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# Potential for Denitrification near Reclaimed Water Application Sites in Orange County, Florida, 2009

By Michael J. Byrne Sr., Richard L. Smith, and Deborah A. Repert

U.S. Department of the Interior
U.S. Geological Survey

**U.S. Department of the Interior**
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**U.S. Geological Survey**
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia 2012

Suggested citation:
Byrne, M.J. Sr., Smith, R.L., and Repert, D.A., 2012, Potential For Denitrification near Reclaimed Water
Application Sites in Orange County, Florida, 2009; U.S. Geological Survey Open-File Report 2012-1123, 54 p.

# Acknowledgments

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# Conversion Factors

| Multiply | By | To obtain |
| --- | --- | --- |
| | Length | |
| foot (ft) | 0.3048 | |
| mile (mi) | 1.609 | kilometer (km) |
| | Area | |
| acre | 4,047 | square meter ($m^2$) |
| acre | 0.4047 | hectare (ha) |
| | Volume | |
| gallon (gal) | 3.785 | liter (L) |
| | Flow rate | |
| million gallons per day (Mgal/d) | 0.04381 | cubic meter per second ($m^3$/s) |

# Abbreviations

DOC       dissolved organic carbon

RIB        rapid infiltration basin

TN         total nitrogen

USGS     U.S. Geological Survey

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
°F=(1.8×°C)+32
Nitrate mg/L as N may be converted to Nitrate mg/L as follows: Nitrate mg/L = Nitrate mg/L as N x 4.43

# Potential for Denitrification near Reclaimed Water Application Sites in Orange County, Florida, 2009

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## Abstract

The potential for denitrification was tested in water samples from four Upper Floridan aquifer wells near a reclaimed water application site, in west Orange County Florida, and two adjacent springs. Results of the study indicate that denitrifying bacteria are present in the groundwater and spring water samples, and that these bacteria can readily denitrify the waters when suitable geochemical conditions exist. The acetylene block technique was used to assess nitrous oxide in the samples that was produced by denitrification. The laboratory incubation experiment consisted of four different treatments to each of the six samples: (1) ambient water (no added nitrate or glucose), (2) ambient water amended with 1.4 milligrams per liter (mg/L) nitrate as nitrogen (N), (3) ambient water amended with 5.0 mg/L nitrate as N, and (4) ambient water amended with 5.0 mg/L nitrate as N and 10 mg/L glucose as $C_6H_{12}O_6$. A companion set of incubations using treatment 2 tracked changes in nitrate and nitrite concentration with time. The rate of denitrification in treatment 2 ranged from 0.059 to 0.124 milligram per liter per day nitrogen [(mg/L)/d N] and in treatment 3 ranged from 0.071 to 0.226 (mg/L)/d N. At all of the sampling sites, treatment 4 yielded denitrification rates at least an order of magnitude greater than those measured for the other treatments; rates ranged from 2.3 to 4.4 (mg/L)/d N. The electron donor supply, dissolved organic carbon, in the groundwater and springwater is sufficient to remove at least 1.1-1.4 mg/L nitrate as N in 20 to 30 days, as indicated by nitrous oxide production rates under ambient conditions (treatment 1). The even higher nitrate removal observed with addition of supplemental carbon in treatment 4 suggests that carbon is a limiting nutrient in this reaction. Denitrifying activity might explain the low ambient nitrate concentrations in the Upper Floridan aquifer in this area.

## Introduction

Springs in central Florida are threatened by elevated concentrations of nitrate, which lead to algal blooms, fish kills, and oxygen depletion (Walsh and others, 2009). The sources of the nitrate include fertilizer, manure, and septic waste, all of which are carried by rainfall into the Upper Floridan aquifer through natural diffuse downward leakage as well as numerous drainage wells, and karstic features such as sinkholes (Katz and others, 1999). The nitrate-rich groundwater then enters the springs through artesian groundwater discharge. Rapid infiltration basins (RIBs) are shallow basins established to dispose of applied, nitrate-containing reclaimed water and additionally to recharge the Upper Floridan aquifer (Adamski and German, 2003). RIBs initially recharge the surficial aquifer that overlies the Upper Floridan aquifer, then most of the water in the surficial aquifer eventually flows downward to the Upper Floridan aquifer in this area (Adamski and German, 2003).

Springs have also been affected by groundwater withdrawals. Groundwater consumption in Orange County, Florida, which is predominantly from the Upper Floridan aquifer, has increased from 87 million gallons per day (Mgal/d) in 1965 to 267 Mgal/d in 2005 (Marella, 2009). Increased groundwater consumption has contributed to decreased water levels in the Upper Floridan aquifer and decreased discharge to the springs in Orange County (Adamski and German, 2003).

Nitrate concentrations in the springs are elevated above background concentrations of 0.2 milligram per liter (mg/L) nitrate as nitrogen (N) (Walsh and others, 2009). Nitrate can be naturally reduced to an inert nitrogen gas by a bacterial process called denitrification, which can serve as a remediation mechanism if the appropriate conditions (a suitable electron supply, such as organic carbon, and anoxia) are present:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_2 \text{ (g)}$$

The process begins with nitrate and the end product of denitrification is non-reactive nitrogen gas (Smith and Duff, 1988). An understanding of the degree to which denitrification occurs, or the "rate of denitrification," in the Upper Floridan aquifer is needed to predict nitrate transport to the springs and the potential amount of nitrate removed within the transport interval.

In 2004, the U.S. Geological Survey (USGS), in cooperation with the Orange County Utilities Department, initiated a study to determine: (1) the source of the nitrate in the Upper Floridan aquifer beneath a RIB site located in west Orange County, Florida (fig. 1); (2) whether denitrification occurs within the aquifer; (3) the age (time since recharge) of the water in the aquifer in this area; and (4) an estimate of the rate of denitrification in the Upper Floridan aquifer. The first two objectives were addressed by Kroening (2007; app. 1). The third objective was addressed by Schlosser and others (2008; app. 2). The final objective of the study is addressed in this report. Estimates of denitrification rates of water from selected springs, in addition to the Upper Floridan aquifer, also are included in this publication.

## Purpose and Scope

The purpose of this report is to describe potential rates of denitrification in water samples from the Upper Floridan aquifer, Wekiwa Springs, and Rock Springs in west Orange County, Florida (fig. 1). In addition, this report incorporates findings from the previous reports completed as part of the study to provide the reader with a single report that addresses all of the study objectives. The "potential" rate of denitrification is defined as the capacity of denitrifying bacteria present in the water to reduce nitrate concentrations when certain optimal conditions exist, (presence of denitrifying bacteria, ample supply of carbon to act as an electron donor source, and reducing conditions related to a low concentration of dissolved oxygen)  and does not necessarily reflect what is occurring in the aquifer under ambient conditions. The potential rate of denitrification was calculated as the rate of nitrate reduction to nitrous oxide within water samples using the acetylene block technique in short-term laboratory incubations (Balderston and others, 1976; Yoshinari and others, 1977). For the current effort, a total of six water quality samples were collected at six sites (four groundwater wells, two springs) in late 2009.

## Previous Investigations

Sumner and Bradner (1996) described the fate and transport of nutrients within the surficial aquifer beneath a rapid infiltration basin along the Lake Wales Ridge in Orange County. Removal of nitrogen by denitrification from the percolating reclaimed water was minimal within the surficial aquifer in the immediate vicinity of the basin, probably because of the lack of reducing conditions and a relative
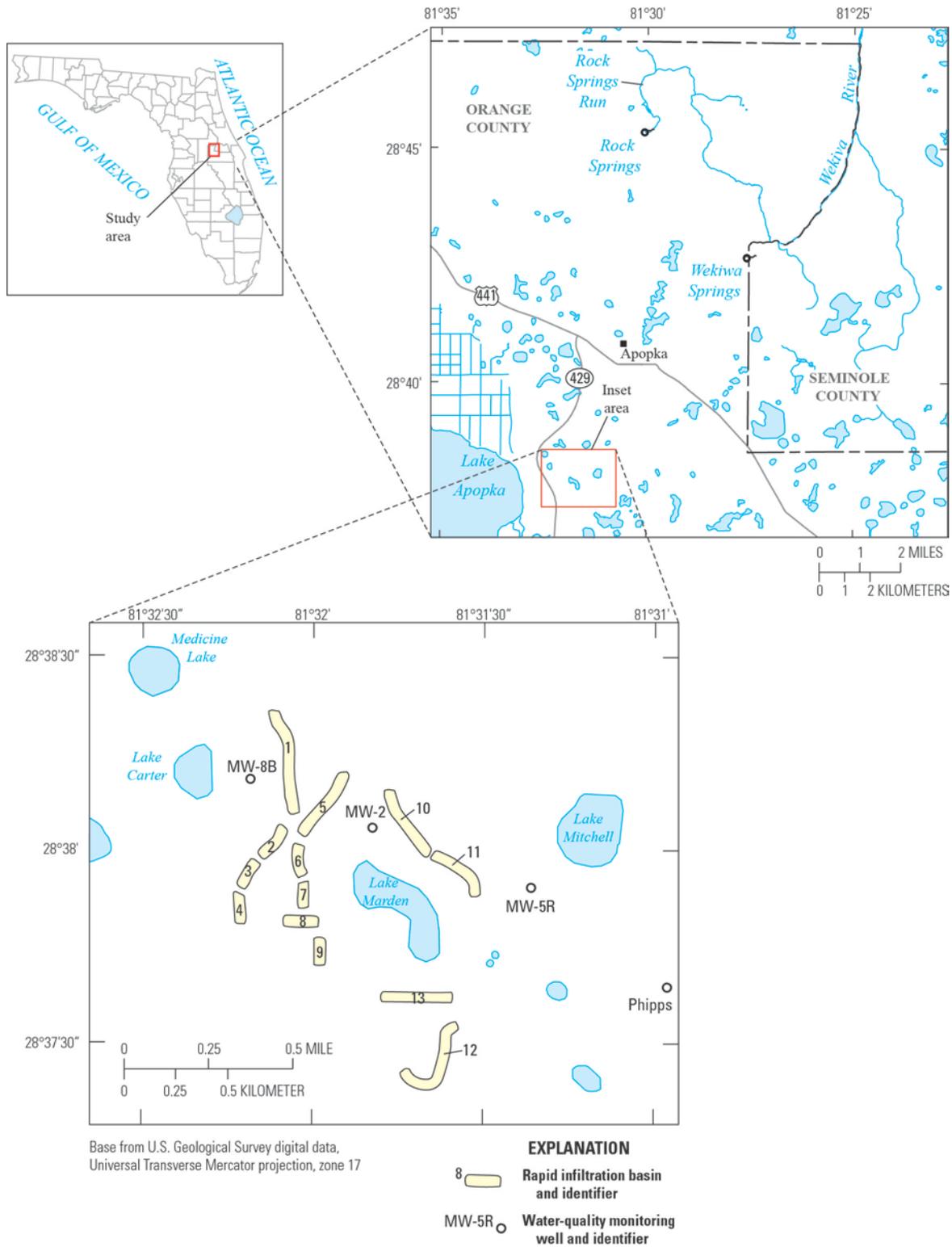
**Figure 1.** Map showing location of study area.

paucity of organic carbon substrates. They also noted that phosphorus concentrations were decreased by about 90 percent from concentrations in applied reclaimed water after moving through the upper 15 feet (ft) of the soil profile. This most likely was a result of adsorption onto abundant iron and aluminum hydrous oxyhydroxide coatings on sand grains. A number of models have been developed that describe the northeasterly groundwater flow in the Upper Floridan aquifer in Orange County and predict the areas of aquifer recharge (Murray and Halford, 1996; O'Reilly, 1998; Sepulveda, 2002). Katz and others (1999) used nutrients, isotopes, and major ions to study the spring water in the Suwannee River Basin and found that (1) the age of the spring water was greater than 20 years, (2) nitrate contamination was positively correlated with volume of fertilizer use, and (3) nitrate and dissolved oxygen concentrations in groundwater were positively correlated. Toth and Fortich (2002) also described how nitrate contamination in Rock Springs and Wekiwa Springs was related to fertilizer use in those areas. Walsh and others (2009) found that nitrate contamination had decreased in Rock Springs and Wekiwa Springs by 2007, but was increasing in other springs.

Denitrification in groundwater can be quantified or inferred using several different techniques. Smith and Duff (1988) used the acetylene block technique to determine rates of denitrification in an unconfined sand and gravel aquifer, and discovered that available carbon limited the reaction. Katz and Böhlke (2000) used isotopic signatures of nitrogen to identify denitrification in a carbonate aquifer in the Suwannee River Basin. Kroening (2007; app. 1) found excess nitrogen gas, the end product of denitrification, in the Upper Floridan aquifer beneath the RIBs site that is the focus of this report, and used nitrogen isotopes to identify fertilizer as the source of the nitrate. Nitrogen-15-enriched nitrate also has been injected into groundwater during natural gradient tracer tests to quantify denitrification *in situ* (Smith and others, 2004).

## Water Quality and Flow to Springs

Historical and recent groundwater quality, as well as estimates of how fast groundwater moves from the RIBs to nearby springs, are presented in this section. The Orange County Northwest Water Reclamation Facility RIBs are located near the west border of Orange County, Florida, more than 7 miles (mi) from Wekiwa Springs and Rock Springs (fig. 1). These RIBs were constructed in 1987, and have a treatment capacity of 7.5 Mgal/d (Morrell and others, 2002). Tertiary wastewater treatment before application consists of grit removal, activated sludge aeration, sand filtration, and disinfection using chlorine.

Although nitrate and dissolved oxygen concentrations are relatively high in the surficial aquifer, indicating potential water-quality degradation beneath the RIBs, results from Kroening (2007) indicate that these effects do not extend to the Upper Floridan aquifer. Nitrate and dissolved-oxygen levels in the surficial aquifer beneath the RIBs were 1.20 to 6.30 mg/L nitrate as N and 1.5 to 8.4 mg/L as $O_2$, respectively (Kroening, 2007; app. 1). Water in the Upper Floridan aquifer beneath the RIBs is suboxic (0.1-0.2 mg/L as $O_2$), and the nitrate concentration is considered to be at background levels (less than 0.2 mg/L nitrate as N; Kroening, 2007, app I). Dissolved oxygen concentrations are low in Wekiwa Springs (0.40 mg/L as $O_2$) and in Rock Springs (1.38 mg/L as $O_2$) (Walsh and others, 2009).

In 1961, the nitrate concentration in Wekiwa Springs was 0.61 mg/L as N (Toth and Fortich, 2002); however nitrate concentrations in 2009 in Wekiwa Springs (1.12 mg/L as N) and Rock Springs (1.38 mg/L as N) were elevated above the background concentration of 0.2 mg/L as N (Walsh and others, 2009). A peak nitrate concentration (2.0 mg/L as N) was measured in Wekiwa Springs in 1995; values have since declined (Toth and Fortich, 2002; Walsh and others, 2009). The declining trend appears to be related to a decrease in citrus acreage, which peaked at 65,000 acres in 1968, dropped substantially to 45,000 acres in 1984 following a hard freeze, and declined further to 10,000 acres by

2001 (Toth and Fortich, 2002). Toth and Fortich (2002) used isotope data to determine that (1) the source of nitrate was fertilizer and animal waste at Wekiwa Springs, and fertilizer at Rock Springs, and (2) the mean age of the water since recharge to the Upper Floridan aquifer at both springs was approximately 17 years.

Groundwater age and time of travel from the RIBs to the springs were estimated from a groundwater flow model and groundwater age-dating and geochemical methods. Model projections, based on particle tracking (MODPATH 4.2) simulations using a calibrated groundwater flow model of the area (O'Reilly, 1998), indicate that it takes more than 100 years for the water in the Upper Floridan aquifer beneath the RIBs to reach Wekiwa Springs (Nicasio Sepulveda, U.S. Geological Survey, oral commun., 2011). Based on isotopic tritium/helium-3 analysis of replicate samples from one well (MW-2), the water currently in the Upper Floridan aquifer beneath the RIBs is estimated to have entered the aquifer 19 years before present (Schlosser and others, 2008; app. 2). Boron, an element used in detergent, was elevated in the RIBs water, but there were only trace levels in the Upper Floridan aquifer. Kroening (2007; app. 1) suggested the Upper Floridan aquifer beneath the RIBs does not contain water from the RIBs based on the low concentration of boron present. Based on analysis of nitrogen and argon gases in groundwater, Kroening (2007; app. 1) inferred that excess nitrogen gas exists in the Upper Floridan aquifer. The excess dissolved nitrogen gas (1-5 mg/L as N), above the naturally occurring concentration in water at the time of infiltration, was attributed to denitrification. Based on the age of the water in the aquifer and the amount of excess nitrogen gas, a rate of denitrification of $5\times10^{-4}$ mg/L as N per day was estimated for this process. Nitrogen isotopic analyses of the excess nitrogen ($N_2$) indicated that the source of the nitrogen in the Upper Floridan aquifer was fertilizer, probably from the orange groves that occupied the site prior to the establishment of the RIBs (Kroening, 2007; app. 1).

## Methods of Investigation

The potential rate of denitrification of water in the Upper Floridan aquifer and Wekiwa and Rock Springs was assessed using laboratory incubations. Sample collection and analysis were made in accordance with standard USGS protocols. Further details on the method are provided in Smith and others (2004).

### Water Sampling

Water samples were collected on November 9 and 30, 2009, from four Upper Floridan aquifer wells (MW-8B, MW-5R, MW-2, and Phipps) located on the RIBs property (fig.1), and two nearby springs, Wekiwa Springs and Rock Springs (fig. 1). Groundwater samples were collected by lowering a submersible pump into the open-hole interval of each well and near the main boil of both springs, and pumping at 2.5 liters per minute (L/min.) until the field readings of specific conductance, pH, dissolved oxygen, and temperature stabilized. A total of 4 liters (L) of water was collected from each site using sterile pump tubing, and was stored in 1-L amber glass bottles that had previously been baked at 500°C. The bottles were flushed with 3 to 5 L of sampled water, filled completely, and capped to avoid an air space. The four bottles from the six sites were then sealed, placed on ice, and shipped overnight to the USGS laboratory in Boulder, Colorado for testing the next day.

