

## **FINAL REPORT**

### **Use of Natural and Artificial Tracers to Detect Subsurface Flow of Contaminated Groundwater in the Florida Keys**

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### **Chapter 1**

#### **FATE OF WASTEWATER-BORNE NUTRIENTS UNDER LOW DISCHARGE CONDITIONS IN THE SUBSURFACE OF THE FLORIDA KEYS, USA**

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**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 ( $^{32}\text{PO}_4^{3-}$ ), or bulk unlabeled nitrate ( $^{14}\text{NO}_3^{-}$ ) 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 hours. 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  $2700 \mu\text{moles m}^{-3} \text{ groundwater hr}^{-1}$ , 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 ( $2.6 \text{ m}^3$  wastewater injected per day), while some facilities in the Keys inject as much as  $750 \text{ m}^3$  per day. Saturation of available adsorption sites and organic substrate availability may limit the efficiency of wastewater nutrient removal under such conditions.

## 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 5,000 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 meters per hour. 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 (Phlips et al., 1995; Phlips and Badylak, 1996; Phlips, et al., 1999; Fourqurean and Roblee, 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; Fourqurean et al., 1992b; Fourqurean et al., 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 of tracer 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 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<sup>3</sup> of secondary treated wastewater per day. Although secondary treatment may remove more than 85 percent 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 meters. 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 meters. 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  $\text{KNO}_3$ , a "slug" of phosphate, as  $\text{KH}_2\text{PO}_4$  and phosphate a second time as  $\text{H}_3^{32}\text{PO}_4$ . All of these non-conservative nutrient tracers were added simultaneously with sulfur hexafluoride ( $\text{SF}_6$ ), an inert conservative tracer (Dillon, 1998; Dillon et al., 1999). Radioactive iodine ( $^{131}\text{I}$ ) was also utilized as a conservative tracer during the  $\text{KNO}_3$  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 liters of tap water and then sparged with concentrated  $\text{SF}_6$  gas



for 20 minutes (the radioactive phosphate was added to 50 liters and the other two salts were added to 200 liters). 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 3 well volumes. Purge water was stored in a 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 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 tartate to form a phosphate complex. This antimony-phospho-molybdate complex is then reduced with ascorbic acid to a 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-cc glass syringes. Following removal of the purge volume, water was collected from wells with these syringes and 1/8-inch copper tubing. A headspace of argon or ultra-high purity nitrogen was then added to the syringe and shaken for two minutes to extract the SF<sub>6</sub> 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<sub>6</sub> 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<sub>6</sub> 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-pressurized 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 uL or less. The gas chromatograph contained a stainless steel column (180 cm x 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<sup>-1</sup>. 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, =  $\mu\text{L/L}$ ) of  $\text{SF}_6$  were determined by reference to a 1.04 ppm standard (Scott Specialty Gases). Headspace concentrations were converted to dissolved concentrations in  $\mu\text{M}$  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 were usually better than 10%.

### 3.3. Phosphorus-32

Water soluble capsules containing a total of approximately  $4.5 \times 10^{11}$  dpm of  $^{32}\text{P}$  ( $t_{1/2} = 14.3$  days) in 3 mL of  $\text{H}_3\text{PO}_4$  were dissolved in 50 liters of  $\text{SF}_6$ -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 FSU and the high-energy beta particles (1.709 MeV) from  $^{32}\text{P}$  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  $\text{mL}^{-1}$ ).

### 3.4. Iodine-131

Iodine-131 samples were collected into 1 or 2 liter polyethylene containers then taken to the on-site lab where a stable carrier (KI) and a radiometric tracer (I-129:  $t_{1/2} = 1.7 \times 10^7$  y), used as a yield determinant, were added to the sample. A series of oxidation / reduction steps, using  $\text{KMnO}_4$  and  $\text{Na}_2\text{SO}_3$ , ensured complete mixing of the sample with the stable carrier and the yield determinant and adjusted the oxidation state of the iodine for precipitation ( $\text{I}^-$ ). The iodine was then quantitatively precipitated as  $\text{AgI}$  from a slightly acidic solution ( $\text{pH} < 4$ ). The precipitates were collected on 47-mm 0.45  $\mu\text{m}$  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 accounts 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 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 radioiodine 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  $\text{KH}_2\text{PO}_4$  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  $\text{SF}_6$ . The measured injection concentrations of phosphate and  $\text{SF}_6$  were 0.83 M and 46.2  $\mu\text{M}$ , respectively. The concentration of dissolved salts were  $\sim 100 \text{ g kg}^{-1}$ , 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. 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.  $^{32}\text{P}$  was added as 3-mL of phosphoric acid diluted in 50 L of tap water and sparged with  $\text{SF}_6$ . Injected concentrations of  $^{32}\text{P}$  and  $\text{SF}_6$  were  $8.66 \times 10^9 \text{ dpmL}^{-1}$  (equal to  $4.3 \times 10^{-4} \mu\text{M PO}_4^{3-}$ ) and  $99.6 \mu\text{M}$ , 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  $\text{SF}_6$  (Fig. 3 and 4). Phosphate concentrations 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 ( $\text{PO}_4^{3-} = 0.1 \mu\text{M}$ ,  $^{32}\text{P} = 1.1 \text{ dpm mL}^{-1}$ ). 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 ( $1.74 \text{ m hr}^{-1}$ ) than in the second ( $0.08 \text{ m hr}^{-1}$ ) based on the maximum peak of  $\text{SF}_6$  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,  $\text{SF}_6$  distribution appeared to be associated with rapid conduit flow (Dillon, 1998). The highest concentration of  $\text{SF}_6$  appeared in this well after just 2.9 hours (Fig. 3 D). During the second phosphate experiment in June, 1998, the highest concentration of  $\text{SF}_6$  was also found in Well# 1-18, but the peak arrival took about 2.5 days rather than just a few

hours (**Fig. 4 D**). 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<sub>6</sub>. During the first experiment, the maximum concentration of SF<sub>6</sub> observed was at well cluster #1 (1-18, 70.4 nM), corresponding to 0.15% of the injected concentration. The phosphate:SF<sub>6</sub> ratio in the injected solution was 18000. 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<sub>6</sub>. The only wells that appeared to contain tracer phosphate were the wells at cluster #1 and the deepest well at cluster #3. The SF<sub>6</sub> 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 meters 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<sub>6</sub> within the 5 meters of travel from the injection well and the first 5 days.

In the June, 1998 <sup>32</sup>P experiment, an even greater loss of phosphate relative to SF<sub>6</sub> was observed. The tracer ratio (<sup>32</sup>P:SF<sub>6</sub>) of the injected fluid (dpmL<sup>-1</sup>:nM) was approximately 87000. Of those measured, the only wells that consistently had detectable <sup>32</sup>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<sub>6</sub> observed was again collected at the deepest well of well cluster #1. The peak occurred after 63 hours 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 meters 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 <sup>32</sup>P experiment in addition to the difference in the amount of total phosphate present in the injection solution. Perhaps 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 compared to 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 differences 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 the Keys Marine Laboratory, a rapid removal of phosphate was initially observed followed by a much slower rate of uptake which declined overtime (**Fig. 6 A 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):

$$\ln C = \ln C_0 - k_1 t \quad (1)$$

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:

$$-\frac{\partial C}{\partial t} = k_1 C - k_{-1}(C_0 - C) \quad (2)$$

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

Applying equation (1) to our phosphate uptake results provides estimates for the first-order adsorption rate constant of  $0.02 - 0.10 \text{ hr}^{-1}$  and  $0.06 - 0.34 \text{ hr}^{-1}$  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 equation (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:SF<sub>6</sub> ratios have reached a steady state (**Fig. 6 A and B**). Calculated desorption rates ranged from  $0.0007 \text{ hr}^{-1}$  in Well# 1-13.5 to  $0.007 - 0.012 \text{ hr}^{-1}$  in Well# 1-18 for both tracer experiments. Griffin and Jurinak (1974) estimated

desorption rates for phosphate of  $0.0002 \text{ hr}^{-1}$  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 hours 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. Phosphate 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  $\text{KNO}_3$  was dissolved in 200 L of tap water, sparged with  $\text{SF}_6$ , and added to the wastewater injection well at the Keys Marine Laboratory. Iodine-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  $\mu\text{M}$ , and  $5.6 \times 10^8 \text{ dpm L}^{-1}$  of nitrate,  $\text{SF}_6$ , and  $^{131}\text{I}$ , respectively, giving a molar tracer ratio ( $\text{NO}_3^-:\text{SF}_6$ ) of 22700. The nitrate and  $^{131}\text{I}$  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 four day period and analyzed for  $\text{SF}_6$ ,  $^{131}\text{I}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  only at well cluster # 1 due to time constraints.

Horizontal groundwater flow rates as high as  $0.46 \text{ m hr}^{-1}$  were calculated based on the maximum concentration of  $\text{SF}_6$  found in the deepest well at cluster #1 (Dillon, 1998). The

maximum SF<sub>6</sub> concentration measured during this experiment was 360 nM (1-18), and while this represents a dilution of approximately 2 orders of magnitude (1.2% of injection concentration), it is actually much less diluted than observed in the other experiments. Dilutions of more than 7 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<sup>6</sup> 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<sub>6</sub> results (**Fig. 7**). Tracer ratios (NO<sub>3</sub><sup>-</sup>:SF<sub>6</sub>) for well cluster #1 were well below the estimated injection ratio indicating removal of N relative to SF<sub>6</sub> (**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<sub>6</sub> (**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 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<sub>6</sub>, 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 7,700 and 10,600, respectively. This suggests that as much as 50% of the nitrate was removed during the first day within 5 meters 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 5m of the injection well after 3.5

days. The amount of nitrate lost is much smaller and the removal ratio 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  $33.0 \pm 0.9 \mu\text{M}$  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 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 Guten et al., 1991; Von Gunten and Zobrist, 1993; Sumner et al., 1998).

High total organic carbon (as high as  $900 \mu\text{M}$ , J.K. Bohlke, U.S.G.S., pers. comm. 1999) and nitrate ( $1000 \mu\text{M}$ ) 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 in contact. Since all of the data presented are from sampling wells located within 5 meters of the injection well and since the majority of the tracer was found in the deeper depths ( $> \sim 15 \text{ m}$ ), the volume of water in this layer can be calculated assuming these dimensions and a porosity of 50% (Monaghan, 1996). We assume that the nitrate will only interact with the layer between 10-20 meters depth over a radial distance of 5 meters from the injection well. This provides a conservative estimate of  $393 \text{ m}^3$  of saturated void (water) volume that the injected solution has come in contact. This void volume is within 40% of the dilution volume estimated by the  $\text{SF}_6$  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  $\sim 90$  moles N removed) during the first 3.5 days, is approximately  $2700 \mu\text{moles m}^{-3}$  groundwater  $\text{hr}^{-1}$ . However, as much as 50% of the injected nitrate was removed within the first day, giving a denitrification rate of at least  $7300 \mu\text{moles m}^{-3}$  groundwater  $\text{hr}^{-1}$ . 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 Bohlke et al. (1997) showed relatively large amounts of excess  $N_2$  in wastewater and in mixed groundwaters near the Keys Marine Laboratory 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.

## 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 meters 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  $0.34 \text{ hr}^{-1}$  for wastewater injected into the subsurface at the Keys Marine Laboratory. 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  $7300 \mu\text{moles m}^{-3} \text{ groundwater hr}^{-1}$ . 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  $2.6 \text{ m}^3$  of wastewater per day. Disposal sites injecting as much as  $750 \text{ m}^3$  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.

## **Acknowledgments**

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**Table 1:** Summary of tracers used and injection concentrations.

Experiment Date	Tracers Added	Injection Concentration	Injection Volume (L)	Wells Monitored <sup>1</sup>
October 1996	K <sub>2</sub> HPO <sub>4</sub> /SF <sub>6</sub>	0.83 M / 46.2 μM	200	1, 2, 3, 4, 5, 6, 7
February 1997 <sup>2</sup>	KNO <sub>3</sub> /SF <sub>6</sub> / <sup>131</sup> I	0.70 M / 30.84 μM / 5.6 X 10 <sup>8</sup> dpm L <sup>-1</sup>	200	1
June 1998	H <sub>3</sub> <sup>32</sup> PO <sub>4</sub> /SF <sub>6</sub>	8.66 X 10 <sup>9</sup> dpm L <sup>-1</sup> / 99.6 μM	50	1, 3

<sup>1</sup>Indicates well cluster number where all tracers in the experiment were monitored.

<sup>2</sup>Nitrate and I-131 injection concentrations are not a direct measurement. Rather, the concentrations were calculated based on the mass of KNO<sub>3</sub> salt (14 kg) and activity of <sup>131</sup>I added to 200L of water.

**Table 2:** Summary of pertinent information for tracer experiments. Ratios of tracer to SF<sub>6</sub> presented were used to estimate percent of nutrient removal relative to the injected ratio.

Experiment Date	Injection Ratio	Well No.	Time to Peak SF6 (days)	Tracer Ratio <sup>1</sup>
October 1996 <sup>2</sup> Bulk PO <sub>4</sub>	18000	1-15	70.8	BD <sup>3</sup>
		1-30	2.0	200
		1-45	0.6	600
		1-60	0.1	1900
		3-60	7.9	100
February 1997 <sup>2</sup> Bulk NO <sub>3</sub>	22700	1-15	3.3	BD
		1-30	3.4	3300
		1-45	1.4	5700
		1-60	0.5	6600
June 1998 <sup>4</sup> <sup>32</sup> P	87000	1-45	>4.5	600
		1-60	2.5	2900

<sup>1</sup>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.

<sup>2</sup>Units of tracer ratio are μM/nM.

<sup>3</sup>Below detection.

<sup>4</sup>Units of tracer ratio are dpm L<sup>-1</sup>/nM.

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

Study	Denitrification Rate ( $\mu\text{moles m}^{-3} \text{ hr}^{-1}$ )
This Study	2700-7300
Trudell et al., 1986	560-9300
Focht and Joseph, 1974	1860-8500
Doner et al., 1974	19000
Bowman and Focht, 1974	28500-57100
Volz et al., 1974	12100-44300

### Figure Captions

Figure 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.

Figure 2. The Keys Marine Laboratory is located on Long Key. The injection well (marked with a cross) receives approximately 2600 liters of wastewater per day from the package plant. The injection well is surrounded by seven monitoring well clusters (solid circles). Samples were collected from monitoring wells, Florida Bay, and a canal south of U.S. 1 which is a direct link to the Atlantic-side of the Keys.

