Tracing Atmospheric Nitrate Deposition in a Complex Semiarid Ecosystem using $\Delta^{17}$O.
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Abstract. The isotopic composition of nitrate collected from aerosols, fog and precipitation was measured and found to have a large $^{17}$O anomaly with $\Delta^{17}$O values ranging from 20 to 30 ‰ ($\Delta^{17}$O = $\delta^{17}$O -.52×$\delta^{18}$O). This $^{17}$O anomaly was used to trace atmospheric deposition of nitrate to a semiarid ecosystem in southern California. We demonstrate that the $\Delta^{17}$O signal is a conserved tracer of atmospheric nitrate deposition and is a more robust indicator of N deposition relative to standard $\delta^{18}$O techniques. The data indicate that a substantial portion nitrate found in the local soil, stream and ground water is of atmospheric origin and does not undergo biologic processing before being exported from the system.

Introduction

The global nitrogen cycle has been altered by human activities such that human N$_2$-fixation annually more than doubles natural fixation and this N flux is expected to again double by 2030 (1-3). The negative impacts of excess N input includes shifts in biodiversity(4), soil acidification and forest decline (5), eutrophication of coastal waters and estuaries(6) and degradation of ground and surface waters (7,8). Nitrogen originating from combustion of fossil fuel has the unique potential to impact ecosystems far from their source including pristine wilderness preserves (5). The direct contribution of atmospheric N to N export is difficult to ascertain, but is estimated to vary from 10-50% (6). Transport of atmospheric fixed N pollutants across local, regional and national boarders also raises questions on how emission reductions strategies should be implemented by local authorities.

Nitrate is a unique form of fixed N because of its high solubility, which allows it to be leached and exported out of ecosystems. This export often leads to accumulation of NO$_3^-$ in
groundwater and EPA regulations dictate that potable water NO$_3^-$ concentrations must not exceed 10 ppm. Atmospheric NO$_3^-$ (NO$_3^{\text{atm}}$) is a mixture of gas phase nitric acid, produced by the oxidation of NO$_x$, and NO$_3^-$ salts formed by heterogeneous reactions involving NO$_y$ on aerosol surfaces (9). The main removal mechanism of NO$_3^{\text{atm}}$ is through dry and wet deposition and it can be a substantial source of new N, but its utilization by biota depends largely on the N retention dynamics of the system in question. Researchers have recently applied $\delta^{18}$O and $\delta^{15}$N methods (10) to determine the fate and transport of NO$_3^{\text{atm}}$ to ecosystems but there are significant limitations to the effectiveness of this methodology. Because of the wide range of observed $\delta^{18}$O and $\delta^{15}$N values for the two main sources of NO$_3^-$, microbial nitrification of organic matter and NO$_3^{\text{atm}}$, it is difficult to detect and quantify NO$_3^{\text{atm}}$ deposition in natural systems using isotopic mass balance (11-13). In addition, kinetic and equilibrium isotopic fractionation processes, such as denitrification and abiotic reductions, can alter NO$_3^-$ $\delta^{18}$O and $\delta^{15}$N values complicating their interpretation beyond the simple isotope mass balance approach (11).

Recent observations have shown that NO$_3^{\text{atm}}$ is anomalously enriched in $^{17}$O (13). Such enrichments are generally quantified by $\Delta^{17}$O notation, $\Delta^{17}$O = $\delta^{17}$O - .52 × $\delta^{18}$O, where $\delta$ = $(R_{\text{sample}}/R_{\text{standard}} - 1)\times1000$ and R is the $^{17}$O/$^{16}$O or $^{18}$O/$^{16}$O ratio of the sample and the standard. The origin and seasonal variation in the observed $\Delta^{17}$O of NO$_3^{\text{atm}}$ is attributed to oxygen atom transfers from ozone (where the $\Delta^{17}$O is well characterized (14,15) to oxides of nitrogen during the conversion of NO$_x$ to NO$_3^{\text{atm}}$(13). Because the production of nonzero $\Delta^{17}$O values is strictly a photochemical affect, NO$_3^-$ produced in soils by nitrification has $\Delta^{17}$O = 0. Further more, post depositional isotopic fractionations such as denitrification will obey the well-established mass
dependent fractionation law \( \delta^{17}O = 0.52 \times \delta^{18}O \) (16), leaving the \( \Delta^{17}O \) unaltered. Therefore, \( \Delta^{17}O \) can be used as a conserved tracer of \( \text{NO}_3^{-, \text{atm}} \) deposition. Hydrologists, ecologists and soil scientists can use such a tracer to better understand the fate of atmospheric deposition.

