Fate of wastewater-borne nutrients under low discharge conditions in the subsurface of the Florida Keys, USA

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Abstract

We designed experiments to evaluate the fate of the addition of wastewater-borne nutrients injected into the shallow subsurface in the Florida Keys. During three different experiments, either bulk unlabeled phosphate, radio-labeled phosphate ($^{32}$P), or bulk unlabeled nitrate ($^{14}$NO$_3^-$) was added simultaneously with conservative tracers (sulfur hexafluoride and I-131) into a wastewater injection well on Long Key. Relative concentration changes monitored over time indicated that both phosphate and nitrate acted non-conservatively in the subsurface. Phosphate showed an initial rapid uptake followed by a slower removal, possibly caused by adsorption–desorption reactions. Based on our observations, we estimate that approximately 95% of the phosphate injected into the subsurface could be removed in 20 to 50 h. There was also evidence for some removal of nitrate, possibly due to denitrification. Approximately 65% of the nitrate was removed over several days, suggesting a denitrification rate of 2700 $\mu$mol m$^{-3}$ groundwater h$^{-1}$, comparable to estimates of denitrification in other groundwater systems. Collectively, our results suggest that nutrients injected in the subsurface are removed rapidly from solution and thus may not have a significant impact on surface waters. However, these experiments were conducted at a relatively small facility (2.6 m$^3$ wastewater injected per day), while some facilities in the Keys inject as much as 750 m$^3$ day$^{-1}$. Saturation of available adsorption sites and organic substrate availability may limit the efficiency of wastewater nutrient removal under such conditions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: nutrients; groundwater; Florida Bay; denitrification; adsorption

1. Introduction

Wastewater practices in the Florida Keys contribute an estimated 897 kg of nitrogen and 215 kg of phosphate to the shallow groundwater system each day (U.S. Environmental Protection Agency, 1996). The addition of these nutrients to an otherwise nutrient-depleted natural environment occurs through approximately 600 sewage disposal (injection) wells, ranging in depth from 10–30 m, 24,000 septic tanks, and an estimated 5000 illegal cesspools (Shinn et al., 1994). Studies conducted by Lapointe et al. (1990) and Lapointe and Clark (1992) have shown significant nutrient enrichment (up to 5000-
fold) in groundwaters contiguous to septic tanks and in dredged boat canals and some nearshore waters of the Keys near areas of wastewater injection.

Canals may be particularly impacted by sewage-derived nutrients due to their low flushing rates and their direct contact with contaminated groundwaters. Paul et al. (1995) conducted two tracer tests on Key Largo and found that bacteriophages added directly to a septic tank and injected into a simulated injection well appeared in a nearby canal in less than a day. Estimated rates of transport ranged from 0.57 to 24.2 m h\(^{-1}\). The greatest tracer concentrations in canals and wells corresponded with major stages of the tide, indicating subsurface flow is at least somewhat dependent on the Atlantic tide. Some stations showed the greatest viral tracer concentration during high tide, while others showed a maximum at low tide. They speculated that the low tides enable drainage of the tracer and wastewater from the limestone, while high tides move the material back into the Keys, to be drained by another low tide. These studies and others performed by Paul et al. (1997), Dillon (1998) and Dillon et al. (1999) suggest that significant quantities of sewage from on-site disposal systems may reach the surficial waters of the Florida Keys on a time scale from hours to days.

In the past decade, Florida Bay has experienced significant ecological changes (Boesch et al., 1993) including seagrass dieoffs, greater frequency of planktonic algal blooms, and poor water quality (Philips and Badylak, 1996; Philips et al., 1995, 1999; Fourqurean and Robblee, 1999). Lapointe and Clark (1992) attribute the algal blooms and poor water quality to an increase in nutrient loading. Lapointe et al. (1990) suggested that sewage-derived inputs of nitrogen and dissolved phosphorus to canals and surface waters may be a key factor in causing the current problems within the bay. In addition, Florida Bay has been shown to be a phosphate-limited environment (Powell et al., 1989; Fourqurean et al., 1992a,b, 1993), therefore, small additions of dissolved phosphate may stimulate significant ecological changes. Unfortunately, there have been no systematic studies to date that quantified the fate of the wastewater-borne nutrients, which are continually being injected into the subsurface. The general consensus has been that nutrients would undergo in situ uptake (water polishing), by such processes as bacterial utilization, adsorption of phosphate by the carbonate matrix, and that significant dilution of the sewage would occur before it reached surface waters. However, if this water polishing does not take place, and if the flux into surface waters is high, then human and ecosystem health would be at risk, and different wastewater disposal methods would be necessary.

The potential for discharging groundwater to have an impact on surface water is greatest in nearshore areas, especially nearshore bodies of water with limited circulation, such as Florida Bay. The importance of groundwater discharge to the coastal environment is dependent on several variables, including the amount and type of nutrient enrichment in the groundwater, water column circulation and tidal flushing, and the groundwater flow rate, which is determined by the porosity and permeability of the underlying strata and the hydraulic head. Additionally, Corbett et al. (1999) have shown that the distribution of natural tracers in Florida Bay is consistent with the hypothesis that the area immediately adjacent to the Keys has the most pronounced interactions between groundwater and surface waters. Based on these observations, the water quality of Florida Bay has the potential of being influenced by groundwater flow due to elevated nutrient concentrations in groundwater associated with wastewater practices and the extremely high permeability of the limestone strata. We report here the subsurface behavior oftracer amounts of the non-conservative species nitrate and phosphate to evaluate the extent of chemical and biological removal processes such as adsorption and denitrification while assessing the physical processes of advection and dispersion with the conservative tracer, sulfur hexafluoride.