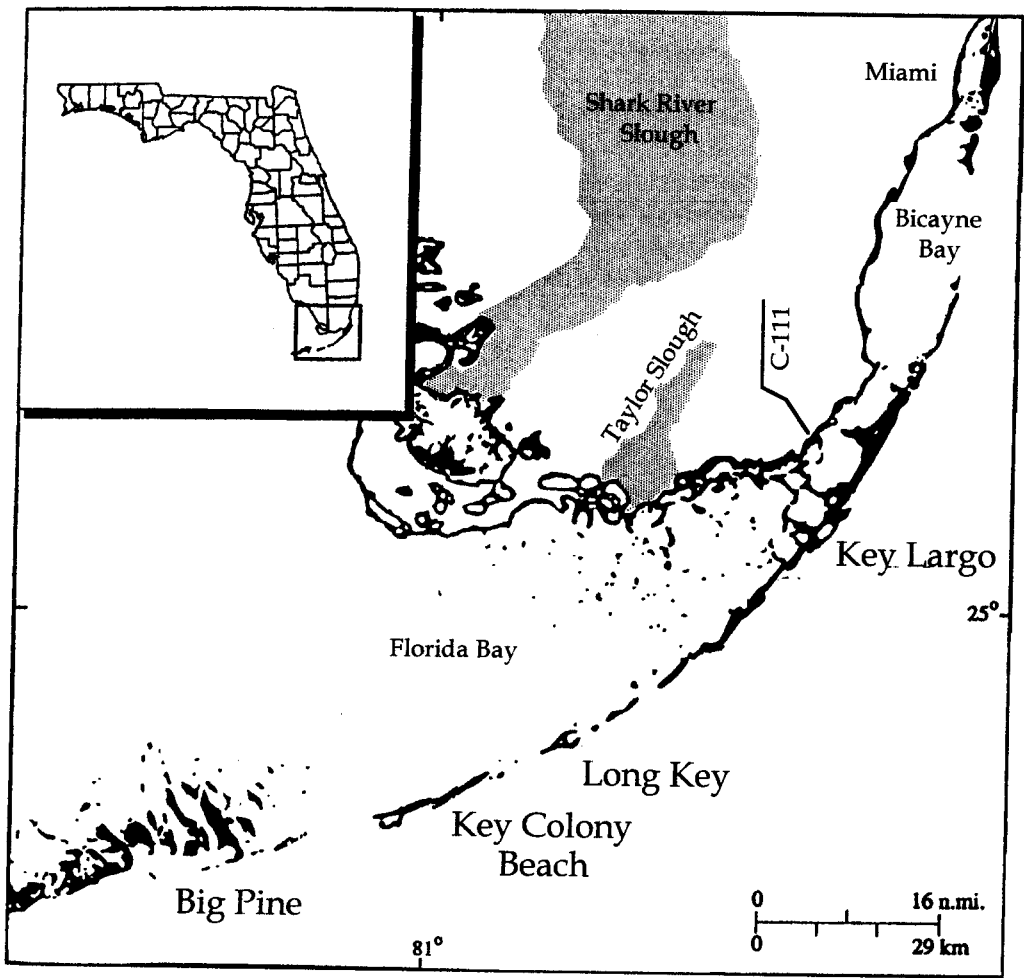
Figure 3. Normalized tracer concentrations over time for SF<sub>6</sub> (closed square) and phosphate (open circle) in well cluster #1-4.5m (A), 9m (B), 13.5m (C), and 18m (D) for the October 1996 experiment. Concentrations are normalized to the initial injection concentrations and multiplied by 10<sup>6</sup> for easier comparison. The SF<sub>6</sub> and PO<sub>4</sub> lines would plot on top of each other if both tracers acted alike, i.e., if PO<sub>4</sub> behaved conservatively. Inset in (C) and (D) show the uptake of phosphate early in the experiment.

Figure 4. Normalized tracer concentrations over time for SF<sub>6</sub> (closed square) and <sup>32</sup>P (open circle) in well cluster #1-4.5m (A), 9m (B), 13.5m (C), and 18m (D) for the June 1998 experiment. Concentrations are normalized to the initial injection concentrations and multiplied by 10<sup>6</sup> for easier comparison. Most of the <sup>32</sup>P samples collected were below detection limit, indicating rapid uptake relative to SF<sub>6</sub>. Note the y-axis break in well# 1-13.5 (C) and 1-18 (D).

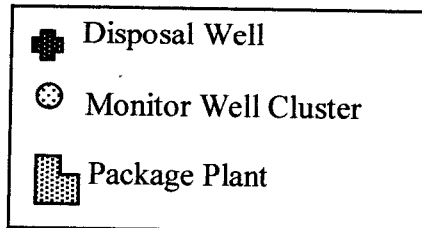
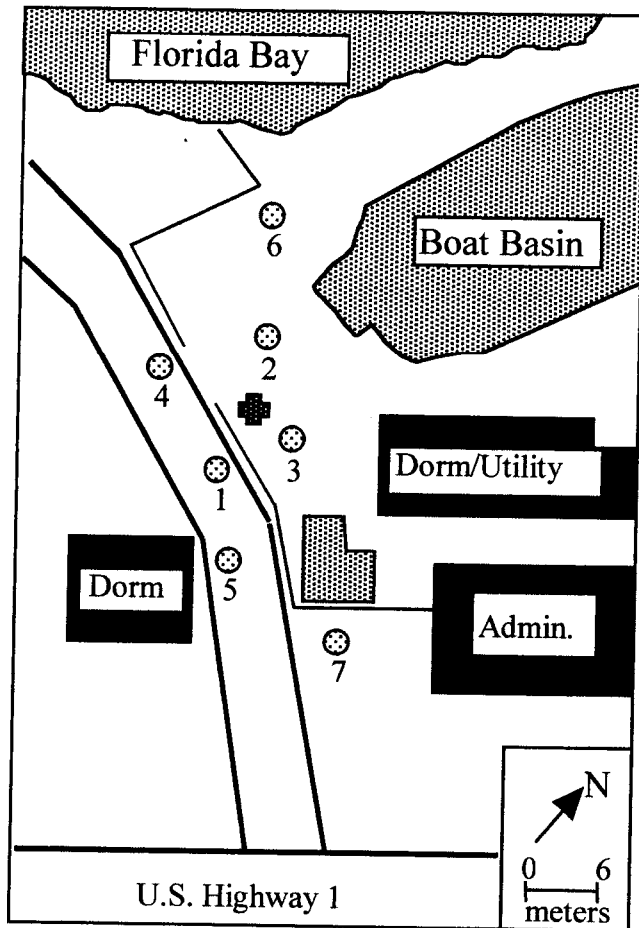
Figure 5. Samples collected from well#1-18 during the phosphate (A), <sup>32</sup>P (B), and nitrate (C) experiments show non-conservative behavior of the nutrients when plotted against the corresponding SF<sub>6</sub> concentration. The solid line represents the ratio of the nutrient to SF<sub>6</sub> trend that would indicate conservative behavior of the nutrient. In each case the nutrient samples fall below the ideal line, while non-reactive <sup>131</sup>I (closed triangles in C) mimics the conservative trend. Note in the <sup>32</sup>P experiment (B) the y-axis has been plotted on a log scale.

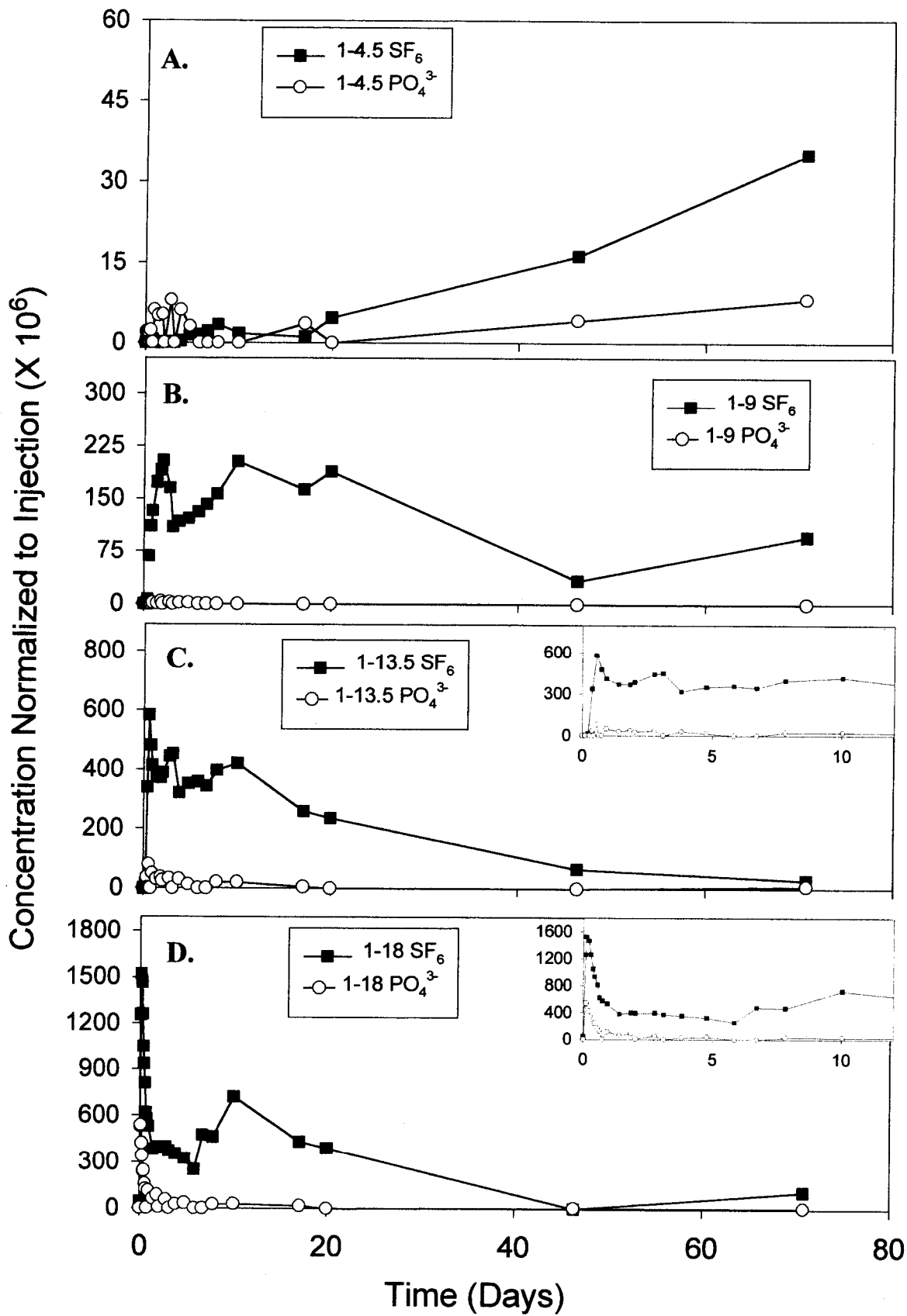
Figure 6. The tracer ratio for the phosphate (A), <sup>32</sup>P (B), and nitrate (C) experiments plotted over time. Both phosphate experiments (A, B) show a rapid uptake followed by a much slower rate of removal. The tracer ratio in these two experiments is also shown to change with depth. The nitrate tracer ratio (C) had apparently already equilibrated by the time the wastewater plume had reached monitor well #1.

Figure 7. Normalized tracer concentrations over time for SF<sub>6</sub> (closed square) and nitrate (open circle) in well cluster #1-4.5m (A), 9m (B), 13.5m (C), and 18m (D) for the February 1997 experiment. Concentrations are normalized to the initial injection concentrations and multiplied by 10<sup>6</sup> for easier comparison.









