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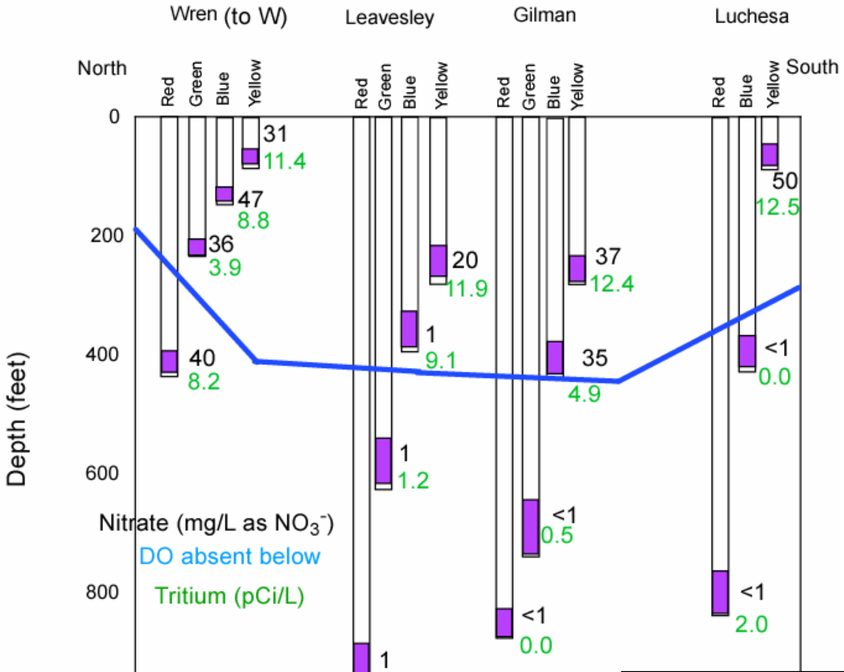
California GAMA Program: Sources and transport of nitrate in shallow groundwater in the Llagas Basin of Santa Clara County, California



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Sources and transport of nitrate in shallow groundwater in the Llagas Basin of Santa Clara County, California

Executive Summary

A critical component of the State Water Resource Control Board's Groundwater Ambient Monitoring and Assessment (GAMA) Program is to assess the major threats to groundwater resources that supply drinking water to Californians (Belitz et al., 2004). Nitrate is the most pervasive and intractable contaminant in California groundwater and is the focus of special studies under the GAMA program. This report presents results of a study of nitrate contamination in the aquifer beneath the cities of Morgan Hill and Gilroy, CA, in the Llagas Subbasin of Santa Clara County, where high nitrate levels affect several hundred private domestic wells.

The main objectives of the study are: 1) to identify the main source(s) of nitrate that issue a flux to the shallow regional aquifer 2) to determine whether denitrification plays a role in the fate of nitrate in the subbasin and 3) to assess the impact that a nitrate management plan implemented by the local water agency has had on the flux of nitrate to the regional aquifer. Analyses of 56 well water samples for major anions and cations, nitrogen and oxygen isotopes of nitrate, dissolved excess nitrogen, tritium and groundwater age, and trace organic compounds, show that synthetic fertilizer is the most likely source of nitrate in highly contaminated wells, and that denitrification is not a significant process in the fate of nitrate in the subbasin except in the area of recycled water application. In addition to identifying contaminant sources, these methods offer a deeper understanding of how the severity and extent of contamination are affected by hydrogeology and groundwater management practices. In the Llagas subbasin, the nitrate problem is amplified in the shallow aquifer because it is highly vulnerable with high vertical recharge rates and rapid lateral transport, but the deeper aquifers are relatively more protected by laterally extensive aquitards. Artificial recharge delivers low-nitrate water and provides a means of long-term remediation. Examination of nitrate concentration in relation to groundwater age indicates that the nitrate management plan has not yet resulted in a decrease in the flux of nitrate to the shallow aquifer in the areas tested.

Introduction and Background

Nitrate contamination of California drinking water supplies is pervasive– about 10% of California public drinking water supply wells produce water that exceeds the regulatory drinking water limit, and a much larger fraction produce water which approaches the limit (CA DHS, 2004). Nitrate contamination of groundwater is a growing concern for drinking water supplies not just in California, but also in many areas in the United States. Between 1993 and 2000, the U.S. Geological Survey's National Water-Quality Assessment program found that 9% of domestic supply wells and 2% of public supply wells exceeded the Environmental Protection Agency's maximum contaminant level (MCL) for drinking water of 45 mg NO_3 L^{-1} (10 mg L^{-1} as N) (Nolan et al., 2002). The human activities that contribute nitrate to groundwater – animal operations, crop fertilization, wastewater treatment discharge, septic systems – are ongoing and essential to the industry and commerce of the State of California. Best management practices can mitigate source loading but not eliminate it. Furthermore, nitrate is expensive to remove from drinking water supplies, especially in public and private systems that rely on untreated groundwater and do not have the necessary water treatment infrastructure. These factors combine to make nitrate the greatest contaminant threat to California's drinking water supply.

The ultimate goal of the *Groundwater Quality Monitoring Act of 2001* (AB599) is the implementation of a comprehensive monitoring program to allow groundwater basin assessment. Assessment is a broad term, but encompasses assessing susceptibility of groundwater to contamination, characterizing current water quality in a basin, and predicting future water quality under different conditions. Because of the potential threat that nitrate poses to drinking water supplies, special studies are focused on basin-scale nitrate contamination. To meet these goals, basin assessment must consider the current inventory of nitrate in basin soils and waters, current and past source loading, groundwater recharge and transport, and nitrogen cycling in the soil, vadose and saturated zone. Nitrate occurs naturally, has relatively low-intensity point, distributed and nonpoint sources, and has a long history of introduction into the environment. Surface nitrogen loading has dramatically increased in the last 50 years, making groundwater ages a useful approach to assessing historical inputs and to determining the effectiveness of relatively recently implemented nitrate management plans.

This study focuses on the aquifers beneath the cities of Morgan Hill and Gilroy, CA, in the Llagas Subbasin of the Gilroy-Hollister Groundwater Basin, where high nitrate levels affect several hundred wells (figure 1). Deep, high capacity public drinking water wells have lower, but rising nitrate concentrations. This is a serious water supply problem because the region relies exclusively on groundwater for its drinking water, and at least 19 public supply wells are in the contaminated portion of this basin, although none has as yet had an MCL exceedence. In a study carried out by the local water agency, over 600 private domestic wells were tested for nitrate concentration, and more than 300 had MCL exceedences (SCVWD, 1998). A previous GAMA California Aquifer Susceptibility study in which public drinking water wells from Morgan Hill and Gilroy were tested for vulnerability parameters concluded that several wells in Gilroy are highly vulnerable to contamination based on observed young groundwater ages (Moran et al., 2004). The same study showed that wells screened exclusively in the deeper aquifers are much less vulnerable to contamination.

The main objectives of this study are: 1) to identify the main source(s) of nitrate that issue a flux to the shallow regional aquifer 2) to determine whether denitrification plays a role in the fate of nitrate in the subbasin and 3) to assess the impact that a nitrate management plan, implemented by the local water agency, has had on the flux of nitrate to the regional aquifer. Application of multiple analytical and isotopic techniques highlights the value of an integrated, multi-faceted approach. In addition, the degree of vertical transport of nitrate to deeper drinking water aquifers, as well as the potential for mobilizing accumulated nitrate during artificial recharge is evaluated. The latter two topics are relevant for evaluating two possible remediation strategies – pumping and treating groundwater from shallow zones before it is transported to deeper zones, and increased artificial recharge of low-nitrate water.

Many studies have used ^{15}N and ^{18}O in nitrate as tracers for the source and fate of nitrate contamination (Choi et al., 2003). Because of the overlap of source isotope values and the variety of potential fractionation processes that affect nitrate, isotopes alone are not always sufficient to provide conclusive evidence of the contamination source (Choi et al., 2003 and Bohlke and Denver, 1995). A successful investigation of nitrate behavior and distribution must take into account the many environmental and historical factors that affect nitrate fate and transport. These include local hydrogeology, changing land use practices, and variable conditions that support an array of natural nitrogen cycling reactions (Kendall and Aravena, 2000). Combining the results of these techniques allows an understanding of nitrate contamination in a larger context and facilitates development of effective management strategies.

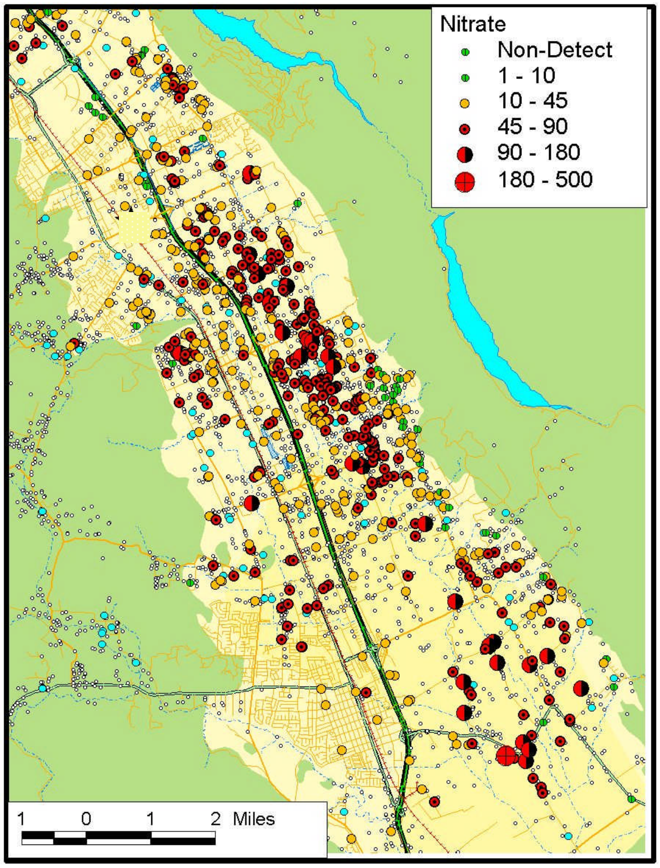

Figure 1 (courtesy of SCVWD). Maximum nitrate concentrations (mg/L as NO_3^-) observed in wells in the Llagas Basin.

This study demonstrates the application of an integrated analytical approach in a nitrate-impacted groundwater basin. Interpretation of nitrate ^{15}N and ^{18}O data to identify contamination sources is enhanced through the use of additional isotopic and chemical tracers. We use well water major ion analyses to delineate the scope of the high nitrate region, and use historical data, collected for nitrate monitoring purposes, to track concentration changes through time. Stable isotopes of water provide information about groundwater sources, and residence time methods using tritium and noble gas measurements further constrain the source history. Possible reactions of nitrate are accounted for by analysis of dissolved gases, which can indicate whether saturated-zone denitrification has taken place. The methods used here could be widely applied in the many groundwater basins where urbanization has created a greater demand for drinking water, and where decades of agricultural activity have left a potential source of nitrate to groundwater.

Site Description and Land Use History

The groundwater basins of the Santa Clara Valley lie in an alluvial trough between the Santa Cruz Mountains on the west and the Diablo range to the east (figure 2a). The Santa Clara Valley Basin fills the southern end of the structural trough containing San Francisco Bay. South of the main subbasin, the Santa Clara Valley Basin narrows through Coyote Valley, then splays to the south with alluvial fan material from Coyote Creek to form the Llagas subbasin, part of the Gilroy-Hollister Valley Basin. Other major sources of alluvial fill material are from Llagas Creek and Uvas Creek off of the Santa Cruz Mountains to the west. Alluvial sediments are more than 1000 feet thick in the southern portion of the subbasin. The northern portion of the Llagas basin and the elevated lateral edges constitute the forebay, with unconfined conditions, recharge from subsurface inflow, percolation through streams, rainfall and irrigation returns, and flow toward the south-southeast, where the basin flattens out. Confining conditions begin at approximately Rucker Avenue (figure 2a), where upper and lower aquifer zones are separated by a major, laterally continuous aquitard that occurs at depths of 20 to 100 feet. The water-bearing materials in the subbasin consist of Pliocene to Holocene age unconsolidated to semi-consolidated alluvial deposits (CDWR, 1981). Discharge takes place at the Pajaro River to the south, and through pumping (CDWR, 1981).

The basin is managed for conjunctive use by the Santa Clara Valley Water District (SCVWD). Approximately 55,000 acre-ft is drawn for public water supply and irrigation from the Llagas and Coyote subbasins (SCVWD Groundwater Management Plan, 2002), with the majority comingfrom the Llagas subbasin. Artificial recharge includes controlled in-stream recharge during the dry season, and off-stream recharge in ponds that are either continuously recharged, or in ponds that are periodically dried. Beginning in 1983, water delivered to the recharge ponds has come from the San Luis Reservoir, which receives water from the Sacramento-San Joaquin Delta. Artificial recharge is therefore a combination of water imported from outside the study area, and locally-captured water. Natural recharge from rainfall (average annual rainfall in San Jose is 14.5 inches) and runoff occurs throughout the basin, and sources of non-natural uncontrolled recharge include leakage from pipelines, seepage through the boundaries of the groundwater basin, and net irrigation return flows.

