



## Biogeochemical budgets in a Mediterranean catchment with high rates of atmospheric N deposition – importance of scale and temporal asynchrony

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**Abstract.** In this study biogeochemical export 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 that would not have been possible with a more limited data set. 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<sup>-1</sup> year<sup>-1</sup> at the crest of the catchment). These high rates of deposition have translated into consistently high levels of NO<sub>3</sub><sup>-</sup> in some streams of the San Bernardino Mountains. However, the streams of the Devil Canyon catchment have widely varying dissolved inorganic nitrogen (DIN) concentrations and export. These differences are also, to a more limited extent, present for dissolved organic carbon (DOC) but not in other dissolved species (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup> and other weathering products). As catchment size increases DIN and DOC concentrations first increase until catchment area is ~ 150 ha but then decrease as catchment scale increases beyond that size. The scale dependence of DIN export implies that catchments at different spatial scales are at different degrees of N saturation. The reason for this scale effect appears to be the dominance of flushing of DIN out of soil at small scales due to the temporal asynchrony between nutrient availability and biological N demand, the groundwater exfiltration of this flushed DIN at intermediate scales and the removal of this DIN from streamflow through in-stream processes and groundwater–surface water interaction 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 export for DIN and DOC.

### Introduction

Studies of catchment biogeochemical budgets have typically focused on a single catchment or several catchments of the same size (e.g. Likens and Bormann 1995; Williams and Melack 1997) or they have focused on comparison of catchment studies that attempt to answer questions about regional or global level controls on biogeochemical export (Lewis et al. 1999; Boyer et al. 2002; Perakis and Hedin 2002; Sickman et al. 2002). This general focus on single catchments or large-scale comparisons is not sufficiently robust to adequately address the influence of fundamental

controlling processes in a given climatic regime or ecosystem on biogeochemical export. Several studies in the past have used multiple neighboring catchments to investigate questions of biogeochemical control on water quality and catchment biogeochemical export has proven effective (e.g. Clow et al. 1996; Creed et al. 1996; Vanderbilt et al. 2003). 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 (e.g. Aber et al. 1989, 1998; Stoddard 1994; Fenn et al. 1998). Nitrogen saturation is a phenomenon where previously N limited ecosystems begin to leak nitrogen. According to Stoddard (1994), stage 0 of N saturation is when no impact of N deposition on stream chemistry is observable, stage 1 occurs when some inorganic N leaks out on a seasonal basis, stage 2 is when concentrations are elevated year round, and stage 3 is when the system leaks more N than is input into the system. An underlying assumption of the Stoddard N saturation hypothesis is that we can infer terrestrial ecosystem N status from measurements of stream inorganic nitrogen concentrations.

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 ( $40\text{--}90\text{ kg ha}^{-1}\text{ year}^{-1}$  along the crest; Fenn et al. 2003). Although N deposition is high throughout the Devil Canyon catchment,  $\text{NO}_3^-$  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 land use history (Goodale et al. 2000) deposition rate (Fenn and Poth 1999), forest floor processes (Gundersen et al. 1998), flow pathways (Creed et al. 1996), residence time (Peterson et al. 2001), in-stream processes (Grimm and Fisher 1984), riparian processes (Sabater et al. 2003) 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 paper we seek to answer the following questions regarding biogeochemical export from seasonally dry catchments:

- (1) How does biogeochemical export vary with 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?

## Methods and procedures

### *Site description*

Observations were collected for the Devil Canyon catchment, six sub-catchments and one groundwater spring. Devil Canyon is heavily impacted by atmospheric