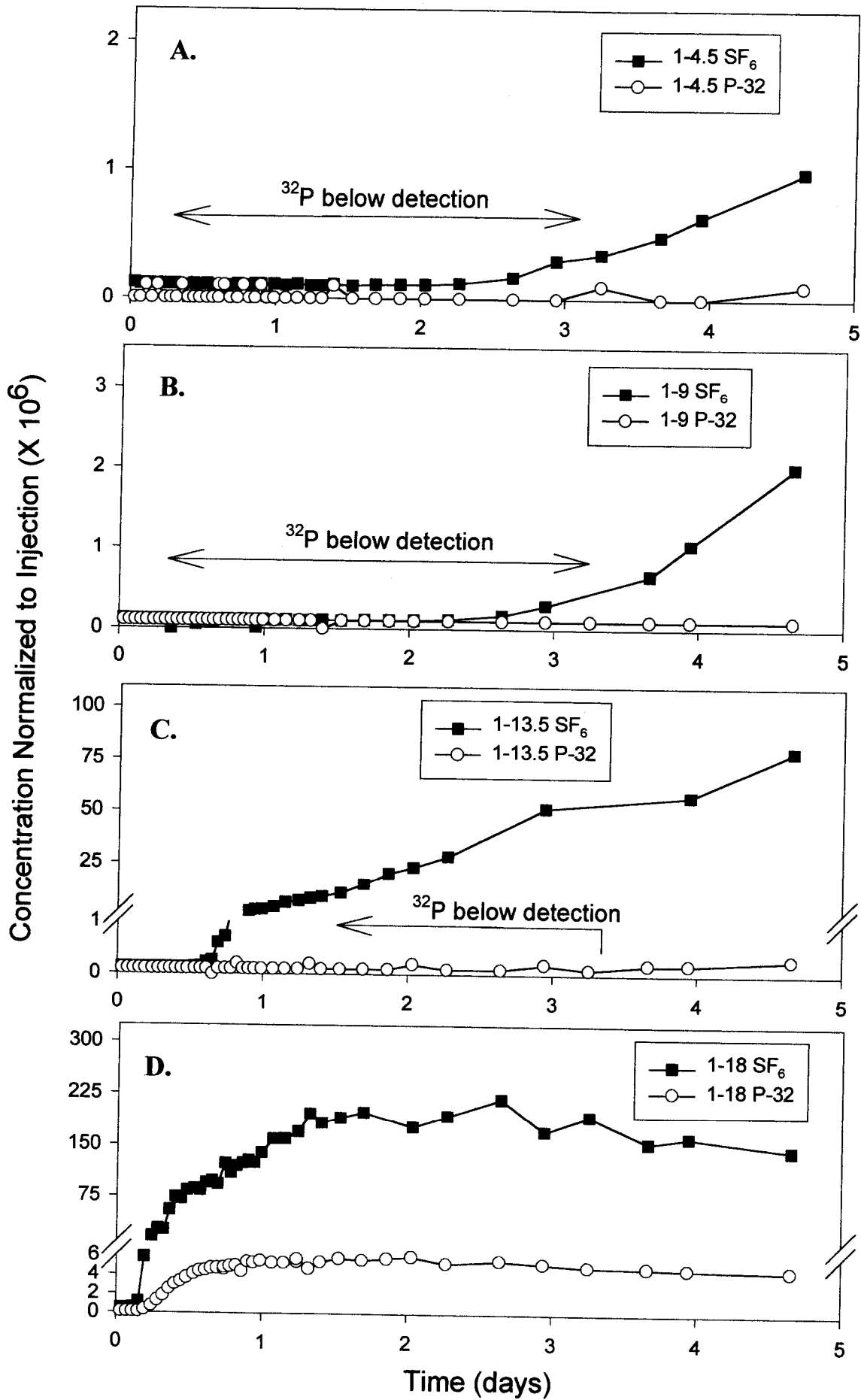
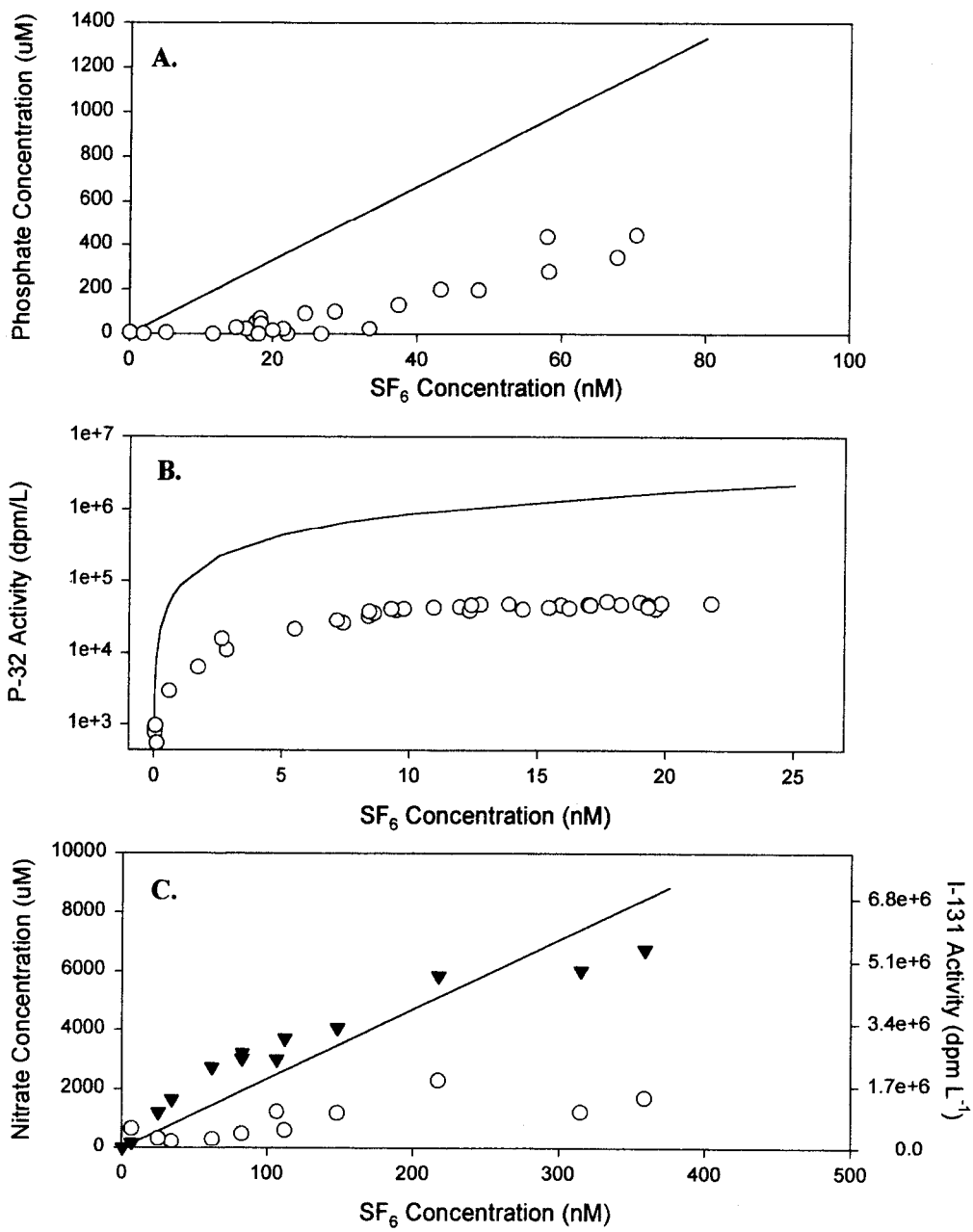


Figure 5



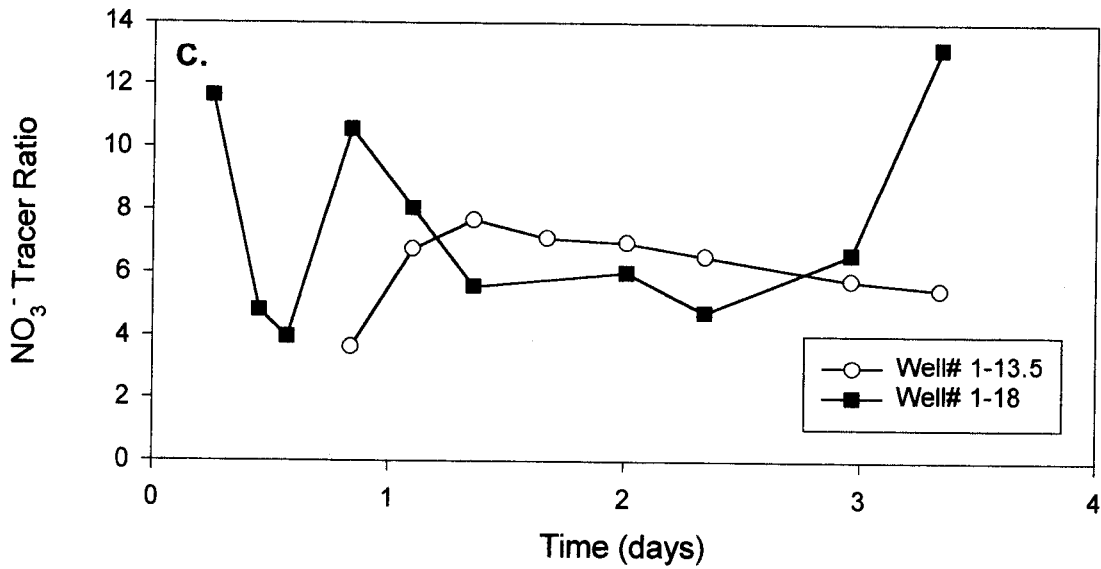
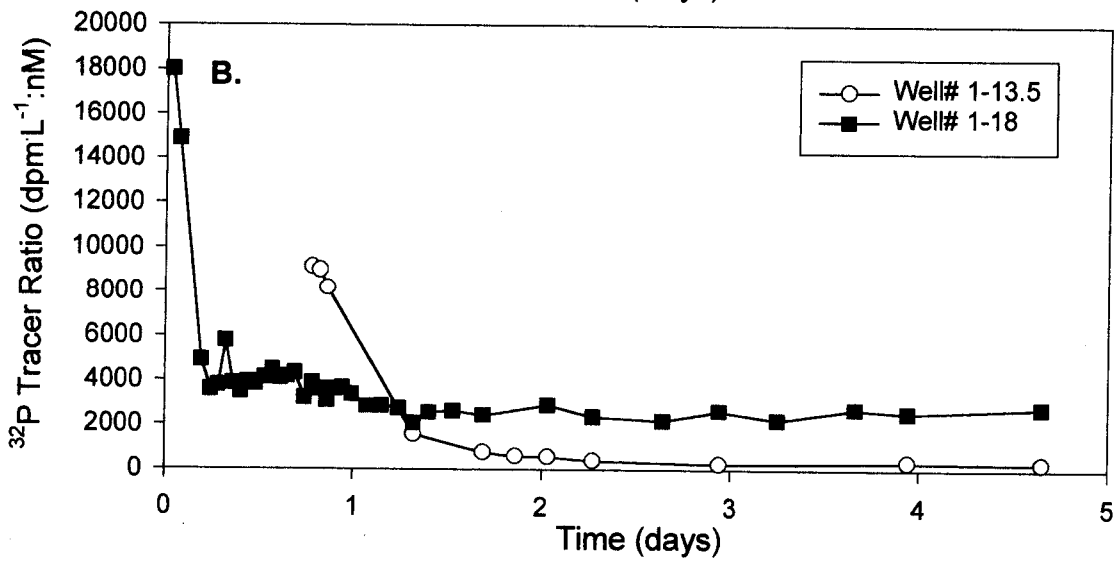
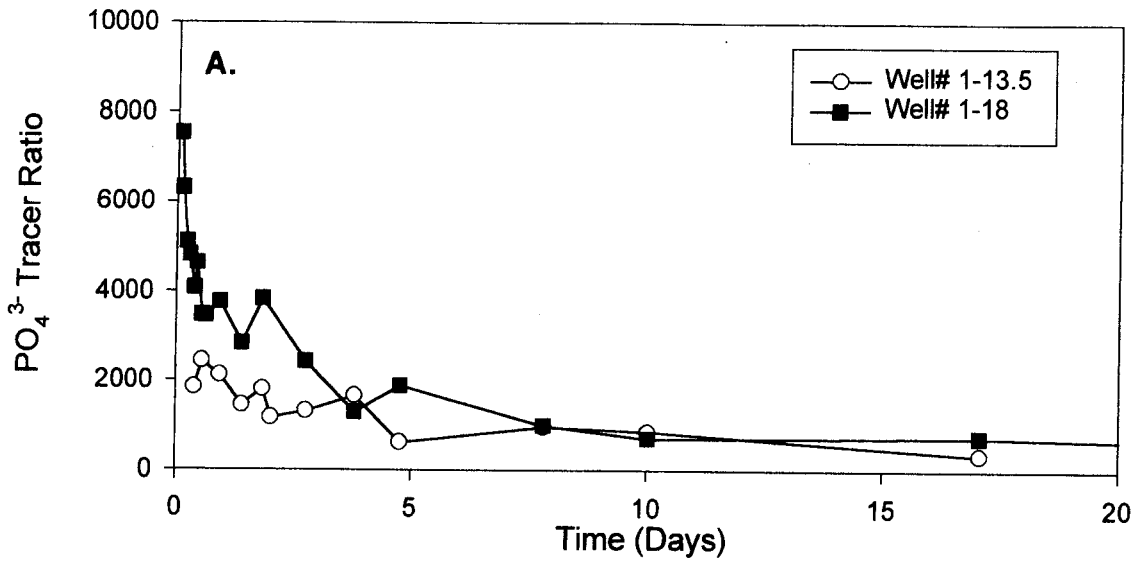


Figure 3

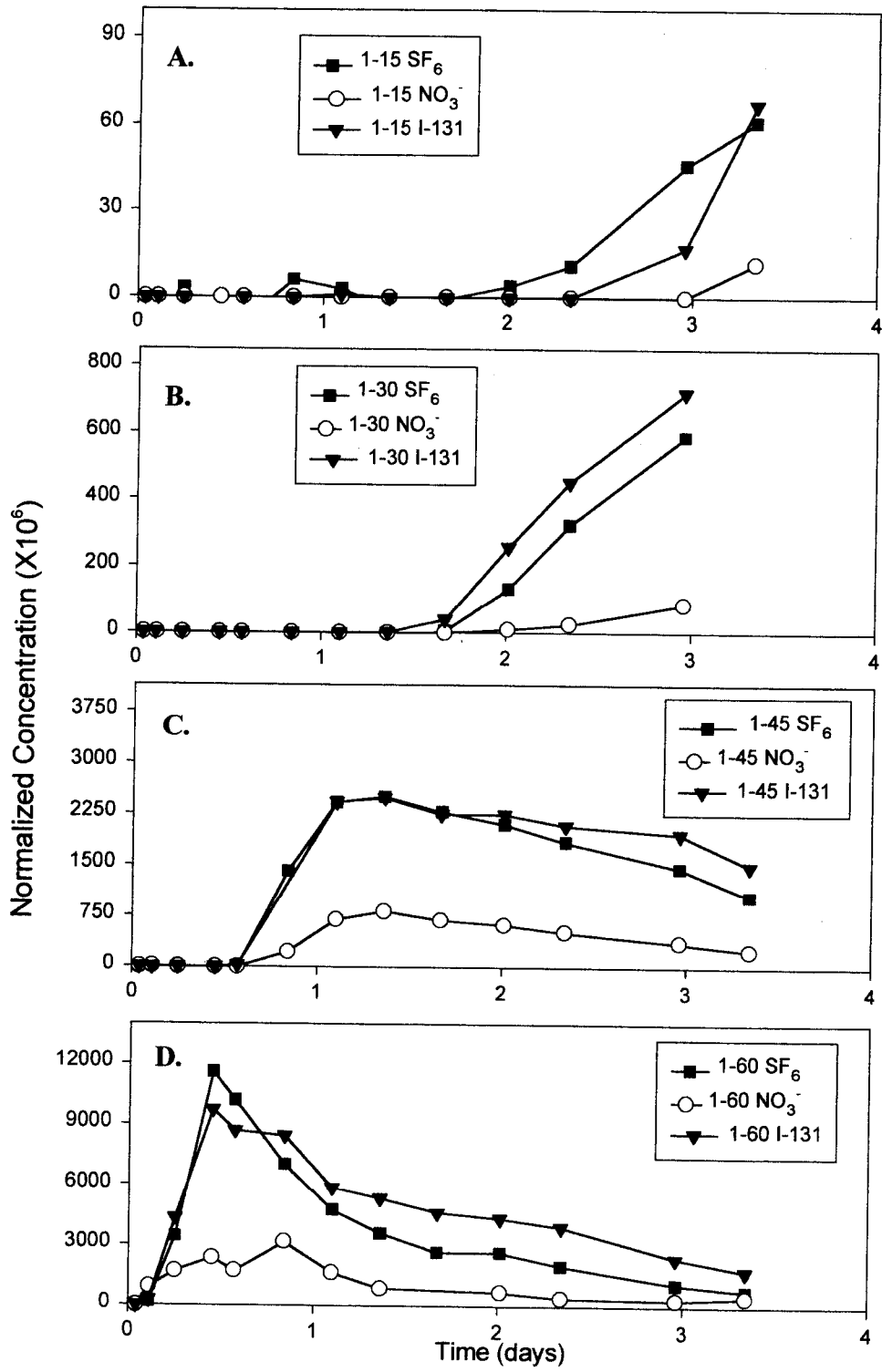


Figure 7

Chapter 2.

FATE OF WASTEWATER-BORNE PHOSPHATE UNDER HIGH DISCHARGE  
CONDITIONS INTO KARST KEY LARGO LIMESTONE

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## **Abstract:**

Two artificial tracer experiments were conducted in a ground water system surrounding a high a volume (500-1200 m<sup>3</sup>/d) wastewater disposal well in the Florida Keys. Bimodal groundwater transport was observed both horizontally and vertically. Slow, dispersive-type flow rates were estimated to be below 0.3 m/d while the most rapid conduit type flow was characterized by flow rates from 7.9 to as high as 123.3 m/d. This highest rate of flow was only observed immediately adjacent to the point of injection, however, at two monitoring wells placed within 4 m of the injection well, which are highly influenced by the continuous injection of wastewater. Vertical transport rates were of the same magnitude as horizontal rates, because of density differences between the fresh waste water plume and the salty groundwater. The wastewater rapidly buoyed to the surface, indicating it is probably not transported under ground kilometers offshore. The shape of the wastewater plume resembled an inverted funnel, with the pointed side down. Transport rates were approximately five times higher in October 1999 than those observed in June 1998 as wastewater discharge increased from  $6.33 \times 10^5$  to  $2.32 \times 10^6$  L/d. Salinity data indicate that the waste water plume extends beneath the entire well field, as far as 175 m from the injection well.