### Sample Preparation and Incubation

For each of the six samples, one 1-L bottle was filtered and preserved for nitrate, nitrite, ammonium, dissolved organic carbon (DOC) and total dissolved nitrogen (TN) analyses (Savoie and

others, 1998). A second 1-L bottle of unfiltered water for each sample was placed immediately into an anaerobic glovebox. In the glovebox, the water was dispensed into triplicate 60-milliliter (mL) serum bottles for each of four treatments to assess denitrification potential. The bottles were stoppered and flushed with helium to replace the glovebox gas (a mixture of nitrogen, hydrogen, and carbon dioxide gases). Anoxic, stock solutions of 250 mg/L $NaNO_3$ as N and 500 mg/L glucose as $C_6H_{12}O_6$, were then added, as appropriate, to prepare the following treatments: (1) ambient (no added nitrate or glucose), (2) amended with 1.4 mg/L nitrate as N, (3) amended with 5 mg/L nitrate as N, and (4) amended with 5 mg/L nitrate as N and 10 mg/L glucose as $C_6H_{12}O_6$. The glucose plus nitrate addition was included to serve as a positive control to confirm that proper conditions existed for denitrification to occur. Oxygen-free acetylene gas was then added to the headspace of each bottle. Acetylene blocks the reduction of nitrous oxide (an intermediate in the denitrification pathway) to nitrogen gas. Accordingly, in the presence of acetylene, nitrous oxide production over time is used to quantify rates of denitrification. Rates are designated as "potential" denitrification when *in situ* conditions are altered, such as by adding nitrate and (or) glucose. After the addition of acetylene, the sample bottles were placed on a rotator, set to 4 revolutions per minute, and incubated at room temperature (22°C). The bottles were analyzed for nitrous oxide concentration in the headspace after 1 hour, at daily intervals for 10 days, and (thereafter) once every few days for 1 to 2 months. At the end of the experiment, water samples were removed by syringe from the serum bottles, filtered, and preserved for nitrate, nitrite, ammonium, and DOC/TN analysis.

Nitrate/nitrite concentrations also were monitored over time in a separate, companion set of incubation bottles as a control for the experiment to measure denitrification without the acetylene block. These were triplicate, 100-mL unfiltered water samples in serum bottles to which nitrate was added to obtain a concentration of 1.4 mg/L as N. The bottles were flushed with helium to replace the glovebox gas, but no acetylene was added. This second set of bottles was rotated at room temperature, and water samples were removed by syringe and filtered and preserved for nitrate and nitrite analysis each time a nitrous oxide measurement was made in the headspace of the acetylene-amended bottles. At the end of the experiment, water samples were removed from the companion bottle set and filtered and preserved for nitrate, nitrite, ammonium, and DOC/TN analyses.

### Analytical Procedures

Nitrous oxide production was measured using an HNU gas chromatograph equipped with an electron capture detector. Concentrations were calibrated using authentic standard gas mixtures. Nitrate and nitrite were analyzed using a Dionex Model DX500 ion chromatograph with an AS4A-SC 4-millimeter (mm) analytical column, sodium carbonate/bicarbonate mobile phase, and conductivity detection. Ammonium was measured using a Dionex Model DX300 ion chromatograph with a CS12A 4-mm analytical column, a gradient mobile phase of 5- to 25-mN (millinormal) sulfuric acid, and conductivity detection. Dissolved organic carbon and total dissolved nitrogen were analyzed simultaneously on a Shimadzu combined TOC-VCSN and TNM-1 analyzer with high temperature combustion and chemiluminiscent detection. Alkalinity was measured using a Radiometer Model ABU93 auto-titrator.

## Potential Rates of Denitrification

The potential rate of denitrification was calculated as the rate of nitrate reduction to nitrous oxide within water samples, quantified by nitrous oxide production. All samples tested exhibited potential denitrifying activity, as evidenced by the accumulation of nitrous oxide in the presence of

acetylene (fig. 2). All groundwater samples except the Phipps Well sample required an addition of nitrate or nitrate plus glucose for denitrification, whereas both springwater samples demonstrated denitrifying activity under all conditions tested. Most of the incubations showed an initial 1 to 2 day lag period, followed by a period of linear (steady) nitrous oxide production, and a subsequent tapering off in production with the exhaustion of the nitrate pool. Estimates of rates of denitrification were determined using linear regression over the initial portion of the nitrous oxide production curve (fig. 2). In three of the four wells, MW-2, MW-5R, and MW-8B, the ambient nitrate concentrations were too low (below 0.04 mg/L as N) to establish a denitrification rate using treatment 1. In the Phipps Well sample, the ambient nitrate concentration was 0.13 mg/L as N (table 1 and the denitrification rate for treatment 1 was 0.050 milligram per liter nitrogen per day [(mg/L)/d] N (table 1). When nitrate was added for treatments 2 and 3, the denitrification rate doubled (table 2). Wekiwa Springs water had an ambient nitrate concentration of 1.12 mg/L as N and the denitrification rate for treatment 1 was 0.072 (mg/L)/d N; treatments 2 and 3 yielded higher denitrification rates. Rock Springs water had an ambient nitrate concentration of 1.38 mg/L as N and a denitrification rate of 0.071 (mg/L)/d N for treatment 1; treatments 2 and 3 yielded higher denitrification rates. Water from well MW-2 had a denitrification rate of 0.059 (mg/L)/d N for treatment 2 with a higher rate of 0.087 (mg/L)/d N for treatment 3 (table 2). At all of the sampling sites, treatment 4 yielded denitrification rates at least an order of magnitude greater than those measured for the other treatments; rates ranged from 2.3 to 4.4 (mg/L)/d N as shown in figure 2 and table 2.

At four of the six sites, the calculated denitrification rate was similar in treatments 2 and 3 (fig. 2). This finding may indicate that when nitrate exceeds about 1.4 mg/L as N, the denitrification rate is not limited by available nitrate. Rock Springs deviated the most; the denitrification rate in this sample for treatment 3 was 2.4 times as high as treatment 2 (table 2, fig. 2). For all the samples, the order of magnitude increase in the denitrification rate produced by the addition of carbon in the form of glucose (treatment 4) indicates that carbon availability may be the primary control on nitrous oxide production. Ambient dissolved organic carbon (1-3 mg/L), which is the electron donor supply in the groundwater and spring water, is sufficiently abundant to remove at least 1.1-1.4 mg/L nitrate as N in 20 to 30 days, even in situations where the background nitrate concentration in groundwater is low. The rate of nitrate consumption was determined at all sites for the companion set of sample bottles that were amended with 1.4 mg/L nitrate as N using the linear section of the nitrate consumption curves in figure 3 (table 2). At most sites, the rate of nitrate consumption exceeded the rate of nitrous oxide production; this difference is primarily attributable to nitrite production. One exception, however, was the sample from Rock Springs, for which the rate of nitrate consumption for treatment 3 and nitrous oxide production were comparable [0.226 (mg/L)/d N and -0.218 (mg/L)/d N, respectively, table 2]. The slowest rate of nitrate consumption, 0.09 (mg/L)/d N, occurred in the groundwater sample from well MW-5R, and the fastest, 0.27 (mg/L)/d N, occurred in the Wekiwa Springs sample. Consumption rates for all other sites ranged between 0.17 and 0.23 (mg/L)/d N.

Using the ambient nitrous oxide production rates, the number of days required to consume available nitrate was calculated for the three sites that had above-background nitrate concentrations. The available nitrate would be consumed in 15, 2.6, and 20 days at Wekiwa Springs, Phipps Well, and Rock Springs, respectively, assuming that the rates remain constant as nitrate concentrations decrease.

In a separate laboratory control sample experiment, bottles, without an acetylene block and amended with 1.4 mg/L nitrate as N were also measured over several weeks. In these samples all available nitrate was removed through denitrification in 4 to 6 days, with an initial lag, leaving only background concentrations of 0.04 mg/L nitrate as N.

**Table 1.** Site identification and ambient water-quality data Site identification and ambient water-quality data.

[mg/L, milligrams per liter; mg/L as N, milligrams per liter as nitrogen]

| Site name | Well number | Date of sample | Well depth, in feet below land surface | Water temperature, in ºC | pH, in standard units | Specific conduc-tance, in μS/cm | Dissolved oxygen, in mg/L | Nitrate, in mg/L as N | Total[b] Nitrogen, in mg/L as N | Dissolved Organic Carbon, in mg/L as C |
|---|---|---|---|---|---|---|---|---|---|---|
| MW-2 | 283803081314901 | 11/09/09 | 160 | 25.7 | 7.46 | 504 | 0.23 | 0.042 | 0.436 | 2.229 |
| MW-5R | 283754081312101 | 11/09/09 | 165 | 25.7 | 7.84 | 333 | 0.16 | 0.020 | 0.076 | 1.064 |
| MW-8B | 283809081321001 | 11/09/09 | 170 | 26.0 | 7.95 | 278 | 0.32 | 0.032 | 0.116 | 1.263 |
| Phipps Well | 283738081305801 | 11/30/09 | 165 | 24.1 | 7.53 | 308 | NA | 0.129 | 0.197 | 1.088 |
| Rock Springs | 2234610 | 11/30/09 | --- | 23.4 | 7.61 | 269 | 1.38[a] | 1.385 | 1.521 | 0.673 |
| Wekiwa Springs | 2234600 | 11/30/09 | --- | 24.0 | 7.30 | 357 | 0.40[a] | 1.117 | 1.254 | 1.129 |

[a] Median concentration from Walsh and others (2009).

[b] Difference between Total Nitrogen and Nitrate is predominately ammonia

**Table 2.** Denitrification rates of water samples based on laboratory analysis.

[(mg/L)/d N, milligrams nitrogen per liter per day; mg/L nitrate, milligrams nitrate-nitrogen per liter; NA, not applicable]

| Site name | Date | 1st treatment ambient denitrification rate, in (mg/L)/d N | 2nd treatment ambient sample amended with 1.4 mg/L nitrate denitrification rate, in (mg/L)/d N | 3rd treatment ambient sample amended with 5.0 mg/L nitrate denitrification rate, in (mg/L)/d N | 4th treatment ambient sample amended with 5.0 mg/L nitrate and 10 mg/L glucose denitrification rate, in (mg/L)/d N | Nitrate consumption rate sample amended with 1.4 mg/L nitrate, in (mg/L)/d N |
|---|---|---|---|---|---|---|
| MW-2 | 11/10/09 | NA | 0.059 | 0.087 | 2.3 | -0.227 |
| MW-5R | 11/10/09 | NA | 0.083 | 0.071 | 4.0 | -0.090 |
| MW-8B | 12/15/08 | NA | 0.120 | NA | NA | NA |
| MW-8B | 11/10/09 | NA | 0.118 | 0.127 | 2.3 | -0.205 |
| Phipps Well | 12/01/09 | 0.050 | 0.099 | 0.105 | 4.4 | -0.173 |
| Wekiwa Spring | 12/01/09 | 0.072 | 0.124 | 0.142 | 2.4 | -0.269 |
| Rock Spring | 12/01/09 | 0.071 | 0.095 | 0.226 | 3.4 | -0.218 |
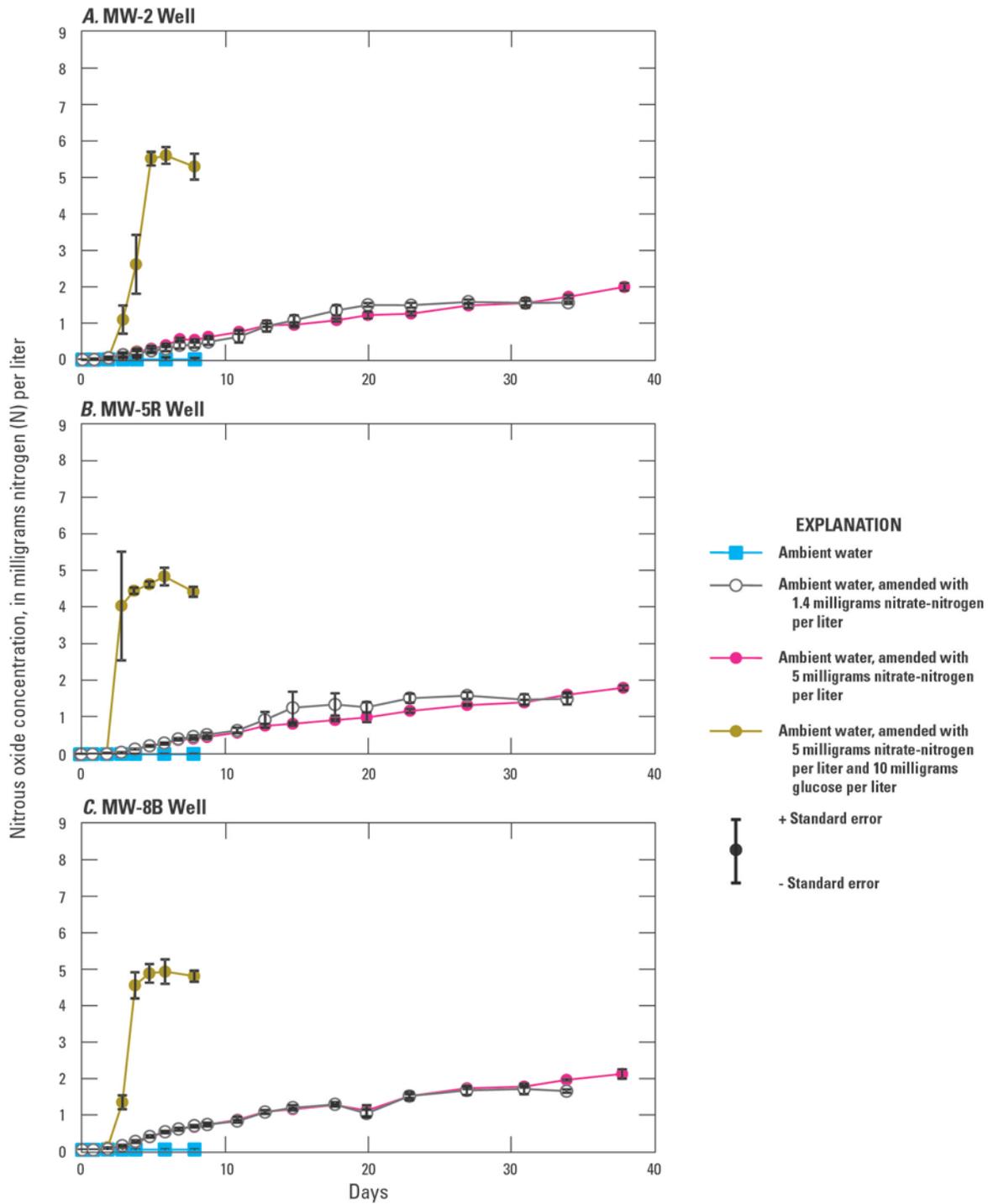
**Figure 2.** Graphs showing time course of nitrous oxide production by well water and spring-water samples during laboratory incubations to measure denitrification potential.
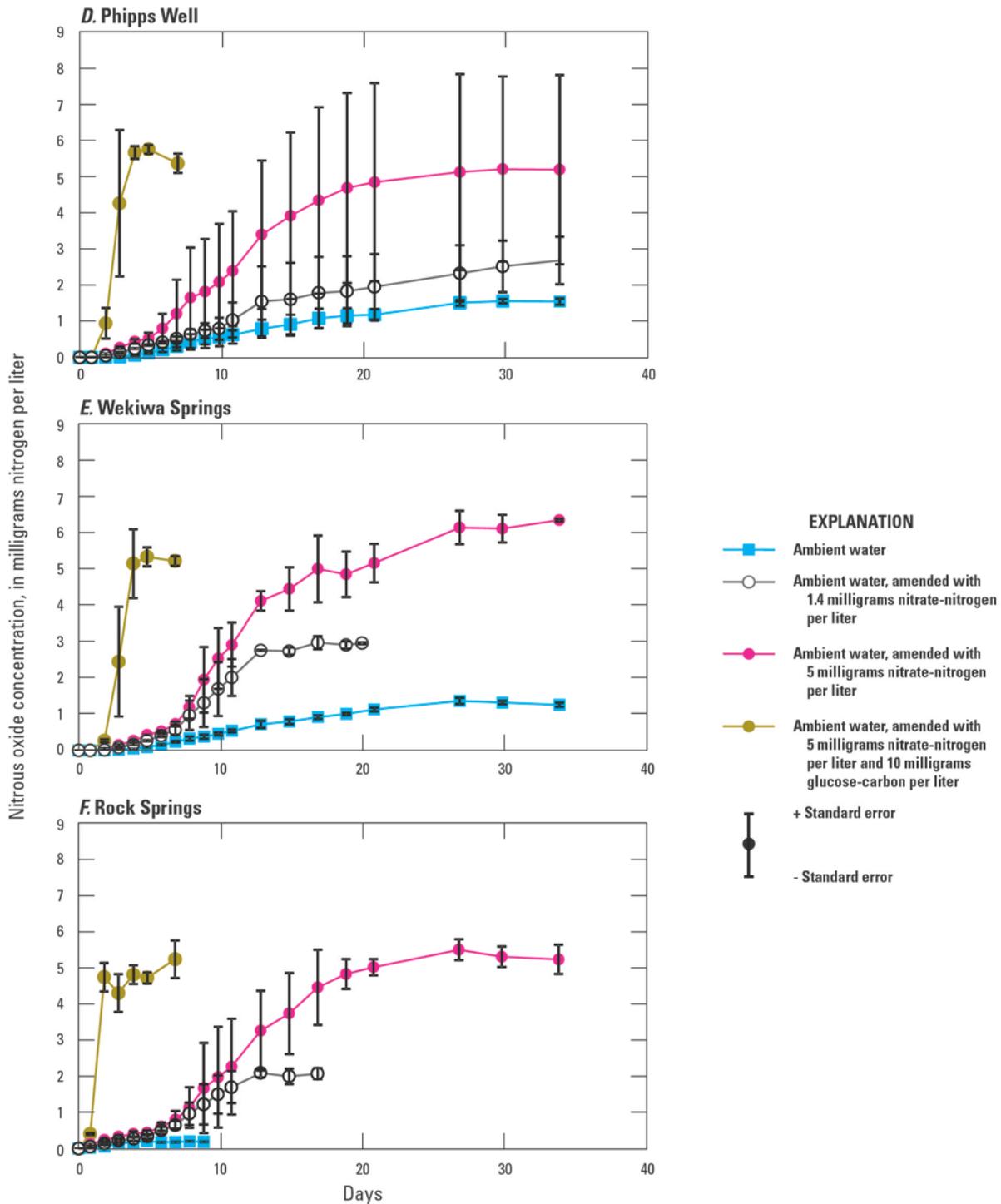
**Figure 2.** Graphs showing time course of nitrous oxide production by well water and spring-water samples during laboratory incubations to measure denitrification potential.—Continued
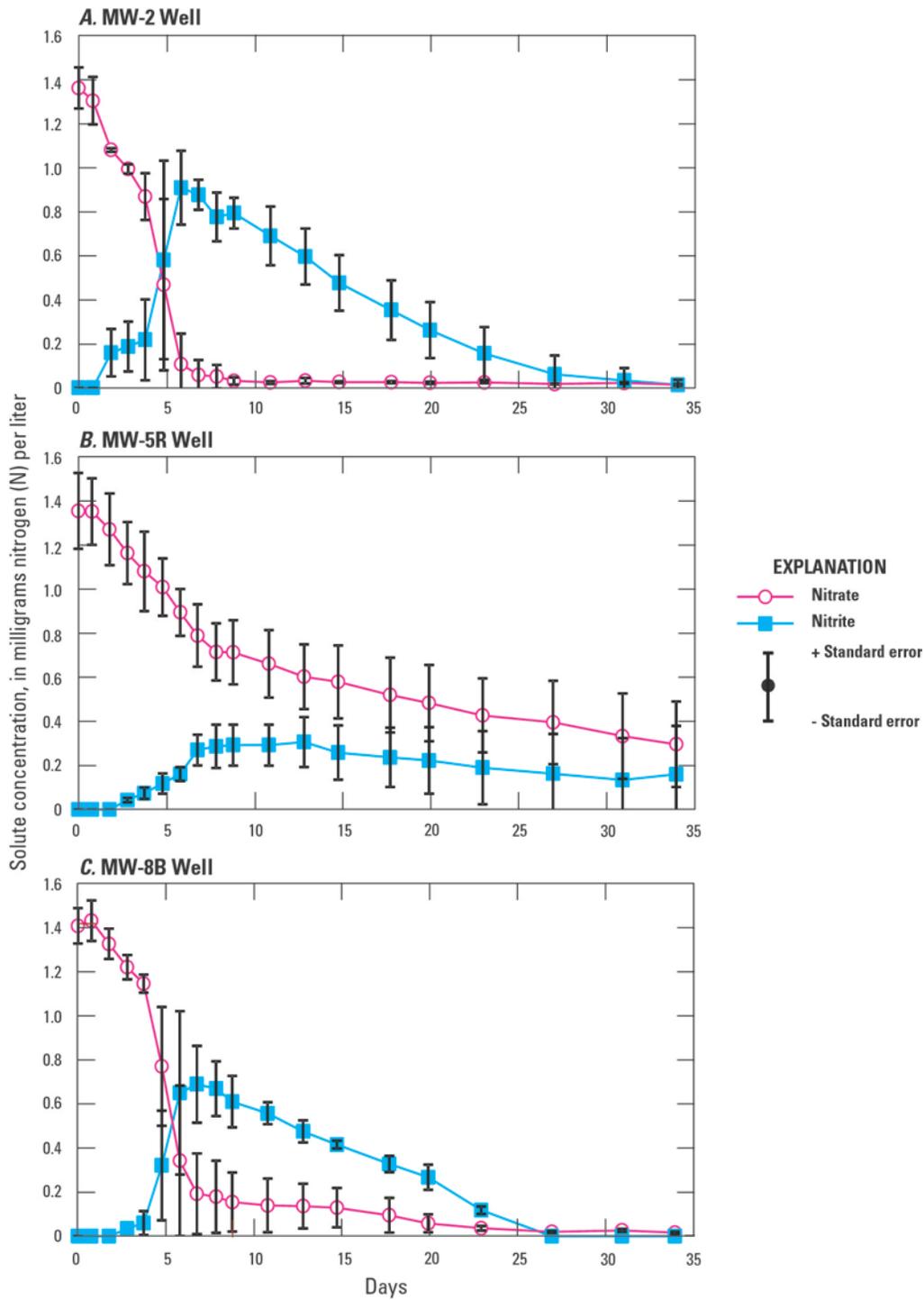
**Figure 3.**  Graphs showing time course of nitrate and nitrite concentration change in well water and spring-water samples during laboratory incubations.