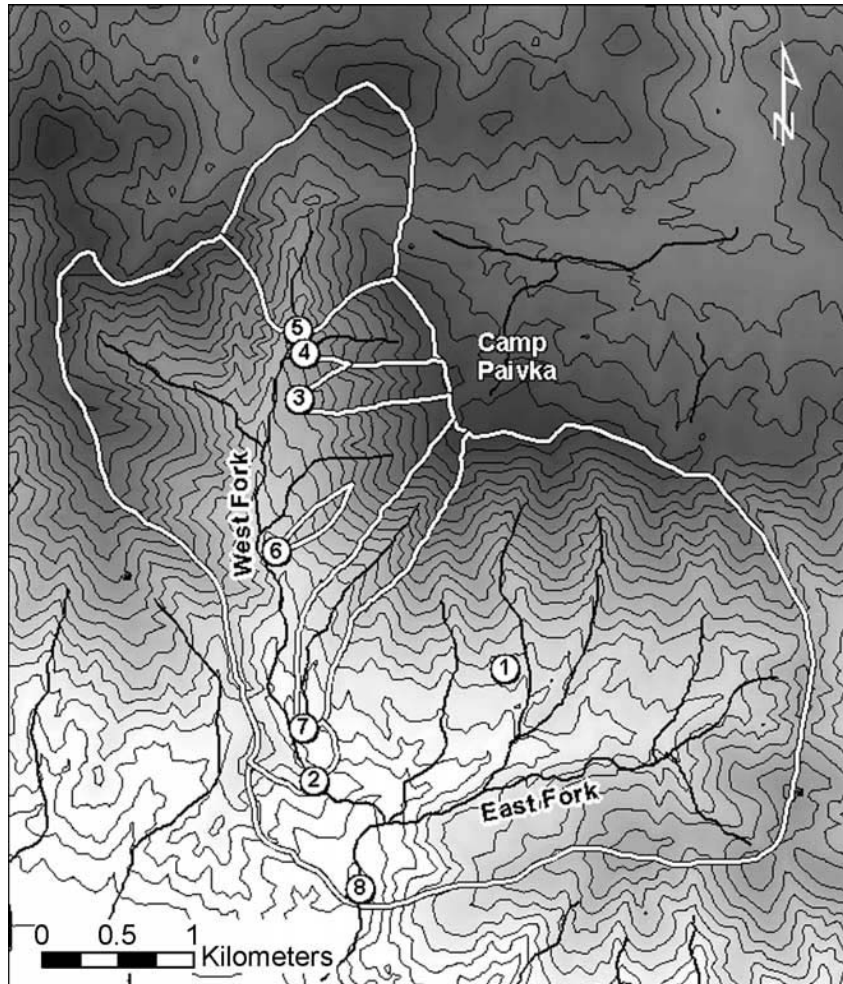


Figure 1. Sampling site locations in the Devil Canyon catchment. Site 8 is coincident with a USGS Gauging Station. Site 1 is a spring sampled at its source.

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  $\text{NO}_3^-$  concentrations despite being within several kilometers of each other. Camp Paivka 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

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	66	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%)

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) due to the active tectonic activity and Mediterranean climate the bedrock is well weathered.

Mean annual precipitation for the catchment varies from 610 mm year<sup>-1</sup> at the bottom of the catchment to 987 mm year<sup>-1</sup> 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 eight 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<sub>4</sub><sup>+</sup> concentrations in runoff are generally undetectable at Devil Canyon and in chaparral catchments in general (Riggan et al. 1985), NO<sub>3</sub><sup>-</sup> is equivalent to dissolved inorganic nitrogen (DIN).

#### Field and laboratory methods

The eight catchments have been sampled to varying degrees since the fall of 1995. Sampling and analysis previous to 2000 was reported in Fenn and Poth (1999). The data from 1995 through 1998 is used in this paper to calculate mass fluxes and mean concentrations using additional data from this study. Grab sampling was conducted at all eight 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 h 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<sub>2</sub>SO<sub>4</sub>. Samples for metal analysis were acidified within one day after sampling. All samples were stored in the dark at 4 °C 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<sub>3</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>) and soluble reactive phosphorus (SRP). A Varian ICP-OES was used with filtered and acidified samples for the analysis of calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), 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 DOC in the samples. Comparisons between the two methods have been made with our samples and indicate that the difference in concentration between the two methods is less than 10%, in our case. For all analyses United States National Institute of Standards and Technology standards and blind spikes were used to ensure the accuracy of the analysis. Duplicates were analyzed to ensure analytical precision.

#### *Atmospheric deposition*

Atmospheric deposition to the Devil Canyon catchment was estimated using 64 ion exchange resin column throughfall collectors (Fenn et al. 2002) spread 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 2-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 (*Q. dumosa*, *Ceanothus crassifolius*, *U. californica*), hardwood (*Quercus chrysolepsis*, *A. 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.

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

Catchment	$r^2$	No. of obs.	% error
2	0.851	60	25
3	0.903	14	28
4	0.508	65	43
5	0.750	61	35
6	0.696	48	40
7	0.309	66	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

### 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 (VWM) 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  $\sigma^2$  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 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:

$$E_t = (E_A^2 + E_B^2)^{1/2}$$

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 3–7 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.

## **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 runoff as depth 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

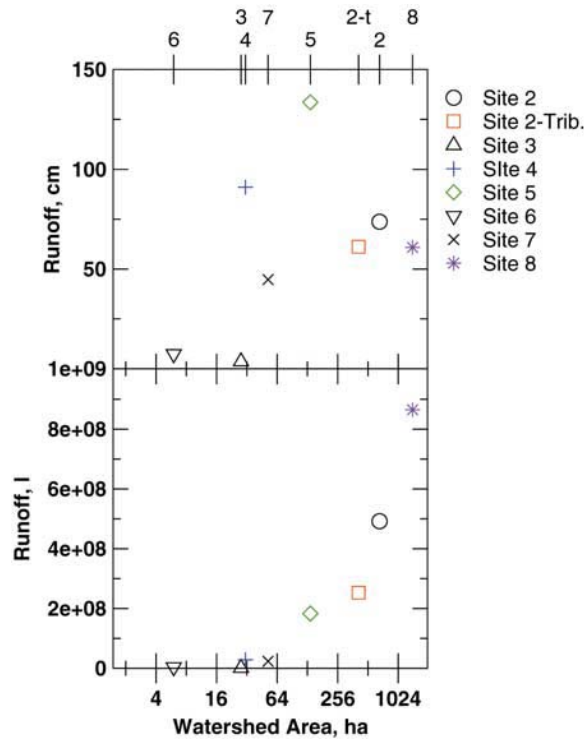


Figure 2. Mean annual runoff from the seven Devil Canyon stream locations in liters and centimeters. Graph shown with x-axis as catchment size. Catchments from left to right are 6, 3, 4, 7, 5, 2, 2-tributaries, and 8 (as labeled across the top of the figure). Runoff depth is highly variable with catchment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

shows profound inter-annual variability reflecting the highly variable precipitation patterns of southern California (Table 3). Based on rainfall data for this area for the last two years, we report mean runoff coefficients in Table 4.

