Title

Landscape level controls on nitrate-nitrogen in forested and chaparral catchments of southern California

Author

Meixner, Thomas

Publication Date

2003-08-01

Landscape level controls on nitrate-nitrogen in forested and chaparral catchments of southern California

Author - Thomas Meixner

Dept. of Environmental Sciences, University of California, Riverside, Room 2208 Geology
email – thomas.meixner@ucr.edu

UC- Water Resources Center Technical Completion Report - W-931
August 2003

Keywords and phrases – Nitrogen deposition, semi-arid, Mediterranean climate, catchment, forested ecosystems, hydrology

Abstract

In this study water quality in a set of catchments that vary from 6 ha to almost 1500 ha is investigated. Studying catchments across this large range of scales enables us to investigate the scale dependence and fundamental processes controlling catchment biogeochemical export. The Devil Canyon catchment, in the San Bernardino Mountains, California, has some of the highest atmospheric N deposition rates in the world (40-90 kg ha^{-1} yr^{-1} at the crest of the catchment). These high rates of deposition have translated into consistently high levels of NO_3^- in some streams of the San Bernardino Mountains. However, the streams of the Devil Canyon catchment have widely varying dissolved inorganic nitrogen (DIN) concentrations, variability, and export. These differences are also, to a more limited extent, present for dissolved organic carbon (DOC) but not in other dissolved species (Cl^-, SO_4^{2-}, Ca^{2+} and other weathering products). As catchment size increases DIN and DOC export first increases until catchment area is ~150 ha but then decreases as catchment scale increases beyond that size. Inorganic nitrogen and DOC also share similar temporal variability within the catchments. The reasons for these phenomena appear to be the dominance of flushing of dissolved constituents out of soil at small scales, the groundwater exfiltration of these flushed materials at intermediate scales and the removal of biologically active materials from streamflow through riparian processes at larger scales. While the particular scale effect observed here may not occur over the same range in catchment area in other ecosystems, it is likely that other ecosystems have similar scale dependant processes. In-stream removal processes are a particularly relevant process for understanding the loss processes controlling the fate and transport of nutrients derived from agricultural and urban land uses.

Introduction

Studies of catchment biogeochemical budgets typically focus on a single catchment or several catchments of the same size (e.g. (Williams and Melack, 1997; Likens and Bormann, 1995) or they have focused on comparison of catchment studies that attempt to answer questions about regional or global level controls on biogeochemical export (Lewis Jr. *et al*., 1999; Perakis and Hedin, 2002; Boyer *et al*., 2002; Sickman *et al*., 2002). This focus is not sufficiently robust to adequately address the influence of fundamental controlling processes in a given climatic regime or ecosystem on biogeochemical export. Neighboring catchments can be used to understand the potential impacts and responses to atmospheric deposition at the catchment scale. Studies across several catchments may increase our understanding of ecosystem susceptibility to nitrogen saturation and the link between aquatic observation and terrestrial ecology and can indicate the processes limiting the adverse impacts of environmental pollution on water quality (e.g. (Aber *et al*., 1989; Aber *et al*., 1998; Stoddard, 1994; Fenn *et al*., 1998).

The Devil Canyon catchment in the western San Bernardino Mountains, 100 km east of Los Angeles, has been the site of catchment biogeochemical export studies since the fall of 1995. This catchment receives some of the highest rates of N deposition in the world (40-90 kg ha^{-1} $year^{-1}$ along the crest; Fenn *et al.* 2003). Although N deposition is high throughout the Devil Canyon catchment, NO_3^- concentrations vary considerably across the sub-catchments. This variability provides a unique opportunity to investigate the differences in process level controls on biogeochemical export among these catchments. Among the processes that may influence biogeochemical export are deposition rate (Fenn and Poth, 1999), flow pathways (Creed *et al*., 1996), residence time (Peterson *et al*., 2001), riparian processes (Grimm and Fisher, 1984) and denitrification (Hill, 1979). A suite of geochemical and hydrologic measurements have been made in these catchments in order to identify what processes might be controlling biogeochemical export from these catchments. In this report we seek to answer the following questions regarding biogeochemical export from seasonally dry catchments:

1) How does biogeochemical export vary with time and scale in Mediterranean catchments?
2) Do differences in atmospheric deposition rate determine the differences in export?
3) What are the controls on biogeochemical export in catchments with Mediterranean climates and how do these controls change with catchment size and time?

Methods and Procedures

Site Description

Observations were collected for the Devil Canyon catchment, 6 sub-catchments and 1 groundwater spring. Devil Canyon is heavily impacted by atmospheric deposition from the urban Los Angeles air mass. In previous studies (Fenn and Poth, 1999) it was demonstrated that the eight locations in this study had vastly different NO_3^- concentrations despite being within several kilometers of each other. Camp Paivika is located at the top of the catchment at 1580 m, while the USGS stream gauge station (Station no. 11063680) (site 8 in Figure 1) is at an elevation of 632 m. Vegetation is mixed conifer near the crest of the catchment but grades to chaparral at lower elevations with riparian areas dominated by white alder (*Alnus rhombifolia* Nutt.) with intermediate elevation and riparian zones having large areas of California bay laurel (*Umbellularia californica*), scrub oak (*Quercus dumosa*) and coast live oak (*Quercus agrifolia*). The geology of the Devil Canyon catchment is composed of crystalline and sedimentary rocks

ranging from ancient Precambrian to quaternary deposits. Much of Devil Canyon is underlain by plutonic igneous rocks of Mesozoic age, predominately quartz monzonite and granodiorite (Fenn and Poth, 1999).

Mean annual precipitation for the catchment varies from 610 mm $year^{-1}$ at the bottom of the catchment to 987 mm $year^{-1}$ at the top of the catchment at Camp Paivika. Precipitation is profoundly seasonal with more than 80% of precipitation occurring as rain during the period from December to March. The 8 catchments being sampled vary greatly in catchment area, dominant riparian and catchment wide vegetation types as well as mean slope (Table 1) (Fenn and Poth, 1999). Since NH_4^+ concentrations are generally undetectable at Devil Canyon and in chaparral catchments in general (Riggan *et al*., 1985), NO_3^- is equivalent to dissolved inorganic nitrogen (DIN).

Field and Laboratory Methods

The 8 catchments have been sampled to varying degrees since 1996. Sampling and analysis previous to 2000 was reported in *Fenn and Poth* (1999). The data from 1996 through 1998 is used in this paper to calculate mass fluxes and mean concentrations using additional data from this study. For this study, grab sampling was conducted at all 8 sites weekly in winter and monthly in summer. Grab samples were filtered (0.45 μm membrane filters) immediately in the field into triple-rinsed plastic bottles. Simultaneous to all grab sampling, stream flow was measured either by the velocity profile method or by recording the time it takes to fill a container of known volume. Grab sampling was supplemented by the use of autosamplers (Sigma 900 max). Samples were taken every 4 hours with an autosampler and composited into a single bottle for each day. On some occasions, samples were taken in discrete bottles to understand how the catchments behaved during storm events. During these storm events an autosampler was maintained at site 2 while two other autosamplers were rotated between sites such that we attempted to capture several significant rain events for each of the sites. Separate grab samples were collected for organic carbon analysis. Organic carbon samples were collected in combusted glass bottles with Teflon lined lids. Organic carbon samples were filtered with combusted glass fiber filters (Whatman GF-F) within 2 days of returning from the field and samples were acidified with H_2SO_4. Samples for metal analysis were acidified within one day after sampling. All samples were stored in the dark at 4 ^oC until analysis; DOC and nitrogen analyses were completed within 1 month of field collection.

A Technicon TRAACS 800 Autoanalyzer (Tarrytown, NY) was used to analyze for nitrate (NO_3^-), ammonium (NH_4^+) and soluble reactive phosphorus (SRP). A Varian ICP-OES was used with filtered and acidified samples for the analysis of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), and silica (Si) concentrations. Total dissolved organic carbon (DOC) concentrations were determined using a Shimadzu TOC-V. Some early samples were analyzed with a Dohrmann-Xertex TOC analyzer that utilizes persulfate oxidation of organic carbon and ultraviolet radiation to determine the amounts of dissolved organic carbon in the samples.

Atmospheric Deposition

Atmospheric deposition to the Devil Canyon catchment was estimated using 64 ion exchange resin column throughfall collectors (Fenn *et al.*, 2002). These collectors were located throughout the catchment under different species, and several collectors were placed in open locations where precipitation could enter the collectors unimpeded by vegetation. These collectors measure total bulk deposition and bulk throughfall. The ion exchange resin columns were exchanged every 7-

9 months over a two-year period from October 2000 to October 2002. Estimates of atmospheric deposition to the catchments were calculated by averaging deposition rates for individual vegetation types including: chaparral (*Quercus dumosa, Ceanothus crassifolius, Umbellurario californica*), hardwood (*Quercus chrysolepsis, Alnus rhombifolia, Juglans californica*), and conifer estimates (Fenn *et al.* 2003). The mean estimates for deposition under the different vegetation types were then used to calculate a weighted average of annual deposition to each catchment. These weighted averages were calculated by multiplying the deposition estimates by the fractional coverage of each vegetation type for each of the catchments (reported in Table 1). Standard deviations for the estimates of the deposition were calculated by combining the errors associated with each of the vegetation types in a weighted manner by the area of each vegetation type within each catchment.

Flow Estimates

It was not possible to instrument all of these sites with stage recorders and develop rating curves. For the purposes of calculating mass export from these catchments and for calculating volume weighted mean concentrations, we developed simple linear regression equations with the flow measurements we made at each of the sites with the data from site 8 where a USGS recording gauge is located. Some sites had better correlations than others (sites 2, 3, 5 and 6 all having r^2 of 0.7 or more) (Table 2). The correlation coefficients generated from these equations were then used to generate continuous flow time series for each of the sites. Errors for these extrapolations are included in our analysis and reported in the results section. Variance in flow predictions was calculated as:

$$\sigma^2 = \frac{SSE}{n-2}$$

where σ^2 is the variance in the flow predictions, SSE is the sum of squared errors between the flow predicted by the linear regression and the observed flow and n is the number of observations. The standard deviation is then calculated as the square root of the variance and then divided by the mean observed flow in each catchment to generate the reported % error (Table 2). Mean annual flow for the USGS gauge at site 8 is reported as downloaded from the USGS NWIS online database (http://waterdata.usgs.gov/nwis/sw USGS Station no. 11063680, Table 3)

Calculating Mass Budgets and Error Analysis

Using all of the available stream chemical analyses we calculated annual mass export, export per unit area and volume weighted mean (VWM) concentrations for the year (Williams and Melack, 1997). The error in these calculations was determined by combining the error in our extrapolations in flow for each of these sites and the error introduced by our sampling and analytical error according to the equation:

$$E_t = (E^2_A + E^2_B)^{1/2}$$

where E_A and E_B are two errors, in our case the error introduced by our flow estimates and that estimated using Tukey's jackknife method (Sokal and Rohlf, 1981). In Tukey's jackknife method, variability in mean solute concentrations is calculated by removing an observation from consideration in calculating the mean and repeating for each sample. The variability of these calculations is then used to calculate a standard error (Williams and Melack, 1997).

