

Problem and Research Objectives.

Introduction to the Problem - Major uncertainty surrounds the importance and magnitude of nitrogen (N) input into local environments in Arizona. Wet and dry deposition of ammonia, amines, and oxidation products of nitrogen oxides represent major inputs of N onto land, where enhanced rates of nitrogen fixation have been observed as a result of anthropogenic activity, including fossil fuel combustion (e.g. Smil, 1990; Vitousek and Matson, 1993; Ayers et al., 1994; Galloway et al., 1995). Some of the highest levels of N deposition in the western United States (29 kg per ha per year) were reported for desert sites near Phoenix, Arizona (AZ); yet, nitrogen “deposition rates are unknown for most areas in the West” (Fenn et al., 2003), including Tucson, AZ. In addition, high altitude regions and ecosystems, which are common in Arizona, are especially vulnerable to the effects of N deposition. Recent measurements in the Rocky Mountain region indicate that N deposition fluxes have increased nearly 20-fold since pre-industrial times (Galloway et al., 1982, 1995; Hedin et al., 1995; Beem et al., 2009). Nitrogen deposition is intimately linked to regional water quality - an issue that is underappreciated in terms of attention and research in Arizona. In addition to N-species, major uncertainty also surrounds the nature and magnitude of organic carbon (OC) deposition to terrestrial surfaces (Goldstein and Galbally, 2007). While wet deposition of OC (in the form of dissolved organic carbon, DOC) has received attention with regard to quantifying its average global chemical signature and deposition rate (Willey et al., 2000), dry deposition of OC remains even less understood.

Nitrate is one of the most common contaminants degrading water quality world-wide (e.g. WHO, 2006). In Arizona, over 1,000 groundwater wells contain nitrate concentrations above the EPA drinking water standard (10 mg/L NO₃-N). Nitrate contamination is attributed to agricultural activities, feedlots and effluent discharge from wastewater treatment plants and septic systems (Rahman and Uhlman, 2009). Recent studies in the Tucson Basin, using multiple-isotope tracers (¹⁷O, ¹⁸O, ¹⁵N of NO₃), show that atmospheric deposition of N may also be a significant contributor to nitrate contamination to surface and ground water (up to 50%) (Dejwakh, 2008). Extending this study, a new NSF-funded research project (PI Lohse) is currently investigating the importance of atmospheric nitrate deposition on the water quality of storm runoff in urban landscapes (Tucson and Phoenix). At the margins of such basins, the majority of groundwater is derived from recharge in high elevation mountain blocks, which may also receive atmospheric deposition of nitrogen, leading to the question:

What is the contribution of nitrogen and organic carbon from atmospheric deposition in mountain systems surrounding these urban environments that may impact groundwater quality?

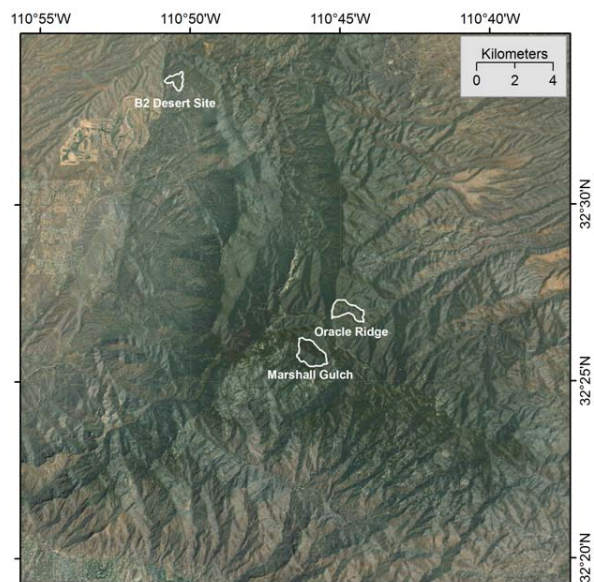


Figure 1: Satellite image of the Santa Catalina Mountains in southeastern Arizona, north of Tucson. This study focused two watersheds (outlined in white) – the Marshall Gulch high elevation site at the top of Mt. Lemmon, and the B2 Desert site near the base of the mountains.

Research Objectives – The primary objective of this project was to determine the amount, sources, and cycling of nitrogen and carbon deposition in the Santa Catalina Mountains in southeastern Arizona, north of Tucson. In addition, we aimed to evaluate how much of the N and C from atmospheric deposition are naturally reacted in soils and/or transported to surface water and groundwater. To meet this objective, we measured N-species composition (NO_3 , NO_2 , NH_4 , amines, organic-N) and dissolved organic carbon (DOC) in atmospheric deposition, soil waters and surface waters at the B2 desert site at the base of the Santa Catalina Mountains, and at the Marshall Gulch and Mt. Bigelow sites at the top of the mountains (Fig. 1). Stable isotopes (^{15}N , ^{18}O , ^{17}O) of wet and dry deposition, soil pore waters, and surface waters are currently being analyzed. Nutrient data was coupled with hydrologic measurements (e.g. amount of precipitation, stream discharge) and catchment characteristics (e.g. soil depth, bedrock lithology) to investigate controls on nutrient dynamics. Specific questions addressed were:

- (1) How does bedrock lithology control organic carbon and nitrogen cycling?*
- (2) How does landscape position effect organic carbon and nitrogen cycling?*
- (3) What are the amounts, sources, and seasonality of species in atmospheric deposition?*
- (4) How does variability in precipitation effect organic carbon and nitrogen cycling?*

Methodology.

Study Site – The Santa Catalina Mountains are primarily composed of fractured granite with local occurrences of schist and other bedrock types. There is an extreme climate (precipitation and temperature) gradient from Sonoran Desert Scrub at the base (800 m) to Mixed Conifer Forest at the top (2600 m). Most of the precipitation is delivered in the winter as mixed snow and rain, and in the summer as rain from intense monsoon storm events. Infiltration of precipitation into the fractured bedrock migrates downgradient to the adjacent alluvial aquifers, providing an important source of recharge; the amount of N being transported from these mountain systems to groundwater basins is an important endmember that is still yet unknown.

During the timeframe of this project, there were two instrumented hydrologic and biogeochemical research sites established in the Santa Catalina Mountains at different elevations on schist and granite hillslopes: (1) a low elevation (1164 m) site near Biosphere 2; (2) a high elevation (2590 m) site near Summerhaven, AZ, including Marshall Gulch watershed and Mt. Bigelow (Fig. 1). The low and high elevation sites have hydrometeorology stations, stream gauges with autosamplers, automated tipping bucket rain gauges, soil moisture probes, and nested lysimeters to capture variations in soil water chemistry and transit times with hillslope position and depth.

During summer 2010, the B2 Desert site produced very little surface or soil water. The lysimeters were completely dry, and are currently being reinstalled in case the problem was poor installation. Thus, we have focused most of our analyses on data from the high elevation site – Marshall Gulch.

A third mid-elevation site (~2000 m; Oracle Ridge site) was recently (Spring 2011) established on the north side of the Santa Catalina Mountains; this site will have similar instrumentation as the other two sites. We plan to collect soil solution and surface water samples from Oracle Ridge, starting Summer 2011, to better constrain the influence of elevation gradients (e.g. change in temperature, precipitation, vegetation type) on nutrient dynamics.

Procedures and Methods - To distinguish the sources of N in the Santa Catalina Mountains, reaction in soils, and transport to adjacent alluvial basins, we collected and analyzed:

(1) Atmospheric deposition – Aerosol samples were collected at two sites representing the base and summit of the Santa Catalina Mountains. These included a B2 desert site, and the University of Arizona High-Altitude Laboratory (32.26° N, -110.46° W, 2791 m ASL) at the summit of Mt. Lemmon. The sampling systems (installed as part of this project) consisted of an inlet designed to remove contamination from precipitation and large debris. It was determined that precipitation events did not contaminate collected samples. Sampled air containing aerosol particles were passed through a filter sampler (URG), consisting of several sections. The sampled air first travels through a 2.5 µm impactor to remove particles with diameters exceeding 2.5 µm. The air stream is then passed through a series of three denuders to remove inorganic and organic vapors that could bias the aerosol measurements. Aerosol particles were then collected on 47 mm quartz filter fibers (PALL Life Sciences) that were all prebaked and sterilized to remove contaminants prior to sampling. The filter sampler was equipped with a critical orifice to maintain a constant volumetric air flow rate of approximately 16 LPM. A pump downstream of the critical orifice drew vacuum on the sampled air. A total of 8 samples were collected at the mountain-top site and 11 at mountain-base site, spaced between March 2010 and January 2011. Sampling typically lasted for a period of a week to collect sufficient material on the filters for a variety of different types of analyses. Filters were stored in a freezer after collection up until the point of chemical analyses.

