). Peak SF_6 concentrations were 25% of those at well 1-60 for the phosphate experiment, and less than 10% of those at well 1-60 for the nitrate experiment. Even at this extent of dilution, significant concentrations of phosphate were expected at well 1-30, yet concentrations above background were not observed. Essentially all phosphate had been removed from the patch by the time it reached the well 1-30 sampling position 1-2 days after injection. In contrast, significant nitrate remained in the patch 3 days after injection. However, the observed nitrate concentration after 3 days was ·50% of that expected, indicating that some preferential removal (adsorption or reduction) of nitrate had occurred.

Discussion

The early measurement of elevated concentrations of both the tracer and phosphate in well 1-60 suggests strong advective flow through the karstified limestone substrate, with a rate of transport on the order of 2-3 m/hr. The reduction of the ratio of phosphate to the tracer over time indicates that PO_4 is being preferentially removed from the tracer patch, on times-

cales of days. The elevated tracer levels found in the wells at shallow depths indicates that there is vertical dispersion.

The injectant had a density that was greater than that of the deep groundwater ($20kg/200L = 100$ per mil). Although this dense solution would not tend to be buoyed to the surface, it was chased by a considerable slug wastewater with very low salinity, which tended to add buoyancy to the tracer. The shallow well's low salinity (3 to 18 psu) does not allow the injectant to rise into the shallow mixing zone through buoyant forces, so inferred vertical flow velocities are probably dominated by dispersive rather than buoyant flow.

The persistence of elevated phosphate concentrations at wells 1-60 and 1-45 at times when the appearance of the patch at well 1-30 was unaccompanied by any phosphate, suggests that the passage of the patch in the near-field leads to an exchange equilibrium with the carbonate bedrock. Further from the point of injection there is insufficient phosphate remaining to establish a measurable equilibrium phosphate concentration. Had the injection continued at the original concentration, this equilibrated "front" presumably would have migrated further and further from the point of injection. This suggests that under heavy wasteater loading, high concentrations of phosphate will be established under equilibrium partitioning in a wastewater plume. Measurements of uptake capacity for the Key Largo limestone will be made this summer, using columns constructed from core materials at KML or Key Colony Beach.

QUALITY ASSURANCE

This section presents our assessment of the quality of our data, specifically our nutrient analyses. In general, detection limits were no problem, given that we were analyzing wastewater or diluted wastewater, for which nutrient concentrations were typically in excess of 10^{-5}M, well above our MDL. The following analysis is repeated from past quarterly reports; little analysis was performed in the last six months of the project, and much of that effort was dedicated to switching to autoanalyzer methods for nutrient analysis (as described in the QAPP for the new award).

Field Quality Control

The first step in checking the quality of our work is to collect each groundwater sample in duplicate (Dup I and Dup II). The next step towards quality control was to analyze each of these duplicates twice for each analysis. Therefore, for each Dup, there are replicate analytical

results: Rep a and Rep b. This gives a total of four results for each well depth for each of the measured parameters.

Calibrations

Of the groundwater analyses conducted at PSU, six of them use colorimetric techniques: dissolved ammonium, dissolved nitrate, and dissolved inorganic phosphate (soluble reactive phosphate). These analyses utilize the Spectronics 601 Spectrophotometer. For these methods, a calibration curve is run prior to sample analysis using standards prepared for the analyte of interest. A linear regression was performed for all of our calibration runs. The lowest r value for both campaigns, out of all the calibration curves for all the analyses, is 0.97. And in 98% of the cases, the r value is at least 0.99. Therefore, the calibration curves all show excellent linearity, which in turn leads to more dependable concentration calculations from these linear regressions. For both campaigns, r^2 values exceed this limit in all instances except one, in which case that calibration curve was not used. And in 89% of the calibration curves, the r^2 value is at least 0.99.