Radiolabelled phosphate experiments showed an initial rapid uptake by the limestone followed by a slower release. Evidence of desorption was observed in several of the wells. The limestone matrix underlying the study site seems to acting as a phosphate buffer, removing PO<sub>4</sub> from solution until an equilibrium concentration of approximately 25 μM is reached. The mechanisms controlling this buffering capacity are poorly understood at this time. We hypothesize that the mechanism is a simple surface reaction process where “old” adsorbed PO<sub>4</sub> is displaced by “new” PO<sub>4</sub> molecules entering the system.



## INTRODUCTION

Although sewage disposal practices are becoming more efficient at nutrient removal, the sheer volume of wastewater to be handled continues to increase at an alarming rate. In addition, monetary interests and logistics often limit the degree to which wastewater can practically be treated and disposed. The Florida Keys is a prime example, as the isolation of these popular islands limits the disposal methods to on-site treatment facilities such as septic tanks and small treatment plants; the latter typically dispose of advanced treated wastewater via injection wells that are 18 - 27 m deep. The fate of these disposed nutrients in the subsurface has become a concern as water quality in the historically oligotrophic waters near the Keys has declined in recent years (Phlips and Badylak, 1996; Phlips et al., 1995, 1999; Fourqurean and Robblee, 1999).

Elevated nutrient concentrations have been observed in canals and nearshore waters in the Keys (LaPointe et al. 1990, LaPointe and Clark, 1992). Jones (REF TALK?) has observed a small but steady increase in total phosphate concentrations in the waters of the Florida Keys National Marine Sanctuary off Key Largo over the last ten years. Due to the oligotrophic nature of the aquatic ecosystem of the Florida Keys, even small increases in nutrient levels may have severe environmental impacts such as an increase in coral reef mortality, proliferations of nuisance algae and decreases in seagrass abundances just to name a few. Phosphate ( $\text{PO}_4$ ) is of particular concern as it has been shown to be the limiting nutrient in Florida Bay (Powell et al., 1989; Fourqurean et al., 1992a,b, 1993) as well as nearshore waters of the Keys (Lapointe, 1987, 1989, 1992). There is most likely a concert of influences effecting water quality in the Keys. Pinpointing and quantifying these sources is essential if restoration steps (which are

currently underway) for Florida Bay are to be successful. Until recently, groundwater input of nutrients into surface waters has been largely ignored in and around the Florida Keys.

Previous studies in the Keys have shown that substances injected into the subsurface whether it be via septic tanks (which are just above or at the water table) or disposal wells (18-27 m depths) can be transported to nearby surface waters in a matter of hours to days (Paul et al., 1997; Dillon et al. 1999; Dillon et al, 2000) due to the high permeability of the Key Largo Limestone (KLL) underlying the Keys. KLL is composed of ancient hermatypic corals with intra and interbedded calcarenites and thin beds of quartz sand (Halley et al., 1995). The feature is extremely porous due to conduits and interconnected pore spaces created by ancient coral growth and meteoric diagenesis (Harrison and Coniglio, 1985; Dodd and Siemers, 1971; Vacher et al., 1992). Porosity estimates from cores collected at Key Colony Beach were ~50% in cores with complete recovery although void areas characterized by poor core recovery were common (Elliott, 1999; Dillon, personal observation). Estimates of hydraulic conductivity (K) for KLL range from 1400 -  $3.84 \times 10^4$  m/d (Vacher et al., 1992; Halley et al., 1995; Dillon et al, 1999).

Estimates of horizontal groundwater transport rates less than 0.14 m/h have been associated with the KLL's primary porosity while rates as high as 3.28 m/hr have been attributed to rapid conduit flow (Dillon et al., 1999; Dillon et al., 2000). In the case of disposal wells, it has been shown that wastewater buoys upwards after injection due to the density differences between the wastewater and the ambient hypersaline waters (Shinn et al., 1994) at rates as high as 8.4 m/d (Dillon et al., 2000). Conduits or preferential flow paths may also act to channel the wastewater upward.

The ability of calcium carbonate to adsorb  $\text{PO}_4$  has documented by many researchers (Cole et al., 1953; Kuo and Lotse, 1972; Griffin and Jurinak, 1973; McGlathery et al., 1994). Corbett et al. (2000) investigated the fate of wastewater borne nutrients at a low discharge (2600 L/day) waste water disposal well and determined that both phosphate and nitrate were removed from solution in the subsurface. There was an initial rapid uptake of  $\text{PO}_4$  presumably due to adsorption to the KLL followed by a removal at a slower rate, which was hypothesized to be due to adsorption-desorption processes. Nitrate removal was also observed to a lesser degree most likely due to denitrification in the anoxic carbon-rich waters surrounding the injection well (IW). The results from this study suggested that nutrients are removed from solution and thus may not have a significant impact on surface waters. However Corbett et al. (2000) do point out that their study was conducted at a low discharge well and that processes may be different at a larger volume IW due to saturation of available adsorption sites and higher organic substrate availability.

This report investigates the largest wastewater disposal well in the Keys using a dual tracer approach similar to that of Corbett et al. (2000) to evaluate groundwater flow patterns as well as the fate of  $\text{PO}_4$  in the subsurface. To evaluate the fate of a reactive compound, such as  $\text{PO}_4$ , one needs to employ a conservative tracer that can be used to account for dilution and other physical mixing processes that affect the solutions being injected. In this case, sulfur hexafluoride ( $\text{SF}_6$ ) was employed as such a tracer. Previous studies have shown that it behaves conservatively in subsurface mediums such as sand and carbonates (Wilson and Mackay, 1993; Dillon et al., 1999; Dillon et al., 2000). It also has the advantage of a low detection limit making it an effective tracer in systems with high dilution rates (Wanninkhof et al., 1991).

Radiolabelled phosphate ( $^{32}\text{PO}_4$ ) was chosen as our reactive tracer for several reasons. A tracer was needed that would behave similarly to stable  $\text{PO}_4$  yet would still allow us to discriminate between our injected tracer and the elevated concentrations of ambient  $\text{PO}_4$  that have developed after 5 years of injection into the disposal wells. In addition, sample collection and processing needed to be relatively quick due to the large numbers of samples that would be generated in a short time. Another advantage of  $^{32}\text{PO}_4$  is that its short half life (14.3 days) results in the tracer decaying away in a matter of months, making additional tracer studies possible without concern with residual tracer affecting the results.

The main objective of this study was to replicate the study of Corbett et al. (2000) at a high discharge site to see if the  $^{32}\text{PO}_4$  would behave differently under high discharge conditions. We hypothesized that phosphate adsorption rates would not be as great due to higher flow and greater organic loading. We questioned if the  $\text{PO}_4$  removal properties of the limestone would be overwhelmed or saturated by this high volume injection well. Our objectives with this study were to test this hypothesis as well as to determine groundwater flow rates (vertical and horizontal) using artificial groundwater tracers. Additional objectives were to characterize the size of the wastewater plume and to document the evolution of such a plume beneath a high volume wastewater facility. Additional research efforts investigating denitrification rates in the subsurface is currently ongoing and will be presented elsewhere.

## METHODS

### Study site and injection methods

Key Colony Beach (KCB) is a man-made island on the Atlantic side of the Florida Keys just northeast of the city of Marathon (Figure 1). The island was built up in the 1950's from

submerged KLL using dredge material from newly excavated canals and an imported marl like mud which was laid over the limestone dredge material. Like all of the upper Keys, the salinity of the ambient groundwater is high (>35 ‰), so it is not potable and is not used for irrigation purposes. Cores collected show that the mud layer is very impermeable, extends to depths of approximately 3-6 m and is underlain by Key Largo limestone, which has a very high porosity. Elliott (1999) calculated porosities of 52-60% in cores with high recovery (>90%). The approximately 500 to 1200 m<sup>3</sup> of wastewater that is generated daily on the island undergoes secondary treatment in an on-site wastewater treatment facility and is then injected into the subsurface to a depth of 18 - 27 m via an array of 5 injection wells (IWs). Under normal conditions the effluent is injected into only 1 or 2 of the centermost IWs. Twelve monitor well clusters have been installed around the centermost IW, which receives the most effluent. Each cluster contains two or three monitor wells drilled to various depths ranging from 3 to 18 m.

Initially, only 7 well clusters were installed (clusters A - G) in order to conduct a preliminary tracer experiment to determine groundwater flow rates and directions. Wells were installed as described Shinn et al. (1994). A more detailed description of well construction, development, and recovered core material can be found in Elliott (1999). Wells are referred to by their cluster letter followed by their depths in meters. For example, the 18.3 m well in cluster A is referred to as A-18.

In June 1998, an injection slug was prepared by sparging a 900 L parcel of tap water with SF<sub>6</sub> for 80 minutes to saturate the slug with this gaseous tracer. Fluroscein was also used as a tracer to serve as a visual aid in the early stages of the experiment so the plume's movement could be roughly evaluated while sampling the well field, but no fluroscein results are included in this report. After the slug was prepared, it was then sampled for the tracers and

was then pumped into the center disposal well at a rate of 70 L/min. The surrounding monitor well clusters were then sampled for the presence of the tracers for 83 days. Canals to the east and west of the well field were also sampled for SF<sub>6</sub>. Daily disposal well flow rates were obtained from the staff of the KCB sewage treatment plant. Nutrient samples (NH<sub>4</sub>, NO<sub>2</sub> + NO<sub>3</sub>, and PO<sub>4</sub>) were collected from each well on June 6, 1998 as described by Elliott (1999).

After the initial experiment was completed, the well field was reevaluated and 5 more monitor well clusters (clusters H-L, Figure 1) were installed in May 1999 to obtain better coverage. After these new wells were developed and allowed to equilibrate for several months, the dual tracer experiment (SF<sub>6</sub>/<sup>32</sup>P) was conducted.

In September 1999, an injection slug was prepared by sparging 1040 L of tap water with SF<sub>6</sub> for 90 minutes. Next, 500 mCi of radiolabelled PO<sub>4</sub> was added to the slug as H<sub>3</sub>PO<sub>4</sub>. After mixing the slug with a high circulation pump, it was injected into the centermost well at a rate of 86 L/min. The surrounding monitor well clusters were then sampled for SF<sub>6</sub> and <sup>32</sup>PO<sub>4</sub> for 30 days. Salinity was measured at each well prior to starting the experiment. Well heads were also measured regularly during the experiment in order to determine the piezometric surface and the resultant flow directions at various depths of the well field. In addition, nutrient samples (PO<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub> and NH<sub>4</sub>) were collected from each well on day 8 of the experiment to evaluate the size of the subterranean wastewater plume.

Well water heights were measured with a Solinst water level meter (Model 101). Well heights for monitor well clusters A-G were surveyed with a computerized theodolite surveying system, which could reproduce measurements with an average standard deviation of 0.5 cm. Each well's height was measured relative to a USGS monument designation with a stated elevation relative to mean sea level.

Ground water transport rates were determined for each sampling location by dividing the distance from the IW by the arrival time of the peak concentration. Multiple well depths at each well cluster also allowed vertical transport rates to be calculated. For these estimates, the wells' depths were subtracted from the minimum injection depth (18.3 m) and then divided by the arrival time of peak tracer concentration. Thus these vertical rates represent lower limits if the injectate went to deeper depths initially.

### Sampling methods

Each well was purged for 3 well volumes before being sampled. Purge water was stored in a large tank for the first 9 days of the experiment, after which it had to be injected into the main disposal well due to lack of further storage space for the accumulating purge water. Due to the tendency for SF<sub>6</sub> to bind to plastics, each well had its own unique piece of sampling tubing. All samples were collected with a peristaltic pump. SF<sub>6</sub> samples from wells were collected in 30 mL serum bottles while those from canals were collected in 160 mL serum bottles. After rinsing the tubing and the serum bottle three times, each sample was pumped into the bottle with the tubing at the bottom and allowed to overflow for approximately three volumes. The sample was then sealed with a rubber septa. To prevent loss of SF<sub>6</sub> through the septa, the samples were stored upside down until analysis.

Two types of radiolabelled phosphate samples were collected for the dual tracer experiment: a 20 mL sample for direct counting by a liquid scintillation counter and a 1 L sample from which the PO<sub>4</sub> was concentrated and then counted to allow for greater sensitivity and a lower limit of detection. <sup>32</sup>PO<sub>4</sub> sample containers were not rinsed with sample water

prior to sample collection due to the tendency of  $^{32}\text{P}$  to bind to surfaces. Tubing was rinsed with sample water prior to sample collection. For the 20 mL samples, a plastic 20 mL scintillation vial was filled with sample water only and sealed with a plastic cone cap. The 1 L samples were pumped into clean plastic containers, which were then sealed and transported to the Keys Marine Laboratory where the samples were processed and preliminary measurements were made with a portable scintillation counter. More accurate counts (which are reported here) were made on all  $^{32}\text{PO}_4$  samples upon arrival at the FSU radiation research facility. Results from the portable scintillation counter can be found in Kim et al. (in press).

Nutrient samples from June 1998 were pumped directly into 500 mL polyethylene bottles without filtration while September 1999 nutrient samples were filtered through ashed glass fiber filters (Whatman GF/F, nominal pore size = 0.7 microns) and collected in 250 mL polyethylene bottles. In each case, sample bottles were rinsed with sample filtrate 3 times, filled and frozen until analysis could be performed. All nutrient samples were analyzed within one month of collection.

## **Analytical methods**

### Sulfur hexafluoride

Sulfur hexafluoride samples were analyzed with a Shimadzu model 8A gas chromatograph equipped with an electron capture detector. The gas chromatograph contained a stainless steel column (180 cm x 0.1 cm ID.) packed with molecular sieve 5A (80/100 mesh).



Ultra-high purity nitrogen was used as the carrier gas. Column and detector temperatures were set at 90°C and 220°C, respectively. SF<sub>6</sub> was extracted from the samples with a variation of a headspace extraction technique: samples were extracted in the lab by adding a small headspace (typically 4 mL) of ultra-high purity nitrogen to the sample. To allow room for the added headspace, a volume of water from the sample bottle had to be simultaneously removed and discarded. The serum bottles were slightly over pressurized with 1 cc of nitrogen to allow several injection volumes (100 µL or less) for the gas chromatograph (GC) to be pulled from each sample. The samples were shaken for two minutes to extract the SF<sub>6</sub> from solution into the headspace. The minimum detection limit for this method is 1.0 pM (1 pM = 10<sup>-12</sup> M) for 30 mL samples and 0.1 pM for 160 mL samples. A more detailed description of this headspace extraction technique can be found in Dillon et al. (2000).