Tributary Calculations

Catchments 3, 4, 5, 6 and 7 are all tributary to the west fork of Devil Canyon at site 2. This structure to our sampling allows us to calculate the difference between export at site 2 and export from the combination of these five catchments. This calculation of catchment 2 export minus the export from its tributaries indicates the relative export coming from the remaining 413 ha of catchment 2 (from now on these calculations will be discussed as catchment 2 minus tributaries (catchment 2-tribs). The chemical load from the tributaries was calculated then subtracted from the export of catchment 2 and the difference was then divided by the difference in flow to calculate VWM concentrations. There are two relatively unsampled streams (unlabeled in Figure 1) that are tributary to site 2. One has not been observed to flow during this study. For the other we have very limited data. The few samples we have indicate concentrations similar to catchment 4.

Longitudinal Surveys and Stream Tracer Experiments

To investigate the longitudinal variability of stream chemical composition we sampled stream water quality along the reach between site 5 and site 2 at a distance of every 250'. Samples were collected unfiltered and later filtered in the lab. These samples were analyzed in the laboratory for the same suite of constituents as the standard sampling. In the summer of 2001 temperature loggers (tidbit's) were also placed in the field at the longitudinal survey sample points. The loggers were left in the field for one week. Loggers would indicate groundwater exfiltration via decreased variability in stream temperature relative to areas without groundwater exfiltration.

We conducted several stream tracer injection experiments to investigate the ability of the stream to consume inorganic nitrogen. Three experiments were conducted one in September of 2001, one in December of 2001 and one in March of 2001. In each experiment a concentrated solution of NaBr and $NaNO_3$ was injected at a constant rate using a peristaltic pump. The stream was then sampled 40 and 290 meters downstream of the injection site. Br transport was assumed to be conservative and thus could identify sources of dilution to the stream. Relatively greater loss in NO_3 as compared to Br would indicate some sort of biological or chemical loss mechanism in the stream.

Results

Runoff

Runoff from the seven catchments increases in total volume as scale increases (Figure 2 – bottom). When calculated as runoff depth, runoff at first increases with increasing scale but then decreases as the catchment size becomes larger (Figure 2 – top). To some degree this increase and then decrease in effective runoff reflects the fact that as catchment size increases the mean catchment elevation decreases and precipitation decreases as well due to the strong orographic effect in the San Bernardino Mountains (Minnich, 1986) (Figure 2). Mean annual runoff at site 8 shows profound inter-annual variability reflecting the highly variable precipitation patterns of southern California (Table 3). We have rainfall data for this area for the last two years and we report mean runoff coefficients for these two years (Table 4).

Temporal Variability in Nitrate Concentration

The temporal variability of NO_3^- concentration shows a profound seasonality for the three main stem catchments (Catchments 2, 5 and 8) with highest concentrations during the winter coinciding with the highest stream flows, while the smaller catchments show a more divergent

pattern of NO_3^- variability. Some locations such as site 1 (a groundwater spring) and catchment 6 (sampled just downhill from an ephemeral groundwater spring) have consistent concentrations. Other tributary streams like catchment 4 and catchment 7 have patterns that are somewhat similar to the main stem streams. Finally, the ephemeral stream at catchment 3 has a sharp peak in NO_3^- concentration at the onset of flow and then a sharp decline in concentration as time progresses (Figure 3). Other species do not show this temporal variability with season

Correlation with flow of Concentration

Looking at NO_3^- variation versus flow as well as Ca^{2+} and DOC concentration versus flow helps illustrate the dominant processes governing NO_3^- concentrations in these 8 catchments (Table 5). A strong correlation between NO_3^- and DOC concentration and flow is seen at sites 2, 4, 5, and 8 (r^2 of 0.85, 0.48, 0.63, and 0.86 for NO_3^-, 0.55, 0.45, 0.65 and 0.47 respectively for DOC). Conversely there is generally a negative (but weak) correlation between flow and Ca^{2+} concentration at these same sites (for sites 2, 4, 5 and 8 an r^2 of 0.22, 0.09, 0.7, 0.18).

Volume Weighted Mean Concentrations

Reported VWM concentrations against catchment size are widely variable among the chemical species studied. For VWM NO_3^- concentration there is a strong increase in concentration until catchment size reaches 137 ha (Catchment 5). Further increases in size are associated with a decline in VWM concentrations. DOC shows a general trend with respect to scale if catchments 3 and 8 are censored. Catchment 3 and 8 have DOC concentrations much higher than the other locations most likely due to the large amount of vegetative litter in and near the stream directly upstream from these two sampling sites. Given this data censoring, the highest DOC concentrations are at catchment 5 and decline as catchment scale becomes larger or smaller. VWM Ca^{2+} concentrations exhibit a general increase in concentration with scale, although with considerable variability. For Cl^- there is little trend with catchment size, except that catchment 7 and catchment 8 had higher Cl^- concentrations. Inter-annual variability indicates dilution for Cl^- and Ca^{2+} with wet years (1998 and 2001) having lower concentrations than dry years (2002). The same is not true for NO_3^- concentrations. Instead NO_3^- concentrations are generally higher in wet years 1996, 1998, and 2001 while dry years such as 2002 have lower concentrations. Nitrate concentrations do not fit this pattern in 1997 when concentrations were low, notwithstanding the somewhat wet conditions. With only 2 years of data little can be said about inter-annual variability in DOC concentrations (Table 6 and Figure 4).

Uncertainty in Estimates

The uncertainty in our estimates of mass fluxes and VWM concentrations is relatively large due to the error in estimates of flow (Table 2). However, the error due to our sampling regime was small (generally less than 1%) and is therefore not reported. The small sampling error is likely due to our frequent sampling and the relatively stable nature of water quality in our catchments (Meixner *et al*., 2001). Combined errors are not reported but coefficients of variation are equivalent to errors in flow estimates due to much larger error in flow as compared to sample error.

Deposition Estimates

Nitrogen deposition in throughfall varied among the species we sampled under (Table 7), although these differences are not statistically significant due to the large variability in our data. *Quercus chrysolepsis* had the highest average deposition rate (26 kg ha^{-1} $year^{-1}$) while the other hardwood species (*Alnus rhombifolia and Juglans californica*) had lower rates (17 and 16 kg ha^{-1} $year^{-1}$ respectively). The chaparral species (*Quercus dumosa, Ceanothus crassifolius*, and *Umbellaria californica*) had lower mean deposition rates (13, 17 and 14 kg ha^{-1} $year^{-1}$ respectively). These estimates of deposition are lower than those for conifer forests at Camp Paivika (the high point of the catchment, rates are estimated as 40-90 kg ha^{-1} $year^{-1}$). Throughfall deposition data from earlier studies for the mixed conifer forest were used for the higher elevations of the catchments. While these studies indicate deposition rates as high as 90 kg ha^{-1} $year^{-1}$ we used a conservative estimate of 40 kg ha^{-1} $year^{-1}$ since we do not know the spatial extent to which these very high rates occur (Fenn *et al.* 2002; 2003).

Riparian Losses

The 413 ha catchment (catchment 2 – tribs) had consistently lower NO_3^- export, VWM NO_3^- concentrations, and NO_3^- yield compared to catchment 2 (Figure 4). This indicates that there is a net loss of NO_3^- as water flows to catchment 2 through the large riparian corridor of the catchment. This result indicates some loss mechanism is operating within this area. Other chemical species also indicate a slight net loss to a strong gain between the tributaries and site 2. The longitudinal data indicates that NO_3^- concentrations generally decline as distance downstream increases but with noticeable increases in concentrations in areas where the decreased variability in stream temperature indicates that the source of stream NO_3^- is from exfiltrating groundwater (Figure 5). The tracer studies indicate a significant loss mechanism for NO_3^- in September when streamflow was low but similar very small losses of NO_3^- during December and March. These results indicate that the loss of NO_3^- from the stream is via a heterotrophic microbial process. If plant uptake were important we would expect a significant difference between the December (alder has no leaves) and March (leaves are starting to come out) experiments (Figure 6). This difference in the experiments indicates that, not surprisingly, increased streamflow leads to reduced NO_3^- loss thus explaining the variability of NO_3^- and possibly DOC with increases in flow.

N Retention and Yield

These species level differences in deposition resulted in slightly different estimated deposition rates to the catchments. These differences do not affect our overall results dramatically but may partially explain why catchment 5 has higher NO_3^- export since it also has the highest N deposition rates (Table 7). Nitrogen deposition, retention and yield results for each catchment are reported (Table 7 and Figure 7). In addition, nitrogen yield as % is reported against catchment area for all of the years of available data (1996, 1997, 1998, 2001, and 2002). These results again indicate the increasing yield of nitrogen from these catchments as catchment size increases to 137 ha and then decreases at larger scales. Retention is high in % terms for most catchments but lower for catchment 5. Retention figures in terms of mass are more divergent due to difference in deposition among the catchments.

Discussion

Temporal Variability

The sites group into categories that will help further discussion. Sites 1, 3, 4, 6, and 7 are tributaries to the main stem of Devil Canyon while sites 5, 2 and 8 (in that order) are a downstream transect along the stream (Figure 1). Both site 1, a spring sampled at the source, and site 7, a relatively constant flow stream with a long course and narrow watershed (Figure 1), have relatively stable NO_3^- concentrations (average values of 50 μmoles L^{-1} for site 1 and 70 μmoles L^{-1} for site 7) throughout the year (Figure 3). The three sites with the largest area and largest flow, sites 2, 5 and 8 (USGS site) have a distinctive rise in concentration in the winter months (as high as 220, 360 and 105 μmoles L^{-1} respectively) and a subsequent decline in concentration during the summer months (to minimum concentrations of 1, 16 and 25 μmoles L^{-1} respectively) (Figure 4). The two sites with relatively little flow and the lowest concentrations (often below detection limits), site 6 and site 3, are similar in their low levels of inorganic N, but Site 3 has a notable flushing of NO_3^- (peak concentration of 105 μmoles L^{-1}) at the onset of flow (site 3 is in an ephemeral stream) while concentrations at site 6 are remarkably stable (Figure 3). Site 4 is somewhat of an intermediate stream, it has an annual variation in NO_3^- concentration but its concentration values (peak of 66 μmoles L^{-1} and a minimum of 15 μmoles L^{-1}) are smaller than the large sites (2, 5 and 8) and somewhat higher than the two shallow flow dominated sites 3 and 6 (Figures 3 and 4).

