Bimodal Transport of a Waste Water Plume Injected into Saline Ground Water of the Florida Keys

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Abstract

Two experiments were conducted on Long Key, Florida, United States, to examine the fate of waste water following sewage disposal in 10 to 30 m deep injection wells. This waste disposal practice introduces extraordinary amounts of nutrients into the ground water of the Florida Keys. In these experiments, artificial ground water tracers, sulfur hexafluoride (SF_6) and radioiodine (^{131}I) were used to determine transport rates and directions of soluble nonreactive substances injected into the saline ground water underlying the Keys. Two types of transport were observed: (1) rapid flow (0.20 to 2.20 m/hr) presumably due to the many conduits present in the limestone; and (2) slower flow (less than 0.003 to 0.14 m/hr) associated with the limestone's primary porosity. Vertical flow was comparable to horizontal flow due to either the density-driven buoyancy of the waste water plume or to preferential flowpaths that allow upward advection or combination of both. These experiments showed that conservative artificial tracers injected into the subsurface reach surface water in a matter of days and can remain in the immediate vicinity of the injection well for several months.

Introduction

Florida Bay is a shallow lagoon bordered by the Florida Keys and the Florida mainland. It covers an area of approximately 2200 km^2 and has an average depth of about 1.8 m with its western margin open to the Gulf of Mexico. Shallow carbonate mud banks divide the bay into discrete basins, restrict circulation, and attenuate tidal influences from the Gulf (Robblee et al. 1991; Fourqurean and Robblee 1999). Most fresh water enters the bay from the north through Taylor Slough, C-111 (a man-made canal in the northeast corner of the bay that channels water from the Everglades), or as sheet flow from the Everglades. Salinity in the bay oscillates between brackish and hypersaline. In 1989, Zieman et al. estimated that seagrasses covered more than 80% of the bay. Many commercially important types of fish and crustaceans depend on these grass beds as a habitat or nursery grounds (Robblee et al. 1991).

Around 1987, water quality in Florida Bay began deteriorating (Robblee et al. 1991). The clear and quiescent water that once characterized the bay began appearing green and turbid. Seagrass die-offs and algae blooms became commonplace. It has been hypothesized that the system may be undergoing a shift from domination by benthic primary production to domination by water column photosynthesis. Some blame these changes on elevated salinity or increased nutrient loading resulting from the rapid urbanization of south Florida and the Florida Keys (U.S. EPA 1991). Others believe that the ecological changes are part of the system's natural variability (Fourqurean and Robblee 1999). There is no simple explanation available for what has caused these dramatic changes, but it is likely that they are related to a combination of natural phenomena and anthropogenic activities. Many facets of Florida Bay are now being studied to aid in the development of a model to characterize its physical, chemical, and biological conditions. Since this model will be used to predict what restoration steps would be most beneficial, it is important that it takes into consideration all significant nutrient sources to the bay.

Ground water has been shown to contribute significant quantities of nutrients to some coastal areas. Studies of Great South Bay, New York, by Capone and Bautista (1985) and Capone and Slater (1990) have shown that more than 50% of the nitrate delivered to that bay is contributed via ground water discharge. Ground water discharge has also been shown to be a factor in the nutrient budgets of Discovery Bay, Jamaica (D'Elia et al. 1981), Tomales Bay, California (Oberdorfer et al. 1990), and salt marshes in Massachusetts (Valiela et al. 1990). Until recently, possible ground water contributions of nutrients into Florida Bay have been largely ignored.

The majority of the ground water underlying the Keys is saline. Meteoric fresh water lenses exist on some of the lower Keys (i.e., Big Pine Key) due to the lower permeability of the Miami oolite compared to the Key Largo limestone (KLL), which characterizes the upper Keys (Vacher et al. 1992). KLL is composed of ancient hermatypic corals with intra- and interbedded calcarenites and thin beds of quartz sand (Halley et al. 1995). The formation is extremely porous and permeable due to conduits and interconnected pore spaces created by ancient coral growth and meteoric diagenesis (Halley et al. 1995). Due to this high degree of permeability, meteoric fresh water lenses do not occur in the upper Keys.

Approximately 600 sewage disposal (injection) wells ranging in depth from 10 to 30 m have been installed in the Florida Keys

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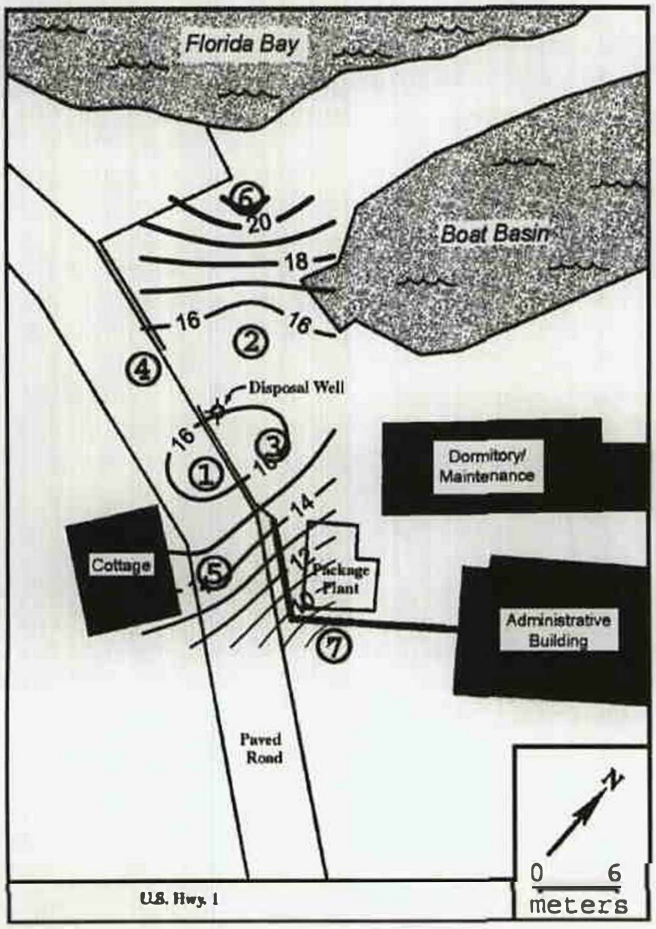

Figure 1. Sampling site located at the Keys Marine Laboratory. The canal that was used as an indicator of the Atlantic tide and sampled for artificial tracers is located southeast of U.S. Highway 1. Contour lines represent wellheads in centimeters measured on day 2 of the October experiment.

(Shinn et al. 1994). In addition, there are also some 30,000 septic tanks and an estimated 10,000 illegal cesspools (U.S. EPA 1996) that may contribute to elevated nutrient levels in shallow ground water. The U.S. EPA (1996) calculates that approximately 897 kg of nitrogen and 215 kg of phosphate are put into the subsurface ground water daily by these three methods of waste disposal. Lapointe et al. (1990) have shown significant nutrient enrichment (up to 5000-fold) in ground water contiguous to septic tanks on Big Pine Key. In another study, Lapointe and Clark (1992) showed that phosphate and dissolved inorganic nitrogen levels were elevated in canals and in some nearshore water of the Keys. Canals may be particularly impacted by sewage-derived nutrients due to their low flushing rates and their direct contact with contaminated ground water.

Evidence suggests that significant quantities of sewage from on-site disposal systems may reach the surficial water of the Florida Keys (Lapointe and Clark, 1992; Shinn et al. 1994; Paul et al. 1995; Paul et al. 1997; Dillon et al. 1999). Although there is certain to be significant dilution, that alone may not be important if the total flux of nutrients reaching surface water is high. If the waste water plume reaches surface water rapidly with little dilution or nutrient uptake (water polishing) or if the flux into surface water is high, then human and ecosystem health could be at risk and different waste water disposal methods would be needed.