#### Radioactive phosphate (<sup>32</sup>PO<sub>4</sub>)

The 1 L <sup>32</sup>PO<sub>4</sub> samples were first acidified with concentrated HCl to pH ~2. Then, 1 mL 20 mM of PO<sub>4</sub> carrier (KH<sub>2</sub>PO<sub>4</sub>) was added, which is on the same order of expected natural PO<sub>4</sub> concentration in the pure wastewater, which is approximately 25 µM. The samples were then vigorously stirred to equilibrate the natural PO<sub>4</sub> and carriers, and 1 mL 300 mM of Zr carrier (ZrOCl<sub>2</sub> • 8H<sub>2</sub>O dissolved in water) was added to precipitate the ZrPO<sub>4</sub>. The samples were stirred again while the precipitates formed. The samples were allowed to settle for at least 30 minutes and were then filtered through Whatman GF/B filters. Filters were then placed in a scintillation vial with a cocktail / acid mixture and then counted with a Wallac 1414 scintillation counter. After each sample batch, all filtration apparatus were thoroughly cleaned with 6 M HCl followed by deionized water to prevent cross contamination. Untreated 20 mL

$^{32}\text{PO}_4$  samples were counted with a Wallac scintillation counter. All  $^{32}\text{P}$  activities were decay corrected back to the time of injection. The detection limit with this method was below the background beta activity (~ 32 dpm/L). A more thorough explanation of this protocol is described by Kim et al. (in press).

### Nutrients

For June 1998 ammonia, nitrate + nitrite, and phosphate were measured by automated spectrophotometry on a Technicon Autoanalyzer II according to EPA methods as described by Elliott (1999).

Nutrient analysis for September 1999 are described herein. Nitrate + nitrite was measured with a chemiluminescence detector after being reduced to nitric oxide in an acidic medium containing vanadium (III) at 80-90° C. The nitric oxide is removed from the reaction solution by scrubbing with helium carrier gas and is then detected by the chemiluminescence  $\text{NO}_x$  detector. This method is very sensitive and requires less than 1 mL of sample. Nitrite concentrations were determined colorimetrically as described by Parson and Strickland (1972). Nitrate concentrations were then determined by the difference. The lower limit of detection for  $\text{NO}_3$  and  $\text{NO}_2$  were 0.5 and 0.1  $\mu\text{M}$ . Ammonium was measured colorimetrically with a modification of the phenol-hypochlorite method described by Parson and Strickland (1972). Soluble reactive phosphate was also determined colorimetrically as described by Parson and Strickland (1972). The lower limits of detection for  $\text{NH}_4$  and  $\text{PO}_4$  were both 0.5  $\mu\text{M}$ .

## RESULTS

### Preliminary artificial tracer experiment - June 1998

Nutrient concentrations of groundwater from each well are presented in Table 1. On June 6, 1998 the injected wastewater had a  $\text{PO}_4$  concentration of  $92.99 \mu\text{M}$ . Wells A-18, B-18 and C-9 had  $\text{PO}_4$  concentrations of 52.63, 50.69 and  $25.51 \mu\text{M}$ , respectively. Well F-8 located 80 m north of the IW had a  $\text{PO}_4$  concentration of  $9.69 \mu\text{M}$ . Wells E-9 and G-9 had respective  $\text{PO}_4$  concentrations of 1.94 and  $1.61 \mu\text{M}$ . All other wells had  $\text{PO}_4$  levels less than  $1 \mu\text{M}$ .

During the first 11 days of the June 1998 experiment, the average wastewater injection rate was  $6.33 \times 10^5 \text{ L/d}$  with a standard deviation of  $7.95 \times 10^4 \text{ L/day}$ . The 900 L injection slug had a  $\text{SF}_6$  concentration of  $27.32 \pm 3.41 \mu\text{M}$ . Peak tracer concentrations and times are summarized in Table 2 along with the calculated transport rates. At no time during this experiment was tracer observed in any of the shallow wells (4.6 m) which are located within the impermeable mud layer. Elliott (1999) has shown that water from this depth is hypersaline, anoxic and ammonium rich. The mud layer appears to act as an aquitard, preventing exchange between groundwater below the mud layer and recharge from above.

The first major flow path observed was toward well C, 9.1m (15 m southeast of IW).  $\text{SF}_6$  concentrations here rose rapidly, reaching a peak concentration of  $3.98 \pm 0.05 \text{ nM}$  after 5.9 days (Figure 2a), a dilution of approximately 6900 times the injection slug. Note that the salinity data indicates that this dilution was primarily from wastewater that has accumulated under the study site. A horizontal transport rate (HTR) of 2.52 m/d and a vertical transport rate (VTR) of 1.54 m/d were calculated from this well. No  $\text{SF}_6$  was detected in the deep well (18.3 m) at well cluster C. At well cluster B (15 m southwest of the disposal well), however,  $\text{SF}_6$  was

only observed at the deep well (18.3 m) reaching a maximum concentration of  $1.96 \pm 0.01$  nM at 10.0 days, yielding a HTR of 1.50 m/d (Figure 2b). The tracer was observed at both depths at well cluster A, 15 m due south of the IW (Figure 2c). After 18.8 days, the deep well (18.3 m) reached a peak concentration of  $0.33 \pm 0.08$  nM (HTR = 0.80 m/d) while at the shallower well (9.1 m) concentrations began to rise slowly after about 2 weeks eventually rising to 0.51 nM after 55.1 days (HTR = 0.27 m/d, VTR = 0.17 m/d). Tracer was next observed in well cluster D (~78 m east of IW) at a depth of 9.1 m after approximately 3 weeks and continued to climb to 0.81 nM after 55.1 and 65.0 days. This concentration is only four times less than that observed at the 9.1 m well at cluster C, suggesting that a large fraction of the wastewater plume is advected in an easterly direction after buoying up to the mud layer.

SF<sub>6</sub> samples collected from canals also support evidence of a predominately easterly transport direction during this experiment. Canals to the east and west were each sampled for SF<sub>6</sub> at three different locations. The west canal is approximately 84 m from the wastewater injection well while the east canal is about 200 m away. Despite the large disparity in their distances from the IW, both canals began to show traces of SF<sub>6</sub> after 35 days (Figure 3). The west canal reached a peak concentration of  $1.24 \pm 0.01$  pM at canal station 3 after 55 days. The east canal, however reached a higher maximum concentration of  $4.15 \pm 1.1$  pM at canal station 5 after 65 days. HTR's of 3.08 and 1.52 m/d were calculated for the west and east canal, respectively. The higher concentrations observed in the east canal along with the rapid transport in this direction also suggest that the bulk of the wastewater plume was transported to the east.

#### Dual-tracer experiment - September 1999

In May 1999, 5 more wells were installed to obtain better coverage of the well field. Monitor well cluster H and I were installed just to the north and south of the IW in order to evaluate how rapidly the wastewater plume rises. Well cluster J and K were installed along the eastern transect of well clusters to better describe the eastern transport of the wastewater plume. Well L was placed within the treatment plant to determine whether a significant portion of the plume was transported northward. Well B-9 was lost before the dual tracer experiment was conducted. The well became clogged with sediment after a Hurricane Georges and could not be cleared.

The average wastewater injection flow during the first 19 days of the experiment was  $1.65 * 10^6 \pm 5.94 * 10^5$  L/day. This average actually represents only 11 of the 19 days as the treatment plant is closed on weekends and thus measurements were not made on Saturdays or Sundays. Since the population on KCB likely increases during the weekend due to increased tourism, this average is most likely a minimum value. In addition, there was also one day when the plant's flow meter was inoperative. The  $PO_4$  concentration of both  $NO_3$  and  $PO_4$  were much less than those measured in June 1998 (Tables 1 and 3) due to technological improvements made in the treatment plant. Well head measurements were made throughout the dual tracer experiment. As observed by Elliott (1999), well heads at all clusters oscillated up and down with the Atlantic tide. Several studies observing this type of groundwater movement has also been observed elsewhere in the Keys (Shinn et al., 1994; Machusak and Kump, 1997; Dillon et al., 1999; Corbett et al., 1999; Dillon et al., 2000). There was no measurable time lag (> 30 min) between different well clusters' fluctuations and the Atlantic tide, indicating a very high hydraulic conductivity for the KLL at this location.

Since all the well head fluctuations were synchronized, there was very little overall variation in the hydraulic gradient across the study site during the time of the experiment. Figure 4 shows typical piezometric surfaces at two different depths of the well field and illustrates the driving force for groundwater movement at this site. Arrows indicate groundwater flow directions. At 18.3 m, there is radial movement of wastewater away from the "mound" of water caused by continuous injection of wastewater. After buoying up to the mud layer due to density differences, the plume is advected downgradient in an easterly direction. At 9.1 m, the hydraulic gradient is sloped from the west to the east, most likely due to water level differences between Florida Bay and the Atlantic Ocean.

Nutrient and salinity measurements made from the monitor well clusters during the dual-tracer experiment (Table 3) also illustrate the movement of the wastewater plume beneath Key Colony Beach. A map view of the plume's phosphate concentrations can be seen in figure 5. Low salinities and elevated nitrate concentrations were highly correlated with increasing phosphate concentrations. Phosphate concentrations as high as injected wastewater ( $25.85 \mu\text{M}$ ) were found up to 15 m from the disposal well at various depths of the well field. Concentrations at the 18.3 m wells drop rapidly with increasing distance from the IW to 0.73, 0.52, and  $1.61 \mu\text{M}$  at wells E-18, J-18 and F-18, respectively. Well cluster G's deep well (G-18) showed a slightly elevated concentration of  $2.8 \mu\text{M}$ . At a depth of approximately 9 m, the plume extends much further east. In fact, phosphate levels were slightly higher at well K-8 ( $7.90 \mu\text{M}$ ) than at well D-9 ( $6.19 \mu\text{M}$ ) even though well cluster K is approximately 100 m further from the IW than cluster D. Nitrate concentrations at well K-8 ( $492.39 \pm 1.52 \mu\text{M}$ ) were actually higher than that of the wastewater being injected at the time of sampling ( $381.40 \pm 1.99 \mu\text{M}$ ). These data most likely indicate that wastewater richer in nutrients was injected

weeks or months prior to our experiment. The phosphate concentration in the east canal was below detection while the  $\text{NO}_3$  concentration was  $3.97 \mu\text{M}$  (Table 3).

On September 29, 1999 a 1040 L injection slug laden with both  $\text{SF}_6$  and  $^{32}\text{PO}_4$  was injected into the centermost disposal well at a rate of 87 L/min. The  $\text{SF}_6$  concentration of this slug was  $23.81 \pm 1.58 \mu\text{M}$  and the  $^{32}\text{P}$  activity was  $9.34 \times 10^8$  dpm/L. For convenience, both  $\text{SF}_6$  and  $^{32}\text{PO}_4$  data have been normalized to the injection slug's  $\text{SF}_6$  concentration and  $^{32}\text{P}$  activity, respectively, and then multiplied by  $10^6$  to put the numbers on a better scale. Treating the data in this fashion allows differences in the tracers' subsurface behaviors to be easily seen. If both tracers acted conservatively, their normalized breakthrough curves would be identical. If the  $^{32}\text{PO}_4$  curve lies beneath that of the  $\text{SF}_6$  then  $\text{PO}_4$  uptake can be inferred. On the other hand, a normalized  $^{32}\text{P}$  ratio greater than that of the  $\text{SF}_6$  implies  $^{32}\text{PO}_4$  is being released back into solution from the KLL.

Canals were not sampled for  $^{32}\text{PO}_4$  during the dual-tracer experiment due to the short half-life of  $^{32}\text{P}$ , high dilution rates and expected phosphate uptake (as observed by Corbett et al., 1999) that occurs as the plume travels to the canals. It was reasoned that the radioactive tracer would likely be undetectable by the time it reached the canals due to radioactive decay, dilution and adsorption to the KLL and that time would be better invested concentrating our sampling efforts on the well field.

Results from the two different methods of  $^{32}\text{P}$  measurements were highly correlated ( $r^2 = 0.99$ ,  $n=120$ ). Due to the lower limit of detection and the higher sensitivity of the precipitation method, only data obtained with this method is presented in this report. A more detailed discussion and comparison of the two methods can be found in Kim et al. (in press).

A summary of normalized peak tracer times and ratios as well as the calculated transport rates (both horizontal and vertical) from the dual-tracer experiment are summarized in Table 4. As was expected, both tracers were seen rapidly at well clusters H (3.7 m south of the IW) and I (2.5 m north of IW). These cluster each have 3 wells with depths of 9.1, 13.7, and 18.3 m. Peak tracer concentrations were measured within 48 and 74 minutes (for H and I, respectively) of injection at the deepest wells at these two clusters. The breakthrough curves for both tracer ratios at well I-18 are shown in Figure 6.

Approximately 45% of the  $^{32}\text{PO}_4$  was immediately removed from solution as can be seen by the disparity between the peaks of the two tracers' normalized breakthrough curves. The deep well at cluster H indicated even more removal with 77% of the  $^{32}\text{PO}_4$  being stripped from solution. Tracer concentrations in the shallowest wells (9.1 m) of clusters I and H peaked after 2.2 and 4.5 hrs and indicated removal of 79 and 95% of the  $\text{PO}_4$ , respectively.

The mid-depth (13.7 m) wells at clusters H and I showed a different pattern as can be seen in Figure 7a. At both of these wells, the peak  $\text{SF}_6$  concentrations took much longer to arrive (40.4 and 16.7 hrs for H-14 and I-14, respectively; Table 4). Corresponding  $^{32}\text{PO}_4$  activities were near or below background levels, indicating total removal of the radiolabelled tracer from solution. After 15 days, the normalized  $^{32}\text{P}$  ratio at these intermediate depth wells slowly began to increase above the  $\text{SF}_6$  normalized ratio. The slow tracer arrival as well as the greater  $^{32}\text{PO}_4$  removal rate suggests that there is a relatively dense area of KLL around these well's screened portions. This wastewater flow through this less permeable feature appears to be much slower and thus allows for much greater removal of  $^{32}\text{PO}_4$  due to greater surface area of KLL with which the wastewater comes into contact. The rapid appearance of both tracers at the shallow wells at clusters H and I does suggest that this feature isn't very large, as there



seems to be flow around or through it via less permeable limestone, conduits and/or dysgenic features.

After the initial adsorption of the  $^{32}\text{PO}_4$  to the limestone, there seems to be a remobilization of the tracer due to desorption reactions that aren't well understood at this time. After 0.5 days, the  $^{32}\text{PO}_4$  ratio rises above the  $\text{SF}_6$  ratio at well I-18 (Figure 6) indicating remobilization of the  $^{32}\text{PO}_4$ . Smaller desorption rates were also observed at wells I-9, H-9 and H-18 (after 1.9, 6.4 and 15.1 days, respectively). In each of these wells,  $^{32}\text{PO}_4$  ratios remained above the  $\text{SF}_6$  ratios for the duration of the experiment (30 days) as was also observed in wells H-14 and I-14.

