Estimating Wet and Dry Deposition of Nitrogen to Southern California Streams: Final Report of IA DW-12-92326401-0

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Executive Summary

The purpose of this report is to summarize the findings of a research study designed to characterize the flux of atmospheric nutrients to southern California watersheds conducted with the support of the U.S. Environmental Protection Agency under Interagency Agreement DW 12923264010. Atmospheric deposition (wet and dry) is potentially one source of "background" nutrients to streams. The load of nutrients to aquatic habitats from atmospheric deposition, relative to other potential sources of nutrients, are not well characterized in California. In particular, little data are available on the dry deposition of atmospheric nutrients, which may constitute roughly 90% of the total annual atmospheric loads in semi-arid regions. Studies were conducted to address the following research objectives:

- Evaluate methods for assessment of wet and dry deposition rates of nitrogen and phosphorus from the atmosphere.
- Estimate the spatial and temporal variability in nitrogen and phosphorus deposition from the atmosphere to five, relatively undisturbed catchments in Southern California.
- Evaluate the utility of stable isotopic tracers, specifically the dual isotopes of nitrate ($\delta^{18}O$ and $\delta^{15}N$) to assess the contribution of atmospheric nitrate to reference streams.

Following are the major findings of this study:

1. Of the surrogate surfaces tested under controlled circumstances, the water surface samplers seemed to produce the most reliable results.
    a. Surface water samplers produced a strong linear relationship with air concentration; however, use of the water surface samplers is hampered by practical considerations such as evaporation and freezing of the water in the dish, which greatly limit when and where the samplers can be deployed.
    b. Nitric acid deposition onto Nylasorb filters showed some promise; however they did not show as strong of a linear relationship with ambient concentration as water samplers and the flux of nitric acid onto the filters was significantly less than that calculated from the water samplers.
    c. Ammonium deposition onto the acid trap filters showed no significant relationship with ambient concentration, suggesting acid traps either degrade with exposure releasing ammonia back into the atmosphere or are not strong enough ligands to hold onto the ammonium ion.

2. Across all sites, dry nitrogen and phosphorus deposition was a significant fraction of the total annual atmospheric deposition of nutrients (average nitrogen dry deposition is ~70% and average phosphorus dry deposition is ~30% of the total load), demonstrating the

importance of characterizing this fraction when assessing atmospheric nutrient loads.

  a. There was a large degree of spatial and temporal variability in both wet and dry deposition, demonstrating that atmospheric nutrient deposition is somewhat site/time specific.
  b. There appears to be a slight seasonal trend in dry deposition with the highest values occurring in the spring and lower values occurring in the fall for all nutrient species; however, there do not appear to be any spatial trends.

3. In Southern California there has been an assumption that nitrogen deposition should be dominated by oxidized forms of nitrogen due to domination by automobile exhaust; however this study shows that is not necessarily the case.

  a. Water surface sampler deposition data show that in general, ammonium dry deposition is nearly twice as high as nitrate dry deposition.
  b. Similarly, for some sites ammonium wet deposition may dominate the nitrogen deposition pool.
  c. The prevalence of ammonium may be due to the proximity of agriculture in the airsheds of these reference site.

4. The dual isotopic signatures of $\delta^{18}O$ and $\delta^{15}N$ in atmospheric nitrate deposition in Southern California is consistent with literature values for atmospheric nitrate showing characteristically high $\delta^{18}O$ values. The distinctiveness of the high $\delta^{18}O$ value for atmospheric nitrate across all sites suggests that the dual isotopic composition of nitrate could be an excellent tracer for direct deposition of atmospheric nitrate into water bodies.

  a. Stream dissolved nitrate did not reflect the isotopic composition of atmospheric nitrate, suggesting that direct deposition of nitrate to streams is likely minimal. This is not surprising given the relatively small surface area of headwater streams.
  b. However, this is not to say that atmospheric deposition is not a significant source of nitrate to streams; rather, atmospheric deposition of nutrients is more likely indirectly accumulated in streams, by first depositing on the landscape and entering the streams through surface runoff or groundwater.

Acknowledgements

Disclaimer

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1. Introduction

1.1. Background and Purpose of Report

Streams and rivers are known to provide a wide range of essential and economically valuable services (ecosystem services) that support the health of watersheds, including opportunities for recreation, habitat for aquatic life use and protection of aquatic biodiversity, and nutrient cycling. In semi-arid regions, stream ecosystems are especially vital because they provide freshwater oases on which a multitude of native wildlife species are dependent for survival. In addition, wadeable streams play a critical role in denitrification, the important pathway for permanent loss of nitrate by conversion to nitrogen (N) gas. Denitrification within streams can reduce the total N load from runoff and groundwater to N-sensitive coastal marine environments (Howarth et al. 1996; Alexander et al. 2000).