The filter extraction procedure consisted of ultrasonication (15 min) of glass vials containing filter punches and 10 mL of 18.2 mega-ohm Milli-Q water. The filter extract liquid was then sent through a syringe filter (Acrodisc filters, 25 µm) to a separate vial. This procedure was repeated two more times to collect a total of 30 mL of extracted liquid for analysis. This liquid was then

partitioned into fractions for separate types of analyses, including measurements of the total N associated with NH_4 , total N, total organic carbon (TOC), N isotope analysis, and ion chromatography analysis (NO_2^- , NO_3^- , SO_4 , Cl). Sections of each filter will remain archived for any future analyses that becomes of interest based on the initial set of results. Both water blanks and filter blanks were included in these analyses as well.

A complementary aerosol dataset was also obtained and analyzed to provide a longer statistical record to use along-side the measurements above that span one year in time. The other dataset includes measurements from a decade-long measurement campaign at the University of Arizona High-Altitude Laboratory on top of Mt. Lemmon between 1992 and 2002 (Matichuk et al., 2006). That studied relied on almost an identical sampling strategy using filters and water-extraction techniques to study the water-soluble composition of the aerosol.

(2) *Surface water and soil water samples* – Surface waters in Marshall Gulch were collected approximately every 7 days, starting in February 2009 through November 2010 at four locations: the granite hillslope outlet, the schist hillslope outlet, a seep on the schist hillslope, and a weir after the confluence of streams draining the granite and schist hillslopes (Fig. 2). Stream discharge at the weir was also measured using a pressure transducer. In addition, 11 soil lysimeters, installed on the schist and granite hillslopes, were sampled during the same time period as the surface waters, when water was available (Fig. 3). Seven water samples were collected from the B2 desert site from a seep on the schist hillslope, soil lysimeters in the schist and granite hillslopes, and surface water from the CDO wash. Due to the limited number of samples that were collected (dry conditions most of the study period), we did not include these samples in our analysis.

Surface water and soil water samples (730 total) were analyzed for pH, and filtered and analyzed for total dissolved inorganic carbon (TIC or DIC), total dissolved organic carbon (TOC or DOC), and total dissolved nitrogen (TN or TDN) on a Shimadzu carbon and nitrogen analyzer in Dr. Jon Chorover's laboratory in the Soil, Water, Environmental Sciences department at the University of Arizona. Anions, including NO_3 , NO_2 , Cl, SO_4 , PO_4 , F and Br were measured on an ion chromatograph in Dr. Chorover's lab.

A subset of water samples (30 total) were collected for triple isotope analyses (^{18}O , ^{17}O , ^{15}N) of nitrate: 14 from soil lysimeters and 7 from surface waters in Marshall Gulch; 4 from soil lysimeters and 3 from surface waters in the B2 Desert site; and 2 samples of Sabino Creek at the Sabino Dam. Samples were collected in May, June and August 2010. These samples have been shipped to Dr. Greg Michalski at Purdue University. Dr. Michalski had indicated that he could complete the isotope analyses in Fall 2010; however, the instrument was down until December 2010. He is currently analyzing the samples, and we expect results in the next ~3 months.

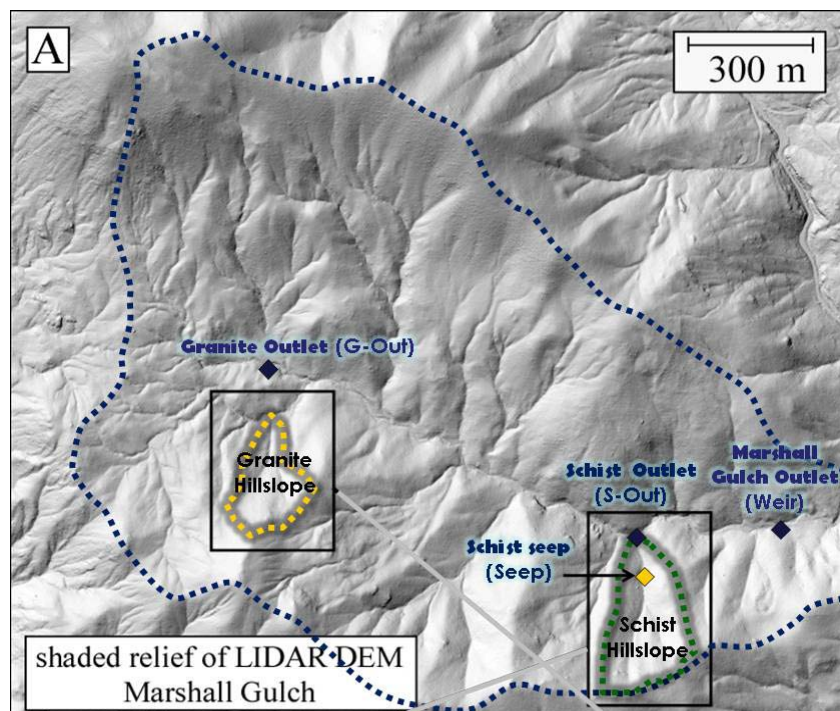


Figure 2: Land surface image of the Marshall Gulch watershed, showing the 2-paired hillslopes, and instrumentation installed as part of the NSF Jemez River Basin-Santa Catalina Mountains Critical Zone Observatory project. Figure courtesy of Angela Jardine and Matej Durcik.

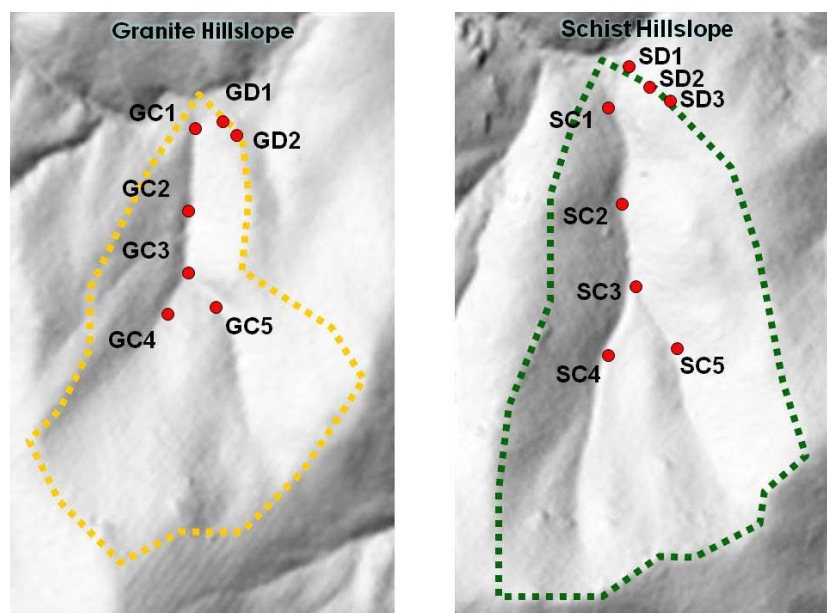


Figure 3: Zoomed-in view of the granite and schist hillslopes, showing the location of the soil solution samplers (soil lysimeters). Figure courtesy of Angela Jardine and Matej Durcik.

The triple isotope approach ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$) will be used to distinguish sources of N (terrestrial vs. atmospheric), as well as to constrain biological reactions (denitrification and nitrification) taking place in soils and surface waters. There is often a lot of scatter in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ relations of NO_3 due to variable sources of N. By adding $\Delta^{17}\text{O}$, we can subtract the contribution from atmospheric N and better identify denitrification and nitrification reactions.

Principle Findings and Significance.