Land use in the study area is approximately 40% agricultural, 25% urban, 20% rural residential, 5% open space and parks, and the remaining 10% of mixed use (1995 Santa Clara County General Plan). A gradual retiring of agricultural land to suburban housing has taken place over the past 30 years. In rural residential areas, nearly every parcel has a septic tank for wastewater treatment, and a previous study (SCVWD, 1994) estimated potential nitrate loading from septic tanks at 53 to 151 thousand pounds per year over the study area (Table 1). The other sources considered in the study were agricultural lands fertilized by commercial N-fertilizer (227 thousand pd/yr), agricultural lands fertilized by cattle manure (8 to 30 thousand pd/yr), rainwater (14 thousand pd/yr), 4 existing dairies (4.6 to 6.9 thousand pd/yr), 20,000 to 50,000 cattle, including some small feed lots of up to 200 cattle (162 to 538 thousand pd/yr assuming no waste management), 4 egg farms (one with 230,000 chickens; 90 to 151 thousand pd/yr assuming no waste management), wastewater from three food packaging operations (3.5 to 5.2 thousand pd/yr), process wastewater from 2 wineries, wastewater from a cogeneration facility that converts agricultural waste into electrical energy, a sewage treatment facility (2.1 to 3.1 thousand pd/yr), and 602 acres of greenhouse operations (11 to 54 thousand pd/yr). Several of the potential sources have decreased in number or extent in the study area over the past few decades. For example, before about 1970 several large feedlots with more than 2000 cattle existed in the area, and the number of dairies has likewise decreased from more than 20 to 4 since the 1960's. The study concludes that the two main sources are likely septic discharges and inorganic fertilizer from agricultural lands. Nursery crops, the highest cash crop produced in the area, and greenhouse operations are considered potentially large and growing contributors.

Table 1. Estimated potential nitrogen loadings to groundwater (SCVWD, 1996)

Source	Total Potential N Loading (thousands of pounds per yr)
Septic Tanks	53-151
Agricultural Lands Fertilized by Commercial N fertilizer	227
Agricultural Lands Fertilized by Manure	8.1-26.9
Rainwater	14
Dairies	4.6-6.9
Cattle Feed Lots	162-538*
Egg Farms	90-151
Food Packaging Operations	3.5-5.2
Cogeneration Facility	2.2-3.3
Sewage Treatment Facilities and disposal pits	2.1-3.8
Greenhouse Operations	11-54

* assuming no nitrate waste management

In 1997, SCVWD began implementation of a Nitrate Management Program based on a study of nitrate contamination in shallow groundwater that included an assessment of potential sources of nitrate (SCVWD, 1996). One of the main elements of the program consists of assisting growers in evaluating and adopting the use of in-field nitrate testing and N management planning to improve fertilizer use efficiency and profitability. Routine field monitoring and comparative trials utilizing in-field soil and petiole testing is carried out to confirm the utility of in-field soil nitrate testing for N-fertilizer scheduling on crops with sprinkler or drip irrigation. Also, an evaluation of whether in-field quick soil and petiole testing could allow reduced fertilizer application for crops on drip systems for warm season crops like peppers was carried out at individual fields. In addition, educational resources and on-site soil and water testing are made available through use of a mobile lab, test kits are distributed to growers, and educational seminars are carried out at local schools and agricultural extension venues. The efficacy of the program in reducing nitrate flux to groundwater has not been assessed. Many of the activities associated with the program began in earnest in 2000, only four years before the time of sampling for this study.

METHODS

Sample Collection

The fifty-six well sampling locations are shown in Figure 2b and described in Table 2a. At SCVWD and South County Regional Wastewater Authority (SCRWA) monitoring wells, samples were taken using a portable submersible pump. At private domestic wells and City of Gilroy monitoring wells, dedicated well pumps were used. Most ion and isotope samples were filtered in the field with a 0.45µm in-line filter. Nitrate isotope samples were loaded onto anion exchange columns within 24 hours of sampling at LLNL, and ion analyses were performed within 48 hours of sampling. For excess nitrogen analyses, dissolved gases (nitrogen, oxygen, and argon) were collected in 40-mL vials (VWR TraceClean^{TM}, amber borosilicate; 0.125-inch septum liner) with no headspace. Samples were stored in coolers on ice and analyzed within 24 hours of sampling. A 1-L Pyrex bottle with a polypropylene plug seal cap was filled for tritium analysis and a 30-mL clear, French-square type glass bottle with a Qorpak^{TM} polyseal-lined cap was filled for analysis of stable isotopes O and H in water. Approximately 10 mL of groundwater was collected in copper tubes pinched by metal clamps for noble gas samples.

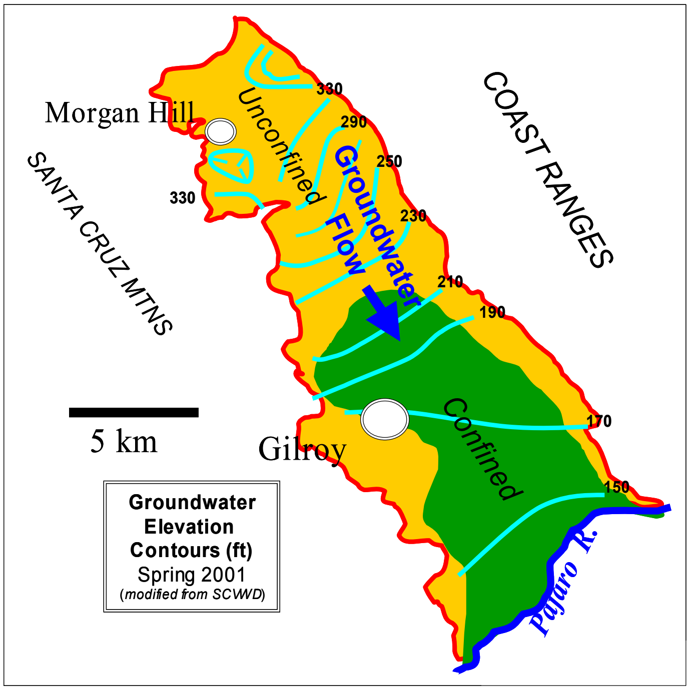

Figure 2a. Map of the Llagas subbasin showing subbasin boundaries, major geographic features and groundwater elevation contours for Spring, 2001 (after SCVWD).

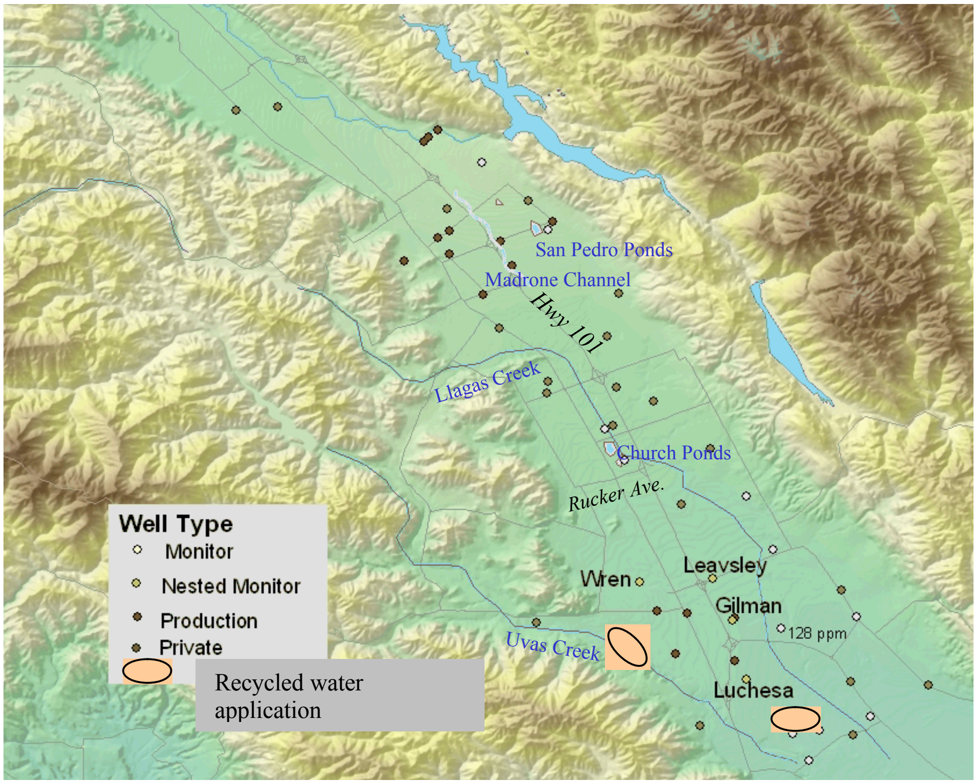

Figure 2b. Map showing wells sampled for the study. Named wells and recharge areas are referred to in the text.

Laboratory Methods

Nitrate isotope samples were analyzed at the Environmental Isotopes Lab at the University of Waterloo, all other analyses were performed at LLNL. After extraction as silver nitrate, nitrogen gas for the measurement of $\delta^{15}N$ was produced by the sealed tube Cu/copper oxide method (Kendall and Grim, 1990; Flatt and Heemskerk, 1997) and CO_2 for measurement of $\delta^{18}O$ was produced by combustion with graphite. The isotope ratios of these gases were measured on a PRISM isotope ratio mass spectrometer. $\delta^{15}N$ results are reported as per mil relative to AIR and $\delta^{18}O$ results are referenced to VSMOW. Anions and cations were measured by ion chromatography on a Dionex IC DX-600 with a precision of ±2.7% relative standard deviation for nitrate. Oxygen isotopes of water were measured on a VG PRISM isotope ratio mass spectrometer. Results are reported as per mil with reference to VSMOW and have a precision of ±0.1‰. Deuterium was measured on the VG PRISM after extraction of hydrogen by the zinc reduction technique. Results are reported as per mil with reference to VSMOW and have a precision of ±0.9‰. Dissolved gases for examination of excess nitrogen were measured by membrane inlet mass spectrometry (MIMS) with an SRS RGA200 quadrupole mass spectrometer (Kana et al., 1994). ^3He and ^4He were measured on a VG5400 mass spectrometer, Ar was measured using a high-sensitivity capacitive manometer, and Ne, Kr, and Xe were measured on an SRS RGA200 quadrupole mass spectrometer. Tritium was determined by measuring the rate of ^3He accumulation. Residence time calculations were made by combining measurements of tritium with measurements of its decay product, ^3He, and excess air was determined from measured Ne concentrations. In this calculation, noble gas data was used to separate tritiogenic helium from that from other sources (Ekwurzel, 2004).

Isotope and Dissolved Gas Techniques

A variety of nitrate fractionation processes lead to unique isotopic signatures for different nitrate sources. As a result, isotope values of nitrogen and oxygen can be useful in identifying the origin of groundwater nitrate (figure 3). Synthetic fertilizers generally have $\delta^{15}N$ values between –2‰ and +4‰ (Kendall et al., 1998). By the time it reaches the groundwater, however, fertilizer nitrogen tends to be enriched by several per mil over the original source, often making it indistinguishable from soil organic nitrogen, which tends to have $\delta^{15}N$ values of +3‰ to +8‰ (Bohlke and Denver, 1995). Due to volatile loss of ammonia from manure, nitrate from animal waste has higher $\delta^{15}N$ values, usually greater than +10‰, and so can often be distinguished from other sources. All animals produce waste with similar $\delta^{15}N$ values, though, so isotopes alone are usually not useful in differentiating between septic waste and other animal wastes (Kendall, 1998; Choi et al., 2003).

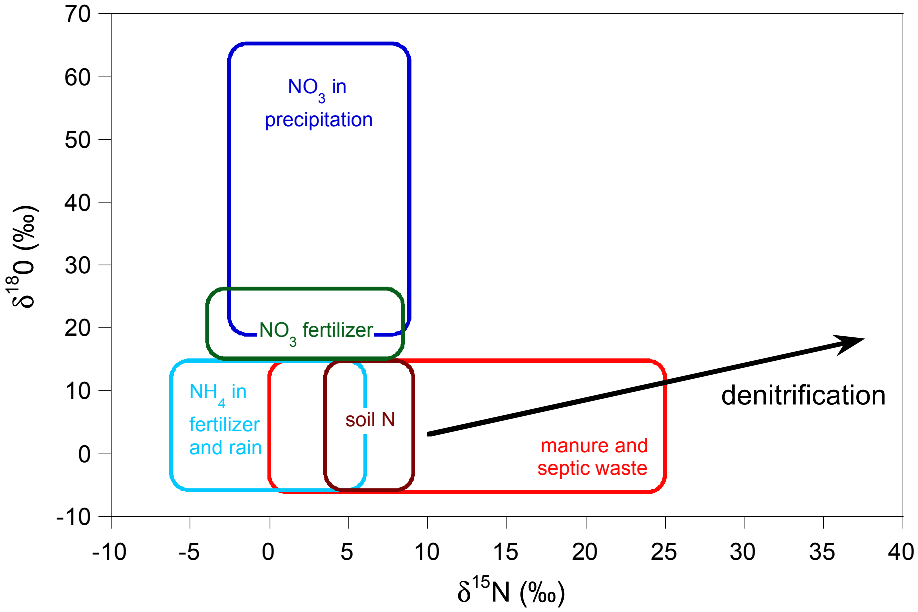

Figure 3: Isotopic composition of nitrogen and oxygen in nitrate from different sources (after Kendall, 1998).