The primary purpose of this study was to determine directions and rates of ground water transport on Long Key and compare our results with other studies conducted at the site (Shinn et al. 1994; Paul et al. 1997). Only the flow of waste water itself, not the behavior of nutrients in the subsurface, is addressed in this report. A companion study describes the fate of nutrients that were simultaneously injected into the disposal well (Corbett et al. 1999a). Our second objective was to determine how much dilution occurs before contaminated ground water reaches nearby surface water, something that previous studies have not been able to achieve. To examine the problem, we used sulfur hexafluoride (SF_6) and radioactive iodine (^{131}I) as artificial tracers of ground water at a deep well (18 to 28 m) injection site at the Key Marine Laboratory (KML) on Long Key.

SF_6 is a stable, slightly water-soluble gas that can be measured at low concentrations. It is well suited as a ground water tracer because it is nontoxic, has extremely low background concentrations (5×10^{-17} moles/L [M]; Watson and Liddicoat 1985) and has been shown to be a conservative tracer in saturated sandy media with low organic content (Wilson and Mackay 1993). While SF_6 was used in both experiments in this study, ^{131}I was used only in the second experiment. ^{131}I has the advantage of disappearing from a system in a short time period, unlike SF_6, which can persist in a system for as long as a year (Dillon 1998; Dillon et al. 1999). ^{131}I has a half-life of 8.02 days, making it a useful tracer on short time scales, as the tracer will decay to below detection in a matter of weeks.

Methods

Study Sites and Injection Methods

A class V sewage injection well at the KML was used to introduce the tracers to the subsurface. This well is a relatively low volume disposal well with an average daily injection volume of 2600 L. This type of injection well is used by multiunit residences such as hotels, trailer parks, campgrounds, and small communities in the Keys (Paul et al. 1997). The injection well at the KML is 27.7 m deep and cased to 18.3 m, allowing for waste water to enter the subsurface at the bottom 9.4 m of the well. After secondary treatment in a package plant, waste water is gravity fed into the injection well. There are seven monitor well clusters surrounding the injection well (Figure 1). Each well cluster consists of four 1-inch wells drilled to depths of 4.6, 9.2, 13.8, and 18.3 m. Each well is screened at the lower 1.2 m portion of the well. The void space around each well is packed with sand, and each well is sealed from the other well depths with portland cement. A more detailed discussion of the well construction and development, as well as the recovered core material, can be found in Monaghan (1996). Porosity of the Key Largo limestone varies widely due to the heterogeneity of the ancient coral matrix. Monaghan (1996) estimated porosity by weight using recovered core material from this site and considers an average porosity of 50% to be a conservative value.

Tracer experiments were conducted on two occasions: October 1996 and February 1997. In each case, slug injections were prepared by bubbling 200 L of tap water with concentrated SF_6 gas for 20 minutes. Salts containing phosphate and nitrate were also added to the slugs for a companion study investigating nutrient removal in the subsurface (Corbett et al. 1999a). For the February experiment, 200 millicuries (mCi) of ^{131}I were also dissolved into a 50 L injection slug to serve as a second tracer. For both experiments, the solutions were siphoned into the injection well during a low Atlantic tide. Approximately 1000 L of waste water (salinity = 0 ppt) were then injected from the package plant's holding tank as a chaser to drive the solution into the aquifer. Although the added salts increased the salinity of the injection slugs to 70 and 100 ppt in the October and February experiments, respectively, we believe that subsequent dilution by the chaser volume, in addition to dilution by waste water within the well casing (465 L), resulted in solutions with salinity below that of the saline ground water. If the 200 L slug was fully mixed with the water, the salinities would have been 8.4 ppt (parts per thousand) in October and 12.0 ppt in February. After injection, the surrounding well clusters were monitored for the presence of the tracer(s). Before each well cluster was sampled, each well was first purged to remove three well volumes. Purge water was stored in a large holding tank for the duration of both experiments to prevent contamination.

Atlantic tides for Long Key were obtained from the computer tide program, Tides and Currents for Windows (version 2.0, Nautical Software). Measurements taken from the canal across U.S. Highway 1 confirm that the program was accurate for this location (Dillon 1998). Well water heights were measured with modified conductivity probes, marked off at 0.1 cm intervals, connected to electrical signaling systems. All well heights were surveyed with a computerized theodolite surveying system, which could reproduce measurements with an average standard deviation of 0.5 cm. We measured each well's height relative to a USGS monument designation with a stated elevation relative to mean sea level. In both experiments, the hydraulic gradient across the study site was determined from three depths (4.6, 13.8, and 18.3 m) using data from well clusters 6 and 7.

Ground water transport rates were determined for each sampling location by dividing the distance from the injection well by the arrival time of the peak concentration. During the first experiment, tracer concentrations in some wells were still rising at the end of the experiment and thus the peak concentrations may not have been observed. For these cases, the time of the last measurement was used to estimate an upper limit of the transport rate. 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 injection depth (18.3 m) and then divided by the arrival time of peak tracer concentration. The resultant rates are the horizontal and vertical components of the transport rates.

Sampling Methods

Sulfur hexafluoride samples were collected with two variations of a head space extraction technique (Wanninkhof et al. 1991). In October 1996, samples were collected from wells with syringes and ⅛-inch copper tubing. Approximately 2 m of tubing was inserted into a well after three well volumes had been purged using a peristaltic pump. A glass syringe was attached to the tubing with a three-way stopcock and a small piece of Tygon tubing. After clearing the sample tubing and syringe of all air bubbles, three syringe volumes were drawn and discarded to act as a rinse. The sample was then pulled into the syringe. A headspace of argon or ultra-high-purity nitrogen was then added to the syringe, which was shaken for two minutes to extract the SF_6 from solution. Approximately 8 mL of headspace was then injected into a 4 mL Vacutainer(tm). Standards stored in this fashion showed no loss of SF_6 from the Vacutainer over 500 days (Dillon 1998). Samples were analyzed within a month of collection.

Although the Vacutainer method was adequate, it proved to be time intensive. To reduce sampling time, extraction was delayed until the samples were to be analyzed. Samples were collected in 30 mL serum bottles with a peristaltic pump. To prevent contamination, each well or water body being sampled had its own dedicated piece of tubing. After rinsing the tubing and the serum bottle with well or surface water, 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 and a crimp cap leaving a small air bubble. To prevent loss of SF_6 from the air bubble through the septa, the samples were stored on their sides until they were extracted and analyzed. 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.

Iodine-131 samples were collected into 1 or 2 L polyethylene containers and taken to the on-site lab, where we added a stable carrier (KI) and a radiometric tracer (^{129}I: $t_{1/2} = 1.7 \times 10^7$ y [year]), which served as a yield determinant. A series of oxidation/reduction steps, using $KMnO_4$ and Na_2SO_3, adjusted the oxidation state of the iodine for precipitation as I-. The iodine was quantitatively precipitated as AgI (silver iodine) from a slightly acidic solution (pH<4). The precipitate was then collected on 47 mm 0.45 μm polypropylene filters, washed with dilute ammonia, which removes any silver chloride and silver bromide present and rinsed with deionized water. The filters were then dried and counted with a sodium iodide detector.

Analytical Methods

SF_6 samples were analyzed with a Shimadzu model 8A gas chromatograph equipped with an electron capture detector. Injection volumes were typically 100 μL or less. The GC contained a stainless steel column (180 cm × 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. Due to problems with carrier gas contamination, we switched to ultra-high-purity nitrogen as a carrier at the same flow rate. Column and detector temperatures were set at 90°C and 220°C, respectively.