2. Background and approach

The Florida Keys are a low-lying archipelago off the southern-tip of Florida (Fig. 1). Geologically, the Keys consist primarily of two formations: the Key Largo Limestone and the Miami Limestone. The Key Largo Limestone, associated with islands north of Big Pine Key (including our study site), consists of ancient hermatypic corals with intra- and interbedded calcarenites and thin beds of quartz. The formation is
Fig. 1. Florida Bay separates the Florida Keys, located off the southern tip of Florida, from the mainland. Tracer experiments were conducted at the Keys Marine Laboratory located on Long Key.

extremely porous due to an intricate maze of conduits and interconnected pores created by coral growth and meteoric diagenesis. The Miami Limestone, found on Big Pine Key and further south, consists of well-sorted ooids with varying amounts of skeletal material (e.g., corals, echinoids, mollusks, and algae) and some quartz sand (Halley et al., 1995). The Miami Limestone is much less permeable than the Key Largo Limestone and supports small freshwater lenses in some areas (Vacher et al., 1992).

The hydrology of the Florida Keys is much more complicated than a simple homogeneous unconfined aquifer. Subsurface water masses in the upper and middle Keys are typically saline to hyper-saline, and except for the occasional shallow freshwater lens in the lower Keys, the driving force for groundwater flow is tidal rather than topographic (Halley et al., 1994; Shinn et al., 1994). Therefore, the direction of groundwater flow beneath the Keys oscillates as the fluctuating Atlantic tides create a differential head with respect to Florida Bay, where tides are extremely damped. Although the groundwater flow in this region can change directions more than once a day, Halley et al. (1995) presented some evidence that sea level in Florida Bay is higher on average than that on the Atlantic side of Keys, suggesting net groundwater flow is towards the Atlantic.

The study site for this investigation was the Keys Marine Laboratory (KML) located on Long Key (Fig. 1). The laboratory has a wastewater injection well onsite that currently injects approximately 2.6 m$^3$ of secondary treated wastewater per day. Although secondary treatment may remove more than 85% of the biological oxygen demand (BOD) and suspended solids, it does not remove significant amounts of dissolved nitrogen, phosphorus, heavy metals, or many pathogenic bacteria and viruses (Davis and Cornwell, 1991). Thus, low salinity
wastewater (salinity = ~ 0.5) with typical concentrations of soluble reactive phosphate and nitrate greater than 250 µM and 1000 µM, respectively, is injected into a saline aquifer (salinity = ~ 37) with low phosphate and nitrate concentrations, creating a buoyant nutrient-rich plume (Monaghan, 1996).

The treatment facility at KML is similar to those used at many multi-unit residences in the Keys such as hotels, trailer parks, campgrounds, and small communities. However, the amount of wastewater currently injected at the KML facility is much smaller than most facilities in the Keys (Paul et al., 1997) because the facility was originally designed to be used as a tourist center (Shark World) with up to 700 visitors per day, rather than to be used as a marine laboratory. Although the amounts injected are smaller, the approach is the same. Wastewater is initially pumped into a holding tank and aggressively aerated with diffusion stones. Water is then pumped to a clarifying tank, followed by chlorination, and finally gravity fed into the injection well. Sludge left in the clarifying tank is pumped back to the aeration tank for further decomposition, with some undecomposed sludge removed from the system on a regular schedule.

The injection well at KML is a 15-cm diameter hole drilled to 27 m and cased to 18 m below ground level, allowing wastewater to move into the limestone aquifer within the deepest 9 m. Seven monitor well clusters have been established (Fig. 2) by Penn State and USGS researchers in close proximity to the KML injection well (Monaghan, 1996). Each well cluster contains four wells drilled to depths of 4.5, 9, 13.5, and 18 m (core barrel lengths were 1.5 m), and screened at the bottom 1.2 m. Wells were not drilled deeper than 18 m since the buoyant wastewater plume was expected to move out laterally at the base of the injection well casing.

We conducted three tracer experiments with a "slug" of nitrate, as KNO₃, a "slug" of phosphate, as KH₂PO₄ and phosphate a second time as H₅₃²PO₄. All of these non-conservative nutrient tracers were added simultaneously with sulfur hexafluoride (SF₆), an inert conservative tracer (Dillon, 1998; Dillon et al., 1999). Radioactive iodine (¹³¹I) was also utilized as a conservative tracer during the KNO₃ tracer experiment. Experiments were conducted in October 1996, February 1997, and June 1998. In each case, the nutrient of interest (P or N) was dissolved in either 50 or 200 l of tap water and then sparged with concentrated SF₆ gas for 20 min (the radioactive phosphate was added to 50 l and the other two salts were added to 200 l). The solution was siphoned into the injection well during a low Atlantic tide, followed by approximately 1000 l of wastewater (salinity = ~ 0.5) from the package plant. Salinity profiling of the injection well indicated that the wastewater moves out laterally at the base of the casing (18 m) with little penetration to greater depths. This may be attributed to the buoyant nature of the wastewater with respect to the ambient groundwater. The surrounding well clusters were then monitored for the presence of all added tracers (Table 1). Prior to sampling each well, they were purged to remove three well volumes. Purge water was stored in a
Table 1