Eutrophication in streams is manifested symptoms such as accumulation of high biomass of stream benthic algae, a shift in the algal community structure towards lower diversity and stress tolerant taxa, and wide variation in diel ranges of oxygen and pH. These changes cause trophic level shifts in benthic macroinvertebrates and higher level consumers that prey upon them. Recent studies have shown that increasing eutrophication decreases the capacity of stream to denitrify N, thus directly degrading the nutrient-related ecosystem services and beneficial uses the provided by stream. Recent data from the Storm Water Monitoring Coalition (SMC) Regional Stream Monitoring Program indicate that approximately 30% of stream miles in southern California exhibit heavy algal cover, indicating a pervasive problem with eutrophication. This problem persisted at a similarly high rate at sites with predominantly undisturbed catchments, suggesting that an unknown "background" source of nutrients may be present at these locations.

Atmospheric deposition (wet and dry) is potentially one source of "background" nutrients to streams. Atmospheric dry deposition is the process by which atmospheric pollutants are transferred to terrestrial and aquatic ecosystems in the absence of precipitation. Studies have indicated that dry deposition loadings may be equal or greater to those of wet deposition and therefore the effects of dry deposition on ecosystems may be substantial (Dolske and Gatz, 1985). The load of nutrients to aquatic habitats from atmospheric deposition, relative to other potential sources of nutrients, are not well characterized in California. In particular, little data are available on the dry deposition of atmospheric nutrients, which may constitute roughly 90% of the total annual atmospheric loads in semi-arid regions.

This purpose of this report is to provide a summary of the data collected to fill the data gap regarding the significance of atmospheric deposition to stream eutrophication in Southern California. Studies were conducted to address the following research objectives:

- Evaluate methods for assessment of wet and dry deposition rates of nitrogen and phosphorus from the atmosphere.
- Estimate the spatial and temporal variability in nitrogen and phosphorus deposition from the atmosphere to five, relatively undisturbed catchments in Southern California.
- Evaluate the utility of stable isotopic tracers, specifically the dual isotopes of nitrate ($\delta^{18}O$ and $\delta^{15}N$) to assess the contribution of atmospheric nitrate to reference streams.

1.2. Report Organization

This report is organized into an executive summary and four chapters:

Executive Summary
Chapter 1: Introduction, purpose, and organization of report, site descriptions, and general study design
Chapter 2: Comparison of Methods to Improve Capacity for Measurement of Dry Deposition of Nitrogen-Containing Air Pollutants
Chapter 3: Rates of Atmospheric Nitrogen Flux to Reference Streams in Southern California
Chapter 4: Utility of Stable Isotope Tracers to Identify Atmospheric Nitrogen-Containing Pollutants in Southern California Reference Streams

A summary of quality assurance results is provided in Appendix 1.

1.3. Site Descriptions

University of California, Riverside.

The first study objective, evaluation of different measurement techniques to assess dry atmospheric deposition of nitrogen and phosphorus, was conducted at the University of California, Riverside. Experiments were conducted in custom laboratory flux chambers, which were set up to deliver three concentration levels of nitrogen deposition for comparison (Padgett et al., 2004)

Stream Bioassessment Reference Sites.

The second and third study objectives, estimation of the spatial and temporal variability in nitrogen and phosphorus deposition from the atmosphere and evaluation of the utility of stable isotopic tracers to assess the contribution of atmospheric nitrate to reference streams, were conducted at five regional stream bioassessment reference sites in southern California. Sites were selected to represent different natural land cover types, e.g., forested vs. chapparal, and were required to be located next to a stream which was deemed as "reference" in the regional

stream bioassessment database in which "reference" sites were required to have greater than 90% open space in the stream catchment. Table 1.1 lists the five relatively undisturbed sites selected for this study.

Table 1.1. Study sites for assessment of wet and dry atmospheric deposition of nitrogen and phosphorus contaminants.