Oxygen isotope values of nitrate can help clarify source identification, especially to separate nitrate fertilizer input from other sources, which produce nitrate by nitrification of ammonium or organic nitrogen. The $\delta^{18}O$ in nitrate fertilizers has a value close to the atmospheric value of +23‰. Other sources of nitrate incorporate two oxygen atoms from water and one from dissolved oxygen gas, leading to lighter $\delta^{18}O$ values dependent on the oxygen isotopes in the water (Kendall and Aravena, 2000). Nitrate from ammonium nitrate fertilizers will have $\delta^{18}O$ values that reflect both processes (Aravena et al., 1993).

Nitrate isotope data are also valuable as indicators of the occurrence of denitrification; as denitrification occurs, nitrogen and oxygen in nitrate are enriched in a characteristic 2:1 ratio (Kendall, 1998). Saturated zone denitrification can also be identified by the presence of its end product, excess nitrogen, dissolved in groundwater. Atmospheric nitrogen is distinguished from excess nitrogen by comparison with dissolved argon, the dominant source of which is atmospheric (Kana et al., 1994; Vogel et al., 1981). We employ both methods to check for possible denitrification.

Geochemical Modeling

Geochemical modeling, using the U.S. Geological Survey's PHREEQC geochemical model (Parkhurst and Appelo, 2002), was used to identify and explain trends in the water quality parameters (major cations, anions, and pH) that correlated with nitrate concentrations and other sample attributes to assist in identifying source signatures. PHREEQC's inverse geochemical modeling capability was utilized to understand the role of carbonate mineral equilibration (calcite, dolomite) in buffering water chemistry in response to possible acidification reactions involving oxidation of NH_3 and/or associated organic material as part of a putative nitrate source loading model.

RESULTS AND DISCUSSION

Nitrate occurs at high concentrations in shallow-screened wells

Historically, nitrate contamination is greatest in wells east of Highway 101, in the central and southern portions of the subbasin, where a large fraction of the wells have had concentrations above the MCL (figure 1). In data collected for this study (Table 2a,b,c), concentrations higher than expected for pre-development levels occur across the subbasin but the highest concentrations are recorded in the southeastern portion of the study area. The origin of the contamination is not clear from concentration patterns, and some of the highest concentrations recorded during the study are in the confined portion of the basin, not in the recharge areas to the north. Current and historical data consistently record higher nitrate concentrations in shallow monitoring and domestic wells than in deep wells. This is illustrated in figure 4, in which wells with top perforations above 250 ft may have high or low nitrate concentrations, but wells with top perforations deeper than about 250 ft have near-zero nitrate concentrations (with one exception at the deep Wren well).

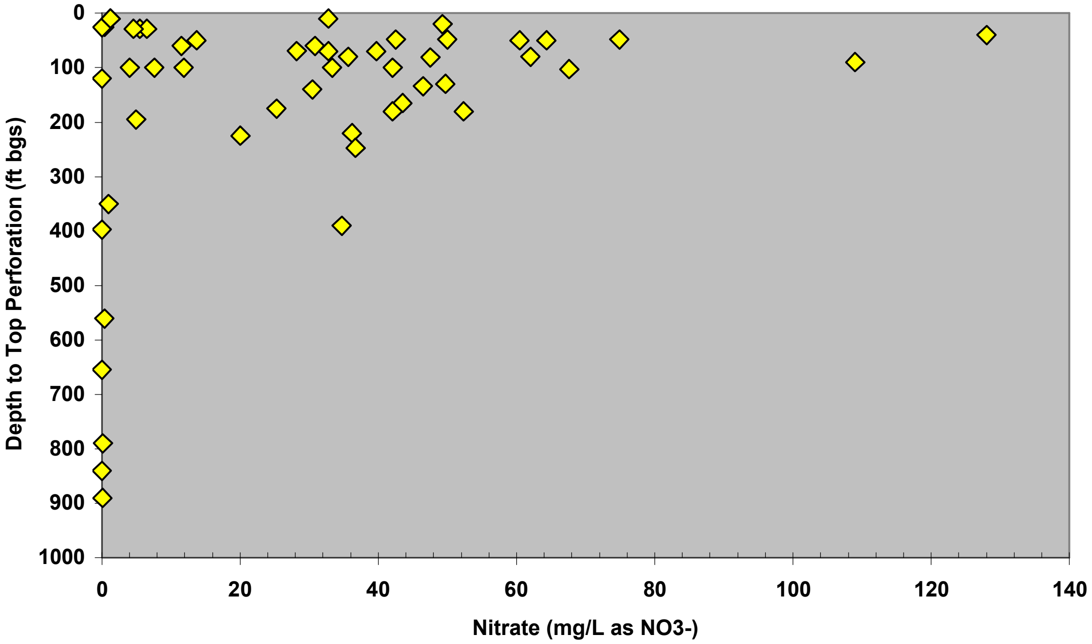

Figure 4. Nitrate concentrations measured in wells from figure 2b versus depth to top perforation show that anthropogenic nitrate does not occur in the deep aquifer.

Several geochemical parameters (dissolved oxygen, tritium, and some major ions) in addition to nitrate exhibit vertical stratification, which is most clearly observed in the nested monitoring wells in Gilroy (figure 5). The four sets of nested monitoring wells owned by the City of Gilroy are particularly useful - they allow examination of parameters' spatial patterns in 3 dimensions and are located in contaminated areas. Chemically stratified groundwater could be the result of a transition to reducing conditions at depth, in which case denitrification could potentially account for the observed drop in nitrate concentrations. As illustrated in figure 5, dissolved oxygen concentrations drop off sharply below about 400 ft in the center of the subbasin and below about 200 ft on the basin margins. Similarly, however, tritium concentrations abruptly decrease to less than 1 pCi/L at the same depths. (An exception occurs at the Wren site where young, nitrate-laden water is found at 400 ft.) The transition from high nitrate to low nitrate groundwater could therefore be due to hydrogeologic factors; i.e., the presence of laterally extensive aquitards with recently recharged, nitrate contaminated groundwater above, physically isolated from old, 'pristine' groundwater below. In the latter case, the time scale for recharge to the deep aquifer, and the heterogeneity of the aquifer system become important factors for predicting the fate and transport of nitrate on a basin scale.

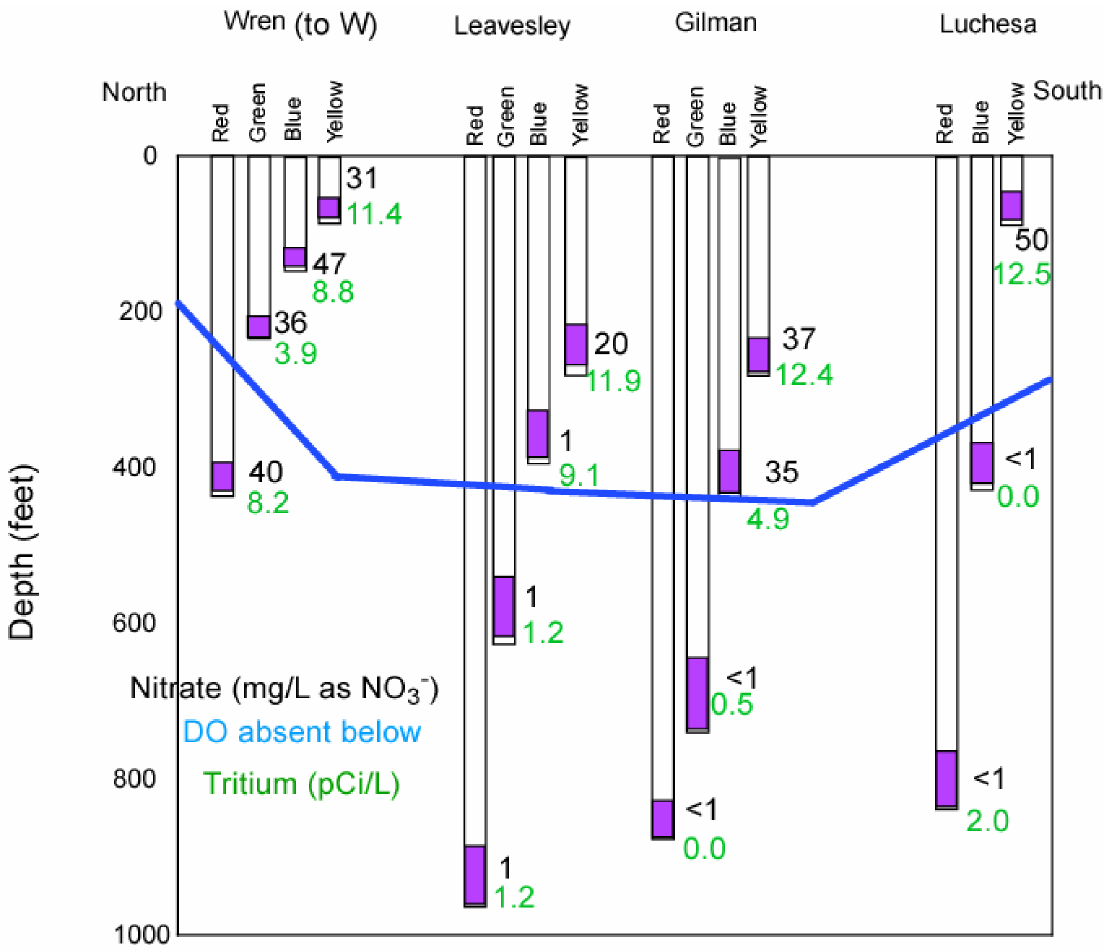

Figure 5. Schematic cross section showing screened intervals (in purple) of nested monitoring wells in Gilroy. Groundwater is stratified with respect to nitrate, tritium, and dissolved oxygen (blue line signifies depth below which dissolved oxygen is near-zero).

CO_2 partial pressure values (P_{CO2}) were estimated using PHREEQC from pH and major ion concentration measurements (the quantity of HCO_3^- in each water sample was not directly measured but was inferred by charge balance). Elevated P_{CO2} would be expected in association with vegetation occurring in recharge areas (as a result of microbial respiration in the root zone) or, in particular, from mineralization of organic carbon associated with manure and/or septic discharge. The distribution of calculated P_{CO2} values suggests a significant fall-off with depth (Figure 6), with the highest values generally occurring in the southeast portion of the subbasin where well screens are generally the shallowest. However, a clearly discernable trend between nitrate concentrations and P_{CO2} is absent (Figure 7). As such, the calculated P_{CO2} values probably do not support manure and/or septic discharge as being dominant sources of nitrate in the water samples studied.

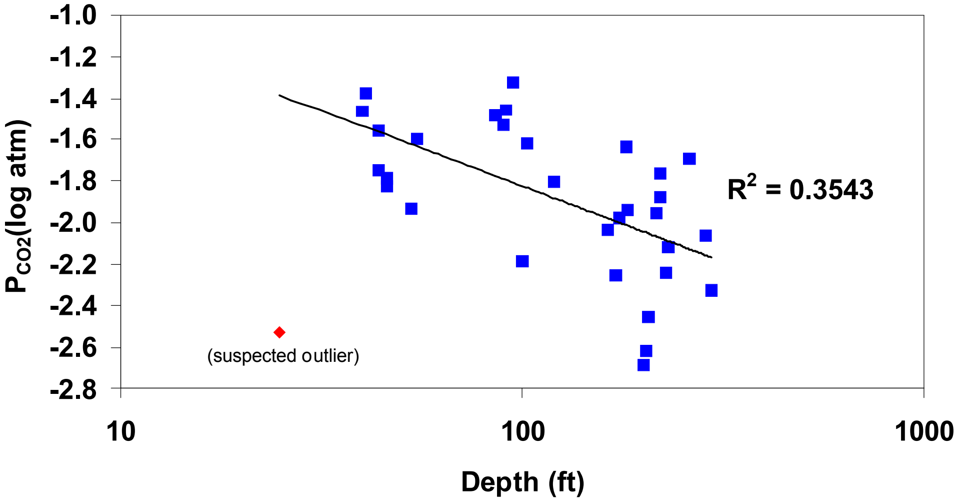

Figure 6. Calculated CO_2 partial pressures vs. well depth.

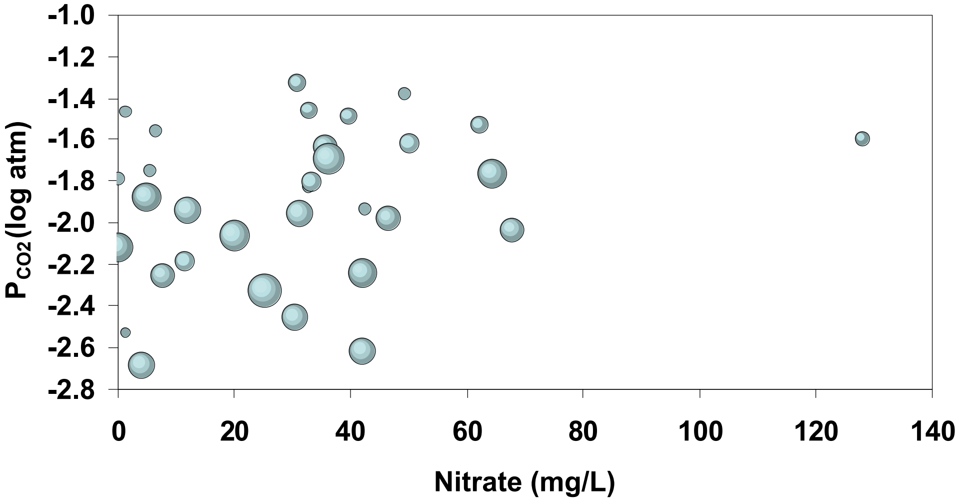

Figure 7. Observed nitrate concentrations, calculated CO_2 partial pressures, and well depth (width of circles corresponds to well depth).