Importance of Flow Variability

The strong correlation with flow for both NO_3^- and DOC at these sites indicate that similar processes or source waters control the concentration of both of these chemicals in the waters of Devil Canyon. Similarly the negative correlation for Ca^{2+} indicates that a different process is controlling the concentration of Ca^{2+} in the Devil Canyon watershed. Possibly a flushing out of soils of water and dissolved materials may be responsible for the high NO_3^- and DOC concentrations seen at higher flows. However, pore water flushing tends to produce a profound hysteresis (rising limb concentrations are usually higher than falling limb concentrations) in stream water DOC and NO_3^- concentrations, and at least at the larger sites (2, 5 and 8) we do not observe hysteresis. An alternative hypothesis for the higher NO_3^- and DOC concentrations observed at higher flows may be due to increased hydraulic gradients in the subsurface decreasing the residence time of waters in the subsurface and limiting the amount of time for denitrification to occur. Since both DOC and NO_3^- are substrates in the microbial reactions of denitrification (Hedin *et al*., 1998) increased residence time would decrease the concentrations of both NO_3^- and DOC if denitrification were a major process controlling these two chemicals. This second explanation could explain the variability observed in the larger ground water dominated streams of Devil Canyon since there are extensive riparian areas and much of the sampling is during baseflow conditions and not during active storm events.

The site groupings identified above can be further described by the physical processes that appear to be controlling NO_3^- concentrations. Two sites appear to be dominated by deep groundwater, site 1 and site 7. Site 1 is a spring sampled at its source so we know that it has little interaction with a riparian zone of any sort. Site 7 has relatively consistent and large flows and geochemically is enriched in Ca^{2+} (concentrations of almost 100 mg L^{-1} as opposed to average for the other sites of 60 mg L^{-1}) indicating that it has deep groundwater as its source. Site 3 and 6 appear to be dominated by water from relatively shallow flowpaths (low Ca^{2+} concentrations of ~20 mg L^{-1}) possibly more indicative of terrestrial processes than the groundwater dominated streams like site 1 and site 7. Both have relatively low flows with site 3 being an ephemeral stream and site 6 having very low flows consistently throughout the year

(and sometimes drying out as it has this past summer) with often times very low NO_3^- concentrations, high DOC concentrations, and relatively low Ca^{2+} concentrations with the exception that at site 3, at the onset of streamflow, there is a very distinct flush of high NO_3^- concentrations followed by low concentrations as has been observed at many ephemeral streams in seasonally dry climates (Riggan *et al*., 1985; Schlesinger *et al*., 1999; Tate *et al*., 1999). Site 3 also has a noticeable concurrent and similar flush of DOC (data not shown). These observations indicate that these two sites are most closely tied to the terrestrial biogeochemistry of their watersheds. The remaining sites (2, 4, 5, and 8) might be termed the perennial streams. These streams generally have a very strong correlation (positive or negative) between flow and NO_3^-, DOC, and Ca^{2+} (correlations are weakest for site 4 with Ca^{2+} being especially weak) unlike the ephemeral streams (sites 3 and sites 6). These streams are no doubt the most perennial of the streams we sampled since their riparian areas are dominated by alder trees and are deep groundwater dominated streams for most of the sampling period. They also represent the streams most likely to be surveyed as indicators of ecosystem processes (whether terrestrial or aquatic) in southern California, since they actually flow throughout much of the year and would generally be accessible from the valley floor. It might be assumed that much of the NO_3^- we observe in these streams originated as N fixed by the white alder that is commonly present in the riparian zones of these 4 streams. Alders are not a likely source since all other evidence points to the riparian areas being net N sinks (lower concentrations of NO_3^- at site 2 and even lower ones at site 8 as compared to site 5). Additionally we have conducted several longitudinal surveys down the stream and the results of these surveys indicate consistently dropping NO_3^- concentrations between site 2 and site 5 in all seasons.

Effect of Scale on Chemical Export

The differential pattern of increase and subsequent decrease of NO_3^- export and DOC export with catchment size compared to the other chemical species indicates that similar processes control these two species, while the other chemical species are controlled by a different set of processes. All species exhibit the expected increased total flux with catchment area (Figure 4 and Table 6) since runoff increases with catchment size and flowpath length and residence time are expected to increase with increasing catchment area (Clow *et al*., 1996). Catchments with more runoff per unit area have greater export of each chemical species with some exceptions. For example, catchment 8 has much larger fluxes of Ca^{2+} and other weathering products, and Cl^- and SO_4^{2-}, again possibly due to the longer flowpaths and residence times at larger scales (Clow *et al*., 1996). Catchment 3 does not follow the general trend as well and has very small fluxes per unit area; probably because it is an ephemeral stream.

Most illuminating and most representative of the average biogeochemical processes for the catchments is the VWM concentration results because this represents the mean chemical composition of an average liter of water in the catchment. The VWM concentrations indicate that NO_3^- and DOC share a process level control as VWM concentrations first increases with catchment area before decreasing again as catchment area continues to increase (this censors DOC concentrations for catchment 8 and catchment 3 from the data set). Catchment 3 has a lot of litter debris in its riparian area as does the area immediately up-stream of site 8 while other locations do not have as much litter present in their riparian areas. Weathering products exhibit considerable variability indicating catchment-to-catchment differences superimposed on a general increase with catchment area. The variability of Cl^- and SO_4^{2-} shows little relationship with catchment scale, instead being indicative of catchment-to-catchment variability with high

Cl^- and SO_4^{2-} in catchments 7 and 8 and the other catchments generally having similar Cl^- and SO_4^{2-} concentrations.

Inter-Annual Variability in Export

There is considerable inter-annual variability in VWM concentrations as well as total flux and flux per area. For Cl^- and Ca^{2+} this inter-annual variability appears to be due solely to a dilution effect in years with more runoff. For NO_3^- a generally inverse pattern is seen, with wetter years having higher VWM concentrations and drier years having lower concentrations. There are some exceptions to this; for example, 1997 had similar runoff as 1996 (Table 3) but VWM NO_3^- concentrations were lower, and 2001 had much less runoff than 1998 but similar or higher VWM NO_3^- concentrations. This pattern may be due to differences in antecedent conditions among the years; 1997 was preceded by a relatively wet year while 2001 was preceded by 2 relatively dry years. This pattern indicates inter-annual storage of NO_3^- in the unsaturated zone of these catchments, which is not surprising given the relatively dry nature of the system and the large potential evapotranspiration flux for Mediterranean catchments.

The results here are reported with a significant degree of uncertainty (Table 2). However, this uncertainty is probably overestimated for the VWM concentration data since concentrations and concentration patterns are fairly stable (as evidenced by the less than 1 % error we calculated using Tukey's jackknife). We have our highest confidence in the VWM concentration results and somewhat lower confidence in the results derived for the flux per area and total flux from each catchment due to the relatively large errors in flow (Table 2).

Deposition and Retention

The deposition measurements we have made at Devil Canyon do indicate differences among species in terms of total rates of deposition on an annual time scale (Table 7). The larger flux for *Quercus chrysolepsis* (canyon live oak) may be due to the expansive canopy of these trees, thus serving as a large receptor for atmospheric pollutants. Varying deposition under different vegetation types translates into differences in total deposition to the catchments as based on estimated land cover in each catchment (Table 1 and (Fenn and Poth, 1999))). Differences in deposition may be in part responsible for the higher VWM NO_3^- concentrations observed in catchment 5 since this catchment has the highest rates of estimated deposition. However, catchments 3 and 4 have significant coniferous areas and slightly higher N deposition than most catchments, but this doesn't lead to high NO_3^- export. Catchment 5 has the peak NO_3^- yield (in mass), the peak retention of nitrogen (in mass terms), but the lowest percent N retention due to the much higher deposition it receives (Figure 7). Instead, some set of hydrologic and biogeochemical processes lead to increases in nitrogen export from the 6 ha to 137 ha scale and then to a decline in nitrogen export as scale increases from there.

Riparian Control

Data for the 413 ha scale catchment (catchment 2 – tribs) in all of the figures suggests what the controlling process on nitrogen export might be as we move from the 137 ha scale to larger scales. This 413 ha scale represents export or VWM concentration at catchment 2 minus the flows and concentrations from the tributaries. For example, the negative concentrations for the 413 ha scale in 2002 are notable (Figure 4). Although a negative concentration is not physically possible, it indicates that export from catchment 2 was less than the combined export from all of the monitored tributaries. This result means that between the tributaries and the outlet of

catchment 2 there is a significant N loss process. These riparian losses also appear to operate in years with higher flow as evidenced by the considerable downtick in VWM concentration and nitrogen export at catchment 2-tribs for the other available years of data (Figure 4). For DOC there was a similar decline in concentration and export for catchment 2 minus its tributaries indicating that the loss process is shared (possibly denitrification) between DOC and NO_3^-. The longitudinal survey data further supports the riparian hypothesis since decreases in stream NO_3^- occur in the downstream direction and increases coincide with regions of groundwater exfiltration (Figure 5). The stream tracer data indicates that the riparian loss mechanism is most likely heterotrophic microbial activity in the near stream hyporheic zone (Figure 6).

What processes explain the observed spatial pattern?

Inorganic nitrogen export from this set of 8 catchments shows a pattern of increased flux with catchment size until 137 ha and then decreased flux as catchment size becomes larger. A combination of processes explains this spatial pattern. At the smallest scale (6 ha and 31 ha, catchment's 6 and 3 respectively) the streams are ephemeral and there is possibly a large unmeasured vertical flux below these catchments because both sampling sites are located on top of bedrock, a substrate that is highly fractured in the San Bernardino Mountains (Graham et al., 1994). Pulses of NO_3^- occur at these two locations at the onset of flow (pulses are much larger at catchment 3 than at catchment 6), but the pulse is short lived and flow is typically very low during these initial flow periods (Meixner *et al*., 2001). As scale increases flow becomes more perennial, and export and VWM concentration of NO_3^- and DOC increase to a point before declining. The low export and concentrations in the ephemeral streams may be a result of close contact with terrestrial processes or that residence time in the catchment is longer (due to drier conditions) so that inorganic nitrogen is lost through some process (i.e., plant uptake or denitrification) prior to surface water export.

Past studies of nitrogen export in Mediterranean climates have consistently found that NO_3^- concentrations increase sharply with increases in flow and particularly during the first couple of storms following the long dry summer (Riggan *et al*., 1985; Avila *et al*., 1992; Holloway and Dahlgren, 2001; Tate *et al*., 1999; Dahlgren *et al*., 2001). This pattern of pulses of NO_3^- with storms and especially the first storm at the end of a dry period is also present in the Devil Canyon catchment (Meixner *et al*., 2001). The source of this NO_3^- is generally ascribed to NO_3^- that has accumulated in soils and groundwaters during the long dry season in California from mineralization, nitrification and atmospheric deposition processes. The higher export in the larger streams may also be partially caused by an increase in mineralization and nitrification, and soil inorganic N pools with soil wetting that has been observed in many other studies (Ryan *et al.*, 1998; Davidson, 1992; Smart *et al.*, 1999). These studies have also typically shown that microbial immobilization, root growth and plant uptake typically take a period of days to weeks to start depleting the mineral nitrogen pool (Cui and Caldwell, 1997; Cabrera, 1993). Others have argued that the period of soil rewetting and delayed microbial immobilization in seasonally dry climates contributes to a loss of N capital, thus favoring nitrogen fixation in these ecosystems to replace losses of inorganic N at the onset of seasonal transitions (Vitousek and Field, 1999; Vitousek and Field, 2001; Schimel, 2001). In the Devil Canyon catchment this natural process of inorganic nitrogen losses at the seasonal transition is emphasized with the long dry summer during which polluted air masses from the greater Los Angeles air basin result in chronic N deposition to the catchment (Fenn and Bytnerowicz, 1993; Fenn *et al*., 1996a; Fenn and Poth, 1999; Meixner *et al*., 2001).

