

**The Use of Multi-Isotope Ratio Measurements  
as a New and Unique Technique  
to Resolve NO<sub>x</sub> Transformation, Transport and Nitrate Deposition  
in the Lake Tahoe Basin**

Final Report

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## **Abstract**

The enrichment of oxygen 17 ( $^{17}\text{O}$ ) observed in photochemically produced nitrate is a powerful tracer of the deposition and transformation of atmospherically derived nitrogen (N) to watersheds. This novel approach was applied, on a small scale, to address the question of the importance of atmospheric N deposition to Lake Tahoe eutrophication. Measurements of  $^{17}\text{O}$  oxygen isotopes in nitrate aerosols collected in the Tahoe Basin showed similar enrichments as those analyzed from southern California with an average  $\Delta^{17}\text{O}$  of 24‰. This atmospheric isotopic signal was assumed to be the same at Lake Tahoe based on comparative measurements, which was deposited to the lake surface generating a water column nitrate  $\Delta^{17}\text{O}$  average of 4‰. This means that ~20% of water column nitrate has retained its photochemical isotopic character and has not been recycled by biota. Using N deposition estimates from other Tahoe researchers, we derive a lake average nitrification rate of 1 mg/m<sup>2</sup>/yr. A significant number of atmospheric and lake nitrate samples were lost during the analytical process due to unexpected loading of organic material in the solutions. Consequently, a portion of the samples collected have been archived and will be analyzed and reported to the ARB once a more effective analytical method has been developed. Initial test results on this new analytical method suggest that it will be applicable by the end of 2007.

## **Executive Summary**

### **Background**

Nitrogen oxides ( $\text{NO}_x$ ) emitted by combustion processes, such as internal combustion engines in automobiles, is converted by photochemical reactions in the atmosphere to nitrate (nitric acid and mineral nitrates), which can be deposited and used as a nutrient in watershed ecosystems. It has been shown that during these photochemical reactions, the  $^{17}\text{O}$  isotope is enriched in the product nitrate relative to that found in nitrate produced by oxidation of organic nitrogen compounds via nitrifying bacteria (Michalski et al. 2004). This  $^{17}\text{O}$  tracer can therefore be used to track the importance of new nutrients (deposition of atmospheric nitrate) relative to the recycling of existing nutrients (nitrification). The role of new nutrient addition to Lake Tahoe is critical to understanding the loss of water column clarity due to algal growth that is stimulated by increased nitrogen loading. This work details the results that explored the utilization of  $^{17}\text{O}$  tracer to detect atmospheric nitrate loading within Lake Tahoe's nitrogen budget to assess the link between atmospheric nitrogen pollution and water clarity of the lake.

### **METHODS**

The primary goal of the research was to establish the  $\Delta^{17}\text{O}$  values (the measure of  $^{17}\text{O}$  excess relative to  $^{18}\text{O}$ ) of two nitrate sources to Lake Tahoe (atmospheric deposition and microbial nitrate) and to measure the  $\Delta^{17}\text{O}$  values of lake nitrate as a function of space and time. The atmospheric nitrate isotopic end member was determined based on nitrate collected on a hi-volume total suspended particle (TSP) sampler. The sampler was installed at the old Lake Forest Fish Hatchery site currently used by UC Davis' Tahoe Research Group (TRG). Fifty-two, week-long TSP samples were collected at a flow rate of 1 meter<sup>3</sup>/min on 8 by 11 inch glass fiber filters. Filters were rinsed and analyzed for their anion composition using ion chromatography. Nitrate was isolated and analyzed for its oxygen isotopic composition by methods described by Michalski et al. (2002).

Lake water nitrate was collected during 8 field trips, at two locations on the lake and at 5 depths (surface, 100, 200, 300, and 400 meters). To attain sufficient nitrate analysis, 20-40 liters of water were collected and the anions were concentrated onto an anion exchange resin as described by Chang et al. (1999). Stream water discharging into the lake was also collected once during the field work, in April of 2005, at 10 streams surrounding the lake. One soil pit was also excavated and nitrate was extracted. Columns were eluted as described by Silva et al. (2000) and isotopic analysis was performed.

### **Results**

Anion analysis of TSP filters showed no seasonal trends in nitrate concentrations, but did show a seasonal fluctuation in sulfate loading. Aerosol nitrate extracted from TSP filters showed  $\Delta^{17}\text{O}$  values similar to those observed in aerosol and rainwater nitrates collected in southern California. Analytical difficulties (see below) limited the

data set and obscured the expected seasonal trend in nitrate  $\Delta^{17}\text{O}$  values. Regardless, the data were sufficient to establish the atmospheric nitrate  $\Delta^{17}\text{O}$  end-member value at 24‰. By end-member we mean one of two end points on a mixing line, in this case two distinct  $\Delta^{17}\text{O}$  values, 24‰ for atmospheric nitrate and 0‰ for nitrification. This second  $\Delta^{17}\text{O}$  end-member, (microbial) was confirmed to be zero by analysis of soil extracted nitrate which had no observable  $\Delta^{17}\text{O}$  value as was expected from biologic nitrate.

Lake water column nitrate had observable positive  $\Delta^{17}\text{O}$  values. This indicates that the recycling of biomass nitrogen is sufficiently slow, relative to the atmospheric deposition of photochemical nitrate, to retain the deposition signal. Average water column  $\Delta^{17}\text{O}$  values were 3-4‰, which translates to approximately ~15% of the lake water nitrate has not been recycled by algal uptake, death, decay and nitrification. From these data combined with previous deposition rate estimates, we can estimate the total amount of nitrate derived by nitrification, from which the residence time can be calculated and, by proxy, the time required for nitrogen levels to drop and lake clarity to recover. Using a 0.13 g N m<sup>2</sup>/yr deposition estimate by Jassby et al.(1994), we derive a lake wide nitrification rate of 1.0 g N m<sup>2</sup>/yr, which is in good agreement with incubation experiments of Paerl (1972). Seasonal fluctuations in column depth nitrate  $\Delta^{17}\text{O}$  values shows evidence of surficial deposition (higher  $\Delta^{17}\text{O}$  values) and sediment nitrification (decreasing  $\Delta^{17}\text{O}$  values) as a function of time during stratified conditions. Stream water  $\Delta^{17}\text{O}$  values were lower than lake values, suggesting vadose zone processes during stream transport are more effective at recycling nitrate than lake processes.

The study was hindered by analytical limitations of the existing method. While we attained sufficient data to make some qualitative and semi-quantitative interpretations of N deposition and recycling in the Tahoe Basin, a number of samples yielded no isotopic data, and obscured potential seasonal and spatial trends. The issues revolved around unknown dissolvable organic material (DOC) in aerosol and watershed samples. This unknown substance, some DOC derivative, evaded cleanup methodology that worked in previous studies. The carbon from the material reacted with O<sub>2</sub> derived from the nitrate analysis creating CO and CO<sub>2</sub> that is unfit for  $\Delta^{17}\text{O}$  analysis. As this contaminant issue became apparent, we halted isotopic analysis and archived the remaining aerosol and lake samples for nitrate until this issue can be resolved analytically. We have spent the last year developing a new methodology that is unaffected by DOC and are currently conducting control experiments. We expect to complete these controls by the end of 2006 and analysis of the remaining samples in early 2007. At that juncture, we will evaluate the data and publish the completed results.

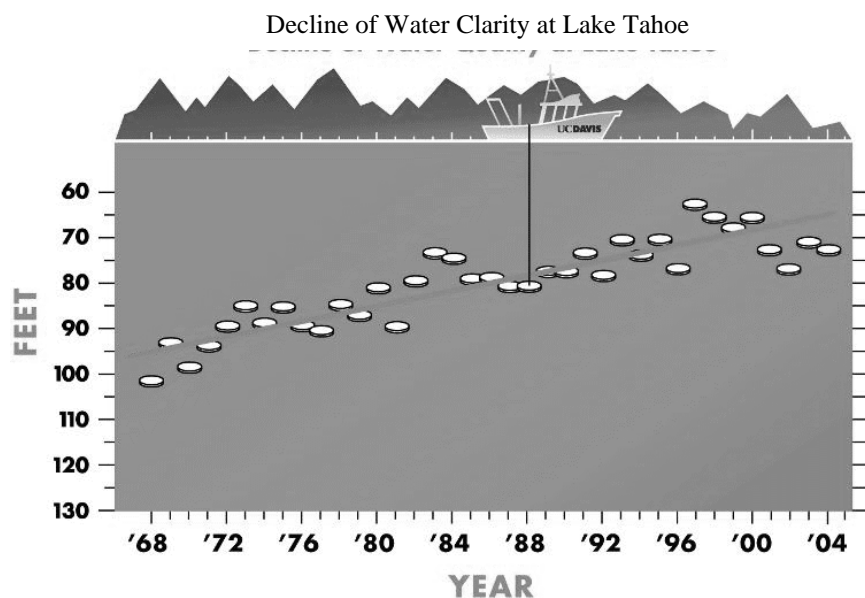
### **Conclusion**

The two primary goals of the project were completed: the establishment of nitrate  $\Delta^{17}\text{O}$  mixing endmember values (atmospheric and biologic) and the detection and quantification of these two sources within Lake Tahoe. These estimates on the biologic and deposition nitrate fluxes based on stable isotopes have established constraint on nitrogen dynamics on a lake-wide scale and verified that local, point studies can be scaled to a larger area without significant error. Additional data that will evolve from the newly developed methodology will help clarify seasonal and spatial isotopic variations.



## INTRODUCTION

The water clarity of Lake Tahoe is world renown, but Secchi plate measurements, shown in figure 1, have shown that the clarity has been steadily decreasing since the late 1960s (Goldman, 1988). The primary cause is still uncertain, but it is firmly established that clarity loss and increases in water column algal concentrations are directly correlated, indicating algal growth is a (dominant) factor (Goldman, 1988; Holm-Hansen et al., 1976; Vincent and Goldman, 1980). Research suggests that the increase in algal growth is primarily due to increases in the limiting nutrients, phosphorous and nitrogen. Over this same time frame, the lake has gone from a classic alpine nitrogen-limited lake (excess phosphorous) to one where phosphorous is now the limiting nutrient (Burgy and Knight, 1974; Goldman, 1988; Hatch et al., 1999). This indicates that since the 1960's the lake has accumulated a significant amount of bioavailable nitrogen, which has spurred algal growth, leading to decreased water clarity.



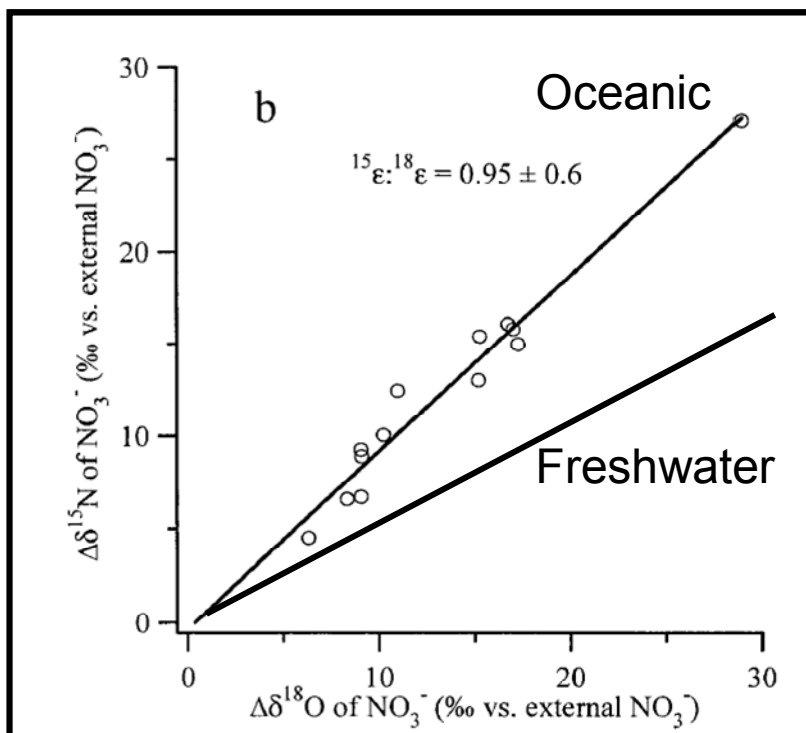
**Figure 1.** Loss of optical depth based on Secchi plate measurements conducted by the Tahoe Research Group at UC Davis. Loss of over 30% since the late 1960s is thought to be mainly due to algal growth in the water column and increased sediment loading from development and traffic. Adapted from the Tahoe research Group <http://terc.ucdavis.edu/clarity.html>