Here we demonstrate the effectiveness of using \( \Delta^{17}O \) for detecting and quantifying the proportion of \( \text{NO}_3^{-, \text{atm}} \) found in \( \text{NO}_3^- \) that was collected from streams and soils along a pollution gradient in southern California. Additionally we use these results to gain insight into the processes controlling the fate and transport of nitrogen in the soil and catchment environments.

**Experimental**

**Site description.** We sampled nitrate in streams, soils, zero-tension soil lysimeters, and atmospheric pollutants along two air pollution gradients in southern California (Fig. 1). Each receives at least 35-45 kg N ha\(^{-1}\) year\(^{-1}\) on the NW end nearest Los Angeles and roughly 5 kg N ha\(^{-1}\) year\(^{-1}\) at the SE terminus furthest from the city (17-19). This nitrogen deposition has been implicated in the recent decline of the coastal sage scrub ecosystems of southern California(20,21) and is linked to elevated \( \text{NO}_3^- \) concentrations in local streams(22,23).

Streamwater, fog and wet deposition samples were collected from the San Dimas Experimental Forest, a low elevation high-pollution chaparral site in the San Gabriel Mountains northeast of Los Angeles. Streamwater samples were also collected in the Devil Canyon watershed (high N deposition site), also predominantly chaparral vegetation, located on the western edge of the San Bernardino Mountains (Fig. 1). Camp Paivika is a high pollution mixed
Figure 1 The mountain gradient (proceeding from 1 to 3) begins 30 km northeast of Los Angeles in the San Gabriel Mountains (1), which contains the Camp Paivika/Devil Canyon watershed (2) and reaches to the eastern end of the San Gorgonio wilderness (3) in the San Bernardino Mountains, 130 km east of Los Angeles. Both of these sites are dominated by mixed conifer forest at high elevations and change to chaparral vegetation at lower elevations. The valley gradient (1 to 5), predominantly coastal sage scrub habitat begins in Riverside, Ca., (4) and ends near Lake Skinner (5)(100 km). La Jolla (6) is approximately 140 km SW and Bakersfield (7) is 160 km NW of the gradients. Atmospheric samples were collected at these last two sites in addition to the Riverside, Ca. location.

Geographic data from The California Spatial Information Library (CASIL), available at http://www.gis.cs.gov/
conifer site located at the crest of Devil Canyon. At Camp Paivika nitrate samples were obtained from soil, soil lysimeters, fog and wet deposition.

Study sites with relatively low or moderate levels of N deposition included Camp Osceola and Barton Flats located near the eastern end of the mixed conifer zone in the San Bernardino Mountains, where N deposition is 5-7 times lower than at Camp Paivika. Both soil and fog samples at these two sites were obtained for nitrate analysis. Streamwater samples were also collected from creeks in southern edge of the San Gorgonio Wilderness (moderate N deposition) (Fig. 1). Two additional field sites were located in the coastal sage scrub ecotone of southern California. One is situated on the campus of the University of California, Riverside (UCR) and the other was located at the Lake Skinner conservation reserve. The UCR site is subject to high rates of deposition and the Lake Skinner site is a lower deposition site. At both sites, only soils were sampled, as stream flow is rare and were not observed during the study period.

**NO₃⁻ collection and analysis.**

Each sample ultimately ends up as a dilute aqueous solution of soluble anions (Cl⁻, NO₃⁻ and SO₄²⁻) and dissolved organic material. The organics are removed and the anions concentrated on 5 ml anion resin columns (Bio-Rad AG1-X8 200-400 mesh) as described by Silva et al. (2000). After loading all resin columns were kept at 5° C prior to isotopic analysis. The NO₃⁻ atm samples were collected as precipitation, fog and aerosols. The precipitation collections utilized Aerochem wet/dry bucket samplers following guidelines detailed by the National Atmospheric Deposition Program (NADP). Fog water was collected by actively pulling the fog through a bank of Teflon collector strings that funnel the droplets into a pre-cleaned Nalgene bottles (24). Aerosol NO₃⁻ was collected for 3 days on pre cleaned glass fiber
filters using a hi-volume aerosol sampler (flow rate = 1200 l min\(^{-1}\)) equipped with a 4 stage, size-segregating impactor. Aerosol samples were collected in La Jolla Ca, a coastal urban site, Riverside Ca. an inland urban center near UCR and Bakersfield Ca. a suburban farming community in the California central valley (Fig. 1). The aerosol samples are considered a mixture of aerosol NO\(_3\)\(^-\) atm and gaseous HNO\(_3\) because HNO\(_3\) is know to react with material on the filter surface to form nitrate salts (25). The soluble salts were extracted by repeatedly sonicating the filters in 50ml of Millipore water.