This large accumulation of summer dry deposition and increased mineral N pools and losses at the onset of winter rains indicates an asynchrony between when mineral N is available to terrestrial plants in the Devil Canyon catchment and when those plants are able to utilize mineral N. Our data support this asynchrony hypothesis; ephemeral streams have low inorganic nitrogen export indicating that the landscape as a whole is still relatively nitrogen limited. Additionally, nitrogen limitation of plant growth has been demonstrated in N fertilization studies in the mixed conifer forest at Camp Paivika on the crest of Devil Canyon (Fenn and Poth, 2001). The condition of N limitation in the forests of Devil Canyon indicates that they are at the early stages of N saturation (stage 0 or 1) but the stream data we have (Fenn and Poth , 1999, Meixner *et al.* 2001 and Figure 3) indicate that the ecosystem is at stage 2. This conflict indicates a flaw in the N saturation hypothesis possibly explained by our asynchrony hypothesis.

During the first rain events of the wet season pulses of nitrate are presumably flushed from the soil profile and are either lost immediately to runoff or leached below the rooting zone thus contributing to groundwater recharge. This NO_3^- rich groundwater later supplies the large inorganic N flux we observe at the larger scale in these streams. The flushing of inorganic nitrogen to groundwater during the wet season has been hypothesized and demonstrated previously (Creed *et al*., 1996; Burns *et al*., 1998). Creed *et al.* (1996) hypothesized that flushing of inorganic N out of the soil profile during periods of low biotic N demand or during spring snowmelt recharge groundwater with high N content waters later to be released in stream baseflow. Burns *et al.* (1998) found that springs recharged by snowmelt waters had high NO_3^- concentrations and that these springs were largely responsible for increased NO_3^- flux from the Neversink catchment during the summer months. Our results and previous results (Berg *et al*., 1991; Fenn and Poth, 1999; Meixner *et al*., 2001) argue for the flushing mechanism as the source of NO_3^- loss from the small ephemeral catchments (early season flush from soil followed by low concentrations) and the groundwater draining mechanism (leading to high total export and high summer concentrations) to explain the heightened nitrogen export at the intermediate scale.

The decrease in NO_3^- concentrations and export at the larger scale is probably due to in-stream and riparian losses from groundwater and surface water within the large productive riparian alder forest that thrives along the main West Fork stem of Devil Canyon between sampling site 5 and sampling site 8. Numerous researchers have shown that small headwater streams are significant sinks for inorganic nitrogen (Peterson *et al*., 2001; Alexander *et al*., 2000). The pathway for this in-stream and riparian loss of NO_3^- is not singular; it may be due to denitrification (Groffman *et al*., 1999; Holmes *et al*., 1996) microbial assimilation (Hedin *et al*., 1998; Sobczak *et al*., 2003) or plant uptake. While the processes of in-stream loss are well studied and there are numerous examples of longitudinal studies demonstrating NO_3^- loss in streams (e.g. (Burns, 1998),(Cooper, 1990; Hill *et al*., 2000) the importance of in-stream loss at the catchment scale is less extensively studied. Most studies have focused on particular catchments (e. g. McDowell, 2001; Mulholland, 1992; Mulholland and Hill, 1997) and not on the relative importance of riparian losses with increases in catchment scale.

Processing length describes the distance it takes for a given amount of a nutrient to be consumed along a stream (Peterson *et al*., 2001). With longer processing length nutrient removal in a stream is less for the same physical stream distance. While processing length varies with season and discharge (longer processing lengths at high flows than at low), it is clear that with increasing stream length the capacity for N uptake and loss increases. Our data indicates that from the intermediate scale up, DIN concentrations decline (Figure 6). The riparian loss mechanism also explains the observed inter-annual variability in NO_3^- export. Because wetter

years have higher flows, residence time is shorter and thus more NO_3^- would move through the riparian system and evade biological assimilation. This pattern is what we have observed (Figure 4). This result and the underlying mechanism are further supported by the longitudinal and tracer experiment results (Figures 5 and 6).

Implications for the N Saturation Hypothesis

Similar to results in the Catskill Mountains of New York (Lovett *et al*., 2000), we have found that neighboring catchments have significantly different N export and by extension we would assume that they are at different stages of N Saturation. As discussed above, there are two main causes for these differences in export: 1) perennial streams receiving groundwater contributions have higher N exports than more ephemeral streams and export increases as catchment size increases up to approximately 150 ha and 2) riparian and in-stream losses of NO_3^- cause DIN export to decrease as scale becomes large (~ 400 ha). These two causes of spatial variability are expected to be common across a wide range of ecosystems. Others have also shown that groundwater contribution can disrupt the underlying logic of the N saturation hypothesis (Burns *et al*., 1998; Stoddard, 1994; Aber *et al*., 1998; Aber *et al*., 1989) in that streams are not necessarily perfect mirrors of the landscapes they flow through. It is possible also that the N saturation hypothesis needs to be tempered by groundwater residence time and groundwater contribution factors. Such a correction might look like the corrections made to the N saturation hypothesis in a study of several Norwegian catchments some of which had relatively large lakes that increased water residence time in the catchments (Kaste *et al*., 2003). The riparian loss mechanism also confounds interpretation of the degree of N saturation since in-stream losses can give the appearance that the terrestrial system is exporting less N than it really is. Catchment 8 in this study is a case in point; streamwater data from catchment 8 suggest that it is less N saturated than tributary streams in catchment 2 or 5.

Conclusions

There are several important lessons to be learned from this study that can be used by water resource managers in California.

1) The high rates of atmospheric deposition near the urban areas of California are likely to adversely impact stream water quality. These levels are not high enough to violate the drinking water standard but could be an issue as relates to surface water eutrophication and the use of wildland runoff to dilute high nitrate concentrations in groundwater contaminated by historical and current agricultural activities.
2) California's wild ecosystems have a noticeable seasonal flush of nitrate at the onset of flow. This observation has been made repeatedly, including in this study. The reason for this observation may be the long dry preceding fall rains and the inability of terrestrial ecosystems to quickly immobilize mineralized nitrogen once the soils wet up. This asynchrony of N availability and N demand is most likely a common trait for Mediterranean ecosystems.
3) In stream losses help explain the seasonal pattern of stream nitrate concentrations observed here and the data points toward a microbial process being the controlling factor.

4) Finally, the in stream loss processes are important in urban and agricultural systems in California where they could represent a significant additional sink for nutrients that is not currently represented in water quality regulations in the state.

Publications

Fenn, M. E., Baron, J. S., Allen, E. B., Rueth, H. M., Nydick, K. R., Geiser, L., Bowman, W. D., Sickman, J. O., Meixner, T., Johnson, D. W., and Neitlich, P. 2003. 'Ecological effects of nitrogen deposition in the western United States', *BioScience,* **53**, 404-420.

Meixner,T., Allen,E.B., Tonnessen,K., Fenn,M.E. & Poth,M.A. **Atmospheric nitrogen deposition: Implications for managers of western U.S. parks**. *Park Science* Denver, Colorado: National Park Service. (2002).

Meixner, T., Fenn, M. E., and Poth, M. A. 2001. 'Nitrate in polluted mountainous catchments with Mediterranean climates', *The Scientific World,* **1**, DOI 10.1100/tsw.2001.324.

Acknowledgements

This research was funded by the University of California Water Resources Center and by the University of California Agricultural Experiment Station. Pete Clark, Jeff McGovern, Megan Robinson, Bridgette Valeron, Tony Davila, Jim Strong and Peggy Resketo assisted in field sampling and laboratory analyses that contributed to this manuscript.

References

Aber, J. D., McDowell, W., Nadelhoffer, K. J., Magill, A., Berntson, G., Kamakea, M., McNulty, S., Currie, W., Rustad, L., and Fernandez, I. 1998. 'Nitrogen saturation in temperate forest ecosystems - Hypotheses revisted', *BioScience,* **48**, 921-934.

Aber, J. D., Nadelhoffer, K. J., Steudler, P., and Melillo, J. M. 1989. 'Nitrogen Saturation in northern Forest ecosystems', *BioScience,* **39**, 378-386.

Alexander, R. B., Smith, R. A., and Schwarz, G. E. 2000. 'Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico', *Nature,* **403**, 758-761.

Anderson, M. A., Graham, R. C., Alyanakian, G. J., and Martynn, D. Z. 1995. 'Late Summer Water Status of Soils and Weathered Bedrock in Giant Sequoia Grove', *Soil Science,* **160**, 415-422.

Avila, A., Pinol, J., Roda, F., and Neal, C. 1992. 'Storm solute behavior in a montane Mediterranean forested catchment', *J. Hydrol.,* **140**, 143-161.

Berg, N., Dunn, P., and Fenn, M. 1991. 'Spatial and temporal variability of rime ice and snow chemistry at five sites in California', *Atmos. Environ.,* **25A**, 915-926.

Boyer, E. W., Goodale, C. L., Jaworski, N. A., and Howarth, R. W. 2002. 'Anthropogenic nitrogen sources and relationships to riverine export in the northeastern U. S. A.', *Biogeochemistry,* **57/58**, 137-169.

Boyer, E. W., Hornberger, G. M., Bencala, K. E., and McKnight, D. M. 1997. 'Response Characteristics of doc flushing in an alpine catchment', *Hydrol. Processes,* **11**, 1635-1647.

Burns, D. A. 1998. 'Retention of NItrate in an upland stream environment: a mass balance approach.', *Biogeochemistry,* **40**, 73-96.

Burns, D. A., Murdoch, P. S., Lawrence, G. B., and Michel, R. S. 1998. 'Effect of groundwater springs on NO3- concentrations during summer in Catskill Mountain streams', *Water Resources Reseach,* **34**, 1987-1996.

Cabrera, M. L. 1993. 'Modeling the Flush of Nitrogen Mineralization Caused by Drying and Rewetting Soils', *Soil Sci. Soc. Am. J.,* **57**, 63-66.

Clow, D. W., Mast, M. A., and Campbell, D. H. 1996. 'Controls on surface water chemistry in the upper Merced River basin, Yosemite National Park, California', *Hydrol. Procecces,* **10**, 727-746.

Cooper, A. B. 1990. 'Nitrate depletion in the riparian zone and stream channel of a small headwater catchment', *Hydrobiologia,* **202**, 13-26.

Creed, I. F. and Band, L. E. 1998. 'Exploring functional similarity in the export of nitrate-N from forested catchments: A mechanistic modeling approach', *Water. Resourc. Res.,* **34**, 3079-3093.

Creed, I. F., Band, L. E., Foster, N. W., Morrison, I. K., Nicolson, J. A., Semkin, R. S., and Jeffries, D. S. 1996. 'Regulation of nitrate-N release from temperate forests: a test of the N flushing hypothesis', *Water. Resourc. Res.,* **32**, 3337-3354.