The source of this additional nitrogen is still questioned. Development of wetlands surrounding the lake have eliminated riparian zones that normally act as nutrient filters for runoff from the surrounding watershed (Coats and Goldman, 2001; Hatch et al., 1999; Hatch et al., 2001; Leonard et al., 1979; Naslas et al., 1994). Basin population increases and the establishment of recreational activities have increased fertilizer usage within the basin and increased the potential for leakage from pipes that export sewage from the basin, both potential sources of available nitrogen and phosphorus (Burgy and Knight, 1974; Loeb and Goldman, 1979; Mitchell and Reisenauer, 1974). A large transient tourist population has contributed a significant amount nitrogen oxides, emitted from automobiles, and fixed nitrogen is also likely imported from urban pollution outside the basin (Jassby et al., 1995; Jassby et al., 1994; Tarnay et al., 2001; Tarnay, 2001; Zhang et al., 2002). Deposition studies suggest that a major component of lake nitrogen is derived from direct deposition of this atmospheric nitrogen to the lake surface (Jassby et al., 1994). However, deriving the amount of nitrogen deposited relies upon accurate estimates of wet and dry deposition taken at by a relatively limited

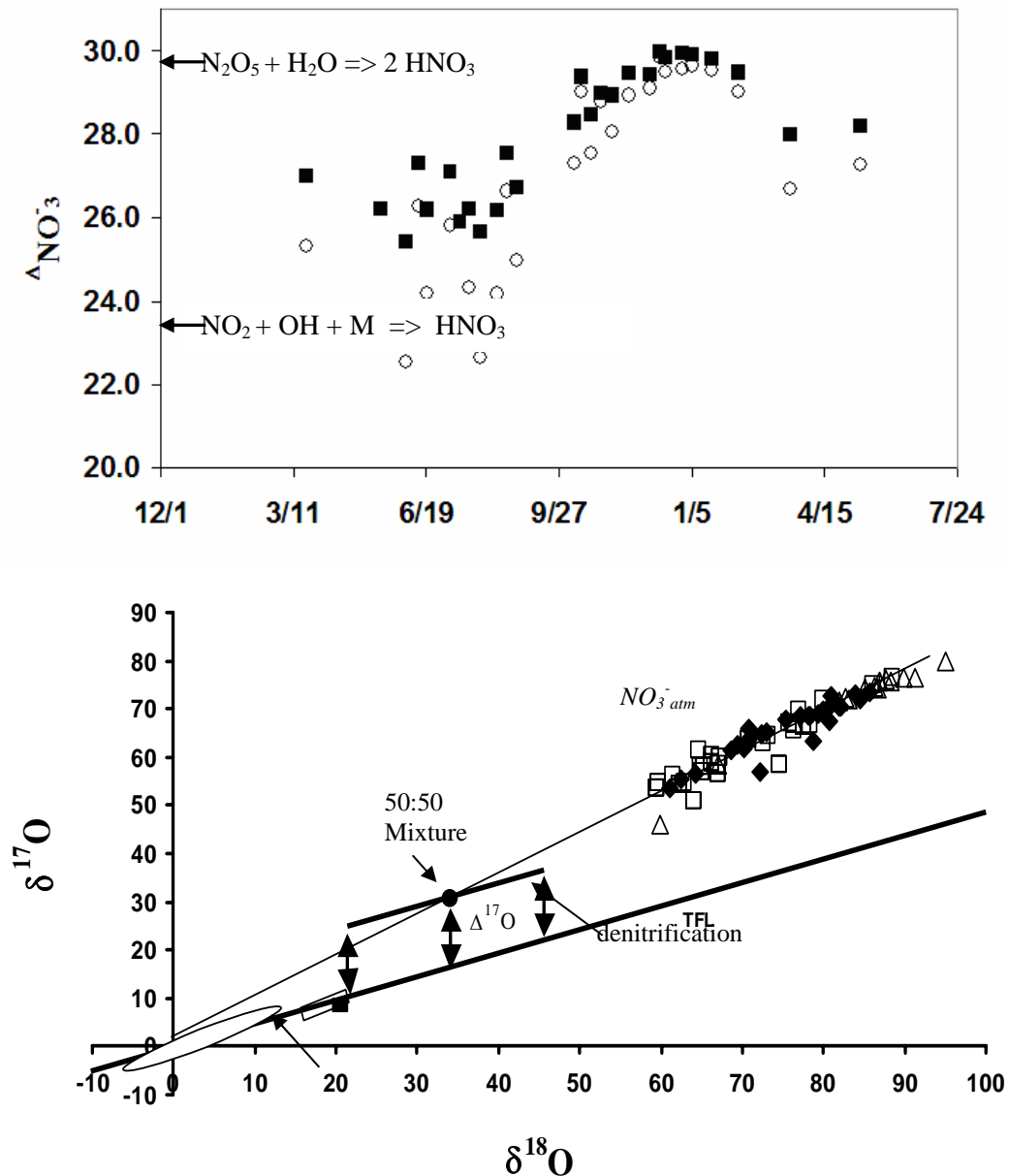
spatial/temporal network and accurately extrapolating these estimates across the large surface area of the lake. Both measurement errors and extrapolation methods/models are subject to significant error.

Even less is known about the rate of N deposition relative to internal biologic recycling of nitrogen. Algae growing in the photic zone (~100 meters) eventually dies, sinks, decomposes and is converted to inorganic nitrogen (nitrate and ammonium) by water column and sedimentary bacteria (Abbott et al., 1984; Goldman, 1988; Holm-Hansen et al., 1976; Paerl et al., 1975). Inorganic nitrogen (primarily as nitrate) is then mixed throughout the lake by currents and annual vertical mixing, returning nutrients to the photic zone for re-utilization (Paerl et al., 1975). Direct deposition of atmospheric nitrate ( $\text{NO}_3^-_{\text{atm}} = \text{HNO}_3 + \text{mineral NO}_3^-$ , the end product of automobile exhaust and biomass burning) is mixed with nitrified N from biomass and represents new nitrogen addition to the system. Attempts to constrain nitrogen dynamics using nitrate concentration measurements are not feasible as they are spatially and temporally variable, depending on mixing, biologic loading, season, temperature and numerous other highly variable parameters, including the limited sampling capability at such a large lake. Stable isotopes of oxygen in nitrate have potential to resolve such source and sink budgets where concentration analysis fail.

Nitrate exists primarily as the  $^{14}\text{N}^{16}\text{O}_3$  specie but may also exist as an isotopomer, primarily by the single substitution of either a  $^{15}\text{N}$ ,  $^{18}\text{O}$ , or  $^{17}\text{O}$  atom. The production of nitrate (biological or photochemical) generates isotopomers based on the isotopic composition of the sources (nitrogen and oxygen) and kinetic or equilibrium



**Figure 2.** Dual isotope plots of  $\delta^{15}\text{N}$  versus  $\delta^{18}\text{O}$  for nitrate as a function of nitrate loss. Loss of nitrate by algal uptake in oceanic environments fractionates  $^{15}\text{N}$  and  $^{18}\text{O}$  in a 1:1 manner. In freshwater, loss of nitrate by denitrification results in  $^{15}\text{N}$  and  $^{18}\text{O}$  of the residual nitrate being increased in 1:2 manner by a process that likely depends on kinetics or equilibrium isotope effects. These linear arrays can thus be used as tracers of biological function. Figure taken from (Granger et al., 2004)



**Figure 3.** The bottom plot shows the terrestrial fractionation line (TFL) for oxygen isotopes predicted by equilibrium and kinetic isotope effects (nitrification and fertilizer nitrate fall on this line (oval)) and the range of  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values for various nitrate compounds found in nature.  $\text{NO}_3^-_{\text{atm}}$  (aerosols and rainwater from Riverside ( $\square$ ), La Jolla ( $\blacklozenge$ ), and Bakesfield ( $\Delta$ ) in southern California collected from 1997-2002) are offset from the TFL (data points), having  $\Delta^{17}\text{O}$  values ranging from 20-32‰. A 50:50 mixture of nitrate derived from microbial nitrifiers and  $\text{NO}_3^-_{\text{atm}}$  that is subsequently denitrified lies on a line parallel to the TFL, but the  $\Delta^{17}\text{O}$  value is preserved (vertical arrows). The  $\text{NO}_3^-_{\text{atm}}$  portion of total nitrate can be quantified using the bulk  $\Delta^{17}\text{O}$  value, even as the  $\delta^{18}\text{O}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{17}\text{O}$  values change, making  $\Delta^{17}\text{O}$  a conserved tracer. Upper plot shows the  $\Delta^{17}\text{O}$  values of nitrate aerosols collected in La Jolla, CA. in 1997-1998 ( $\circ$ ) and estimates based on photochemical modeling ( $\blacksquare$ ). Note the seasonal influence of ozone on the  $\text{NO}_3^-_{\text{atm}}$   $\Delta^{17}\text{O}$  values, showing how oxygen isotopes can be used to trace changes in oxidation chemistry. High amounts  $\text{N}_2\text{O}_5$  hydrolysis ( $\Delta^{17}\text{O} \sim 30\text{‰}$ ) increases the  $\text{NO}_3^-_{\text{atm}}$   $\Delta^{17}\text{O}$  value in winter, while homogenous reactions with OH ( $\Delta^{17}\text{O} \sim 20\text{‰}$ ) lower the values in spring/summer. Isotopic abundances given are ratios (R) of the minor isotope relative to the main isotope, which for oxygen is  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$ . Small changes in isotopic abundances ( $\delta$ ) are reported relative to the ratio of an accepted standard, whose  $\delta$  is defined as zero. These small changes are given in units of parts per thousand, e.g. per mil (‰).

$$\delta^{18}\text{O}(\text{‰}) = [(R_{\text{sample}} - R_{\text{stand.}})/R_{\text{stand.}}] * 1000 \quad (\text{EQ. 1})$$

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - .52 \delta^{18}\text{O} \quad (\text{EQ. 2})$$

$\Delta^{17}\text{O}$  is a measure (verticle distance) of the offset from terrestrial fractionation line.

fractionation factors associated its formation (Kendall, 1998; Mayer et al., 2001).

Kinetic or equilibrium imprints can also be generated by biotic fractionations during nitrate loss processes such as denitrification. One example is the oxidation of ammonium to nitrate by nitrifying bacteria. During the addition of oxygen atoms during nitrification, two of the added atoms are derived from surrounding cell water and one derives from dissolved  $O_2$  (Andersson and Hooper, 1983). The  $\delta^{18}O$  value of water is highly variable in space and time and is impacted by longitude, latitude, altitude, time of year, temperature, evapo-transpiration, evaporation and condensation (Bowen and Wilkinson, 2002). Likewise, while the  $\delta^{18}O$  of air,  $O_2$  is essentially constant, its value in soil pore spaces or the water column varies due to fractionations related to respiration, diffusion and chemical oxidation of minerals (Angert et al., 2001; Blunier et al., 2002). Therefore the  $\delta^{18}O$  of nitrate from nitrification in a given microenvironment is unique and is a function of hydrologic and biogeochemical factors. This uniqueness of both  $\delta^{18}O$  and  $\delta^{15}N$  signatures allows them to be used as a tracer of both biologic activity and hydrologic transport. Loss processes can also isotopically imprint the residual nitrate. Denitrification preferentially utilizes lighter isotopes leaving the residual nitrate isotopically enriched (Boettcher et al., 1990; Kendall, 1998; Spoelstra et al., 2001). It has been observed that, while this enrichment is different for  $^{15}N$  and  $^{18}O$ , they are linearly related (Figure 2). This linearity is due to mass dependant fractionation where the relative mass difference is critical. For example, fractionation factors due to diffusion are a function of the square root of molecular mass, which for  $^{15}NO_3$  is 1.008 and for  $N^{18}O^{16}O_2$  is 1.016 (each relative to  $^{14}N^{16}O_3$ ) or 8‰ and 16‰. In other words twice the fractionation occurs in the  $^{18}O$  substituted molecule compared with the  $^{15}N$  substituted because of the 2:1 atomic mass change ( $^{18}O - ^{16}O = 2$ ,  $^{15}N - ^{14}N = 1$ ). Linear changes of two or more isotopes with changes in concentration are indicative of mass dependent loss process, distinguishing them from the mixing of isotopic reservoirs.