Site	Latitude	Longitude	Elevation	Stream	Watershed
Bear Creek	N 34° 14.520'	W 117° 53.202'	1688 feet	Bear Creek	San Gabriel River
Cattle Creek	N 34° 13.661'	W 117° 45.829'	1941 feet	Cattle Creek	
Forest Falls	N 34° 04.734'	W 116° 52.911'	6404 feet	Mill Creek	Santa Ana River
Heart Bar	N 34° 09.288'	W 116° 47.040'	6858 feet	Santa Ana River	
Palomar	N 33° 20.774'	W 116° 54.402'	4560 feet	French Creek	San Luis Rey River
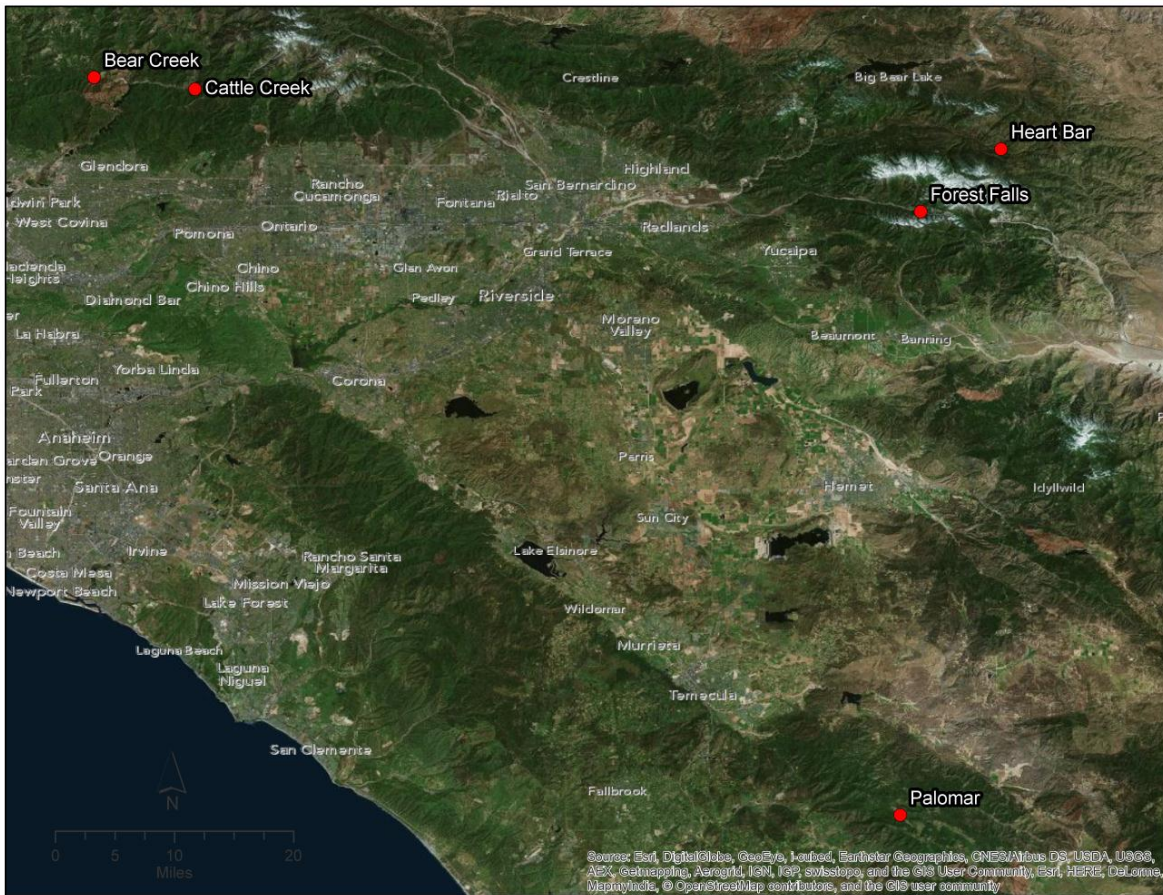
Figure 1.1. Location of reference sites.

1.4. Study Design

The general study design of this project was to use passive sampling methods to extrapolate the wet and dry deposition of nitrogen and phosphorus containing contaminants to undisturbed catchments in southern California and determine the temporal variability in these deposition rates and whether atmospheric sources of nitrate could be traced into headwater streams. The project has 3 primary tasks all related to improving the understanding of the contribution of atmospheric deposition, particularly dry deposition, to eutrophication of surface waters:

> **Task 1. Improve the capacity for measuring dry deposition of nitrogen-containing air pollutants.** Several new passive monitoring methods for determining dry deposition fluxes in semi-arid regions were evaluated under controlled conditions. The relationship between atmospheric concentration and deposition value was evaluated for consistency and reproducibility among the deposition proto-types.

Task 2. Establish the rates of atmospheric nitrogen flux to reference streams used in eutrophication studies of coastal waters and estuaries in Southern California. Passive samplers were deployed at five regional stream bioassessment reference sites established by the Southern California Coastal Waters Research Program for the study of water quality in Southern California. Measurements were taken six times over two years. Resin-based wet deposition collectors were co-deployed at each of the reference sites for a full year (with an exchange at 6 months) to determine the contribution of nitrogen and phosphorus from rain. These data were used to calculate a total annual deposition load was calculated for each site as well as an average for Southern California.

Task 3. Improve the ability to identify sources of atmospheric nitrogen-containing pollutants contributing to terrestrial and aquatic eutrophication. A pilot study was conducted using stable isotopes (^{18}O and ^{15}N of nitrate) collected by deposition samplers to define an end-member value for the deposition of nitrate into southern California streams as a means of identifying source contribution to eutrophication. This is an emerging technique that has shown promise in source apportionment and biogeochemical cycling (see Kendall and McDonald, 1998, Elliot et al. 2007). Co-incident measurements of dissolved nitrate in local streams were also collected to determine if the atmospheric signature was apparent.