Stream water samples were collected in the field in clean, triple rinsed Nalgene sample bottles. Water samples were filtered (0.45µ pore size) within two days following field collection. Soils were sampled at several depth intervals down to 30 cm below the surface, including the litter layer of the soil profile. Soil samples were stored frozen prior to extraction. Soluble ions were extracted from the soils by mixing them in a 1:10 ratio with Millipore water and shaken for two hours. The soil extracts were then centrifuged and filtered through a 0.45 µm filter and stored in the dark at 4°C until ready for concentrating on to anions resin columns.

The anions were eluted from the column and the NO\(_3\)\(^-\) was purified and converted to AgNO\(_3\) as described by Silva et al. For samples with high loads of dissolved organics carbon (DOC) the eluent was further purified by SPE using C-18 resin and by anion separation using a high capacity ion chromatograph (26). The AgNO\(_3\) was freeze-dried directly in silver capsules, converted to O\(_2\) and analyzed for \(\delta^{17}\)O and \(\delta^{18}\)O using a duel inlet Finnigan-Mat isotope ratio mass spectrometer (26). All oxygen isotopic data presented are measured with respect to SMOW and have accuracy and precision of \(\pm 1.5%\) for \(\delta^{18}\)O and for \(\Delta^{17}\)O it is \(\pm 2%\) (26).
Results and Discussion

Oxygen Isotopic Composition of Atmospheric Nitrate

The oxygen isotopic compositions of the NO$_3^{\text{atm}}$ samples are given in Table 1. The data are also plotted in an oxygen three-isotope space, which shows the large $^{17}$O isotope enrichments relative to the terrestrial isotopic mass fractionation line (Fig. 2). The average NO$_3^{\text{atm}}$ $^{17}$O value is 26‰ with a spread of ± 3 ‰ and are in the same range as previously reported NO$_3^{\text{atm}}$ $^{17}$O values. We have also included, in figure 2, the NO$_3^{\text{atm}}$ $^{17}$O results from our previous study (La Jolla) (13) to give a clear representation of the range of $^{17}$O values observed. In that study the $^{17}$O values for NO$_3^{\text{atm}}$ were modeled by tracing NO$_x$ oxidation pathways that shifted depending on the season and oxidant species. Those results showed that the NO$_3^{\text{atm}}$ formed during the winter months had consistently higher $^{17}$O values than NO$_3^{\text{atm}}$ produced in the spring or summer. The precipitation and aerosol samples from Riverside and Bakersfield were predominately collected during the winter when the $^{17}$O values in NO$_3^{\text{atm}}$ are highest. This bias of predominately winter sampling in this study only over estimates the NO$_3^{\text{atm}}$ $^{17}$O by about 1‰ and we have taken the annual average NO$_3^{\text{atm}}$ $^{17}$O as ~25‰.

