

# The Use of Artificial Tracers to Determine Ground-Water Flow and the Fate of Nutrients in the Karst System Underlying the Florida Keys.

By Kevin S. Dillon<sup>1</sup>, D. Reide Corbett<sup>2</sup>, William C. Burnett<sup>1</sup>, and Jeffrey P. Chanton<sup>1</sup>

<sup>1</sup> Dept. of Oceanography, Florida State University, Tallahassee, FL 32306

<sup>2</sup> Dept. of Geology, East Carolina University, Greenville, NC 27858

## Abstract

To determine the fate and movement of sewage derived contaminants and their possible interaction with surface waters in the Florida (USA) Keys, several types of experiments were conducted using SF<sub>6</sub> as an artificial tracer. The first type of experiment examined fluid flow from septic tanks placed in Miami Oolite on Big Pine Key, where there is a shallow freshwater lens overlying saline ground waters. Here ground water transport rates were constrained to be between 0.11 to 1.87 m/hr, traveling in an easterly direction (Dillon et al., 1999). The second type of experiment took place on Key Largo where there is no freshwater lens and the matrix of the aquifer is solely the more porous Key Largo limestone (KLL). Here we injected the tracer into a shallow well, which was screened from 0.6 to 10 m. This allowed us to evaluate groundwater movement in the shallow upper portion of the aquifer, the area to which inputs by septic tanks occur. Groundwater transport rates in the Upper Keys were as great as 3.7 m/hr and were controlled by the Atlantic tide (Dillon et al., 1999). SF<sub>6</sub> laden groundwater plumes moved back and forth due to tidal pumping. SF<sub>6</sub> reached nearby surface waters within 8 hours. Our results indicate that wastewater injected into the shallow subsurface can travel rapidly and may reach marine surface waters within a few hours.

Three dual tracer experiments were conducted on Long Key, Florida USA 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 waters of the Florida Keys. In three experiments, artificial ground water tracers, sulfur hexafluoride (SF<sub>6</sub>) and radioiodine (<sup>131</sup>I) were used to determine transport rates and directions of soluble non reactive substances injected into the saline ground waters underlying the Keys. Simultaneously, reactive tracers (bulk unlabeled phosphate, PO<sub>4</sub>, and nitrate, NO<sub>3</sub>, and radio-labeled phosphate (<sup>32</sup>PO<sub>4</sub>)) were also added to determine the fate of nutrients in the subsurface. Two types of transport were observed: (1) rapid flow (0.20 - 2.20 m/hr) presumably due to the many conduits present in the limestone and (2) slow diffusive flow (< 0.003 - 0.14 m/hr) associated with the limestone's primary porosity (Dillon et al., 2000). Vertical flow was comparable to horizontal flow due to either the density driven buoyancy of the waste water plume or to preferential flow paths which allow upward advection or combination of both. These experiments showed that conservative artificial tracers injected into the subsurface reach surface waters in a matter of days and can remain in the immediate vicinity of the injection well for several months.

At this low discharge site (2600 L/day) the reactive tracers' behaviors in the subsurface indicate that PO<sub>4</sub> and NO<sub>3</sub> are both partially removed from solution in the subsurface. Phosphate showed an initial rapid uptake followed by a slower removal, caused by adsorption-desorption reactions with the KLL (Corbett et al., 2000). Based on our observations, we estimate that approximately 95% of the PO<sub>4</sub> injected into the subsurface could be removed in 20-50 hours. There was also evidence for some removal of nitrate from solution, most likely due to denitrification. Approximately 65% of the nitrate was removed over several days, suggesting denitrification rates between 2700 and 7000 μmoles m<sup>-3</sup> hr<sup>-1</sup>. Collectively, our results from this site suggest that much of the nutrients injected into the subsurface are removed from solution and may not have a significant impact on surface waters. However, these experiments were conducted at a relatively small facility, while some facilities in the Keys inject as much as 750,000 L per day. Saturation of available adsorption sites and organic substrate availability may limit the efficiency of waste water nutrient removal under such conditions.

To evaluate the fate of waste water at a high volume injection well facility, another dual tracer study using  $^{32}\text{PO}_4$  and  $\text{SF}_6$  was conducted. During this study, rapid conduit flow as high as 7.9 m/day was observed. At this site, waste water rises rapidly after injection to 18-27 m due to the buoyancy of the low salinity waste water plume. It buoys upward until it meets an impermeable mud layer at about 5 m that overlies the KLL. The majority of the plume is then advected to the east due to the local hydraulic gradient that exists across this site. Initially, phosphate was rapidly adsorbed as observed at the Long Key site. After approximately 36 hours, however we began to see radio labeled  $\text{PO}_4$  returning to solution, indicating that phosphate is being desorbed from the KLL and slowly returning to solution. The KLL underlying this site seems to be acting as a phosphate buffered system. As a result, the  $\text{PO}_4$  concentrations 15 m from the injection well seem to be maintained at approximately 25  $\mu\text{M}$ . This is supported by column experiments (Elliot, 1999), which also show that adding low phosphate water to KLL that is saturated with  $\text{PO}_4$  will cause desorption of  $\text{PO}_4$  until an equilibrium value of approximately 25  $\mu\text{M}$  is reached.

Denitrification assays (Acetylene-block technique) suggest rates of denitrification as high as 3000  $\mu\text{moles m}^{-3} \text{ hr}^{-1}$ , comparable to estimates from the Long Key study. Seagrass and macroalgae samples collected from surface waters around the site indicate that isotopically heavy nitrogen, which is indicative of sewage derived nitrogen (McClelland et al., 1997), is being incorporated into the biomass of these primary producers. Macroalgae collected in a canal to the east of the disposal well showed a  $\delta^{15}\text{N}$  value of +13.55 per mil. Stable nitrogen isotopic samples of subsurface  $\text{NO}_3$  as well as  $\text{N}_2/\text{Ar}$  samples have been collected and should provide a clearer picture of the fate of  $\text{NO}_3$  in the subsurface at this site.

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