By coupling new measurements of organic carbon and N-species in atmospheric deposition, soil

waters and stream waters, with precipitation and discharge data, we were able to determine the amount, sources and fate (e.g. transport and cycling) of C and N in the Santa Catalina Mountains, one of many sky island ecosystems in the southwestern United States that provide important water resources via mountain block recharge to adjacent alluvial basins and population centers. Major findings and significance are discussed below, organized by research question.

(1) How does bedrock lithology control organic carbon and nitrogen cycling?

We expected to observe differences in nutrient retention between the granite and schist hillslopes in Marshall Gulch due to differences in soil development. The schist hillslope has much thicker soils (80 to 120 m) than the granite hillslope (40 to 90 m), likely because schist bedrock is less resistant to weathering than granite. Total nitrogen (TN), NO₃-N and NO₂-N concentrations in stream waters draining the granite hillslope are slightly higher than the schist hillslope (Table 1; Fig. 4). Dissolved organic carbon (DOC) concentrations in the schist and granite hillslope outlets are similar, but the concentrations are more variable in the schist outlet. This suggests that N-species and organic carbon may be retained more in schist hillslopes possibly because of greater cation exchange capacity in more developed soils. DOC and N may be more easily flushed from granite hillslopes.

Table 1. Dissolved organic carbon (DOC), total nitrogen (TN), nitrate (NO₃-N), and nitrite (NO₂-N) concentrations at the Marshall Gulch outlet, Schist outlet and Granite outlet.

	DOC (ug/L)				TN (ug/L)		
	MG out	Sout	Gout		MG out	Sout	Gout
mean	7306	10633	10649	mean	594	733	622
median	6225	6234	9604	median	461	491	512
STD	3685	18346	7474	STD	530	821	462
Min	2429	476	4281	Min	0	0	0
Max	26414	63104	65495	Max	3578	4543	2364

	NO ₃ -N (ug/L)				NO ₂ -N (ug/L)		
	MG out	Sout	Gout		MG out	Sout	Gout
mean	528	521	628	mean	112	152	171
median	306	346	338	median	70	84	96
STD	694	568	752	STD	127	165	200
Min	1	1	18	Min	10	7	20
Max	3393	2976	3522	Max	516	530	995

Mean and median concentrations for DOC, TN, NO₃-N (median only) and NO₂-N decrease downgradient between the granite and schist hillslope outlets, and Marshall Gulch outlet (Table 1; Fig. 4). This may suggest in-stream processing of organic carbon and N, dilution, or absorption of DOC; future synoptic sampling of stream waters downgradient should be done to address these hypotheses.

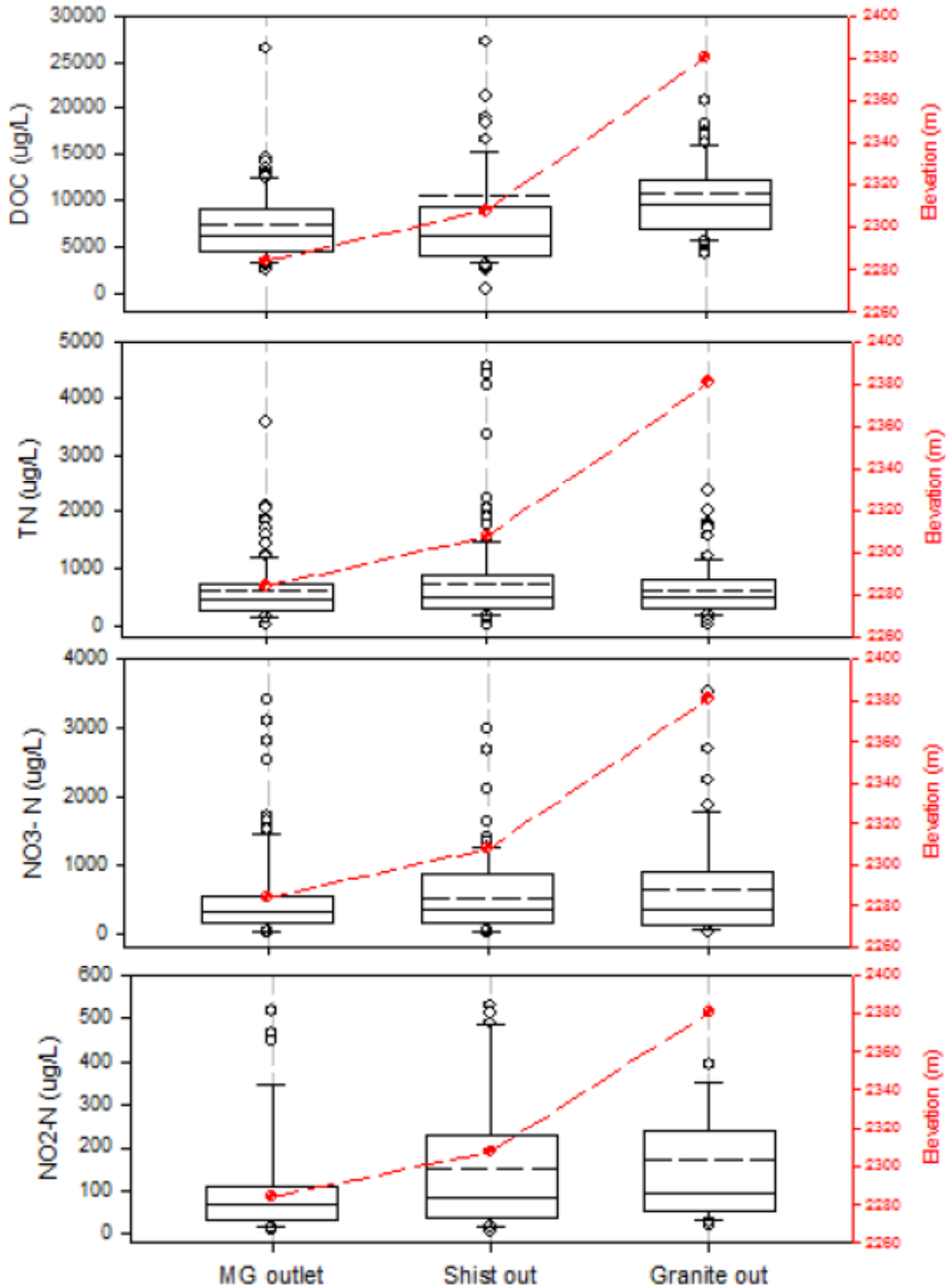


Figure 4: Dissolved organic carbon (DOC), total nitrogen (TN), nitrate ($\text{NO}_3\text{-N}$), and nitrite ($\text{NO}_2\text{-N}$) concentrations in stream waters, from the granite outlet to the Schist outlet, to the Marshall Gulch (MG) outlet (see Fig. 2 for sample locations).

(2) How does landscape position effect organic carbon and nitrogen cycling?

We expected to observe differences in nutrient concentrations in soils waters within each hillslope dependent on landscape position (i.e. up slope vs. riparian areas, and upstream vs. downstream riparian areas). Across the schist hillslope, DOC and TN concentrations are higher in the mid-elevation zone, and NO₃-N and NO₂-N values do not vary significantly along the elevation gradient (Table 2; Fig. 5). In the granite hillslope, DOC, TN, and NO₂-N concentrations are highest at the bottom of the elevation gradient, while NO₃-N concentrations do not vary along the hillslope (Table 3; Fig. 6). Differences in TN values may be a function of organic-N or NH₄, which were not measured in this study; future sampling campaigns will include these analyses. The highest DOC and TN values in the mid-elevation and bottom slope positions in the schist and granite hillslopes, respectively may indicate accumulation of solutes in downslope positions. Further investigation is needed to better understanding within catchment variability of nutrient concentrations.

Table 2. DOC, TN, NO₃-N and NO₂-N concentrations of soil water along the Schist hillslope.