#### *Temporal variability in nitrate concentration*

The temporal variability of  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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 catchments 4 and 7 have patterns that are somewhat similar to the main stem streams. Finally, the ephemeral stream at catchment 3 has a peak in  $\text{NO}_3^-$



Table 4. Mass flux (kg) and runoff from each catchment (2001 and 2002 data)

Catchment	Runoff (mm)	Precip. (mm) <sup>1</sup>	Runoff coeff.	NO <sub>3</sub> <sup>-2</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	DOC	K <sup>+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Si	SO <sub>4</sub> <sup>2-</sup>
2	74	550	0.13	1600	61000	7000	1500	2900	12000	12000	4400	24000
3	3.6	550	0.006	0.78	190	27	5.8	10	21	31	6.3	40
4	91	550	0.17	21	1600	220	56	80	320	310	260	580
5	134	550	0.24	1200	22000	2700	810	890	3500	4101	1400	5900
6	7.4	550	0.013	1.6	230	53	8.0	10	60	80	51	87
7	45	550	0.081	44	2400	510	66	84	630	580	310	2200
8	61	550	0.11	1800	150000	51000	4300	9300	43000	45000	14000	97000
2-tribs	61	550	0.11	270	35000	3500	550	1900	7800	6400	2400	15000

<sup>1</sup>Mean precipitation average of 2001 and 2002 water years, the only years for which we have reliable data. For reporting purposes same mean precipitation was used for all catchments since we had insufficient data to determine precipitation differences among the catchments.

<sup>2</sup>NO<sub>3</sub><sup>-</sup> means are for period of 1996–2002 using data from this study and Fenn and Poth (1999).

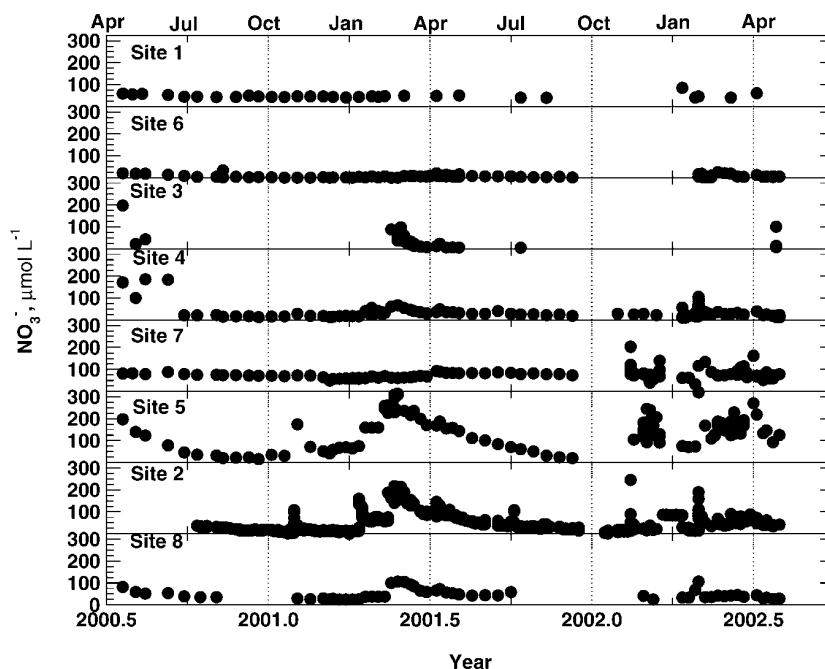


Figure 3. Temporal graph of  $\text{NO}_3^-$  concentration for all sites. For purposes of presentation, top graph is main stem sites 2, 5 and 8; bottom graph is tributary locations sites 1, 3, 4, 6 and 7. Main stem sites have profound seasonal variability with peak  $\text{NO}_3^-$  coinciding with peak flow. Tributary sites differ in their seasonal variability from little variability (site 1) to variability similar to the main stem sites (site 4).

concentration at the onset of flow and then a sharp decline in concentration as time progresses (Figure 3).

#### *Chemical mass flux*

Mass fluxes of several chemical species are reported in terms of total mass flux from each catchment, flux per ha and VWM concentration. The fluxes for  $\text{NO}_3^-$ , DOC,  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  are reported graphically while all of the measured species are reported in tables. These four chemicals were selected because  $\text{NO}_3^-$  and DOC are not conservative in stream systems,  $\text{Ca}^{2+}$  is representative of the rest of the weathering products and  $\text{Cl}^-$  is a conservative tracer. As expected, due to the increase in flow with catchment size, the flux of most chemical species increases with catchment size. It is important to note that  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  both show consistent increases with catchment size while  $\text{NO}_3^-$  and DOC exhibit some deviation from this pattern (Figure 4 and Table 4). There is also considerable year-to-year variability in chemical export from these catchments. Notably, wet years like 1998