Accuracy

Accuracy is expressed as the percent recovery (%R) of standards of known concentration. It is calculated as the ratio of the observed concentration and the known concentration, multiplied by 100. The standards used to determine the method's accuracy are called calibration check standards (CCS). They determine the state of calibration of the instrument (the spectrophometer in this case) after the initial calibration. For our analyses, we run three CCS' every 20 samples or every 4 hours. These standards include: a method reagent blank; a low level, near-the-MDL, standard of 0.10 ppm; and a high level standard of 1.00 ppm. At the end of the analysis of samples, the full suite of standards used in the initial calibration curve are analyzed again as a final calibration check. The %R determined for each CCS is then plotted on a control chart which monitors results over time. The means control chart is constructed from the mean and standard deviation (s) (calculated from historical data) of the percent recovery of the CCS. The upper and lower warning limits (WL) on the control charts are set at +2s from the mean, and the upper and lower control limits (CL) at +3s from the mean. The warning limits are intended to flag possible analytical problems before they become too severe. If two out of three successive points exceed the WL, another CCS is analyzed; if it is within the WL, the analysis continues; if it exceeds the WL, the analysis is discontinued and the problem must be identified and corrected. The control limits represent the maximum and minimum percent recoveries allowed given the historical standard deviation and mean for that analysis. If a point exceeds the CL, the

analysis must be repeated immediately. If the repeat is within the CL, analysis continues; if it exceeds it, the analysis is discontinued and the problem must be identified and corrected. Since the limits calculated for the control charts are based on historical results which tend to change dramatically from one campaign to the next, we also refer to Standard Method's Table 1020:I "Acceptance limits for duplicate samples and known additions to water and wastewater" for a general range to compare results.

The range of percent recovery for nutrient analyses is 80-120%. Again, this general range serves as an additional means of assessing each method's analytical accuracy. Since these control charts were only constructed after the completion of our last analyses from the May campaign, we have used them to determine the methods' accuracy as it was for each campaign, and to identify areas which need improvement.The standard deviations and means used to determine the control chart limits are presented in Table 1.

Table 1. Typical standard deviations and mean of percent recovery of calibration check standards, for each analysis.

Analysis	Trip	s	mean
Phosphate	Sept. '95	18.18	99.58
	Feb. '96	7.99	98.05
	May '96	8.83	97.01
Nitrate	Sept. '95	17.32	97.32
	Feb. '96	19.17	83.95
	May '96	14.16	101.19
Ammonia	Sept. '95	18.48	99.05
	Feb. '96	4.04	100.00
	May '96	8.83	95.64
Sulfide	Sept. '95	1.60	102.13
	Feb. '96	1.69	100.21
	May '96	6.61	99.07
Sulfate	May '96	5.31	100.01

In general, the CCS percent recoveries cluster around the historical mean with a small number of points exceeding the warning limits, and only a few points exceeding the control limits. For all of the analyses, our greatest error is with the lowest, near-MDL standard of 0.10 ppm. All but one of the points which exceed the control limits are 0.10 ppm standards. Of the points which exceed the warning limits, more than half are 0.10 ppm standards.

Replicate Precision

Precision is generally expressed as a standard deviation. However, this value can vary depending on the units of measurement involved.

Therefore, a percent relative standard deviation (%RSD), or coefficient of variation, can be a more useful measure of precision for various analyses because it equals the ratio of the standard deviation and the mean, multiplied by 100. Since for the February and May campaigns we collected each well depth in duplicate, and analyzed each in replicate, we have four data points for most samples (some underwent further reanalyses, or were collected in triplicate) with which we can determine the %RSD. Standard Methods suggests using another type of control chart, one of normalized ranges, to represent precision in duplicate analyses. Since duplicate analyses are not performed one right after the other as in replicate analyses, inspection of their precision through the use of these charts provides the most insight into each method's analytical precision. Replicate precision, however, is addressed here, with the average %RSD of each method's replicates, and of all four replicates taken together, listed in Table 2 for comparison.