	DOC (ug/L)							TN (ug/L)					
	Sout	SC1	SC2	SC3	SC4	SC5		Sout	SC1	SC2	SC3	SC4	SC5
mean	10633	26235	33682	27419	18722	17307	mean	733	1242	1843	1730	1696	1346
median	6234	15110	27487	15352	11326	14827	median	491	918	1642	1128	1354	1264
STD	18346	48044	20979	54458	20670	6766	STD	821	1108	824	1806	1201	405
Min	476	5470	16079	143	6233	10943	Min	0	296	962	627	425	438
Max	131983	334018	119829	358850	118848	32603	Max	4543	6729	3912	11594	5124	1996

	NO ₃ -N (ug/L)							NO ₂ -N (ug/L)					
	Sout	SC1	SC2	SC3	SC4	SC5		Sout	SC1	SC2	SC3	SC4	SC5
mean	521	1158	744	739	1190	744	mean	153	348	65	145	114	117
median	346	401	177	353	349	179	median	84	104	59	129	77	85
STD	568	1851	1248	954	1790	1145	STD	165	711	40	116	88	89
Min	1	36	16	38	32	31	Min	7	36	19	25	24	35
Max	2976	9628	5909	3556	6554	3969	Max	530	2828	164	579	417	373

Table 3. DOC, TN, NO₃-N and NO₂-N concentrations of soil water along the Granite hillslope.

	DOC (ug/L)					TN (ug/L)			
	Gout	GC1	GC2	GC3		Gout	GC1	GC2	GC3
mean	10649	18564	13958	15644	mean	622	1338	1336	1794
median	9604	13002	12778	16049	median	512	989	1153	1939
STD	7474	16179	4703	4046	STD	462	1110	774	767
Min	4281	9132	8624	9183	Min	0	428	370	675
Max	65495	82606	29766	22492	Max	2364	6599	3057	3194

	NO ₃ -N					NO ₂ -N			
	Gout	GC1	GC2	GC3		Gout	GC1	GC2	GC3
mean	628	516	638	496	mean	171	668	293	84
median	338	417	470	195	median	96	84	99	59
STD	752	662	691	672	STD	200	2263	772	104
Min	18	10	24	18	Min	20	26	26	31
Max	3522	3445	3184	2472	Max	995	9149	3711	376

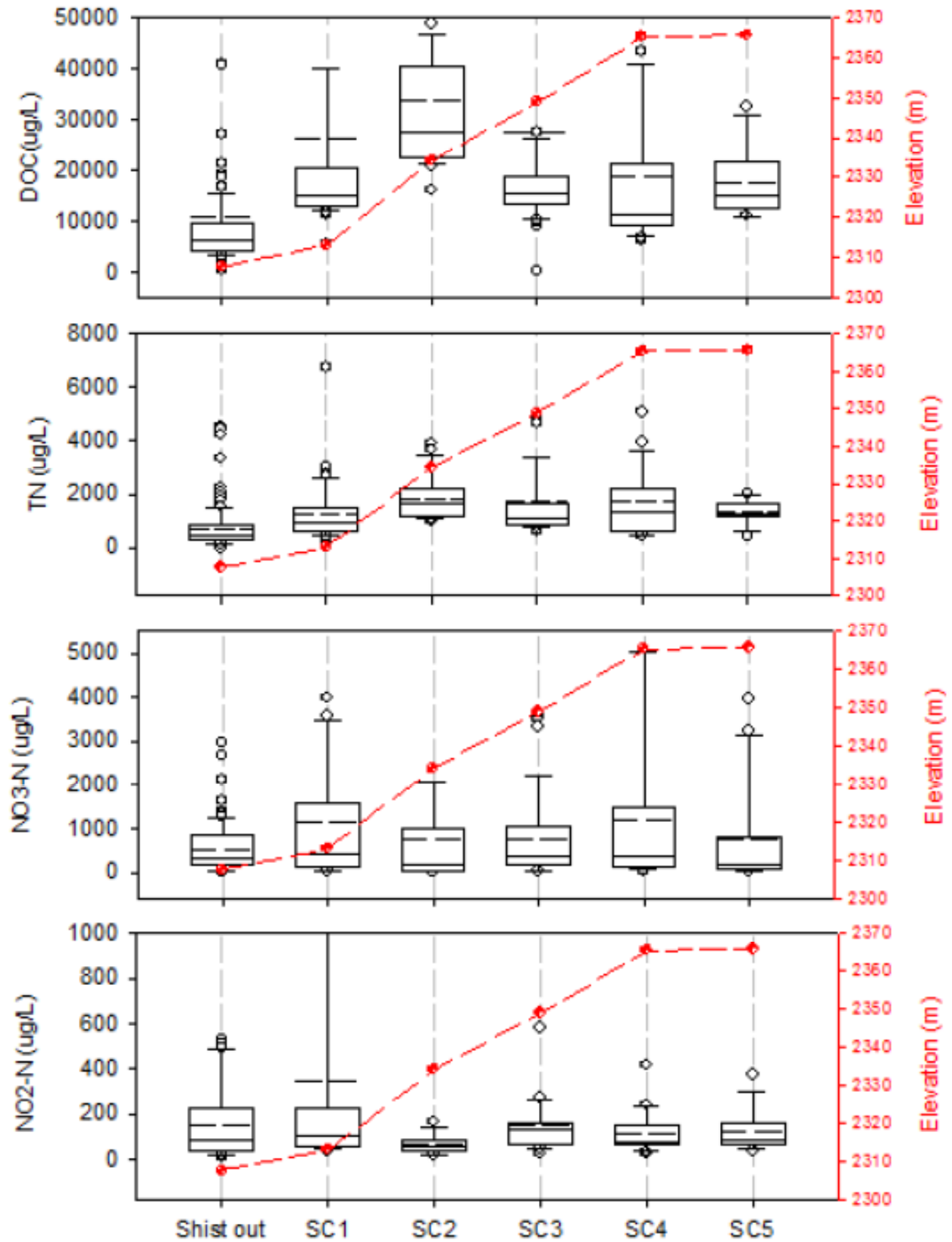


Figure 5: Dissolved organic carbon (DOC), total nitrogen (TN), nitrate ($\text{NO}_3\text{-N}$), and nitrite ($\text{NO}_2\text{-N}$) concentrations in soil waters along the schist hillslope (see Fig. 2 for sample locations).