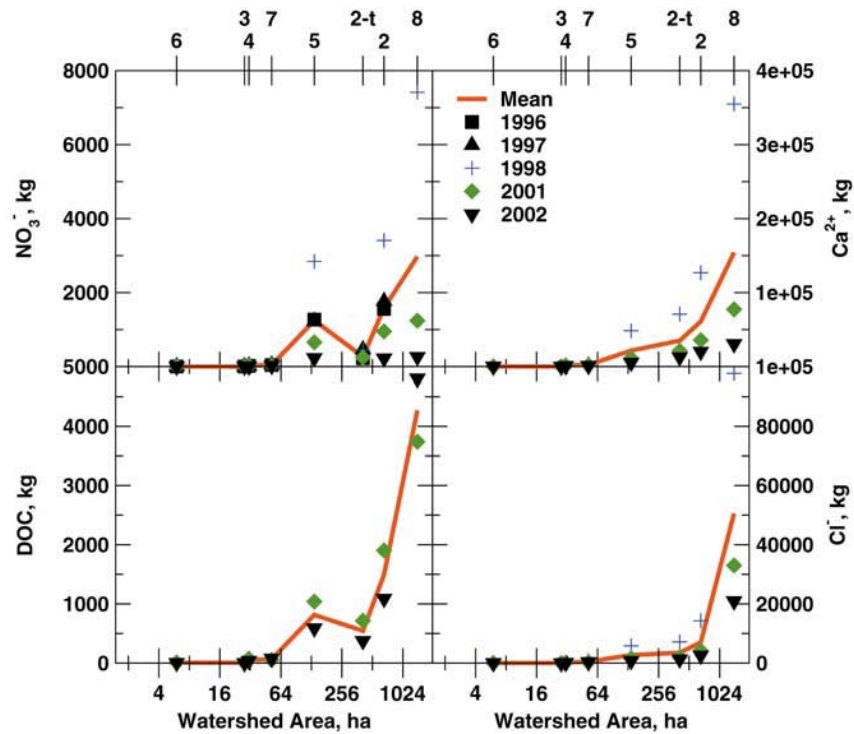


Figure 4. Annual total export of  $\text{NO}_3^-$ , DOC,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  from the seven monitored catchments as well as catchment 2 minus tributaries. Data shown with catchment size on  $x$ -axis. Catchments from left to right are 6, 3, 4, 7, 5, catchment 2 minus tributaries, 2 and 8 (as labeled across the top of the figure). Export increases for all species with catchment size, although to a lesser degree for  $\text{NO}_3^-$  and DOC.

have much larger exports while dry years like 2002 have much lower exports (Figure 4).

#### *Chemical mass flux per unit area*

When looking at catchment flux per unit area ( $\text{kg ha}^{-1}$ ), response patterns differ from those seen with the total flux data ( $\text{kg}$  per catchment). There is a noticeable peak in chemical export per ha from catchment 5, in the middle of the catchment size distribution;  $\text{NO}_3^-$ , DOC,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  all show this peak (Figure 5). While  $\text{NO}_3^-$  and DOC export per ha decline from this peak,  $\text{Cl}^-$  later increases further;  $\text{Ca}^{2+}$  shows a similar pattern, although to a lesser degree. Again inter-annual variability observed with total export is also seen here, with flux per unit area in wet years greater than average and dry years less than average. In part, the peak in flux

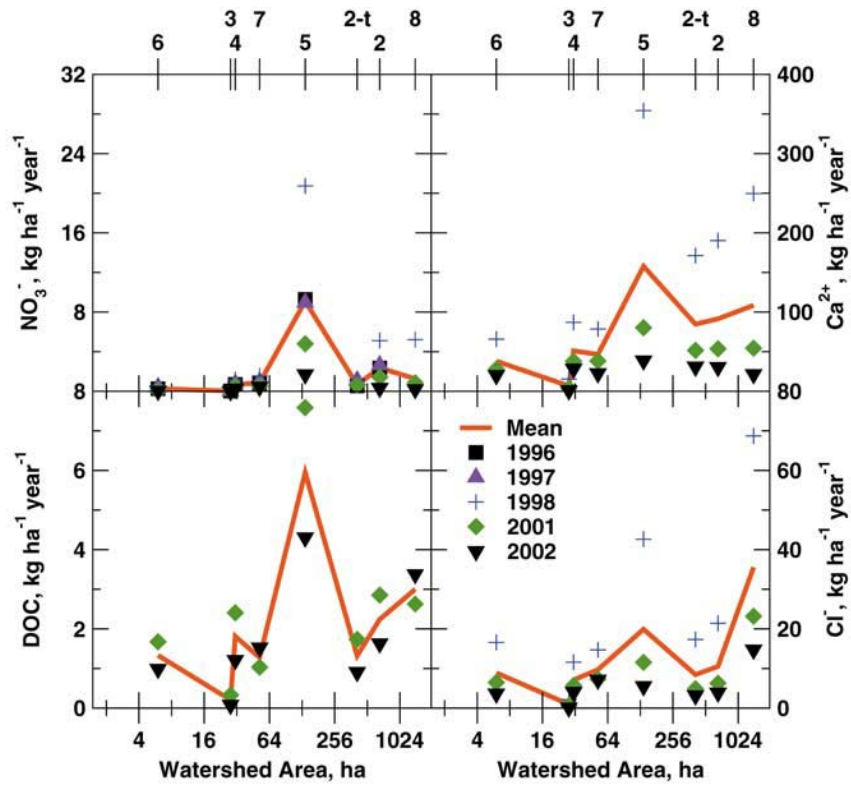


Figure 5. Annual flux per area for  $\text{NO}_3^-$ , DOC,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  from the seven monitored catchments as well as catchment 2 minus tributaries. Data shown with catchment size on x-axis. Catchments from left to right are 6, 3, 4, 7, 5, catchment 2 minus tributaries, 2 and 8 (as labeled across the top of the figure). Flux per area shows a noticeable peak at the intermediate catchment scale particularly for  $\text{NO}_3^-$  and DOC.

per unit area at catchment 5 (Figure 5 and Table 5) is due to the increase in runoff per unit area (Figure 2).