Cui, M. and Caldwell, M. M. 1997. 'A large ephemeral release of nitrogen upon wetting of dry soil and corresponding root responses in the field', *Plant Soil.,* **191**, 291-299.

Dahlgren, R. A., Tate, K. W., Lewis, D., Atwill, E. R., Harper, J. M., and Allen-Diaz, B. H. 2001. 'Watershed research examines rangeleand management effects on water quality', *California Agriculture,* **55**, 64-71.

Fenn, M. E. and Bytnerowicz, A. 1993. 'Dry deposition of nitrogen and sulfur to Ponderosa and Jeffrey pine in the San Bernardino National Forest in southern California', *Environmental Pollution,* **81**, 277-285.

Fenn, M. E. and Bytnerowicz, A. 1997. 'Summer throughfall and winter deposition in the San Bernardino Mountains in southern California', *Atmos. Environ.,* **31**, 673-683.

Fenn, M. E. and Poth, M. A. 1999. 'Temporal and Spatial Trends in Streamwater Nitrate Concentrations in the San Bernardino Moutains, Southern California', *Journal Environmental Quality,* **28**, 822-836.

Fenn, M. E., Poth, M. A., Aber, J. D., Baron, J. S., Bowman, B. T., Johnson, D. W., Lemly, A. D., McNulty, S. G., Ryan, D. F., and Stottlemyer, R. 1998. 'Nitrogen excess in North American ecosystems: A review of geographic extent, predisposing factors, ecosystem responses, and management strategies', *Ecological Applications,* **8**, 706-733.

Fenn, M. E., Poth, M. A., and Johnson, D. W. 1996b. 'Evidence for nitrogen saturation in the San Bernardino Mountains in southern California', *Forest Ecology Management,* **82**, 211-230.

Fenn, M. E., Poth, M. A., and Johnson, D. W. 1996a. 'Evidence for nitrogen saturation in the San Bernardino Mountains in southern California', *Forest Ecology Management,* **82**, 211-230.

Fisher, S. G., Grimm, N. B., Marti, E., Holmes, R. M., and Jones Jr., J. B. 1998. 'Material sprialing in stream corridors: a telescoping ecosystem model', *Ecosystems,* **1**, 19-34.

Grimm, N. B. and Fisher, S. G. 1984. 'Exchange between interstitial and surface water: Implications of stream metabolism and nutrient cycling', *Hydrobiologia,* **111**, 219-228.

Groffman, P. M., E. Holland, D. D. Myrold, G. P. Robertson, and X. Zou, Denitrification, in *Standard soil methods for long-term ecological research,* edited by G. P. Robertson, D. C. Coleman, C. S. Bledsoe, and P. Sollins*,* Oxford University Press, New York, 1999.

Hedin, L. O., von Fisher, J. C., Ostrom, N. E., Kennedy, B. P., Brown, M. G., and Robertson, G. P. 1998. 'Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces', *Ecology,* **79**, 684-703.

Hill, A. R. 1979. 'Denitrification in the nitrogen budget of a river ecosystem', *Nature,* **281**, 291-293.

Hill, A. R., Devito, K. J., Campagnolo, S., and Sanmugadas, K. 2000. 'Subsurface denitrification in a forest riparian zone: Interactions between hydrology and supplies of nitrate and organic carbon', *Biogeochemistry,* **51**, 193-223.

Holloway, J. M. and Dahlgren, R. A. 2001. 'Seasonal and event-scale variations in solute chemistry for four Sierra nevada catchments', *J. Hydrol.,* **250**, 106-121.

Holmes, R. M., Jones Jr., J. B., Fisher, S. G., and Grimm, N. B. 1996. 'Denitrification in a nitrogen-limited stream ecosystem', *Biogeochemistry,* **33**, 125-146.

Lewis Jr., W. M., Melack, J. M., McDowell, W. H., McClain, M., and Richey, J. E. 1999. 'Nitrogen yields from undistrubed watersheds in the Americas', *Biogeochemsitry,* **46**, 149-162.

Likens, G. E. and F. H. Bormann, *Biogeochemistry of a forested ecosystem second edition* Springer-Verlag, New York, 1995.

Lovett, G. M., Weathers, K. C., and Sobczak, W. V. 2000. 'Nitrogen saturation and retention in forested watersheds of the Catskill Mountains, New York', *Ecological Applications,* **10**, 73-84.

McDowell, W. H. 2001. 'Hurricanes, people and riparian zones: controls on nutrient losses from forested Carribean watersheds', *Forest Ecology Management,* **154**, 443-451.

Meixner, T., Fenn, M. E., and Poth, M. A. 2001. 'Nitrate in polluted mountainous catchments with Mediterranean climates', *The Scientific World,* **1**, DOI 10.1100/tsw.2001.324.

Minnich, R. A. 1986. 'Snow levels and amounts in the mountains of southern California', *J. Hydrol.,* **89**, 37-58.

Mulholland, P. J. 1992. 'Regulation of nutrient concentrations in a temperate forest stream: Roles of upland, riparian, and instream processes', *Limnol. Oceanogr.,* **37**, 1512-1526.

Mulholland, P. J. and Hill, W. R. 1997. 'Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects', *Water. Resourc. Res.,* **33**, 1297-1306.

Perakis, S. S. and Hedin, L. O. 2002. 'Nitrogen loss from unpolluted South American forests mainly via dissolved organic compunds', *Nature,* **415**, 416-419.

Peterson, B. J., Wollheim, W. M., Mullholland, P. J., Webster, J. R., Meyer, J. L., Tank, J. L., Marti, E., Bowden, W. B., Valett, H. M., Hershey, A. E., McDowell, W. H., Dodds, W. K., Hamilton, S. K., Gregory, S., and Morall, D. D. 2001. 'Controls of nitrogen export from watersheds by headwater streams', *Science,* **292**, 86-90.

Riggan, P. J., Lockwood, R. N., and Lopez, E. N. 1985. 'Deposition and processing of airborne nitrogen pollutants in Mediterranean-type ecosystems of southern California', *Envirnomental Science and Technology,* **19**, 781-789.

Schimel, J. P., Biogeochemical Models: Implicit versus explicit microbiology, in *Global Biogeochemical Cycles in the Climate System,* edited by D. G. Schulze, M. Heimann, S. Harrison, E. Holland, J. Lloyd, I. C. Prentice, and D. Schimel, pp. 177-183, Academic Press, New York, 2001.

Schlesinger, W. H., Abrahams, A. D., Parsons, A. J., and Wainwright, J. 1999. 'Nutrient loss in runoff from grassland and shurbland habitats in southern New Mexico: I. rainfall simulation experiments', *Biogeochemistry,* **45**, 21-34.

Schlesinger, W. H., Ward, T. J., and Anderson, J. 200. 'Nutrient losses in runoff from grassland and shurbland habitats in southern New Mexico: II. field plots', *Biogeochemistry,* **49**, 69-86.

Sickman, J. O., Melack, J. M., and Stoddard, J. L. 2002. 'Regional analysis of inorganic nitrogen yield and retention in high-elevation ecosystems of the Sierra Nevada and Rock Mountains', *Biogeochemistry,* **57/58**, 341-374.

Sobczak, W. V., Findlay, S., and Dye, S. 2003. 'Relationships between DOC bioavailability and nitrate removal in an upl;and stream: An experimental approach', *Biogeochemistry,* **62**, 309-327.

Sokal, R. R. and F. J. Rohlf, *Biometry: The Prinicples and Practice of Statistics in Biological Research*W. H. Freeman, New York, 1981.

Stoddard, J. L., Long-term changes in watershed retention of nitrogen - its causes and aquatic consequences, in *Environmental Chemistry of Lakes and Reservoirs,* edited by L. A. Baker, pp. 223-284, American Chemical Society, Washington, DC, 1994.

Tate, K. W., Dahlgren, R. A., Singer, M. J., Allen-Diaz, B., and Atwill, E. R. 1999. 'Timing, frequency of sampling affect accuracy of water-quality monitoring', *California Agriculture,* **53**, 44-48.

Vitousek, P. M. and Field, C. B. 1999. 'Ecosystem constraints to symbiotic nitrogen fixers: a simple model and its implications', *Biogeochemistry,* **46**, 179-202.

Vitousek, P. M. and C. B. Field, Input/output Balances and Nitrogen Limitation in Terrestrial Ecosystems, in *Global Biogeochemical Cycles in the Climate System,* edited by E. D. Schulze, M. Heimann, S. Harrison, E. Holland, J. Lloyd, I. C. Prentice, and D. Schimel, pp. 217-225, Academic Press, New York, 2001.

Williams, M. R. and Melack, J. M. 1997. 'Atmospheric deposition, mass balances, and processes regulating streamwater solute concentrations in mixed-conifer catchments of the Sierra Nevada, California', *Biogeochemistry,* **37**, 111-144.

Table 1 Catchment characteristics

Catchment	Area (ha)	Catchment slope (%)	Conif. cover (%)	Hard. Cover (%)	Chap cover (%)	Riparian	Fire – (Year, % of WS)
1	N/A	N/A	5	12	77	N/A	1954 (91%), 1980 (40%)
2	667	49	12	22	65	Alder	1954 (74%), 1980 (52%)
3	28	49	27	39	34	Oak	1954 (84%), 1980 (14%)
4	31	50	36	56	8	Alder	1954(91%)
5	137	47	67	21	12	Alder	1954(17%)
6	6	51	0	1	99	Bay	1954 (100%), 1980 (71%)
7	52	50	13	4	81	Chap.	1954 (99%), 1980 (32%)
8	1421	50	10	15	75	Sycamore	1954 (91%), 1980 (40%)
2 – tribs	413	49	0	17	83	Alder	1954 (87%), 1980 (78%)

Table 2 Correlation Statistics for catchment streamflow with USGS gauge (site 8)

Catchment	r^2	# of obs.	% error
2	0.851	60.00	25
3	0.903	14.00	28
4	0.508	65.00	43
5	0.750	61.00	35
6	0.696	48.00	40
7	0.309	66.00	57

Table 3 Mean annual flow for Site 8

Year	Mean Annual Flow (l s^{-1})
1996	98
1997	118
1998	220
1999	40
2000	38
2001	40
2002	7

Table 4 Runoff from each catchment (2001 and 2002 data)

Catchment	Runoff (mm)	Precip. (mm)	Runoff Coeff.
2	74	550	0.13
3	3.6	550	0.006
4	91	550	0.17
5	134	550	0.24
6	7.4	550	0.013
7	45	550	0.081
8	61	550	0.11
2 -tribs	61	550	0.11

Table 5 - Regression Results for DOC, NO_3^- and Ca^{2+} against Stream Discharge

	DOC vs. Flow			NO_3^- vs. Flow			Ca^{2+} vs. Flow		
Site	Pearson R	R^2	Bonferroni P	Pearson R	R^2	Bonferroni P	Pearson R	R^2	Bonferroni P
1	0.363	0.132	0.097	0.677	0.458	0.001	-0.118	0.014	0.598
2	0.745	0.555	0.000	0.926	0.857	0.000	-0.464	0.215	0.017
3	0.691	0.477	0.009	0.557	0.310	0.038	-0.501	0.251	0.140
4	0.671	0.450	0.000	0.689	0.475	0.000	-0.298	0.089	0.097
5	0.804	0.646	0.000	0.797	0.635	0.000	-0.837	0.700	0.000
6	0.451	0.203	0.008	0.045	0.002	0.791	-0.228	0.052	0.226
7	0.545	0.297	0.001	0.507	0.257	0.002	-0.045	0.002	0.806
8	0.686	0.470	0.000	0.927	0.860	0.000	-0.415	0.172	0.077

Table 6 Volume weighted mean chemical concentration1 (2001 and 2002 data)

Catchment	NO_3^-	Ca^{2+}	Cl^-	DOC	K^+	Mg^{2+}	Na^+	Si	SO_4^{2-}
2	83	1353	183	3.1	61	495	451	330	261
3	16	1515	236	5.7	107	492	406	242	187
4	33	905	145	1.9	45	325	317	329	142
5	170	1110	170	4.6	47	333	396	284	154
6	13	890	219	2.1	38	387	509	473	137
7	88	1714	436	3.0	62	768	726	477	682
8	64	1498	799	6.5	158	1215	1471	796	743
2 -tribs	24	1565	176	2.2	74	615	486	348	323

[1] Concentrations are in μM except for DOC which is in mg L^{-1}

[2] NO_3^- means are for period of 1996-2002 using data from this study and Fenn and Poth 1999.