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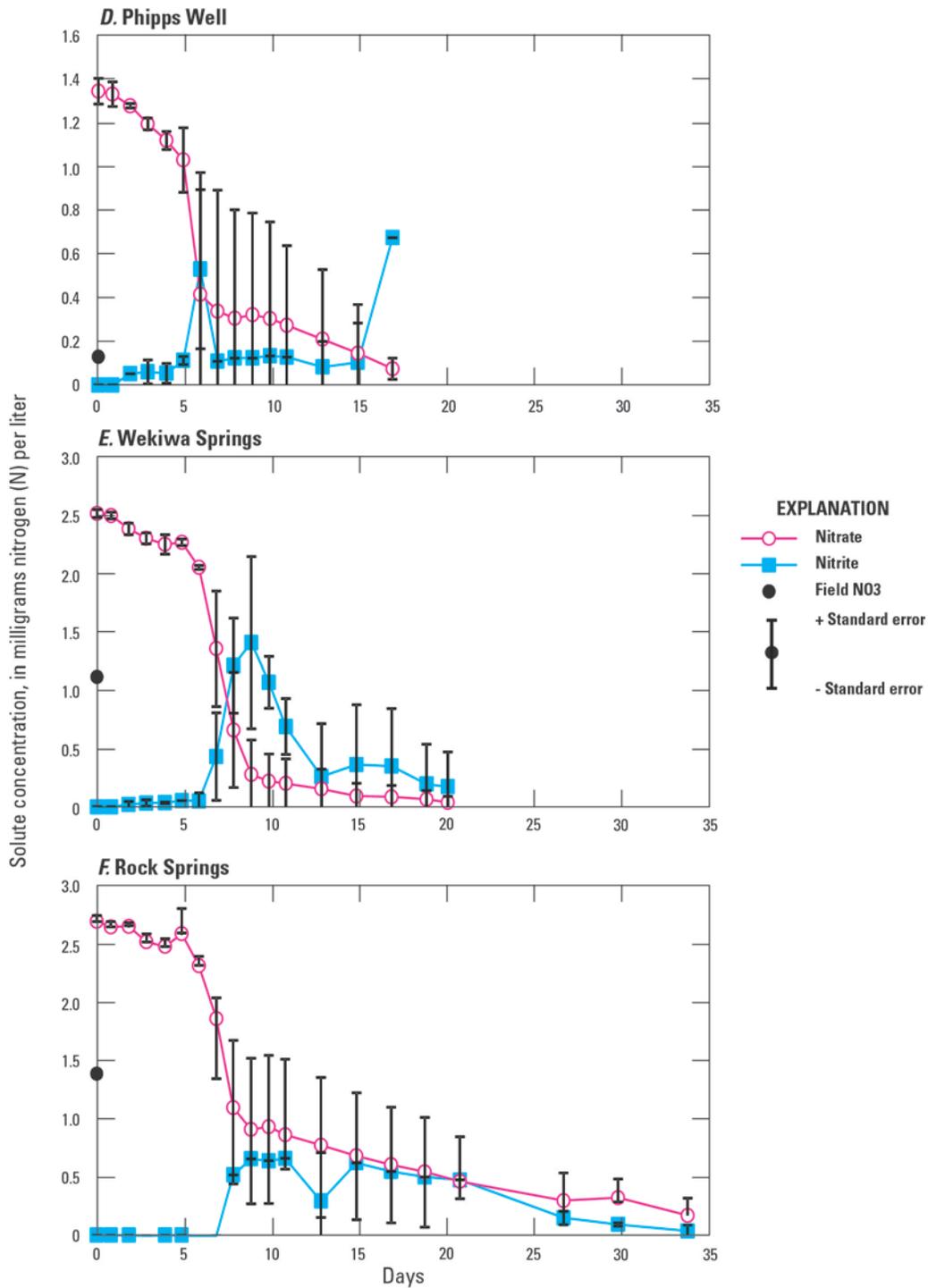
**Figure 3.** Graphs showing time course of nitrate and nitrite concentration change in well water and spring-water samples during laboratory incubations.—Continued

## Limitations

Smith and others (1996) in a prior study of a surficial aquifer, suggest that potential rates of denitrification determined with the anoxic laboratory samples are likely greater than rates that occur in the aquifer due to elevated dissolved oxygen concentration in the shallow aquifer of that study. However, because the Upper Floridan aquifer has low dissolved oxygen concentrations, it is doubtful that a disparity in laboratory and aquifer dissolved oxygen would bias applicability of the laboratory-derived denitrification rates to the Upper Floridan aquifer. The addition of nitrate and glucose would tend to stimulate denitrification during laboratory incubations since the relevant bacteria require nitrate and glucose to colonize and, therefore, would bias laboratory-derived denitrification rates higher than *in situ* aquifer rates. The laboratory results also are only relevant to denitrifying bacteria and carbon suspended in the groundwater; the experiments did not measure rates of denitrification for bacteria attached to possible carbon-rich biofilms on aquifer solids. If attached bacteria actively consume nitrate by denitrification in *in situ* aquifer conditions, neglect of biofilm denitrification would bias laboratory-derived denitrification rates lower than *in situ* aquifer rates. The data presented in this study suggest that carbon is the limiting nutrient for this reaction in the Upper Floridan aquifer.

Low nitrate concentrations in the Upper Floridan aquifer in this area make tracer studies impractical under ambient aquifer conditions and retrieval of injected enhanced-nitrate tracers is challenging in the fast-moving, conduit flow within this aquifer.

# Summary

Water samples from four Upper Floridan aquifer wells and two springs were tested to determine the potential for denitrification near reclaimed water application sites in west Orange County, Florida. Tests were conducted to quantify the potential rates of denitrification using the acetylene block technique; the potential rate of denitrification was calculated as the rate of nitrate reduction to nitrous oxide within water samples, quantified by nitrous oxide production. The experiment consisted of four different treatments: (1) ambient water (no added nitrate or glucose); (2) ambient water amended with 1.4 mg/L nitrate as N, (3) ambient water amended with 5.0 mg/L nitrate as N, and (4) ambient water amended with 5.0 mg/L nitrate as N and 10 mg/L glucose as $C_6H_{12}O_6$. Nitrate/nitrite concentrations also were monitored over time in a separate, companion set of incubation bottles subjected to treatment 2 but without addition of an acetylene block (laboratory control). These control samples were denitrified in 4-6 days with an initial lag and final concentrations of 0.04 mg/L nitrate as N.

Results of the study indicate that denitrifying bacteria were present in the groundwater and spring water samples, and these bacteria readily facilitated denitrification when placed in suitable conditions. In three of the four well sites, the ambient nitrate concentrations were too low (less than 0.04 mg/L as N) to establish a denitrification rate using treatment 1. But in the fourth well, where the ambient nitrate concentration was 0.13 mg/L as N, the nitrous oxide production rate for treatment 1 was 0.050 milligram per liter per day [(mg/L)/d] N. When nitrate was added for treatments 2 and 3, the denitrification rate increased. In four of the six sites, the denitrification rate was similar in treatments 2 and 3. This finding may indicate that when nitrate exceeds about 1.4 mg/L as N, the denitrification rate is not limited by available nitrate. The denitrification rate, in all the samples ranged from 0.059 to 0.124 (mg/L)/d N (treatment 2) and 0.071 to 0.226 (mg/L)/d N (treatment 3). Treatment 4 yielded nitrous oxide production rates at least an order of magnitude greater than those measured for the other treatments, at all of the sampling sites; rates ranged from 2.3 to 4.4 (mg/L)/d N. The electron donor supply, dissolved organic carbon, in the groundwater and springwater is sufficient to remove at least 1.1-1.4 mg/L nitrate as N in 20 to 30 days, as indicated by nitrous oxide production rates under ambient

conditions (treatment 1). The even higher nitrate removal observed with addition of supplemental carbon in treatment 4 suggests that carbon is a limiting nutrient in this reaction. Denitrifying activity might explain the low ambient nitrate concentrations in the Upper Floridan aquifer. The *in situ* rates of denitrification were calculated as $5\times10^{-4}$ mg/L as N per day based on groundwater age and excess nitrogen gas concentrations data collected by Kroening(2007).  The potential rates of denitrification determined in the low dissolved oxygen laboratory incubations during this study may represent *in situ* rates of denitrification because, in contrast to previous studies of shallow aquifers with oxygenated conditions that retard denitrification,  low dissolved oxygen concentrations prevail in the Upper Floridan aquifer.

The potential for denitrification exists in the Upper Floridan aquifer near a reclaimed water application site in west Orange County, Florida. The necessary conditions for denitrification, including the presence of denitrifying bacteria, relatively low dissolved oxygen concentrations, and ample dissolved organic carbon are met. The laboratory-derived rates of denitrification in this study represent a reasonable approximation for actual rates in the Upper Floridan aquifer in the study area. Fertilizer appears to be the primary source of nitrate in the Upper Floridan aquifer beneath the rapid infiltration basin sites.

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# Appendix 1.  Sources of Nitrate and Evaluating the Potential for Denitrification in the Surficial and Upper Floridan Aquifers, Central Florida

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# Sources of Nitrate and Evaluating the Potential for Denitrification in the Surficial and Upper Floridan Aquifers, Central Florida

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## Abstract

The sources of nitrate and potential for denitrification were evaluated in the karstic Upper Floridan aquifer (UFA) and overlying surficial aquifer beneath and upgradient from a reclaimed water facility in Central Florida. Nitrate-N concentration (<0.02 to 6.3 mg/L) in ground water in this area likely originated from past fertilizer use in citrus agriculture or treated wastewater applied to rapid-sand infiltration beds. Chemical, isotopic, and dissolved gas data were evaluated from water samples collected from nine wells to determine nitrate sources and if conditions were conducive for denitrification. Surficial aquifer wells ranged from 3.7 to 23.8 m deep, and UFA wells ranged from 46 to 102 m deep. $\delta^{15}N$ and $\delta^{18}O$ values of nitrate in well water samples indicated that treated wastewater likely is the source of nitrate in the surficial aquifer wells, whereas the sources of nitrate in the UFA were likely treated wastewater and fertilizer. Denitrification likely occurs in the UFA, but may only occur to a limited extent in the surficial aquifer. Dissolved oxygen concentrations generally were less than 1 mg/L in the UFA and greater than 2 mg/L in the surficial aquifer. Dissolved gas and isotopic data indicated that denitrification had occurred in water from 4 of 5 UFA wells. Excess nitrogen gas ($N_2$), the end product of denitrification, was estimated for four UFA wells based on the concentrations of dissolved $N_2$ and argon in ground water. Excess $N_2$ concentrations ranged from 1 to 5 mg/L. $\delta^{15}N$ values associated with $N_2$ in these same wells also were substantially greater (+0.97 to +2.14 ‰) than for $N_2$ in equilibrium with air-saturated water. Denitrification may naturally attenuate some nitrate in the UFA before it is transported to natural springs in the area.

## Introduction

Karstic aquifer systems supply water to approximately 25 percent of the world's population (Williams, 1993) and are extremely susceptible to nitrate contamination due to the rapid recharge of these systems through sinkholes and other subsidence features, sinking streams, and preferential flow paths created by conduits. High nitrate concentrations in these systems pose a threat to the quality of potable water supplies and may affect the ecosystems surrounding karstic springs, which evolved under nutrient-limited conditions in parts of the U.S. (Stevenson et. al., 2004). Specifically, the nuisance growth of filamentous algae may be associated with increased nitrate concentrations and were identified as a problem for recreational use and aquatic life support in springs (Stevenson et. al., 2004).

The karstic Upper Floridan aquifer (UFA) is the primary source of water in Central Florida (St. Johns River Water Management District, 2006a) and discharges to numerous

natural springs. Approximately $3.3 \times 10^6$ m$^3$/day were withdrawn from the UFA in Central Florida in 2000 (Marella, 2004). Ground water use is projected to increase about 60 percent by the year 2025 due to projected population increases for the area (St. Johns River Water Management District, 2006b). Ground water from the UFA is being withdrawn near the maximum sustainable rate (St. Johns River Water Management District, 2006a), and measures are being implemented to replenish this aquifer system to help ensure that adequate water supplies are available to meet projected water-supply demands and sustain the ground water inflow to the many natural springs. Artificial recharge with treated wastewater, or reclaimed water, is one management technique which is becoming widely utilized to recharge the UFA in Florida and aquifer systems in other parts of the U.S. (York et. al. 2002; U.S. Environmental Protection Agency 2004; St. Johns River Water Management District 2006a). In many of these applications, reclaimed water is discharged to rapid-sand infiltration basins (RIBs) and allowed to percolate into the ground (Brooke and Godlewski 1995; O'Reilly 1998; U.S. Environmental Protection Agency 2004).