The NO$_3^{\text{atm}}$ δ$^{18}$O values are also highly enriched and are in reasonable agreement with δ$^{18}$O values reported for nitrate in wet deposition (10,11,27). Since the $^{17}$O enrichments in NO$_3^{\text{atm}}$ are the result of NO$_x$ oxidation by ozone (13,28), which is equally enriched in both $^{17}$O and $^{18}$O (29), during its conversion to HNO$_3$, it is not surprising to find the δ$^{18}$O values following trends similar to $^{17}$O. The higher variability observed in NO$_3^{\text{atm}}$ δ$^{18}$O values is likely the result of fluctuations in the δ$^{18}$O tropospheric water vapor, which is incorporated into NO$_3^{\text{atm}}$. 
Figure 2 Oxygen three isotope plot of NO$_3$ atm from the Riverside Air Basin (□), La Jolla Ca, (♦), and Bakersfield Ca. (△) showing an average Δ$^{17}$O of 25 ± 4 ‰ and a high correlation between δ$^{17}$O and δ$^{18}$O. The solid bold line is the terrestrial fractionation line (TFL) that describes most non-photochemical isotopic compositions (δ$^{17}$O = 0.52×δ$^{18}$O) including NO$_3^-$ from nitrification (white oval), fertilizer NO$_3^-$ (open rectangle) and air O$_2$ (solid square). Mixing between NO$_3$ atm and NO$_3^-$ from nitrification or fertilizer decreases the Δ$^{17}$O proportionally to the respective source strengths (solid circle). Once mixed, any subsequent kinetic or equilibrium isotopic fractionations (denitrification/reduction) follow δ$^{17}$O = 0.52×δ$^{18}$O, i.e. parallel to the terrestrial fractionation line, leaving the Δ$^{17}$O unaltered (arrows). Our overall NO$_3$ atm δ$^{18}$O values are larger (60-95‰) than other studies (40-75‰) but with similar spreads (35‰) and is likely due to recent evidence showing offline NO$_3^-$ δ$^{18}$O experimental methods suffer from scaling factors for samples that differ significantly from δ$^{18}$O near 23‰.(30)
during heterogeneous hydrolysis and the NO$_2$ + OH $\rightarrow$ HNO$_3$ reaction (13). Kinetic isotope effects for the numerous reactions involved in the NO$_x$ cycle may also be playing a role in the $\delta^{18}$O variability. Its is unlikely the fluctuating $\delta^{18}$O values are the signature of multiple NO$_x$ sources as previously suggested (11), since industry and emission do not radically vary with season in the Los Angeles basin. Rather, the $\delta^{18}$O variations are also the result of shifts in oxidation chemistry (the increased importance of N$_2$O$_5$ hydrolysis) that vary with sunlight, temperature and oxidant levels (13).

**Oxygen Isotopic Composition of Stream and Soil NO$_3^-$**

All soil and aquatic NO$_3^-$ samples in this study had positive $\Delta^{17}$O values (Table 1, Fig. 3), unambiguously showing that every sample of soil and water has some degree of NO$_3^-$ atm input. This result is in stark contrast to detecting NO$_3^-$ atm deposition using the $\delta^{18}$O methodology, which would indicate only 15-30% of the samples had detectable NO$_3^-$ atm (Fig. 3). The correlation between $\Delta^{17}$O and $\delta^{18}$O values observed in the atmospheric samples (Fig. 2) is absent in the terrestrial samples (Fig. 3) showing, that while $\Delta^{17}$O scales with the degree of NO$_3^-$ atm deposition, some unknown processes are affecting the $\delta^{18}$O values. The divergence may be due to variability of microbial NO$_3^-$ $\delta^{18}$O values that can range from $-5$ to $15\permil$ depending on isotopic composition of the pore water and O$_2$, soil characteristics, pH, N speciation, and bacterial species (12). These factors require that the microbial $\delta^{18}$O end-member be determined by *in situ* experiments at each individual site. The $\Delta^{17}$O is zero for all microbial nitrification because the oxygen reservoirs utilized in nitrification are water and atmospheric O$_2$, which both have measured $\Delta^{17}$O of $\sim 0$, and the nitrification process itself is a mass-dependent process. Therefore no knowledge of the soil conditions or the isotopic composition of the pore water or pore O$_2$, both of which have
Figure 3 NO$_3^-$ from stream (○) and soil (●) samples and δ$^{18}$O and mass balance mixing lines between NO$_3$ atm (solid oval) and nitrification NO$_3^-$. Nitrification utilizes O atoms from atmospheric O$_2$ (δ$^{18}$O = 23.5‰, $\Delta^{17}$O = -0.15) and soil water in a 1:2 ratio$^{21}$. Precipitation (H$_2$O) for this study had δ$^{18}$O = -8 ± 0.3 ‰, $\Delta^{17}$O = 0 which would result in nitrification δ$^{18}$O ~ +3‰, $\Delta^{17}$O ~ -0.1 (y-axis terminus of solid line), assuming no isotopic fractionation occurs when O$_2$ diffuses into the soil. Other studies indicate the O$_2$/H$_2$O ratio shifts with changing conditions and can produce NO$_3^-$ with δ$^{18}$O values ranging from −5 to 15 ‰ (y-axis terminus of dot-dash lines)$^{21,24}$. NO$_3$ atm detection limits using δ$^{18}$O are shown as horizontal dotted lines for natural systems (N) where nitrification and NO$_3$ atm are the only NO$_3^-$ sources and for agricultural regions (A) where fertilizer NO$_3^-$ (δ$^{18}$O ~18-23‰, $\Delta^{17}$O ~ -0.2) is an additional source. Points above these lines are considered to having detectable NO$_3$ atm. Detection limit using $\Delta^{17}$O (vertical dash line, D) is based on our analytical precision/accuracy of .2‰, with points to the right of the line being samples with detectable NO$_3$ atm.
variable $\delta^{18}O/\delta^{17}O$ values, need be known to apply $\Delta^{17}O$ for estimating $NO_3^{-}_{atm}$ deposition.