Headspace concentrations in ppmv (parts per million by volume, μL/L) of SF_6 were determined by reference to a 1.04 ppm standard (Scott Specialty Gases). The 1.04 ppm standard was run at the beginning of each day, after every 10 sample injections, and at the end of the day. Headspace concentrations were converted to dissolved concentrations in μM (10^{-6} M) as shown here:

$$[SF_6]\ (\mu M) = ((\mu L/L)/\ (R((L\ atm)/(mol\ K))\ *\ T\ (K))\ *\ E \qquad (1)$$

where R is the gas constant from the ideal gas law (PV = nRT), and T is temperature in degrees K. The parameter E is the extraction efficiency, which is determined by repeated extractions of some of the water samples. All headspace gas is purged from the syringe or bottle between extractions. The repeated extractions are continued until 99% of the SF_6 has been extracted. The extraction efficiency is then calculated as the quantity of gas in the first extraction divided by the quantity of gas in the summed extractions. Extraction efficiencies for the two methods of sampling used in this study were at least 95% (Dillon 1998). Dilutions of the standard show a linear

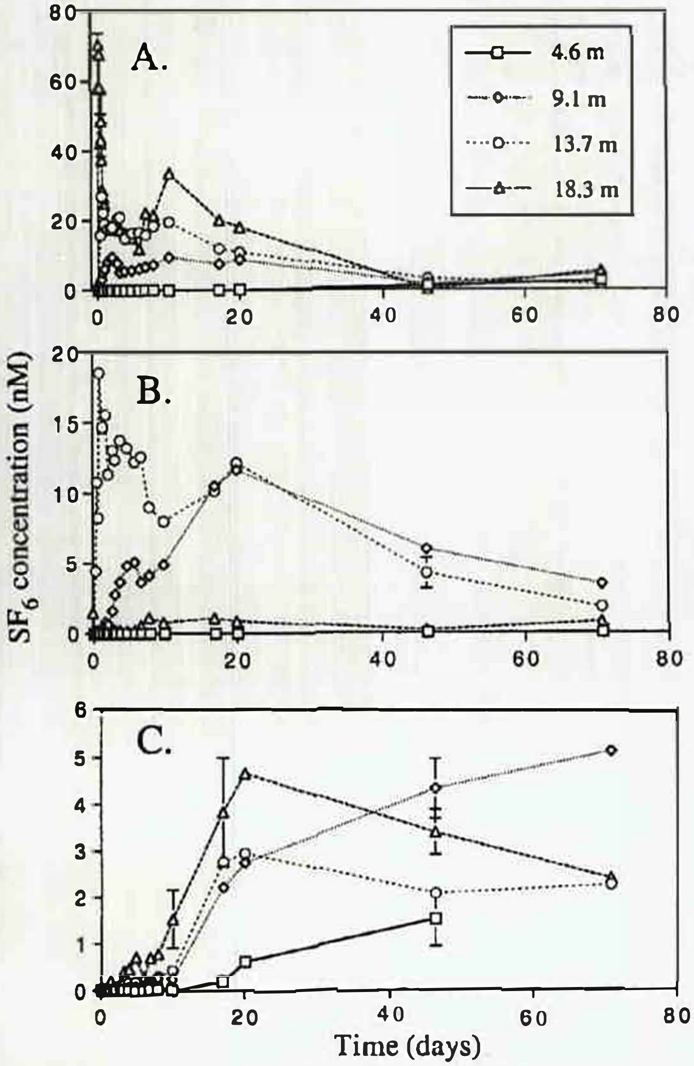

Figure 2. SF_6 results for the wells (4.6 m, 9.1 m, 13.7 m, and 18.3 m) at well clusters 1, 3, and 2 during the October 1996 experiment. Well cluster 1 (panel A) indicates rapid horizontal flow, especially at 18.3 m depth, as well as the vertical movement of the plume. Well cluster 3 (panel B) represents rapid vertical flow, especially at 13.7 m depth. Well cluster 2 (panel C) indicates slower movement representative of the limestone's primary porosity.

relationship between SF_6 concentration and the response of the GC between injections ranging from 0.04 to 42.53 picomoles (1 pmole = 10^{-12} moles). Replicates were collected for 10% of the samples. In addition, duplicate injections were run on the GC every fifth injection. Precision between replicate samples and duplicate injections were usually better than 10%. The lower limit of detection for SF_6 was 0.1 pM.

Iodine-131 samples were counted on one of two NaI (sodium iodine) detectors for the quantification of both ^{131}I and ^{129}I. Iodine-129 was quantified using the low energy photo-peaks (29.0 to 40.0 kiloelectron volts, [keV]), which accounts for 78.3% of the available photons. The 364 keV peak (81.2% photon intensity) was used to calculate the ^{131}I activity. A small correction was made to the ^{129}I total counts because a small percentage (4% of the ^{131}I photon intensity) of counts in this region are attributed to the ^{131}I decay. After these corrections, the radiometric yield can be determined using ^{129}I, and the ^{131}I sample activity can then be estimated. Several samples were recounted after the short-lived ^{131}I had decayed away to verify the radiometric yield results. The majority of all the iodine recoveries were greater than 95%. None were less than 80%. The lower limit of detection for ^{131}I was 41 dpm L^{-1}.

Table 1
October 1996 Data Summary
Times of peak SF_6 concentrations and transport rates (HTR and VTR) for each sampling location during the October 1996 experiment on Long Key. The initial 200 L injection slug had a SF_6 concentration of 46.25 ± 1.21 μM.

Sampling Location	Depth (m)	Time (days)	Maximum SF_6 Conc. (nM)	HTR (m/hr)	VTR (m/hr)
Well 1	4.6	70.8	2.50	< 0.003	< 0.008
	9.1	2.0	9.45	0.10	0.18
	13.7	0.6	27.00	0.37	0.35
	18.3	0.1	70.38	1.74	—
Well 2	4.6	46.3	1.51	< 0.003	< 0.008
	9.1	70.8	5.11	< 0.003	< 0.005
	13.7	20.0	2.95	0.01	0.01
	18.3	20.0	4.65	0.01	—
Well 3	4.6	70.8	0.04	< 0.003	< 0.008
	9.1	20.1	11.66	0.01	0.02
	13.7	1.0	18.54	0.22	0.2
	18.3	7.9	1.11	0.03	—
Well 4	4.6	69.1	0.07	< 0.003	< 0.008
	9.1	69.1	6.79	< 0.003	< 0.005
	13.7	17.1	2.14	< 0.003	< 0.002
	18.3	69.1	0.21	< 0.003	—
Well 5	4.6	0.3	0.80	1.61	2.2
	9.1	17.1	1.94	0.004	0.008
	13.7	70.8	0.21	< 0.003	< 0.005
	18.3	70.8	0.33	< 0.003	< 0.002
Well 6	4.6	69.1	5.09	< 0.01	< 0.008
	9.1	69.1	3.30	< 0.01	< 0.005
	13.7	69.1	0.01	< 0.01	< 0.002
	18.3	69.1	0.19	< 0.01	—
Well 7	4.6	69.1	0.04	< 0.01	< 0.008
	9.1	69.1	6.10	< 0.01	< 0.005
	13.7	69.1	0.16	< 0.01	< 0.002
	18.3	69.1	0.01	< 0.01	—
Canal		6.2	0.0014	0.74	—

RESULTS

October 1996 Experiment

During the first two weeks of the October experiment, there was heavy daily rainfall. On the second day of the experiment, all of the wells' hydraulic heads were measured and the hydraulic gradient across the site was calculated for three of the well depths (4.6, 13.8, and 18.3 m). The piezometric surface at 13.8 m obtained for one of these sampling rounds is shown on Figure 1. The gradient was found to be sloped to the south with values ranging from 0.35 to 0.50 cm/m. These measurements were conducted hourly over a 10-hour period and showed that the gradient between well clusters 6 and 7 did not change more than 0.15 cm/m, although the wellheads oscillated up and down following the Atlantic tide. In addition to illustrating the flow to the south, the contour lines shown in Figure 1 also suggest that the injected waste water is flattening out the piezometric surface around the injection well.