#### VWM concentrations

Reported VWM concentrations against catchment size are more widely variable than export or export per unit area among the chemical species studied. For VWM  $\text{NO}_3^-$  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. Catchments 3 and 8 are both ephemeral and thus have large litter accumulations during the dry season that are a source of DOC to these streams. Given

Table 5. Chemical export  $\text{kg ha}^{-1}$  (mean of 2001 and 2002)

Catchment	$\text{NO}_3^-$ <sup>1</sup>	$\text{Ca}^{2+}$	$\text{Cl}^-$	DOC	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Na}^+$	Si	$\text{SO}_4^{2-}$
2	2.37	91.44	10.54	2.24	4.37	18.45	17.25	6.59	35.46
3	0.03	6.72	0.96	0.21	0.35	0.76	1.11	0.23	1.42
4	0.68	51.09	7.12	1.81	2.57	10.37	10.01	8.35	18.50
5	9.09	157.79	19.92	5.95	6.44	25.26	29.93	10.00	42.72
6	0.26	37.99	8.91	1.33	1.62	10.01	13.23	8.47	14.52
7	0.85	46.46	9.72	1.28	1.61	12.11	11.22	5.94	42.62
8	1.25	108.46	35.56	3.00	6.57	29.92	32.02	10.02	68.40
2-tribs	0.65	84.67	8.47	1.32	4.48	18.93	15.50	5.81	36.05

<sup>1</sup> $\text{NO}_3^-$  means are for period of 1996–2002 using data from this study and Fenn and Poth (1999).

Table 6. VWM chemical concentration<sup>1</sup> (2001 and 2002 data)

Catchment	$\text{NO}_3^-$ <sup>2</sup>	$\text{Ca}^{2+}$	$\text{Cl}^-$	DOC	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Na}^+$	Si	$\text{SO}_4^{2-}$
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

<sup>1</sup>Concentrations are in  $\mu\text{M}$  except for DOC which is in  $\text{mg l}^{-1}$ .

<sup>2</sup> $\text{NO}_3^-$  means are for period of 1996–2002 using data from this study and Fenn and Poth (1999).

this data censoring, the highest DOC concentrations are at catchment 5 and decline as catchment scale becomes larger or smaller. However due to the data censoring needed to show this pattern the strength of this pattern is obviously fairly weak. VWM  $\text{Ca}^{2+}$  concentrations exhibit a general increase in concentration with scale, although with considerable variability. For  $\text{Cl}^-$  there is little trend with catchment size, except that catchments 7 and 8 had higher  $\text{Cl}^-$  concentrations. Inter-annual variability indicates dilution for  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  with wet years (1998 and 2001) having lower concentrations than dry years (2002). The same is not true for  $\text{NO}_3^-$  concentrations. Instead  $\text{NO}_3^-$  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 6).