Time series reconstructions of past nitrate concentrations at individual wells using SCVWD's monitoring data show statistically significant upward trends from the 1960's to the present in many of the wells from the affected areas (SCVWD, 1998). Superimposed on the long term upward trend is a seasonal cycle with wintertime highs and summertime lows in several affected wells (Figure 8). In general, the most recent data (collected in August, 2004) continue to show flat or slightly increasing trends, when compared with previous summertime results. This observation is noteworthy because a nitrate management plan has been in place since about 1997. The pattern displayed at individual wells suggests that a store of nitrate is present in the shallow vadose or soil zone, and is intercepted during the winter when water levels rise due to decreased local and regional pumping and increased precipitation. This could also explain the continuing increase in concentrations with time even though loading may have decreased in response to the nitrate management plan. Alternatively, the observed seasonal pattern could result from late-season irrigation or leaching from fallow fields during the rainy season. Those processes flush accumulated excess nitrate from fertilizer through the soil zone to shallow groundwater.

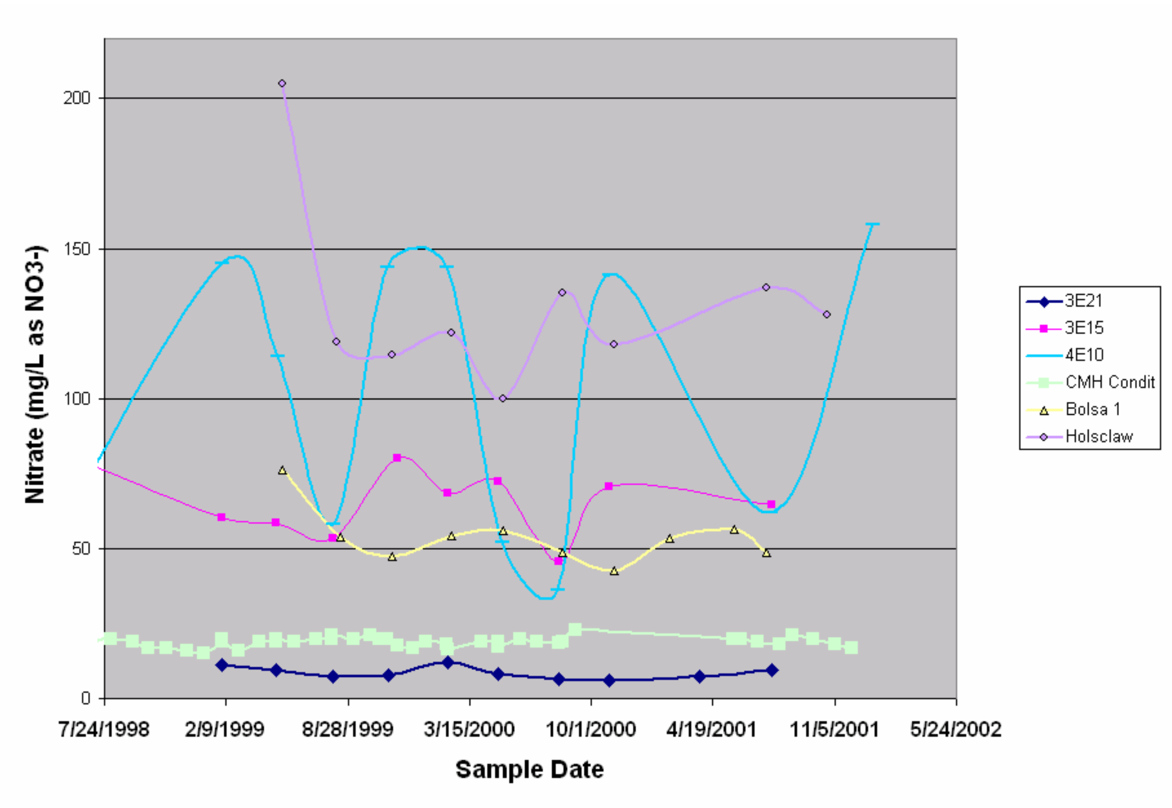

Figure 8. Measured nitrate concentrations show seasonal variations, especially in wells with shallow top perforations in the southern portion of the basin.

Isotopes of water and groundwater ages reveal distributed recharge of local and imported water

Stable isotopes of the water molecule help to establish groundwater provenance, while tritium-helium is used to determine groundwater residence time; both stable and radioactive isotopes of water can help delineate recharge areas, groundwater flowpaths, and nitrate sources. The $\delta^{18}O$ vs. $\delta^{2}H$ positions of all of the 2003 data fall below the Global Meteoric Water Line and have a trend generally parallel to it, providing little evidence of evaporation on a large scale. Exceptions are the two wells adjacent to artificial recharge ponds (Church 457, Church 452, see figure 2b) and one of the wells in the wastewater application area (Obata 22), which show evidence for significant evaporation. Two other wells adjacent to the San Pedro recharge ponds are depleted compared to most well values, indicating the presence of imported water. Recharge water in the subbasin is a combination of locally-derived precipitation and runoff from within the watershed and imported San Felipe Project (SFP) water, which is transported from the Sacramento-San Joaquin Delta and artificially recharged in Madrone Channel and in off-stream recharge facilities. Locally derived water in this relatively warm, low-lying subbasin has an observed range in δ^{18}O of –5‰ to –7‰ (Coplan and Kendall, 2000). Originating mostly in the northern Sacramento River watershed at high elevations, the imported water is isotopically lighter than local precipitation (–10.6‰ to –9.9‰ δ^{18}O; n = 2). Imported SFP water recharges the aquifer in the Madrone Channel, San Pedro ponds and Main Avenue ponds. Wells with δ^{18}O values of less than –7‰ likely produce a component of this imported water. As seen in figure 9, these wells occur near artificial recharge areas in the northern part of the study area, and in shallow wells near Llagas Creek. Local water is delivered to Church Avenue ponds.

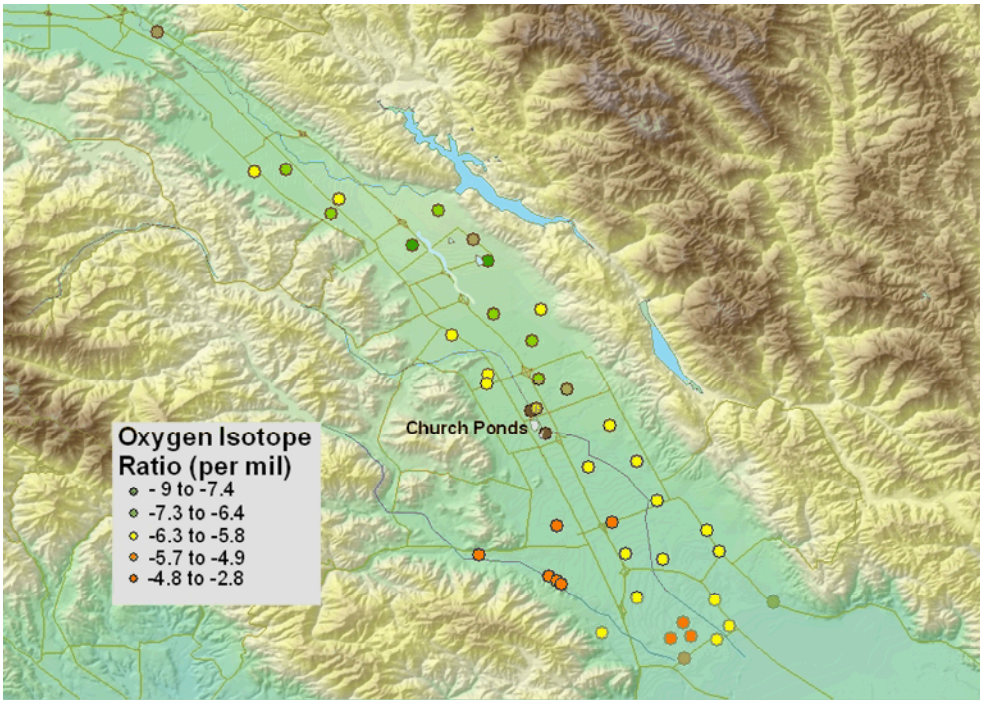

Figure 9. Observed oxygen isotope ratios show the influence of isotopically-enriched evaporated water recharge near Church Ponds and isotopically-depleted imported water in other wells where artificial recharge water comprises a component of groundwater.

A plot of δ^{18}O versus nitrate reveals that wells recharged by imported water (depleted δ^{18}O values), and wells recharged by evaporated water (enriched δ^{18}O; from recharge ponds) have extremely low nitrate concentrations (figure 10). All of the wells with high nitrate concentrations have local water stable isotope signatures, indicating that nitrate source areas do not coincide with areas of artificial recharge. Imported Sacramento-San Joaquin Delta water itself contributes little nitrate, with an average concentration over the last 10 years of 2.5 mg L^{-1} (State of California, Department of Water Resources, Water Data Library, Water Quality Data).

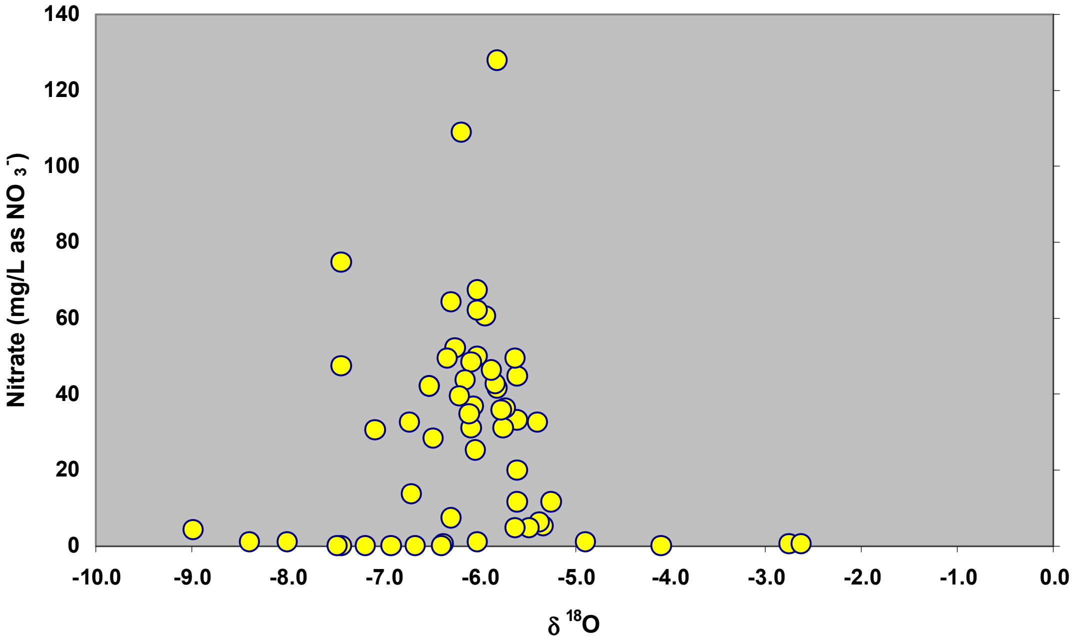

Figure 10. High nitrate concentrations in wells with 'local' isotopic ratios suggest that nitrate source areas do not coincide with artificial recharge areas.

Tritium concentrations and tritium-helium age data (Table 2c and figure 11) reveal a very dynamic shallow aquifer flow system, with significant recharge and relatively rapid groundwater flow over a large part of the subbasin. Tritium concentrations are remarkably uniform and in good agreement with the expected concentration in modern day precipitation. Thirty-five of fifty-five samples analyzed for tritium fall in the narrow range of 9 to 14 pCi/L (figure 12). Nineteen of these samples have $^3He/^4He$ ratios in the narrow range of $1.35x10^{-6}$ to $1.41x10^{-6}$ (close to the value expected for water in equilibrium with air and no tritiogenic ^3He), and corresponding calculated tritium-helium ages of less than 10 years. Wells along Uvas Creek (Christmas Hill, Thomas) and on the basin margins (Buena Vista, Leavesley 1), along with wells adjacent to artificial recharge facilities (Maple, San Pedro, Church, Coleman, Coyote Narrows, and Obata) have residence times of less than three years, and delineate the areas of active recharge.