<table>
<thead>
<tr>
<th>Experiment date</th>
<th>Tracers added</th>
<th>Injection concentration</th>
<th>Injection volume (l)</th>
<th>Wells monitored</th>
</tr>
</thead>
<tbody>
<tr>
<td>October 1996</td>
<td>K$_2$HPO$_4$/SF$_6$</td>
<td>0.83 M/46.2 μM</td>
<td>200</td>
<td>1–7</td>
</tr>
<tr>
<td>February 1997$^b$</td>
<td>KNO$_3$/SF$_6$/I$^{131}$</td>
<td>0.70 M/30.84 μM/56 × 10$^4$ dpm l$^{-1}$</td>
<td>200</td>
<td>1</td>
</tr>
<tr>
<td>June 1998</td>
<td>H$_3$PO$_4$/SF$_6$</td>
<td>8.66 × 10$^7$ dpm l$^{-1}$/99.6 μM</td>
<td>50</td>
<td>1, 3</td>
</tr>
</tbody>
</table>

$^a$Indicates well cluster number where all tracers in the experiment were monitored.

$^b$Nitrate and I-131 injection concentrations are not a direct measurement. Rather, the concentrations were calculated based on the mass of KNO$_3$ salt (14 kg) and activity of $^{131}$I added to 200 l of water.

large holding tank for the duration of each experiment. Water samples were collected with glass syringes or peristaltic pumps.

3. Analytical methods

3.1. Nutrients

Water samples taken in the field were kept frozen in the dark until analysis. Both nitrate and soluble reactive phosphate (SRP) were analyzed by standard methods with an automated spectrophotometer at the Pennsylvania State University. Nitrate concentrations were measured colorimetrically following reduction via a copper–cadmium column (EPA Method 353.2; U.S. Environmental Protection Agency, 1979). The procedure for the quantification of phosphate uses ammonium molybdate and antimony potassium tartrate to form a phosphate complex. This antimony–phospho-molybdate complex is then reduced with ascorbic acid to an intense blue-colored solution and the concentration is measured colorimetrically (EPA Method 365.1; U.S. Environmental Protection Agency, 1979).

3.2. Sulfur hexafluoride

Sulfur hexafluoride samples were collected with two different variations of a head space extraction technique. During the October 1996 experiment, samples were extracted on site with 30-cm$^3$ glass syringes. Following removal of the purge volume, water was collected from wells with these syringes and 1/8-in. copper tubing. A headspace of argon or ultra-high purity nitrogen was then added to the syringe and shaken for 2 min to extract the SF$_6$ into the headspace. Approximately, an 8-ml headspace was then injected into a 4-ml Vacutainer$^®$. Standards stored in this fashion showed no loss of SF$_6$ from the vacutainer for more than 500 days. Samples were analyzed within a month of collection Dillon, 1998.

In order to reduce the time spent in the sampling process, samples were later collected in 30-ml serum vials with a peristaltic pump and extracted just before analyses. After purging the well, a sample was pumped into a serum vial and allowed to overflow for three bottle volumes. The vial was then sealed with a rubber septum and a crimp cap. To prevent loss of SF$_6$ through the septa, the samples were stored on their sides until the samples could be extracted and analyzed. Samples were extracted in the lab by adding a small headspace (typically 4 ml) of argon or ultra-high purity nitrogen to the sample. Simultaneously, a volume of water from the sample had to be removed and discarded to allow for the headspace. The serum vials were slightly over-presurized with 1 ml of nitrogen to allow several withdrawals for analysis (100 μl or less) by the gas chromatograph (GC) to be pulled from each sample.

Sulfur hexafluoride samples were analyzed with a Shimadzu model 8A gas chromatograph equipped with an electron capture detector. Typically, the volume injected was 100 μl or less. The gas chromatograph contained a stainless steel column (180 × 0.1 cm I.D.) packed with molecular sieve 5A (80/100 mesh). Initially, a P5 mixture (95% argon, 5% methane) was used as a carrier gas with a flow rate of 25 ml min$^{-1}$. After having problems with carrier gas contamination, we switched to ultra-high
purity nitrogen as a carrier at the same flow rate. Column and detector temperatures were set at 90°C and 220°C, respectively.

Headspace concentrations in ppmv (parts per million by volume, = µl/l) of SF₆ were determined by reference to a 1.04 ppm standard (Scott Specialty Gases). Headspace concentrations were converted to dissolved concentrations in µM with the ideal gas equation. Replicates were collected for 10% of the samples. In addition, duplicate injections were run on the gas chromatograph every fifth injection. Precision between replicate samples and duplicate injections was usually better than 10%.

3.3. Phosphorus-32

Water soluble capsules containing a total of approximately 4.5 × 10¹³ dpm of $^{32}$P ($t_{½} = 14.3$ days) in 3 ml of $\text{H}_3\text{PO}_4$ were dissolved in 50 l of SF₆-saturated tap water. Samples were collected in plastic containers from monitoring wells with a peristaltic pump. Aliquots of each sample were transferred to 20-ml borosilicate scintillation vials in the field laboratory. Samples were returned to Florida State University and the high-energy beta particles (1.709 MeV) from $^{32}$P were counted by Cerenkov radiation on a Wallac 1414 liquid scintillation counter. The amount of light particles detected is proportional to the absolute activity of the solution, which was obtained with a standard curve using the same approach (efficiency = 56%; MDA = 1.1 dpm ml⁻¹).