A similar mass dependant relationship exists between the three stable isotopes of oxygen, with  $\delta^{17}O \sim 1/2\delta^{18}O$  and most terrestrial compounds plotting of a line of slope 1/2 (the terrestrial fractionation line) in dual isotope space (Fig. 3) (Miller et al., 2002; Young et al., 2002). Notable exceptions to this rule is isotope partitioning during ozone formation where  $\delta^{17}O = \delta^{18}O$  (Heidenreich, III and Thiemens, 1983; Thiemens and Heidenreich, III, 1983) and this deviation from the terrestrial fractionation line is quantified by  $\Delta^{17}O = \delta^{17}O - .52 \times \delta^{18}O$  (Miller, 2002). Positive  $\Delta^{17}O$  values are common in compounds where oxygen atoms are transferred during oxidation reactions involving ozone (Savarino et al., 2000; Savarino and Thiemens, 1999). Most notable is  $HNO_3$  produced by oxidation of  $NO_x$ , which has  $\Delta^{17}O$  values of 20-30‰ (Michalski et al., 2003; Michalski et al., 2004). Because primary pools of oxygen available for nitrification ( $H_2O$  and  $O_2$ ) have  $\Delta^{17}O$  values of zero, any measure of  $\Delta^{17}O$  in soils or watersheds must be due photochemical  $HNO_3$  making  $\Delta^{17}O$  measurements a hyper-sensitive tracer of N deposition (Michalski et al., 2004) and the percentage of atmospheric nitrate in the total nitrate pool is easily determined (Figure 4,5). Also, kinetic fractionations associated with abiotic or biotic (denitrification) reactions do not alter  $\Delta^{17}O$  values, as they follow normal mass dependent fractionations (Figure 4). The sensitivity of this tracer of  $NO_3^-_{atm}$  is orders of magnitude better than  $\delta^{18}O$  techniques (Kendall, 1998) which lead to ambiguous results when applied to watershed studies (Mayer et al., 2002). Because

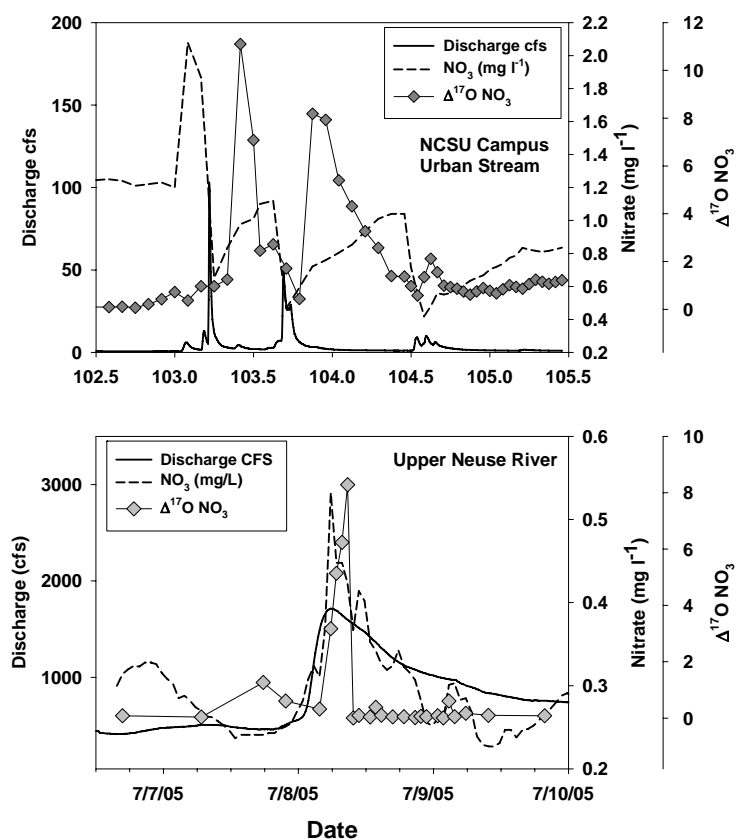
$\Delta^{17}\text{O}$  evaluations of  $\text{NO}_3^-_{\text{atm}}$  is only limited by the analytical error, not by isotopic budgets (e.g., all other sources and processes have zero  $\Delta^{17}\text{O}$  values) the 0.1‰ analytical resolution leads to a detection limit for  $\text{NO}_3^-_{\text{atm}}$  of 0.5% of total nitrate (Michalski et al., 2004).

### Using $\Delta^{17}\text{O}$ values of $\text{NO}_3^-$ in the Lake Tahoe Watershed

We can approximately quantify nitrates from source to outflow by applying isotopic and mass balance. For Lake Tahoe, we can assume that the system is in steady state with respect to nitrate balance and so the nitrate fluxes (F) can be characterized by

$$F_{\text{atm}} + F_{\text{bio}} = F_{\text{water}} + F_{\text{denit}} + F_{\text{uptake}}$$

Since denitrification and uptake chemically alter nitrate to other N compounds, in



**Figure 4.**  $\Delta^{17}\text{O}$   $\text{NO}_3^-$ , discharge and nitrate concentrations in a small urban stream and the upper river near Raleigh NC. The  $\Delta^{17}\text{O}$  on the right axis can be converted to  $\text{NO}_3^-_{\text{atm}}$  by dividing by 21‰, this regions deposition value. If the assumption of a homogenous nitrate pool that is incorporated into hydrologic models were true, we should see no change in isotopes with changing source strength. This is clearly not observed. The  $\Delta^{17}\text{O}$  peak values do not correspond to the peak nitrate concentrations or the discharge peaks, but occur during falling portions of the hydrographs. This behavior is due changes of export probability of  $\text{NO}_3^-_{\text{atm}}$  that accumulated on the surface during the dry season, which is being flushed past the plant and bacterial biomass by the rain. The upper Neuse River exhibits different behavior with  $\text{NO}_3^-_{\text{atm}}$  more closely aligned with discharge and concentration changes. This highlights then nitrate source flux differences for biogeochemically different systems.

terms of mole fractions of nitrate ( $x$ )

$$x \cdot F_{\text{atm}} + (1-x) \cdot F_{\text{bio}} = F_{\text{water}} \quad (\text{EQ. 3})$$

We propose to independently determine  $x$ , the proportion of atmospherically derived nitrate, by using  $\Delta^{17}\text{O}$  analysis and applying isotopic mass balance

$$\Delta^{17}\text{O}_{\text{water}} = x \cdot \Delta^{17}\text{O}_{\text{atm}} + (1-x) \cdot \Delta^{17}\text{O}_{\text{bio}} = x \cdot 23\text{‰} + (1-x) \cdot 0\text{‰}$$

$$x = \Delta^{17}\text{O}_{\text{water}} / 23\text{‰}$$

In the above, the 23‰ is the average  $\Delta^{17}\text{O}$  value for nitrate aerosols from southern California and the 0‰ value for biological nitrate are estimates from known nitrification oxygen reservoirs ( $\text{O}_2$  and  $\text{H}_2\text{O}$ ). These two values will be determined empirically for the Lake Tahoe Basin by nitrate aerosol isotopic analysis and soil nitrate analysis. Once these two end-members are quantified, the appropriate  $x$  values (percent of atmospheric nitrate retained in the lake) can be determined.

An example of using the high sensitivity of the  $\Delta^{17}\text{O}$  signature in detecting atmospherically deposited nitrate can be seen in data from the Neuse River basin in North Carolina. The NC peak  $\Delta^{17}\text{O}$   $\text{NO}_3^-$  values are not observed with peak discharge or peak nitrate concentrations in an urban stream or at an upper river site (Showers, unpublished data, Figure 6). Using a  $\Delta^{17}\text{O}$  precipitation value of +21 for this site, the integrated mass flux of ADN is 20-25%, slightly higher in the stream than in the main river. The changes of  $\delta^{18}\text{O}$  nitrate do not match trends of  $\Delta^{17}\text{O}$  nitrate, indicating that other processes such as nitrification and denitrification may be affecting the  $\delta^{18}\text{O}$  nitrate values at this site (Figure 7).

We have had success in assessing N deposition in streams in southern California and North Carolina using  $\Delta^{17}\text{O}$  signatures in nitrate collected in the watershed. In southern California site, near UC Riverside, we observed various proportions of  $\text{NO}_3^-_{\text{atm}}$  in soils ranging from >90% in surface litter to ~10% in nitrate found to depths of 1 meter. We also observed high variability in the proportion of  $\text{NO}_3^-_{\text{atm}}$  found in stream water nitrate. This variation is related to export dynamics such as the importance of overland flow relative to groundwater inputs to the streams (Michalski et al. 2004). Similar dynamical effects have been observed in reaches of the Neuse River in North Carolina (Figure 4, Showers, unpublished data). Note that the nitrate  $\Delta^{17}\text{O}$  values can peak with nitrate concentration increases or be out of phase of the increase. In phase phenomena is likely the result of overland flow regimes, where dry deposited nitrate is directly washed to the stream, which then shows as simultaneous increases in nitrate concentration and  $\Delta^{17}\text{O}$  increases. Out of phase isotope/concentration data are the result of the movement of precipitation through the soil profile, where hydrological pressure is pushing soil nitrate, generated by microbial processes, out into the stream first, followed by atmospheric nitrate that must move a greater distance through the soil column and therefore lags the biotic nitrate peak (Figure 4). This data highlights the ability to distinguish the importance atmospheric nitrate within the total nitrate pool by using  $\Delta^{17}\text{O}$  analysis.