Table 2. Percent relative standard deviation (%RSD) of replicate analyses of Duplicate I (Dup I %RSD), Duplicate II (Dup II %RSD), and of all four replicates taken together (%RSD) for each analysis, for each campaign. (Note: a "-" indicates either that the analysis was not performed, or only one set of replicates was analyzed).

| Analysis | February | | | May | | |
	Dup I %RSD	Dup II %RSD	%RSD	Dup I %RSD	Dup II %RSD	%RSD
Phosphate	5.83	7.49	9.14	4.17	5.29	11.77
Nitrate	5.97	4.58	65.41	11.93	1.25	32.39
Ammonia	2.03	3.16	34.33	2.29	9.30	12.60
Total N	0.86	0.53	19.59	8.30	9.16	19.68
Total P	9.64	14.52	22.64	5.60	5.39	10.18
pH	0.56	0.31	0.90	0.45	0.32	0.82
Alkalinity	0.57	0.62	3.30	0.82	0.55	3.62
Sulfide	-	-	10.81	-	-	14.68
Sulfate	-	-	-	-	-	1.79

Triplicate Precision

Ten percent of the samples were collected in triplicate for interlaboratory comparison for both the February and May campaigns. These three samples, selected at random, were analyzed at Florida International University (FIU). The %RSD for each sample, for each nutrient analysis, for each campaign, are listed in Table 3:

Table 3. Percent relative standard deviation (%RSD) of triplicate analyses of three samples from each campaign, calculated for each nutrient analysis.

February Sample	%RSD Phosphate	Nitrate	Ammonia	Total N	Total P
3A-60	52.50	79.63	8.45	21.36	69.30
5B-30	18.75	90.35	50.82	11.87	56.02
7A-15	53.82	104.53	22.81	15.33	72.87
May Sample	%RSD Phosphate	Nitrate	Ammonia	Total N	Total P
1A-60	33.16	34.99	22.24	27.57	69.43
4B-15	65.15	223.61	22.27	38.10	26.30
6A-45	13.62	63.41	20.88	37.74	66.84

In general, the %RSDs are worse here than they are for just our data, suggesting our results are very different from FIU's. There are a few points to note, however. The phosphate and total phosphorous results for both campaigns, and the nitrate May results, are all under the 0.05 ppm MDL. Therefore, these results shouldn't be compared since there could be relatively large errors (at such low levels) in their final concentrations. (On the range control charts, these data points are included, but they are denoted as being less than the MDL.) Also, many of these results include one or more zeros, which produces very high %RSDs no matter how small the other results are, such as May's nitrate %RSD for sample 4B-15, which has one value of 2.7 mM, and four 0.0 mM values. For the other analyses which have >MDL results, some of the high %RSDs are due to (bad) luck-of-the-draw. Since the samples were collected at random, there was no way of knowing if we had selected samples with >MDL concentrations, or if these samples would have problems with intralaboratory precision (let alone interlaboratory precision). For instance, nitrate's February samples all have very high %RSDs due to the contracted Water Lab's afore-mentioned lack of precision between duplicates. It just happens that two of these three samples (7A-15 and 5B-30) were the top two worst samples for duplicate reproducibility out of all the samples from that campaign. So intralaboratory precision was already bad before we added FIU's results. In a similar fashion, ammonia's February results show the range of good and bad luck-of-the-draw, with 3A-60 representing one of the Water Lab's best duplicate results, and 5B-30, one of it's worst. The average %RSD of these ammonia triplicates is 26.70, close to May's triplicate average of 21.80, which both lie between the duplicate results for February and May (Table 2). In general, FIU's nitrate, ammonia, and total nitrogen results were higher than ours for each sample. They found that freezing the samples was not enough to remove sulfide interference, and suggested that lower results would be obtained if the interference was not dealt with more efficaciously. Therefore, one strong positive point to come from

this interlaboratory comparison is the discovery that our technique for removal of sulfide interference may not be complete. It is also clear that a more valuable comparison is gained by submitting samples with >MDL concentrations for triplicate analysis (if that can be determined before-hand).