3.4. Iodine-131

Iodine-131 samples were collected into 1- or 2-l polyethylene containers then taken to the on-site lab where a stable carrier (KI) and a radiometric tracer (I-129: $t_{½} = 1.7 \times 10^7$ year), used as a yield determinant, were added to the sample. A series of oxidation/reduction steps, using KMnO₄ and Na₂SO₃, ensured complete mixing of the sample with the stable carrier and the yield determinant and adjusted the oxidation state of the iodine for precipitation ($I^-$). The iodine was then quantitatively precipitated as AgI from a slightly acidic solution (pH < 4). The precipitates were collected on 47-mm 0.45 µm polypropylene filters. The filters were then washed with dilute ammonia, to remove any silver chloride and silver bromide present, and then rinsed with deionized water.

All filters were counted on one of two NaI detectors for the quantification of both I-131 and I-129. Iodine-129 was quantified using the low energy photo-peaks (29.0–40.0 keV), which account for 78.3% of the available photons. The 364 keV peak (81.2% photon intensity) was used to calculate the I-131 activity. A small correction was made to the I-129 total counts, due to a small percentage (4% of the I-131 photon intensity) of counts in this region which are attributed to the I-131 decay. After these corrections, the radiometric yield was determined using I-129 and the I-131 sample activity was then calculated. Several samples were re-counted after the short-lived I-131 had decayed away to verify the radiometric yield results. Most radiiodine recoveries were greater than 95%.

4. Results and discussion

4.1. Phosphate

Two experiments were performed to evaluate the potential non-conservative nature of inorganic phosphate, associated with waste disposal, in the limestone strata of Long Key. We conducted an initial experiment in October 1996 and injected approximately 20 kg of $\text{K}_2\text{HPO}_4$ into the wastewater injection well, followed by 1000 l of wastewater. The phosphate salt was first dissolved in approximately 200 l of tap water followed by sparging of the same water with SF₆. The measured injection concentrations of phosphate and SF₆ were 0.83 M and 46.2 µM, respectively. The concentration of dissolved salts was $\sim 100$ g kg⁻¹, or approximately three times the salt content of the groundwater. The 1000-l wastewater “chaser” may have reduced the total salt content below that of seawater. Samples were collected from all well clusters over a period of 70 days.

During this first phosphate experiment, the density of the injection water was raised by approximately 10% (even greater than the density of the saline groundwater). This led to a concern that the experiment could be compromised by unrealistic density effects associated with the salt difference as well as potential swamping of the system with a very
concentrated slug of injection water. Radioactive phosphorus was used in the final experiment (June 1998) to avoid the potential density anomalies present in the first two experiments. The use of a radioactive tracer allows for a significant amount of tracer to be added without changing the density or ambient concentrations within the system, i.e., relatively few atoms of phosphate are added to the aquifer, providing a more realistic experimental approach. $^{32}$P was added as 3 ml of phosphoric acid was diluted in 50 l of tap water and sparged with SF$_6$. Injected concentrations of $^{32}$P and SF$_6$ were $8.66 \times 10^9$ dpm l$^{-1}$ (equal to $4.3 \times 10^{-4}$ µM PO$_4^{3-}$) and 99.6 µM, respectively. Phosphate activities were only measured in two well clusters (#1 and #3) due to time and analytical constraints. These two wells were chosen as being the best for our observations based on data collected during the initial experiments.

Phosphate concentrations were extremely attenuated in both experiments relative to the conservative SF$_6$ (Figs. 3 and 4). Phosphate concentrations mea-

![Fig. 3. Normalized tracer concentrations over time for SF$_6$ (closed square) and phosphate (open circle) in well cluster #1–4.5 m (A), 9 m (B), 13.5 m (C), and 18 m (D) for the October 1996 experiment. Concentrations are normalized to the initial injection concentrations and multiplied by $10^6$ for easier comparison. The SF$_6$ and PO$_4$ lines would plot on top of each other if both tracers acted alike, i.e., if PO$_4$ behaved conservatively. Insets in (C) and (D) show the uptake of phosphate early in the experiment.](image-url)
Fig. 4. Normalized tracer concentrations over time for SF₅ (closed square) and ^32^P (open circle) in well cluster #1–1.45 m (A), 9 m (B), 13.5 m (C), and 18 m (D) for the June 1998 experiment. Concentrations are normalized to the initial injection concentrations and multiplied by 10^6 for easier comparison. Most of the ^32^P samples collected were below detection limit, indicating rapid uptake relative to SF₅. Note the y-axis break in well #1–13.5 (C) and 1–18 (D).