Highlights of the October 1996 tracer results are shown in Figure 2a-c. Times of peak concentrations, maximum concentrations, and calculated transport rates for each well cluster are shown in Table 1. The 200 L injection slug had a SF_6 concentration of 46.25 ± 1.21 μM. The slug also contained 14 kg of potassium phosphate. Due to a spill of purge water into the boat basin during the first few hours of the experiment, samples from Florida Bay water are not presented for this experiment. The SF_6 concentration in the bay was elevated (17.00 nM or 17×10^{-9} M) immediately after the spill and decreased exponentially until it was undetectable after 17.63 days. When the next sample was collected at 20.07 days, however, the SF_6 concentration had increased to 0.76 nM.

The first major ground water flowpath detected was southward. Two hours after injection, the SF_6 concentration at well 1 (5 m south of the injection well) rose to 58.06 nM at the 18.3 m depth and further increased to a maximum of 70.38 nM after 2.9 hours (Table 1, Figure 2a), yielding a horizontal transport rate (HTR) of 1.74 m/hr. The maximum SF_6 concentration observed at this well was 0.1% of the injected concentration. After six hours, SF_6 was detected in well cluster 1 at shallower depths (13.7 and 9.1 m) at concentrations of 0.74 and 0.30 nM (Figure 2a). By 13.2 hours, well 1 (13.7 m) reached a peak concentration of 27.0 nM. The 9.1 m well peaked at 48.5 hours with a concentration of 9.45 nM. The results of these two depths indicates horizontal transport rates of 0.37 and 0.10 m/hr, respectively. Vertical transport rates (VTRs) for these two depths were calculated to be 0.35 and 0.18 m/hr, respectively. These shallow flowpaths illustrate the rapid movement of the plume both horizontally and vertically after injection into the saline aquifer. The 4.6 m well took much longer to show traces of SF_6 and was still rising as of the last sampling period (70 days).

A small peak (1.49 nM) was also observed at well 3; 18.3 m (5 m east of injection well; Figure 2b) during the first hour of the experiment suggesting a HTR of 5.2 m/hr. However, this peak was smaller than the peak observed at well 1, and following this peak concentrations quickly dropped to below 0.25 nM until 6.75 days. At 6.75 days, the SF_6 concentration began to climb and reached 1.11 nM at 7.88 days. If one uses this point as the peak, then an HTR of 0.03 m/hr results. Well cluster 3 showed indications of rapid, vertical flow in the 13.7 m well (Figure 2b). Concentrations at this depth reached a peak value of 18.54 nM 24 hours after injection, yielding an HTR of 0.22 m/hr and a VTR of 0.20 m/hr. The 9.1 m well took longer (20.1 days) to reach its maximum SF_6 concentration of 11.66 nM (HTR = 0.01 m/hr, VTR = 0.02). The SF_6 concentration at the 4.6 m well at this cluster took much longer to show traces of SF_6 and was still rising 70.8 days after injection.

Another small peak comparable to that of well 3 (18.3 m) was also observed at well 5 at the shallowest depth, 4.6 m, after 6.2 hours (Table 1). Well 5 is 10 m south of the injection well. SF_6 concentrations here rose to 0.80 nM, a dilution of 10,000-fold relative to the injected concentration. This yields an HTR of 1.61 m/hr, close to that calculated for well 1 (18.6 m). and a vertical transport rate (VTR) of 2.2 m/hr. This vertical transport is roughly four times faster than was observed at the intermediate depths at well 1.

Results from well 2, located 5 m north of the injection well, illustrate the slower transport similar to that observed in well (9.1 m). Concentrations at all depths here increased slowly over a one- or two-week period (Figure 2c). The two deeper wells (13.7 and 18.3 m) reached their maxima (2.96 and 4.65 nM) at 20 days and then declined. This yields transport rates of 0.01 m/hr for both horizontal and vertical transport. The concentrations in the shallower wells (4.6 and 9.1 m) were still rising as of the last sampling periods, yielding HTRs of <0.005 m/hr and <0.003 and VTRs of <0.01 and <0.005 m/hr, respectively. These are maximum estimations of transport rates since these SF_6 concentrations were still rising as of the last sampling round.

The remainder of the well clusters—4, 6, and 7—took much longer than the others to show signs of SF_6 and generally exhibited much lower concentrations than the peak concentrations observed

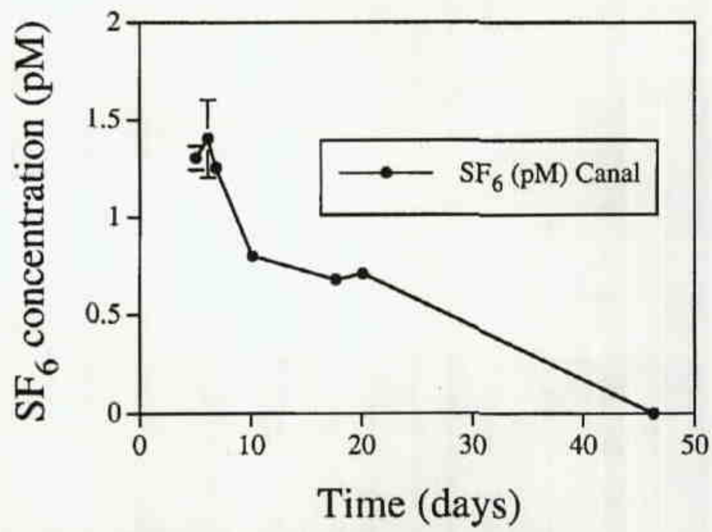

Figure 3. October 1996 SF_6 results from the canal sampled across U.S. Highway 1. This indicates that waste water has the potential to reach Atlantic surface water within days, although it is greatly diluted.

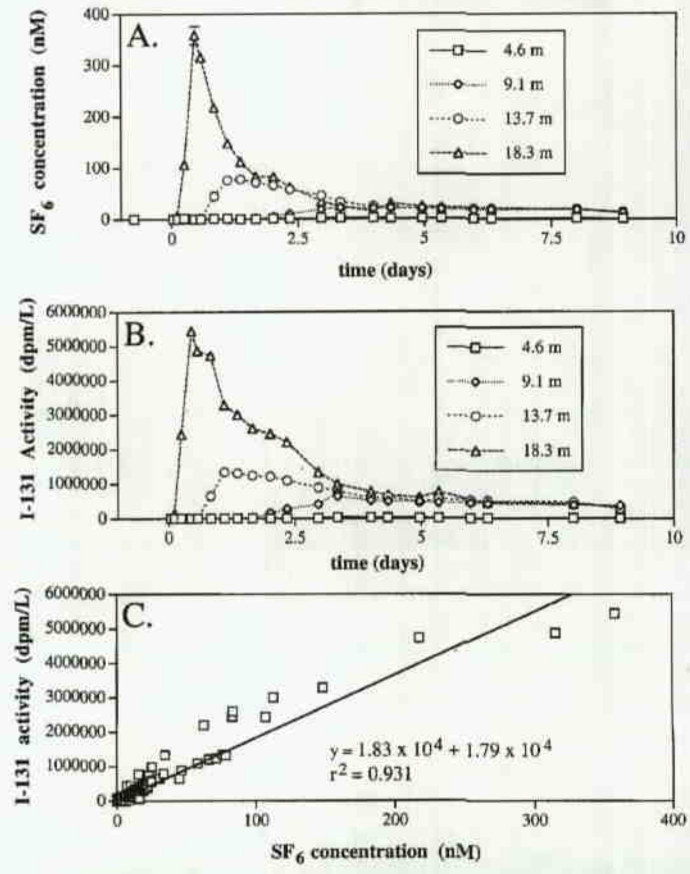

Figure 4. (a) SF_6 results for well cluster 1 during the February 1997 experiment. (b) February 131I results for well cluster 1. (c) SF_6 correlation with ^{131}I for the February 1997 experiment. All samples collected during the experiment are shown.

at the wells shown in Figure 2 (Table 1). Intermediate well depths (9.1 and 13.7 m) at cluster 4 showed peaks values of 5.90 and 2.14 nM, respectively, after 17 days. After 20 days, these levels dropped to 1.69 and 0.43. By the last sampling period (70 days), tracer concentrations in these wells were increasing and were comparable to their previous maxima. The shallow and deep wells at this cluster showed slight traces (<0.2 nM) of SF_6 only on day 70. Well clusters 6 and 7 did not start showing traces of SF_6 until after 40 days. After 70 days, the concentrations at cluster 6 were 5.10, 3.30,

Table 2
February 1997 Data Summary
Times of peak SF_6 concentrations and transport rates (HTR and VTR) for each sampling location during the February 1997 experiment on Long Key. Initial injection slug had a SF_6 concentration of 30.84 ± 1.90 μM.