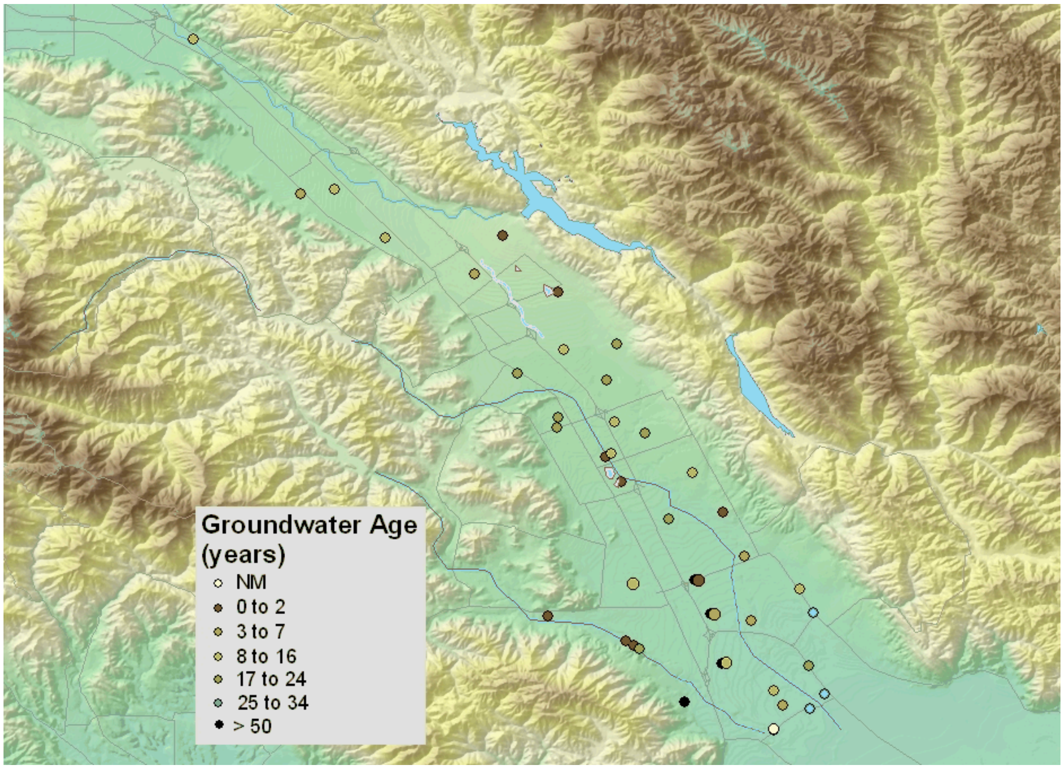

Figure 11. Very young calculated tritium-helium groundwater ages occur over a large portion of the basin and indicate high groundwater contamination vulnerability and active recharge to the shallow aquifer. For nested monitoring wells, the symbol on top is for the shallowest well – the deepest intervals have non-detectable tritium (> 50 year ages), but also have dissolved helium isotope ratios that reflect a mantle helium component.

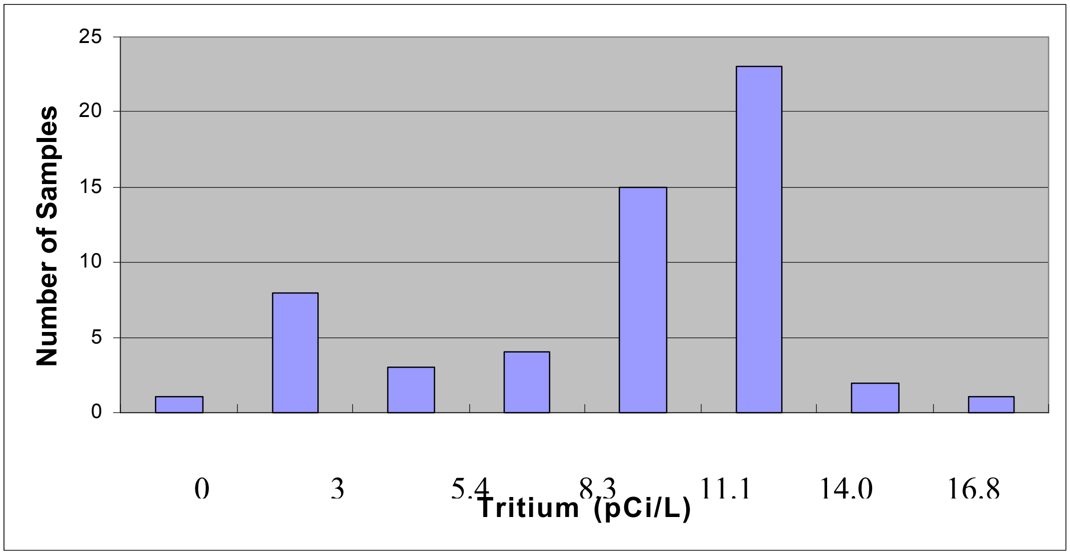

Figure 12. Histogram showing the prevalence of wells that produce groundwater with near modern tritium concentrations (8 to 14 pCi/L).

Significant, active recharge along Uvas Creek is further evidenced by very low excess air concentrations and low recharge temperatures observed in the wells adjacent to the creek. Low excess air is characteristic of stream recharge wherein the streambed meets the local water table and interaction between infiltrating water and vadose zone gas is minimal. Noble gas recharge temperatures for most wells in the study area cluster around 16C, the approximate mean annual air temperature, while wells along Uvas Creek have recharge temperatures of about 13C. The lower temperatures point to wintertime recharge when flows are high and streambeds are scoured of fine sediment that can inhibit recharge.

The shallowest wells in the three nested sets along the valley axis in Gilroy all have very young ages, indicating that the area of active recharge and rapid groundwater flow extends to the center of the subbasin. Most significantly, the wells with the highest nitrate concentrations, including Holsclaw, Leavesely 1, and Buena Vista 1, all have young groundwater ages (4 yr, 1yr, and <1 year, respectively), which means that a high nitrate flux to groundwater is ongoing in areas of 'natural recharge'. A major source of recharge in these areas may be irrigation return flow, so rapid recycling of high-nitrate groundwater used for irrigation is a plausible scenario.

Lateral flow in the shallow zone is therefore quite rapid, with significant spatial variability in the flow rate. An increasing groundwater age gradient that could be used to delineate lateral flowpaths is not evident, and recharge to the shallow system, while significant at artificial recharge areas, is widely dispersed. A sampling of flow velocities along possible flowpaths, determined from tritium-helium ages, exhibits a wide range. From the Buena Vista well to downgradient Leavesley 1, a flow velocity of approximately 1300 ft/yr is calculated, while a flowpath to the shallow Gilman well from Llagas Creek gives a velocity of approximately 6000 ft/yr. Vertical flow rates, determined from groundwater ages at the nested wells Maple 1 and 2 and Gilman are 5.3 ft/yr and 4.3 ft/yr, respectively.

Longer groundwater residence times indicate a less active flow regime and more distant recharge. In the Llagas subbasin, several wells in the northern area east and west of the main basin axis between Madrone Channel and Church Ponds recharge facilities have groundwater ages greater than 20 years (figure 11). Similarly, a group of 5 wells in the southeastern corner of the study area have distinctly older mean groundwater ages, and indicate that the area is likely fully confined with slower groundwater flow. Six wells (5 are deep, nested monitoring wells) in the study area have a component of dissolved gas from the earth's mantle, indicating upwelling of deep fluids with a primordial Helium isotope signature. As mentioned above, wells screened exclusively below 200 ft (including 4 of the 5 with a mantle He component) have no detectable tritium, indicating residence times of greater than 50 years. These wells provide an archive of groundwater that is not influenced by modern human activity. Wells with long screened intervals invariably produce groundwater with a broad age distribution – a mixture of tritiated nitrate-laden water combined with a component of tritium and nitrate-free water. For example Crumrine, a well with a nitrate concentration of 109 mg/L and $\delta^{15}N$ of 6.1‰ (suggesting a synthetic fertilizer source as described below), has a long well screen and a resulting mean age of 16 yr. This well draws in young groundwater, contaminated with nitrate, along with a calculated 60% fraction of 'pre-modern' water, which likely adds little if any nitrate (Table 2c).

Nitrate in the most contaminated wells has a fertilizer source signature

Major dissolved gases were analyzed in order to test for the possible presence of excess dissolved nitrogen in groundwater. Dissolved nitrogen and argon trends do not show the presence of detectable excess nitrogen, demonstrating that saturated zone denitrification is not prevalent (Table 2b). This result is consistent with low dissolved organic carbon (< 1.5 mg/L TOC; n=8); a sufficient flux of organic carbon is necessary for heterotrophic denitrification. With the exception of the wells just adjacent to recharge ponds, shallow-screened wells in the study area have high dissolved oxygen concentrations that indicate an aerobic system with low reduction potential. Groundwater nitrate isotope data, therefore, may be interpreted directly as indicative of nitrate source, without accounting for enrichment due to denitrification along the flowpath.

Nitrate-$\delta^{15}N$ results, plotted in Figure 13, help identify the major sources of nitrate in wells from the study area. Wells in the southwestern portion stand out as having high nitrate-$\delta^{15}N$ and relatively low nitrate concentrations. Their higher nitrate-$\delta^{15}N$ values suggest an animal waste source. As noted above, application of recycled water from the SCRWA is applied to agricultural fields at Obata Farms, adjacent to the wastewater treatment facility, and at Christmas Hill Park in Gilroy. Three wells at each of those locations show evidence for a different source of nitrate than the rest of the study area. In addition, two other wells (Bolsa-2 and Bloomfield-1) in the southwest area near the areas of recycled water irrigation are likely affected by recycled water recharge, as evidenced by relatively high measured $\delta^{15}N$. The $\delta^{15}N$ values, though not as high as the range expected for treated wastewater effluent (between 13.0‰ and 29.2‰; 41, 42), are at least 2‰ higher than the narrow range observed outside of the area of recycled water application. The measured values may reflect a mixture of the recycled water source and a soil or fertilizer source that is less enriched in $\delta^{15}N$.

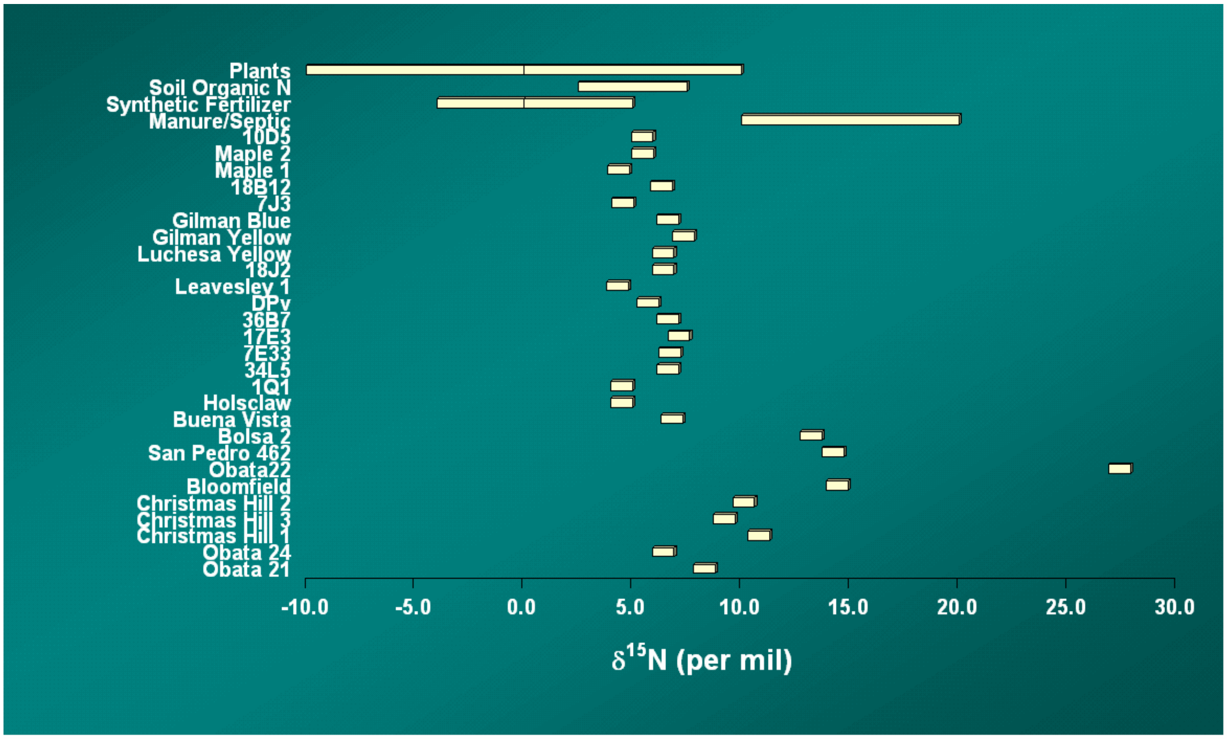

Figure 13. Bar graph shows the small range in δ^{15}N centered around +6‰ observed at most wells; wells in areas influenced by recycled water recharge have more positive values, due to denitrification.

Many of the wells with high δ^{15}N values also stand out as having high δ^{18}O (figure 14), suggesting some degree of denitrification. For example, Obata-22 shows a clear signal of denitrification, with extremely enriched δ^{15}N and δ^{18}O values, a very low nitrate concentration of 1.3 mg/L, and being on a line of slope close to ½ from Obata-21 (Figure 14). This denitrification has likely taken place during wastewater treatment, rather than in the aquifer, as excess nitrogen was not found.

A high δ^{15}N also distinguishes the San Pedro well (just adjacent to San Pedro Recharge Pond) from the majority of the results. Its accompanying high δ^{18}O nitrate, low dissolved oxygen concentration, and low nitrate concentration (1.2 mg/L) make it highly likely that this is another area affected by denitrification. (The similarly situated Church Pond wells had nitrate concentrations too low to carry out isotopic analyses. Furthermore, excess nitrogen from denitrification of only a few mg/L of nitrate would not be detectable.) As noted above, source waters in these areas have low starting nitrate concentrations, so denitrification near artificial recharge facilities is not expected to play a significant role in the overall fate of nitrate in the basin. A more extensive study near recharge facilities is necessary to determine whether these areas may be effective for long-term remediation.