Measured in most of the monitoring wells were below detection. Results from well #1, closest to the injection well, are presented for both experiments, since most of the data are above the detection limit for both approaches (PO₄³⁻ = 0.1 μM, ^32^P = 1.1 dpm ml⁻¹). Tracer concentrations have been normalized to the injection concentration (measured concentration divided by the injected concentration) and multiplied by 10^6, allowing easier comparison. Normalizing each parameter to the amount injected allows for a quick evaluation of the extent of dilution and conservative behavior, i.e., when plotted, both parameters should overlap if phosphate behaved conservatively.
Groundwater movement in the first experiment was faster (1.74 m h\(^{-1}\)) than in the second (0.08 m h\(^{-1}\)) based on the maximum peak of SF\(_6\) measured in the deepest well from cluster #1 (well #1–18; wells are numbered by cluster location and screen depth in meters). In the October 1996 experiment, SF\(_6\) distribution appeared to be associated with rapid conduit flow (Dillon, 1998). The highest concentration of SF\(_6\) appeared in this well after just 2.9 h (Fig. 3D). During the second phosphate experiment in June 1998 the highest concentration of SF\(_6\) was also found in well #1–18, but the peak arrival took about 2.5 days rather than just a few hours (Fig. 4D). The difference in groundwater movement is thought to be due to the variations in the differential head of Florida Bay and the Atlantic, created by differences in tidal amplitude and potentially from different weather patterns occurring at the time of each experiment. The Atlantic Ocean can have tides on the order of 1 m, while tides in Florida Bay are only about 0.25 m near Long Key. Halley et al. (1994) showed that there are positive and negative head differentials of the surface of the Atlantic relative to that of the Bay, and the difference can be as great as 0.7 m. In addition, during the October experiment, there were heavy rains and high winds for the first two weeks. Florida Bay’s water level is strongly dependent on winds, which can pile water up in the bay. Northerly winds during the October experiment elevated the mean bay tidal level on Long Key relative to the June experiment, when conditions were relatively calm. The second experiment (June 1998) was conducted during a relatively dry period. These conditions are thought to have created the large difference in flow rate between the two experiments.

Although weather conditions and absolute groundwater flow velocities varied between the two experiments, it was evident that phosphate did not act conservatively in either case (Fig. 5A and B). However, there is a large difference between the two experiments in the attenuation of phosphate relative to SF\(_6\). During the first experiment, the maximum concentration of SF\(_6\) observed was at well cluster #1 (1–18, 70.4 nM), corresponding to 0.15% of the injected concentration. The phosphate:SF\(_6\) ratio in the injected solution was 18,000. This tracer ratio, after approximately 5 days, was systematically lower than the injection ratio in all wells where phosphate was significantly higher than background levels (Table 2). This ratio, which accounts for dilution, should give an indication of the extent of the non-conservative behavior of phosphate, i.e., a decreasing tracer ratio indicates removal of phosphate relative to the conservative SF\(_6\). The only wells that appeared to contain tracer phosphate were the wells at cluster #1 and the deepest well at cluster #3. The SF\(_6\) data indicated that the highest transport rates were along the north/south axis of the island during this experiment (Dillon, 1998). Since well cluster #3 lies approximately 5 m east of the injection well, the tracer plume would require more time to reach this well. Thus, further depletion of phosphate than that observed at well cluster #1 would be expected and is evident in the tracer ratio. It is apparent that there is an increasing removal of phosphate as the tracer moves away from its injection site. Based on the tracer ratios observed in well cluster #1, more than 85% of the phosphate was removed relative to the SF\(_6\) within the 5 m of travel from the injection well and the first 5 days.

In the June 1998 \(^{32}\)P experiment, an even greater loss of phosphate relative to SF\(_6\) was observed. The tracer ratio (\(^{32}\)P:SF\(_6\)) of the injected fluid (dpm \(1^{-1}\):nM) was approximately 87,000. Of those measured, the only wells that consistently had detectable \(^{32}\)P activities were the two deepest wells at well cluster #1 (Fig. 4). As with the previous experiment, the greatest flow occurred along a north/south axis of the island, however, the plume was more dilute and moved much slower in June 1998. The maximum concentration of SF\(_6\) observed was again collected at the deepest well of well cluster #1. The peak occurred after 63 h and had a concentration of 21.8 nM, only 0.02% of the injected concentration. The tracer ratios observed after approximately 2 days were 2900 and 600 for the deepest (1–18) and next to deepest (1–13.5) wells, respectively. Based on these observations, we calculate that more than 95% of the phosphate was removed within the first 2 days from the wastewater within 5 m of travel through the subsurface. The difference in the phosphate removal between the two experiments may be attributed to slower flow rates in the June \(^{32}\)P experiment in addition to the difference in the amount of total phosphate present in the injection solution. Perhaps
Fig. 5. Samples collected from well #1–18 during the phosphate A, $^{32}$P (B), and nitrate (C) experiments show non-conservative behavior of the nutrients when plotted against the corresponding SF$_6$ concentration. The solid line represents the ratio of the nutrient to SF$_6$ trend that would indicate conservative behavior of the nutrient. In each case, the nutrient samples fall below the ideal line, while non-reactive $^{131}$I (closed triangles in C) mimics the conservative trend. Note in the $^{32}$P experiment (B) the y-axis has been plotted on a log scale.

The available sites for phosphate adsorption were saturated near the point of injection more quickly during the first (more concentrated, October) experiment, allowing further transport of measurable phosphate concentrations.