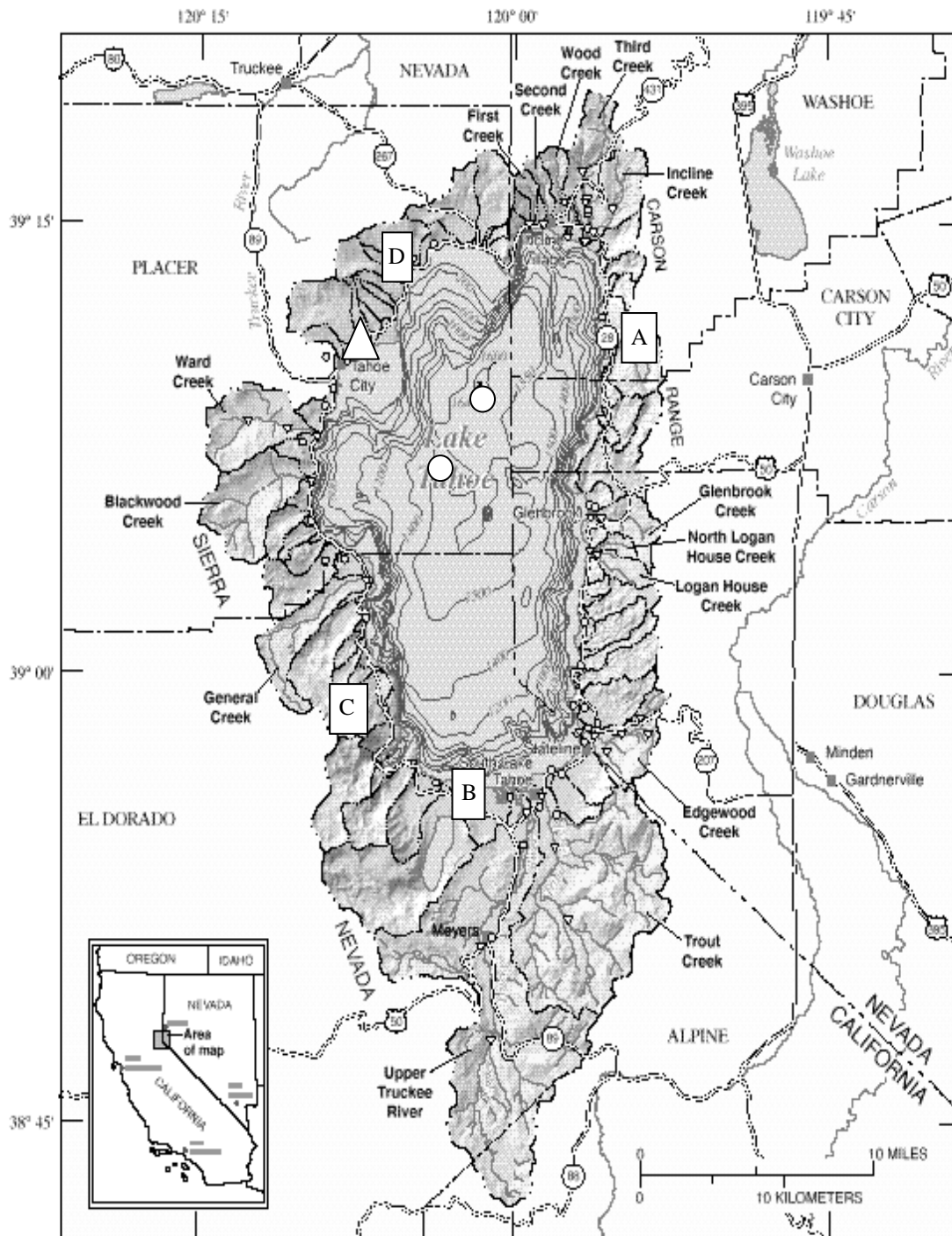
## **MATERIALS AND METHODS**

### **Sample Collection**

Aerosol samples were collected using a high-volume whole air total suspended particle collector (ThermoAndersen). Samples were collected at the Tahoe Research Group's Lake Forest research station located in Tahoe City, CA on the north western shore of Lake Tahoe. Air was pulled through an 8 by 11 inch glass fiber filter at a rate of 1.1 m<sup>3</sup>/min using a Fuji regenerative blower motor (model VFC200P-5T). The sample collections spanned ~7 days for a total sampling volume of ~1 × 10<sup>4</sup> m<sup>3</sup>. Filters were placed in a large Ziplok plastic baggie to which 60ml of Millipore water was added. The bag was sealed and mechanically shaken for 2 min, and then allowed to stand for an additional 5 minutes. One corner of the bag was clipped and the filter was squeezed so the extract was purged into a 50 ml centrifuge tube. Filter absorption of the extract was typically 10 ml, so while anion concentration analysis is based on 50 ml, mass calculations are assessed on the initial 60 ml. The filter extract was filtered at 0.2 micron using a Steriflip device. Anion analysis was performed with a Dionex 2020i ion chromatograph using 20 mmol carbonate/bicarbonate eluent and acid suppressed electrical conductivity detection.

Watershed samples were obtained during 8 lake field trips and one basin perimeter transect of various streams (April 2005). The stream samples were collected at the sites detailed in Figure 5. Lake water samples were collected at two locations called Mid-Lake (39° 06.851' N; 120° 03.441' W ) and Bouy (39° 06.612' N; 120° 04.521' W ) at depths of 100, 200, 300, and 400 meters, plus surface water. Samples were collected using large volume Niskin bottle casts, with the water being transferred to pre washed 20L Naglene carboy bottles. The water was transported to the Lake Forest station and was drawn by gravity siphon (10 feet) through a 0.45 micron filter and anion exchange resin (Biorad 50 mesh) overnight (Chang et al., 1999; Silva et al., 2000). The anion resin cartridges were capped and refrigerated until the day of extraction. Stream waters were collected in the same fashion. Several well water samples from the basin were obtained from Jim Thomas at the Desert Research Institute and processed in the same manner. The anion resins were stripped using 15 ml of 1 M HBr, with the Br<sup>-</sup> displacing the lake water anions such as sulfate, nitrate, and carbonate that was concentrated on the resin. The excess HBr was neutralized by using pre-washed Ag<sub>2</sub>O and the resulting solid AgBr and AgCO<sub>3</sub> was removed by centrifuging. At this point, the solution is primarily Ag<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> ions.

Initial tests on the lake water collection methodology (Chang et al., 1999; Silva et al., 2000) revealed that using the suggested 200 mesh resin bead size resulted in slow drip rates and up to 5 days of gravity flow to completely filter the 20 liter volumes. These resins were also subject to blockage from particulate matter clogging the flow path. Therefore, we tested 50 mesh resin beads and found that rapid flow (>100 ml/min) still trapped ~90% of solution nitrate and did not alter the isotopic composition. After the second lake collection, we switched to this larger bead size and 20 liter water feeds were completed in ~5 hours.



Base from U.S. Geological Survey digital data, 1:24,000 and 1:100,000, 1969-85. Universal Transverse Mercator projection, Zone 11

Bathymetric contours from Rush, 1973. Compiled from soundings made by the U.S. Coast and Geodetic Survey (1923)

**EXPLANATION**

- |  |  |
|--|--|
|  Selected hydrologic basin used in this study |  Bathymetric contour, in feet below highest legal lake-surface altitude (6,229.1 feet above U.S. Bureau of Reclamation datum of 1929) |
|  Boundary of Lake Tahoe Basin                 |  Surface-water site   |
|  Boundary of subbasin                         |  Ground-water site  |

**Figure 5.** Map of the stream locations where water samples were collected in April, 2004. Sites included General Creek, Blackwood Creek, Ward Creek, Second Creek, First Creek, Logan House Creek, Sand Harbor (A), Eagle Falls (B), Meeks Bay Creek (C), and Dollar Hill (D). Lake sampling sites are shown as white circles and aerosol collections were conducted near Tahoe City (white triangle).



an identical procedure. A slight stoichiometric excess of 1 M BaCl<sub>2</sub> is added to the solutions to precipitate sulfate as BaSO<sub>4</sub>, which was removed by centrifugation. Excess Ba<sup>2+</sup> and other cations are exchanged for H<sup>+</sup> by passing through cation resin (Biorad AG1-50x). The resin also removes organic acids and other components of DOC. The acidic solution is again neutralized with Ag<sub>2</sub>O and filtered to remove solid AgCl (from excess BaCl<sub>2</sub>), and then freeze-dried. The dried solids are re-hydrated, filtered at 0.2 micron, and tested for purity by ion chromatography and dissolution completion (this should be AgNO<sub>3</sub>, which is highly soluble). The solution is again freeze-dried, then re-hydrated with 75 micro liters of Millipore water and pipetted into a pre-weighed solid silver capsule. The capsule containing the AgNO<sub>3</sub> solution is dried in a centrifugal freeze drier. The capsules are then reweighed to determine the mass of AgNO<sub>3</sub>.

The silver boats containing the sample AgNO<sub>3</sub> are thermally decomposed under vacuum as described by (Michalski et al., 2002). The resulting O<sub>2</sub>/NO<sub>2</sub> mixture is purified to O<sub>2</sub> by cryogenically removing NO<sub>2</sub> in two liquid nitrogen traps. The O<sub>2</sub> yield is measured using a capacitance manometer and a calibrated volume containing 5A molecular sieve. The O<sub>2</sub> is then transferred to a Finnigan-Mat 251 isotope ratio mass spectrometer and <sup>17</sup>O/<sup>16</sup>O and <sup>18</sup>O/<sup>16</sup>O ratios are determined by monitoring masses 32, 33, and 34. Oxygen delta values are reported with respect to Vienna Standard Mean Ocean Waters (VSMOW), the internationally accepted oxygen isotope standard.

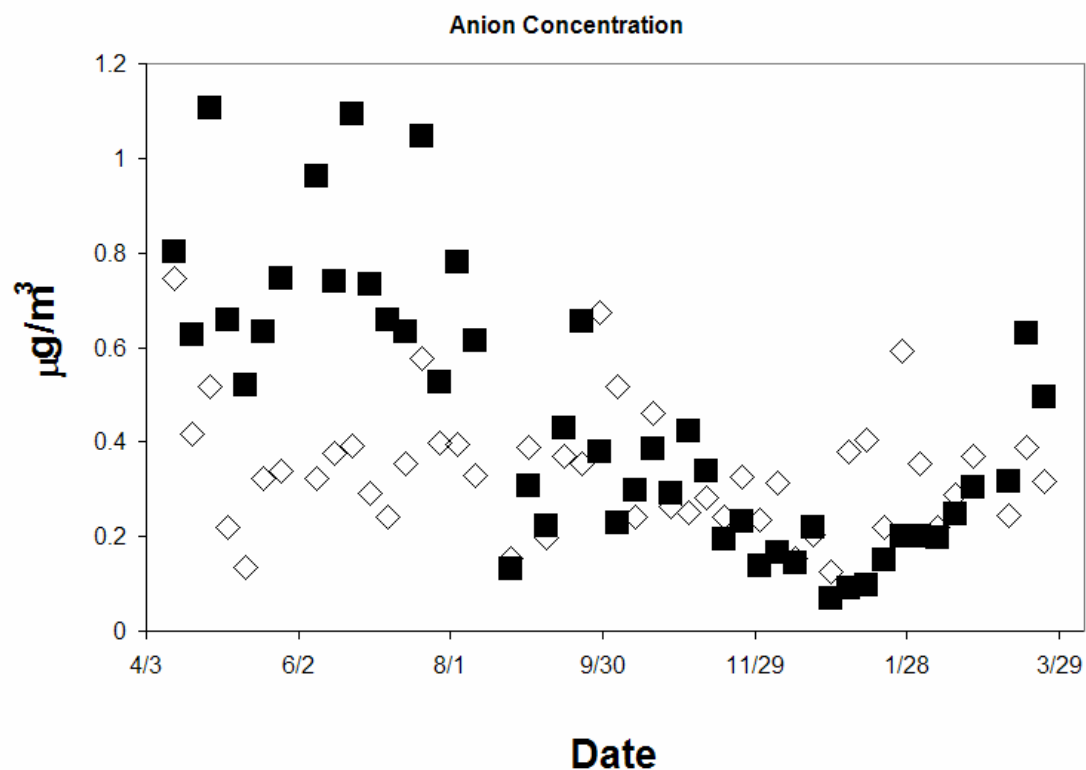
## **RESULTS**

### **Aerosols**

The aerosol sulfate and nitrate concentrations measured at the Tahoe City site are shown in Figure 6. Nitrate concentrations ranged from 0.13 to 0.75 μg/m<sup>3</sup> with an average of 0.34 μg/m<sup>3</sup> and standard deviation of 0.13 μg/m<sup>3</sup>. There is no apparent seasonal trend in aerosol nitrate concentrations, but five dates throughout the year have concentrations in excess of the standard deviation of the mean indicating episodic NO<sub>x</sub> events. These values agree well with measurements from the IMPROVE network which showed the annual concentration of atmospheric nitrate at Lake Tahoe to be 0.4 μg/m<sup>3</sup> with little seasonal variation. The aerosol nitrate concentration analysis is based on two assumption 1) that "aerosol nitrate" is in fact a combination of nitrate salts in aerosol form and gaseous HNO<sub>3</sub> that reacts on the filter media or existing aerosols retained on the filter over the sampling period. 2) That no volatilization of nitrate has occurred. Volatilization occurs because the nitrate salt NH<sub>4</sub>NO<sub>3</sub> has a significant vapor pressure, depending on ambient temperature and humidity, and can be lost over time. No NH<sub>4</sub><sup>+</sup> data was attained during this study, so it is difficult to assess how the NH<sub>4</sub>NO<sub>3</sub>/NO<sub>3</sub><sup>-</sup> varied with season and how much NH<sub>4</sub>NO<sub>3</sub> was lost during the week long sampling periods. Chang et al. (2005, ARB final report "Sampling and Analysis for the Lake Tahoe Atmospheric Deposition Study" , 2005) showed that from 20 to 100% of ammonium nitrate volatilized in aerosol sample collected in Tahoe City in 2002, with an average in excess of 60%. Their average nitrate concentration of .45 μg/m<sup>3</sup> is larger to our 0.32 μg/m<sup>3</sup>, but this would scale to ~ 0.52 μg/m<sup>3</sup> if similar percent volatilization had occurred in our study. Comparing our collection efficiency to that of Chang et al. would require knowledge of NO<sub>x</sub> concentrations, which are not available for our site, but given that annual variations at individual sites are not likely to vary widely, we believe that ~

30% of the nitrate in our samples was likely lost to volatilization. Chang et al. (2005) showed that nitrate concentrations are variable among different sampling locals in the basin. Our goal was to establish how isotopic signatures vary with nitrate concentration and not to evaluate concentration and mass fluxes to the lake, therefore for the purposes of this work these concentration differences between local need not be considered.