#### 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

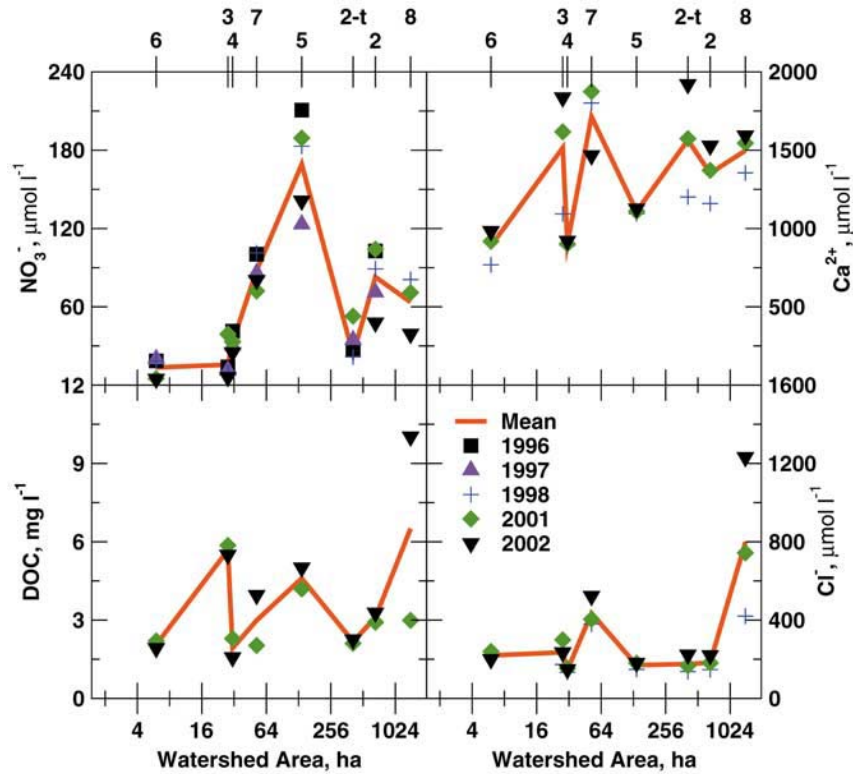


Figure 6. VWM stream concentrations for  $\text{NO}_3^-$ , DOC,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  from the seven monitored catchments as well as catchment 2 minus its tributaries. Data shown with catchment size on x-axis. Catchments from left to right are 6, 3, 4, 7, 5, catchment 2 minus tributaries, 2 and 8 (as labeled across the top of the figure). VWM concentrations show a noticeable peak for  $\text{NO}_3^-$  at the intermediate size. Other constituents show considerably more variability.

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

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

Species (common name)/Catchment	No. of collectors	Mean NO <sub>3</sub> <sup>-</sup> -N (std. Dev.) kg ha <sup>-1</sup> year <sup>-1</sup>	Mean NH <sub>4</sub> <sup>+</sup> -N (SD) kg ha <sup>-1</sup> year <sup>-1</sup>	N (Std. Dev.) kg ha <sup>-1</sup> year <sup>-1</sup>
<i>Q. chrysolepsis</i> (canyon live oak)	12	14 (8)	13 (6)	26 (13)
<i>Q. dumosa</i> (scrub oak)	7	6 (2)	7 (3)	13 (5)
<i>A. rhombifolia</i> Nutt. (white alder)	11	7 (3)	9 (4)	17 (5)
<i>C. crassifolius</i> (buckthorn)	11	7 (4)	9 (7)	17 (8)
<i>U. californica</i> (California bay-laurel)	7	7 (2)	6 (2)	14 (4)
<i>J. californica</i> (walnut)	4	8 (3)	8 (2)	16 (4)
Open	7	4 (1)	7 (3)	11 (3)
Others <sup>1</sup>	3	5 (2)	7 (2)	11 (3)
Conifer <sup>2</sup>		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)

<sup>1</sup>One each of *Salix gooddingii*, *Cercocarpus betuloides*, and *Salvia apiana*.

<sup>2</sup>From Fenn et al. (2003).

variability in our data. *Quercus chrysolepsis* had the highest average deposition rate (26 kg ha<sup>-1</sup> year<sup>-1</sup>) while the other hardwood species (*A. rhombifolia* and *J. californica*) had lower rates (17 and 16 kg ha<sup>-1</sup> year<sup>-1</sup> respectively). The chaparral species (*Q. dumosa*, *C. crassifolius*, and *U. californica*) had lower mean deposition rates (13, 17 and 14 kg ha<sup>-1</sup> year<sup>-1</sup> 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<sup>-1</sup> year<sup>-1</sup>).

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<sup>-1</sup> year<sup>-1</sup> we used a conservative estimate of 40 kg ha<sup>-1</sup> year<sup>-1</sup> since we do not know the spatial extent to which these very high rates occur as the study sites where the 90 kg ha<sup>-1</sup> year<sup>-1</sup> has been observed occur at the absolute crest of the mountains. These study sites were originally selected as sites expected to have high ozone concentrations and high deposition rates and therefore may not be representative of the wider forest area (Fenn et al. 2002, 2003).

#### *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

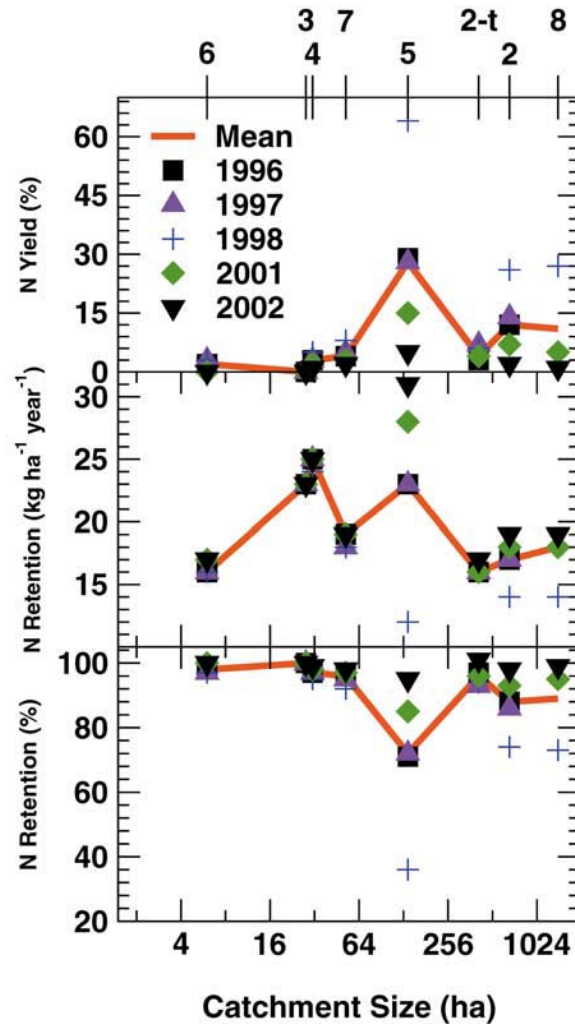


Figure 7. Catchment nitrate yield for the seven monitored catchments as well as catchment 2 minus its tributaries. Data shown with catchment size on *x*-axis. Catchments from left to right are 6, 3, 4, 7, 5, catchment 2 minus tributaries, 2 and 8 (as labeled across the top of the figure). Nitrate yield 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.

results dramatically but may partially explain why catchment 5 has higher  $\text{NO}_3^-$  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 (1996–1998, 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.