The concentration of dissolved reactive phosphate has been shown to be significantly lower in waters in contact with sediments containing high weight percentages of calcium carbonate than in other sediments (Fanning and Pilson, 1971; Serruya, 1971; Berner, 1974; De Kanel and Morse, 1978). Early experiments of the kinetics of phosphate uptake in lake sediments showed an initial chemisorption onto the calcite matrix, followed by a quiescent period and then a rate of uptake which increased with time (Stumm and Leckie, 1970). Experiments conducted by De Kanel and Morse (1978) with synthetic seawater, aragonite, and calcite initially showed similar results to those of Stumm and Leckie (1970). However, De Kanel and Morse (1978) observed a rapid initial uptake followed by a slow decreasing rate of phosphate uptake with time. They attributed the dif-
Table 2
Summary of pertinent information for tracer experiments. Ratios of tracer to SF6 presented were used to estimate percent of nutrient removal relative to the injected ratio.

<table>
<thead>
<tr>
<th>Experiment date</th>
<th>Injection ratio (%)</th>
<th>Well no.</th>
<th>Time to peak SF6 (days)</th>
<th>Tracer ratio*</th>
</tr>
</thead>
<tbody>
<tr>
<td>October 1996*</td>
<td>18,000</td>
<td>1–15</td>
<td>70.8</td>
<td>BD^c</td>
</tr>
<tr>
<td>(bulk PO_4^3–)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1–30</td>
<td></td>
<td>2.0</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>1–45</td>
<td></td>
<td>0.6</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>1–60</td>
<td></td>
<td>0.1</td>
<td>1900</td>
</tr>
<tr>
<td></td>
<td>3–60</td>
<td></td>
<td>7.9</td>
<td>100</td>
</tr>
<tr>
<td>February 1997*</td>
<td>22,700</td>
<td>1–15</td>
<td>3.3</td>
<td>BD</td>
</tr>
<tr>
<td>(bulk NO_3^–)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1–30</td>
<td></td>
<td>3.4</td>
<td>3300</td>
</tr>
<tr>
<td></td>
<td>1–45</td>
<td></td>
<td>1.4</td>
<td>5700</td>
</tr>
<tr>
<td></td>
<td>1–60</td>
<td></td>
<td>0.5</td>
<td>6600</td>
</tr>
<tr>
<td>June 1998*</td>
<td>87,000</td>
<td>1–45</td>
<td>&gt; 4.5</td>
<td>600</td>
</tr>
<tr>
<td>(^31)P</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1–60</td>
<td></td>
<td>2.5</td>
<td>2900</td>
</tr>
</tbody>
</table>

*Tracer ratios were calculated after 5 days for the October 1996 experiment, after 3.5 days for the February 1997 experiment, and after 2 days for the June 1998 experiment. These times were selected based on the equilibration of the tracer ratio, i.e., when the slope of the ratio vs. time approached zero.

^cUnits of the tracer ratio are in μM/nM.

^dBelow detection.

^eUnits of the tracer ratio are in dpm l^{-1}/nM.

ferences to either lower phosphate concentrations or different mechanisms operative in seawater and freshwater.

Uptake of phosphate observed in our experiments showed almost identical trends to those of De Kanel and Morse (1978). During both experiments conducted at KML, a rapid removal of phosphate was initially observed followed by a much slower rate of uptake which declined overtime (Fig. 6A and B). This trend is most evident in well #1–18 for both the October 1996 and June 1998 experiments. This general trend was observed in all the wells with concentrations above background. De Kanel and Morse (1978) described this process with the Elovichian Chemisorption model, which uses activation energy and available adsorption sites to describe the trends in the data. They concluded that there is an initial rapid physical adsorption on active sites with low activation energies. This initial process is then followed by a much slower rate, attributed to a linear increase of the activation energy and/or exponential decrease in the number of available reaction sites. These two very different rates were successfully modeled by the Elovichian process, and this same process may be occurring in the waters below the wastewater injection well. However, if rapid adsorption onto active sites initially removes phosphate from the subsurface waters, there must be a mechanism to reactivate the sites for subsequent injections, since we have observed the same trends at the same site more than once. Laboratory experiments currently being conducted suggest the potential for rapid adsorption followed by phosphate mineralization (K. Elliott, unpublished data). An additional mechanism may be the transport of groundwater with low phosphate concentration across the site following an injection. This may increase desorption of phosphate, reactivating the adsorption sites for subsequent injections.

Assuming the initial decrease in the tracer ratio is dominated by adsorption, i.e., desorption is small, then the observations can be used to obtain a first-order rate constant ($k_1$) using a well-known rate expression (Frost and Pearson, 1961):

$$\ln C = \ln C_0 - k_1 t$$  \hspace{1cm} (1)

where $C$ is the concentration of phosphate, $C_0$ is the concentration at the start of the experiment, and $t$ is the elapsed time. Using this approach, a plot of $\ln C$ versus time should be linear, allowing calculation of the rate constant from the slope of the line. In addition, a desorption rate may be estimated, assuming adsorption no longer dominates the system after the initial rapid removal of the phosphate. Moore (1972) described a first-order rate expression for opposing surface reactions as:

$$\frac{dC}{dt} = k_1 C - k_{-1} (C_0 - C)$$  \hspace{1cm} (2)

where $k_{-1}$ is the first-order desorption reaction rate constant and the other variables are the same as Eq. (1). Assuming steady state or equilibrium conditions, the ratio of adsorption to desorption can be estimated (Griffin and Jurinak, 1974).