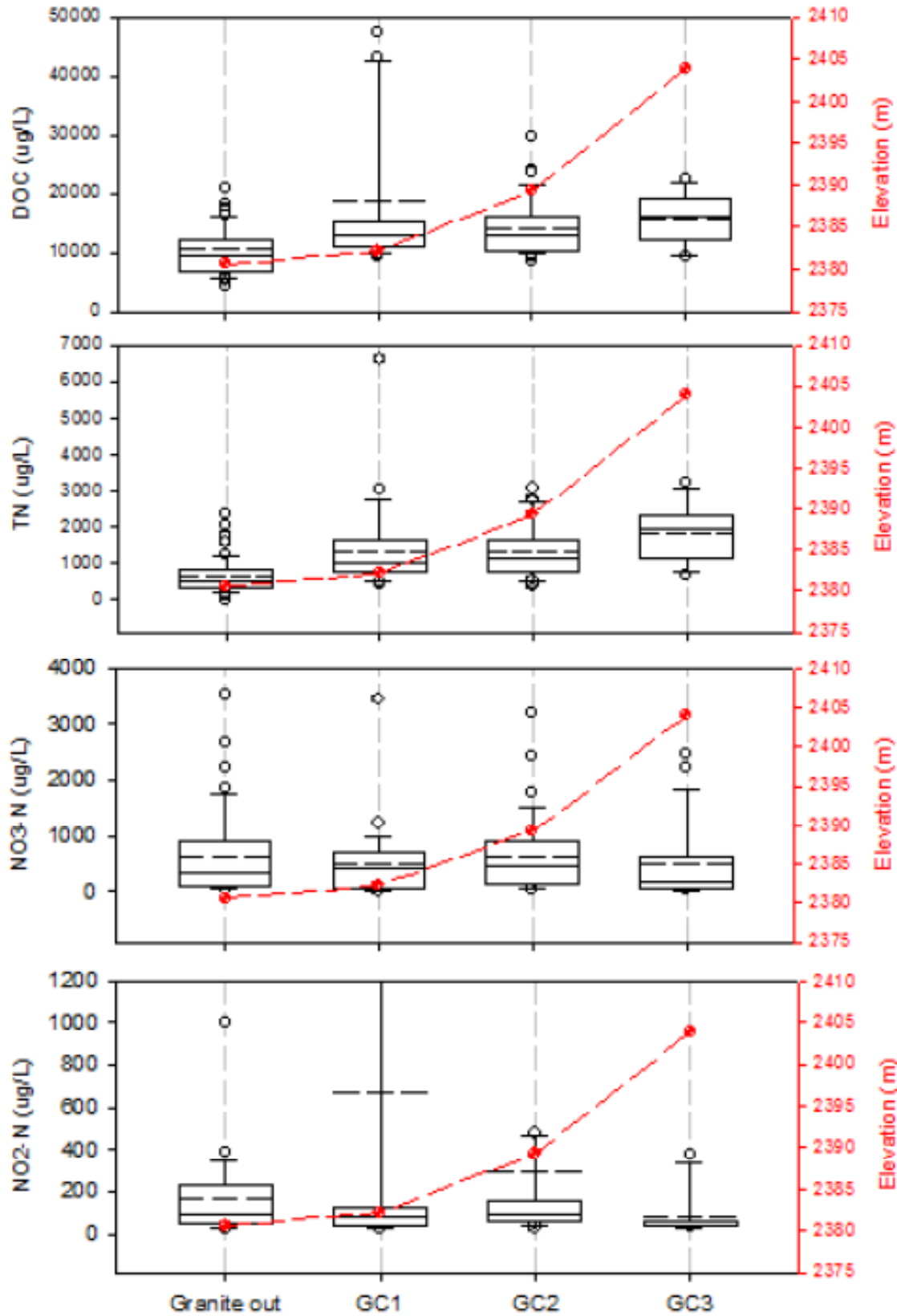


Figure 6: Dissolved organic carbon (DOC), total nitrogen (TN), nitrate (NO₃-N), and nitrite (NO₂-N) concentrations in soil waters along the granite hillslope (see Fig. 2 for sample locations).

(3) What are the amounts, sources, and seasonality of species in atmospheric deposition?

Aerosol measurements are used in this study to draw connections between particles that settle to the surface via dry deposition and the composition of soil water and surface waters downgradient of deposition areas. Temporal trends in aerosol concentrations and chemical composition of particles are dictated largely by meteorology, emissions sources, and air mass source origin. The summit of Mt. Lemmon is influenced by the Tucson urban plume during summer months when the mixing layer deepens as a result of higher ambient temperatures and more vigorous atmospheric convection. During the winter months, this high altitude site is exposed only to local sources (e.g. vehicular emissions by nearby town of Summerhaven and wood-burning) and free tropospheric aerosol, while the low-altitude B2 desert site is influenced by pollution sources in the metropolitan Tucson area. Aerosol particles are impacted by both natural and anthropogenic sources, where the predominant source of dry deposition at the summit of Mt. Lemmon is hypothesized to be dust, owing to its coarse size and prevalence at these high altitudes during spring and summer months.

Table 4: Concentrations of chloride, sulfate, nitrate, and nitrite in atmospheric deposition, measured as part of this study from the Mt. Lemmon and B2 sites.

Collection Site	Start	End	$\mu\text{g m}^{-3}$ Cl	$\mu\text{g m}^{-3}$ SO4	$\mu\text{g m}^{-3}$ NO3	$\mu\text{g m}^{-3}$ NO2
Mt Lemmon	6/8/10	6/16/10	0.0497	0.5572	0.1891	0.0172
Mt Lemmon	7/14/10	7/22/10	0.0169	0.4649	0.1272	0.0127
Mt Lemmon	8/15/10	8/20/10	0.0337	0.5041	0.1278	0.0018
Mt Lemmon	9/4/10	9/10/10	0.0044	0.4393	0.1202	
Mt Lemmon	10/14/10	10/27/10	0.0074	0.4021	0.0179	0.0092
Mt Lemmon	10/27/10	11/5/10	0.0035	0.3396	0.0267	0.0082
Mt Lemmon	12/3/10	12/17/10	0.0043	0.2333	0.1008	0.0179
Mt Lemmon	1/25/11	1/30/11	0.0044	0.2933	0.0652	
B2	3/2/10	3/3/10	0.0489	0.3763	0.1647	
B2	5/21/10	5/22/10	0.1389	1.1164	0.1408	0.0194
B2	6/18/10	6/24/10	0.1247	1.3563	0.3555	0.0496
B2	7/27/10	8/2/10	0.0585	1.4236		0.0087
B2	8/27/10	9/5/10	0.0335	0.9320	0.1895	0.0127
B2	9/26/10	10/6/10	0.0172	0.7499	0.1190	0.0152
B2	10/26/10	11/15/10	0.0254	0.5116	0.1682	0.0096
B2	12/4/10	12/17/10	0.0701	0.4550	0.2081	0.0132

A number of species were investigated in this study, including nitrate, nitrite, sulfate, chloride, and organic carbon. Particulate nitrate (NO_3^-) mainly originates from oxides of nitrogen resulting from combustion processes. Submicrometer NO_3^- is typically present in the form of ammonium nitrate, produced via the reaction between gaseous ammonia (NH_3) and nitric acid (HNO_3), where sufficient NH_3 must be present to first fully neutralize SO_4^{2-} prior to formation of ammonium nitrate (NH_4NO_3). Nitrate in $\text{PM}_{2.5}$ can also be associated with the lower tail of a coarse mode due to reactions of HNO_3 (or precursors) with sea salt and dust (Lee et al., 2008; note that sea salt can be ruled out as a major aerosol component in southern Arizona). Nitrite (NO_2^-) similarly can partition into the aerosol phase as a result of uptake and reactions of nitrogen oxides on the surface of mineral particles such as dust (Grassian et al., 2001). While nitrate is a common constituent of atmospheric aerosol particles, there are sparse measurements of particulate nitrite as it usually is in low concentrations and is easily oxidized (e.g. Lammel and Cape, 1996). It is thought that nitrite is associated with local pollution and mineral particles (e.g. Acker et al., 2008). Sulfate originates mainly from anthropogenic pollution (i.e. SO_2 emissions) and is produced via photochemical reactions and therefore is most abundant during summer

months as a result of vigorous solar radiation. Its production is also more rapid in the aqueous phase, and thus is produced most efficiently at high relative humidity and especially in clouds. The major sources for organic carbon (OC) include prescribed and natural wildfires, residential wood combustion, anthropogenic emissions, biogenic emissions, and suspended soil dust. Particulate organics can be formed via direct emission (e.g. primary biological aerosol particles such as pollen, fungi, and bacteria) and by secondary gas-to-particle conversion processes as a result of volatile organic compound (VOC) emissions. Similar to sulfate, secondary production of OC is expedited with high relative humidity and high solar radiation. Chloride originates from mineral aerosols (sea salt, dust), coal combustion (Ye et al., 2003), and biofuel combustion. This species is predicted to be most abundant at our two measurement sites in the spring and summer months.

We hypothesized that the highest concentrations of all species studied in dry deposition aerosol samples should be observed during the spring and summer months owing to the largest influence of dust aerosol and the Tucson urban plume at both the low elevation (B2) and high elevation (Mt. Lemmon) sites. Dust emissions in Arizona are highest between April and July, and subsequently decrease as a result of monsoon precipitation suppressing the lofting of dust aerosol from surfaces. However, during the episodic monsoon storms, massive dust plumes are associated with gust fronts that also have the ability to impact both measurement sites. Satellite imagery confirms that massive dust storms extending from the surface to higher than 5 km in altitude frequently pass through southern Arizona and have a great potential to impact both measurement sites.

As predicted, the highest concentrations of Cl, SO₄, and NO₃ were measured in aerosol particles from the low elevation (B2) and high elevation (Mt. Lemmon) sites in the summer months (May-August 2010; Table 4) when dust deposition is the highest, and the Tucson urban plume (including NO_x emissions) reaches the top of Mt. Lemmon. NO₂ values in dry deposition were highest in June-July and December at the Mt. Lemmon site, and May-June at the B2 site. A plausible explanation for the high concentration of NO₂ measured in dry deposition (up to 0.0496 ug/m³) is that heterogeneous processes on dust surfaces allow this species to partition to the aerosol phase. Enhanced sulfate levels in atmospheric deposition during the summer time at the Mt. Lemmon site show that concentrations of dry deposited species at high-altitude sites can be governed to a large extent by variability in atmospheric mixing layer height, which is driven by solar radiation and convection.