Artifically-recharged water from RIBS, while providing beneficial recharge to the ground water system, may potentially contaminate the UFA with nitrate. Wastewater disposal to RIBS in other parts of the U.S. resulted in nitrate contamination of the ground water (Aulenbach and Tofflemire, 1975; LeBlanc, 1984). Disposal of treated wastewater for over 60 years in the Cape Cod, Massachusetts resulted in a 3.5 km-long plume containing nitrate concentrations greater than 3 mg/L (LeBlanc, 1984). Knowledge of the source and fate of nitrate in the ground water system is necessary in order to develop effective management strategies to prevent or remediate nitrate contamination. Denitrification, nitrate reduction to $N_2$ gas, generally is considered the primary nitrate attenuation mechanism in contaminated aquifers (Korom 1992). Numerous studies have documented the potential for denitrification in surficial sand and gravel aquifers (Wassenaar 1995; Starr and Gillham 1993; Smith and Duff 1988). Denitrification in karstic aquifers, such as the UFA, often is believed to be insignificant due to the rapid transport velocities of oxygenated water through these systems (Coxon 1999), however, the potential for denitrification has been reported in several karstic aquifers based on dissolved gas or stable isotope data (Panno et. al. 2001; Wilson et. al. 1990; Mariotti et. al. 1988).

This paper presents the results of a study conducted from 2004-2006 by the U.S. Geological Survey in cooperation with Orange County, Florida to determine the nitrate sources in the karstic UFA and surficial aquifer system (SAS) beneath and upgradient from a wastewater treatment and reuse facility (WWTRF). Chemical data were used to determine whether conditions in these aquifers were conducive for denitrification to occur. Nitrogen and oxygen isotope ratios on the nitrate in water samples and N isotope ratios on the $N_2$ gas dissolved in the water samples were examined for evidence of denitrification and were used to determine nitrate sources. Dissolved gas ($N_2$ and Ar) concentrations were used to estimate recharge temperatures and the amount of $NO_3^-$ consumed by denitrification. $N_2O$ concentration data were used to identify whether active areas of denitrification were present.

*Study Area*

The study was conducted in the SAS and UFA in a nine km$^2$ area in Central Florida (Fig. 1). The mean annual air temperature in this area is approximately 22.0°C (Adamski and German, 2005). Regional ground-water flow in the UFA generally is from the southwest to the northeast (Kinnaman, 2006), and ground water discharge occurs through several springs to the north and northeast of the study area, most notably Wekiwa and Rock Springs. The UFA is characterized by primary and secondary porosity (Spechler and Halford 2001), and generally is separated from the SAS by a confining unit consisting of low permeability Miocene or early Pliocene-age carbonate and siliceous deposits, except where the confining unit is breached by sinkholes. Within the study area, the UFA is mantled by about 140 to 150 feet of post-Miocene and Miocene-age deposits, and the uppermost deposits generally are described as consisting of fine-grained sand which grades into silty and clayey fine sands (Morrell et. al. 2002).

A WWTRF occupies approximately one-third of the study area and has been operated since 1987 to treat domestic waste. Other land uses in the study area include agriculture and low- and medium-density residential developments, which are primarily located to the north and east of the WWTRF. Current agricultural land use consists of ornamental nurseries, abandoned tree crops, and pasture. Prior to the construction of this facility, citrus agriculture likely was the predominant land use (Florida Department of Environmental Protection, 2004).

Rainfall and treated wastewater effluent are the predominant sources of recharge water to SAS and UFA in the study area. Central Florida typically receives about 130 cm of rainfall per year, with the majority occurring from June through September (Adamski and German 2004). The WWTRF discharged approximately 61.8 x 10$^6$ m$^3$ of treated wastewater to 13 RIBs from 1990-2003. Most of the wastewater was discharged to RIB 1 (34 percent), 5 (16 percent), and 12 (12 percent), which have the greatest infiltration rates (1.6-1.9 m/day) (Post Buckley Schuh & Jernigan, Inc., 1993). The other RIBs each received less than 6 percent of the treated wastewater.


**Methods**

*Site Selection*

Nine SAS and UFA wells were sampled for this study at five sampling sites (Fig. 1). Eight of these wells were located in the vicinity of the WWTRF and one UFA well was located upgradient of the facility. Existing UFA wells, ranging from about 46 to 102 m deep were sampled at sites 2 (45.7 m deep), 4 (51.8 m deep), and 5 (102 m deep). A 64.0-m deep UFA well was installed at site 3 in December 2004 to replace an existing monitoring well. At site 1, a vertical sequence of SAS wells (wells 1-A, 1-B, 1-C, and 1-D), ranging from 3.7 to 23.8 m deep, and one UFA well (well 1-E, 62.5 m deep) were installed in December 2004 (Fig. 2) to replace an existing UFA monitoring well and characterize any vertical gradient in
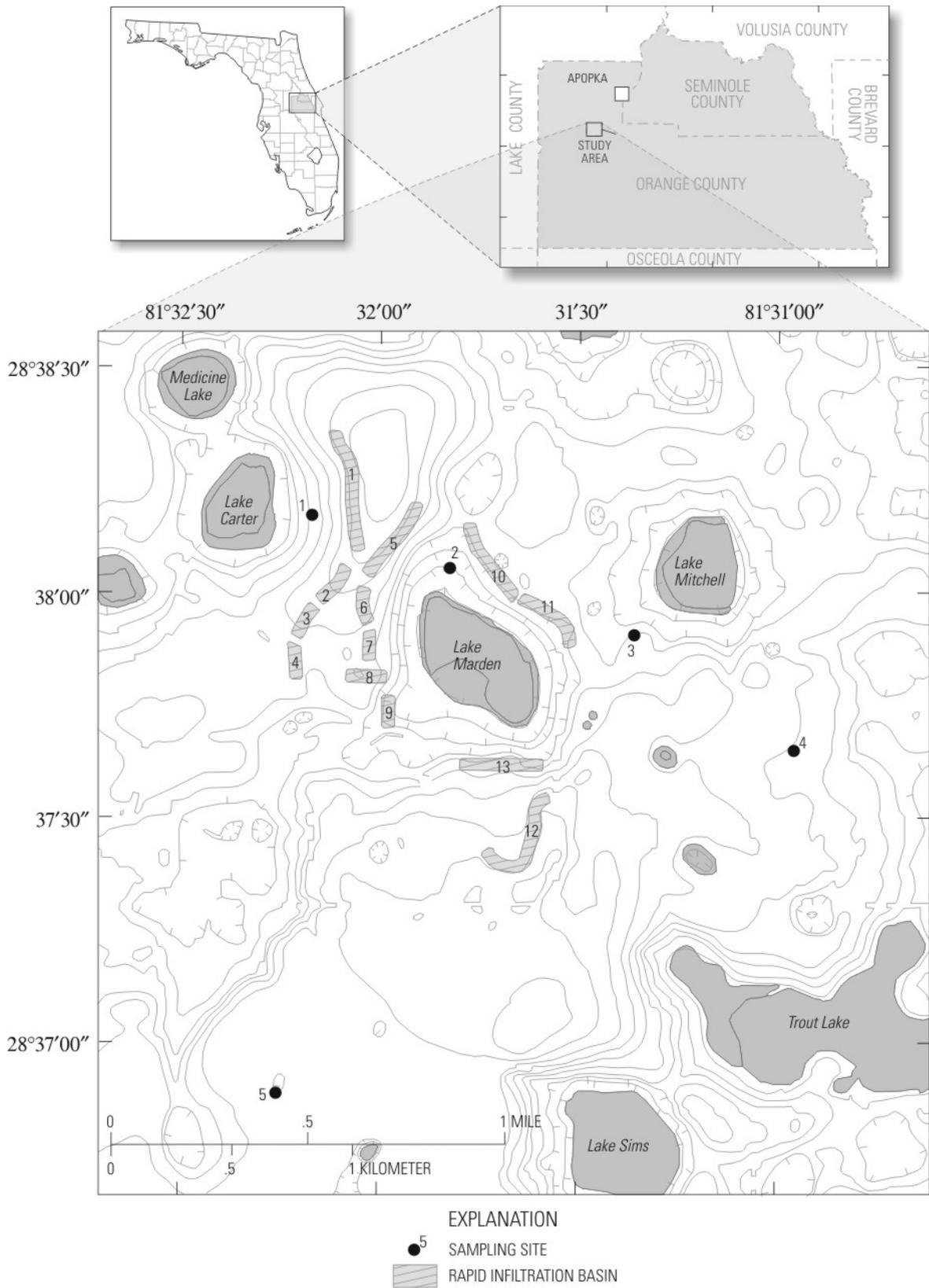
**Figure 1.** Location of the study area, rapid-infiltration basins, and sampling sites.

the denitrification potential. SAS wells were screened to 1.5-3.0 m intervals. The UFA wells were not screened and the open-hole interval for these wells ranged from 3.0-31.7 m. UFA Well 5 had the longest open-hole interval. The open-hole intervals for the other UFA wells were 15.2 m or less.

Lithologic and ground-water level data collected at site 1 in 2004 showed the direction of the vertical head gradient was downward and there was substantial confinement between most of the SAS wells. Ground-water level measurements showed there was a downward vertical head gradient among the SAS and UFA wells at site 1 during all sampling events. Lithologic data collected prior to drilling at this site showed clay layers were interbedded among the sands comprising the SAS, which resulted in substantial water confinement between most of the SAS layers. The most substantial confinement occurred between wells 1-B through 1-D. The median difference in ground water levels between wells 1-B and 1-C was 9.4 m, and the median difference in ground water levels between wells 1-C and 1-D was 3.4 m. Of all the SAS wells, ground water levels in wells 1-A and 1-B were the most similar, with a median difference in ground water levels of 0.2 m.
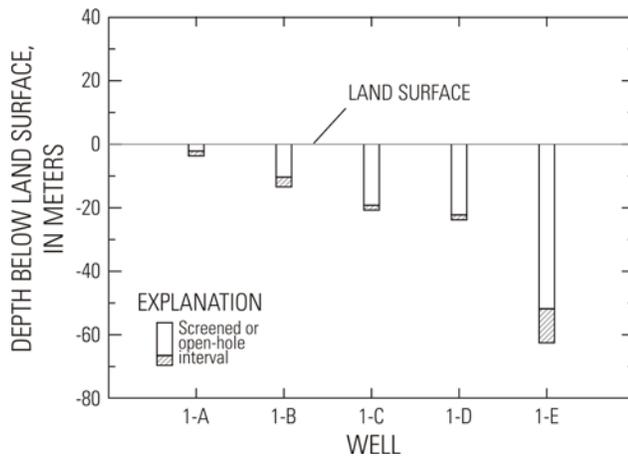


**Figure 2.** Placement of well cluster at site 1.

*Water-quality sampling*

Water samples were collected from October 2004 to April 2006. All wells except number 5 were sampled using a stainless steel submersible pump with PVC tubing. Well 5 supplied potable water to a toll plaza. Water samples were withdrawn from this well at a point upgradient of the pressure tank using the dedicated submersible pump. Samples collected for analysis of $N_2O$ dissolved in the ground water were collected only in 2006, and samples were not collected from well 1-A because the well was dry. Most samples were collected using standard techniques (Wilde et. al., 1999) after a minimum of three well-bore volumes of water were purged and field readings of specific conductance, pH, dissolved oxygen, and temperature stabilized. A closed flow-through chamber was used to measure water temperature, specific conductance, and pH. Dissolved oxygen concentrations were measured using a polargraphic probe during October 2004-2005 and using a colorimetric reagent in ampoules and a battery-operated spectrophotometer (Chemetrics Inc. Calverton

VA, USA) (use of trade names is for identification purposes only and does not imply endorsement by the U.S. Government) in 2006. Water samples for N and O isotope analysis were filtered using an encapsulated 0.45 μm filter into 125-mL plastic bottles and kept frozen until analysis. Water samples for $N_2$, Ar, $CO_2$, and $CH_4$ determinations were collected in 150-mL serum bottles without headspace. For $N_2O$ determinations, 20-mL water samples were collected in a syringe and injected into stoppered 30-mL serum vials containing 0.2 mL of 12.5 N KOH in a He headspace.

*Analytical procedures*

$NO_3^-$, $NO_2^-$, and $NH_4^+$ were analyzed in water samples using established methods (EPA 300.0; Fishman, 1993) at the USGS laboratory in Denver, Colorado or the Orange County laboratory in Orlando, Florida. Organic carbon and boron were analyzed using established methods (EPA 200.7, SM5310C) at the Orange County laboratory in Orlando, Florida. Dissolved $N_2$, Ar, $CO_2$, and $CH_4$ gases in the samples were analyzed by gas chromatography after extraction in headspaces of glass samplers (Busenberg et. al. 1998). The isotopic composition of $N_2$ in the water samples, $\delta^{15}N$ of $N_2$, was measured in the leftover headspace after the $N_2$, Ar, $CO_2$, and $CH_4$ analysis. The headspace was pressurized with He, expanded into a 0.1 mL loop, then flushed with He through a 5A mole sieve gas chromatograph to separate $O_2$+Ar from $N_2$ (modified from Revesz et al., 1999; Smith et al., 2006). These peaks were passed through an open split to the ion source of a Finnigan Delta Plus XL mass spectrometer (use of trade names is for identification purposes only and does not imply endorsement by the U.S. Government) and monitored in continuous-flow mode at m/z 28, 29, 32, 34, 36, and 40. Relative peak areas at m/z 28 and 40 (from $N_2$ and Ar) were used to confirm sample integrity between the concentration measurements and the isotopic analyses. Values of $\delta^{15}N$ are reported with respect to atmospheric $N_2$ (0 ‰) and were calibrated by analyses of air-saturated water samples (+0.65 ‰) that were collected in serum bottles and treated the same way as the samples, with estimated uncertainties of approximately ± 0.1 ‰ (1-sigma). N and O isotopes in aqueous $NO_3^-$, $\delta^{15}N$ of $NO_3^-$ and $\delta^{18}O$ of $NO_3^-$, were analyzed by bacterial conversion of nitrate to nitrous oxide and subsequent measurement on a continuous flow isotope ratio mass spectrometer as described by Sigman et. al. (2001), Casciotti et. al. (2002), Coplen et. al. (2004), and Revesz and Casciotti (2005). Nitrogen isotope ratios are reported relative to $N_2$ in air (Mariotti, 1983). $\delta^{15}N$ of $NO_3^-$ values were normalized to values of +4.72 ‰ for International Atomic Energy isotopic standard NO-3 and +180.0 ‰ for USGS-32. $\delta^{18}O$ of $NO_3^-$ values were reported on a scale such that the Vienna Standard Mean Ocean Water (VSMOW) was 0 ‰ and the Standard Light Antarctic Precipitation was -55.5 ‰ relative to the VSMOW (Coplen, 1988, 1994). The reported $\delta^{18}O$ data were calibrated by assuming the following values for internationally distributed nitrate isotopic reference materials (Böhlke and others, 2003): IAEA-NO-3 (+25.6 ‰), USGS32 (+25.7 ‰), USGS34 (-27.9 ‰), and USGS35 (+57.5 ‰). The analytical uncertainties for $\delta^{15}N$ of $NO_3^-$ and $\delta^{18}O$ of $NO_3^-$ results were ±0.5 and ±1.0 ‰, respectively (2-sigma). $N_2O$ concentrations were determined by gas chromatography with an electron capture detector as described by Smith and Duff (1988) at the USGS laboratory in Boulder, Colorado.

*Reconstruction of Initial Nitrate Concentration and Isotopic Composition*

The initial concentration and isotopic composition of $NO_3^-$ was estimated for wells where excess $N_2$ gas resulting from denitrification was estimated to be present. The initial $NO_3^-$ concentration present in the ground water prior to the onset of denitrification was estimated as the sum of the measured $NO_3^-$ and excess $N_2$. The initial isotopic composition of the $NO_3^-$ concentration, $\delta^{15}N$ of $NO_3^{-o}$, present in the ground water prior to the onset of denitrification, was estimated by an isotopic mass balance as described by Böhlke et. al. (2002).

## Results and Discussion

*Chemical and Isotopic Composition of the Treated Effluent*

The treated effluent discharged to the RIBS contained high concentrations of $NO_3^-$-N, organic carbon, and boron. Measured $NO_3^-$ concentrations from 2004-2006 ranged from 1.37-6.93 mg/L as N. Organic carbon and boron concentrations measured in an effluent sample in November 2004 were 6.1 mg/L as C and 0.24 mg/L, respectively. $\delta^{15}N$ of $NO_3^-$ values from effluent samples had a wide variation (+9.46 to +29.07 ‰) which resulted from periodic denitrification of the effluent at the WWTRF.

*Evidence for Denitrification*

Chemical conditions were conducive for denitrification to occur in the UFA but generally not in the SAS. The UFA wells contained organic carbon, varying amounts of $NO_3^-$, and little $O_2$. Dissolved $O_2$ concentrations in water from all UFA wells were less than 1 mg/L. Ground waters exhibiting evidence of denitrification typically have concentrations less than approximately 2 mg/L (Böhlke et. al., 2002). Organic carbon was present in all UFA wells at concentrations ranging from 0.4-1.7 mg/L, and was highest (0.9-1.7 mg/L) in water samples from well 5. $NO_3^-$ was present in water from UFA wells 1-E, 2, and 4, but was not detectable in samples from wells 3 and 5. $NO_3^-$ concentrations were highest in well 1-E (1.78-3.17 mg/L as N) and 4 (0.44-0.77 mg/L as N). $NO_3^-$ was detected at low concentrations (0.02-0.05 mg/L as N) in water from well 2 from 2004-2005 but was not detected in water samples collected in 2006. Water from the SAS wells typically contained oxic water with higher concentrations of organic carbon and $NO_3^-$ compared to the UFA. Dissolved $O_2$ concentrations in the SAS wells ranged from 1.5-8.4 mg/L, and organic carbon concentrations ranged from 0.6-3.9 mg/L. $NO_3^-$ concentrations generally were elevated in the SAS wells compared to the UFA and ranged from 1.20-6.30 mg/L as N. Aerobic degradation of organic carbon likely was occurring in the part of the SAS represented by well 1-B, which resulted in increased $CO_2$ concentrations and lower pH values in water from this well. Water from well 1-B had $P$CO$_2$ values ranging from 5.1-7.3 kPa, which were approximately 150-200 times higher than values in ambient air. Water pH values also were lower in well 1-B (5.1-6.2 units) due to the high $P$CO2 values and were about 1 unit lower than the pH of water from well 1-A which represents an overlying part of the SAS.