Applying Eq. (1) to our phosphate uptake results provides estimates for the first-order adsorption rate constant of 0.02–0.10 h^{-1} and 0.06–0.34 h^{-1} for
well #1–13.5 and well #1–18, respectively. These estimates are based on both tracer experiments, with the experiment employing the radioactive phosphate producing the larger rate constant in both wells. Desorption rate constants were calculated using Eq. (2) and assuming that the system has reached equilibrium. It is apparent that after 5 and 2 days for the October 1996 and June 1998 experiments, respectively, that the phosphate:SFe ratios have reached a steady state (Fig. 6A and B). Calculated desorption rates ranged from 0.0007 h\(^{-1}\) in well #1–13.5 to 0.007–0.012 h\(^{-1}\) in well #1–18 for both tracer experiments. Griffin and Jurinak (1974) estimated desorption rates for phosphate of 0.0002 h\(^{-1}\) in laboratory experiments using calcium carbonate and distilled water.

Using the estimated adsorption rate constants from the deepest well (1–18), it would only take between 10 and 50 h to remove approximately 95% of the phosphate from the injected water. However, this calculation does not account for desorption, which probably occurs after the initial rapid uptake. Phos-
phate is remobilized from the near-injection surface sites between injections, as the system evolves toward equilibration with phosphate-free ambient groundwaters. This desorption reactivates these near-injection surfaces, allowing for rapid scavenging of phosphate from subsequent injections. The remobilized phosphate is dispersed further from the point of injection, but is likely efficiently scavenged by adsorption. We see little likelihood that significant phosphate is reaching surface waters at this site.

4.2. Nitrate

In February 1997, approximately 14 kg KNO$_3$ was dissolved in 200 l of tap water, sparged with SF$_6$, and added to the wastewater injection well at KML. I-131 was also added to the injection well as a conservative tracer during this experiment. The concentration of tracers in the injection slug was 0.70 M, 30.8 µM, and 5.6 × 10$^7$ dpm l$^{-1}$ of nitrate, SF$_6$, and $^{131}$I, respectively, giving a molar tracer ratio (NO$_3^-$:SF$_6$) of 22,700. The nitrate and $^{131}$I injection concentrations are based on the amount of salt (14 kg) and total activity added to the injection slug, not a direct measurement of the water injected. While it is impossible to judge the uncertainty of such an assumption precisely, a direct measurement and an estimate based on the mass added was done for the phosphate experiment and the difference was about 10%. We expect it should be about the same in this case. Samples were collected over a 4-day period and analyzed for SF$_6$, $^{131}$I, NH$_4^+$, and NO$_3^-$ only at well cluster #1 due to time constraints.

Horizontal groundwater flow rates as high as 0.46 m h$^{-1}$ were calculated based on the maximum concentration of SF$_6$ found in the deepest well at cluster #1 (Dillon, 1998). The maximum SF$_6$ concentration measured during this experiment was 360 nM (1–18), and while this represents a dilution of approximately two orders of magnitude (1.2% of injection concentration), it is actually much less diluted than observed in the other experiments. Dilutions of more than seven orders of magnitude were measured by the time the tracer was observed in surface waters. As before, all tracer concentrations were normalized to their injection concentration and multiplied by 10$^6$ for easier comparison (Fig. 7). It is clear from these plots that nitrate does not act conservatively in the subsurface as the normalized concentrations do not overlap. The radioactive iodine, however, did act conservatively, overlapping the normalized SF$_6$ results (Fig. 7). Tracer ratios (NO$_3^-$:SF$_6$) for well cluster #1 were well below the estimated injection ratio indicating removal of N relative to SF$_6$ (Table 2). Most of the nitrate samples analyzed in the two shallower depths (1–4.5 and 1–9) were below detection (0.7 µM). It is thus apparent that nitrate is removed relative to the conservative SF$_6$ (Fig. 5C), assuming the tracer ratio of the injected solution is correct. Ignoring results which were below detection limits, the tracer ratio in the deepest well at cluster #1 (1–18) appears to remain around an average value over the duration of the experiment (Fig. 6C), rather than systematically falling as did the phosphate ratios. The tracer ratio in the next-to-deepest well at cluster #1 (1–13.5) shows an initial increase (ignoring results below detection), potentially due to a lag in nitrate relative to SF$_6$, followed by a decreasing trend, probably a result of denitrification (see below). In both wells, the tracer ratio initially present is much lower than that of the estimated injection ratio, suggesting a very rapid loss of nitrate following injection. The tracer ratios in the two deepest wells (1–13.5 and 1–18) associated with the peak concentration of nitrate were 7700 and 10,600, respectively. This suggests that as much as 50% of the nitrate was removed during the first day within 5 m of the injection well. In addition to this rapid removal, the tracer ratio tends to decrease from the deeper to the shallower sampling depths, indicating continual removal with increasing travel distance from injection (Table 2). Based on these ratios, which account for dilution effects, more than 65% of the nitrate added to the system was lost within the first 5 m of the injection well after 3.5 days. The amount of nitrate lost is much smaller and the removal ratio is much slower than that of the phosphate, indicating different removal mechanisms.

Ammonia was measured throughout the experiment and showed very little change over time, averaging 33.0 ± 0.9 µM for all the samples collected. Therefore, the reduction of nitrate to ammonia in this environment did not appear to play an important role. However, the occurrence of denitrification in groundwaters has been documented from chemical and bacteriological evidence in many field and lab-
Fig. 7. Normalized tracer concentrations over time for SF$_6$ (closed square) and nitrate (open circle) in well cluster #1–4.5 m (A), 9 m (B), 13.5 m (C), and 18 m (D) for the February 1997 experiment. Concentrations are normalized to the initial injection concentrations and multiplied by $10^6$ for easier comparison.