(4) How does variability in precipitation effect organic carbon and nitrogen cycling?

Water year (WY Oct-Sept) 2010 was relatively wet compared to 2009, with significantly more precipitation (Fig. 7; 397 mm vs. 675 mm, respectively). There was also a relatively large snowpack that developed on Mt. Lemmon during winter 2010 that led to higher spring snowmelt pulses in surface waters. Thus, we expected to see differences in the nutrient concentrations in stream waters between WY 2009 and 2010. In addition, we expected to see differences within years between the spring snowmelt, dry summer, and monsoon seasons.

A

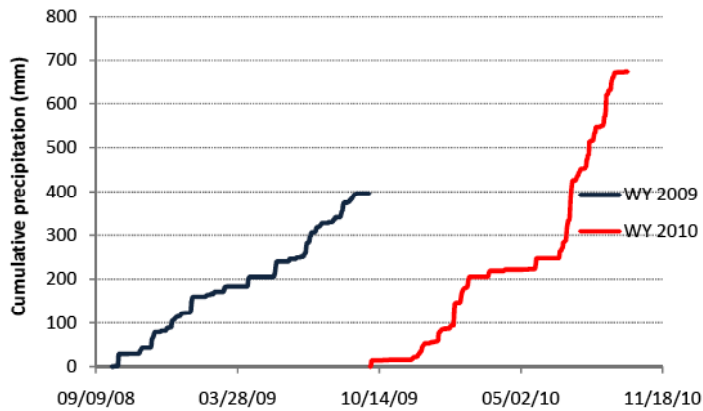
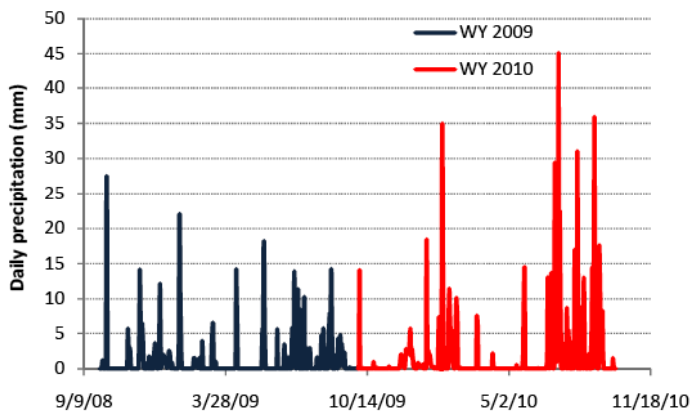


Figure 7: Comparison of precipitation amounts in the Santa Catalina Mountains between water years (WY; Oct 1-Sept 30). A) Cumulative precipitation, showing higher amounts in 2010. B) Daily precipitation values, showing higher precipitation during the winter and summer

B



Dissolved organic carbon (DOC; same as total organic carbon (TOC)) values in the Marshall Gulch outlet stream waters were highest during the spring and summer, likely due to flushing of shallow soils during snowmelt (Fig. 8). In addition, DOC concentrations were significantly greater in 2010 than 2009. We hypothesize that greater precipitation amounts in 2010 enhanced DOC production in soils, which was then transported to streams.

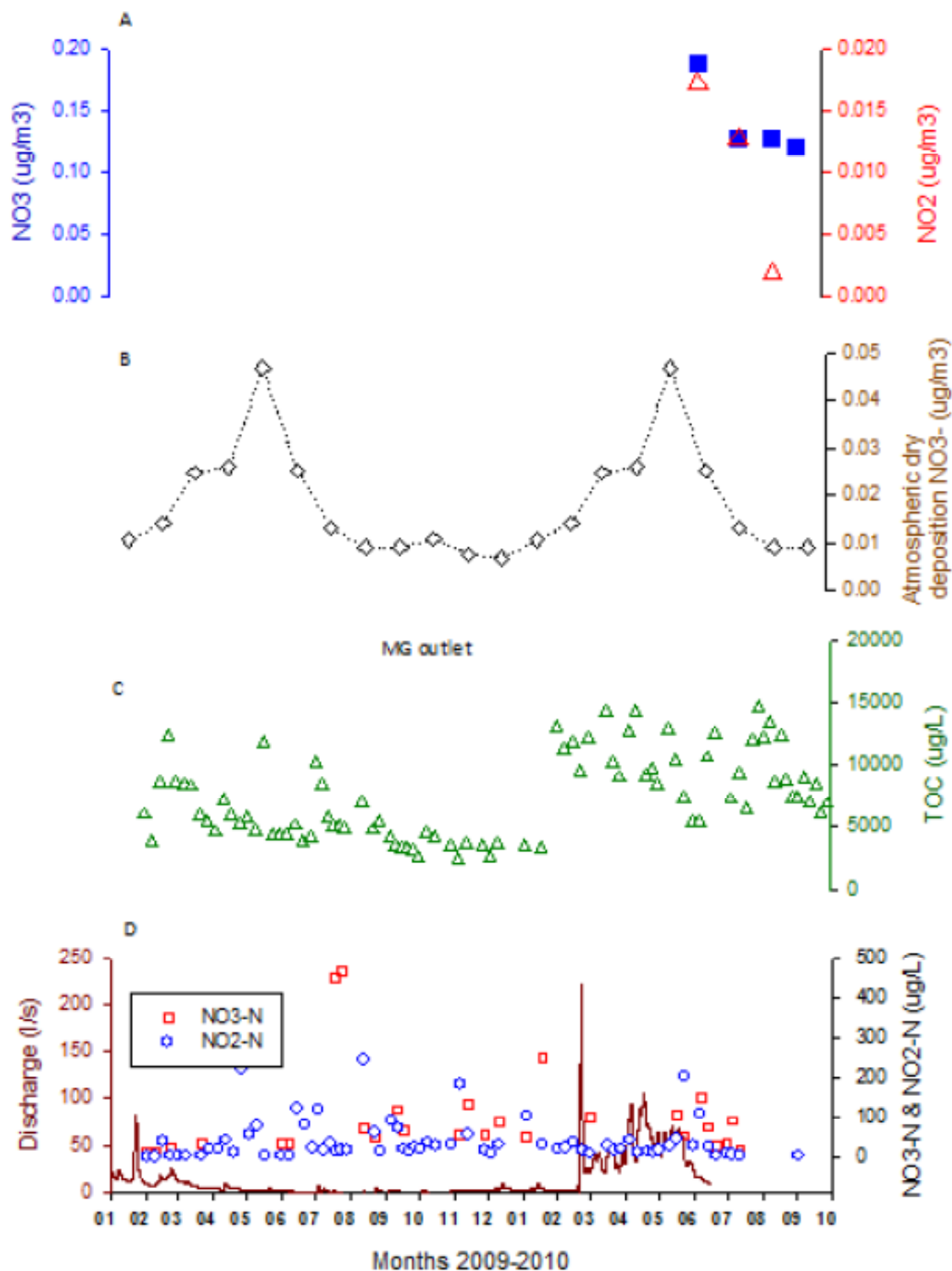


Figure 8. Comparison of atmospheric deposition to stream water quality of the Marshall Gulch outlet. A) Measured NO_3 and NO_2 concentrations in atmospheric deposition at Mt. Lemmon (this study). B) NO_3 levels atmospheric dry deposition (longer-term dataset courtesy Dr. Eric Betterton). C) Time series of total organic carbon (TOC) concentrations in stream waters from the Marshall Gulch (MG) outlet. D) Discharge data from Marshall Gulch outlet, and nitrate ($\text{NO}_3\text{-N}$) and nitrite ($\text{NO}_2\text{-N}$) concentrations of stream waters.