Sampling Location	Depth (m)	Time (days)	Maximum SF_6 Conc. (nM)	HTR (m/hr)	VTR (m/hr)
Well 1	4.6	3.3	2.68	0.06	0.17
	9.1	3.4	22.44	0.06	0.11
	13.7	1.4	77.97	0.15	0.14
	18.3	0.5	358.73	0.46	—
Well 2	4.6	*	*	—	—
	9.1	*	*	—	—
	13.7	8.0	15.87	0.03	0.02
	18.3	3.0	3.19	—	—
Well 3	4.6	*	*	—	—
	9.1	2.9	14.49	0.07	0.13
	13.7	3.3	21.81	0.06	0.06
	18.3	0.8	1.52	0.26	—
Well 4	4.6	*	*	—	—
	9.1	3.0	19.72	0.07	0.13
	13.7	*	*	—	—
	18.3	*	*	—	—
Well 5	4.6	*	*	—	—
	9.1	*	*	—	—
	13.7	*	*	—	—
	18.3	*	*	—	—
Well 6	4.6	*	*	—	—
	9.1	*	*	—	—
	13.7	*	*	—	—
	18.3	*	*	—	—
Well 7	4.6	*	*	—	—
	9.1	*	*	—	—
	13.7	*	*	—	—
	18.3	*	*	—	—
Canal		*	*	—	—
Bay		*	*	—	—

*SF_6 samples that never rose above background concentrations in the nine-day sampling period.

0.01, and 0.19 nM at 4.6, 9.1,13.7, and 18.3 m, respectively. The same depths at cluster 7 had concentrations of 0.04, 6.1, 0.16, and 0.01 nM.

A canal across U.S. Highway 1 was sampled five days after injection and showed an SF_6 concentration of 1.3 pM (Figure 3). At six days, a maximum of 1.4 pM was reached (HTR = 0.74 m/hr), then levels declined to just below 1 pM from days 10 to 20. The canal's maximum concentration is more than seven orders of magnitude less than that of the injection slug. After 46 days, no SF_6 was detected in the canal.

February 1997 Experiment

In February 1997, a dual tracer experiment was conducted to verify the results from the October experiment. Due to the previous work done on site, a background concentration of less than 2 nM SF_6 was found at all the wells. This relatively low background did not hinder our observation of the major flowpaths, although the resolution of the slow type of transport was obscured. The second tracer (^{131}I) was not useful for detecting the slower transport due to its short half-life ($t_{1/2}$ = 8.02 days). For these reasons, the February experiment was monitored for only nine days.

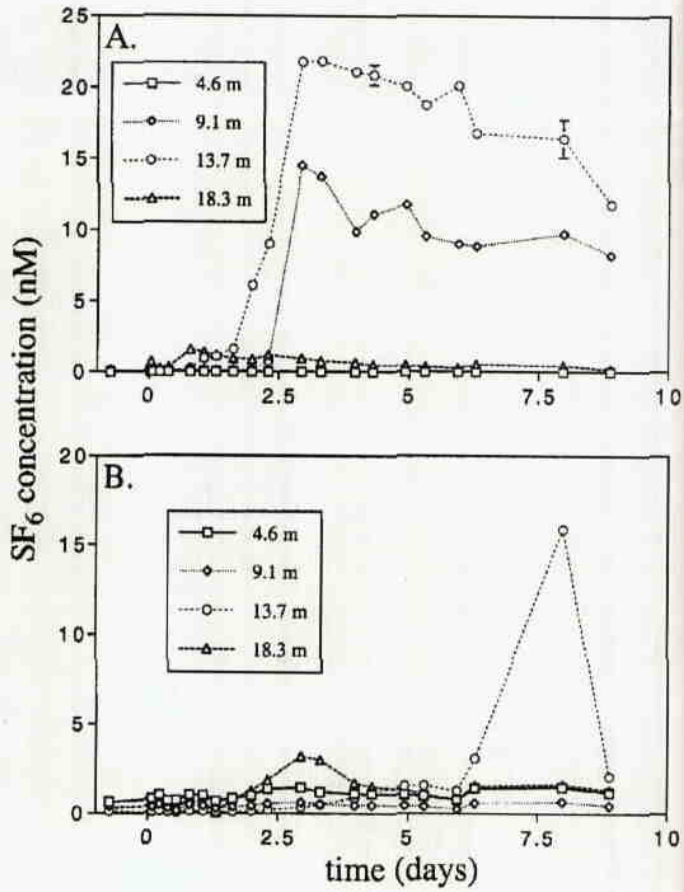

Figure 5. SF_6 results for the wells (4.6 m, 9.1 m, 13.7 m, and 18.3 m) at well clusters 3 and 2 during the February 1997 experiment.

There was no significant rainfall during the course of this experiment. The hydraulic gradient was determined from the water level in well clusters 6 and 7 at three depths (4.6, 13.8, and 18.3 m) during the first two days of this experiment and was found to be sloped toward the south with values ranging from 0.36 to 0.53 cm/m during several tidal cycles. This hydraulic gradient was almost identical to that measured in October.

The two tracers were prepared as two slugs that were injected simultaneously. A 200 L parcel of tap water was sparged with concentrated SF_6 for 20 minutes while a capsule containing 200 mCi ^{131}I was dissolved in 50 L of tap water. The 200 L injection slug had an SF_6 concentration of 30.84 ± 1.90 μM and contained 20 kg of potassium nitrate. The 50 L slug had an estimated ^{131}I activity of 1.0 mCi L^{-1}, which is equivalent to 2.24×10^9 dpm L^{-1}.

The ^{131}I results mimicked those of SF_6, therefore only the latter will be described in detail. Both tracers behaved conservatively and were highly correlated (Figure 4a-c). SF_6 results of the February 1997 experiment were similar to and confirmed results from October (Figure 4a). The first flowpath observed in February was once again southward at well 1 (18.3 m) with a peak concentration of 358 nM SF_6 after 11 hours (HTR = 0.46 m/hr; Table 2). This horizontal flow rate is an order of magnitude slower than the previous estimate at this location, and the SF_6 concentration is four times greater. The 13.7 m well's concentration climbed to 78 nM SF_6 in about 33 hours, corresponding to flow rates of 0.14 m/hr both vertically and horizontally. The 9.1 and 4.6 m wells at this location each took about 80 hours to reach their maximum concentrations of

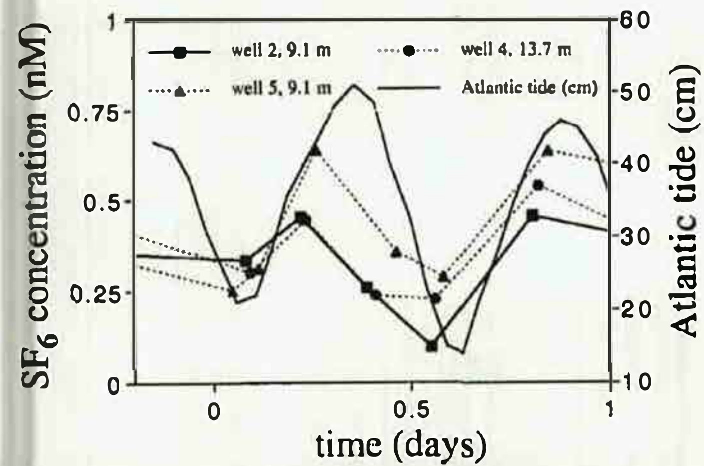

Figure 6. February 1997 SF_6 concentrations (presumably residual from October 1996 experiment) for wells 2, 4, and 5. Only one well is shown for each well cluster. Solid line is Atlantic tide. Note how SF_6 concentrations seem to follow tidal fluctuations.