After 1.9 days, maximum  $\text{SF}_6$  ratios of 180.6 and 31.3 were calculated for wells A-18 and C-18, respectively (Table 4). At well A-18 (Figure 7b),  $\text{SF}_6$  ratios dropped exponentially to a value of 0.4 at day 30 while  $^{32}\text{PO}_4$  ratios slowly began to rise, eventually climbing to 5.6 after 30 days, suggesting that  $^{32}\text{PO}_4$  desorption is occurring up to 15 m from the IW. At well C-18, radiotracer activity was near or below background levels for the entire experiment, indicating the radiolabelled phosphate was stripped to levels below detection in the 1.9 days it took the  $\text{SF}_6$  to reach this well. Evidence of phosphate desorption was not observed at well C-18.

Well C-9 showed maximum concentrations of both tracers at 3.1 d with initial  $^{32}\text{PO}_4$  ratios being approximately 10% of the  $\text{SF}_6$  ratios, indicating 90% initial adsorption (Table 4). After 15 days, there is evidence for small amounts of  $^{32}\text{PO}_4$  desorption although it is much less than that observed at the other wells (data not shown). Well J-6 was the next well to show a peak in  $\text{SF}_6$  concentrations, reaching a maximum  $\text{SF}_6$  ratio of 41 after 4.2 days (Table 4). The

very small  $^{32}\text{P}$  activity that was measured at this well indicated a  $^{32}\text{PO}_4$  uptake of 99.5%.  $^{32}\text{P}$  activities at this well then fell below detection and remained so for the duration of the experiment.

A small  $\text{SF}_6$  peak was observed at well A-9 after 15 days although no  $^{32}\text{P}$  was detected (Table 4). Small concentrations of  $\text{SF}_6$  were beginning to appear in wells D-9, E-18 and J-14 when the last samples were collected at 30 days. No detectable  $^{32}\text{P}$  was observed in either of these wells (Table 4). Very small background concentrations of  $\text{SF}_6$  were observed at well E-9 and at well D-14 (data not shown). The minute  $\text{SF}_6$  concentrations ( $<2$  pM) at these wells were present before the injection occurred and didn't change significantly during the experiment indicating that this was residual  $\text{SF}_6$  from the previous tracer experiment. No other wells showed detectable levels of either tracer during the experiment.

## DISCUSSION

A comparison of nutrient data collected from well cluster D (Tables 1 and 3) shows that the wastewater plume's phosphate concentrations appear to be increasing with time despite the fact that WW  $\text{PO}_4$  concentrations has decreased significantly due to changes in the treatment process within the package plant. Although  $\text{PO}_4$  concentrations 15 m from the injection well (wells A-18 and B-18) have decreased to reflect this difference, the  $\text{PO}_4$  concentrations at well D-9 have increased tenfold from  $0.65$   $\mu\text{M}$  in June 1998 to  $6.19$   $\mu\text{M}$  in September 1999. The same cannot be said of  $\text{NO}_3$  concentrations, which were lower during the September dual tracer experiment and seem to be much more variable over time (data not shown) most likely

due fluctuations in the treatment process. Additional data were collected to examine the fate of nitrate in the subsurface and will be presented elsewhere (Dillon et al., in prep)

Bimodal flow was observed in both experiments conducted in this study as was reported by Dillon et al. (2000) at a low volume disposal well. Typical groundwater transport rates at Key Colony Beach ranged from 0.27 to 19.23 m/d in wells located at least 15 m from the injection well. Rates as high as 123.33 m/d were measured in well clusters H and I, which are both within 4 m of the injection well and are highly effected by the continuous injection of wastewater. Typical rates in this study were lower than those reported for a low discharge facility, which were as high as 52.8 m/d (Dillon et al., 2000). The slower flow rates are likely due to the larger plume size at this site which may provide a deeper, larger mixing zone.

Transport rates were approximately 5 times more rapid at KCB in September 1999 than those in June 1998 most likely due to the greater daily wastewater injection rate in September 1999 ( $1.65 * 10^6$  L/day) than in June 1998 ( $6.33 * 10^5$  L/day). A greater difference between the water levels of Florida Bay and the Atlantic Ocean may have also contributed to the increased transport rates. There was greater precipitation before and during the September 1999 campaign, which may have contributed to the steeper gradient at this time. Although the impermeable mud layer acts to prevent recharge on KCB, there is a storm water injection well north of the sewage treatment plant that receives stormwater from a shallow holding pond during times of heavy rainfall. No records are kept of this volume of stomwater injected into the subsurface but it may have contributed to the elevated gradient in September 1999. The nutrient concentration of this storm water has not been characterized and may represent an additional source of nutrients to the subsurface.

Both experiments showed that the wastewater plume rises quickly after injection and is then advected eastward by the regional groundwater flow at this depth. Results from well cluster A indicate that the plume movement can vary temporally most likely due to different injection rates into the disposal wells. In June 1998, the SF<sub>6</sub> maximum was observed in the 9.1 m well after approximately 3 weeks then in the 18.3 m well after 55 days. In September 1999, the SF<sub>6</sub> peak was observed in just 1.9 days at the deep well while a smaller peak was observed at the 9.1 m well after 2 weeks. Higher rates of wastewater injection may push the plume deeper or wider into the subsurface, possibly allowing it to extend further from the injection well before buoying upward.

Transport rates for the dual tracer experiment can be used along with the hydraulic gradient at this time to estimate the Key Largo Limestone's hydraulic conductivity using Darcy's law:

$$v = (-K/n)dh/dl$$

where  $v$  is the groundwater velocity,  $K$  is the hydraulic conductivity,  $n$  is the porosity, and  $dh/dl$  is the hydraulic gradient. The hydraulic gradient measured during this experiment was typically  $1.14 \times 10^{-3}$ . If one assumes an eastern flow rate of 7 m/d (Table 4) and a porosity value of 50%, then a value for  $K$  of 3063 m/d can be calculated. This is near the lower end of the range (3144 to  $3.84 \times 10^4$  m/d) estimated by Dillon et al. (1999) and more than twice the value of 1400 m/d estimated by Halley et al. (1995).

Dilution rates determined from SF<sub>6</sub> peak concentrations in the well field ranged from 3 to 6 orders of magnitude during both experiments. The SF<sub>6</sub> maxima detected in the canals in

June 1998 were diluted by approximately 7 orders of magnitude compared to the injected concentration. It should be noted however, that these dilution rates represent dilution of the injection slug primarily by wastewater itself in addition to some mixing with ambient groundwater. Low salinity waters of the plume extend beneath the entire study area. Salinities below 10 psu were measured as far east from the IW as 175 m (wells K-6 and K-8) and as far south as 67 m (well G-9). Estimates based on salinity and stable oxygen isotopes (Elliott, 1999) determined that wastewater comprised 85 - 100% of the water collected at 9.1 m depth at clusters A, B, C, D, E, F, and G. The low salinities observed 175 m from the IW at cluster K (Table 3) indicate that water from this well is 91-94 % wastewater.

By making some general assumptions about the plume's size and transport rate it is possible to estimate the  $\text{PO}_4$  loading to the east canal. For this calculation, we have assumed that the plume's shape is a half ellipse in cross section with the wider portion contacting the mud layer. If one assumes that the plume is 140 m wide (as shown in Figure 5) and 7.5 m tall (best estimate) by the time it reaches the east canal, has a  $\text{PO}_4$  concentration of  $4.5\mu\text{M}$  (average concentration from well K-5 and K-8, Table 3) and it is advected 1.5 m/d (conservative estimate from Table 2) then one can estimate that 2.78 moles of  $\text{PO}_4$  (3.6 % of the daily injected  $\text{PO}_4$ ) is delivered to the east canal every day. This is equivalent to dumping 1.5 lbs of sodium phosphate salt into the canal each day.

Results from the dual tracer experiment showed rapid initial  $^{32}\text{PO}_4$  uptake followed by a slower rate of desorption. Other studies have also observed rapid phosphate removal followed by a much slower rate of uptake which declined over time by KLL (Corbett et al., 2000; Elliott, 1999), calcite and aragonite (DeKanel and Morse, 1978); and carbonate sediments (McGlathery et al., 1994; Carignan and Vaithyanathan, 1999; Gomez et al., 1999). Corbett et al. (2000)

hypothesized that adsorption / desorption reactions may explain this gradual decrease in the  $\text{PO}_4$  removal rate. Elliott (1999) conducted column experiments with cores collected in KLL and showed that after additions of phosphate-enriched solutions (fresh water and saline)  $\text{PO}_4$  was rapidly stripped from solution. A leveling off of adsorption rates then followed until equilibrium concentrations of approximately  $25 \mu\text{M}$  ( $0.8 \text{ mg/L}$ ) were reached. In one case, Elliott added seawater with low phosphate levels ( $<0.1 \mu\text{M}$ ) to the phosphate-loaded KLL column and observed an increase in  $\text{PO}_4$  concentration as the solution was recirculated over the limestone until a concentration of approximately  $25 \mu\text{M}$  was reached. Interestingly, the  $\text{PO}_4$  concentration of WW being injected into the subsurface in September 1999 was  $25.85 \mu\text{M}$ .

The data presented here in conjunction with Elliott's column experiments indicate that the KLL underlying Key Colony Beach seems to be acting as a phosphate buffer. Phosphate in such a system may be subject to adsorption, desorption, precipitation, and dissolution reactions (Froelich, 1988) and can be influenced by pH, dissolved phosphate concentrations, competing anions, and the composition of solid phase phosphate (Carignan and Vaithyanathan, 1999). Similar buffering capacities have been documented in carbonate sediments (McGlathery et al., 1994; Carignan and Vaithyanathan, 1999; Gomez et al., 1999). In the case of KCB, it appears that  $\text{PO}_4$  molecules are quickly adsorbed onto the KLL after injection into the subsurface. As "new"  $\text{PO}_4$  is introduced to the system it is rapidly bound to the limestone. Simultaneously, "old"  $\text{PO}_4$  is "bumped" from the limestone by either desorption or dissolution and transported further down the flow path.

A first order rate constants for adsorption and desorption can be calculated as described by Corbett et al. (2000) using a well known rate expression (Frost and Pearson, 1961):

$$\ln A = \ln A_0 - k_1 t$$

where A is the normalized activity of  $^{32}\text{PO}_4$ ,  $C_0$  is the initial normalized activity at the start of the experiment, and t is the elapsed time. A desorption rate may also be estimated assuming adsorption no longer dominates the system after the initial rapid removal of phosphate. A variation of Moore's (1972) first-order rate expression for opposing surface reactions can be stated as:

$$-\partial C/\partial t = k_1 A - k_{-1}(A_0 - A)$$

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

Applying equation (1) to our radiolabelled phosphate results provides estimates for the first-order adsorption rate constant of 0.06, 0.23, and 0.22  $\text{hr}^{-1}$  for wells I-9, I-18 and H-18, respectively. This is within the range of 0.02-0.34 reported by Corbett et al. (2000), despite the higher organic loads at this location. Estimates of the first order desorption rates ranged from 0.03 to 0.05  $\text{hr}^{-1}$  for the same three wells. This desorption rate is more than three times greater than that calculated by Corbett et al. (2000). This may be a consequence of the higher loading rates at this location. Higher influx of  $\text{PO}_4$  at this high volume facility may cause  $\text{PO}_4$  to be more mobile due to higher competition for binding sites on the KLL.

The rather rapid rate at which these adsorption / desorption processes occurs may make mineral precipitation such as apatite formation unlikely. Additional column experiments and

core analysis need to be conducted to address this issue. It is unclear what the long-term effects phosphate loading will have on this study site. In September 1999 after approximately 6 years of continuous injection, equilibrium phosphate concentrations of approximately 25  $\mu\text{M}$  existed 15 m from the injection well. It seems likely that as  $\text{PO}_4$  is continued to be added to the system, more bound  $\text{PO}_4$  molecules will be remobilized and move further and further from the source. At the edge of the plume, low  $\text{PO}_4$  loaded limestone will come into contact with elevated  $\text{PO}_4$  concentrations. Initially, the limestone may adsorb the  $\text{PO}_4$  until an equilibrium concentration (presumably 25  $\mu\text{M}$ ) is reached. This phosphate-equilibrated plume will most likely continue to expand with additional phosphate loading. It is difficult to predict the rate at which this will occur. More column experiments are needed to address this issue. These experiments should investigate the adsorption / desorption reactions that occur in pristine KLL at low  $\text{PO}_4$  concentrations (<5  $\mu\text{M}$ ) and should then observe these reactions as the  $\text{PO}_4$  load to the column is slowly increased to an equilibrium concentration.



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Table 1. Salinity, ammonia, nitrate+nitrite, and phosphate concentrations from samples collected June 6, 1998. "bd" indicates the parameter was below the limit of detection (1.39, 0.03 and 0.10  $\mu\text{M}$  for  $\text{NH}_4$ ,  $\text{NO}_2+\text{NO}_3$  and  $\text{PO}_4$ , respectively). "NA" means that the data was not available.

<u>sample</u>	<u>salinity</u> <u>(psu)</u>	<u>[NH<sub>4</sub>]</u> <u>(<math>\mu\text{M}</math>)</u>	<u>[NO<sub>2</sub>+NO<sub>3</sub>]</u> <u>(<math>\mu\text{M}</math>)</u>	<u>[PO<sub>4</sub>]</u> <u>(<math>\mu\text{M}</math>)</u>
A-9	6.1	7.86	584.29	bd
A-18	29.5	bd	292.86	52.63
B-9	7.1	22.86	72.14	bd
B-18	13	bd	512.14	50.69
C-9	6.7	bd	821.43	25.51
C-18	38.8	4.29	bd	0.65
D-9	NA	bd	435.00	0.65
D-14	36.9	22.14	0.79	0.65
E-9	6.4	7.14	33.79	1.94
E-18	29.8	22.14	2.43	bd
F-8	9.7	329.29	bd	9.69
F-14	35.4	22.14	43.50	bd
F-18	37.2	8.57	bd	bd
G-9	8	52.14	2.50	1.61
G-18	36.6	23.57	1.00	0.65
WW	4.8	36.43	1307.14	92.99

Table 2. Peak SF<sub>6</sub> concentrations, times and calculated transport rates. VTR is the vertical transport rate and HTR is the horizontal transport rate.