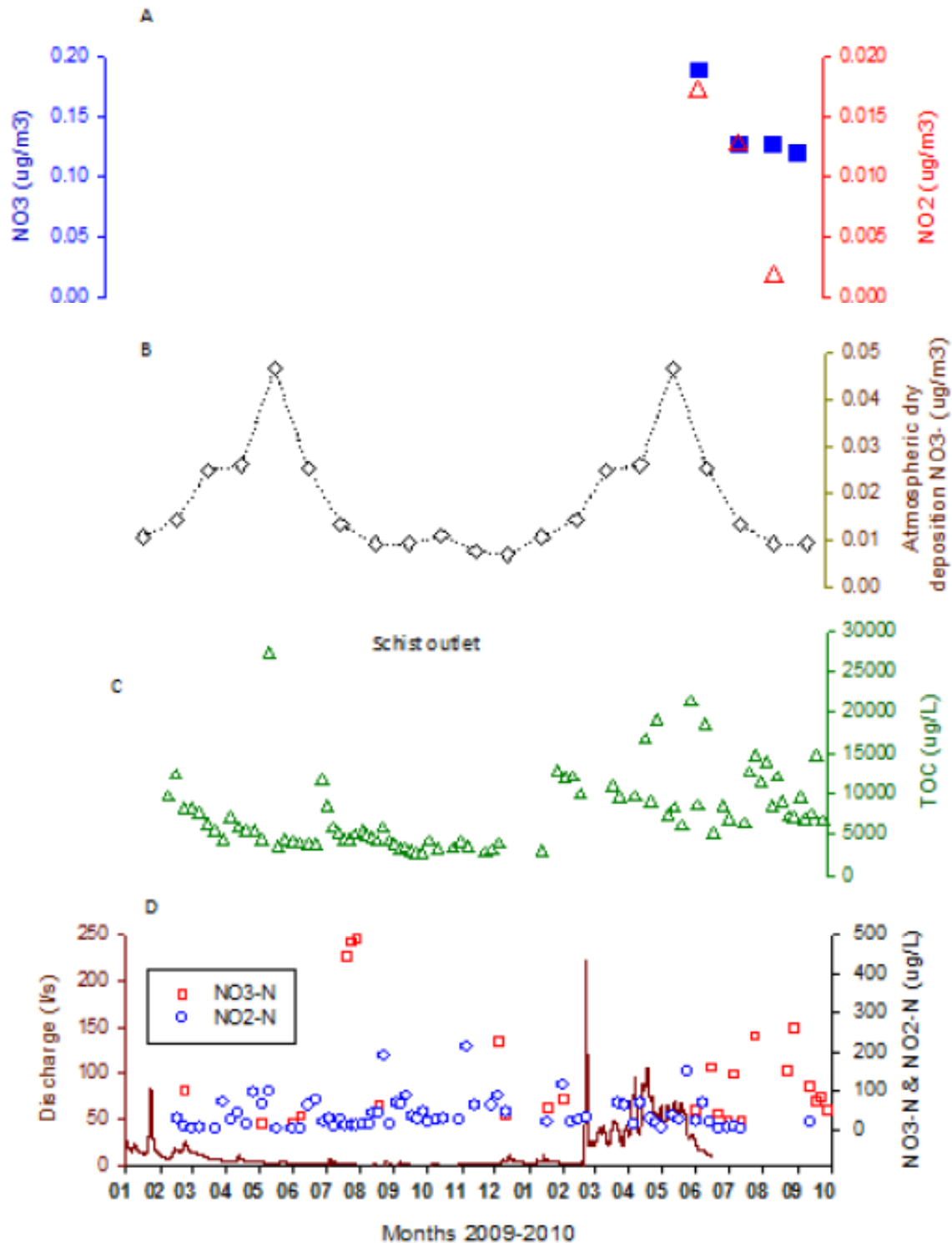


Figure 9. Comparison of atmospheric deposition to stream water quality of the Schist hillslope outlet. A) Measured NO_3 and NO_2 concentrations in atmospheric deposition at Mt. Lemmon (this study). B) NO_3 levels atmospheric dry deposition (longer-term dataset courtesy Dr. Eric Betterton). C) Time series of total organic carbon (TOC) concentrations in stream waters from the Schist hillslope outlet. D) Discharge data from Marshall Gulch outlet, and nitrate ($\text{NO}_3\text{-N}$) and nitrite ($\text{NO}_2\text{-N}$) concentrations of stream waters from the Schist hillslope outlet.

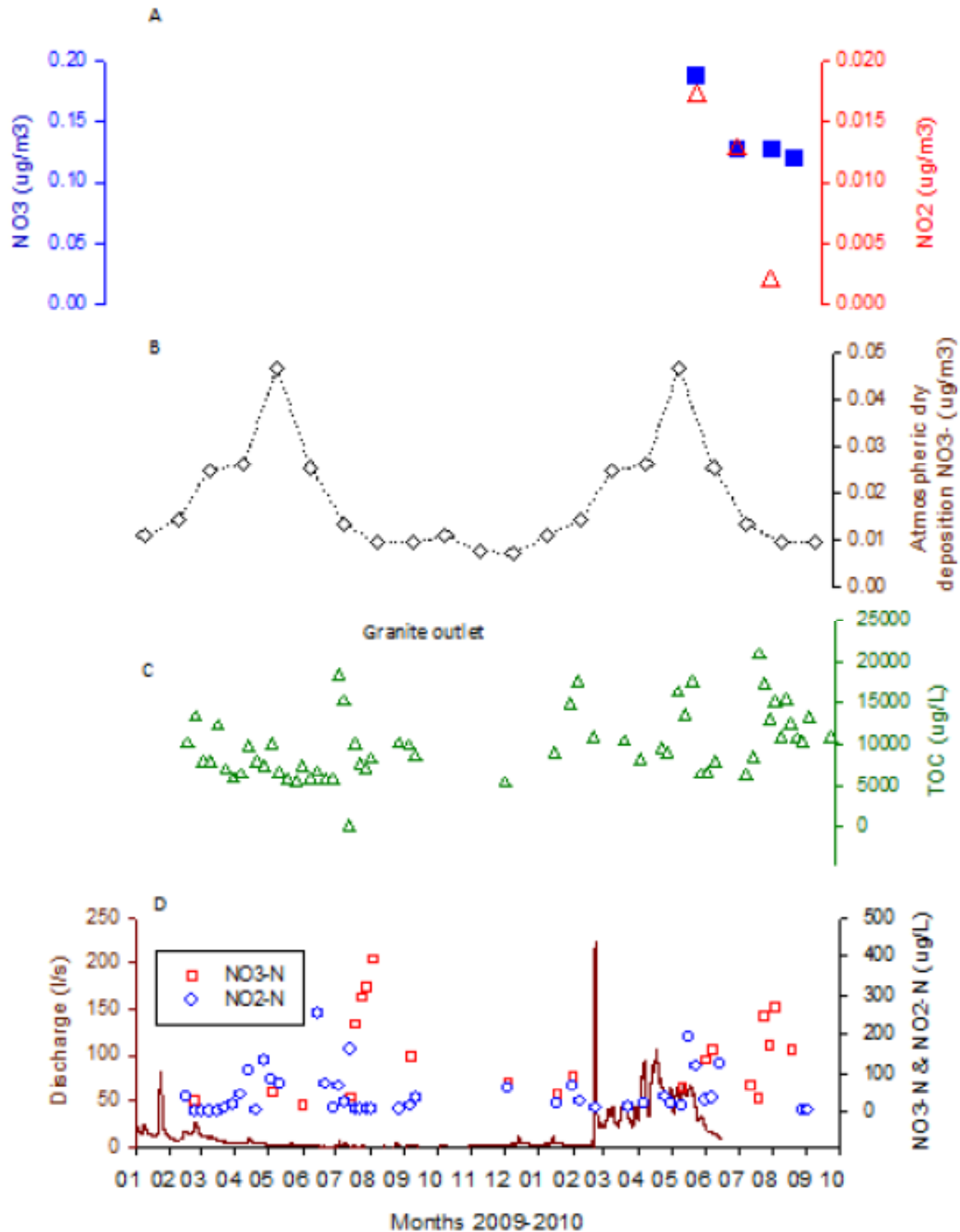


Figure 10: Comparison of atmospheric deposition to stream water quality of the granite hillslope outlet. A) Measured NO_3 and NO_2 concentrations in atmospheric deposition at Mt. Lemmon (this study). B) NO_3 levels atmospheric dry deposition (longer-term dataset courtesy Dr. Eric Betterton). C) Time series of total organic carbon (TOC) concentrations in stream waters from the granite hillslope outlet. D) Discharge data from Marshall Gulch outlet, and nitrate ($\text{NO}_3\text{-N}$) and nitrite ($\text{NO}_2\text{-N}$) concentrations of stream waters from the granite hillslope outlet.