Table 7 Atmospheric nitrogen deposition by plant species and catchment (2001 and 2002)

Species (common name)/Catchment	number of collectors	Mean NO_3^--N (stdev.) kg ha^{-1} $year^{-1}$	Mean NH_4^+-N (stdev.) kg ha^{-1} $year^{-1}$	N (stdev.) kg ha^{-1} $year^{-1}$
Quercus chrysolepsis (canyon live oak)	*12*	14 (8)	13 (6)	26 (13)
Quercus dumosa (scrub oak)	*7*	6 (2)	7 (3)	13 (5)
Alnus rhombifolia Nutt. (white alder)	*11*	7 (3)	9 (4)	17 (5)
Ceanothus crassifolius (buckthorn)	*11*	7 (4)	9 (7)	17 (8)
Umbellularia californica (California bay-laurel)	*7*	7 (2)	6 (2)	14 (4)
Juglans californica (walnut)	*4*	8 (3)	8 (2)	16 (4)
Open	7	4 (1)	7 (3)	11 (3)
Others [1]	3	5 (2)	7 (2)	11 (3)
Conifer[2]		20 (5)	20 (5)	40 (7)
2		9 (6)	9 (7)	18 (11)
3		11 (7)	12 (7)	23 (11)
4		13 (8)	13 (7)	26 (12)
5		16 (6)	16 (6)	33 (9)
6		6 (5)	7 (8)	14 (10)
7		8 (5)	9 (7)	18 (10)
8		8 (6)	9 (8)	18 (11)
2 - tribs.		7 (6)	8 (8)	17 (11)

[1] 1 each of willow, mountian mahogany, and white sage

[2] from Fenn et al. 2003

Figure 1 – Sampling site locations in the Devil Canyon catchment. Site 8 is coincident with a USGS Gauging Station. Site 1 is a spring sampled at its source.

Figure 2 – Mean annual runoff from the 7 Devil Canyon stream locations in liters and centimeters. Graph shown with x-axis as catchment size. Catchments from left to right are 6, 3, 4, 7, 5, 2, 2-tributaries, and 8 (as labeled across the top of the figure). Runoff depth is highly variable with catchment scale while runoff volume increases consistently with catchment size.

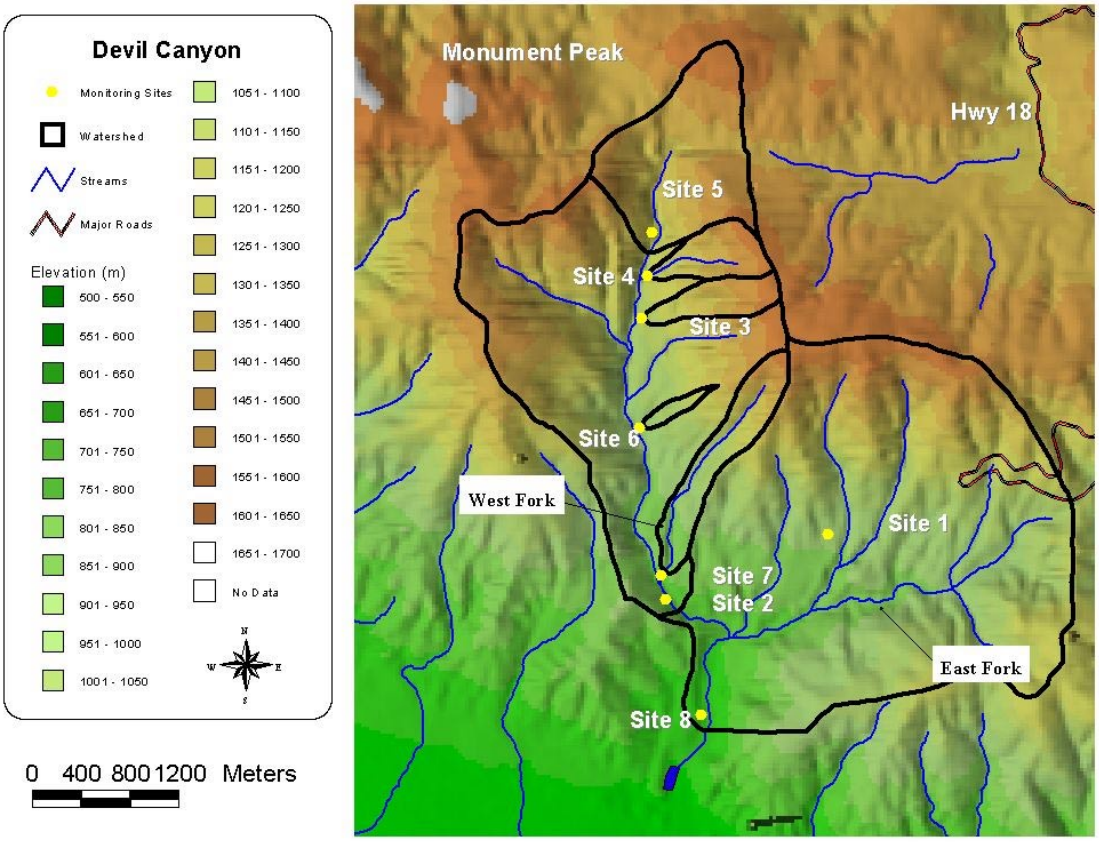
Figure 3 – Temporal graph of NO_3^- concentration for all sites. For purposes of presentation, top graph is main stem sites 2, 5 and 8; bottom graph is tributary locations sites 1, 3, 4, 6 and 7. Main stem sites have profound seasonal variability with peak NO_3^- coinciding with peak flow. Tributary sites differ in their seasonal variability from little variability (site 1) to variability similar to the main stem sites (site 4).

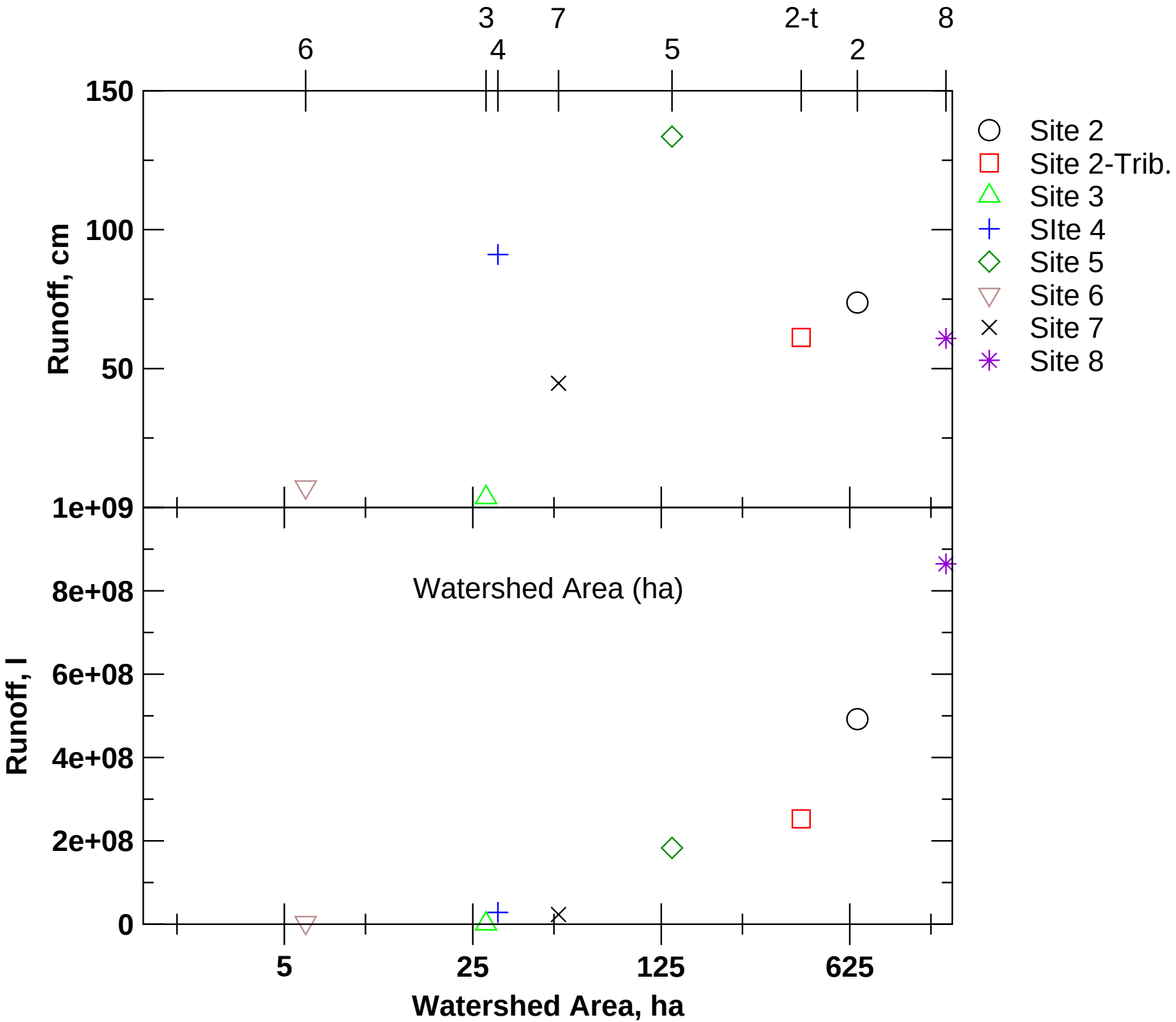
Figure 4 – Annual total export of NO_3^-, DOC, Ca^{2+} and Cl^- from the 7 monitored catchments as well as catchment 2 minus tributaries. Data shown with catchment size on x-axis. Catchments from left to right are 6, 3, 4, 7, 5, catchment 2 minus tributaries, 2 and 8 (as labeled across the top of the figure). Export increases for all species with catchment size, although to a lesser degree for NO_3^- and DOC.