Anomalously high apparent recharge temperatures calculated based on the $N_2$ and Ar data in 4 of the 5 UFA wells indicated there was an additional source of $N_2$ in the ground water, which was attributed to denitrification. Concentrations of dissolved $N_2$ and Ar in water from the SAS wells and UFA well 5 were consistent with atmospheric equilibrium of the air during recharge with the addition of small amounts of excess air (<4.8 cm$^3$ STP/L). Apparent ground water recharge temperatures ranged from 14.0°C to 22.7°C in the SAS wells and from 20.3 to 22.2°C in UFA well 5. The wide variation in apparent recharge temperatures from the SAS wells likely resulted from the seasonal temperature fluctuations of the treated effluent discharged to the RIBS combined with the high infiltration rate. Apparent recharge temperatures were anomalously high in UFA wells 2 (30.1-36.9°C), 3 (36.8-37.8°C), and 4 (30.2-33.9°C), and were near or slightly higher than the mean annual air temperature in well 1-E (21.5-25.4°C). It was interpreted from these high recharge temperatures there was another source of $N_2$ in the ground water besides recharge water in equilibrium with atmospheric air and the entrainment of excess air. This additional source of $N_2$ most likely resulted from the denitrification of $NO_3^-$. The amount of $N_2$ resulting from denitrification was estimated to range from near zero to 4.8 mg/L, assuming the water in these wells was recharged at the median recharge temperature calculated for well 5 (21.4°C), which is close to the mean annual air temperature for the area. Concentrations were lowest in well 1-E (near zero to 1.5 mg/L) and highest in wells 2 (2.8-4.6 mg/L) and 3 (4.7-4.8 mg/L). The amount of excess $N_2$ may be underestimated for well 1-E. Water may be recharged to this well at a temperature similar to those determined for the SAS wells (14.0°C to 22.7°C). A lower recharge temperature would result in a higher estimate of the amount of $N_2$ resulting from denitrification, and would range from 2.7-4.1 mg/L at 15°C and 1.4-2.8 mg/L at 18°C.

Elevated $\delta^{15}N$ of $N_2$ values measured in wells 1-E and 2-4 confirmed denitrification had occurred in these UFA wells. $\delta^{15}N$ of $N_2$ values in wells 1-E and 2-4 (+0.94 to +2.14 ‰) were notably higher than values associated with air-saturated water, approximately +0.75 ‰. $\delta^{15}N$ of $N_2$ values in the SAS wells (+0.61 to +0.75 ‰) and UFA well 5 (+0.70 to +0.84 ‰) were similar to air-saturated water values. The isotopic enrichment associated with denitrification was estimated to range from -2 to -8 ‰, which generally is smaller compared to the ranges reported for denitrification (Kendall and Aravena, 2000). Smaller enrichment factors reported in this study likely resulted from the well water samples containing a mixture of denitrified and undenitrified waters.

Detections of $N_2O$ and $NO_2^-$ indicated active denitrification occurred in selected parts of the UFA. $N_2O$ and $NO_2^-$-N were detected in water samples from two UFA wells, 1-E and 4. $N_2O$ concentrations in well 1-E ranged from 20.4-25.7 µg/L, and $NO_2^-$ concentrations in this well ranged from below method reporting limits (0.008 mg/L as N) to 0.04 mg/L as N. $N_2O$ concentrations were lower in well 4 compared to well 1-E and ranged from 3.1-11.9 µg/L, and $NO_2^-$ concentrations in this well ranged from below method reporting limits (0.016 mg/L as N) to 0.04 mg/L as N. $N_2O$ also was detected in SAS wells 1-B, 1-C, and 1-D at concentrations ranging from 3.1-20.2 µg/L, although the highest concentrations were measured in well 1-D (16.6-20.0 µg/L). These $N_2O$ detections may have resulted from: 1) the initial onset of denitrification before any appreciable build-up of $N_2$ in the ground water because some $O_2$ concentrations measured were near the upper limit for ground waters exhibiting evidence for denitrification, and $\delta^{15}N$ of $N_2$ values were similar to those in air-saturated water, 2) the water in the well contains a mixture of denitrified and nondenitrified waters, or 3) nitrification of ammonium in the ground water. However, ammonium only was

detected at concentrations near method detection limits in the water from these wells (0.01 mg/L), which is considerably lower than concentrations previously reported in ground water in which nitrification was occurring (Smith et. al., 2006). This suggests the potential for nitrification in the SAS may be limited.

*Sources of Nitrate and Initial Nitrate Concentrations*

Measured $\delta^{15}N$ of $NO_3^-$ and $\delta^{18}O$ of $NO_3^-$ values indicated that the source of nitrate was treated effluent in the SAS. $\delta^{15}N$ of $NO_3^-$ and $\delta^{18}O$ of $NO_3^-$ values in water from these wells were consistent with values measured in the effluent and were within the typical range of values in wastewater (Fig. 3). Elevated boron concentrations also indicated the source of the high nitrate concentrations in the SAS wells was treated wastewater. Boron is a common component of detergents and often is used as a tracer of wastewater in ground water systems (Repert et. al., 2006; Verstraeten et. al., 2005). Boron concentrations measured in the SAS wells ranged from 0.17-0.23 mg/L and were slightly lower than those measured in the treated effluent.
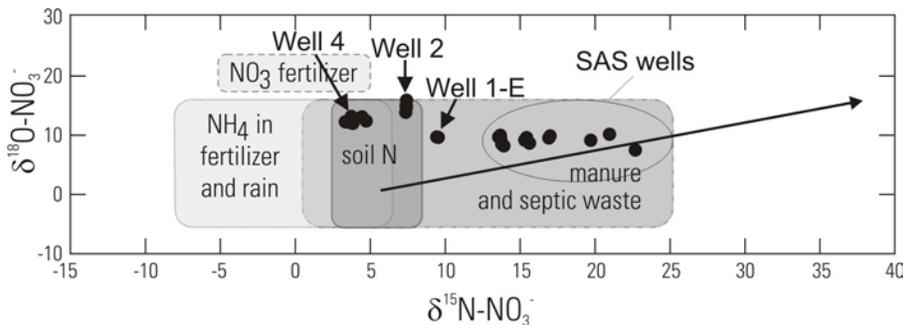


**Figure 3.** $\delta^{15}N$ and $\delta^{18}O$ of $NO_3^-$ values from SAS wells and UFA wells 1-E, 2, and 4 and typical ranges of values. Values for UFA wells represent the initial isotopic composition and were calculated assuming a recharge temperature of 21.4°C for wells 2 and 4 and 18°C for well 1-E. Typical ranges of values were from Kendall and Aravena, 2000.

Reconstructed initial N isotope values indicated that treated wastewater and fertilizer were the $NO_3^-$ sources in the UFA wells. Estimated initial nitrate concentrations in the UFA wells ranged from 2.58-6.77 mg/L, depending upon the recharge temperature assumed for well 1-E. Initial nitrate concentrations in wells 2-4 ranged from 3.10-4.82 mg/L. In well 1-E, the initial nitrate concentrations ranged from 2.58-3.67 mg/L as N if the assumed recharge temperature was 21.4°C and was higher for lower assumed recharge temperatures (for example 5.77-6.77 mg/L as N at a recharge temperature of 15°C). $\delta^{15}N$ of $NO_3^{-o}$ values were estimated for three UFA wells: 1-E, 2, and 4. $\delta^{15}N$ of $NO_3^{-o}$ values could not be estimated for wells 3 and 5 because there was insufficient $NO_3^-$ in water samples to determine its current isotopic composition. $\delta^{15}N$ of $NO_3^{-o}$ values in wells 1-E and 2 (Fig. 3), which are located near two of the most heavily-loaded RIBS, indicated the nitrate source likely was treated wastewater. Lower $\delta^{15}N$ of $NO_3^{-o}$ values in well 4 indicated the nitrate source was past

fertilizer use, which may have originated from citrus agriculture. The distribution of boron concentrations in the UFA wells supports this interpretation of the isotope data. The highest boron concentrations in the UFA were measured in wells 1-E (0.06-0.10 mg/L) and 2 (0.06-0.08 mg/L), and concentrations in the other UFA wells ranged from 0.01-0.03 mg/L.


## Summary and Conclusions

The potential for denitrification and sources of nitrate were evaluated in the karstic Upper Floridan aquifer (UFA) and overlying surficial aquifer beneath and upgradient from a wastewater treatment and reuse facility in Central Florida. Prior to the construction of this facility, the land use likely was citrus agriculture. Nitrate-N concentration (<0.02 to 6.3 mg/L) in ground water in this area likely originated from past fertilizer use in citrus agriculture or treated wastewater applied to rapid-sand infiltration beds. Chemical, isotopic, and dissolved gas data were evaluated from water samples collected from 9 wells to determine nitrate sources, the potential for denitrification, and identify areas of active denitrification. Sampled surficial aquifer wells ranged from 3.7 to 23.8 m deep, and UFA wells ranged from 46 to 102 m deep. $\delta^{15}N$ of $NO_3^-$ and $\delta^{18}O$ of $NO_3^-$ values in well water samples indicated that treated wastewater likely is the source of nitrate in the surficial aquifer wells, whereas reconstructed initial $\delta^{15}N$ of $NO_3^-$ values indicated the sources of nitrate in the UFA were treated wastewater in wells closest to the RIBS and fertilizer in the well located further away from the facility. Denitrification likely occurs in the UFA, but may only occur to a limited extent in the surficial aquifer. Dissolved oxygen concentrations generally were less than 1 mg/L in the UFA and greater than 2 mg/L in the surficial aquifer. Dissolved gas and isotopic data indicated that denitrification had occurred in water from 4 of 5 UFA wells. Excess nitrogen gas ($N_2$), the end product of denitrification, was estimated to be present in water from four UFA wells based on the concentrations of dissolved $N_2$ and Ar in the ground water. Excess $N_2$ concentrations which likely resulted from denitrification typically ranged from 1 to 5 mg/L. $\delta^{15}N$ values associated with $N_2$ in these same wells also were substantially greater (+0.97 to +2.14 ‰) than for $N_2$ in equilibrium with air-saturated water. Denitrification may naturally attenuate some nitrate in low dissolved oxygen zones of the UFA before it is transported to natural springs in the area. The chemical character of groundwater in karst can change rapidly during recharge events (Doctor et al., 2006). More frequent sampling of well water during conditions of water table fluctuation, especially during periods of RIB loading, may provide additional information on controls on conditions leading to denitrification within the study area.


## Acknowledgments

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**Biographical Sketch**
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# Appendix 2.  Laboratory Report of Tritium/He Measurements for USGS Project

Prepared by the Noble Gas Laboratory Lamont-Doherty Earth Observatory of Columbia University, New York. Explanatory information provided for the reader precedes the reprinted document. Refer to Schlosser and others (2008) in the references cited section for the complete report citation.

Tritium/helium measurements may be used to determine the elapsed time since water in an aquifer lost contact with the atmosphere, commonly referred to as the "age" of the water. Tritium is a radioactive form of hydrogen containing 1 proton and 2 neutrons, often written as $^3$H. Tritium is a rare, naturally occurring isotope with typical concentrations near 1-3 tritium units (TU) in current rain samples. From 1952 to 1963, tritium was also produced as a byproduct of above ground testing of nuclear bombs.  Tritium is incorporated into the water molecule, making it an effective environmental tracer that is useful in age dating relatively young groundwater. Tritium concentrations peaked in 1963 at over 1,000 TU in precipitation at some locations in the U.S. In Miami from the mid-1960s to 1990, the tritium concentration in precipitation ranged from 35 TU to the background concentration of 1-3 TU (Walsh and Price, 2010).

The half-life of tritium is 12.43 years (Unterwegar and others, 1980) and the end product is radioactive helium, $^3$He$_{trit}$ (Turrin, 2012).  As a result of radioactive decay since the peak production of tritium, an accurate measurement of the concentration of $^3$He$_{trit}$ is also required to estimate groundwater age. Helium is predominately in the form of $^4$He, but $^3$He is naturally occurring in the earth's mantle and the atmosphere.  In order to determine the precise concentration of $^3$He$_{trit}$ in groundwater, the following variables need to be accounted for: concentrations of $^4$He and neon dissolved in groundwater and the temperature and elevation at which recharging water was no longer in equilibrium with the atmosphere (Turrin, 2012). For further detail on $^3$H/$^3$He dating methods, see Schlosser and others (1988).

The nine water samples presented in this lab report were collected to determine the age of water in the surficial and Upper Floridan aquifer from wells located at or near the Northwest Water Reclamation Facility in Orange County, Florida (fig. 1). Not all of these results are included in the main report because some analyses were inconclusive or not used for the study.  Description of well depths and location reported by Kroening (2007) are included in appendix I; however, the well names were different in that report. Cluster wells 1-B, 1-C, 1-D in Kroening (2007) are reported in this appendix as Cluster Well 2, Cluster Well 3, and Cluster Well 4, respectively.  Cluster Well 1-E in Kroening (2007) is Monitoring Well 8R, and sites 2, 3, 4, and 5 are reported here as Monitoring Well 2, Monitoring Well 5R, Phipps Well and Toll Plaza Well, respectively. Keene Road Well 14, which was not used in this study, is an Upper Floridan Well located in the landfill on the northeast boundary of the RIBs site. This well is 172 ft deep with a 10 ft open interval. Three wells are in the surficial aquifer and the remaining 6 wells are in the Upper Floridan aquifer. Information on well depths, casing, and hydrogeology are in Kroening (2007) under Site Selection.

The wells were sampled January 24, 25, 31 of 2006, using the method described by Schlosser (undated). Nine sets of duplicate samples were submitted to the laboratory. Analysis methodology is described by Schlosser and others (1988). Laboratory results and measured concentrations are listed in this appendix. For further explanation of the meaning of uncorrected age and corrected age data listed in the laboratory report see U.S. Geological Survey (undated). Tritium was measured in samples from all nine wells, and ranged in concentration from 0.08-5.46 TU. The $^3$He, $^4$He, and neon concentrations were measured in the samples from five wells. Neon concentration was also measured in the sample from one additional well. Various reasons are listed in the laboratory report for the possible problems associated with the samples. Two sites where problems affected laboratory analysis were Cluster Well 4 (surficial aquifer) and replicate samples from Monitoring Well 2 (Upper Floridan aquifer). For the purpose of this study, 19 years was used as an estimate for the age of the water from the Upper Floridan aquifer.

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# DATA RELEASE NO. 08-1.15.0 (USGS report; 03/24/2008)

## TRITIUM/HE MEASUREMENTS FOR THE USGS PROJECT
'Fl-Kroening-1(a)' (SAMPLES SUBMITTED BY Kroening)

Peter Schlosser, Brent D. Turrin, and Millie Klas

Lamont-Doherty Earth Observatory
Palisades, N.Y. 10964

TRITIUM/HELIUM MEASUREMENTS FOR THE USGS PROJECT:

## Fl-Kroening-1(a)    Submitted by Kroening

Data Summary:

Number of He/Ne Samples Submitted in Duplicate ............................................... 9
Number of He/Ne Measurements/Extractions Performed ................................... 11
Number of He/Ne Data Reported ................................................................... 5
Number of He/Ne Samples Re-measured ........................................................ 2

Problems    USGS ............................................................................... 1
            LDEO ............................................................................... 5
            Checks .............................................................................. 1

USGS Charge

    Number of Samples Measured/Extracted ............................................ 11-1-5
    minus Number of Checks, minus Number of LDEO Problems ......................... 5

Number of Tritium Samples Submitted ............................................................. 9
Number of Tritium Measurements Performed .................................................... 11
Number of Tritium Data Reported ................................................................... 11
Number of Tritium Data Re-measured .............................................................. 3

Problems    USGS ............................................................................... 0
            LDEO ............................................................................... 0
            Checks .............................................................................. 3

USGS Charge

    Number of Samples Measured ........................................................... 11-3-0
    minus Number of Checks, minus Number of LDEO Problems ......................... 8

**Total Number He/Ne Samples Charged** ........................................................ **5**
**Total Number Tritium Samples Charged** ....................................................... **8**

# USGS-FI-Kroening-1(a)

| Item# | Sample ID # | Tritium (TU) | δ3he | 4He x10-8 cm3STP/g | Ne x10-8 cm3STP/g | Comment |
|---|---|---|---|---|---|---|
| 1 | Cluster Well 2/H2072 | 1.03 | -- | -- | 63.97 | High ΔNe indicates air contamination. Sample pumped due to either high concentration of dissolved gases or sampling problem. Tritium measurement looks OK, |
|  | Cluster Well 2/T1610 | 0.51 |  |  |  | Tritium measurement looks OK |
| 2 | Cluster Well 3/H2074 |  |  | -- | -- | No more sample |
| 3 | Cluster Well 4/H2076 | 1.02 | 2.46 | 68.84 | 64.70 | High ΔHe and ΔNe indicates air contamination Tritium measurement looks OK |
| 4 | Keene Road Well 14/H2080 | 5.46 | -- | -- | -- | Tritium measurement looks OK |
| 5 | Monitoring Well 2/H2066 | 1.46 | 10.12 | 5.91 | 23.50 | Tritium measurement looks OK |
|  | Monitoring Well 2/H2067 | 1.27 | 6.64 | 3.30 | 10.07 | Negative ΔHe and ΔNe indicates sample gas was stripped as the result of a sampling problem. Sample most likely fractionated. Do not use age. Tritium measurement looks OK |
| 6 | Monitoring Well 5R/H2078 | 2.65 | -- | -- | -- | Tritium measurement looks OK, 4He bulb blank slightly elevated |
|  | Monitoring Well 5R/T1613 | 3.01 |  |  |  | High 4He bulb blank |