Sulfate concentrations exhibited a significantly large degree of variation, ranging from a high of 1.1 to a low of 0.07  $\mu\text{g}/\text{m}^3$ . In contrast to nitrate, the sulfate aerosols did show a seasonal trend, with the highest values occurring in the spring and summer and lowest concentrations in the winter. Both the sulfate mass amounts and the seasonal trends are comparable to those in other studies. The IMPROVE sampling station in South Lake Tahoe showed sulfates ranging from a summer high of 1.1  $\mu\text{g}/\text{m}^3$  to a winter

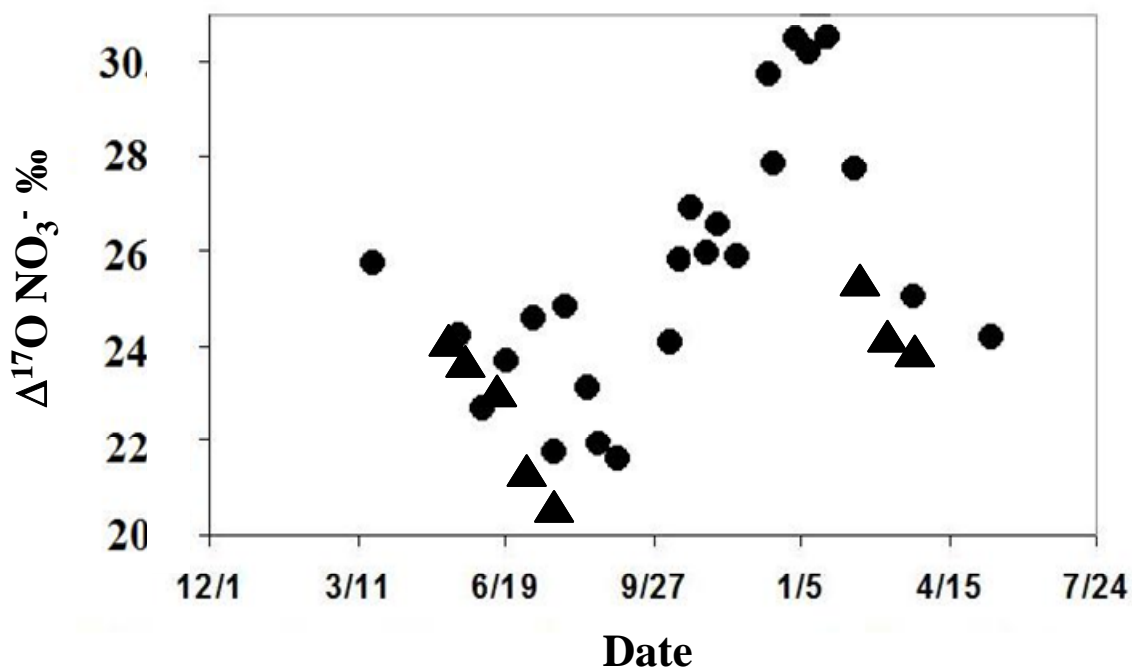


**Figure 6.** Nitrate (open diamond) and sulfate (solid square) concentrations at Tahoe City in ambient air in  $\mu\text{g}$  per cubic meter. Estimated uncertainty of the absolute concentration is  $\pm 10\%$  and relative concentration is  $\pm 2\%$ . Nitrate concentrations exhibit a fairly consistent value of  $0.3 \mu\text{g}/\text{m}^3$  with occasional episodic events. Sulfate shows a clear seasonal trend with decreased loading in the winter months in agreement with measurements by the IMPROVE network <http://vista.cira.colostate.edu/improve/>

average low of  $0.4 \mu\text{g}/\text{m}^3$ .

The absence of any correlation between nitrate and sulfate over the course of the year suggests that the nitrogen and sulfur cycles are decoupled in the Tahoe Basin. While  $\text{NO}_x$ , and hence aerosol nitrate, is overwhelmingly from combustion sources, sulfate has additional important sources, including oxidation of sulfide minerals and stratospheric mixing. It is likely that the increase of sulfate over the nitrate is from sulfate contained in local soils and dust because if it were due to transport from outside basin we should expect to see a similar increase in nitrate concentrations, which is not observed. Isotopic analysis could help resolve the potential source. Sulfide mineral is usually isotopically distinct from photochemical sulfate both in oxygen and sulfur isotopes. However, this is beyond the scope of the current project but could be explored in future studies.

Analysis of the isotopic composition of nitrate aerosols collected during the late spring and summer indicates similar  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values as those observed in southern California. Aerosol nitrate  $\delta^{18}\text{O}$  values ranged from 53 to 63‰ and  $\Delta^{17}\text{O}$  values were between 20 and 25‰ (Figure 7).



**Figure 7.**  $\Delta^{17}\text{O}$  values of nitrate aerosols from Lake Forest (NW of Lake Tahoe, CA; solid triangles).  $\Delta^{17}\text{O}$  values for aerosols from La Jolla (N of San Diego, CA) collected in 1999 (solid circles) for reference. Seasonal trend observed in La Jolla can not currently be resolved due to interference of organic material during the analysis. The data average suggest a lower value  $\sim 23\text{‰}$ . However similarities between spring and summer values suggest that the average  $\Delta^{17}\text{O}$  value for both regions are the similar. The higher values in winter at La Jolla are due to temperature dependence of the  $\Delta^{17}\text{O}$  (increased  $\text{N}_2\text{O}_5$  hydrolysis) and such a winter maximum would theoretically occur in the Tahoe basin. Based on these data and near consistent  $\text{NO}_3^-$  aerosol concentrations though the year, we estimate the annual average  $\Delta^{17}\text{O}$  value of nitrate deposited to the lake is  $24\text{‰}$ . This adjustment has little bearing in the interpretation of lake data discussed in late sections.

## Analytical Difficulties with $\text{NO}_3^-$ Isotopic Analysis Due to Organic Carbon Contamination

While initial results and analytical were successful and encouraging, analytical difficulties arose in during processing of subsequent aerosol and lake nitrate samples. Beginning in the fall, nitrate aerosol isotopic analyses were not successful. While ion chromatographic testing of the purified filter extracts showed only nitrate, the  $\text{AgNO}_3$  combustion process yielded no  $\text{O}_2$  to conduct the mass spectrographic analysis. A small amount, roughly 10%, of the expected yield of non-condensable gas was generated, but mass spectral scans of the gas indicated that it was carbon monoxide (CO) not  $\text{O}_2$  as expected. The lack of detectable anions other than nitrate, the presence of CO and the complete loss of  $\text{O}_2$  indicate that an unknown source of carbon was present in the filter extracts and was not removed by established methods. This carbon then reacted with  $\text{O}_2$  during the combustion phase to produce  $\text{CO}_2$  and CO, with the  $\text{CO}_2$  being cryogenically removed with the  $\text{NO}_2$  in the liquid nitrogen traps. The notion of a increase in organic carbon loading is supported by previous work that showed a mark increase of fine fraction aerosol organic compounds during the transition from summer to fall and winter (Figure 7). We have begun new explorations into additional clean up processes including cation exchange, solid phase extraction (SPE) using C-18 resin, PVP absorption (Haberhauer and Blochberger, 1999), silica gel and high capacity ion chromatography separation. The basis for selecting these purification compounds is their individual absorption characteristic. Cation resin will absorb positively charged organic molecules as well and replacing cations with  $\text{H}^+$ . The slight acidification produced by the cation resin helps protonate weak organic acids making them less negatively charged and more likely to be absorbed by the subsequent compounds. Silica gel absorbs slightly polar compounds, while Polyvinylpyrrolidone (PVP) has been shown to absorb humic substances associated with soil organic matter. C-18 resin is a matrix material with a 18 chain hydrocarbon attached and is effective at absorbing hydrophobic, non polar compounds.

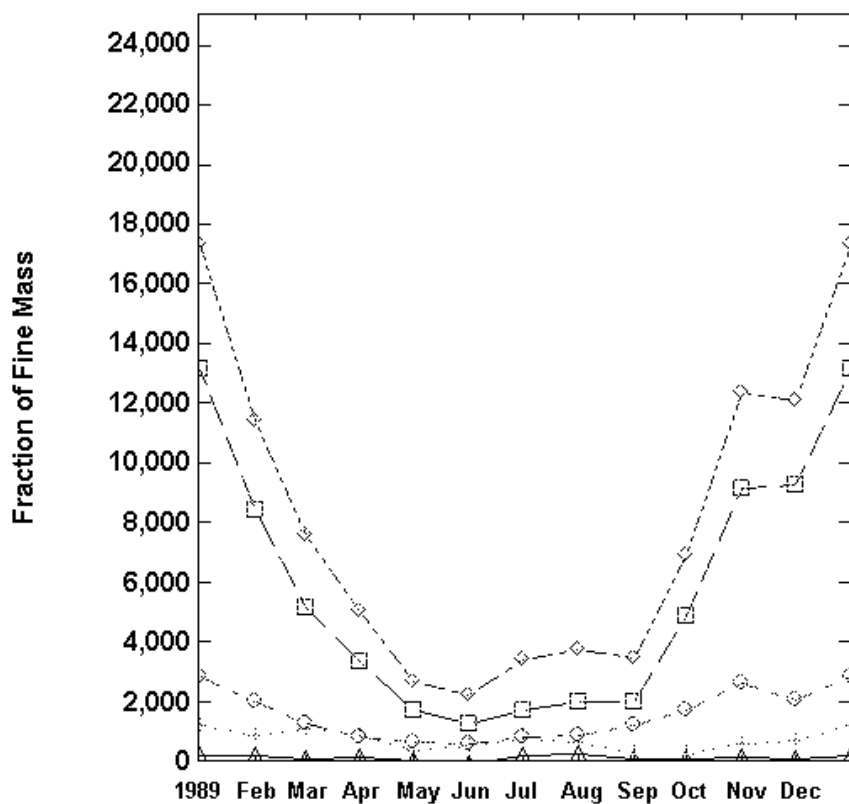
We tested the ability of the nitrate anion to pass through the various absorption media. Nitrate passed through 5 ml bed volumes of each compound with > 95% efficiency. The ultimate procedure consisted of assembling a 30 ml disposable chromatography column (Biorad inc.) which was filled with ~ 5 ml of each compound from bottom to top (PVP, C-18, Silica gel, cation resin) and rinsing with 200 ml of Millipore water. Tests of these columns on samples with high organic loads, solutions having a mild tea color, resulted in strong absorption of the organic material resulting a clear eluent and brown/black discoloration of the resin materials. After purification through the columns, the solutions were pumped on to a high capacity anion column and the anions were separated using carbonate eluent and acid suppression. The resulting  $\text{HNO}_3$  solution was converted to  $\text{AgNO}_3$  using a cation exchangeable membrane in  $\text{Ag}^+$  form (Dionex  $\text{H}^+$  converted by exchange with  $\text{Ag}^+$ ).

None of these methods individually, or in tandem, was successful in eliminating the unknown carbon source. We encountered similar analytical difficulties in lake and stream samples. Initial analyses were successful in attaining isotopic values of evolved  $\text{O}_2$  (see below), but subsequent nitrate analyses were randomly converted to  $\text{CO}_2$ . This must be due to a residual organic material retained in our nitrate solutions that is

retained upon drying of the  $\text{AgNO}_3$  solutions. This organic then reacts with the hot oxygen generated during the combustion to produce  $\text{CO}_2$ . As polar, non polar, and positively charged compounds should be removed by the clean up procedure, this must be a negatively charged base of an organic acid. Why the compound(s) is not being isolated by the ion chromatography is less clear, though slow bleed of organic acids from anion columns has been observed. Since the size of our nitrate samples was near the analytical limit for most of the samples in this study, the amount of organic contaminant need not be large to generate the interference. Given the large amounts of organic material observed in Tahoe aerosols (Figure 8) and waters/soils, even 99% organic removal is not sufficient given the small concentration of nitrate relative to organic material.

Given the time and resources already committed to the field work and sample processing, it was decided to halt the isotopic analysis until this carbon contamination issue could be resolved. This decision was based on the development of a new isotopic technique, known as the denitrifier method, developed by Sigman et al. at Princeton University (Casciotti et al., 2002; Sigman et al., 2001). This method uses denitrifying bacteria to convert nitrate to  $\text{N}_2\text{O}$ , which in turn can be converted to  $\text{N}_2$  and  $\text{O}_2$  for mass

S. Lake Tahoe - Bliss State Pk. Difference



**Figure 8.**

*Composition of fine aerosol mass from Lake Tahoe taken from the two IMPROVE sites sampling PM<sub>2.5</sub>. The high organic loading in the fall and winter made purification of the relatively small amounts of  $\text{NO}_3^-$  difficult.*



spectral analysis. The advantage of this method is that neither other oxygen-bearing anions nor organic material in the analyte solution interfere with the denitrification process, and the sample amount can be reduced by two orders of magnitude (e.g. 100 nmol).