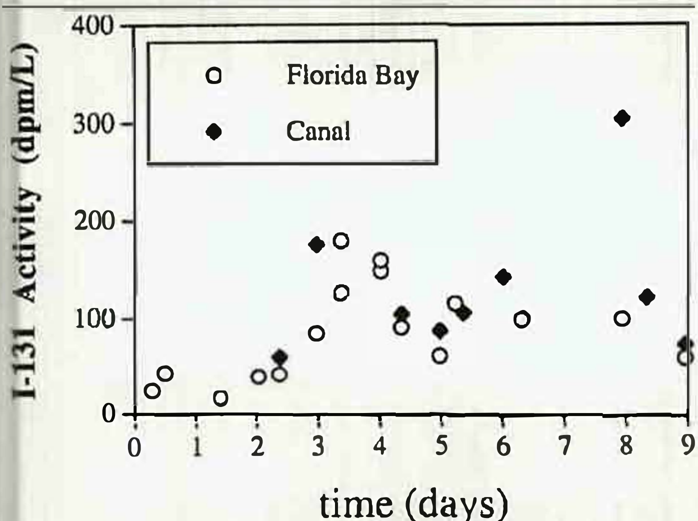

Figure 7. ^{131}I activity in the bay and the canal over time during the February 1997 experiment. Activity of tracer tends to increase over time in surface water indicating that waste water has the potential to reach both the bay and the Atlantic in a few days. Limit of detection was 41 ± 18 dpm/L.

22.4 and 2.7 nM SF_6, respectively. The HTR for both depths was calculated to be 0.06 m/hr while the VTRs were 0.11 and 0.17 m/hr, respectively. With the exception of the shallowest well, which reached a peak SF_6 concentration of 2.68 nM after 79 hrs (HTR = 0.06 m/hr, VTR = 0.17 m/hr), the transport of the tracer to well 1 was slower and the concentrations observed were greater than in the previous experiment.

At well cluster 3, the shallow well (4.6m) showed no increase in SF_6 concentration (Figure 5a). The deepest well (18.3m) showed a small peak of 1.52 nM at 19.2 hours and then began to decrease slowly, yielding a flow rate of 0.26 m/hr (Table 2). At the intermediate depths (9.1 and 13.7 m), tracer concentration peaked at 2.94 and 3.31 days, respectively, with much higher concentrations of 14.49 and 21.81 nM. These results suggest transport rates horizontally of 0.07 and 0.06 m/hr and vertically of 0.13 and 0.06 m/hr. Similar results were seen at well 4 (9.1 m) where concentrations began increasing at 1.08 days, reaching a maximum of 19.72 nM after 2.96 days (71 hrs). This yields an HTR of 0.07 m/hr and a VTR of 0.13m/hr. None of the other depths at well 4 showed any significant increase in SF_6 concentrations.

The remainder of the wells for the February experiment showed no signs of rapid conduit flow and were all similar to the results at well cluster 2 (Figure 5b). Although no rapid flow was observed at these well clusters, the results do suggest that the Atlantic tide can influence ground water movement. During the first day of the experiment, we closely monitored SF_6 concentrations in most wells (1, 2, 3, 4, and 5) and tidal levels in the Atlantic. The SF_6 background concentrations at clusters 2, 4, and 5 showed fluctuations in tracer concentration that corresponded with tidal height variations, suggesting that tidal forcing may play a role in the transport of substances in the water table (Figure 6). Peak residual background SF_6 concentrations at each well cluster (all depths) corresponded to a rising tide for the first day of the experiment, while the lowest concentrations were observed during low tide. Since the piezometric surface at this time was sloped to the south, these fluctuations must be due to up and down movement of the water table following tidal fluctuations. After one day, the sampling intervals were increased and this fine resolution of background fluctuations was lost. Well clusters 6 and 7 weren't monitored as intensely for SF_6 and could not be compared to the tidal data.

The SF_6 concentrations measured in both the bay and the canal across U.S. Highway 1 were near the limit of detection in the February experiment. Due to the previous work done at this site, it is difficult to evaluate whether these low levels of SF_6 were from the October or the February injection. However, the iodine data in surface water show that water from the February injection did reach surface water (Figure 7). After approximately three days, 131I consistently showed up in the Atlantic and the bay's surface water at similar activities (100 to 300 dpm L^{-1}). These activities are approximately seven orders of magnitude more dilute than the injection slug. This dilution is similar to the dilution of the SF_6 that we observed in the canal during the October experiment.

The well coverage at this study site made it possible to roughly estimate what portion of the SF_6 injected could be accounted for by the results. The objective of these calculations was to determine if we were following the majority of the SF_6 or only a small insignificant portion of it. The accuracy of this estimate depends on the physical characteristics of the aquifer itself, as well as the distribution of monitoring wells. In a homogeneous, isotropic aquifer that flows in only one direction, this calculation would be straightforward. Many modeling programs are currently available for such applications. There are none, however, for fresh water masses injected into a saline, tidally affected, anisotropic aquifer that is riddled with innumerable holes and conduits. This lithology is not only evident from the cores obtained during well installation (Monaghan 1996), but also can be seen in the many canals that have been cut into the Keys. The remnants of ancient coral heads, as well as cracks and cavities that formed as these reefs developed, can easily be seen. Due to the heterogeneity of this system, the buoyancy of the observed flow, and the limited distribution of monitoring wells, it was impractical to use any available modeling programs to quantify the observed plume.

For these reasons, we used a simple interpolation of the data by dividing the study area into a stack of eight 2 m tall cylinders, which were sliced evenly into eight wedges with the injection well at the center (Figure 8). Each wedge had an inner and outer portion. The eight inner slices contained the four monitor well clusters closest to the injection well (clusters 1, 2, 3, and 4) The outer eight portions contained well clusters 5, 6, and 7. Porosity was assumed to be 50% (Monaghan, 1996). Several other assumptions