<u>Well</u>	<u>peak concentration (nM)</u>	<u>time (days)</u>	<u>VTR (m/d)</u>	<u>HTR (m/d)</u>
A - 9	0.51	55.10	0.17	0.27
A - 18	0.33	18.80	-	0.80
B - 18	1.96	10.03	-	1.50
C - 9	3.98	5.94	1.54	2.52
C - 18	0.01	3.95	-	3.80
D - 9	0.81	55.10	0.17	1.41
West canal	$1.21 \times 10^{-3}$	55.1	-	1.52
East canal	$4.15 \times 10^{-3}$	65.01	-	3.08

Table 3. Salinity and nutrient concentrations for monitoring wells at Key Colony Beach. Salinity measurements were made September 26, 1999. Nutrient samples were collected October 5, 1999. "bd" indicates the parameter was below the limit of detection (0.4, 0.5, 0.1 and 0.5  $\mu\text{M}$  for  $\text{NH}_4$ ,  $\text{PO}_4$ ,  $\text{NO}_2$ , and  $\text{NO}_3$ , respectively).

<u>sample</u>	<u>Salinity</u> <u>psu</u>	<u>[NH<sub>4</sub>]</u> <u>(<math>\mu\text{M}</math>)</u>	<u>st dev</u>	<u>[PO<sub>4</sub>]</u> <u>(<math>\mu\text{M}</math>)</u>	<u>st dev</u>	<u>[NO<sub>2</sub>]</u> <u>(<math>\mu\text{M}</math>)</u>	<u>st dev</u>	<u>[NO<sub>3</sub>]</u> <u>(<math>\mu\text{M}</math>)</u>	<u>st dev</u>
G-9	10	77.70	0.18	2.28	0.02	0.98	0.00	6.11	0.05
G-18	39	13.05	0.12	2.80	0.11	bd		bd	
K-5	6	43.42	0.15	0.77	0.09	5.84	0.04	102.76	0.39
K-8	7	bd		7.84	0.03	13.30	0.01	491.31	0.87
K-8 dup	7	bd		7.96	0.00	13.35	0.04	493.46	
J-6	6	148.94	0.75	3.78	0.09	0.27	0.09	86.87	0.47
J-14	32	1.90	0.92	0.76	0.06	1.61	0.05	5.56	0.10
J-14 dup	32	0.94	0.07	0.83	0.12	1.46	0.03	5.42	0.19
J-18	37	4.10	0.01	0.52	0.01	bd		bd	0.01
F-8	13	124.51	1.96	0.92	0.01	0.12	0.01	0.55	
F-14	35	12.21	0.45	3.18	0.02	bd		bd	
F-18	40	6.55	0.25	1.61	0.04	bd		bd	
D-9	7	5.82	0.19	6.19	0.03	7.38	0.04	276.73	0.56
D-14	37	10.11	0.05	1.45	0.04	bd		bd	
E-9	10	27.44	5.79	1.23	0.13	7.63	0.05	69.20	0.15
E-18	22	20.47	0.79	0.73	0.10	0.13	0.02	bd	0.02
A-9	9	12.34	0.12	7.75	0.02	13.32	0.06	232.34	0.70
A-18	6	0.40	0.04	28.94	0.06	0.16	0.04	390.42	0.21
B-18	7	bd		32.23	0.02	0.28	0.00	413.21	0.33
C-9	5	bd		25.98	0.16	bd		380.40	1.15
C-18	21	bd		26.34	0.03	bd		384.01	0.13
I-9	3	9.25	14.16	26.04	0.06	bd		380.43	0.15
I-14	4	bd		19.59	0.00	bd		352.41	0.56
I-18	4	bd		27.24	0.21	bd		366.67	0.60
H-9	5	bd		22.35	0.11	bd		340.06	0.06
H-13	5	0.76	0.32	20.36	0.09	bd		376.87	0.57
H-60	5	bd		30.09	0.08	bd		370.50	0.52
East Canal	36	1.05	0.12	bd		0.27	0.02	3.97	0.07
trough	4	bd		25.85	0.09	bd		382.81	0.22
trough dup	4	bd		26.13	0.06	bd		379.99	0.15

Table 4. Summary of September 1999 dual tracer results for wells that showed elevated SF<sub>6</sub> concentrations.

Well	time (days)	maximum SF <sub>6</sub> ratio	corresponding <sup>32</sup> PO <sub>4</sub> ratio	HTR (m/d)	VTR (m/d)
H-18	0.03	2641.4	601.6	123.33	-
H-14	1.68	449.1	0.2	2.20	3.27
H-9	0.19	502.9	26.9	19.47	48.42
I-18	0.05	1746.9	966.1	50.00	-
I-14	0.70	606.9	bd	3.57	6.57
I-9	0.09	2753.5	581.4	27.78	102.22
A-18	1.89	180.6	0.5	7.94	-
A-9	15.11	14.2	bd	0.99	0.61
B-18	7.30	80.4	0.5	2.05	-
B-9	No data - lost well				-
C-18	1.90	31.3	0.4	7.89	-
C-9	0.78	183.9	0.3	19.23	11.79
J-14	30.09	8.6	bd		< 0.16
J-6	4.16	41	0.2		3.01
D-9	30.08	7.9	bd	< 2.59	0.31
E-18	29.75	5.3	bd	< 0.91	-



# Key Colony Beach

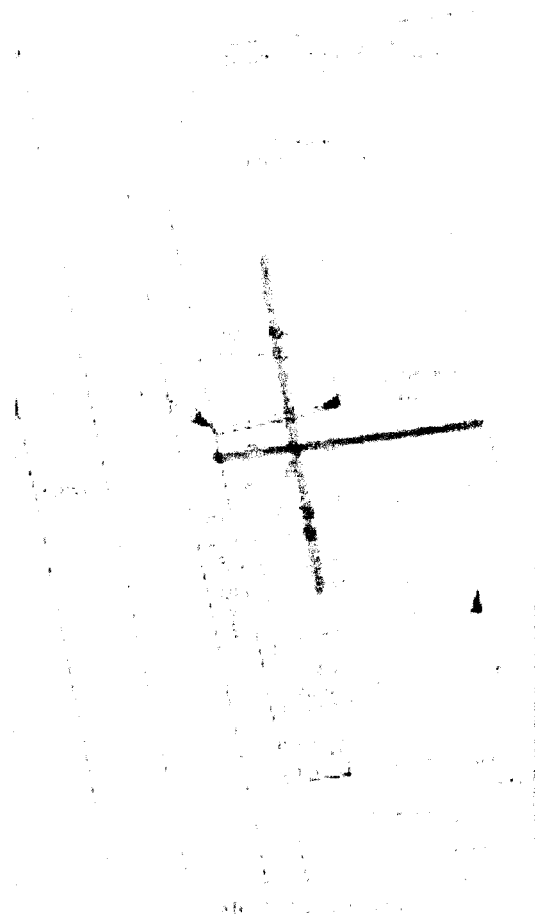
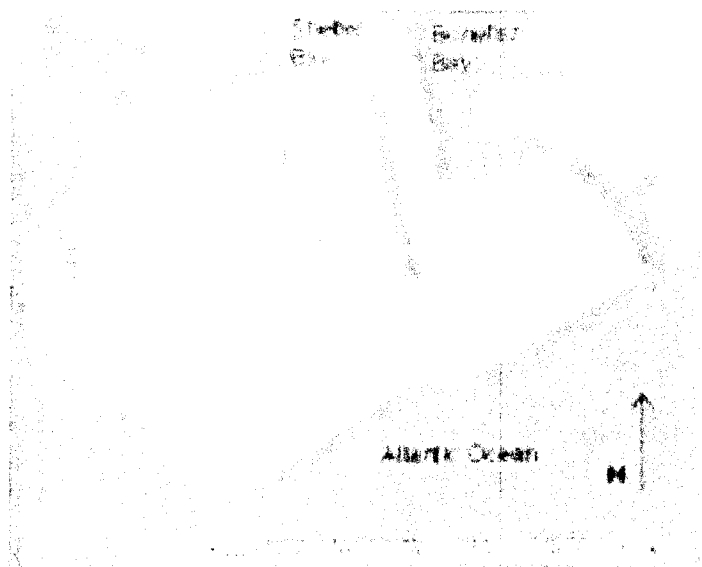


Figure 1. Map of Key Colony Beach, FL. Well cluster positions are shown by their corresponding identification letter.

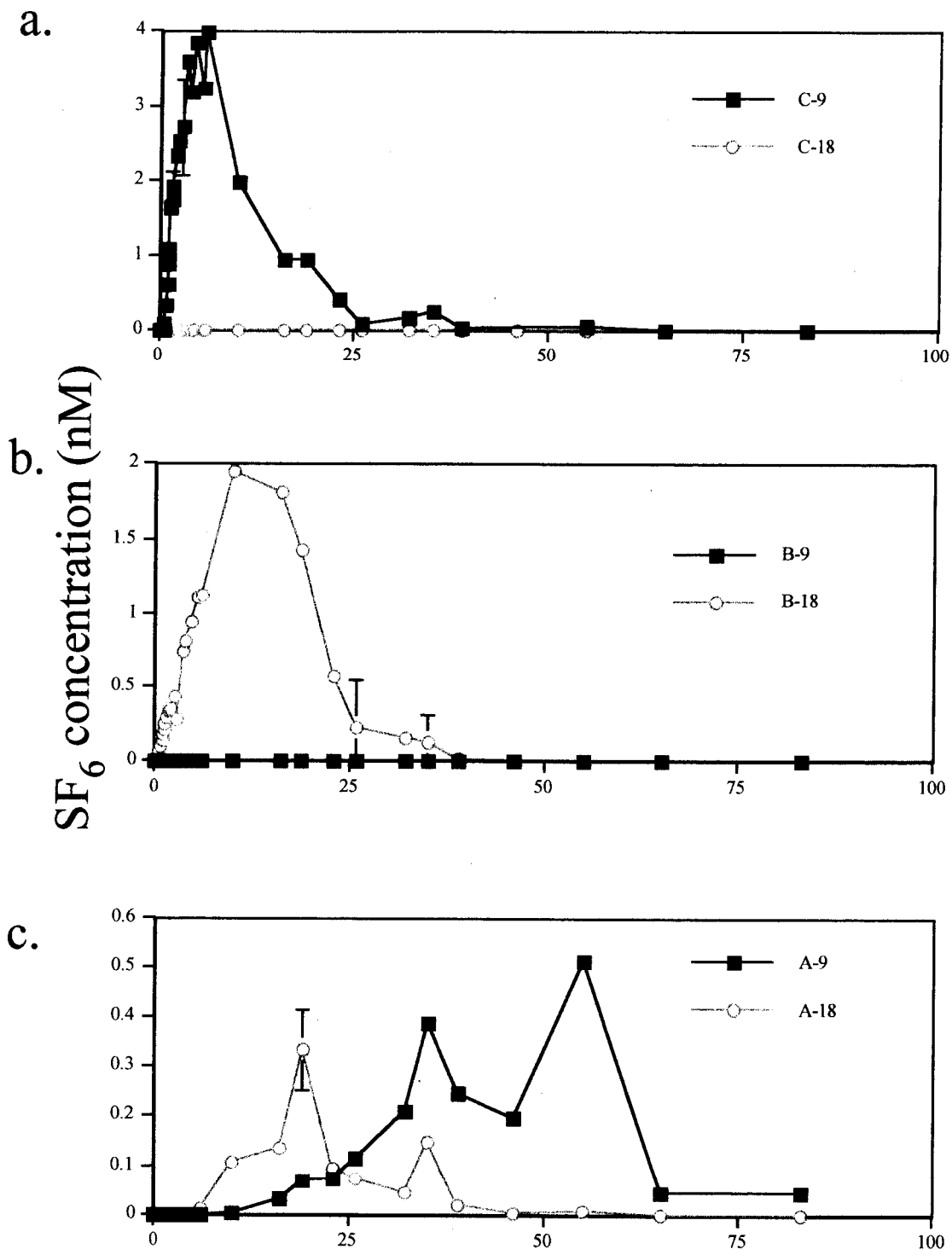


Figure 2. SF<sub>6</sub> breakthrough curves for well clusters A, B, and C from the June 1998 tracer experiment.

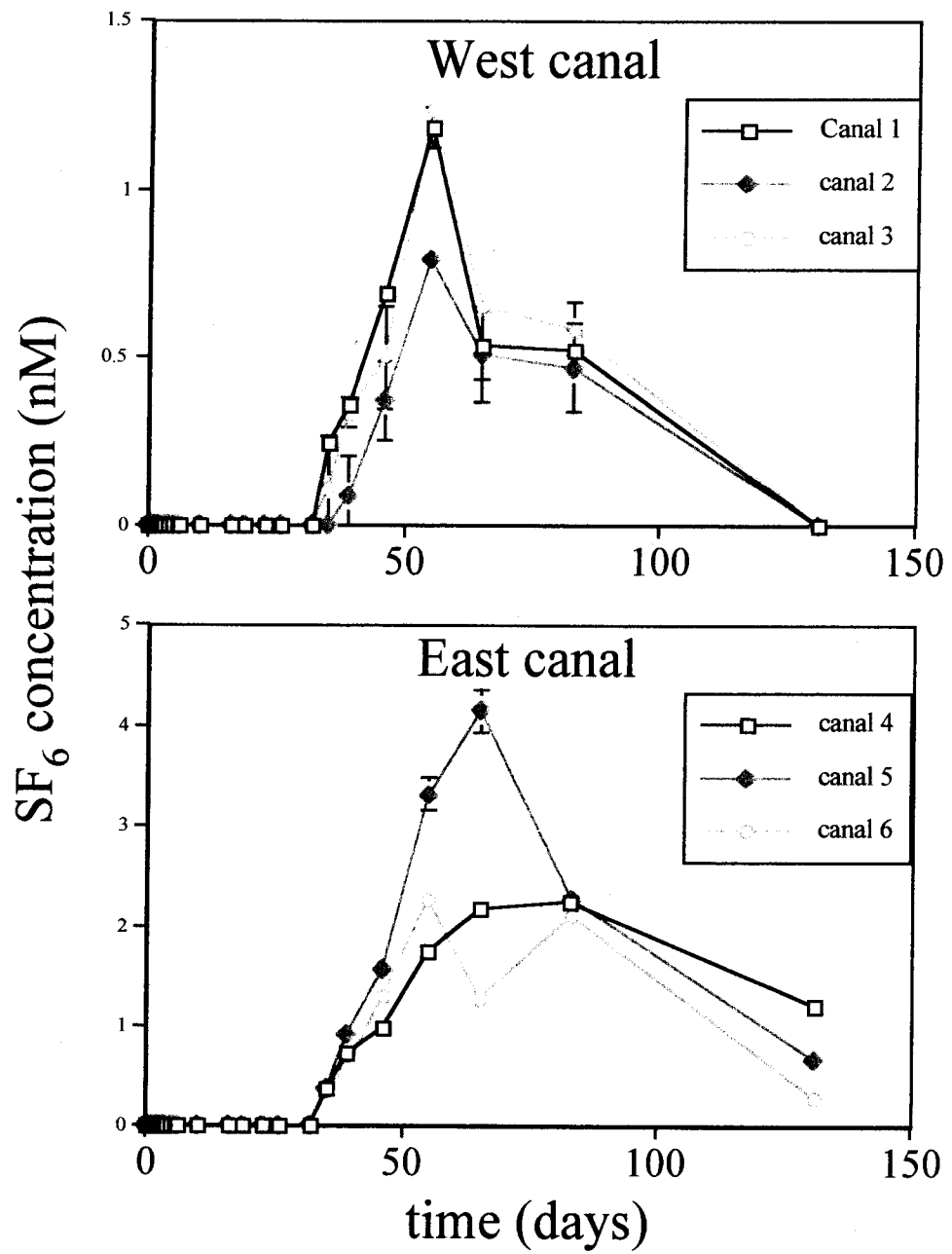
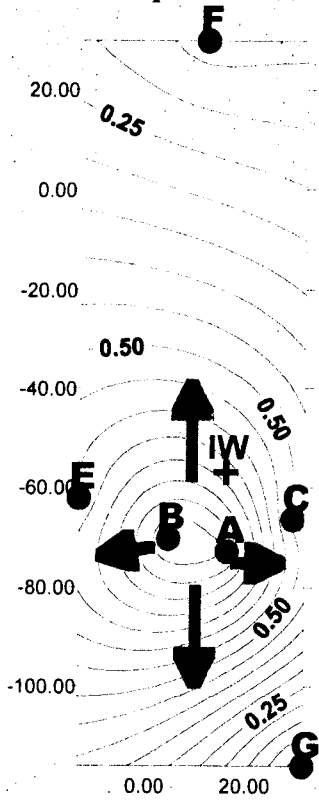


Figure 3. SF<sub>6</sub> breakthrough curves for East and West canals for June 1998 tracer experiment.