$\delta^{18}O$ alterations may also result from known mass-dependent isotopic fractionations such as denitrification (11) or the effect of unmeasured processes, such as soil uptake, plant utilization, abiotic reductions, and ionic transport. For example, isotopic discrimination during leaching has been suggested as one of the causes in the observed $\delta^{15}N$ enrichments with depth in soil $NO_3^{-}$ profiles. Similar increases in the $\delta^{18}O$ values of leached $NO_3^{-}$ would be expected (they have yet to be determined) in roughly a 2:1 fashion relative to $\delta^{15}N$, in a manner similar to the 2:1 $\delta^{18}O:\delta^{15}N$ enrichments observed in denitrifying conditions (11). Although such processes will also alter the $\delta^{17}O$ (in conjunction with $\delta^{18}O$), they do so in a mass-dependent manner, which on a three-isotope plot generates an array of slope .52 parallel to, but offset from, the terrestrial mass fractionation line and leaves the $\Delta^{17}O$ unchanged (see Fig. 2). This emphasizes that although the $\Delta^{17}O$ calculations are made relative to $\delta^{18}O$ values, they are independent of the absolute $\delta^{18}O$ value. For example, the $NO_3^{-}$ found the Devil canyon streams during base flow have $\delta^{18}O$ that differ by 20‰ but have identical $\Delta^{17}O$ (Table 1).

The variability in the isotopic composition of the biologic end-member and fractionation dynamics have been previously cited as the limiting factors in the quantifying $NO_3^{-}_{atm}$ deposition budgets using $\delta^{15}O$ (12). The consequence of these fractionating processes for quantifying $NO_3^{-}_{atm}$ loads can be seen in a comparison of $\delta^{18}O$ and $\Delta^{17}O$ mass balance approaches (Fig. 4). Both overestimations and underestimations of $NO_3^{-}_{atm}$ are prevalent in the $\delta^{15}O$ data, calling into question recent studies that indicate $NO_3^{-}_{atm}$ is not relevant even in watersheds with high N deposition (31). These percentage estimates of $NO_3^{-}_{atm}$ are relative to the terrestrial $NO_3^{-}$ sources and local $\Delta^{17}O$ fluctuations (within each site) are more likely due to the varying local importance
Figure 4 Mass balance estimates of the percentage of NO$_3$ atm in terrestrial NO$_3$ samples using average NO$_3$ atm $\delta^{18}$O = 70‰ and $\Delta^{17}$O = 25‰ and nitrification NO$_3$ $\delta^{18}$O of 3‰, $\Delta^{17}$O = -0.1. The solid line is a 1:1 correlation slope if the $\delta^{18}$O method and the $\Delta^{17}$O method gave the same percentage of NO$_3$ atm. Error bars represent uncertainties using solely the $\delta^{18}$O values due to the range of possible nitrification $\delta^{18}$O values -5‰ to +15‰. Zero or negative % would be interpreted as having no NO$_3$ atm. Peak stream flow during the October storm results in good agreement between $\delta^{18}$O and $\Delta^{17}$O methods. No correlation exists in later storms (March) and there is little agreement during base stream flow conditions or for soil NO$_3$. 
of nitrification rather than deposition differences. Nitrification includes both nitrification of mineralized plant N and the nitrification of NH$_4^+$ that is derived from atmospheric deposition and it is not possible to distinguish between the two N sources using current isotopic methods. The study areas presented here have NH$_4^+$ deposition of roughly equal importance relative to NO$_3^-$ (32,33) so that any N deposition estimates based on NO$_3^-$ atm ($\Delta^{17}O$) are at least a factor of 2 too low. In addition, because the nitrification of atmospheric NH$_4^+$ will have a $\Delta^{17}O = 0$ our N deposition estimates based of $\Delta^{17}O$ calculations may be further diluted, so caution must be used when extrapolating total N from NO$_3$ atm.