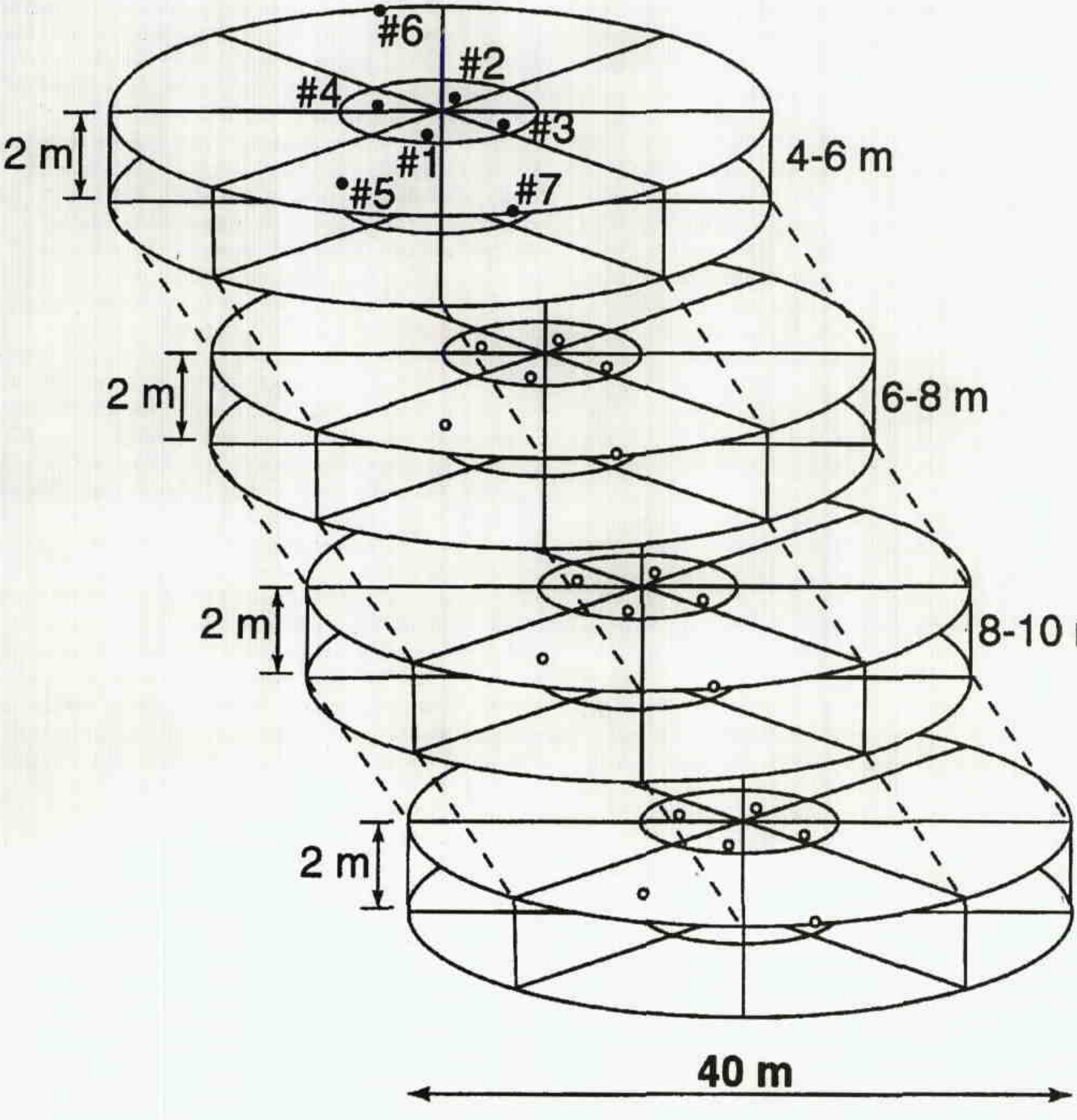

Figure 8. Finite model used to estimate mass balance of SF_6. Each well cluster position is indicated by closed circles and a cluster number. There are eight stacks (only the top four are shown) in the model, each of which is 2 m tall and 40 m in diameter. Each stack contains eight outer wedges and eight inner wedges. The injection well is located in the center of each stack.

had to be made. First, we assumed that the system matrix was homogeneous and the plume spread in a dispersive manner as it rose. We assumed that the tracer concentration measured from a well located within a particular wedge represented the entire wedge. Thus we used known concentrations of individual wells to estimate the concentration of a particular volume in each portion of the model that contains a well. The missing sections of each 2 m tall cylinder were then interpolated horizontally around the inner and outer rings. This gave us the mass of SF_6 in the four cylinders that corresponded to the four well depths at each cluster (4.6, 9.3, 13.8, and 18.3 m). These masses were then used to vertically interpolate throughout the other four cylinders that did not contain any wells. As stated previously, these mass-balance calculations are rough estimates, and thus the calculated amount of SF_6 for each sampling round have large errors associated with them. These calculations were performed only to evaluate whether a significant portion of the tracer could be accounted for by our results.

These mass-balance calculations were carried out for each sampling round of both experiments. The estimated amount of SF_6 for the first experiment ranges between 19% and 34% of the injected amount for the first 10 days. After 17 and 20 days, this estimate rises to 52% and 45%, respectively. After 46 days, 89% of the tracer could be accounted for by this method. After another month ($t = 71$ days), the estimation climbs to 144% of the injected amount. The values shown for the first 10 days may be underestimated due to the fact that the concentrations for each inner slice are based upon concentrations determined from wells located at the outer edge of the pie, not the center. This is particularly true of the deeper depths, close to where the injection occurs. The most concentrated portion of the plume was probably located near the injection well and decreased away from it.

As time continued, this plume probably dispersed in a more even fashion. Presumably our model overestimates the SF_6 in the later sampling rounds due to the large volumes of the outer rings of the finite model. Monitoring wells were located in only three of the eight outer portions. Tracer concentrations of the remaining five pieces had to be interpolated from the known tracer concentrations. These outer rings have huge volumes, and consequently even a small overestimation of concentration can cause the estimated mass of SF_6 to increase drastically. Data from these experiments as well as others (Shinn et al. 1994; Paul et al. 1997) indicate that the highest transport rates were observed along the north/south axis of the island. The monitor well clusters (5, 6, and 7) used to estimate the SF_6 concentrations of the slices in the outer ring of the model are along or near the north-south axis. Consequently, the plume may not ever reach the model's outer slices that are east and west of the injection well. Estimations of the outer rings located east and west of the injection well may be gross overestimates since the interpolations were made using data from well clusters 5, 6, and 7.

In February, approximately 39% of the SF_6 injected in October was still present in the study area. There was an SF_6 background of less than 2 nM at all wells. These data were used to obtain average background concentrations for each portion of the model. These concentrations were then subtracted from the estimations for the second experiment. The first two sampling rounds were conducted 1 and 2.6 hours after injection. These estimates were virtually the same as the background estimate, indicating that a significant portion of the plume hadn't yet reached the monitoring wells. After six hours, the estimated total amount of SF_6 began rising (54%) and continued to climb until 11 hours when a maximum of 164% of the injected mass could be accounted for. During the next 30 hours, the estimate dropped to 74%, then fluctuated between 66% and 140% for the remainder of the experiment. Although crude and rather elementary, this method suggests that a significant portion of tracer injected can be accounted for in both of these experiments. Furthermore, these results indicate that a large portion of the waste water injected at the site remains relatively close to the injection site for several months.

Discussion

Estimated transport rates from the deep well injection experiments on Long Key suggest there are two types of movement for injected waste water (Tables 1 and 2). The first type is characterized by rapid advection through conduits presumably formed by the dissolution of or fractures within the carbonate bedrock. This flow can be as rapid as 1.72 m/hr (41 m/d) horizontally and as great as 2.2 m/hr (53 m/d) vertically. Paul et al. (1997) conducted a similar experiment at this location with viral tracers and found comparable rates of ground water flow (0.12 to 2.0 m/hr) with the greatest advection of the plume being in a southerly direction.

Due to the rapid upward movement of the plume, we believe that hypersaline injection slugs were diluted by the waste water present in the injection well pipe prior to the injection, as well as by the 1000 L waste water "chaser" (salinity ~ 0 ppt). This dilution must have been sufficient to lower the salinity to below that of the ambient ground water (> 35 ppt; Kump 1998). The total volume of the injection well is 704 L, 465 L of which is in the cased region of the well. Due to these large volumes of waste water, it is likely that the slug was diluted significantly by the time it reached the bottom of the injection well and entered the ground water system. If so, the rapid vertical flow could be driven by density differences between the injected waste water and the more saline ambient ground water. Alternatively, upward movement may have been caused by vertical dispersion through preferential flowpaths that direct the waste water upward. Most likely, a combination of these two mechanisms was responsible for the vertical migration of the plume. Small differences in the density of the treated waste water due to temperature could also affect the buoyancy of the waste water plume, although this was not examined in this study.