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# USGS-FI-Kroening-1(a)

| Item# | Sample ID # | Tritium (TU) | δ3he | 4He x10-8 cm3STP/g | Ne x10-8 cm3STP/g | Comment |
|---|---|---|---|---|---|---|
| 7 | Monitoring Well 8R/H2070 | 1.55 | 0.64 | 7.06 | 27.40 | Tritium measurement looks OK. |
|  | Monitoring Well 8R/T1609 | 1.55 |  |  |  | Tritium measurement looks OK, ⁴He bulb blank elevated |
| 8 | Phipps Well/H2064 | 1.79 | -- | -- | -- | Tritium measurement looks OK, |
|  | Phipps Well/H2065 |  |  | -- | -- | Tritium measurement looks OK,  No more sample. |
| 9 | Toll Plaza Well/H2068 | 0.08 | 72.94 | 0.99 | 4.27 | Negative ΔHe and ΔNe indicates sample gas was stripped as the result of a sampling problem.  Sample most likely fractionated. Do not use age. Tritium measurement looks OK, |

| SampleID | Sampling Date | Tritium | ±1σ TU | δ³He | ±1σ (%) | Ratio 10⁻⁴ | ±1σ (%) | ⁴He (10⁻⁴ ccSTP/g) | Ne | %He (terrigen.) | Age ±1σ (yrs) (uncorrected) | Age ±1σ (yrs) (corrected) | published comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cluster Well 2/H2072 | 1/25/2006 | 1.03 | 0.09 | ? | 0.55 | ? | 0.68 | 0.00 (Δ⁴He -100.0) | 63.97 (ΔNe 262.4) | ? | High He pressure, pumped at MS, L-DEO problem. | | High ΔNe indicates air contamination. Sample pumped due to either high concentration of dissolved gases or sampling problem. Tritium measurement looks OK, |
| Cluster Well 2/T1610 | 1/25/2006 | 0.51 | 0.03 | | | | | | | | Tritium data from bottle sample | | Tritium measurement looks OK |
| Cluster Well 3/H2074 | 1/25/2006 | | | ? | ? | | | 0.01 (Δ⁴He -99.9) | 0.00 (ΔNe -100.0) | ? | | | No more sample |
| Cluster Well 4/H2076 | 1/25/2006 | 1.02 | 0.09 | 2.46 | 0.22 | 1.418 | 0.46 | 68.84 (Δ¹He 1477.3) | 64.70 (ΔNe 270.6) | 73.88 | 42.3 ± 1.4 | 101.2 ± 1.5 | High ΔNe and ΔNe indicates air contamination Tritium measurement looks OK |
| | | | | | | | | | | | High pressure at branch, Sample pumped due to either high concentration of dissolved gases or sampling problem. | Terrigenic He, use corrected age | |
| Keene Road Well 14/H2080 | 1/31/2006 | 5.46 | 0.14 | 5952.55 | 0.31 | 83.767 | 0.51 | 0.02 (Δ⁴He -99.6) | 0.00 (ΔNe -100.0) | ? | High pressure at branch, Sample pumped due to either high concentration of dissolved gases or sampling problem. | | Tritium measurement looks OK |
| Monitoring Well 2/H2066 | 1/24/2006 | 1.46 | 0.09 | 10.12 | 0.25 | 1.524 | 0.47 | 5.91 (Δ⁴He 35.2) | 23.50 (ΔNe 34.2) | -3.18 | 22.8 ± 0.8 | 18.9 ± 0.7 | Tritium measurement looks OK |
| Monitoring Well 2/H2067 | 1/24/2006 | 1.27 | 0.09 | 6.64 | 0.34 | 1.476 | 0.52 | 3.30 (Δ⁴He -24.6) | 10.07 (ΔNe -42.5) | 32.45 | 14.9 ± 0.7 | 34.7 ± 1.0 | Negative ΔHe and ΔNe indicates sample gas was stripped as the result of a sampling problem. Sample most likely fractionated. Do not use age. Tritium measurement looks OK |
| | | | | | | | | | | | Terrigenic He, use corrected age | | |
| Monitoring Well 5R/H2078 | 1/24/2006 | 2.65 | 0.11 | 2575.88 | 0.31 | 37.034 | 0.51 | 0.03 (Δ⁴He -99.3) | 0.00 (ΔNe -100.0) | ? | High pressure at branch, Sample pumped due to either high concentration of dissolved gases or sampling problem. | | Tritium measurement looks OK, ⁴He bulb blank slightly elevated |
| Monitoring Well 5R/T1613 | 1/24/2006 | 3.01 | 0.07 | | | | | (Δ⁴He) | (ΔNe) | | Tritium data from bottle sample | | High ⁴He bulb blank |
| Monitoring Well 8R/H2070 | 1/25/2006 | 1.55 | 0.08 | 0.64 | 0.24 | 1.393 | 0.47 | 7.06 (Δ⁴He 60.8) | 27.40 (ΔNe 54.4) | -1.61 | 6.5 ± 0.3 | 0.6 ± 0.0 | Tritium measurement looks OK. |
| Monitoring Well 8R/T1609 | 1/25/2006 | 1.55 | 0.05 | | | | | (Δ⁴He) | (ΔNe) | | Tritium data from bottle sample | | Tritium measurement looks OK, ⁴He bulb blank elevated |
| Phipps Well/H2064 | 1/24/2006 | 1.79 | 0.09 | 5733.40 | 0.28 | 80.734 | 0.49 | 0.01 (Δ⁴He -99.7) | 0.00 (ΔNe -100.0) | ? | High pressure at branch, Sample pumped due to either high concentration of dissolved gases or sampling problem. | | Tritium measurement looks OK, |
| Phipps Well/H2065 | 1/24/2006 | | | | | | | 0.00 (Δ⁴He -99.9) | 0.00 (ΔNe -100.0) | ? | High pressure at branch, Sample pumped due to either high concentration of dissolved gases or sampling problem. | | Tritium measurement looks OK, No more sample. |

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constants: $\delta^3He_{equilibrium}$: -1.8 %; $\lambda_{3H}$ = .05577 yr⁻¹.; $^3He/^4He_{atmos}$ = 1.384 ×10⁻⁶.; crustal terrigenic $^3He/^4He$ ratio: 2 ×10⁻⁸

| SampleID | Sampling Date | Tritium | ±1σ TU | δ³He | ±1σ (%) | Ratio $10^{-4}$ | ±1σ (%) | ⁴He ($10^{-8}$ ccSTP/g) | Ne | %He (terrigen.) | Age ±1σ (yrs) (uncorrected) | Age ±1σ (yrs) (corrected) | published comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Toll Plaza Well/H2068 | 1/24/2006 | 0.08 | 0.07 | 72.94 | 0.28 | 2.393 | 0.49 | 0.99 | 4.27 | 53.41 | High He pressure, pumped at MS, L-DEO problem. | | Negative ΔHe and ΔNe indicates sample gas was stripped as the result of a sampling problem. Sample most likely fractionated. Do not use age. Tritium measurement looks OK. |

$\Delta^4$He  -77.7   ΔNe  -76.3

constants: $\delta^3He_{equilibrium}$: -1.8 %; $\lambda_{3H}$: .05577 yr.$^{-1}$; $^3He/^4He_{atmos}$ = 1.384 ×10$^{-6}$; crustal terrigenic $^3He/^4$He ratio: 2 ×10$^{-8}$

# Noble Gas Laboratory
## Lamont-Doherty Earth Observatory
## Columbia University, New York

| report | Sender | Kroening | Organization | USGS | Program | FI-Kroening-1 |
|---|---|---|---|---|---|---|
| **r** | Sample ID | Cluster Well 2/H2072 | | | | |

| Channel No. | 1 | Tritium Bottle No. | | | Date received | |
|---|---|---|---|---|---|---|
| Sample Date | 1/25/2006 | Sampling Time | 1200 | Altitude 39.62 m | Temp. 25.8 °C | Salinity 0 |

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| T Degas No. | **22605** | T Degas Date | | T Measurement Date | 6/7/2006 |
|---|---|---|---|---|---|

| | | | | | $^4$He bulb blank 0.662 x10$^{-9}$ cm$^3$STP |
|---|---|---|---|---|---|
| **Tritium:** | **1.029** | **± 0.091** | TU (1σ) | 0.091 | Ingrown $^3$He$_{trit}$ 2.267394 x10$^{-15}$ cm$^3$STP |
| T database | | | | | %$^3$He$_{trit}$ 59.3 |
| Alternative tritium value: | | ± | TU (1σ) | comment: | |

---

| He Extraction No. 22605 | | He Extraction Date 3/1/2006 | | | He Measurement Date 7/27/2006 |
|---|---|---|---|---|---|

| $\delta^3$He: | ? | ± 0.55 | % (1σ) | $\delta^3$He$_{cor}$ from other T (see above): 78896 % | $\delta^3$He$_{uncor}$: ? ± 0.55 % (1σ) |
|---|---|---|---|---|---|
| $^3$He$_{trit}$: | 21.89 | ± 0.00 | TU (1σ) | he database | $^3$He: 5.340 x10$^{-14}$ cm$^3$ STP/g |
| | | | | | Sample weight: 39.38 g |

| $^4$He: | 0.000 | ± 0.000 | x10$^{-8}$ cm$^3$STP/g (1σ) | $\Delta^4$He: -99.99 % | Age | Uncorrected ±1σ (y) |
|---|---|---|---|---|---|---|---|
| Ne: | 63.972 | ± 0.280 | x10$^{-8}$ cm$^3$STP/g (1σ) | $\Delta$Ne: 262.37 % | | |

| Average crustal terrigenic $^3$He/$^4$He ratio: 2 x10$^{-8}$: | | | | |
|---|---|---|---|---|
| $\delta^3$He$_{cor}$: | -76.795 | % | | Corrected for terrigenic He |
| $^3$He$_{cor}$: | -75.314 | TU | $^3$He$_{cor}$: 5.695 x10$^{-14}$ cm$^3$STP/g | |
| $^4$He$_{cor}$: | 17.733 | x10$^{-8}$ cm$^3$STP/g | % Terrigenic $^4$He ? | Age ±1σ (y) |
| $^4$He$_{terrigenic}$: | -17.732 | x10$^{-8}$ cm$^3$STP/g | | |

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| Site specific terrigenic $^3$He/$^4$He ratio: | | | | Corrected for terrigenic He |
|---|---|---|---|---|
| $\delta^3$He$_{cor}$ | -76.795 | % | $^3$He$_{cor}$ 5.695 x10$^{-14}$ cm$^3$STP/g | Age ±1σ (y) |
| $^3$He$_{cor}$ | -75.314 | TU | | |

constants: $\delta^3$He$_{equilibrium}$: -1.8 %; $\lambda_{3H}$= .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos}$= 1.384 x10$^{-6}$

| published comments | High He pressure, pumped at MS, L-DEO problem. |
|---|---|
| | High ΔNe indicates possible air contamination. Sample pumped due to either high concentration of dissolved gases or sampling problem. Tritium measurement looks OK. |

| Comments: | |
|---|---|
| | |

# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

| report | Sender | Kroening | Organization | USGS | Program | FI-Kroening-1 |
|---|---|---|---|---|---|---|
| **r** | Sample ID | Cluster Well 2/T1610 | | | | |

| | Channel No. | | Tritium Bottle No. | 1 | | Date received | |
|---|---|---|---|---|---|---|---|
| Sample Date | 1/25/2006 | Sampling Time | 1200 | Altitude | 39.62 m | Temp. 25.8 °C | Salinity 0 |

| T Degas No. | **1009906** | T Degas Date | 2/23/2006 | T Measurement Date | 6/7/2006 |
|---|---|---|---|---|---|

**Tritium:** 0.508 ± 0.034 TU (1σ) 0.034

$^4$He bulb blank 0.695 $\times 10^{-9}$ cm$^3$STP
Ingrown $^3$He$_{trit.}$ 2.814202 $\times 10^{-15}$ cm$^3$STP
%$^3$He$_{trit}$ 65.6

[ T database ]

Alternative tritium value: ± TU (1σ)  comment:

| He Extraction No. | | He Extraction Date | | He Measurement Date | |
|---|---|---|---|---|---|

$\delta^3$He: ± % (1σ) $\delta^3$He$_{cor}$ from other T (see above): % $\delta^3$He$_{uncor}$: ± % (1σ)

$^3$He$_{trit}$: ± TU (1σ) [ he database ] $^3$He: $\times 10^{-14}$ cm$^3$ STP/g

Sample weight: g

$^4$He: ± $\times 10^{-8}$ cm$^3$STP/g (1σ) $\Delta^4$He: % | Age | Uncorrected ±1σ (y)

Ne: ± $\times 10^{-8}$ cm$^3$STP/g (1σ) $\Delta$Ne: %

Average crustal terrigenic $^3$He/$^4$He ratio: $2 \times 10^{-8}$:

$\delta^3$He$_{cor}$: %

Corrected for terrigenic He

$^3$He$_{cor}$: TU $^3$He$_{cor}$: $\times 10^{-14}$ cm$^3$STP/g

$^4$He$_{cor}$: $\times 10^{-8}$ cm$^3$STP/g % Terrigenic $^4$He

$^4$He$_{terrigenic}$: 0.000 $\times 10^{-8}$ cm$^3$STP/g | Age ±1σ (y)

| Site specific terrigenic $^3$He/$^4$He ratio: | | Corrected for terrigenic He |
|---|---|---|

$\delta^3$He$_{cor}$ % $^3$He$_{cor}$ $\times 10^{-14}$ cm$^3$STP/g | Age ±1σ (y)

$^3$He$_{cor}$ TU

constants: $\delta^3$He$_{equilibrium}$: -1.8 %; $\lambda_{3H}$ = .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos.}$ = 1.384 $\times 10^{-6}$

| published comments | Tritium data from bottle sample |
|---|---|
| | Tritium measurement looks OK |

Comments:

# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

| report **r** | Sender | Kroening | Organization | USGS | Program | FI-Kroening-1 |
|---|---|---|---|---|---|---|

| | Sample ID | Cluster Well 3/H2074 |
|---|---|---|

| | Channel No. | 1 | Tritium Bottle No. | | | Date received | |
|---|---|---|---|---|---|---|---|

| Sample Date | 1/25/2006 | Sampling Time | 1000 | Altitude | 39.62 | m | Temp. | 22.1 | °C | Salinity | 0 |
|---|---|---|---|---|---|---|---|---|---|---|---|

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| T Degas No. | **22602** | T Degas Date | | T Measurement Date | |
|---|---|---|---|---|---|

| **Tritium:** | ± | **TU (1σ)** | $^4$He bulb blank | x10$^{-9}$ cm$^3$STP |
|---|---|---|---|---|
| | | | Ingrown $^3$He$_{trit.}$ | x10$^{-15}$ cm$^3$STP |
| T database | | | %$^3$He$_{trit}$ | |

| Alternative tritium value: | ± | **TU (1σ)** | comment: | |
|---|---|---|---|---|

---

| He Extraction No. **22602** | | He Extraction Date 2/23/2006 | | He Measurement Date 7/27/2006 |
|---|---|---|---|---|

| $\delta^3$He: | ± | % (1σ) | $\delta^3$He$_{cor}$ from other T (see above): | | % | $\delta^3$He$_{uncor}$: ? | ± 0.32 | % (1σ) |
|---|---|---|---|---|---|---|---|---|

| $^3$He$_{trit}$: | ± | TU (1σ) | he database | | | $^3$He: | x10$^{-14}$ cm$^3$ STP/g | |

Sample weight: 39.82 g

| $^4$He: | 0.005 | ± 0.000 | x10$^{-8}$ cm$^3$STP/g (1σ) | $\Delta^4$He: | -99.88 | % | Age | Uncorrected ±1σ (y) |
|---|---|---|---|---|---|---|---|---|
| Ne: | 0.000 | ± 0.000 | x10$^{-8}$ cm$^3$STP/g (1σ) | $\Delta$Ne: | -100 | % | | |

| Average crustal terrigenic $^3$He/$^4$He ratio: 2 x10$^{-8}$: | | | | Corrected for terrigenic He |
|---|---|---|---|---|
| $\delta^3$He$_{cor}$: | % | | | |
| $^3$He$_{cor}$: | TU | $^3$He$_{cor}$: | x10$^{-14}$ cm$^3$STP/g | |
| $^4$He$_{cor}$: | -0.799 | x10$^{-8}$ cm$^3$STP/g | % Terrigenic $^4$He 14756.5 | Age ±1σ (y) |
| $^4$He$_{terrigenic}$: | 0.804 | x10$^{-8}$ cm$^3$STP/g | | |

| Site specific terrigenic $^3$He/$^4$He ratio: | | | Corrected for terrigenic He |
|---|---|---|---|
| $\delta^3$He$_{cor}$ | % | $^3$He$_{cor}$ | x10$^{-14}$ cm$^3$STP/g | Age ±1σ (y) |
| $^3$He$_{cor}$ | TU | | |

constants: $\delta^3$He$_{equilibrium}$: -1.8 %; $\lambda_{3H}$= .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos}$= 1.384 x10$^{-6}$

| published comments | High pressure at branch, Sample pumped due to either high concentration of dissolved gases or sampling problem. No more sample |
|---|---|

| Comments: | |
|---|---|

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# Noble Gas Laboratory
## Lamont-Doherty Earth Observatory
## Columbia University, New York

| report | Sender | Kroening | Organization | USGS | Program | FI-Kroening-1 |
|---|---|---|---|---|---|---|
| **r** | Sample ID | Cluster Well 4/H2076 | | | | |

| | Channel No. | 1 | Tritium Bottle No. | | Date received | |
|---|---|---|---|---|---|---|
| Sample Date | 1/25/2006 | Sampling Time | 1330 | Altitude | 39.62 m | Temp. 27.4 °C  Salinity 0 |