The advantages of the $\Delta^{17}O$ methodology for identifying the fraction of NO$_3^-$ atm present are shown by looking at the results from the soil and stream transect sites. At sites closest to Los Angeles, nitrate extracted from surface litter is almost exclusively NO$_3$ atm, with the underlying soil containing up to 17% NO$_3$ atm and significant amounts of NO$_3$ atm detectable throughout the soil profile and in soil lysimeter extracts (Table 1). Soils from the less polluted sites generally contained less than half the amount of NO$_3$ atm relative to the polluted sites even though the deposition rate is a factor of 5 smaller at this local, which suggests that nitrification rates are more dominant in this region. The preservation of the soil nitrate $\Delta^{17}O$ signal indicates that NO$_3$ atm in soils did not undergo complete biological processing prior to being leached from the soil. The stream samples also showed that NO$_3$ atm transported through soil and groundwater in the catchments did not undergo complete biological processing. At the high deposition locations (San Dimas and Devil Canyon) the stream base flow NO$_3$ atm was approximately twice that of moderate-pollution regions (San Gorgonio). These base flow NO$_3^-$ $\Delta^{17}O$ values are not the result of NO$_3$ atm leached into the streams directly from soil because there is no soil/stream hydrologic
connection during dry season base flow conditions. These results suggest that even groundwater in the region is contaminated by NO$_3^-$ atm from atmospheric deposition.

Although we did not analyze changes in $\Delta^{17}O$ values of soil NO$_3^-$ over a detailed time frame, it should be noted the potential use of $\Delta^{17}O$ as a tool in understanding soil N cycling. Since processes such as uptake, utilization and denitrification leave $\Delta^{17}O$ conserved, changes in soil $\Delta^{17}O$ must be the result of net nitrification. This has implications for researchers interested in soil N cycling who are currently studying polluted sites or who are conducting controlled experiments using expensive $^{15}N$ enriched materials. Natural nitrate fertilizer imported from the Atacama region of northern Chile has been determined to have a $\Delta^{17}O\sim20‰$ since they are derived from millennial scale deposition of NO$_3^-$ atm (26,34). This readily available fertilizer offers a low cost alternative to $^{15}N$ for a tracing nitrification dynamics and the fate of NO$_3^-$ as it cycles within ecosystems.