#### *Riparian losses*

The 413 ha catchment (catchment 2 – tribs) had consistently lower  $\text{NO}_3^-$  export, VWM  $\text{NO}_3^-$  concentrations, and  $\text{NO}_3^-$  yield compared to catchment 2 (Figures 4–7). This indicates that there is a net loss of  $\text{NO}_3^-$  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 (Table 6).

### **Discussion**

#### *Effect of scale on chemical export*

The differential pattern of increase and subsequent decrease of  $\text{NO}_3^-$  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 4) 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  $\text{Ca}^{2+}$  and other weathering products, and  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , again possibly due to the longer flowpaths and residence times at larger scales (Clow et al. 1996).

The most representative results of the average biogeochemical processes for the catchments are the VWM concentration results because this represents the mean chemical composition of an average liter of water in the catchment. Additionally we have the most confidence in the VWM concentration results since the catchments with the greatest flow uncertainty have the smallest changes in concentration. This indicates that the estimate of error for flow is probably an overestimate of uncertainty in the VWM concentration estimates.

The VWM concentrations indicate that  $\text{NO}_3^-$  and DOC share a process level control as VWM concentrations first increase with catchment area before decreasing again as catchment area continues to increase (this censors DOC concentrations for catchments 8 and 3 from the data set). Catchments 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. The reason for the litter build up in these channels is the ephemeral nature of the streams at both sample locations. Additionally, Butturini and Sabater (2000) have shown that at the onset of flow in ephemeral streams in Mediterranean climates there can be a large release of DOC possibly from shallow subsurface sources in the stream bed. Weathering products (Table 5 and Figure 5 for  $\text{Ca}^{2+}$ ) exhibit considerable variability indicating catchment-to-catchment differences superimposed on a general increase with catchment area. The variability of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  shows little relationship with catchment scale, instead being indicative of catchment-to-catchment variability with high  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in catchments 7 and 8 and the other catchments generally having similar  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  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  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  this inter-annual variability appears to be due solely to a dilution effect in years with more runoff. For  $\text{NO}_3^-$  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  $\text{NO}_3^-$  concentrations were lower, and 2001 had much less runoff than 1998 but similar or higher VWM  $\text{NO}_3^-$  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 two relatively dry years. This pattern indicates inter-annual storage of  $\text{NO}_3^-$  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 (Swift et al. 1988) indicating relatively small hydrologic throughput as shown by the runoff coefficients for the eight catchments (Table 4).

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 indicate differences among species in terms of total rates of deposition on an annual time scale (Table 7). The larger flux for *Quercus chrysolepis* (canyon live oak) may be due to the

expansive canopy of these trees, thus serving as a large receptor for dry deposition of atmospheric pollutants. The reason for our extensive collection of throughfall is verified by this result since they emphasize the importance of dry deposition in seasonally dry Mediterranean climates (Durand et al. 1992; Domingo et al. 1994). Varying deposition under different vegetation types translates into differences in total deposition to the catchments (Table 7) as based on estimated land cover in each catchment (Table 1 and Fenn and Poth (1999)).

Several factors may be responsible in part for the higher VWM  $\text{NO}_3^-$  concentrations observed in catchment 5. Catchment 5 has the highest rates of deposition (Table 7), it has largely been unburned for the last 50 years (Table 1) (Goodale et al. 2000), and due to these differences it may be farther along in the trajectory of nitrogen saturation and long term deposition is having an affect on forest floor processes (Gundersen et al. 1998). These caveats do not entirely discount the effect of scale on retention and yield we observe. For example catchments 4 and 7 were subjected to burns in the last 50 years and the data for these catchments supports our argument for a scale control on nitrogen export. Catchments 3 and 4 have significant coniferous areas and slightly higher N deposition than most catchments, but this doesn't lead to the high  $\text{NO}_3^-$  export observed for catchment 5.

Catchment 5 has the peak  $\text{NO}_3^-$  yield (in mass), the peak retention of nitrogen (in mass terms), and the lowest percent N retention due to the much higher deposition it receives (Figure 7). The other locations all have relatively high N retention (as %) with the smallest catchments (3, 4, and 6) having the highest rates of retention and with catchment 7, 2, 2-tribs and 8 all having slightly lower percent N retention than these smallest catchments. Catchment 5 is a notable exception with a significantly lower percent rate of N retention due to the higher deposition this catchment receives. Instead, some set of hydrologic and biogeochemical processes lead to increases in nitrogen export from the 6 to 137 ha scale and then to a decline in nitrogen export as scale increases from there.

#### *Riparian/in-stream 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 6). 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 and in-stream losses also appear to operate in years with higher flow as evidenced by the considerable decrease in VWM concentration and nitrogen export at catchment 2-tribs for the other available years of data (Figure 6). For DOC there was a similar decline in concentration and export for catchment 2 minus its

tributaries indicating that the loss process (possibly denitrification) is shared between DOC and  $\text{NO}_3^-$ .