Archived aerosol samples from the Placerville monitoring site, west of Tahoe valley, were obtained from the ARB. All of these samples (n=12) had significant amounts of  $\text{Br}^-$ , whose chromatographic peak overlapped with the nitrate peak and prohibited effective anion separation for these samples. This prevented using established methods as the  $\text{Br}^-$  interference with the conversion to silver nitrate. We are unsure of the origin of the  $\text{Br}^-$ , as this has not been observed in other aerosol samples, including those from the Tahoe basin. It is possible that it is bromine originating from the use of methyl bromide as a fumigant in the farming areas surrounding the Placerville site.

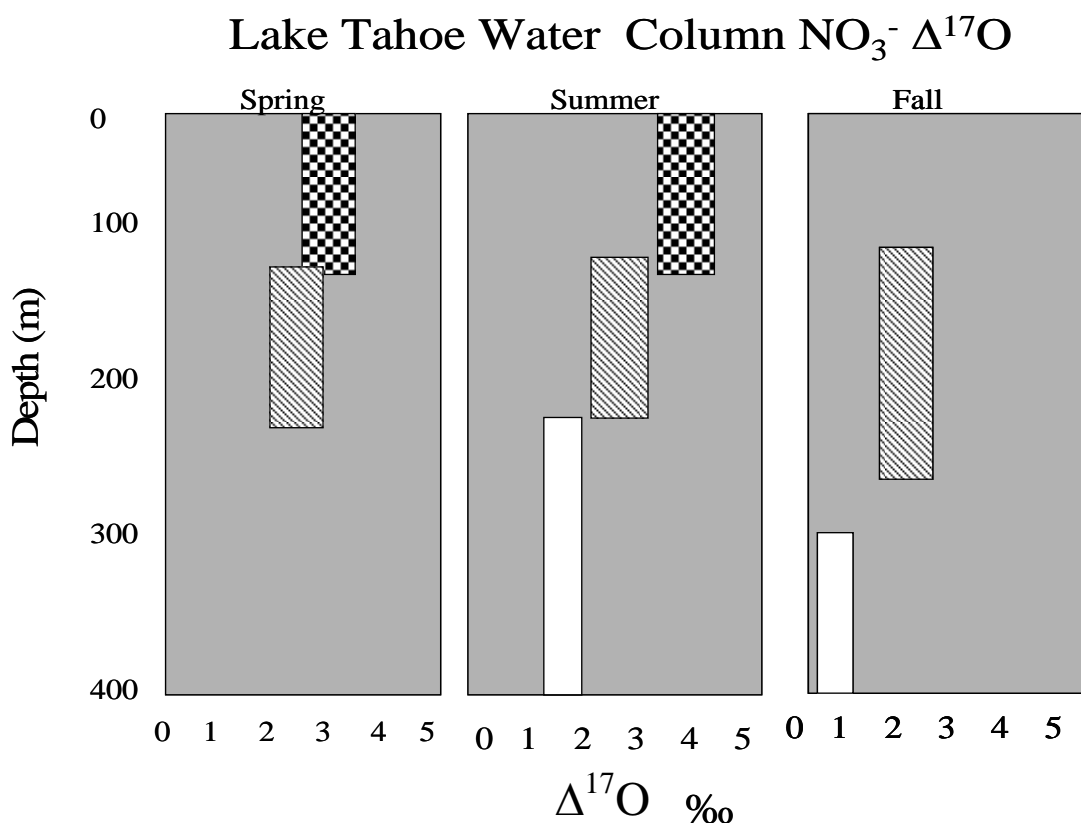
We are currently assembling the extraction interfaces and performing control experiments using the denitrifier method. The conversion to  $\text{N}_2$  and  $\text{O}_2$  over gold (Cliff and Thiemens, 1994) coupled to the denitrifier method represents a new technique. Substantial progress has been made at UCSD and Purdue University and other groups have been successful in completing the development of this method. We anticipate that the archived lake and aerosol nitrates can be analyzed, and reported to the ARB, within the year using this new method. Since initial submission of this report this new method has been further perfected by Kaiser et al. (Kaiser et al., 2006). However additional tests will be required to assess how elution from the anion resins impacts the denitrifier bacteria to function. Other groups have had difficulty using the bacteria when chemical processing of the samples has occurred. We believe these difficulties can be surmounted with due diligence and that all archived lake samples and remaining aerosol nitrate will be analyzed by the end of 2007.

### **Lake and Stream Water $\text{NO}_3^- \Delta^{17}\text{O}$ Values**

Of the 10 streams sampled only 3 yielded purified nitrate. This was due in part because most streams had nitrate concentrations in the low ppb range (except Incline Village, Eagle Falls, and Meeks Bay Creeks), but also because all creeks had high organic loading. The three creeks with low ppm range nitrate did yield nitrate  $\Delta^{17}\text{O}$  values. Both Incline Village and Meeks Bay had  $\Delta^{17}\text{O}$  that were indistinguishable from zero (0.08 and -.11‰ respectively). In contrast, Eagle Falls had measurable  $\Delta^{17}\text{O}$  value of 2.3‰, corresponding to roughly 10% atmospherically derived nitrate. Initial lake water collection yielded sufficient purified  $\text{AgNO}_3$  for isotopic analysis and the water column nitrate  $\Delta^{17}\text{O}$  values versus depth and time of year are shown in Figure 9 for the Buoy Station (Mid-Lake was not sampled until later in the year). Fall surface and photic zone nitrate concentrations were below detection limits and insufficient nitrate was collected, so no analysis was possible. Spring deep water samples were lost to organic combustion during analysis. Two additional field sampling sets, late fall and winter at Buoy and "Mid-lake" sites (20 samples), were completely lost to organic combustion during analysis. It is unclear why column concentration and cleanup procedures work for some lake nitrate samples but not for others. All had sufficient nitrate based on ion chromatography, but production of CO and  $\text{CO}_2$  during combustion suggested organic loading affected the analysis. A decision was made to archive the remaining 4 lake

sampling sets (35 individual samples) until the alternative bacterial method discussed above is developed and validated.

The lake nitrate from all depths and during all seasons clearly showed positive  $\Delta^{17}\text{O}$  values. The spring sample collection indicated an  $^{17}\text{O}$  isotope anomaly in nitrate, which was fairly consistent at  $\Delta^{17}\text{O}$  values of  $3.1 \pm 0.3\text{‰}$  to a depth of 300 meters,. The deep water nitrate sample was lost during analysis, but we believe that the deep water nitrate isotopic composition in spring was similar to surface and mid depth because the lake had undergone vertical mixing within the past month (Reuter, personal communication) and would thus likely be isotopically and concentration homogeneous. While similar values were observed at mid-depth (~200 meters) during the summer and fall, summer surface waters showed a nitrate  $\Delta^{17}\text{O}$  increase to 4.2‰. Interestingly, deepwater (400 and 450 meters) during the summer showed nitrate  $\Delta^{17}\text{O}$  decreases to 1.8‰ that continued to decrease into the fall ( $1.0 \pm .2\text{‰}$ ).



**Figure 9.** Water column nitrate  $\Delta^{17}\text{O}$  values as a function of depth collected during the spring (late April), summer (July) and fall (October). Sampling during these initial field campaigns were at 50 meter intervals, beginning at the surface and going down to 450 meters. Width of the bars is estimated error based on sample size and control analysis. Medium  $\Delta^{17}\text{O}$  values for Spring, Summer and Fall respectively are 3.4‰, 4.3‰, NA (0-150 m), 2.8‰, 3.2‰, 2.2‰ (150-250, )NA, 1.6‰, 1.0‰ (300-400) 1.3‰ (250-300 m Summer only) see appendix table.

## DISCUSSION

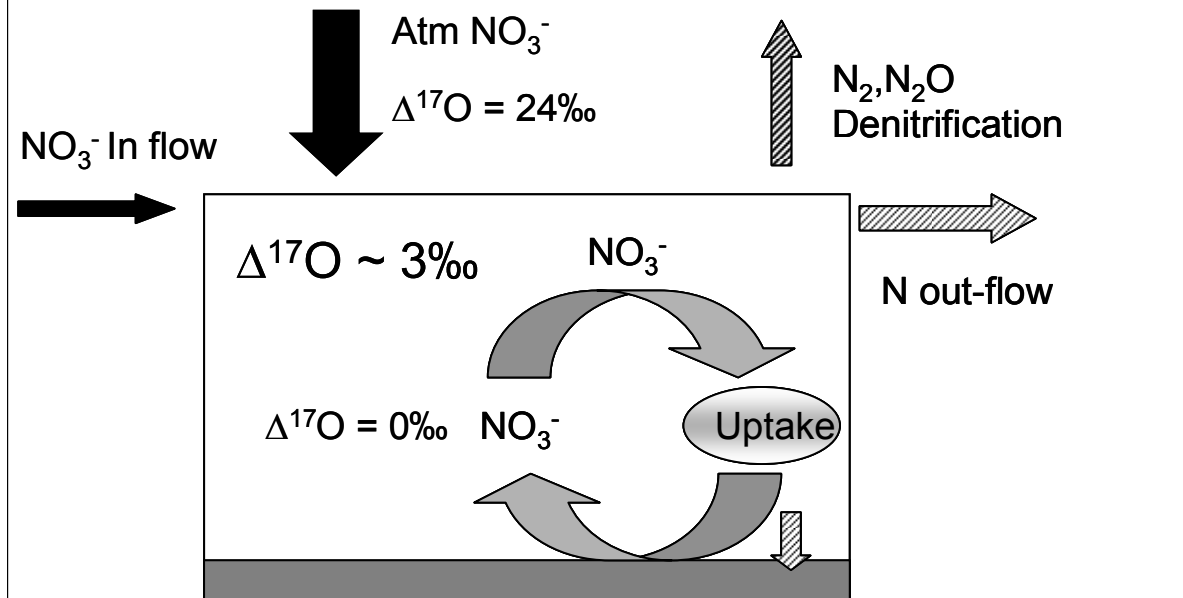
The limited number of aerosol and lake water nitrate samples that yielded useful isotopic data relative to the number of samples was a disappointment. Regardless, the data are useful in addressing the fundamental question proposed by the study: What is the contribution of atmospheric nitrate to the Lake Tahoe nitrate budget? In order to address this question, we needed the two isotopic end-members of Lake Tahoe nitrate. The atmospheric nitrate in the basin had seasonal values similar to those observed in other studies with an average of 23‰. However, we estimate that the “real” average to ~24 to 25‰. This is due to the missing data points for winter sample collections. Atmospheric nitrate  $\Delta^{17}\text{O}$  values rise (see Fig 3) to nearly 30‰ in the winter because of increased  $\text{N}_2\text{O}_5$  hydrolysis driven by cold temperatures. We expect that similar phenomena would occur at Lake Tahoe during the winter months. This slight adjustment of 23‰ to 24‰ will have a minor impact on the discussion below. Nitrate from nitrification processes derives its oxygen primarily from water and  $\text{O}_2$ , both of which have  $\Delta^{17}\text{O}$  values of ~0. Our soil sample ( $\Delta^{17}\text{O} = 0.10\text{‰}$ ) and two of the stream samples ( $\Delta^{17}\text{O} \sim 0\text{‰}$ ), which are dominated by riparian nitrification, support this hypothesis. The one stream that exhibited a positive  $\Delta^{17}\text{O}$  value (Eagle Falls) is from a predominantly granitic basin, with the only soil development being adjacent to the creek and in pockets of pines dotting the escarpment. Therefore, the nitrate deposition is less influenced by soil processes than that in other creeks but is still only a minor component. While it does not appear that stream nitrate is impacted by deposition, this must be treated cautiously. Snow pack watersheds have been shown to be sporadic in their export of nitrate, with large amounts exported during the initial melt. A assessment of magnitude of the impact of nitrate deposition on stream nitrate export would require a much greater temporal sampling effort. However, since concentrations are low and estimates suggest the role of stream nitrate to the lake is minor, this discrepancy would have minor impact on the lake’s nitrate budget.