The second type of ground water movement is a slower transport through portions of the rock with lower permeability. Tracer data from the October experiment show that the tracer reached well clusters 6 and 7, which are the northern and southern most well clusters, at the same time and had similar concentrations. This suggests that hydraulic gradient may undergo reversals that allowed the tracer to move toward both well clusters 6 and 7. Other studies at this site have shown primary transport along this north/south axis as well (Shinn et al. 1994; Paul et al. 1997) but the lack of wells farther to the east and west makes it difficult to evaluate whether there is also significant flow in these directions. This slower transport is most likely a result of diffusion driven by a concentration gradient and mechanical dispersion that may be largely driven by tidal forcing and pumping. Changes and reversals in the local hydraulic gradient driven by meteological events and changes in the water levels of the Atlantic and the bay most likely influenced subsurface transport as well. It is likely that the hydraulic gradient at this location can change dramatically due to the dynamic nature of this ground water system. The flow field is likely somewhat transient, constantly responding to changes of water levels of the Atlantic and the bay as well as being influenced by local recharge. Estimated horizontal flow rates for this slower transport are less than 0.01 m/hr, while vertical rates are less than 0.02 m/hr.

Transport rates observed at well 1 (18.3 m) were four times faster in October than in February. It is unclear why the rates were so different between the two experiments. It may be that the hydraulic gradient was much steeper at the time of injection in October than in February. The wellhead data from October, which are from the day after the injection, show that the gradient at this time was nearly identical to that observed in February. Either the gradient in October decreased dramatically soon after the tracers were injected into the disposal well or some other mechanism(s) are responsible for the difference in flow rates at well 1. Similar differences were also seen at well 3 (13.7 m), which also took longer to reach a peak concentration during the February experiment than it did previously. In October, this well quickly reached a maximum after just 0.95 days (22.8 hours). During the February experiment, however, it took 3.31 days and the maximum concentration was greater.

Trends observed at well 3 (9.1 m) and at well 4 (9.1 m) (east and west of the injection well) suggest that flow rates and directions for the waste water plume can change temporally. At these intermediate depths, a maximum concentration of SF_6 was seen after approximately three days in February. This is in contrast to the October experiment when slightly smaller peak values were seen in these wells after about three weeks. These results seem to indicate that the plume may have moved in a more radial fashion in

February than the plume observed in October. The drastic difference in meteorological conditions between the two experiments may have caused these differences. The similarity of the hydraulic gradients seems to refute this idea, although these measurements were taken a day late during one experiment and were obtained only from well clusters 6 and 7. These head measurements may not accurately describe the hydraulic conditions closer to the injection well, where a small mound of waste water seems to exists in the immediate vicinity of the injection well (Figure 1).

The most likely explanation for the difference in flow patterns between the experiments may be related to the volume of waste water injected in the disposal well after the experiments had begun. No attempt was made to address this issue, but a higher rate of waste water disposal would result in a larger mound of waste water, more radial flow, and consequently higher flow rates near the disposal well. Increased injection volume could also affect flow directions by forcing the plume deeper down the disposal well where it might flow into different cracks or conduits than it did at times of lower flow, thus altering flow directions and affecting mechanical dispersion rates.

Other studies have shown that ground water flow rates through the Key Largo Limestone can be higher at other locations. Paul et al. (1995) conducted two tracer tests on Key Largo. They found that bacteriophages flushed into a toilet and injected into a simulated injection well showed up in a nearby canal within 11 hours. Estimated rates of transport ranged from 0.57 to 24.2 m/h. In their 1997 study, Paul et al. repeated a portion of the Key Largo experiment and found similar transport rates (2.5 to 35 m/hr). In both of these studies, it was shown that transport was influenced by Atlantic tidal fluctuations. In another study on Key Largo, Dillon et al. (1999) showed horizontal ground water transport rates ranging from 0.21 to 3.28 m/hr and also suggested that transport was driven by changes in the Atlantic tide.

Paul et al. (1997) found slower flow rates at KML compared to their Key Largo studies (Paul et al. 1995) and attributed the slower ground water movement to differences in geology or the lack of numerous boating canals cut into the limestone near KML. They found that movement of ground water at this site was predominately along the north/south axis of Long Key and found no indication of tidal influences. However, the higher sensitivity with which SF_6 can be measured allowed the tidal influences on ground water flow at KML to be observed (Figure 6) due to the residual tracer present in all of the wells in February. Although these concentrations were low compared to those observed in October, the observed fluctuations corresponded to changes in the Atlantic tide with the highest concentrations in each well occurring on a rising tide while the lowest concentrations were observed while the tide was falling. The hydraulic gradient during this time indicates that flow across the study site was to the south, suggesting that this correlation with the tide is a result of the plume being forced up and down as the Atlantic tide rises and falls. This up and down motion is in contrast to another study on Key Largo (Dillon et al. 1999) where tracer studies inferred a hydraulic gradient reversal and associated tidal pumping as the Atlantic tide rose and fell as suggested by Halley et al. (1994).

The difference in ground water movement beneath Key Largo and Long Key is due to differences in Florida Bay's tides between the two locations. Eastern Florida Bay near Key Largo is hydraulically isolated from oceanic tides by mud banks and the Keys themselves. Thus the water level in this portion of the Bay is controlled by meteorological condition such as wind forcing (Wang et al. 1994; Halley et al. 1994; Dillon et al. 1999). The hydraulic gradient in the upper Keys can change over a tidal cycle because the water level in Florida Bay remains unchanged, while the tide in the Atlantic oscillates up and down. In contrast, the water level of Florida Bay behind Long Key is influenced more by tidal fluctuations in the Atlantic Ocean and the Gulf of Mexico (Wang et al. 1994). Machusak and Kump (1997) showed a 56% reduction of the Atlantic tide in this region of the Bay. During our study, the measured hydraulic gradients across the study site did not change significantly over time in either experiment, indicating that the bay's water level was consistently higher than the Atlantic's, driving the ground water flow southward. This is not to imply that hydraulic gradient reversals do not occur on Long Key, but no such changes were observed during this study. Several meteorological or tidal mechanisms could raise the Atlantic's water level above that of Florida Bay, causing ground water flow to be northward. As mentioned previously, the plume around the injection well is most likely transient in nature and will constantly move in response to tidal fluctuations or meteorological conditions.

Conclusions

These experiments illustrate the rapid horizontal and vertical transport of relatively low salinity waste waters injected into the saline aquifer of Long Key. Vertical flow rates were comparable to horizontal rates due to either the buoyancy of the plume and/or preferential vertical flowpaths. We interpret the observed rapid flow rates (0.22 to 2.20 m/hr) as conduit flow while the slower rates (< 0.03 m/hr) are representative of the diffusive type of flow associated with the limestone's primary porosity. In addition to these two primary modes of transport, there seems to be some tidal component which, in the case of our experiments, seemed to force the plume up and down with the tide. It is likely that the tide could also lead to a reversal of the hydraulic gradient if some mechanism, meteorlogical or tidal, lowered the bay's water level below that of the Atlantic.

Results from this study indicate that conservative substances injected into the ground water system reach nearby surface water and are diluted by seven orders of magnitude or more by both ground water and the receiving surface water. This dilution rate is representative of the processes that act at this location only; other disposal wells may be more or less hydraulically connected to surface water. High dilution may not totally alleviate environmental concerns if the flux of nutrients from waste water to surface water is high, allowing significant quantities of nutrients to reach surface water over time. Corbett et al. (1999a) have shown that much of the injected nutrients are stripped from the ground water at this location by either quantitative chemical adsorption to the limestone in the case of phosphate or, in the case of nitrate, partial removal by microbial denitrification. However, Corbett et al. (1999b) presents evidence for the influence of ground water derived nitrogen near the Keys within Florida Bay. In the future, we plan to conduct similar experiments at larger volume waste water disposal wells throughout the Keys, one of which injects as much as 7.5×10^5 L/d of waste water to the subsurface, which is about 280 times the waste water volume received by the injection well at KML.

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