**Key Colony Beach  
Piezometric surface at 18.3m (60 ft)  
27 September 1999**



**Key Colony Beach  
Piezometric surface at 30 ft  
27 September 1999**

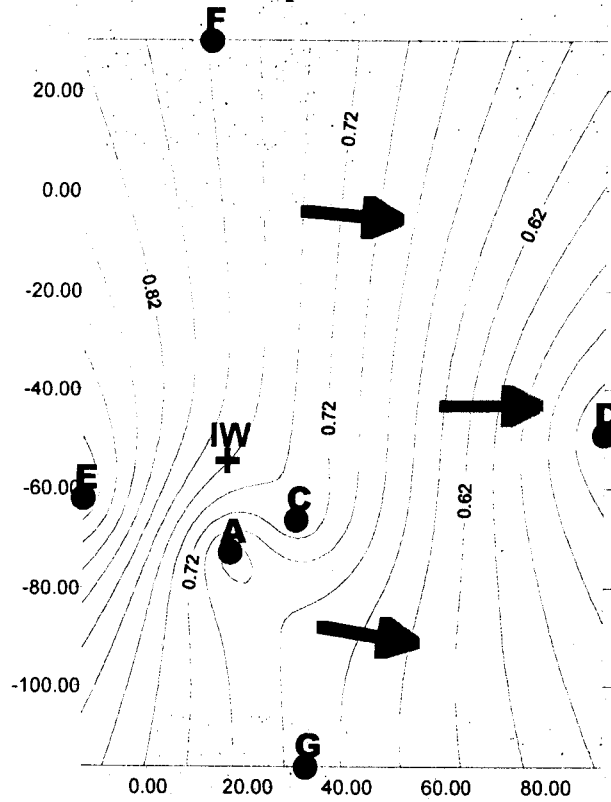


Figure 4. Piezometric surface contours at two different depth in the well field at Key Colony Beach, FL. The location of the injection well is the cross labelled "IW". Arrows illustrate direction of groundwater movement.

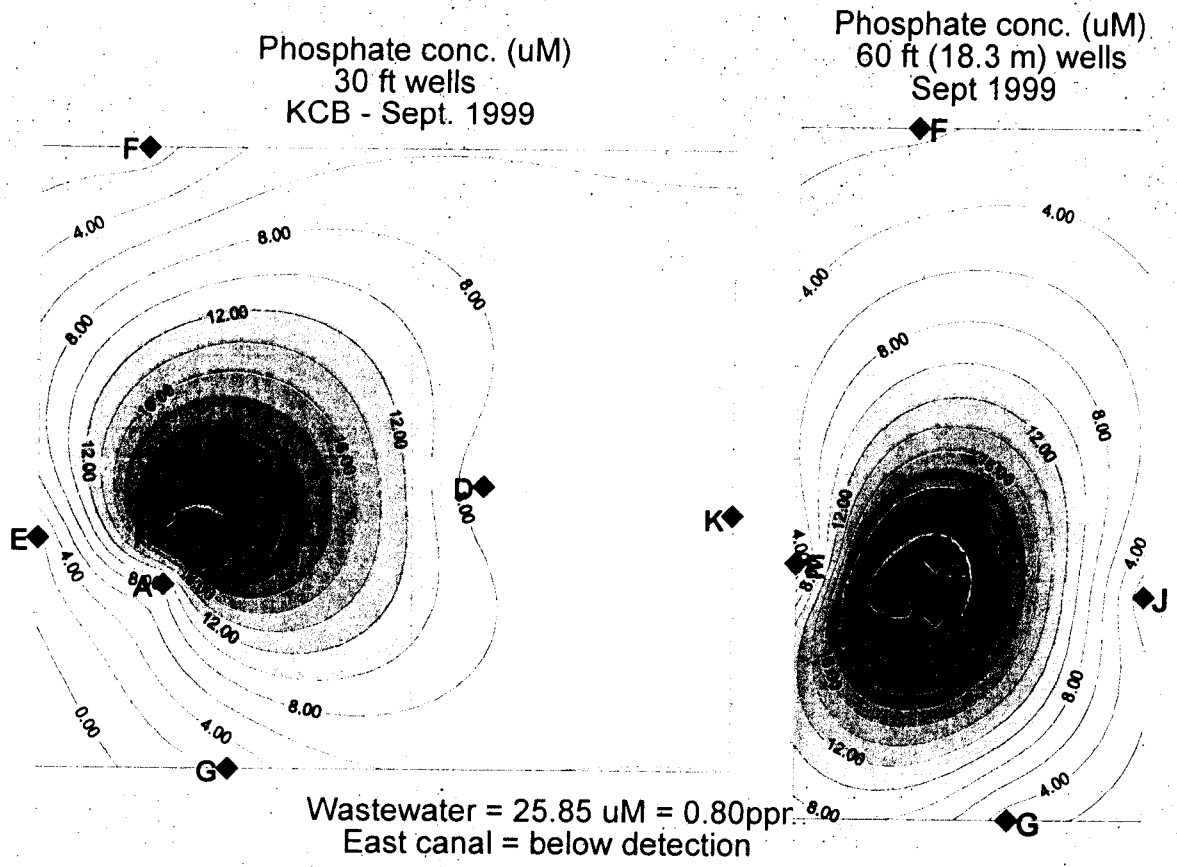


Figure 5. Phosphate concentration contours for two different depth of the well field at Key Colony Beach, FL during the September 1999 dual tracer experiment.

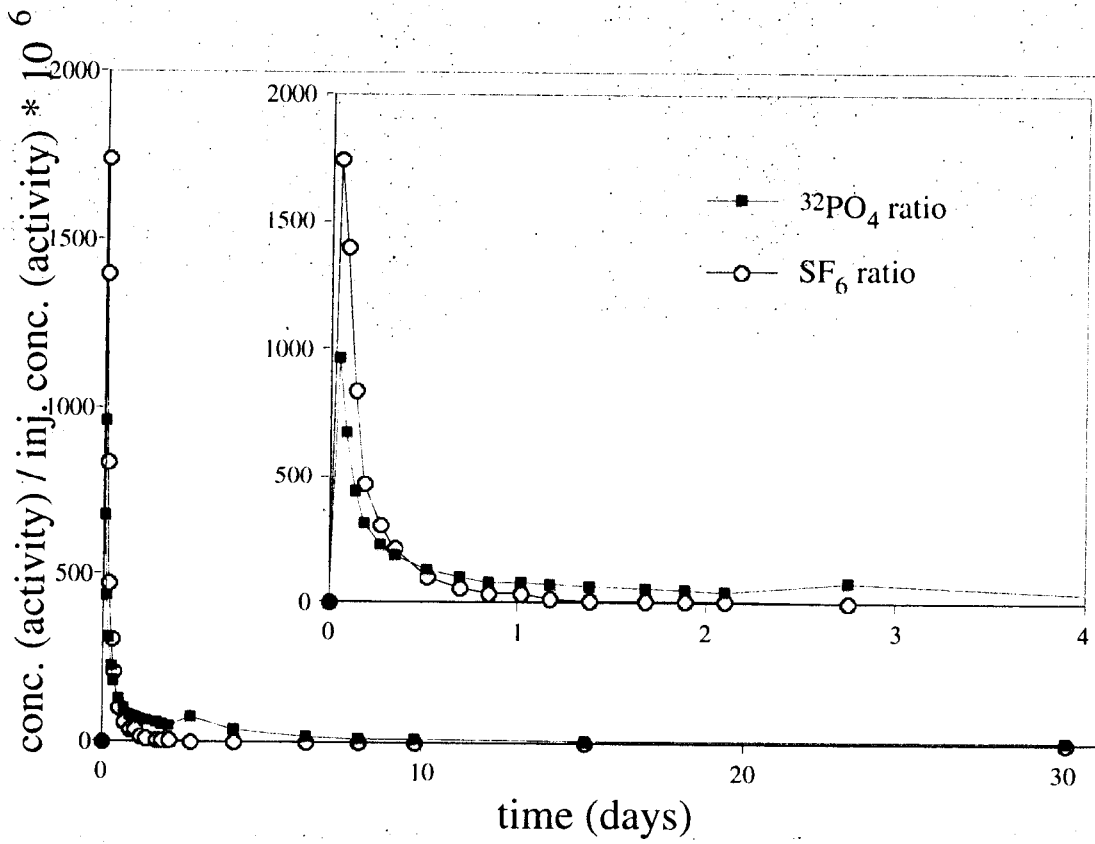
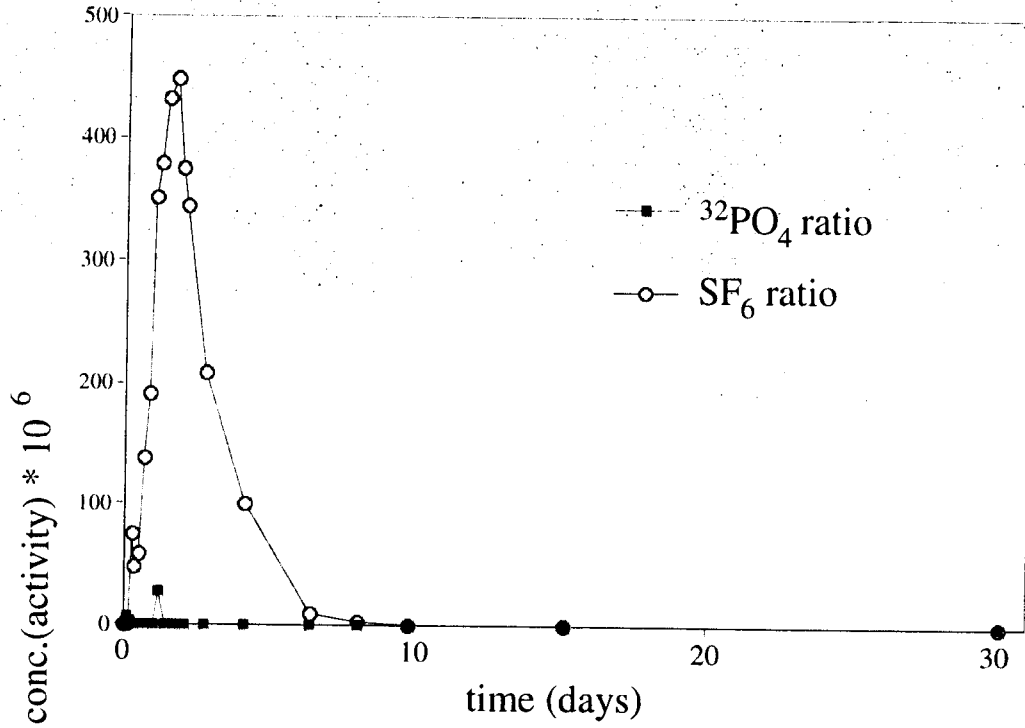


Figure 6. Breakthrough curves for both SF<sub>6</sub> and <sup>32</sup>PO<sub>4</sub> from well I-18 m.

a.



b.

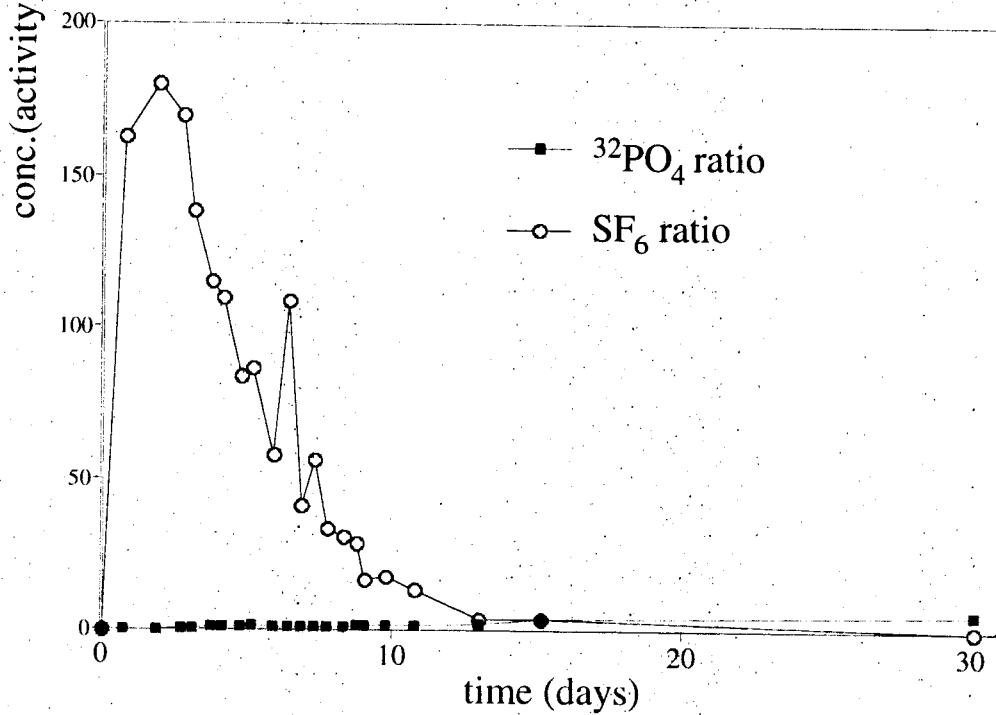


Figure 7.  $\text{SF}_6$  and  $^{32}\text{PO}_4$  breakthrough curves from September dual tracer experiment for (a.) well H-14 and (b.) well A-18