Having established the isotopic signatures of the nitrate mixing end-members, an isotopic constraint on nitrate mass balance can be established using Eq. 3. This model is graphically represented in Figure 10. Nitrate inputs to the lake are by in-flow, from stream and ground water, recycling of organic N through nitrification and by direct deposition from the atmosphere. In a steady state approximation, which is valid on short time-scales, the nitrate inputs are balanced by nitrate outputs via denitrification, nitrate outflow (Truckee River) and burial of N containing organic matter. Nitrate concentration measurements of the stream water multiplied by the annual watershed flux show that inflow is relatively minor relative to direct deposition and internal recycling (uptake/nitrification).

The column-integrated average  $\Delta^{17}\text{O}$  value for nitrate within Lake Tahoe was 3‰, the nitrification  $\Delta^{17}\text{O}$  value is taken as zero, and the atmospheric deposition value is 24‰. Using these values in Eq. 3, we estimate that 13% (3‰/24‰) of the Lake Tahoe nitrate has retained its photochemical isotopic signature. For mass balance, the remaining 87% of the water column nitrate is formed by nitrification of organic matter. This should **not** be interpreted as meaning only 13% of the lake’s nitrate budget derives from the atmosphere, rather this portion has not undergone internal recycling via uptake and nitrification. In other words, all of the nitrogen in the lake could have been derived from the atmosphere, but because the relative rate of nitrification compared to deposition is sufficiently fast, the isotopic signature of the  $\text{NO}_3^-_{\text{atm}}$  has been diminished.



## A Simple Nitrate Isotopic Balance Model



*Figure 10. Simplified version of nitrate cycling within Lake Tahoe. Nitrate inputs and export from stream flow is small relative to the mass of the lake. Denitrification losses are also assumed to be minimal. The isotopic composition of lake nitrate ( $\Delta^{17}\text{O} \sim 3\text{‰}$ ) is then dictated by the rate of nitrate deposition, with a  $\Delta^{17}\text{O}$  value of 24‰, relative to the nitrate generated by nitrification of remineralized organic N whose oxygen isotopes are set by water,  $\Delta^{17}\text{O} = 0$ .*

The uncertainty in this estimate is coupled to the uncertainty of our isotopic measurements. We have never observed a positive analytical artifact associated with the silver nitrate decomposition. In other words when analyzing nitrate standards, including controls on collection and processing, we have never generated a *positive*  $\Delta^{17}\text{O}$  value from a standard known to have a zero  $\Delta^{17}\text{O}$  value. However, contamination can lower positive  $\Delta^{17}\text{O}$  standards, because interfering oxygen is normally has  $\Delta^{17}\text{O}$  values of  $\sim 0$ . The maximum observed dampening by this contamination is 10-15% of the standard value (eg. USGS35 nitrate standard with a  $\Delta^{17}\text{O}$  value of 21‰ can decrease to 19‰). Therefore, the 3‰ value observed in the lake column is a lower bound and the true accurate value may be up to 15% higher, or 3.5‰. However this only shifts our partitioning by 2% (to 15% atmospheric retention) and has little impact on the discussion below.

If we can establish one flux, either atmospheric deposition or nitrification rates, we can calculate the unknown flux based on the mole fractions determined above. Using dry and wet deposition collectors at multiple sites around the lake, Jasby estimated that nitrate deposition is  $0.13 \text{ g N m}^{-2} \text{ yr}^{-1}$ . Tahoe air quality studies have shown that nitrate aerosol concentrations have spatial variability. This local variation of mass may have

alter the estimates of Jasby et al. as their sampling scheme was limited in spatial scale. However, turbulent mixing within the basin likely smoothes this heterogeneity on the scale of the lake. Further the point source  $\text{NO}_x$  emissions are not likely to influence the  $\Delta^{17}\text{O}$  values as these are driven primarily by sunlight availability and the temperature dependence of  $\text{N}_2\text{O}_5$  hydrolysis.

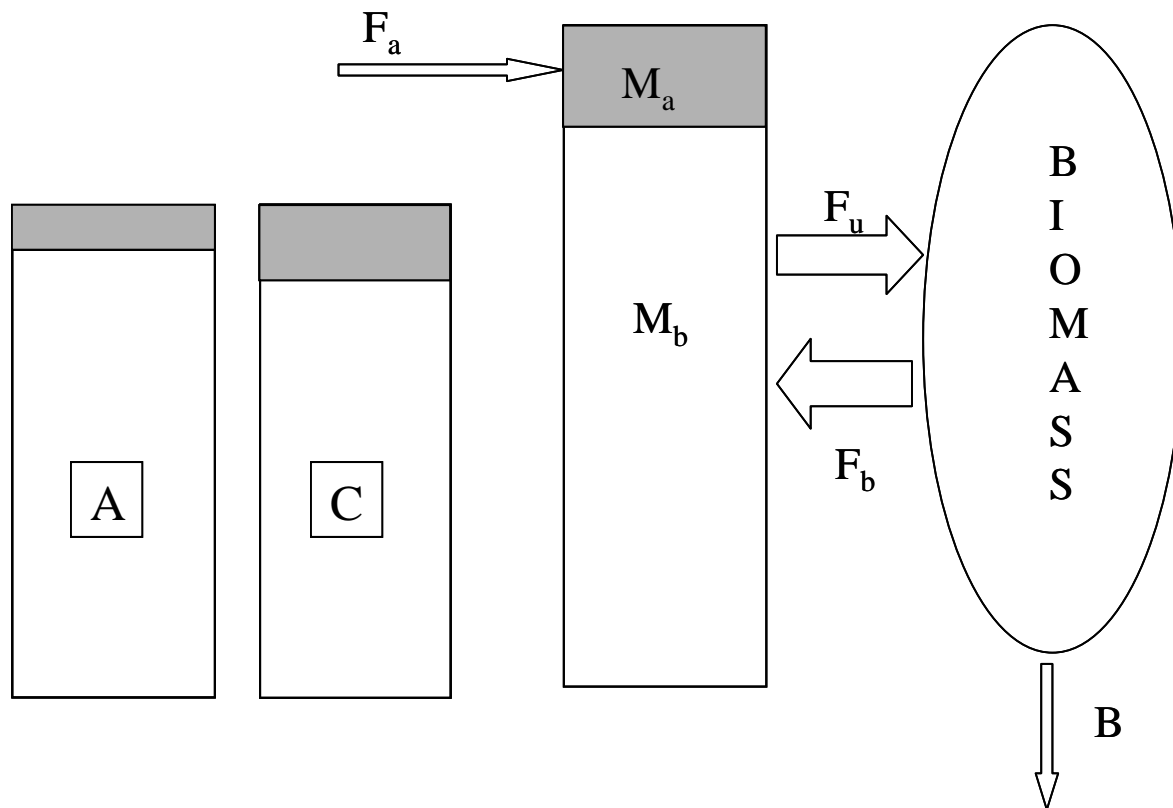
Based on this and our mole fractions derived from the  $\Delta^{17}\text{O}$  data (0.13 deposition, .87 nitrification), we estimate that nitrification rates are  $\sim 0.9 \text{ g N m}^{-2} \text{ yr}^{-1}$  (eg.  $(0.87 \times 0.13) / 0.13$ ). This is in good agreement with incubation studies by Paerl who estimated that lake nitrification was also  $1.0 \text{ g N m}^{-2} \text{ yr}^{-1}$  (Paerl and Goldman, 1972). What this demonstrates is that with only one nitrate input flux (deposition or nitrification) and an average nitrate  $\Delta^{17}\text{O}$  value, we are able to quantify the other flux without an extensive and costly study (as is the case for deposition analysis).

The comparable rates of  $\text{NO}_3^-_{\text{bio}}$  formation and  $\text{NO}_3^-_{\text{atm}}$  deposition are also evident in the nitrate  $\Delta^{17}\text{O}$  values within the depth profiles. In the spring, the homogenous  $\Delta^{17}\text{O}$  values are likely due to the fact that the lake had already undergone vertical mixing in March (TRG-personal communication). Mixing occurs when cold stratified surface water that developed during the winter is displaced by relatively warmer deep water by a spring storm. This generates homogenous nitrate concentrations and would also erase any seasonal isotopic effects that occur during stratified conditions (uptake in the photic zone for example). During the ensuing summer, dry and wet deposition of nitrate to the warm, stratified surface is reflected in the increase in the  $\Delta^{17}\text{O}$  value of surface waters during this time. Meanwhile, sinking and sedimentary organic matter in the deep water is undergoing nitrification and decreasing the nitrate  $\Delta^{17}\text{O}$  in these regions.

What else does the ability to partition the total lake nitrate into  $\text{NO}_3^-_{\text{atm}}$  and  $\text{NO}_3^-_{\text{bio}}$  tell us about nitrogen cycling dynamics in Lake Tahoe? It informs about a critical parameter: the *lifetime* ( $\tau$ ) of  $\text{NO}_3^-_{\text{atm}}$  within the lake defined by  $\tau = M/F$ , where  $M$  is the  $\text{NO}_3^-$  mass and  $F$  is either the source or sink rate (flux), which are equal in steady state systems (see Figure 11).

For the current case the total nitrate mass or  $M_T (\text{NO}_3^-) = M_a (\text{NO}_3^-_{\text{atm}}) + M_b (\text{NO}_3^-_{\text{bio}})$  is the nitrate concentration, based on Paerl's measurements of a constant 10 ppb (N) to 400 meter depth just after turnover mixing (Paerl et al., 1975), multiplied by the lake volume of  $1.51 \times 10^{14}$  liters and is equal to  $1.51 \times 10^9 \text{ g(N)} = M_T$ . At steady state  $F_a + F_b = U + B$ , where  $F_a$  is the nitrate flux from the atmosphere,  $F_b$  is the nitrate flux from nitrification,  $U$  is uptake of nitrate by biomass and  $B$  is burial of organic N. If we impose the condition that  $U = F_b$  then  $B = F_a$ , the lifetime of lake nitrate with respect to atmospheric deposition (or removal by burial) is  $\sim M_T / F_a$ . Again using the nitrate deposition estimate (scaled to area) from Jassby of  $6.5 \times 10^7 \text{ g(N) yr}^{-1}$ , we arrive at a lifetime of  $\sim 23$  years. In contrast, the lake  $\text{NO}_3^-_{\text{atm}}$  content is  $1.96 \times 10^8 \text{ g(N)}$  (based on  $\Delta^{17}\text{O}$  data) divided by a source flux of  $6.5 \times 10^7 \text{ g(N) / yr}$  yields an  $\Delta^{17}\text{O}$  lifetime of 3 years. In other words, if, hypothetically, nitrate deposition could be completely shut off, the water column nitrate  $\Delta^{17}\text{O}$  values would decay to zero within 3 years while the concentration values would require over  $\sim 23$  years to decay. While complete elimination of N deposition is not a possibility, this example does demonstrate that evaluating changes in nitrate dynamics using  $\Delta^{17}\text{O}$  is almost 10 times more sensitive compared to concentration changes.

This concept of  $\Delta^{17}\text{O}$  sensitivity to biologic cycling is shown in Figure 11. The existing situation is the box model including arrows. The question is: What will happen if we reduced nitrate deposition by 20%? If the system remains static, then we expect a 2% decline in nitrate concentration, but since concentrations are already near analytical detection limits, there would be no analytically resolvable change in concentration. However, since the nitrification flux ( $F_a$ ) is large relative to the deposition and thus the uptake/nitrification response to the change will be slow, the water column  $\Delta^{17}\text{O}$  will respond with a 20% decrease quickly (within 3 years). We would then expect a return to the initial  $\Delta^{17}\text{O}$  value on a timescale that depends on the rate of the biomass cycle response, which in turn is an indicator of lake clarity recovery.