2. Comparison of Methods to Improve Capacity for Measurement of Dry Deposition of Nitrogen-Containing Air Pollutants

2.1. Introduction

Nitrogen dry deposition is, in practice, a difficult parameter to measure. While numerous methods have been suggested and applied in various situations, there are currently no standardized methods. The Clean Air Markets Division of EPA runs a dry deposition network called CASTNET that uses air concentrations to model deposition based on deposition velocities of the constituents and various meteorological parameters. It is well recognized that, while it is better than nothing, CASTNET has many failings, among them, the inability to measure ammonia deposition – a significant component in Southern California. Empirical techniques for monitoring site-specific dry deposition have a contentious history, but most scientists agree that the physical and chemical processes driving dry deposition are so site-specific that if one needs to know deposition values at a specific location, one needs to measure it at that specific location.

Use of surrogate surfaces to estimate dry deposition has been increasing. These surfaces are advantageous because they can be used at a variety of locations, including those in very remote areas, and over varying time intervals to delineate spatial and temporal patterns in deposition of pollutants of interest. In addition they have been shown to provide better control over exposure time and extraction methods (Davidson et al. 1985) and are relatively inexpensive and easy to use (Sehmel, 1980). The purpose of this study was to evaluate several techniques using surrogate surfaces for estimating nitrogen deposition in semi-arid environments. Those that showed a consistent relationship with air concentration (as measured by standardized methods) were then deployed at several locations to assess deposition (results of which are discussed in Chapter 3).

2.2. Methods

Study Design. Several new passive monitoring methods for determining dry deposition fluxes were evaluated. Evaluations were conducted in controlled fumigation chambers at the University of California, Riverside (Figure 2.1). Surrogate surfaces were placed into fumigation chambers in which the concentration of ambient nitrate controlled and monitored for each exposure period. Ambient ammonium was not controlled; however, it was monitored over the exposure period. Two experiments were conducted during the first experiment, samples were collected at three time points, 24 hours, 48 hours, and 96 hours to determine the ideal length of deployment. Replicates of each surrogate surface were collected at each time point and three fumigation chambers were used for the experiment. The relationship between atmospheric concentration and deposition value was evaluated for consistency and reproducibility among the deposition proto-types. The second experiment sought to explicitly compare the Nylasorb filters to the water surface sampler. Four fumigation chambers were set up at different levels of ambient nitric acid

air concentration, a control with no additional nitric acid, and chambers with three different levels of ambient nitrate (low, mid, high). Flux of nitric acid onto the two surface samplers were compared.

Figure 2.1. Picture of fumigation chamber set up. Three trays were used to evaluate each time point, 24 hours, 48 hours, and 96 hours. A water surface sampler (from which duplicate samples were drawn) and 2 replicate Nylasorb and glass fiber filters were analyzed for each time point. Air concentrations were measured using a denuder system.

Air Concentration. EPA approved electronic instruments for measuring nitrogen oxides and ozone were used to determine atmospheric concentrations of nitric acid and ammonium. Annular Denuder systems were used as the primary methodology for determining particulate nitrogen nitric acid, and ammonia concentrations. In addition, a recently introduced electronic ammonia analyzer (EcoTech LLC) was also used to determine atmospheric ammonium (NH_3) concentrations.

Dry Deposition. Two methods were evaluated for dry deposition using three surrogate surfaces. The first was a static water surface sampler developed at the Illinois Institute of Technology in Chicago, Illinois and the second was a Knife-Edge Surrogate Surface sampler developed at Clarkson University (Sahu et al., 2007). Both of these sampling devises are aerodynamically designed with sharp leading edges (<10°) which minimize air flow disruption across the surface. The design limits the variables that influence deposition to temperature, relative humidity, atmospheric stability, wind speed and direction. The water surface sampler has a water surface

and is used to measure total nitrate, ammonia, and phosphate deposition (gas and particle). The knife edge sampler uses a Nylasorb filter to measure total nitrate deposition (which was compared to the water surface), and a citric acid impregnated glass-fiber filter which measures the ammonium deposition. Dry deposition was calculated using the following equation:

$$\text{Dry Deposition (mg m}^{-2}\text{ d}^{-1})$$
$$= \text{Nutrient Concentration (mg L}^{-1}) * \frac{\text{Sampler Volume (L)}}{\text{Sampler Surface Area (m}^2) * \text{duration (d)}}$$

Eq. 2.1.

Where nutrient concentration is the concentration of nitrate, ammonia or phosphate measured either on water sampled directly from the water sampler surface dish or from the extracted filter, the sampler volume is either the volume of water remaining in the sampling dish at the end of the exposure or the volume of anion solution used to elute the filters, and duration is the length of time the surrogate surface was exposed.