Laboratory studies (Doner et al., 1974; Howard, 1985; Trudell et al., 1986; Slater and Capone, 1987; Jacobs et al., 1988; Smith and Duff, 1988; Von Gunten et al., 1991; Von Gunten and Zobrist, 1993; Sumner et al., 1998).

High total organic carbon (as high as 900 $\mu$M; Bohlke, USGS, pers. comm., 1999) and nitrate (1000 $\mu$M) injected into the suboxic to anoxic waters beneath Long Key provide an environment conducive toward denitrification. Based on our experimental observations and assuming that the removal of nitrogen is by denitrification alone, a groundwater denitrification rate may be calculated from an assumed volume of water with which the nitrate has come into contact. Since all of the data presented are from sampling wells located within 5 m of the injection well and since the majority of the tracer was found in the deeper depths (> ~ 15 m), the volume of water in this layer can be calculated assuming these dimensions and a porosity of 50%
We assume that the nitrate will only interact with the layer between 10 and 20 m depth over a radial distance of 5 m from the injection well. This provides a conservative estimate of 393 m$^3$ of saturated void (water) volume that the injected solution has come into contact with. This void volume is within 40% of the dilution volume estimated by the SF$_6$ results. The denitrification rate calculated for this injection experiment, based on these volume assumptions and the amount of nitrate apparently removed from the groundwater (i.e., 65% or ~90 mol N removed) during the first 3.5 days, is approximately 2700 $\mu$mol m$^{-3}$ groundwater h$^{-1}$. However, as much as 50% of the injected nitrate was removed within the first day, giving a denitrification rate of at least 7300 $\mu$mol m$^{-3}$ groundwater h$^{-1}$. This rate of denitrification is within the range of other values reported for saturated, sandy soils in previous studies (once converted to the same units; Table 3).

Collectively, our nitrate results indicate an initial rapid denitrification rate at depth (within the first few hours), when nitrate and oxygen-rich wastewaters are mixing with the surrounding reducing saline groundwaters potentially producing a redox gradient, thus facilitating denitrification. This rapid removal is then followed by very little change in the nitrate, other than dilution, over time (Fig. 6). Although conditions for rapid denitrification are ideal following the injection of the wastewater into the subsurface, the lack of a direct measurement of the injected nitrate adds some uncertainty to our interpretation. However, we note that Böhlke et al. (1997) showed relatively large amounts of excess N$_2$ in wastewater and in mixed groundwaters near the KML injection site, and associated this increase with the denitrification of wastewater-borne nitrate. In addition, acetylene-block denitrification assays (Slater and Capone, 1987) conducted on aquifer material and wastewater, obtained during drilling operations further south of Long Key in May 1999 indicate high potential rates of denitrification (Dillon, pers. comm.). This denitrification rate would result in $^{15}$N enriched groundwater nitrate. Corbett et al. (1999) observed $^{15}$N enrichment in algal and seagrass tissues near the Florida Keys, suggesting some groundwater nitrate seeps into surficial waters of Florida Bay.

Table 3
Comparison of denitrification rates estimated in this study to other investigations of denitrification in saturated, sandy soils receiving high concentrations of nitrate

<table>
<thead>
<tr>
<th>Study</th>
<th>Denitrification rate ($\mu$mol m$^{-3}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>2700–7300</td>
</tr>
<tr>
<td>Tradell et al., 1986</td>
<td>560–9300</td>
</tr>
<tr>
<td>Focht and Joseph, 1974</td>
<td>1860–8500</td>
</tr>
<tr>
<td>Doner et al., 1974</td>
<td>19,000</td>
</tr>
<tr>
<td>Bowman and Focht, 1974</td>
<td>28,500–57,100</td>
</tr>
<tr>
<td>Volz et al., 1974</td>
<td>12,100–44,300</td>
</tr>
</tbody>
</table>

5. Summary

The initial rapid removal of phosphorus in subsurface waters, possibly due to chemisorption, indicates the potential for removal of the nutrient in the subsurface following injection. As much as 95% of the phosphate at our site was removed from the injected subsurface fluids within 5 m of the injection well in approximately two days. A first-order rate constant for the adsorption of phosphate onto the carbonate strata was calculated to be as high as 0.34 h$^{-1}$ for wastewater injected into the subsurface at KML. We also found evidence suggesting that nitrate may be removed rapidly upon injection of the wastewater, removing as much as 65% of the nitrate during the first 3.5 days at a rate as high as 7300 $\mu$mol m$^{-3}$ groundwater h$^{-1}$. This loss of nitrate may be due to redox gradients set up by the injection of fresh oxygen-rich wastewater into a reducing saline groundwater, which could promote the rapid removal of nitrate via denitrification. However, it must be emphasized that the site described here is a relatively small waste disposal facility, injecting only about 2.6 m$^3$ of wastewater per day. Disposal sites injecting as much as 750 m$^3$ of wastewater per day are present throughout the Keys. We hypothesize that such high disposal rates could saturate removal sites, especially for phosphate. It is thus possible that the removal of nitrate and phosphate observed during this study may not be as great at such large sites.

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