**Figure 11.** A box model representation of nitrate cycling in Lake Tahoe. New inputs of nitrate are from atmospheric deposition ( $F_a$ ) and losses of N are through organic burial (B). Internal recycling of nitrate via uptake ( $F_u$ ) and nitrification ( $F_b$ ) control the balance of nitrate in the water column. Water column nitrate  $\Delta^{17}\text{O}$  values reflect the relative rate of  $F_a$  and  $F_b$ . Should the deposition rate decrease because of regulatory efforts, what would the effect on the cycle be? The response budgets for lake nitrate sources are shown in A and C. The initial response is isotopic disequilibrium relative to the initial conditions. This is shown in A, where the  $\Delta^{17}\text{O}$  values has shrunk along with the deposition loading decrease(box size, not to scale). This is expected because  $F_u$  and  $F_b$  depend on the amount of the water column algae (Biomass) and therefore one expects  $F_b$  not to be immediately impacted by a small change in  $F_a$ . In other words, since a small shift in deposition only results in a small shift total nitrate, biomass remains effectively unchanged on short timescales, and thus  $F_b$  remains unchanged. Over time both biomass and  $F_b$ , and  $F_u$  will adjust, assuming constant burial. If the shrinkage of biomass is proportional to the deposition decrease, the system should equilibrate isotopically but with a different nitrate concentration (box C). If the system is not directly proportional to deposition, the isotopic balance would end up somewhere between A and C. Long term monitoring of water column nitrate  $\Delta^{17}\text{O}$  is thus an effective proxy for changes in lake algal biomass and could trace spatial productivity inhomogeneities across the lake.

## **SUMMARY AND CONCLUSIONS.**

The goal of this project was to use stable isotopes as a tool for interpreting nutrient cycling in Lake Tahoe in order to assess the role that regional air pollution plays in the water clarity of Lake Tahoe. To assess the importance of atmospheric nitrate deposition and the relative importance of internal nitrogen cycling of lake biomass, we conducted a survey of the isotopic composition of various nitrate sources with the Lake Tahoe Basin. Nitrate produced by photochemical oxidation of nitrogen oxides emitted by vehicles and burning had average  $\Delta^{17}\text{O}$  values of 24‰. Nitrate produced by nitrification of ammonium or organic material had  $\Delta^{17}\text{O}$  value of zero. These two disparate values allowed us to construct a simple two-source mixing model to match our observed lake nitrate  $\Delta^{17}\text{O}$  values of 3‰. The  $\Delta^{17}\text{O}$  data show that 13% of the nitrate in Lake Tahoe has retained its isotopic signature imparted by atmospheric deposition. These data and information of deposition rates allowed us to estimate that nitrification rates throughout the lake average  $1.0 \text{ g N m}^{-2} \text{ yr}^{-1}$ . We demonstrated that in order to assess the effectiveness of remediation efforts on short timescales (10 years) with respect to atmospheric deposition, long term monitoring of water column nitrate  $\Delta^{17}\text{O}$  values is a cost effective and sensitive tracer of the recovery rate of biomass with respect to internal nitrogen cycling.

## **RECOMMENDATIONS**

While the data obtained in this study demonstrated the power of utilizing  $\Delta^{17}\text{O}$  as a tracer of nitrate production and N cycle dynamics, the true effectiveness of an isotopic approach was hampered by analytical shortcomings that derive from the high organic loads in the basin. New analytical developments suggest that sample size can be greatly reduced (two orders of magnitude) and that sample preparation is effectively eliminated. Samples with high organic or anion loading can easily be analyzed without costly and labor intensive procedures. Once proven, this technique would allow much greater spatial and temporal studies of nitrate deposition and internal cycling throughout the basin. In addition, the new techniques are much better at simultaneously assessing  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values in nitrate, which can then be used as tracers of water column nitrogen cycling. Once the analytical hurdles have been cleared, stable isotopes of nitrogen and oxygen hold promise to be one of the most effective tools in assessing water clarity recovery in Lake Tahoe. Until then, the existing technique should be limited to studies where larger nitrate concentrations and less interfering compounds are present.

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## **Glossary**

$\delta$  – Change in isotopic ratio ( $^{18}\text{O}/^{16}\text{O}$  for example) relative to a standard

$\Delta^{17}\text{O}$  – difference (excess) of oxygen 17 isotope relative to that expected from  $\delta^{18}\text{O}$  values. Quantified by the equation  $\Delta^{17}\text{O} = \delta^{17}\text{O} - .52\delta^{18}\text{O}$

$\text{NO}_3^-_{\text{atm}}$  – nitrate from the atmosphere

$\text{NO}_3^-_{\text{bio}}$  – nitrate from biological sources

TSP – total suspended particle

SPE – solid phase extraction

End-member - one end point (isotopic value) on a two point mixing line.

AND - Atmospherically deposited nitrate

NC - North Carolina

TRG - Tahoe Research Group

UC - University of California

UCSD - University of California San Diego

## Tables of Data

### Lake Forest Aerosol Collection Data 2004-2005, 7 day sampling period, continuous



Aerosol Sample ID	Collection Date (2004-05)	NO <sub>3</sub> <sup>-</sup> μg/m <sup>3</sup>	SO <sub>4</sub> <sup>-2</sup> μg/m <sup>3</sup>	NO <sub>3</sub> <sup>-</sup> Δ <sup>17</sup> O ‰	Aerosol Sample ID	Collection Date (2004-05)	NO <sub>3</sub> <sup>-</sup> μg/m <sup>3</sup>	SO <sub>4</sub> <sup>-2</sup> μg/m <sup>3</sup>	NO <sub>3</sub> <sup>-</sup> Δ <sup>17</sup> O ‰
#1	tested				#26	9/28	0.67	0.38	Arch
#2	4/18	0.74	0.80	26	#27	10/5	0.52	0.23	Arch
#3	4/25	0.42	0.63	Arch/CO	#28	10/12	0.24	0.30	Arch
#4	5/2	0.52	1.10	Arch/CO	#29	10/19	0.46	0.39	Arch
#5	5/9	0.22	0.66	24.3	#30	10/26	0.26	0.29	Arch
#6	5/16	0.14	0.52	CO	#31	11/2	0.25	0.42	Arch
#7	5/23	0.32	0.63	Arch/CO	#32	11/9	0.28	0.34	Arch
#8	5/30	0.34	0.75	Arch/CO	#33	11/16	0.24	0.19	Arch
#9	6/1	NA	NA	24.6	#34	11/23	0.32	0.23	Arch
#10	6/8	0.32	0.96	21.6	#35	11/30	0.24	0.14	Arch
#11	6/15	0.38	0.74	CO	#36	12/7	0.31	0.17	Arch
#12	6/22	0.39	1.09	21	#37	12/14	0.15	0.14	Arch
#13	6/29	0.29	0.73	20	#38	12/21	0.20	0.22	Arch
#14	7/6	0.24	0.66	Arch/CO	#39	12/28	0.13	0.07	Arch
#15	7/13	0.35	0.63	Arch/CO	#40	1/4	0.38	0.09	Arch
#16	7/20	0.58	1.05	Arch/CO	#41	1/11	0.41	0.10	Arch
#17	7/27	0.40	0.53	Arch/CO	#42	1/18	0.22	0.15	Arch
#18	8/3	0.40	0.78	CO	#43	1/25	0.59	0.20	Arch
#19	8/10	0.33	0.61	CO	#44	2/1	0.35	0.20	Arch
#20	8/17	power off			#45	2/8	0.22	0.20	Arch
#21	8/24	0.15	0.13	CO	#46	2/15	0.29	0.25	Arch
#22	8/31	0.39	0.31	CO	#47	2/22	0.37	0.30	24.2
#23	9/7	0.20	0.22	CO	#48	3/1	NA	NA	
#24	9/14	0.37	0.43	Arch/CO	#49	3/8	0.25	0.32	CO
#25	9/21	0.35	0.66	Arch/CO	#50	3/15	0.39	0.63	23.8
					#51	3/22	0.32	0.50	23.6

CO = Carbon Monoxide was the main decomposition product

Arch = Sample was archived

Arch/CO = CO main product, but sufficient NO<sub>3</sub><sup>-</sup> to Achieve replicate

Lake Water

Sample ID (Depth)	Collection Date	Local	Depth (m)	liters H <sub>2</sub> O	AgNO <sub>3</sub> (mg)	O <sub>2</sub> yield	Δ <sup>17</sup> O
Tahoe 1.1	4/1/2004	Bouy	Surface	40	2.2	33%	3.4
Tahoe 1.2	4/1/2004	Bouy	100	40	2.4	38%	3.4
Tahoe 1.3	4/1/2004	Bouy	200	40	1.9	34%	2.8
Tahoe 1.4	4/1/2004	Bouy	300	40	0.1	CO	NA
Tahoe 1.5	4/1/2004	Bouy	350	40	0.3	0%	NA
Tahoe 1.6	4/1/2004	Bouy	400	40	0	0%	NA
Tahoe 1.7	4/1/2004	Bouy	450	40	0.2	0%	NA
Tahoe 2.1	8/11/2004	Bouy	Surface	40	NA		na
Tahoe 2.2	8/11/2004	Bouy	100	40	2.3	30%	4.3
Tahoe 2.3	8/11/2004	Bouy	200	40	2.4	30%	3.2
Tahoe 2.4	8/11/2004	Bouy	300	40	2	32%	1.0
Tahoe 2.5	8/11/2004	Bouy	350	40	2.8	35%	1.6
Tahoe 2.6	8/11/2004	Bouy	400	40	2.2	36%	1.8
Tahoe 2.7	8/11/2004	Bouy	450	40	1.9	38%	1.6
Tahoe 3.1	9/17/2004	Midlake	Surface	40	0.2	NA	NS
Tahoe 3.2	9/17/2004	Midlake	100	20	0.1	NA	NS
Tahoe 3.3	9/17/2004	Midlake	200	20	2.2	28%	2.2
Tahoe 3.4	9/17/2004	Midlake	300	20	1.9	0%	NS
Tahoe 3.5	9/17/2004	Midlake	400	20	2.8	4%	NS
Tahoe 3.6	9/17/2004	Bouy	Surface	40	0.1	NA	NS
Tahoe 3.7	9/17/2004	Bouy	100	20	0.3	0%	NS
Tahoe 3.8	9/17/2004	Bouy	200	20	2.4	6%	NS
Tahoe 3.9	9/17/2004	Bouy	300	20	3.1	3%	NS
Tahoe 3.10	9/17/2004	Bouy	400	20	3.3	34%	1.0
Tahoe 4.1	11/15/2004	Midlake	Surface	40	Arch. resin		
Tahoe 4.2	11/15/2004	Midlake	100	20	Arch. resin		
Tahoe 4.3	11/15/2004	Midlake	200	20	Arch. resin		
Tahoe 4.4	11/15/2004	Midlake	300	20	Arch. resin		
Tahoe 4.5	11/15/2004	Midlake	400	20	Arch. resin		
Tahoe 4.6	11/15/2004	Bouy	Surface	40	Arch. resin		
Tahoe 4.7	11/15/2004	Bouy	100	20	Arch. resin		
Tahoe 4.8	11/15/2004	Bouy	200	20	Arch. resin		
Tahoe 4.9	11/15/2004	Bouy	300	20	Arch. resin		
Tahoe 4.10	11/15/2004	Bouy	400	20	Arch. resin		
Tahoe 5.1	2/17/2005	Midlake	Surface	40	Arch. resin		
Tahoe 5.2	2/17/2005	Midlake	100	20	Arch. resin		
Tahoe 5.3	2/17/2005	Midlake	200	20	Arch. resin		
Tahoe 5.4	2/17/2005	Midlake	300	20	Arch. resin		
Tahoe 5.5	2/17/2005	Midlake	400	20	Arch. resin		
Tahoe 5.6	2/17/2005	Bouy	Surface	40	Arch. resin		
Tahoe 5.7	2/17/2005	Bouy	100	20	Arch. resin		
Tahoe 5.8	2/17/2005	Bouy	200	20	Arch. resin		

Tahoe 5.9	2/17/2005	Bouy	300	20	Arch. resin
Tahoe 5.10	2/17/2005	Bouy	400	20	Arch. resin
Tahoe 6.1	4/18/2005	Midlake	Surface	40	Arch. resin
Tahoe 6.2	4/18/2005	Midlake	100	20	Arch. resin
Tahoe 6.3	4/18/2005	Midlake	200	20	Arch. resin
Tahoe 6.4	4/18/2005	Midlake	300	20	Arch. resin
Tahoe 6.5	4/18/2005	Midlake	400	20	Arch. resin
Tahoe 6.6	4/18/2005	Bouy	Surface	40	Arch. resin
Tahoe 6.7	4/18/2005	Bouy	100	20	Arch. resin
Tahoe 6.8	4/18/2005	Bouy	200	20	Arch. resin
Tahoe 6.9	4/18/2005	Bouy	300	20	Arch. resin
Tahoe 6.10	4/18/2005	Bouy	400	20	Arch. resin

NS = No  
sample gas, eg.,  
no O2 was  
detected after  
combustion  
Arch resin =  
Anion resins  
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