*What processes explain the observed spatial pattern?*

Inorganic nitrogen export from this set of eight 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 and 31 ha, catchments 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  $\text{NO}_3^-$  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, Figure 3). As scale increases flow becomes more perennial, and export and VWM concentration of  $\text{NO}_3^-$  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, loss of inorganic nitrogen in the riparian zone of these catchments, 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 gaseous loss during nitrification or denitrification) prior to surface water export. For example, nitric oxide fluxes from soil in N saturated forests and chaparral watersheds in the San Bernardino and nearby San Gabriel Mountains are the highest reported in North America (Anderson et al. 1988; Fenn et al. 1996; Fenn and Poth 2001).

Past studies of nitrogen export in Mediterranean climates have consistently found that  $\text{NO}_3^-$  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; Tate et al. 1999; Dahlgren et al. 2001; Holloway and Dahlgren 2001; Butturini et al. 2003). This pattern of pulses of  $\text{NO}_3^-$  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, Figure 3). The source of this  $\text{NO}_3^-$  is generally ascribed to  $\text{NO}_3^-$  that has accumulated in soils and groundwaters during the long dry season from mineralization, nitrification and atmospheric deposition processes. Butturini et al. (2003) have shown that there can be a large release of  $\text{NO}_3^-$  from near stream sediments as streamwater stage increases at the commencement of the wet season in Mediterranean climates. 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 other semi-arid and arid ecosystems (Davidson 1992; Ryan et al. 1998; Smart et al. 1999). These same studies have shown that microbial immobilization, root growth and plant uptake typically take a period of days to weeks to start depleting the mineral nitrogen pool meaning that this initial burst of mineral nitrogen is available

for export at the beginning of the rainy season as is observed in our study for catchment 3 (Cabrera 1993; Cui and Caldwell 1997). 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, 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 and N accumulation in the catchment (Fenn and Bytnerowicz 1993; Fenn et al. 1996; 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 that the underlying assumption of the Stoddard (1994) nitrogen saturation hypothesis that streams reflect the terrestrial ecosystems they drain is not necessarily always true. This exception to the N saturation hypothesis could be 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  $\text{NO}_3^-$  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 recharges 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  $\text{NO}_3^-$  concentrations and that these springs were largely responsible for increased  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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 sites 5 and 8. This result of decreases in  $\text{NO}_3^-$  runs counter to expectations since the riparian alder forest might be expected to increase stream  $\text{NO}_3^-$  concentrations due to alders ability to fix nitrogen. Numerous researchers have shown that small headwater streams are significant sinks for inorganic nitrogen (e.g. Alexander et al. 2000; Peterson et al. 2001). The pathway for this in-stream and riparian loss of  $\text{NO}_3^-$  is not singular; it may be due to denitrification (Holmes et al. 1996; Groffman et al. 1999) 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  $\text{NO}_3^-$  loss in streams (e.g. Cooper 1990; Burns 1998; 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. Mulholland 1992; Mulholland and Hill 1997; McDowell 2001) 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 (Fisher et al. 1998; 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  $\text{NO}_3^-$  export. Because wetter years have higher flows, residence time is shorter and thus more  $\text{NO}_3^-$  would move through the riparian system and evade biological assimilation. This pattern is what we have observed (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  $\text{NO}_3^-$  cause DIN export to decrease as scale becomes large ( $\sim 400$  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 (Aber et al. 1989, 1998; Stoddard 1994; Burns et al. 1998) 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 catchments 2 or 5.

### Conclusions

The major lessons from this study are that a number of processes control stream chemical export of  $\text{NO}_3^-$  and DOC in Mediterranean catchments and that these processes differ from those controlling most other dissolved species. In particular, the study shows that with increasing scale, inorganic nitrogen export first increases and then decreases. The initial increase is due to increased ground water inflow and the later decrease is due to losses of inorganic N to in-stream and riparian processes. These processes challenge some of the underlying assumptions of the N saturation hypothesis. This statement is not meant to say that the N saturation hypothesis does not work, but that it needs to be carefully applied and judgments need to be based on a wide distribution of streams. If we only had these eight streams to rely on, a concrete judgment would be difficult; however, the more widespread data available in southern California (Riggan et al. 1985; Fenn and Poth 1999) indicates that all Devil Canyon catchments have significantly elevated inorganic N concentrations over background. Some of the Devil Canyon catchments have more highly elevated DIN concentrations than others indicating the importance of catchment and scale specific nutrient loss processes in determining catchment DIN export. The results of nearby forest fertilization experiments indicate that additional nitrogen will still cause increased tree growth despite the fact that our stream data indicates widespread first and second stage N saturation. The temporal asynchrony between N availability and plant N demand, and associated leaching losses of N accumulated from nitrification and N deposition, may cause the high DIN export we observe and result in periods of N deficiency such as during spring plant growth. Also our results suggest that increased N deposition and perhaps less frequent burn history can lead to increased  $\text{NO}_3^-$  export, as shown in catchment 5 which had the highest estimated levels of deposition and has not had a significant burn since 1954. Catchment 5 had the highest export and yield of inorganic nitrogen, and the lowest percent N retention.

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