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| T Degas No. | **22603** | T Degas Date | | T Measurement Date | 6/7/2006 |
|---|---|---|---|---|---|

| | | | | | $^4$He bulb blank 0.660 x10$^{-9}$ cm$^3$STP |
|---|---|---|---|---|---|
| **Tritium:** | 1.024 | ± 0.088 | TU (1σ) | 0.088 | Ingrown $^3$He$_{trit.}$ 2.287344 x10$^{-15}$ cm$^3$STP |
| | | | | | %$^3$He$_{trit}$ 59.8 |

T database

comment:

Alternative tritium value: _____ ± _____ TU (1σ)

---

| He Extraction No. **22603** | He Extraction Date 2/23/2006 | He Measurement Date 7/27/2006 |
|---|---|---|

| $\delta^3$He: | 2.46 | ± 0.22 | % (1σ) | $\delta^3$He$_{cor}$ from other 2.457 % | $\delta^3$He$_{uncor}$: 2.46 ± 0.22 % (1σ) |
|---|---|---|---|---|---|
| $^3$He$_{trit}$: | 9.83 | ± 0.00 | TU (1σ) | T (see above): ~ | $^3$He: 97.612 x10$^{-14}$ cm$^3$STP/g |

he database

Sample weight: 39.32 g

| $^4$He: | 68.837 | ± 0.091 x10$^{-8}$ cm$^3$STP/g (1σ) | $\Delta^4$He: 1477.29 % | | Uncorrected Age ±1σ (y) |
|---|---|---|---|---|---|
| Ne: | 64.699 | ± 0.314 x10$^{-8}$ cm$^3$STP/g (1σ) | $\Delta$Ne: 270.56 % | | 42.3 ± 1.4 |

**Average crustal terrigenic $^3$He/$^4$He ratio: 2 x10$^{-8}$:**

Corrected for terrigenic He

| $\delta^3$He$_{cor}$: | 288.173 | % | | |
|---|---|---|---|---|
| $^3$He$_{cor}$: | 288.606 | TU | $^3$He$_{cor}$: 96.595 x10$^{-14}$ cm$^3$STP/g | |
| $^4$He$_{cor}$: | 17.980 | x10$^{-8}$ cm$^3$STP/g | % Terrigenic $^4$He 73.9 | Age ±1σ (y) |
| $^4$He$_{terrigenic}$: | 50.857 | x10$^{-8}$ cm$^3$STP/g | | 101.2 ± 1.5 |

**Site specific terrigenic $^3$He/$^4$He ratio:** _____

Corrected for terrigenic He

| $\delta^3$He$_{cor}$ | 288.174 | % | $^3$He$_{cor}$ 96.595 x10$^{-14}$ cm$^3$STP/g | Age ±1σ (y) |
|---|---|---|---|---|
| $^3$He$_{cor}$ | 288.606 | TU | | ± |

constants: $\delta^3$He$_{equilibrium}$: -1.8 %; $\lambda_{3H}$ = .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos.}$ = 1.384 x10$^{-6}$

| published comments | Terrigenic He, use corrected age |
|---|---|
| | High $\Delta$Ne and $\Delta$Ne indicates possible air contamination |
| | Tritium measurement looks OK |

**Comments:**

# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

LDEO NGL

| report r | Sender | Kroening | Organization USGS | Program | FI-Kroening-1 |
|---|---|---|---|---|---|

| | Sample ID | Keene Road Well 14/H2080 |
|---|---|---|

| | Channel No. 1 | Tritium Bottle No. | | Date received | |
|---|---|---|---|---|---|

| Sample Date 1/31/2006 | Sampling Time 1000 | Altitude 19.81 m | Temp. 23.7 °C | Salinity 0 |
|---|---|---|---|---|

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| T Degas No. 22606 | T Degas Date | T Measurement Date 6/7/2006 |
|---|---|---|

Tritium: **5.465** ± 0.138 TU (1σ)  0.138

$^4$He bulb blank 0.654 x10$^{-9}$ cm$^3$STP
Ingrown $^3$He$_{trit}$ 8.083985 x10$^{-15}$ cm$^3$STP
%$^3$He$_{trit}$ 88.7

T database

Alternative tritium value: ± TU (1σ)    comment:

---

| He Extraction No. 22606 | He Extraction Date 3/1/2006 | He Measurement Date 7/27/2006 |
|---|---|---|

$\delta^3$He: **5952.55** ± 0.31 % (1σ)  $\delta^3$He$_{cor}$ from other T (see above): 5952. %   $\delta^3$He$_{uncor}$: **?** ± 0.32 % (1σ)

$^3$He$_{trit}$: **6.07** ± 0.00 TU (1σ)

he database

$^3$He: 1.427 x10$^{-14}$ cm$^3$ STP/g
Sample weight: 39.34 g

$^4$He: **0.017** ± 0.000 x10$^{-8}$ cm$^3$STP/g (1σ)   $\Delta^4$He: **-99.61** %
Ne: **0.000** ± 0.000 x10$^{-8}$ cm$^3$STP/g (1σ)   $\Delta$Ne: **-100** %

Age ±1σ (y)   Uncorrected

Average crustal terrigenic $^3$He/He ratio: 2 x10$^{-8}$:

$\delta^3$He$_{cor}$: **-234.333** %
$^3$He$_{cor}$: **10.328** TU   $^3$He$_{cor}$: **1.412** x10$^{-14}$ cm$^3$STP/g
$^4$He$_{cor}$: **-0.759** x10$^{-8}$ cm$^3$STP/g   % Terrigenic $^4$He **4556.4**
$^4$He$_{terrigenic}$: **0.776** x10$^{-8}$ cm$^3$STP/g

Corrected for terrigenic He   Age ±1σ (y)

---

Site specific terrigenic $^3$He/$^4$He ratio:

$\delta^3$He$_{cor}$ **-234.336** %   $^3$He$_{cor}$ **1.412** x10$^{-14}$ cm$^3$STP/g
$^3$He$_{cor}$ **10.328** TU

Corrected for terrigenic He   Age ±1σ (y)

constants: $\delta^3$He$_{equilibrium}$: -1.8 %; $\lambda_{3H}$= .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos}$= 1.384 x10$^{-6}$

published comments | High pressure at branch, Sample pumped due to either high concentration of dissolved gases or sampling problem. Tritium measurement looks OK

Comments:

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# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

| report | Sender | Kroening | Organization | USGS | Program | FI-Kroening-1 |
|---|---|---|---|---|---|---|
| r | Sample ID | Monitoring Well 2/H2066 | | | | |

| | Channel No. | 1 | Tritium Bottle No. | | | Date received | |
|---|---|---|---|---|---|---|---|
| Sample Date | 1/24/2006 | Sampling Time | 1530 | Altitude | 33.53 m | Temp. 27.06 °C | Salinity 0 |

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| T Degas No. | 22598 | T Degas Date | | T Measurement Date | 6/7/2006 |
|---|---|---|---|---|---|

$^4$He bulb blank 0.682 x10$^{-9}$ cm$^3$STP
Ingrown $^3$He$_{trit.}$ 2.930293 x10$^{-15}$ cm$^3$STP
%$^3$He$_{trit}$ 67.6

**Tritium:** 1.458 ± 0.090 TU (1σ) 0.090

T database

Alternative tritium value: ± TU (1σ)    comment:

---

| He Extraction No. 22598 | | He Extraction Date 2/23/2006 | | He Measurement Date 7/27/2006 |
|---|---|---|---|---|

$\delta^3$He: 10.12 ± 0.25 % (1σ)   $\delta^3$He$_{cor}$ from other T (see above): 10.12 %   $\delta^3$He$_{uncor}$: 10.14 ± 0.25 % (1σ)

$^3$He$_{trit}$: 3.75 ± 0.00 TU (1σ)    he database    $^3$He: 9.004 x10$^{-14}$ cm$^3$ STP/g

Sample weight: 39.45 g

$^4$He: 5.908 ± 0.008 x10$^{-8}$ cm$^3$STP/g (1σ)   $\Delta^4$He: 35.15 %   Uncorrected Age ±1σ (y)

Ne: 23.497 ± 0.114 x10$^{-8}$ cm$^3$STP/g (1σ)   $\Delta$Ne: 34.17 %   22.8 ± 0.8

Average crustal terrigenic $^3$He/$^4$He ratio: 2 x10$^{-8}$:

$\delta^3$He$_{cor}$: 6.766 %

$^3$He$_{cor}$: 2.720 TU    $^3$He$_{cor}$: 9.008 x10$^{-14}$ cm$^3$STP/g

Corrected for terrigenic He

$^4$He$_{cor}$: 6.096 x10$^{-8}$ cm$^3$STP/g   % Terrigenic $^4$He  -3.2

$^4$He$_{terrigenic}$: -0.188 x10$^{-8}$ cm$^3$STP/g

Age ±1σ (y)   18.9 ± 0.7

---

Site specific terrigenic $^3$He/$^4$He ratio:

Corrected for terrigenic He

$\delta^3$He$_{cor}$ 6.766 %   $^3$He$_{cor}$ 9.008 x10$^{-14}$ cm$^3$STP/g   Age ±1σ (y)

$^3$He$_{cor}$ 2.719 TU   ±

constants: $\delta^3$He$_{equilibrium}$: -1.8 %; $\lambda_{3H}$= .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos.}$= 1.384 x10$^{-6}$

**published comments** Tritium measurement looks OK

**Comments:**

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# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

| report **r** | Sender | Kroening | Organization USGS | Program Fl-Kroening-1 |
|---|---|---|---|---|
| | Sample ID | Monitoring Well 2/H2067 | | |

| | Channel No. 2 | Tritium Bottle No. | Date received |
|---|---|---|---|

| Sample Date 1/24/2006 | Sampling Time 1530 | Altitude 33.53 m | Temp. 27.06 °C | Salinity 0 |
|---|---|---|---|---|

---

T Degas No. **22990**  T Degas Date  T Measurement Date  4/10/2007

| | | | | | $^4$He bulb blank 0.778 x10$^{-9}$ cm$^3$STP |
|---|---|---|---|---|---|
| **Tritium:** | **1.269** | **± 0.086** | **TU (1σ)** | 0.086 | Ingrown $^3$He$_{trit.}$ 2.844850 x10$^{-15}$ cm$^3$STP |
| | | | | | %$^3$He$_{trit}$ 61.9 |

T database

Alternative tritium value: ± TU (1σ)   comment:

---

He Extraction No. **22990**   He Extraction Date 8/18/2006   He Measurement Date 8/29/2006

| $\delta^3$He: | **6.64** | ± 0.34 | % (1σ) | $\delta^3$He$_{cor}$ from other T (see above): | 6.636 | % | $\delta^3$He$_{uncor}$: | **6.85** | ± 0.34 | % (1σ) |
|---|---|---|---|---|---|---|---|---|---|---|
| $^3$He$_{trit}$: | **1.64** | ± 0.00 | TU (1σ) | he database | | | $^3$He: | 4.866 | x10$^{-14}$ cm$^3$ STP/g | |
| | | | | | | | Sample weight: 19.49 | g | | |

| $^4$He: | **3.297** | ± 0.004 | x10$^{-8}$ cm$^3$STP/g (1σ) | $\Delta^4$He: | -24.58 | % | Age Uncorrected ±1σ (y) |
|---|---|---|---|---|---|---|---|
| Ne: | **10.075** | ± 0.047 | x10$^{-8}$ cm$^3$STP/g (1σ) | $\Delta$Ne: | -42.47 | % | 14.9 ± 0.7 |

Average crustal terrigenic $^3$He/$^4$He ratio: 2 x10$^{-8}$:

| $\delta^3$He$_{cor}$: | **57.157** | % | | | Corrected for terrigenic He |
|---|---|---|---|---|---|
| $^3$He$_{cor}$: | **7.506** | TU | $^3$He$_{cor}$: 4.844 | x10$^{-14}$ cm$^3$STP/g | |
| $^4$He$_{cor}$: | **2.227** | x10$^{-8}$ cm$^3$STP/g | % Terrigenic $^4$He **32.4** | | Age ±1σ (y) |
| $^4$He$_{terrigenic}$: | **1.070** | x10$^{-8}$ cm$^3$STP/g | | | 34.7 ± 1.0 |

---

Site specific terrigenic $^3$He/$^4$He ratio: [ ]   Corrected for terrigenic He

| $\delta^3$He$_{cor}$ | 57.160 | % | $^3$He$_{cor}$ 4.844 | x10$^{-14}$ cm$^3$STP/g | Age ±1σ (y) |
|---|---|---|---|---|---|
| $^3$He$_{cor}$ | 7.506 | TU | | | ± |

constants: $\delta^3$He$_{equilibrium}$: -1.8 %; $\lambda_{3H}$= .05577 yr.$^{-1}$; $^3$He/$^4$He$_{atmos.}$= 1.384 x10$^{-6}$

| published comments | Terrigenic He, use corrected age |
|---|---|
| | Negative ΔHe and ΔNe indicates sample gas was stripped as the result of a sampling problem. Sample most likely fractionated. Do not use age. Tritium measurement looks OK. |

Comments: **RERUN 1/2 duplicate (a)**

# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

| report | Sender | Kroening | Organization | USGS | Program | FI-Kroening-1 |
|--------|--------|----------|--------------|------|---------|----------------|
| **r** | Sample ID | Monitoring Well 5R/H2078 | | | | |

| | Channel No. 1 | | Tritium Bottle No. | | Date received | |
|--|---------------|--|--------------------|--|---------------|--|
| Sample Date | 1/24/2006 | Sampling Time 1400 | Altitude 30.48 m | Temp. 25.1 °C | Salinity 0 | |

| T Degas No. **22604** | T Degas Date | T Measurement Date 6/7/2006 |
|---|---|---|

**Tritium:** 2.649 ± 0.110 **TU (1σ)** 0.110

$^4$He bulb blank 1.138 x10$^{-9}$ cm$^3$STP
Ingrown $^3$He$_{trit.}$ 5.193716 x10$^{-15}$ cm$^3$STP
%$^3$He$_{trit}$ 69.5

T database

Alternative tritium value: ± **TU (1σ)**

comment:

---

| He Extraction No. **22604** | He Extraction Date 2/23/2006 | He Measurement Date 7/27/2006 |
|---|---|---|

**δ$^3$He:** 2575.88 ± 0.31 % (1σ)   δ$^3$He$_{cor}$ from other 2575. %   δ$^3$He$_{uncor}$: ? ± 0.32 % (1σ)

T (see above):

**$^3$He$_{trit}$:** 4.98 ± 0.00 TU (1σ)

he database

$^3$He: 1.178 x10$^{-14}$ cm$^3$ STP/g
Sample weight: 39.43 g

| | | | | | |
|--|--|--|--|--|--|
| **$^4$He:** | 0.032 | ± 0.002 x10$^{-8}$ cm$^3$STP/g (1σ) | Δ$^4$He: -99.28 % | Age | Uncorrected ±1σ (y) |
| **Ne:** | 0.000 | ± 0.000 x10$^{-8}$ cm$^3$STP/g (1σ) | ΔNe: -100 % | | |

Average crustal terrigenic $^3$He/$^4$He ratio: 2 x10$^{-8}$:

| | | |
|--|--|--|
| δ$^3$He$_{cor}$: | -216.071 % | Corrected for terrigenic He |
| $^3$He$_{cor}$: | 9.125 TU | $^3$He$_{cor}$: 1.163 x10$^{-14}$ cm$^3$STP/g |
| $^4$He$_{cor}$: | -0.724 x10$^{-8}$ cm$^3$STP/g | % Terrigenic $^4$He 2375.7   Age ±1σ (y) |
| $^4$He$_{terrigenic}$: | 0.756 x10$^{-8}$ cm$^3$STP/g | |

---

Site specific terrigenic $^3$He/$^4$He ratio:

| | | |
|--|--|--|
| | | Corrected for terrigenic He |
| δ$^3$He$_{cor}$ -216.072 % | $^3$He$_{cor}$ 1.163 x10$^{-14}$ cm$^3$STP/g | Age ±1σ (y) |
| $^3$He$_{cor}$ 9.125 TU | | |

constants: δ$^3$He$_{equilibrium}$: -1.8 %; λ$_{3H}$= .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos}$= 1.384 x10$^{-6}$

| published comments | High pressure at branch, Sample pumped due to either high concentration of dissolved gases or sampling problem. |
|---|---|
| | Tritium measurement looks OK, $^4$He bulb blank slightly elevated |

Comments:

# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

| report | Sender | Kroening | Organization | USGS | Program | FI-Kroening-1 |
|---|---|---|---|---|---|---|
| **r** | Sample ID | Monitoring Well 5R/T1613 | | | | |

| | Channel No. | | Tritium Bottle No. | 1 | | Date received | |
|---|---|---|---|---|---|---|---|
| Sample Date | 1/24/2006 | Sampling Time | 1400 | Altitude | 30.48 m | Temp. 25.1 °C | Salinity 0 |

| T Degas No. | **1009909** | T Degas Date | 2/23/2006 | T Measurement Date | 6/7/2006 |
|---|---|---|---|---|---|

$^4$He bulb blank 6.265 x10$^{-9}$ cm$^3$STP
Ingrown $^3$He$_{trit.}$ 21.66812 x10$^{-15}$ cm$^3$STP
%$^3$He$_{trit}$ 60.0