For wells not influenced by recycled water or by recent artificial recharge, as described above, nitrate-δ^{15}N values fall in a narrow range. In particular, wells in this group with nitrate concentrations greater than 40 mg/L (11 of 27 wells) have nitrate-δ^{15}N values between 3.8‰ and 6.6‰. This range is covered by reported ranges for mineralized inorganic fertilizers and soil organic N, but not by animal wastes or precipitation (Heaton, 1986; Townsend et al., 1994; Kendall, 1998). The wells most clearly affected by anthropogenic nitrate contamination (Holsclaw, Leavesley 1, Maple 1) have the lightest (most depleted) nitrogen isotope values (4.0‰, 3.8‰, and 3.9‰, respectively); solidly in the range expected for synthetic fertilizer. The most likely source of anthropogenic nitrate affecting groundwater concentrations is therefore inorganic fertilizer. Isotopic results do not support the possibility of a significant contribution from animal waste sources including septic and manure outside of areas under the influence of wastewater irrigation. While a significant component from soil organic nitrogen cannot be ruled out, the high concentrations observed are not consistent with results from previous studies in areas where soil nitrogen is the major source, which typically display nitrate concentrations in groundwater of less than 10 mg/L (Edmunds and Gaye, 1997; Williams et al., 1998).

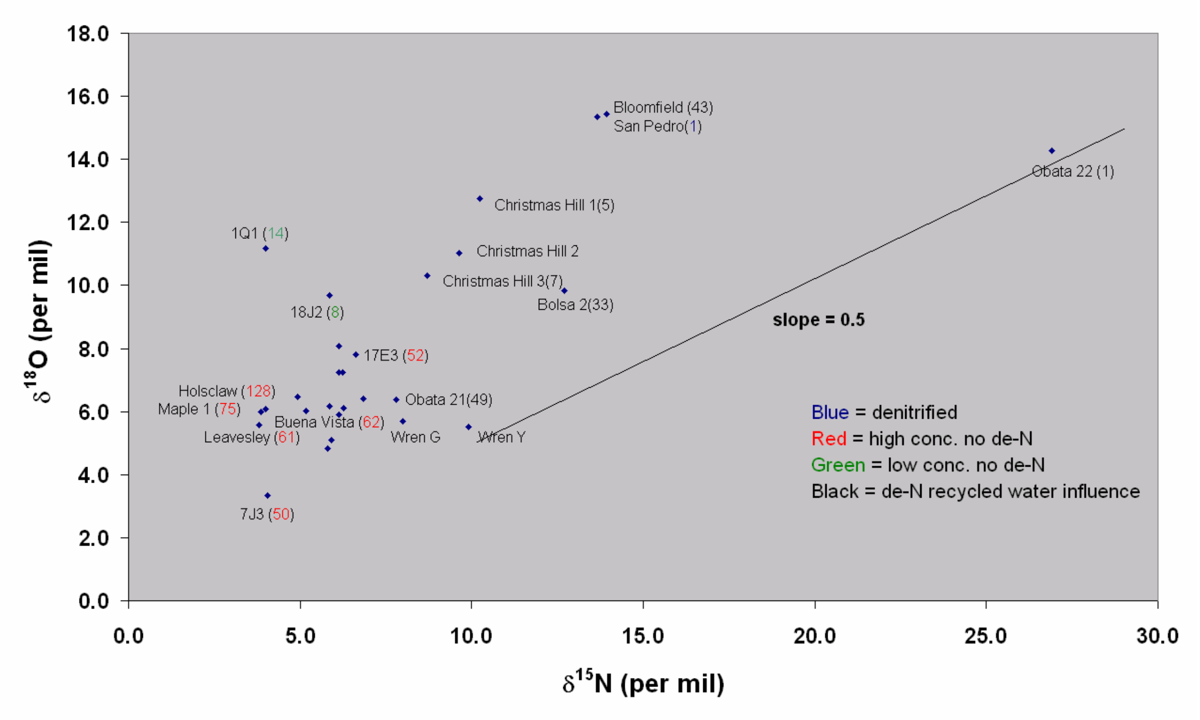

Figure 14. On a plot of $\delta^{15}N$ vs. $\delta^{18}O$ of nitrate, samples with residual nitrate from denitrification (which takes place at the wastewater treatment plant, before recharge) stand out from the majority of samples, for which fertilizer is the most likely source of N. Labels next to points are measured nitrate concentrations, color-coded according to the legend with the interpretation of possible denitrification.

As noted above, nitrate-$\delta^{18}O$ can be useful for distinguishing nitrate sources, especially if nitrate fertilizers are the main source, since they have an expected starting nitrate-$\delta^{18}O$ value of 23‰, the value for atmospheric oxygen. However, if ammonia fertilizer (rather than nitrate fertilizer) is applied and subsequently oxidized to nitrate, then one oxygen atom from air (at +23‰) and 2 from water (at roughly –6‰ for Llagas waters) combine to make up the nitrate-oxygen (Kendall, 1998). The resulting $\delta^{18}O$-nitrate in that case would be +3.6‰, a value somewhat lower than the observed values. Ammonium sulfate is commonly used for fertilization of tomatoes, peppers, and strawberries, major crops grown in the Gilroy area, and may be a major source of nitrate to groundwater. However, a contribution from nitrogen-fixing vegetation cannot be ruled out, and in a climate with a long dry season and soils that do not sustain significant denitrification, the observed nitrate-$\delta^{15}N$ and nitrate $\delta^{18}O$ values fall in the range expected for soil organic nitrogen as a natural nitrate source.

Inverse geochemical modeling calculations via PHREEQC were used to postulate mass transfer reactions that could explain the evolution of select water chemistry parameter values (pH, inferred HCO_3^-, Ca^{2+}, Mg^{2+}) in selected wells from the average chemical composition of reservoirs in the basin that could serve as potential sources of recharge. The allowed mass transfer reactions included NH_3 (as a nitrate source), CO_2, calcite, and dolomite. CO_2, which would be required in an inverse model to explain a water composition affected by mineralization of an animal waste discharge, is a required constituent in wells generally identified as being influenced by wastewater irrigation (figure 15), a finding that is consistent with the nitrogen isotope data.

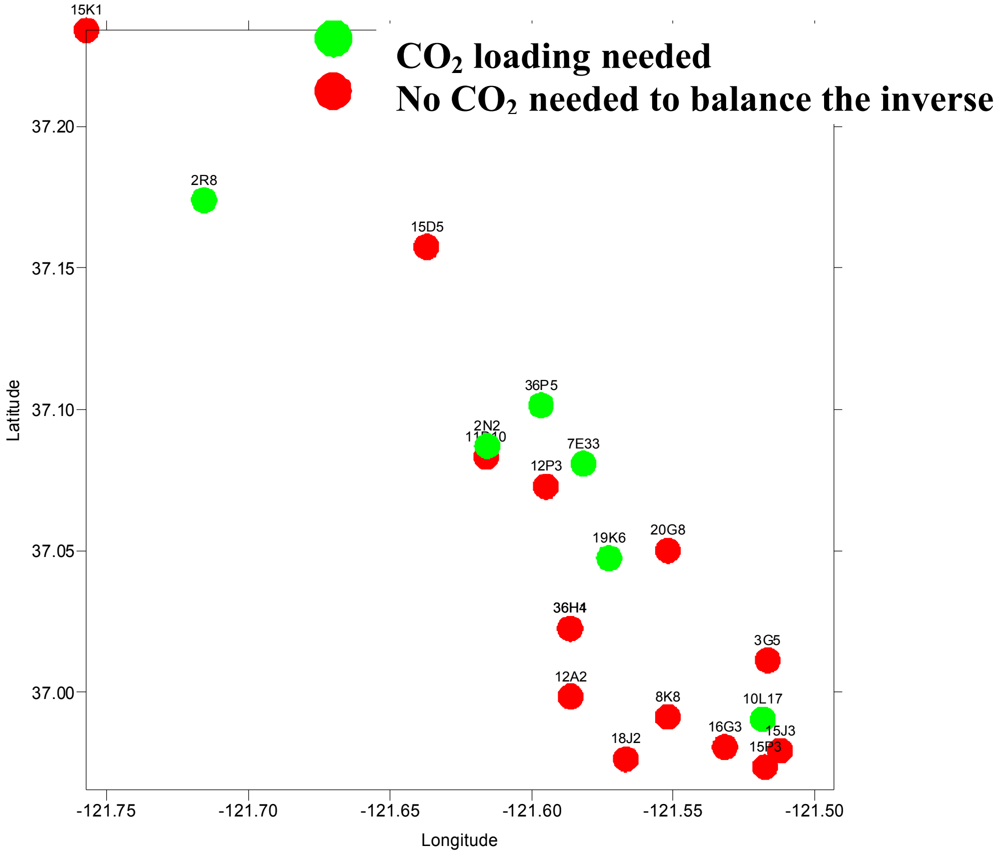

Figure 15. Required CO_2 input in inverse model calculations in select Llagas subbasin wells.

Among the major cations and anions, only magnesium appears to exhibit a discernable correlation with nitrate (figure 16), a feature that is presumably associated with the dissolution of dolomite and/or Mg-rich carbonate minerals. As dolomite is a common soil amendment, the pattern of dolomite distribution could, in principle, reveal clues to as to the distribution of nitrate fertilizer loading. The inverse modeling approach indicates that dolomite dissolution is a necessary component of the inverse models for a number of wells, with the highest values also located toward the southeast portion of the subbasin. This loose association with an animal waste signature in the area raises the possibility that much of the added dolomite simply reflects a natural mineralogical dissolution response of the aquifer material.

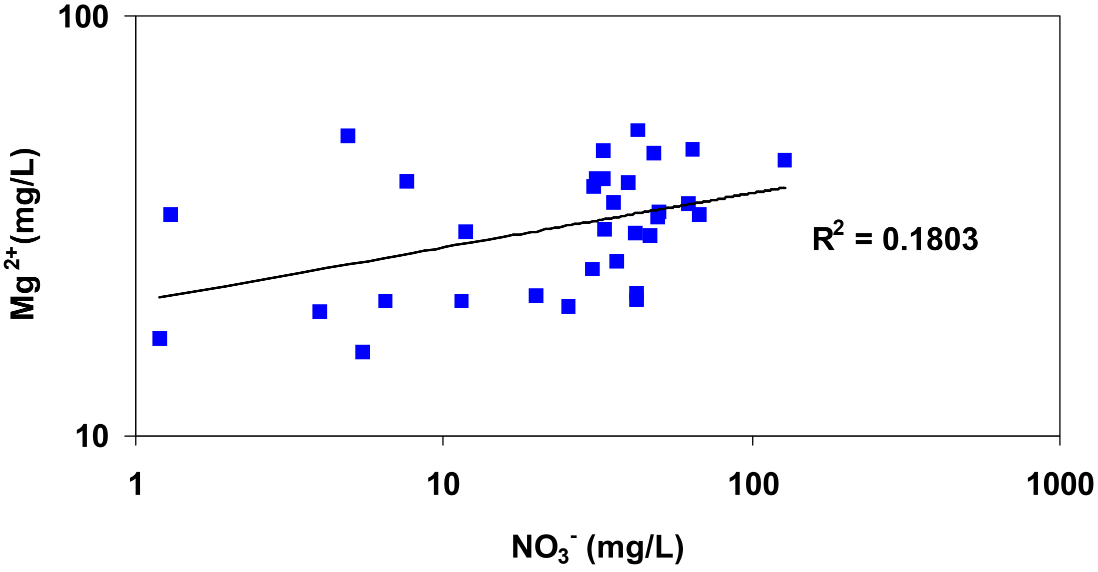

Figure 16. Observed magnesium concentrations versus nitrate in Llagas subbasin wells.

Effectiveness of Nitrate Management Program

As noted above, many of the educational and testing activities that make up the nitrate management program implemented by SCVWD began on a large scale in 2000 and later. Figure 17 shows the locations of 4 key growers that participated in the nitrate management assistance program beginning in January, 2000. Although some of the nitrate management activity took place at the sites shown, these growers have fields in multiple locations, with different crop rotations and different irrigation methods, which makes monitoring the effects of the activities difficult. Two wells, 36P5 and 10D5, are situated just downgradient from Grower B Farms (participated in the program) and Grower A (a major grower not listed as having participated in the program), respectively. The 36P5 well did have a reduction of 29% in its average nitrate concentration, from 59 mg/L (standard deviation 2.6, n=12), to 42 mg/L, as measured in 2003. The 10D5 well fluctuates widely (figure 8; mean concentration 82 mg/L standard deviation 49.8, n=14), but saw an increase above average summertime concentrations in the 2003 sampling.

Without first-encounter monitoring wells emplaced specifically near fields where changes have been instituted, more meaningful assessments based on well data cannot be determined.