Total dissolved nitrogen (TN) and $\text{NO}_3\text{-N}$ concentrations in the Marshall Gulch outlet stream waters were highest during the summer dry period and summer monsoons (Fig. 8). The $\text{NO}_3\text{-N}$ values of stream waters are well below the EPA maximum contaminant level (MCL) of 10 mg/L, with the highest values similar between the schist, granite, and Marshall Gulch outlet samples (3.0, 3.5, and 3.4 mg/L respectively). In contrast, $\text{NO}_2\text{-N}$ concentrations were unusually high for most natural environments, with the highest values recorded during the summer monsoons. Typically, $\text{NO}_2\text{-N}$ is thought to convert rapidly to $\text{NO}_3\text{-N}$ in surface water and soil systems so that concentrations in surface and soil systems are often below detection limit. However, we observed surprisingly high $\text{NO}_2\text{-N}$ concentrations in surface and soil solution waters (7-2828 ug/L, EPA drinking water standard is 1000 ug $\text{NO}_2\text{-N/L}$). These high pulses of N in stream waters in the summer appear to correspond to periods of intense atmospheric deposition of N (mentioned above), thus we hypothesize that high $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ values observed in stream waters during the summer dry period is derived from the atmosphere. Triple isotope analyses of NO_3 should enable us to distinguish atmospheric versus terrestrial sources of N. A similar study using triple isotope analysis of NO_3 is in progress in the Tucson metropolitan area, examining the impacts of urbanization on runoff nitrogen biogeochemistry. This study is also showing high $\text{NO}_2\text{-N}$ concentrations in rainfall and runoff indicating that $\text{NO}_2\text{-N}$ in solution is a longer-lived N form in these hot semi-arid ecosystems (Gallo et al. in revision, Gallo et al. in preparation). The mechanisms explaining higher concentrations of $\text{NO}_2\text{-N}$ are unknown and merit further investigation. Aerosol data point to dust and aerosol deposition being the primary source of $\text{NO}_2\text{-N}$.

The lowest values of TN, $\text{NO}_3\text{-N}$, and $\text{NO}_2\text{-N}$ in stream waters were measured after peak discharges (e.g. snowmelt and monsoons; Fig. 8), which may be due to N removal via uptake or denitrification, in which case the NO_3 should have an isotopic signature indicative of denitrification. Alternatively, lower values might be explained by different source waters and/or flushing of $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ from the soil catchment ecosystem during peak discharge.

There is no positive correlation between $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ as would be expected if both came from the same production pathway (i.e. biological production via two step process of nitrification). Thus, we hypothesize that $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ have different sources, $\text{NO}_2\text{-N}$ via dry/particulate deposition and the $\text{NO}_3\text{-N}$ as wetfall. These hypotheses would have to be further tested with triple isotopes in rainfall, throughfall, dry deposition samples.

Synthesis & Summary of Key Results.

- ⇒ Total dissolved nitrogen (TN), nitrate ($\text{NO}_3\text{-N}$), nitrite ($\text{NO}_2\text{-N}$), and dissolved organic carbon (DOC) concentrations were slightly higher in stream waters draining the granite versus schist hillslopes. We hypothesize that the thicker soils developed on the schist hillslope have higher cation exchange capacities to retain nutrients compared to thinner soils developed on the granite hillslope.
- ⇒ Mean and median concentrations of DOC, TN, $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ decrease downstream between the granite hillslope outlet, the schist hillslope outlet, and the Marshall Gulch outlet. This may suggest in-stream processing of organic carbon and N, dilution or adsorption of DOC.
- ⇒ DOC values in the Marshall Gulch outlet stream waters were highest during the spring

Sources and transport of nitrogen deposition in sky islands

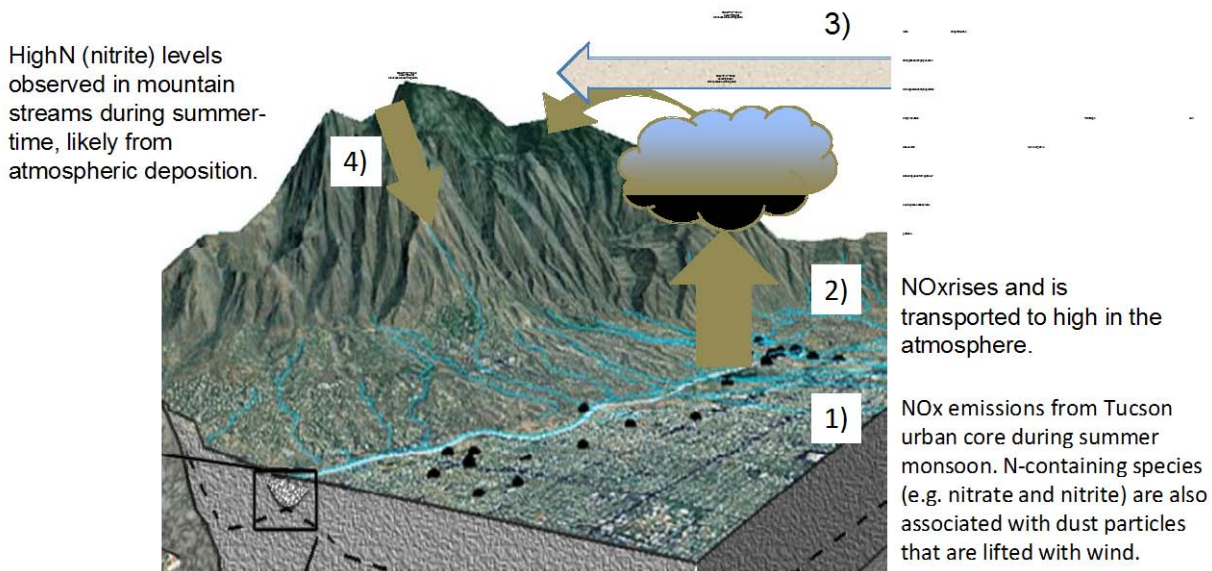


Figure 11: Schematic diagram showing sources of nitrogen deposition and transport in sky-island ecosystems.

and summer, likely due to flushing of shallow soils during snowmelt. In addition, DOC concentrations were significantly higher in 2010 compared to 2009. We hypothesize that greater precipitation amounts in 2010 enhanced DOC production in soils, which was then transported to streams.

- ⇒ Measurement of the composition of aerosol particles at the low and high elevation sites (B2 and Mt. Lemmon, respectively) show that dust aerosol is a major contributor of dry deposition at both sites, during the spring and summer. In addition, NO_3 , NO_2 , and chloride levels are high in aerosols during these dust-impacted months at both sites. High amounts of N deposition in the spring and summer may be related to NO_x emissions from the Tucson urban core and dust, which are transported to the top of Mt. Lemmon (see Fig. 11).
- ⇒ TN, $\text{NO}_3\text{-N}$, and $\text{NO}_2\text{-N}$ concentrations in Marshall Gulch outlet stream waters were highest during the summer dry period and summer monsoons, which corresponds to the period of greatest atmospheric deposition of N. Interestingly, measured concentrations of $\text{NO}_2\text{-N}$ concentrations in stream and soil waters were exceptionally high (in some cases, above the EPA MCL; 1000 $\mu\text{g/L}$ $\text{NO}_2\text{-N}$). Similarly high concentrations of $\text{NO}_2\text{-N}$ have been measured in Tucson urban runoff (Gallo et al., in revision, in preparation), which suggests that nitrite may persist in hot, semi-arid environments.
- ⇒ There is no positive correlation between $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$, which suggests different sources for the N-species. We hypothesize that $\text{NO}_2\text{-N}$ is sourced from dry/particulate atmospheric deposition, while $\text{NO}_3\text{-N}$ is sourced from wet deposition (rainfall).
- ⇒ Ongoing triple isotope analysis of NO_3 will help to constrain atmospheric versus terrestrial sources of N and removal pathways, such as denitrification.
- ⇒ Results from this study enhance our understanding of the sources and amounts of nitrogen being deposited in sky-island ecosystems, and how nitrogen is retained and/or transported from mountain catchments to adjacent groundwater basins. These results are

important for constraining water quality of surface water and groundwater, ecosystem function in semi-arid environments, and atmospheric pollution.

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