**Tritium:** 3.011 ± 0.067 **TU (1σ)** 0.067

T database

Alternative tritium value: ± **TU (1σ)**

comment:

---

| He Extraction No. | | He Extraction Date | | He Measurement Date | |
|---|---|---|---|---|---|

**δ$^3$He:** ± % (1σ)    $^{δ3}$He$_{cor}$ from other T (see above):    %    **δ$^3$He$_{uncor}$:** ± % (1σ)

**$^3$He$_{trit}$:** ± TU (1σ)    [he database]    **$^3$He:** x10$^{-14}$ cm$^3$ STP/g

Sample weight: g

**$^4$He:** ± x10$^{-8}$ cm$^3$STP/g (1σ)    **Δ$^4$He:** %    **Age** Uncorrected ±1σ (y)

**Ne:** ± x10$^{-8}$ cm$^3$STP/g (1σ)    **ΔNe:** %

**Average crustal terrigenic $^3$He/$^4$He ratio: 2 x10$^{-8}$:**

Corrected for terrigenic He

**δ$^3$He$_{cor}$:** %

**$^3$He$_{cor}$:** TU      **$^3$He$_{cor}$:** x10$^{-14}$ cm$^3$STP/g

**$^4$He$_{cor}$:** x10$^{-8}$ cm$^3$STP/g    % Terrigenic $^4$He    **Age** ±1σ (y)

**$^4$He$_{terrigenic}$:** 0.000 x10$^{-8}$ cm$^3$STP/g

---

| Site specific terrigenic $^3$He/$^4$He ratio: | | Corrected for terrigenic He |
|---|---|---|

**δ$^3$He$_{cor}$** %      **$^3$He$_{cor}$** x10$^{-14}$ cm$^3$STP/g    **Age** ±1σ (y)

**$^3$He$_{cor}$** TU

constants: δ$^3$He$_{equilibrium}$: -1.8 %; λ$_{3H}$= .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos.}$ = 1.384 x10$^{-6}$

| published comments | Tritium data from bottle sample |
|---|---|
| | High $^4$He bulb blank |

Comments:

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# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

LDEO NGL

| report **r** | Sender | Kroening | Organization | USGS | Program | FI-Kroening-1 |
|---|---|---|---|---|---|---|

Sample ID  Monitoring Well 8R/H2070

| Channel No. 1 | Tritium Bottle No. | | Date received |
|---|---|---|---|

| Sample Date | 1/25/2006 | Sampling Time | 1045 | Altitude | 39.62 | m | Temp. | 25.09 | °C | Salinity | 0 |
|---|---|---|---|---|---|---|---|---|---|---|---|

---

| T Degas No. **22600** | T Degas Date | | T Measurement Date | 6/13/2006 |
|---|---|---|---|---|

**Tritium:** 1.547 ± 0.083 TU (1σ) 0.083

$^4$He bulb blank 0.457 x10$^{-9}$ cm$^3$STP
Ingrown $^3$He$_{trit.}$ 2.862540 x10$^{-15}$ cm$^3$STP
%$^3$He$_{trit}$ 77.6

[ T database ]

Alternative tritium value: ± TU (1σ)   comment:

---

| He Extraction No. **22600** | He Extraction Date  2/23/2006 | He Measurement Date  7/27/2006 |
|---|---|---|

$\delta^3$He: 0.64 ± 0.24 % (1σ)  $\delta^3$He$_{cor}$ from other .6443 %   $\delta^3$He$_{uncor}$: 0.66 ± 0.24 % (1σ)

T (see above):

$^3$He$_{trit}$: 0.68 ± 0.00 TU (1σ)   $^3$He: 9.834 x10$^{-14}$ cm$^3$ STP/g

[ he database ]   Sample weight: 39.42 g

| | | | | | |
|---|---|---|---|---|---|
| $^4$He: | 7.060 | ± 0.009 x10$^{-8}$ cm$^3$STP/g (1σ) | $\Delta^4$He: 60.8 % | **Age** | Uncorrected ±1σ (y) |
| Ne: | 27.399 | ± 0.133 x10$^{-8}$ cm$^3$STP/g (1σ) | $\Delta$Ne: 54.43 % | 6.5 | ± 0.3 |

Average crustal terrigenic $^3$He/$^4$He ratio: 2 x10$^{-8}$:

| | | | | |
|---|---|---|---|---|
| $\delta^3$He$_{cor}$: | -0.933 | % | | Corrected for terrigenic He |
| $^3$He$_{cor}$: | 0.055 | TU | $^3$He$_{cor}$: 9.836 x10$^{-14}$ cm$^3$STP/g | |
| $^4$He$_{cor}$: | 7.174 | x10$^{-8}$ cm$^3$STP/g | % Terrigenic $^4$He  -1.6 | **Age** ±1σ (y) |
| $^4$He$_{terrigenic}$: | -0.114 | x10$^{-8}$ cm$^3$STP/g | | 0.6 ± 0.0 |

---

Site specific terrigenic $^3$He/$^4$He ratio:

| | | | | |
|---|---|---|---|---|
| | | | | Corrected for terrigenic He |
| $\delta^3$He$_{cor}$ | -0.933 | % | $^3$He$_{cor}$  9.836  x10$^{-14}$ cm$^3$STP/g | **Age** ±1σ (y) |
| $^3$He$_{cor}$ | 0.055 | TU | | ± |

constants: $\delta^3$He$_{equilibrium}$: -1.8 %; $\lambda_{3H}$= .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos}$= 1.384 x10$^{-6}$

| published comments | Tritium measurement looks OK. |
|---|---|

| Comments: | |
|---|---|

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# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

| report | Sender | Kroening | Organization | USGS | Program | FI-Kroening-1 |
|---|---|---|---|---|---|---|
| **r** | Sample ID | Monitoring Well 8R/T1609 | | | | |

| | Channel No. | | Tritium Bottle No. | 1 | | Date received | |
|---|---|---|---|---|---|---|---|
| Sample Date | 1/25/2006 | Sampling Time | 1045 | Altitude | 39.62 m | Temp. 25.09 °C | Salinity 0 |

| T Degas No. | **1009905** | T Degas Date | 2/23/2006 | T Measurement Date | 6/7/2006 |
|---|---|---|---|---|---|

$^4$He bulb blank 2.193 x10$^{-9}$ cm$^3$STP

Ingrown $^3$He$_{trit.}$ 9.089390 x10$^{-15}$ cm$^3$STP

%$^3$He$_{trit}$ 66.5

**Tritium:** 1.549 ± 0.046 **TU (1σ)** 0.046

T database

Alternative tritium value: ± **TU (1σ)**

comment:

---

He Extraction No.　　　　　He Extraction Date　　　　　He Measurement Date

δ$^3$**He:** ± % (1σ)　δ$^3$He$_{cor}$ from other T (see above): %　δ$^3$He$_{uncor}$: ± % (1σ)

$^3$**He$_{trit}$:** ± TU (1σ)　he database　$^3$He: x10$^{-14}$ cm$^3$ STP/g

Sample weight: g

$^4$**He:** ± x10$^{-8}$ cm$^3$STP/g (1σ)　Δ$^4$He: %　Age　Uncorrected ±1σ (y)

**Ne:** ± x10$^{-8}$ cm$^3$STP/g (1σ)　ΔNe: %

**Average crustal terrigenic $^3$He/$^4$He ratio: 2 x10$^{-8}$:**

δ$^3$**He$_{cor}$:** %

Corrected for terrigenic He

$^3$**He$_{cor}$:** TU　$^3$He$_{cor}$: x10$^{-14}$cm$^3$STP/g

$^4$**He$_{cor}$:** x10$^{-8}$ cm$^3$STP/g　% Terrigenic $^4$He　Age ±1σ (y)

$^4$**He$_{terrigenic}$:** 0.000 x10$^{-8}$ cm$^3$STP/g

**Site specific terrigenic $^3$He/$^4$He ratio:**

Corrected for terrigenic He

δ$^3$**He$_{cor}$** %　$^3$He$_{cor}$ x10$^{-14}$cm$^3$STP/g　Age ±1σ (y)

$^3$**He$_{cor}$** TU

constants: δ$^3$He$_{equilibrium}$: -1.8 %; $\lambda_{3H}$= .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos.}$= 1.384 x10$^{-6}$

| published comments | Tritium data from bottle sample |
|---|---|
| | Tritium measurement looks OK, $^4$He bulb blank elevated |

Comments:

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# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

| report **r** | Sender | Kroening | Organization USGS | | Program | FI-Kroening-1 |
|---|---|---|---|---|---|---|

Sample ID: Phipps Well/H2064

| Channel No. 1 | Tritium Bottle No. | | | Date received | |
|---|---|---|---|---|---|

| Sample Date 1/24/2006 | Sampling Time 1150 | Altitude 38.1 m | Temp. 25.07 °C | Salinity 0 |
|---|---|---|---|---|

---

| T Degas No. **22597** | T Degas Date | T Measurement Date 6/13/2006 |
|---|---|---|

**Tritium:** 1.795 ± 0.091 TU (1σ) 0.091

$^4$He bulb blank 0.736 x10$^{-9}$ cm$^3$STP
Ingrown $^3$He$_{trit.}$ 3.615742 x10$^{-15}$ cm$^3$STP
%$^3$He$_{trit}$ 71.6

T database

Alternative tritium value: ± TU (1σ)      comment:

---

| He Extraction No. **22597** | He Extraction Date 2/23/2006 | He Measurement Date 7/26/2006 |
|---|---|---|

$\delta^3$He: 5733.40 ± 0.28 % (1σ)  $\delta^3$He$_{cor}$ from other 5733. %  $\delta^3$He$_{uncor}$: ? ± 0.28 % (1σ)
T (see above):

$^3$He$_{trit}$: 4.98 ± 0.00 TU (1σ)      $^3$He: 1.151 x10$^{-14}$ cm$^3$ STP/g

he database      Sample weight: 39.41 g

$^4$He: 0.014 ± 0.000 x10$^{-8}$ cm$^3$STP/g (1σ)   $\Delta^4$He: -99.68 %   Age  Uncorrected ±1σ (y)

Ne: 0.000 ± 0.000 x10$^{-8}$ cm$^3$STP/g (1σ)   $\Delta$Ne: -100 %

---

Average crustal terrigenic $^3$He/$^4$He ratio: 2 x10$^{-8}$:

$\delta^3$He$_{cor}$: -213.469 %

$^3$He$_{cor}$: 9.021 TU      $^3$He$_{cor}$: 1.137 x10$^{-14}$ cm$^3$STP/g

$^4$He$_{cor}$: -0.724 x10$^{-8}$ cm$^3$STP/g   % Terrigenic $^4$He 5174.8

$^4$He$_{terrigenic}$: 0.738 x10$^{-8}$ cm$^3$STP/g

Corrected for terrigenic He   Age ±1σ (y)

---

Site specific terrigenic $^3$He/$^4$He ratio:

$\delta^3$He$_{cor}$ -213.475 %

$^3$He$_{cor}$ 9.021 TU      $^3$He$_{cor}$ 1.137 x10$^{-14}$ cm$^3$STP/g

Corrected for terrigenic He   Age ±1σ (y)

---

constants: $\delta^3$He$_{equilibrium}$: -1.8 %; $\lambda_{3H}$= .05577 yr.$^{-1}$; $^3$He/$^4$He$_{atmos.}$= 1.384 x10$^{-6}$

published comments: High pressure at branch, Sample pumped due to either high concentration of dissolved gases or sampling problem. Tritium measurement looks OK,

Comments:

# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

| report | Sender | Kroening | Organization | USGS | Program | FI-Kroening-1 |
|---|---|---|---|---|---|---|
| **r** | Sample ID | Phipps Well/H2065 | | | | |

| | Channel No. | 2 | Tritium Bottle No. | | Date received | |
|---|---|---|---|---|---|---|
| Sample Date | 1/24/2006 | Sampling Time | 1150 | Altitude | 38.1 m | Temp. 25.07 °C | Salinity 0 |

| T Degas No. | T Degas Date | T Measurement Date |
|---|---|---|

**Tritium:** ± **TU (1σ)**

$^4$He bulb blank 0.688 x$10^{-9}$ cm$^3$STP
Ingrown $^3$He$_{trit.}$ .9551145 x$10^{-15}$ cm$^3$STP
%$^3$He$_{trit}$ -0.5

T database

Alternative tritium value: ± **TU (1σ)**   comment:

| He Extraction No. | He Extraction Date 9/19/2006 | He Measurement Date |
|---|---|---|

**δ$^3$He:** ± % (1σ)   δ$^3$He$_{cor}$ from other T (see above): %   δ$^3$He$_{uncor}$: -13.68 ± 2.48 % (1σ)

**$^3$He$_{trit}$:** ± TU (1σ)   [he database]   $^3$He: x$10^{-14}$ cm$^3$ STP/g

Sample weight: 39.35 g

| | | | | Uncorrected |
|---|---|---|---|---|
| **$^4$He:** | 0.004 ± 0.000 x$10^{-8}$ cm$^3$STP/g (1σ) | **Δ$^4$He:** -99.91 % | Age | ±1σ (y) |
| **Ne:** | 0.000 ± 0.000 x$10^{-8}$ cm$^3$STP/g (1σ) | **ΔNe:** -100 % | | |

Average crustal terrigenic $^3$He/$^4$He ratio: 2 x$10^{-8}$:

**δ$^3$He$_{cor}$:** %

**$^3$He$_{cor}$:** TU       $^3$He$_{cor}$: x$10^{-14}$ cm$^3$STP/g

|  | | | | Corrected for terrigenic He |
|---|---|---|---|---|
| **$^4$He$_{cor}$:** | -0.724 x$10^{-8}$ cm$^3$STP/g | % Terrigenic $^4$He | 18616.9 | |
| **$^4$He$_{terrigenic}$:** | 0.728 x$10^{-8}$ cm$^3$STP/g | | | Age ±1σ (y) |

Site specific terrigenic $^3$He/$^4$He ratio: [ ]     Corrected for terrigenic He

**δ$^3$He$_{cor}$** %       $^3$He$_{cor}$ x$10^{-14}$ cm$^3$STP/g   Age ±1σ (y)

**$^3$He$_{cor}$** TU

constants: δ$^3$He$_{equilibrium}$: -1.8 %; λ$_{3H}$= .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos}$= 1.384 x$10^{-6}$

| published comments | High pressure at branch, Sample pumped due to either high concentration of dissolved gases or sampling problem. Tritium measurement looks OK, No more sample. |
|---|---|

| Comments: | |
|---|---|

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# Noble Gas Laboratory
# Lamont-Doherty Earth Observatory
# Columbia University, New York

| report | Sender | Kroening | Organization | USGS | Program | Fl-Kroening-1 |
|---|---|---|---|---|---|---|
| **r** | Sample ID | Toll Plaza Well/H2068 | | | | |

| | Channel No. 1 | | Tritium Bottle No. | | | Date received | |
|---|---|---|---|---|---|---|---|

| Sample Date | 1/24/2006 | Sampling Time | 1000 | Altitude | 45.7 | m | Temp. | 23.10 | °C | Salinity | 0 |
|---|---|---|---|---|---|---|---|---|---|---|---|

---

| T Degas No. | **22599** | T Degas Date | | T Measurement Date | 6/8/2006 |
|---|---|---|---|---|---|

$^4$He bulb blank 0.530 x$10^{-9}$ cm$^3$STP
Ingrown $^3$He$_{trit.}$ .8473053 x$10^{-15}$ cm$^3$STP
%$^3$He$_{trit}$ 12.5

**Tritium:** 0.078 ± 0.074 **TU (1σ)** 0.074

T database

Alternative tritium value: ± **TU (1σ)**

comment:

---

| He Extraction No. **22599** | He Extraction Date 2/23/2006 | He Measurement Date 7/26/2006 |
|---|---|---|

$\delta^3$He: 72.94 ± 0.28 % (1σ) $\delta^3$He$_{cor}$ from other 72.93 % $\delta^3$He$_{uncor}$: 72.94 ± 0.28 % (1σ)
T (see above):

$^3$He$_{trit}$: 4.43 ± 0.00 TU (1σ) $^3$He: 2.359 x$10^{-14}$ cm$^3$ STP/g

he database

Sample weight: 39.4 g

$^4$He: 0.986 ± 0.002 x$10^{-8}$ cm$^3$STP/g (1σ) $\Delta^4$He: -77.66 %

$Ne$: 4.272 ± 0.006 x$10^{-8}$ cm$^3$STP/g (1σ) $\Delta Ne$: -76.25 %

Age Uncorrected ±1σ (y)

**Average crustal terrigenic $^3$He/$^4$He ratio: 2 x$10^{-8}$:**

$\delta^3$He$_{cor}$: 269.544 %

$^3$He$_{cor}$: 7.312 TU $^3$He$_{cor}$: 2.348 x$10^{-14}$cm$^3$STP/g

$^4$He$_{cor}$: 0.459 x$10^{-8}$ cm$^3$STP/g % Terrigenic $^4$He 53.4

$^4$He$_{terrigenic}$: 0.526 x$10^{-8}$ cm$^3$STP/g

Corrected for terrigenic He

Age ±1σ (y)

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Site specific terrigenic $^3$He/$^4$He ratio:

Corrected for terrigenic He

$\delta^3$He$_{cor}$ 269.548 % $^3$He$_{cor}$ 2.348 x$10^{-14}$cm$^3$STP/g Age ±1σ (y)

$^3$He$_{cor}$ 7.312 TU

constants: $\delta^3$He$_{equilibrium}$: -1.8 %; $\lambda_{3H}$= .05577yr.$^{-1}$; $^3$He/$^4$He$_{atmos.}$= 1.384 x$10^{-6}$

**published comments**
High He pressure, pumped at MS, L-DEO problem.

Negative ΔHe and ΔNe indicates sample gas was stripped as the result of a sampling problem. Sample most likely fractionated. Do not use age. Tritium measurement looks OK.

**Comments:**