**Stream NO$_3^-$ Isotope Dynamics during Storm Conditions**

The Devil Canyon watershed was also sampled during two storm events, at two locations (Fig 5). Site 2 is in the lower part of the watershed and representative of the total watershed flux and site 7 is one small seasonal tributary in the lower section of the watershed. For both storms during peak flow, close to 40% of the stream NO$_3^-$ originates from atmospheric sources. The NO$_3^-$ $\delta^{18}O$ values differ by 10‰ between locations during storm 1
Figure 5 Stream flow hydrograph for Devil Canyon (solid line), stream NO$_3^-$ concentration for site 2 (dotted line) and site 7 (dashed line) and $\Delta^{17}$O variations for site 2 (■) and site 7 (○) during November and March rainstorms in the Devil Canyon watershed. The November storm was preceded by an 8-month dry period. The March storm came at the end of the rainy season (Table 1) indicating that nitrification/denitrification or some unmeasured isotope effects are locally altering the $\delta^{18}$O, but $\Delta^{17}$O data signify that it is not a decrease in the relative amount of NO$_3^-$atm. The data indicate that during the dry period prior to storm 1, NO$_3^-$atm accumulated on plant and soil surfaces. At the onset of the rainy season, the nitrate is rapidly leached through the dry soil to the shallow ground water, with little time for the surface NO$_3^-$atm to undergo biotic or
abiotic processes that can induce isotopic fractionation, before being discharged into the stream. This description accounts for the parallel $\Delta^{17}O$ and NO$_3^-$ concentration maximums during the initial rains (Fig 5). Silicon concentrations during this first storm were greatly depleted (<1 ppm) relative to base flow conditions (~11 ppm) supporting the shallow ground water hypothesis. The source of the additional NO$_3^-$ atm is not the precipitation itself, since anion analysis of the rainwater gave NO$_3^-$ concentration of ~ 1 ppm which is equal to base flow concentrations. The weak NO$_3^-$/biotic interaction is also evident in the NO$_3^-$ $\delta^{18}O$ values, which are in agreement with NO$_3^-$ atm loading based upon the $\Delta^{17}O$ values (Fig 4), and have been observed in other regions with high N deposition and low N interaction with the soil (10,27). The absence of an increase in the stream NO$_3^-$ concentration during storm 2 suggests most of the NO$_3^-$ in the soil and vegetation has been flushed by previous rains and is either exported or consumed by biological processes. The coincident stream flow and NO$_3^-$ $\Delta^{17}O$ peaks are likely the result of base flow NO$_3^-$ and precipitation NO$_3^-$ atm mixing. During March the base flow is ~ 10 times as great as that observed during November. The silicon concentrations during the March storm (~8ppm) did not dramatically decrease relative to the base flow concentrations (~11ppm) as was observed during the November storm indicating that deep ground water from the rising water table was of greater influence during the time of the year. This would explain the rapid return in NO$_3^-$ $\Delta^{17}O$ values to their base flow values, a phenomena not observed in the November storm where shallow ground water is more important after the long dry period. These observations demonstrate that with more complex nutrient cycling and hydrographic dynamics, $\delta^{18}O$ becomes less robust as a NO$_3^-$ atm tracer, while the $\Delta^{17}O$ tracer is conserved. This supposition is evident in the two soil lysimeter NO$_3^-$ samples where the $\delta^{18}O$ values differ by 40‰, yet the $\Delta^{17}O$ values are identical.
within the experimental error of each other (Table 1). The large % of NO$_3$$_{\text{atm}}$ observed in soil samples conclusively shows that increases in soil NO$_3$$^-$ observed in the soils of southern California ecosystems impacted by air pollution are a direct result of atmospheric deposition. This result is important since increased soil nitrogen concentrations are correlated with ecosystem changes that have been observed in southern California.

Finding so large a fraction (4-40%) of unassimilated atmospherically derived NO$_3$$^-$ in runoff at all sites and the very high percentages (20-40%) in storm runoff in the Devil Canyon catchment has important implications for terrestrial ecology. These results indicate a direct connection between NO$_3$$^-$ concentrations in streamwater and the rate of atmospheric N deposition, although post-depositional processing of N within the watershed is also a major factor influencing runoff NO$_3$$^-$ concentrations. The large amounts of NO$_3$$_{\text{atm}}$ in runoff imply that previous estimates of the fraction of NO$_3$$_{\text{atm}}$ in streams from N-impacted regions may be too conservative (35) in some instances and that some terrestrial ecosystems may not be as efficient in retaining atmospheric N deposition as formerly expected. In particular, seasonally dry ecosystems may leach substantial amounts of inorganic N, especially at the onset of winter rains as seen in our results. This leaching is likely to also impact groundwater and base flow NO$_3$$^-$ concentrations. This study clearly demonstrates that using $\Delta$$^{17}$O signatures to trace the fate of atmospheric nitrate is a powerful technique and can augment the $\delta^{18}$O and $\delta^{15}$N dual isotope method (10,11). This will increase our understanding of N processing and N retention efficiencies within ecosystems that are impacted by atmospheric N deposition.
Table 1 Selected Stream, Soil, and Lysimeter NO$_3^-$ isotopic and concentration data. Percentage of NO$_3^-$ atm estimates are determined using $\delta^{18}O = 70\%$ and $\Delta^{17}O = 25\%$ as average NO$_3^-$ atm values.

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<td>3/18/02</td>
<td>11.4</td>
<td>10.7</td>
<td>4.7</td>
<td>19.7</td>
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<td>Devil Canyon 7</td>
<td>11/13/01</td>
<td>206</td>
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<td>23.9</td>
<td>8.5</td>
<td>35.2</td>
<td>40.7</td>
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<td>11/13/01</td>
<td>250</td>
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<td>19.1</td>
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<td>Devil Canyon 7</td>
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<td>5/2/01</td>
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<td>15.4</td>
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<td>Camp Pavika Surface Litter</td>
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<td>Camp Pavika 0-2 cm</td>
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<td>10/25/01</td>
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<td>Camp Pavika 20-30 cm</td>
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<td>19</td>
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<tr>
<td>Lake Skinner 2-10 cm</td>
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