Nutrient Concentrations. Nutrient concentrations (nitrate, ammonia, and phosphate) were measured on water collected directly from the sampling dish. Nitrate and ammonia concentrations from the Nylasorb and glass fiber filters were measured by extracting the filters in 12 mL of anion eluent solution in an ultrasonic batch for four hours. Nutrients were measured using a continuous flow analyzer and ion exchange chromatograph at the Riverside Forest Service laboratory. Instruments were inspected for physical damage weekly by lab personnel and calibration, instrument drift, and reproducibility were evaluated with each run by lab personnel.

2.3. Results

The experiment was replicated over two weeks. Ambient concentrations of nitrate and ammonia were fairly consistent though both nitrate and ammonium increased slightly in the chambers during the second week. Nitrate ambient concentration was 11.19 ± 1.07 µg-N m^{-3} and varied from a low of 9.79 µg-N m^{-3} at the start of the experiment to a high of 12.67 µg-N m^{-3} towards the end of the experiment. Ammonium ambient concentration was lower than nitrate, because it was not added to the fumigation chambers but had a fairly consistent background concentration of 1.51 ± 0.33 µg-N m^{-3}, varying from a low of 1.45 µg-N m^{-3} at the start of the experiment to a high of 2.05 µg-N m^{-3} at the end of the experiment.

Water surface samplers showed a linear increase in both nitrate and ammonium concentration with time during each replicate experiment (Figure 2.2). Replicate water surface samplers showed very consistent nitrate concentrations at each time point amongst replicate water samplers; however ammonium concentrations, particularly at the 48 hour time point, were slightly more variable. Nylasorb filters also showed a linear increase in nitrate concentration with

time (Figure 2.2.A.) and the concentration accumulated was very similar across replicates taken at each time point. The citric acid impregnated glass fiber filters did not appear to accumulate ammonium over time, with concentrations near 0 mg-N L^{-1} at each time point (Figure 2.2.B.)

A.

B.

Figure 2.2. Concentration of nitrate (A) and ammonium (B) accumulated on different sampling media over time. Nitrate and ammonium dissolved linearly into water dishes and nitrate was also linearly absorbed linearly onto the nylon (Nylasorb) filters. Ammonium was not absorbed onto the citric acid impregnated filters.
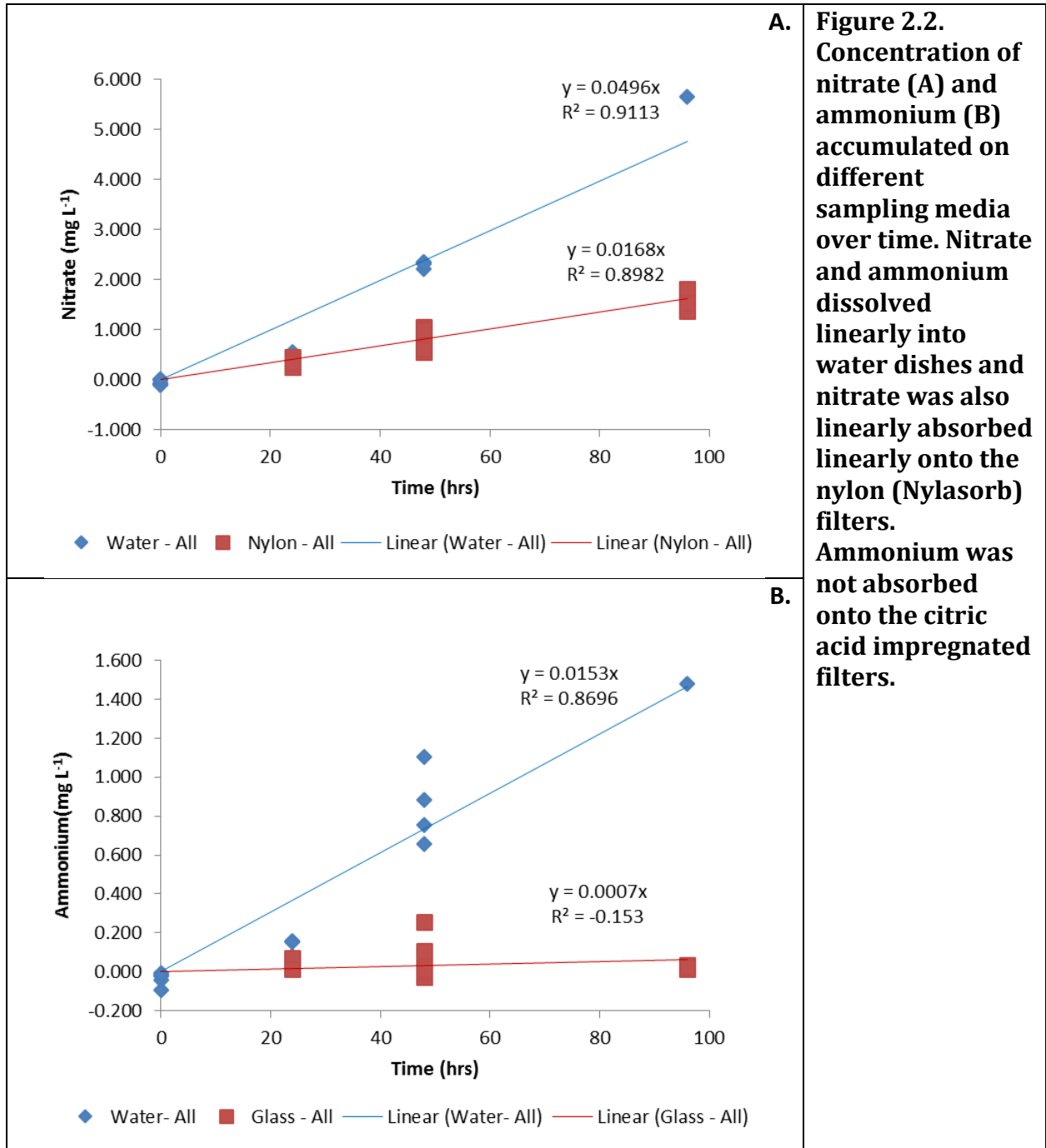
Nitrate and ammonium deposition appears to be linearly related to ambient air concentration when measured with the static water surface sampler (Figure 2.3.A). Nitrate deposition onto the surface water samples increased with stepwise increases ambient concentration (Figure 2.4.A) and was near zero in the fumigation chamber with no addition of nitric acid vapor. Nitrate deposition onto Nylasorb filters also increased with stepwise increases in ambient concentration (Figure 2.4.B), but the linear relationship with ambient air concentration was not as definitive as the water surface sampler (Figure 2.3.B). There was no apparent relationship between ammonium deposition onto citric acid impregnated glass fiber filters and ambient ammonium concentration.