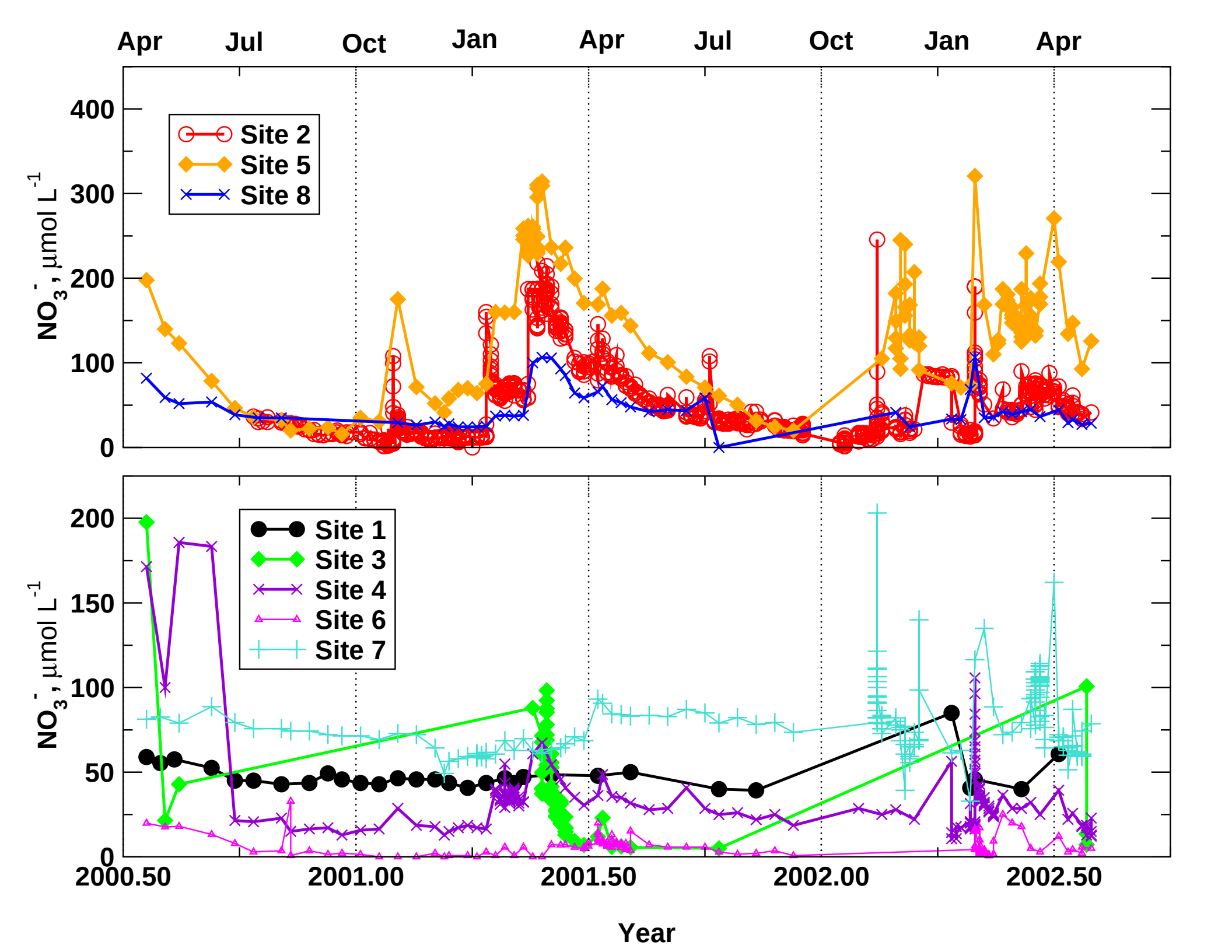
Figure 5 – Data from several stream longitudinal surveys in the Devil Canyon catchment

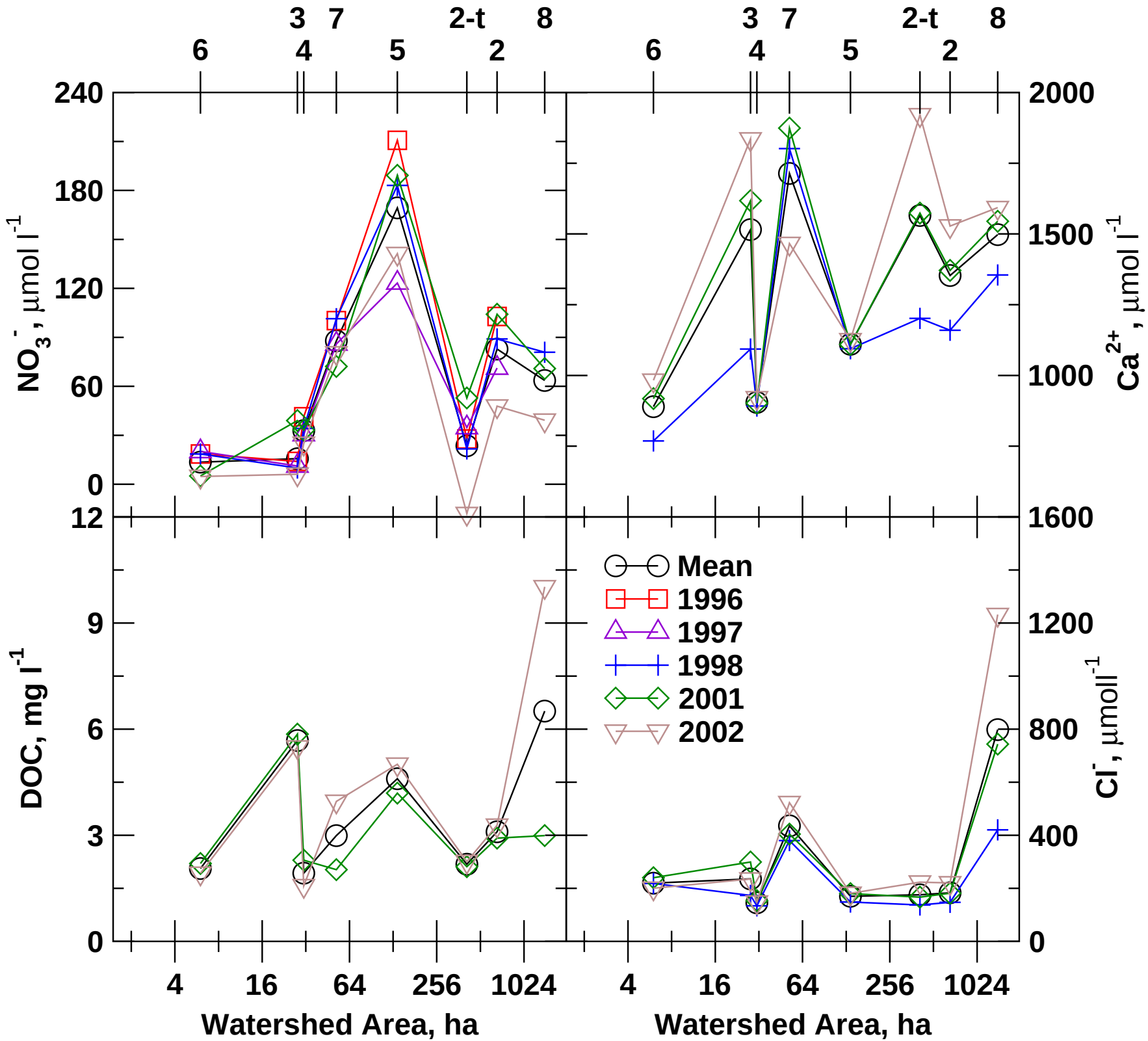
Figure 6 - Results from three stream tracer experiments conducted on the lower reach of the Devil Canyon catchment. Significant loss of nitrogen was observed in September experiment but not in other two experiments.

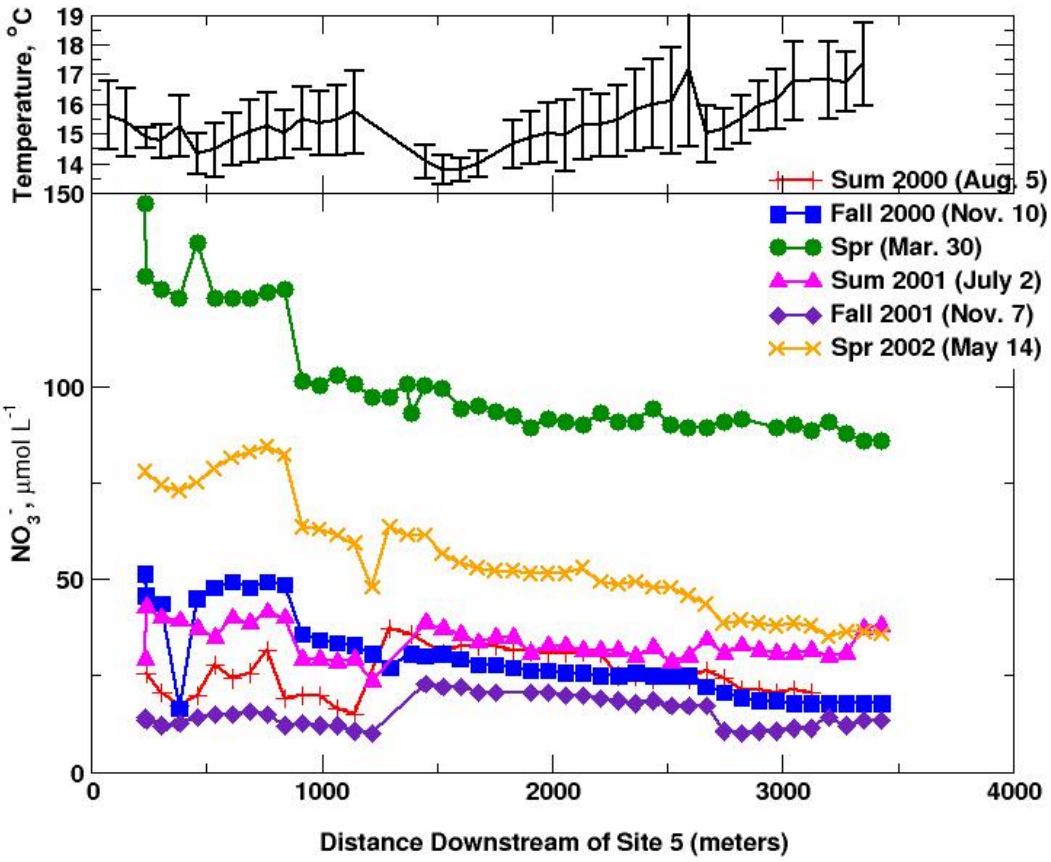
Figure 7 – Catchment nitrate yield for the 7 monitored catchments as well as catchment 2 minus its tributaries. Data shown with catchment size on x-axis. Catchments from left to right are 6, 3, 4, 7, 5, catchment 2 minus tributaries, 2 and 8 (as labeled across the top of the figure). Nitrate yield shows the same general spatial pattern as for the VWM concentration with peak yields for the intermediate catchment sizes. Retention data is more mixed due to differences in deposition among catchments.