Duplicate Precision

The range control chart used to assess duplicate precision involves plotting the normalized range of duplicate analytical results over time, along with the method's mean and the WL and CL (similarly defined as for means control charts, however, only absolute range and limit values are used). The normalized range is defined as the absolute value of the ratio of the difference between the duplicates and their mean. As with the control charts for accuracy, a general range provided by Standard Methods is used as an additional means of comparing results. Table 1020:I gives the acceptance limits for low-level duplicate nutrient analyses as 75-125%, and high-level duplicate nutrient analyses as 90-110%. Low-level refers to concentrations less than 20 times the method detection limit (MDL), high-level, greater than this value. The MDLs for phosphate, nitrate and sulfide are 0.05 ppm, and ammonia's is 0.03 ppm. Therefore, phosphate and nitrate are low-level, sulfide is high-level, and the other analyses lie somewhere in between the two definitions. These percent ranges would translate to absolute normalized ranges of 0.25 for low-level analyses, and 0.10 for high-level ones. In order to produce constructive and useful plots, all duplicates with one value equaling zero had to be omitted from the chart. Any such pair would produce a normalized range of 2 (the maximum value) no matter how close to zero the second value is, because it would be divided by it's half. Also, all values below the method's MDL are plotted as an "x" as a quick and simple way of explaining limit-exceeding points. The mean, WL and CL for each analysis, for each campaign, are presented in Table 4:

Table 4. The mean, warning limit (WL) and control limit (CL) for the normalized range of duplicate analyses (replicate for sulfate) for each method, for each campaign.

Analysis	Trip	Mean	WL	CL
Phosphate	Feb.	0.120	0.280	0.360
	May	0.168	0.418	0.543
Nitrate	Feb.	1.195	2.078	2.519
	May	1.693	1.876	2.468
Ammonia	Feb.	0.573	1.855	2.496
	May	0.158	0.430	0.567
Total N	Feb.	0.337	1.187	1.613
	May	0.278	0.878	1.178
Total P	Feb.	0.244	0.529	0.822
	May	0.122	0.429	0.583
pH	Feb.	0.008	0.044	0.061
	May	0.011	0.060	0.085
Alkalinity	Feb.	0.059	0.318	0.448
	May	0.058	0.520	0.751
Sulfide	Feb.	0.153	0.433	0.572
	May	0.208	0.684	0.922
Sulfate	May	0.025	0.077	0.102

In general, almost all of the >MDL results are within the warning limit, with a small number of points exceeding it, and only a few points exceeding the control limit. Methods with some portion of results below the MDL can attribute almost all of their highest normalized range points (i.e. most imprecise) to these <MDL results.

The range control charts for pH actually represent instrument precision since hardly anything is done to the samples for preparation (they are merely filtered and subsampled). The reproducibility is excellent, with the lowest means and WLs and CLs of all the methods. The range control charts for alkalinity follow the pH results closely. Although precision is still very good, the standard deviations are much higher than those for pH. This should reflect the increase in sample manipulation and operator involvement for alkalinity determination over simple pH measurement. (See previous quarterly reports for range charts.)

In general, it seems that our analytical accuracy and precision are statistically acceptable, with improvement needed for near-MDL standard accuracy, and for nitrate precision. Most of the limit-exceeding results for accuracy can be explained by low recovery of the 0.10 ppm standard, and some of the limit-exceeding results for precision can be explained by low level concentrations, and by compositionally differing duplicates. By using the means control charts to monitor CCS percent recovery as analyses are performed, and by implementing the aforementioned procedural changes to decrease the range between duplicate results, future improvements to analytical accuracy and precision could be made.

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