A.

B.

Figure 2.3. Dry Deposition as a function of air concentration for static water samplers (A) and for filters (B). Ammonium air concentration is on the top axis and ammonium dry deposition is on the right axis. Nitrate air concentration is on the bottom axis and nitrate deposition is on the left axis.
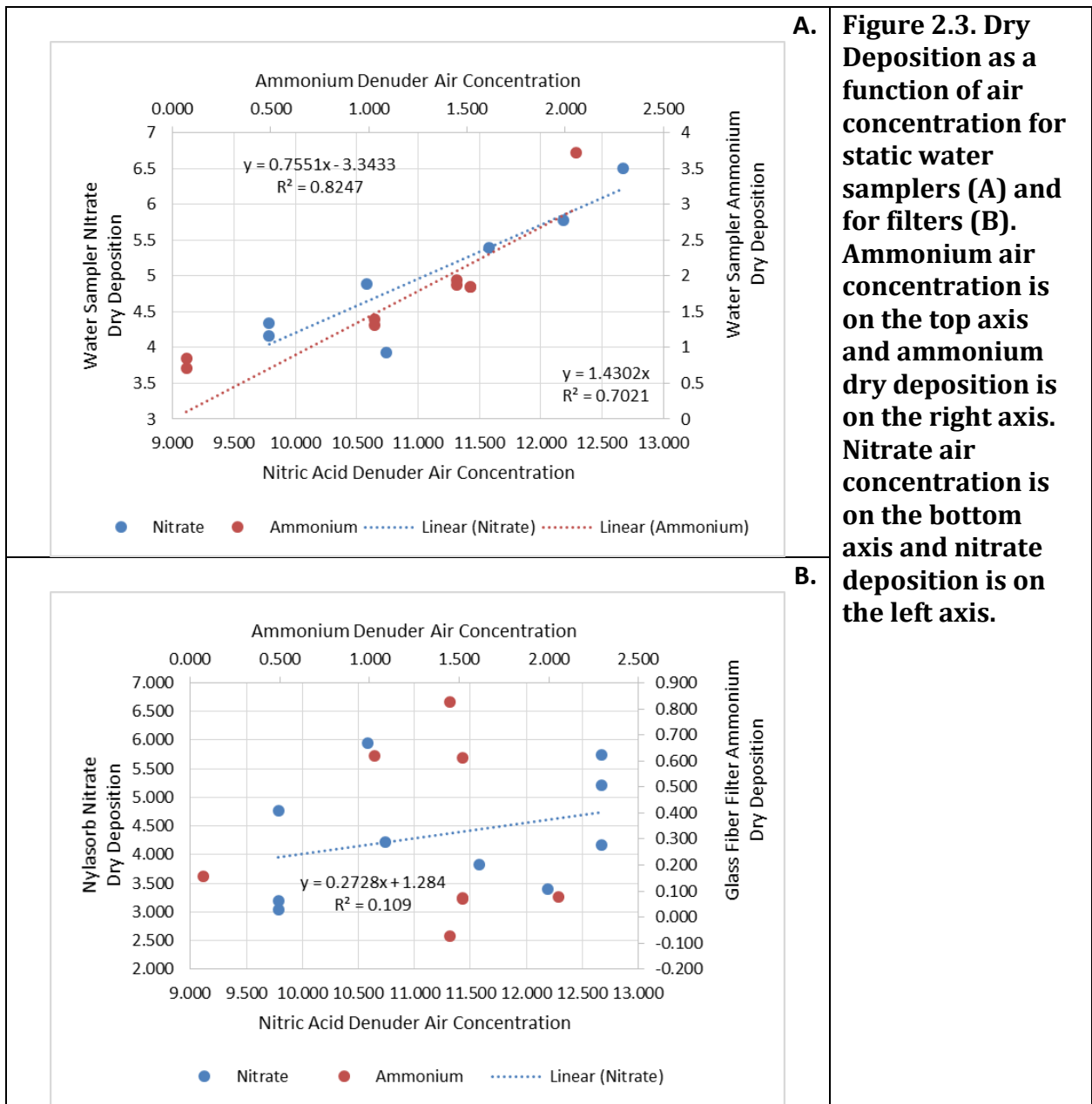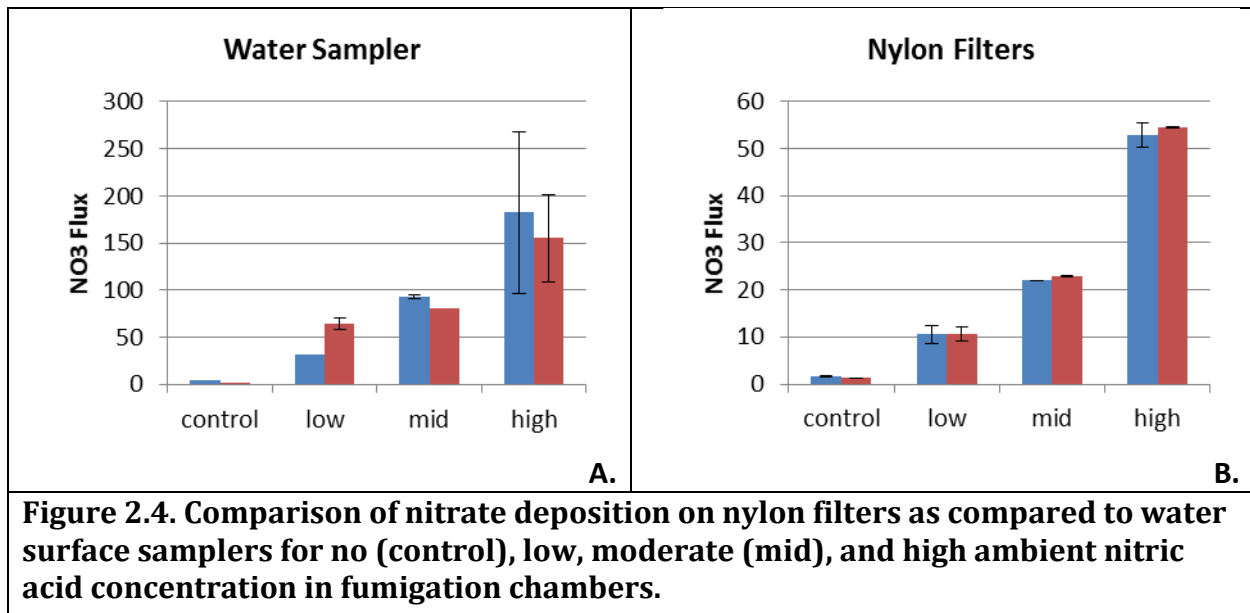
Figure 2.4. Comparison of nitrate deposition on nylon filters as compared to water surface samplers for no (control), low, moderate (mid), and high ambient nitric acid concentration in fumigation chambers.

2.4. Discussion

Under controlled circumstances, measurement of the deposition of nitric acid and ammonium by static water surface sampler appears to be successful. Both nitric acid and ammonium showed a linear relationship with atmospheric concentration with a slope of 0.75 (Figure 2.3.A, Figure 2.4.A.). However use of the water surface samplers is hampered by practical considerations such as evaporation and freezing of the water in the dish. Evaporation was particularly a problem, with most of the sample dishes completely evaporated by the 96 hour time point. These considerations greatly limit when and where the samplers can be deployed (for example, water samplers cannot be deployed during the winter when overnight temperatures will drop below freezing, nor can they be deployed during the driest summer months when low humidity and high temperatures would be expected to evaporate the water before 24 hours of exposure).