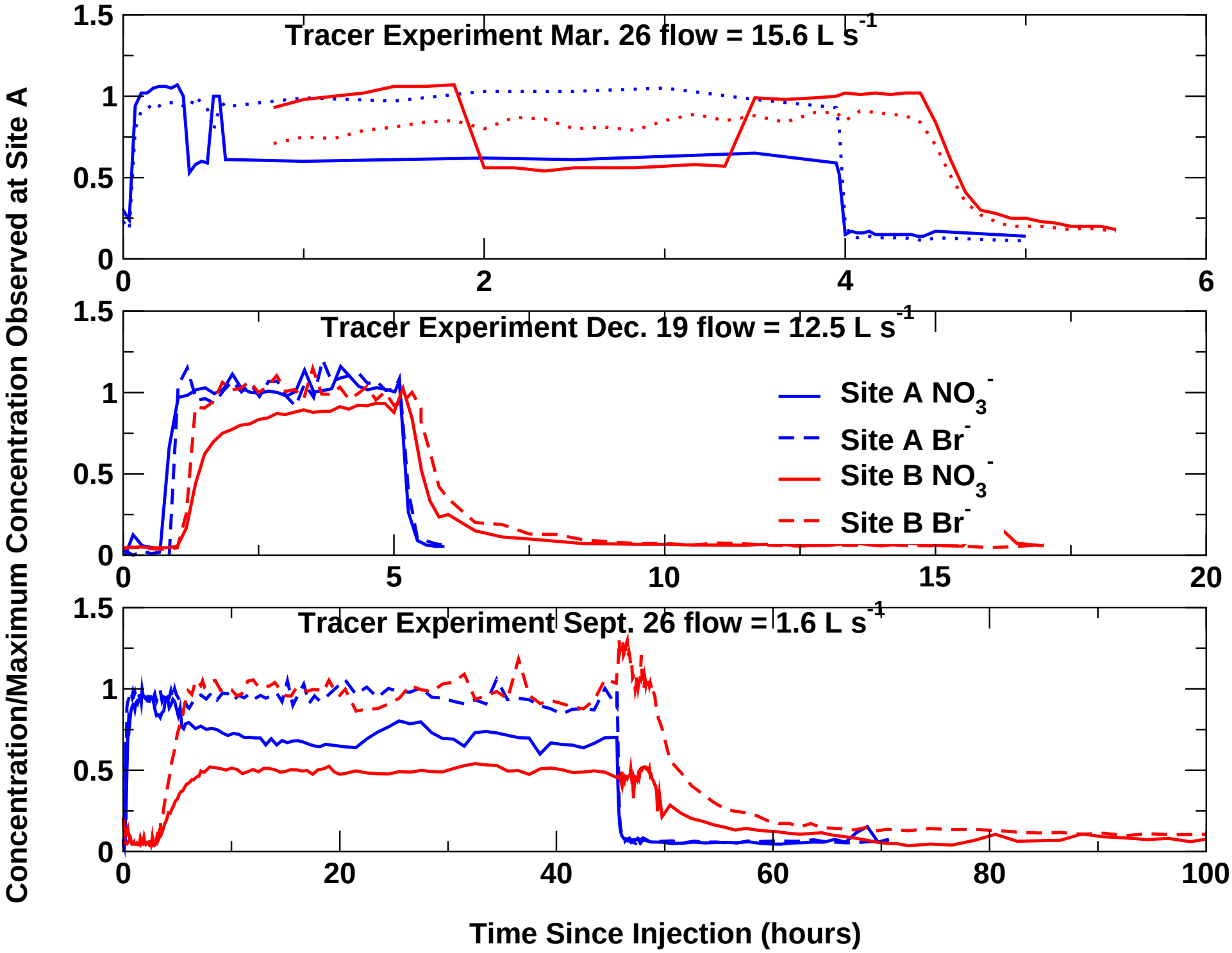

Devil Canyon
Monitoring Sites
Watershed
Streams
Major Roads
Elevation (m)
500 - 550
551 - 600
601 - 650
651 - 700
701 - 750
751 - 800
801 - 850
851 - 900
901 - 950
951 - 1000
1001 - 1050
1051 - 1100
1101 - 1150
1151 - 1200
1201 - 1250
1251 - 1300
1301 - 1350
1351 - 1400
1401 - 1450
1451 - 1500
1501 - 1550
1551 - 1600
1601 - 1650
1651 - 1700
No Data
N
W
E
S
0 400 800 1200 Meters
Monument Peak
Hwy 18
Site 5
Site 4
Site 3
Site 6
West Fork
Site 1
Site 7
Site 2
East Fork
Site 8

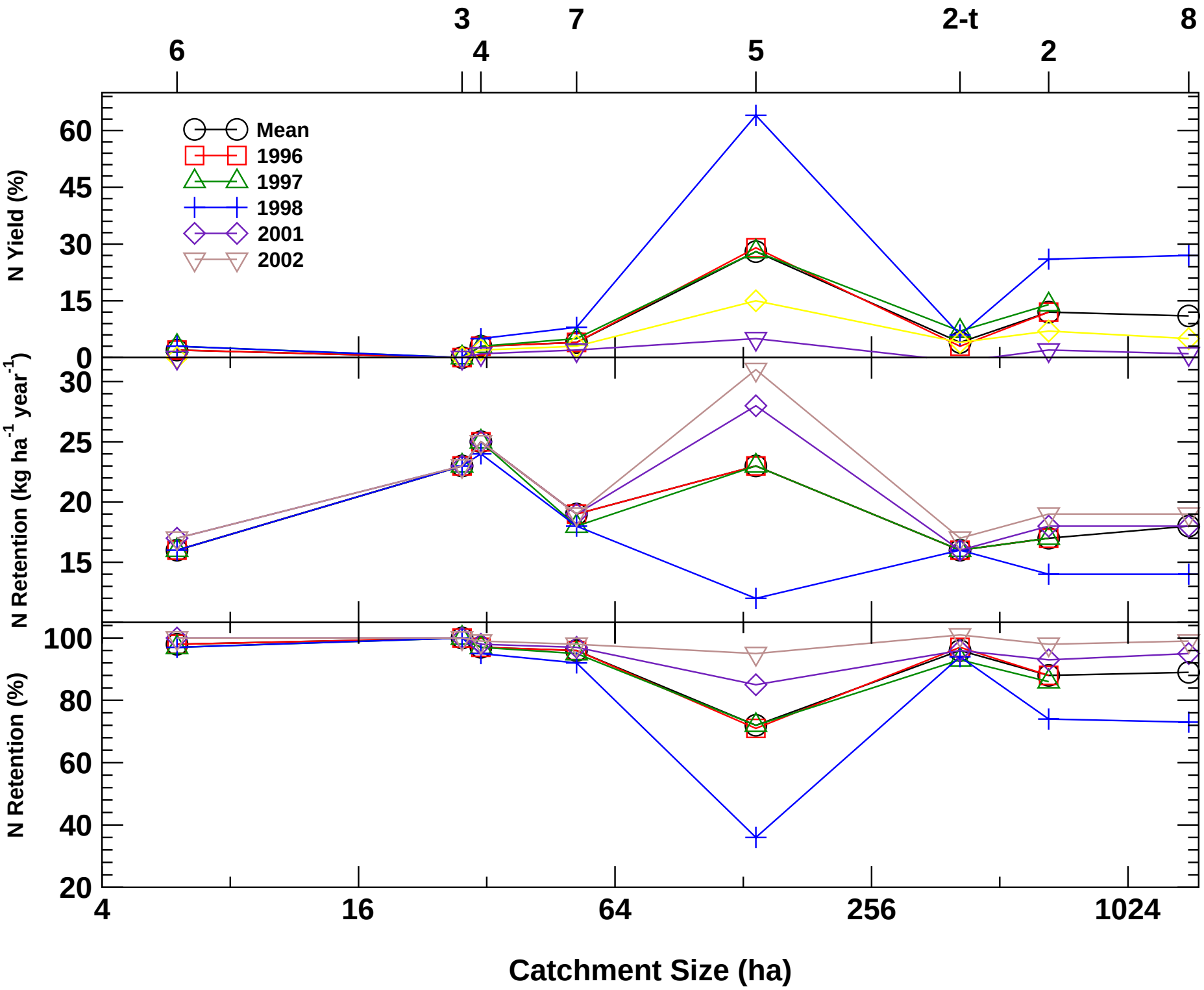

3
7
2-t
8
6
4
5
2
150
100
50
1e+09
8e+08
6e+08
4e+08
2e+08
0
Runoff, cm
Runoff, l
Watershed Area (ha)
5
25
125
625
Watershed Area, ha
Site 2
Site 2-Trib.
Site 3
SIte 4
Site 5
Site 6
Site 7
Site 8


Apr
Jul
Oct
Jan
Apr
Jul
Oct
Jan
Apr
Site 2
Site 5
Site 8
NO_3^-, µmol L^{-1}
0
100
200
300
400
Site 1
Site 3
Site 4
Site 6
Site 7
NO_3^-, µmol L^{-1}
0
50
100
150
200
2000.50
2001.00
2001.50
2002.00
2002.50
Year


6
3
4
7
5
2-t
2
8
240
180
120
60
0
NO_3^-, µmol l^{-1}
2000
1500
1000
Ca^{2+}, µmol l^{-1}
12
9
6
3
0
DOC, mg l^{-1}
1600
1200
800
400
Cl^-, µmoll^{-1}
Mean
1996
1997
1998
2001
2002
4
16
64
256
1024
Watershed Area, ha


Temperature, °C
19
18
17
16
15
14
150
100
50
0
NO_3^-, µmol L^{-1}
0
1000
2000
3000
4000
Distance Downstream of Site 5 (meters)
Sum 2000 (Aug. 5)
Fall 2000 (Nov. 10)
Spr (Mar. 30)
Sum 2001 (July 2)
Fall 2001 (Nov. 7)
Spr 2002 (May 14)


Tracer Experiment Mar. 26 flow = 15.6 L s-1
Tracer Experiment Dec. 19 flow = 12.5 L s-1
Tracer Experiment Sept. 26 flow = 1.6 L s-1
Site A NO3-
Site A Br-
Site B NO3-
Site B Br-
Concentration/Maximum Concentration Observed at Site A
Time Since Injection (hours)
0
0.5
1
1.5
0
2
4
6
0
5
10
15
20
0
20
40
60
80
100


6
3
4
7
5
2-t
2
8
Mean
1996
1997
1998
2001
2002
N Yield (%)
N Retention (kg ha-1 year-1)
N Retention (%)
Catchment Size (ha)
4
16
64
256
1024