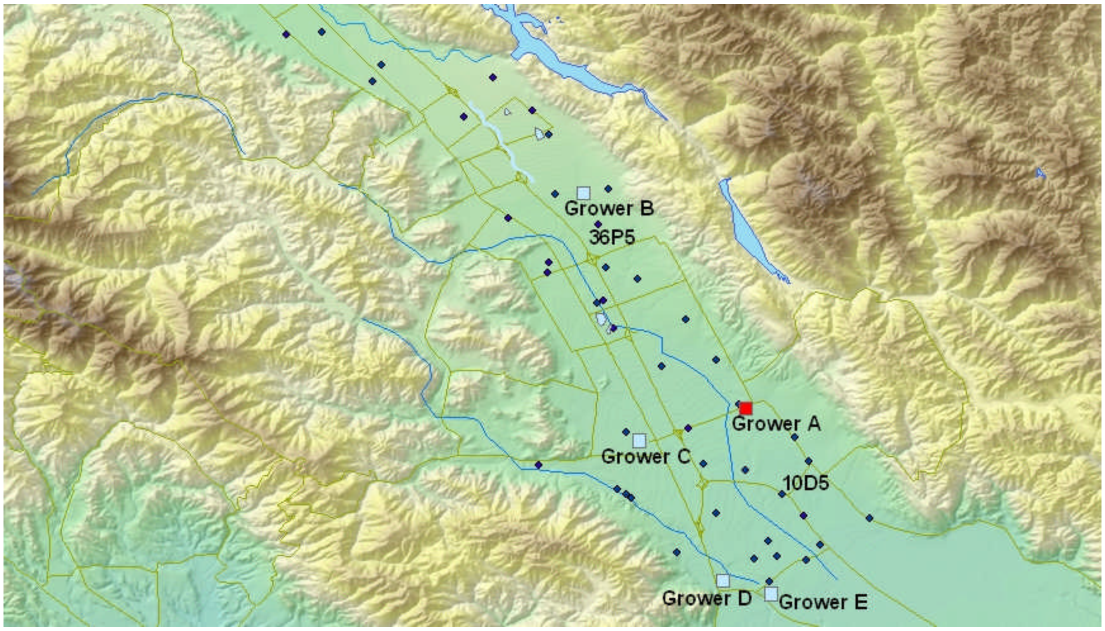

Figure 17. Four of the major growers (B through E) participating in the SCVWD nitrate management plan are shown with light blue symbols, along with one that did not (Grower A). Monitoring wells included in the study are not well situated to monitor changes in the flux of nitrate from those fields.

A more useful exercise for assessing the effect of the nitrate management activities on a regional scale is to examine nitrate patterns in wells with very young groundwater ages. Fourteen wells have calculated ages of less than 4 years, and as such record the most recent flux of nitrate to the saturated zone. Changes to the flux will be observed in these wells first. Of the fourteen wells with very young groundwater, 3 are just adjacent to artificial recharge ponds and have very low concentrations, as discussed above. Another 4 (Obata 22, Christmas Hill 1 and 2, and Bolsa2) are in areas receiving recycled water and have animal waste/denitrified signatures, as discussed above. Five of the remaining wells have low $\delta^{15}N$, indicating anthropogenic nitrate from fertilizer, and are in areas of high historical nitrate levels. Of these wells (Buena Vista-1, Holsclaw, Gilman Yellow, Luchessa Yellow, and Maple-1), 2 (Gilman Yellow and Holsclaw) had insignificant changes from mean concentrations of 1998-2000, 2 (Maple1 and Luchessa Yellow) had significant increases, and only one (Buena Vista-1) had a significant decrease. Groundwater age analyses indicate that the nitrate management plan has not yet resulted in a decrease in the flux of nitrate to the shallow aquifer in the areas tested.

Conclusions and Recommendations:

Inorganic fertilizer is almost certainly the main source of nitrate to shallow groundwater in the Llagas subbasin, so continued efforts to minimize application of fertilizer that is not taken up by plants but rather leached to groundwater is critical. The chemical form of nitrogen in fertilizer, the timing of application, and the method and timing of irrigation are important factors in the propensity for leaching of nitrate from soils. In particular, more efficient irrigation would minimize the chance that significant return flow of high nitrate groundwater leads to continued contamination of wells.

Assessing the effectiveness of the nitrate management program would benefit from installation or identification and testing of first-encounter wells that are just downgradient of fields where the plan is being carried out and where high contamination and young groundwater have been identified. Fields within ½ mile of Leavesley W-1, Holsclaw W-1, or Buena Vista W-1 would be good candidates if growers are participating in the program. Future work ought to include testing the competing hypotheses of contributions to the shallow aquifer from leaching of stored nitrate in the vadose zone, versus enhanced leaching of recently applied nitrate by late season irrigation. This could take the form of a relatively simple study in which vadose zone core samples are leached to determine the nitrate inventory in soil and unsaturated sediment in a few key areas of irrigated agriculture.

Saturated zone denitrification under fields and developed areas is not a significant process for the fate of nitrate, probably because of low organic carbon loading. Artificial recharge brings low nitrate water and may set up conditions necessary for denitrification – enhanced artificial recharge and shallow zone pumping could be used as a long term remediation strategy. A large portion of the shallow aquifer is highly vulnerable to contamination (of any non-reactive constituent), as evidenced by the widespread occurrence of very recently recharged groundwater (see also Moran et al., 2004). To the extent possible, reduction in sources over the large area where groundwater ages are less than 10 years is the optimal scenario for solving the contamination problem in the long term. Areas of lower groundwater vulnerability are to the east of Madrone Channel in Morgan Hill, and the southeastern-most portion of the subbasin in Gilroy. Only deep screened wells in the confined (southern) portion of the subbasin can be expected to be isolated from the input of nitrate for the next several decades. This area could be considered for future drinking water wells.

Acknowledgments

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Table 2a:

Location	LLNL ID	State Well ID	Well Name	Sample Collection	Eleva-tion	Total Well Depth	Perf Top	Temp	Cond	pH	Field DO
						(ft bgs)	*(ft bgs)*	*(°C)*	*(μS)*		*(mg/L)*
Morgan Hill	101665	09S/02E-01Q01 M	1Q1	20030617	237.2	204	50	18.1	440	7.42	
Gilroy	101666	10S/04E-34L05 M	34L5	20030617	199.2	163	90	17.8	746	6.95	
San Martin	101667	10S/04E-17E03 M	17E3	20030617	252.7	200	180	19.5	500	7.27	
San Martin	101668	09S/03E-36B07 M	36B7	20030617	319.2	225	165	19.4	960	7.25	
Gilroy	101669	11S/04E-05C06 M	GILMAN YELLOW	20030617	134.6	305	247	19.6	472	7.47	8.0
Gilroy	101670	11S/04E-05C05 M	GILMAN BLUE	20030617	134.6	435	390	na	na	na	5.0
Gilroy	101671	11S/04E-05C04 M	GILMAN GREEN	20030617	134.6	750	655	22.7	366	8.37	<1
Gilroy	101672	11S/04E-05C03 M	GILMAN RED	20030617	134.6	880	840	22.9	1180	8.06	<1
San Martin	101673	09S/03E-07J03 M	7J3	20030618	314.3	230	130	18.5	634	7.48	
San Martin	101674	09S/03E-18B12 M	18B12	20030618	278.9	84	69	19.3	490	7.35	
San Martin	101675	09S/03E-35C12 M	MAPLE 1	20030618	305.1	61	48	18.9	657	7.06	
San Martin	101676	09S/03E-35C11 M	MAPLE 2	20030618	305.1	91	81	19.0	615	7.39	
Gilroy	101741	11S/04E-10D05 M	10D5	20030618	112.9	325	300				
Gilroy	101766	11S/04E-16K01 M	MW-21 OBATA FARMS	20030819	134.4	41	20	16.8	1020	6.82	
Gilroy	101767	11S/04E-15M02 M	MW-22 OBATA FARMS	20030819	144.6	40	10	17.9	1040	6.75	
Gilroy	101768	11S/04E-16G03 M	MW-24 OBATA FARMS	20030819	149.9	120	100	19.1	920	7.22	
Gilroy	101769	11S/03E-01Q02 M	CHRISTMAS HILL W-1	20030819	169.3	44	29				
Gilroy	101770	11S/03E-12A02 M	CHRISTMAS HILL W-2	20030819	168.0	44	29	19.1	458	7.03	
Gilroy	101772	11S/03E-12A03 M	CHRISTMAS HILL W-3	20030819	158.1	44	29	18.9	570	6.82	
Gilroy	101773	11S/04E-21G03 M	BOLSA W-2	20030820		91	70	18.3	990	6.89	
Gilroy	101774	11S/04E-15J03 M	BLOOMFIELD W-1	20030820		53	48	18.7	910	7.39	
Gilroy	101825	11S/04E-03G05 M	3G5	20031113	183.4	86	70	17.1	907	6.95	
Gilroy	101826	11S/04E-04F07 M	HOLSCLAW W-1	20031113	176.4	55	40	18.1	913	6.90	7.0
Gilroy	101827	10S/04E-20G08 M	BUENA VISTA W-1	20031113	240.8	90	80	19.5	892	6.92	8.0
San Martin	101828	10S/03E-13D08 M	CHURCH 452	20031113	249.3	46	26	19.8	407	7.13	<1
Morgan Hill	101829	09S/03E-23L05 M	SAN PEDRO 462	20031113	350.4	25	10	21.7	456	7.53	
Gilroy	101830	10S/03E-36H04 M	WREN-YELLOW	20031117	207.3	95	60	18.5	808	6.73	4.0
Gilroy	101831	10S/03E-36H03 M	WREN-BLUE	20031117	207.3	174	134	18.3	645	7.28	7.0
Gilroy	101832	10S/03E-36H01 M	WREN-GREEN	20031117	207.3	260	220	18.7	633	7.01	7.0
Gilroy	101833	10S/03E-36H02 M	WREN-RED	20031117	207.3	440	400	20.8	651	7.31	<1

Temp = temperature, Cond = electrical conductivity, DO = dissolved oxygen

Table 2a: con'd

Location	LLNL ID	State Well ID	Well Name	Sample Collection	Eleva-tion	Total Well Depth	Perf Top	Temp	Cond	pH	Field DO
				yyyymmdd	*Ft msl*	*(ft bgs)*	*(ft bgs)*	*(°C)*	*(µS)*		*(mg/L)*
Gilroy	101834	11S/04E-08K08 M	LUCHESSA-YELLOW	20031117	161.2	103	48	17.9	766	7.02	7.0
Gilroy	101835	11S/04E-08K07 M	LUCHESSA-GREEN	20031117	161.2	452	397	17.8	308	9.96	<1
Gilroy	101836	11S/04E-08K06 M	LUCHESSA-RED	20031117	161.2	865	790	17.6	1720	9.66	<1
Gilroy	101837	10S/04E-28M05 M	LEAVESLEY W-1	20031117	193.1	60	50	18.7	929	7.20	5.0
San Martin	101838	10S/04E-07E33 M	7E33	20031119	254.6	228	180	17.6	585	7.40	
San Martin	101839	10S/03E-12C06 M	12C6	20031119	250	206	140	15.8	575	7.58	
Gilroy	101840	10S/04E-19K06 M	19K6	20031119	221.2	295	175	18.0	541	7.57	
Gilroy	101841	11S/04E-11J07 M	11J7	20031119	165.8	230	120	19.7	854	7.68	
Gilroy	101842	11S/04E-15P03 M	15P3	20031119	167.6			18.0	744	7.63	
Gilroy	101843	11S/04E-18J02 M	18J2	20031119	176.8	170	100	18.7	962	7.60	
Gilroy	101844	11S/03E-02E01 M	2E1	20031119	229.7	100	60	16.0	415	7.51	
San Martin	101845	10S/03E-12P03 M	12P3	20031119	238.2	182	100	17.5	527	7.41	
Gilroy	101846	10S/04E-32E06 M	LEAVESLEY YELLOW	20031120	197.8	285	225	18.3	514	7.37	6.0
Gilroy	101847	10S/04E-32E05 M	LEAVESLEY BLUE	20031120	197.8	395	350	19.2	485	7.42	6.0
Gilroy	101848	10S/04E-32E04 M	LEAVESLEY GREEN	20031120	197.8	616	560	18.7	380	9.10	<1
Gilroy	101849	10S/04E-32E07 M	LEAVESLEY RED	20031120	197.8	949	890	19.4	1350	11.22	<1
Coyote	101850	08S/02E-15K01 M	COYOTE NARROWS 1	20031215	203.4	220	195	18.2	626	7.33	3.0
Gilroy	101851	09S/03E-36P05 M	36P5	20031120	287	203	100	18.3	605	7.80	8.0
Gilroy	101852	09S/03E-34P01 M	34P1	20031120	296.7	163	103	18.2	661	7.17	9.0
Gilroy	101853	09S/03E-21C03 M	21C3	20031120	315.9	200	100	16.4	505	7.71	
Morgan Hill	101854	09S/02E-02R08 M	2R8	20031215	272.3	220	50	16.8	712	7.08	6.0
Morgan Hill	101855	09S/03E-15D05 M	COYOTE PUMP STATION	20031215	246.1	46	10	18.8	616	7.15	7.0
San Martin	101856	10S/03E-13K10 M	CHURCH 457	20031215	255.9	50	25	19.7	379	7.29	1.0
San Martin	101857	10S/03E-02N02 M	2N2	20031215	303.8	215		18.1	586	7.19	6.0
San Martin	101858	10S/03E-11D10 M	11D10	20031216	303.8	181	80	17.0	575	6.91	7.0
San Martin	101859	11S/04E-10L17 M	10L17	20031216	223.8	150			17	8.25	7.2
San Martin	101860	09S/03E-36B07 M	36B7	20031216	319.2	225	165				

Temp = temperature, Cond = electrical conductivity, DO = dissolved oxygen

Table 2b:

LLNL ID	$\delta^{18}O_{SMOW}$ in water	δD_{SMOW} in water	$\delta^{15}N$ in nitrate	$\delta^{18}O$ in nitrate	Chloride	Nitrate	Sulfate	N_2	O_2	Ar
	(‰)	*(‰)*	*(‰)*	*(‰)*	*(mg/L)*	*(mg/L)*	*(mg/L)*	*(cm^{3}STP/g)*	*(cm^{3}STP/g)*	*(cm^{3}STP/g)*
101665	-6.7		4.0	11.2	34.0	13.7	42.6	1.85E-02	5.13E-03	4.45E-04
101666	-6.2		6.1	7.3	83.8	109.0	51.0	2.21E-02	6.32E-03	5.29E-04
101667	-6.3		6.6	7.8	63.5	52.4	23.6	1.75E-02	6.11E-03	4.38E-04
101668	-6.1		6.1	8.1	102.5	43.5	20.7	2.16E-02	6.32E-03	5.19E-04
101669	-6.0		6.8	6.4	29.4	36.7	41.7	2.16E-02	4.69E-03	5.03E-04
101670	-6.1		6.1	5.9	25.7	34.7	29.4	2.12E-02	4.95E-03	5.07E-04
101671	-7.4				50.7	0.0	30.1	1.51E-02	3.22E-03	3.61E-04
101672	-7.5				491.8	0.0	17.7	1.95E-02	1.11E-03	4.31E-04
101673	-6.3		4.0	3.4	26.4	49.7	51.0	1.89E-02	7.24E-03	4.54E-04
101674	-6.5		5.8	4.8	18.3	28.2	27.3	1.87E-02	4.37E-03	4.52E-04
101675	-7.4		3.9	6.0	57.2	74.9	53.3	1.57E-02	6.09E-03	3.79E-04
101676	-7.4		4.9	6.5	56.2	47.5	45.8	2.00E-02	7.18E-03	4.71E-04
101741										
101766	-5.6		7.8	6.4	149.8	49.3	76.9	2.34E-02	3.09E-03	5.34E-04
101767	-4.9		26.9	14.3	177.0	1.3	114.5	3.00E-02	1.35E-03	6.12E-04
101768	-5.6		5.9	6.2	41.9	33.3	55.1	2.54E-02	3.21E-03	5.28E-04
101769	-5.5		10.3	12.8	17.1	4.6	29.6	2.00E-02	3.12E-03	4.50E-04
101770	-5.3		9.6	11.0	26.7	5.5	32.6	2.23E-02	2.49E-03	5.25E-04
101772	-5.4		8.7	10.3	45.9	6.5	54.2	2.08E-02	2.78E-03	4.90E-04
101773	-5.4		12.7	9.8	157.5	32.8	87.6	3.43E-02	1.31E-03	7.58E-04
101774	-5.8		13.9	15.4	57.1	42.5	120.7	3.49E-02	1.90E-03	5.94E-04
101825	-6.2				47.4	39.7	32.8	2.41E-02	5.05E-05	4.79E-04
101826	-5.8		4.0	6.1	35.2	128.0	73.9	1.50E-02	4.96E-03	3.58E-04
101827	-6.0		6.3	6.1	57.4	62.0	59.1	1.42E-02	5.25E-03	3.33E-04
101828	-4.1				9.3	0.0	15.9	1.55E-02	1.13E-04	3.70E-04
101829	-8.0		13.7	15.4	58.6	1.2	38.1	1.44E-02	1.41E-03	3.44E-04
101830	-5.7		9.9	5.5	44.4	30.8	63.0			
101831	-5.9				34.8	46.5	37.2			
101832	-5.7		8.0	5.7	32.5	36.2	35.4	2.08E-02	4.36E-03	4.54E-04

Table 2b: (con'd)

LLNL ID	$\delta^{18}O_{SMOW}$ in water	δD_{SMOW} in water	$\delta^{15}N$ in nitrate	$\delta^{18}O$ in nitrate	Chloride	Nitrate	Sulfate	N_2	O_2	Ar
	(‰)	*(‰)*	*(‰)*	*(‰)*	*(mg/L)*	*(mg/L)*	*(mg/L)*	*(%)*	*(%)*	*(%)*
101833	-5.8		13.4		35.5	40.3	56.4	2.68E-02	1.63E-03	4.92E-04
101834	-6.0	-40	5.9	5.1	17.0	50.0	61.2	2.12E-02	4.78E-03	4.54E-04
101835	-6.7	-44			25.3	0.0	46.6	2.03E-02	2.57E-03	4.45E-04
101836	-6.9	-46			722.9	0.1	1.0	4.09E-02	6.30E-04	4.97E-04
101837	-5.9		3.8	5.6	19.6	60.5	31.4	2.05E-02	3.71E-03	4.52E-04
101838	-6.5	-45	6.2	7.2	40.6	42.1	39.8	2.06E-02	5.42E-03	4.69E-04
101839	-7.1	-51			47.5	30.5	41.4	1.93E-02	5.15E-03	4.28E-04
101840	-6.0		5.2	6.0	30.0	25.3	34.1	2.17E-02	5.21E-03	4.72E-04
101841	-6.4				46.5	0.0	42.1	2.06E-02	1.18E-03	4.23E-04
101842	-5.8				26.0	41.6	65.8	1.76E-02	5.52E-03	3.96E-04
101843	-6.3		5.9	9.7	89.8	7.6	87.5	2.00E-02	8.04E-04	4.45E-04
101844	-5.6				10.6	11.5	32.9	1.37E-02	2.08E-03	3.45E-04
101845	-5.2	-36			6.9	11.8	17.3	2.06E-02	2.89E-03	4.39E-04
101846	-5.6	-41			19.1	20.1	29.5	2.65E-02	4.38E-03	5.51E-04
101847	-6.0	-41	Insuff NO_3	Insuff NO_3	0.3	1.0	0.2	2.45E-02	4.53E-03	5.22E-04
101848	-6.4	-44	Insuff NO_3	Insuff NO_3	0.4	0.4	0.5	2.22E-02	7.68E-04	4.60E-04
101849	-7.2	-52	Insuff NO_3	Insuff NO_3	409.8	0.1	3.9	2.79E-02	9.98E-04	5.46E-04
101850	-5.6	-45			23.9	4.9	29.8	1.58E-02	2.10E-03	3.76E-04
101851	-6.5	-46			46.8	42.1	39.4	2.59E-02	7.02E-03	5.63E-04
101852	-6.0	-41			45.2	67.6	50.3	2.22E-02	6.56E-03	4.94E-04
101853	-9.0	-67			72.1	4.0	39.7	2.30E-02	5.62E-03	4.89E-04
101854	-6.3	-45			39.5	64.3	47.5	1.61E-02	3.30E-03	3.74E-04
101855	-6.7	-50			33.6	32.8	48.5	1.32E-02	5.56E-03	3.33E-04
101856	-2.8	-24			7.5	0.4		1.70E-02	5.97E-04	3.90E-04
101857	-6.1	-43			42.0	31.2	27.8	2.25E-02	4.75E-03	4.74E-04
101858	-5.8	-44			40.7	35.6	29.6	2.15E-02	5.64E-03	4.52E-04
101859	-6.1	-43			30.8	48.2	56.5	2.15E-02	1.72E-03	4.45E-04
101860	-5.6	-40			117.5	44.6	82.6	2.18E-02	2.31E-03	4.73E-04

Table 2c:

LLNL ID	Tritium	Tritium error	Excess Air	^{4}He radiogenic	Radiogenic Age	Percent pre-modern	Recharge Temp	Recharge Temp error
	(pCi/L)	*(pCi/L)*	*(ccSTP/g)*	*(ccSTP/g)*		*(%)*	*(°C)*	*(°C)*
101665	14.9	0.76	7.36E-03	<1E-10	15.9	0.44	15.4	1.4
101666	11.1	0.61	1.37E-02	1.8E-10	16.0	0.59	11.2	1.7
101667	11.1	0.61	1.84E-02	<1E-10	15.2	0.57	16.8	2.7
101668	2.7	0.34	1.58E-02	<1E-10	23.9	0.94	17.2	2.4
101669	12.4	0.67	1.13E-02	8.49E-09	0.6	0.55	16.5	1.8
101670	4.9	0.39	1.39E-02	4.34E-09	34.0	0.96	17.1	2.2
101671	0.5	0.22	3.65E-03	4.37E-07			11.9	1
101672	0.0	0.16	4.49E-03	7.55E-07	180.1*	1.00	10.8	1
101673	15.6	2.3	1.44E-02	1.22E-06			15.7	2.1
101674	11.7	1.58	1.11E-02	2.03E-08	11.3	0.50		
101675	10.9	0.54	4.74E-03	1.49E-09	3.9	0.56	15.4	1.2
101676	10.1	0.51	1.06E-02	1.28E-09	9.9	0.57	18.3	1.9
101741	11.9	0.59	2.51E-02	<1E-10	38.5	0.93	18.7	3.8
101766	19.7	1.61	7.33E-03	1.15E-07	66.7*		14.4	1.3
101767	13.7	0.72	5.69E-03	<1E-10	2.8	0.47		
101768	13.8	0.69	1.04E-02	<1E-10	15.6	0.48	14.1	1.6
101769	10.0	0.51	3.03E-03	6.92E-10	0.0	0.65	15.9	1.1
101770	13.2	0.63	3.87E-03	<1E-10	<1		13.7	1.1
101772	9.4	0.47	4.05E-03	<1E-10	16.9	0.67	13.8	1.1
101773	12.7	0.6	8.67E-03	<1E-10	2.4	0.51	15.5	1.5
101774	7.0	0.39	4.15E-03	<1E-10	26.6	0.88	14.6	1.1
101825	2.2	0.18	1.57E-02	<1E-10	28.9	0.97	16.9	2.4
101826	11.9	0.49	2.50E-03	<1E-10	3.9	0.52	14.9	1
101827	6.4	0.31	2.26E-03	2.73E-10	<1		17.8	1
101828	10.7	0.44	4.50E-03	<1E-10	<1		12.0	1
101829	11.2	0.45	2.51E-03	<1E-10	<1		16.9	1
101830	11.4	0.5	6.76E-03	1.11E-08			15.1	1.3
101831	8.8	0.43	1.54E-02	<1E-10	27.1	0.85	15.6	2.2
101832	3.9	0.24	1.25E-02	<1E-10	26.2	0.93	15.1	1.9
101833	8.2	0.39	1.27E-02	3.35E-08			14.2	1.8

Table 2c: (con'd)

LLNL ID	Tritium	Tritium error	Excess Air	^{4}He radiogenic	Radiogenic Age	Percent pre-modern	Recharge Temp	Recharge Temp error
	(pCi/L)	*(pCi/L)*	*(ccSTP/g)*	*(ccSTP/g)*		*(%)*	*(°C)*	*(°C)*
101834	12.5	1.39	1.02E-02	<1E-10	2.6	0.52	14.9	1.6
101835	-0.3	0.73				1.00		
101836	2.3	1.05	1.00E-02	5.71E-06	163.9*	1.00	7.8	1.2
101837	12.7	0.52	1.12E-02	<1E-10	6.3	0.46	15.0	1.7
101838	10.6	0.46	1.40E-02	<1E-10	22.1	0.73		
101839	11.3	0.46	1.26E-02	<1E-10	10.9	0.52	15.9	2
101840	11.7	0.56	1.56E-02	<1E-10	23.5	0.73	16.0	2.3
101841	0.1	1.01						
101842	13.1	0.54	1.40E-02	<1E-10	27.2	0.78	15.0	2
101843	1.2	0.14	7.19E-03	7.62E-07			12.8	1.3
101844	8.5	0.44	1.25E-03	<1E-10	2.0	0.68	13.5	0.9
101845	11.1	0.48	1.27E-02	5.83E-10	12.4	0.54	15.7	1.9
101846	11.9	0.58	1.56E-02	<1E-10	25.8	0.77	14.5	2.2
101847	9.1	0.46	1.40E-02	<1E-10	28.9	0.87	15.1	2
101848	1.2	0.15	8.93E-03	4.8E-08				
101849	1.6	0.25	8.70E-03	1.3E-06	138.0*	1.00	8.9	1.2
101850	13.4	0.54	3.40E-03	<1E-10	9.3	0.42	17.0	0.8
101851	11.3	0.51	1.58E-02	<1E-10	20.3	0.67	16.0	2.3
101852	9.8	0.43	2.10E-02	<1E-10	20.6	0.72	15.9	2.9
101853	10.7	0.46	1.70E-02	<1E-10	6.8	0.55	17.3	2.6
101854	11.5	0.46	3.73E-03	1.33E-08	4.4	0.53	17.0	0.8
101855	10.1	0.42	4.26E-04	<1E-10	1.0	0.63	17.2	0.8
101856	12.4	0.48	4.97E-03	<1E-10	2.5	0.52	19.0	0.9
101857	10.9	0.45	1.36E-02	<1E-10	21.2	0.70	17.0	1.2
101858	11.4	0.46	2.20E-02	<1E-10	19.8	0.66	16.0	1.7
101859	6.1	0.26	6.69E-03	<1E-10	20.3	0.82	15.3	0.9
101860								

*Calculated age is useful only as an indicator of the presence of mantle helium