Nitric acid deposition onto Nylasorb filters showed some promise and these filters are not hampered by the same practical considerations as the water sampler. Deposition was shown to increase as the ambient concentration was increased (Figure 2.4.B.); however the time series did not show as strong of a linear relationship with ambient concentration as the water samplers (Figure 2.3.B) and the flux of nitric acid onto the filters was significantly less than that calculated from the water samplers.

Ammonium deposition onto the acid trap filters, citric acid in this case, was problematic showing no significant relationship with ambient concentration. This suggests that the acid traps either degrade with exposure releasing ammonia back into the atmosphere or are not strong enough ligands to hold onto the ammonium ion under high temperatures and low humidity.

3. Rates of Atmospheric Nitrogen Flux to Undisturbed Catchments in Southern California

3.1. Introduction

In Southern California, the Mediterranean climate combined with the physiography of the region creates a unique opportunity to study dry deposition. The region is well known for its air pollution, and the fact that air pollution has been shown to have a seasonal component. On shore breezes during the summer dry months keep air pollution loads high and the dominate deposition process is dry. During the winter months air masses tend to move off shore thus improving air quality and making wet deposition of pollutants relatively low. In Riverside about 60 miles from the coast, 85% to 90% of the total deposition occurs as dry deposition.

Several studies have shown that dry deposition of nitrogen containing compounds may be significantly contributing to the declining health of coastal ecosystems by promoting eutrophic conditions that inhibit beneficial use. Eutrophication in streams is manifested symptoms such as accumulation of high biomass of stream benthic algae, a shift in the algal community structure towards lower diversity and stress tolerant taxa, and wide variation in diel ranges of oxygen and pH. These changes cause trophic level shifts in benthic macroinvertebrates and higher level consumers that prey upon them. Recent data from the Storm Water Monitoring Coalition (SMC) Regional Stream Monitoring Program indicate that approximately 30% of stream miles in southern California exhibit heavy algal cover, indicating a pervasive problem with eutrophication. This problem persisted at a similarly high rate at sites with predominantly undisturbed catchments, suggesting that an unknown "background" source of nutrients may be present at these locations. Atmospheric deposition (wet and dry) is potentially one source of "background" nutrients to streams. The purpose of this study component was to measure the deposition of nitrogen and phosphorus pollutants to undisturbed catchments in Southern California to assess this potential "background" source of nutrients to "reference" streams. The hypothesis is that atmospheric deposition is contributing substantial loads of nitrogen to these stream reaches and thus increasing eutrophication.

3.2. Methods

Study Design. Atmospheric deposition measurements (wet and dry), were made at five locations upstream of the coastal estuaries. The sites were chosen from a pool of "reference" sites know to have no local disturbance or sources of contaminating runoff, yet seem to have high levels of in stream nutrient loads and were selected to cover a broad geographic area to capture spatial variability in deposition rates (Chapter 1). Measurements were made at six time points from the early spring through fall of two years to capture the temporal variability in the measurement (Figure 3.1.).

Dry Deposition. A combination of methods were used to measure rates of dry atmospheric deposition. Two static water samplers were deployed at each of the five reference sites as the primary method used to measure dry deposition of nitrate, ammonia, and phosphate. This limited deployments to spring through fall when overnight temperatures were above freezing (May through September). Some measurements during the summer were also excluded from the study due to excessive evaporation from the sampling dishes.

In an effort to mitigate evaporation problems, two modifications were evaluated under local conditions at the Riverside Forest Service facility. 1. Increasing ionic strength by using 1M KCl and 2. Loading the petri dishes with 10g mixed bed ion exchange resins; the same material used in the wet deposition collectors. The salt solutions interfered with the analytical methods and appeared to interfere with deposition sorption, thus were rejected. The ion exchange resins worked well under controlled conditions. 100% of the detectable nitrate and ammonia was absorbed by the resins and 95% of the analytes were recovered after a two-step extraction procedure, similar to that used with the wet deposition resins. Field trials on site in Riverside were also encouraging, but the mechanics of transferring the resins both into and out of the petri dishes quantitatively was challenging due to the electro-static characteristics of the resins. One round of field application at the study sites was attempted in May 2013. Serious problems in quantitation transfer were encountered at all locations by all personnel. The resins were collected, extracted and analyzed. But, the approach was abandoned for later deployments.

Five Nylasorb and five acid trap filters were co-deployed with water samplers for comparison of nitrate and ammonium deposition, respectively. Methods are described in detail in Chapter 2. Water samplers were deployed for 2 days and Nylasorb and acid trap filters were deployed for four days. All measurements included a field and laboratory blank.

Wet Deposition. Annual wet deposition of nutrients will be measured using a resin technique (Simkin et al. 2004). Five passive resin samplers for wet deposition will be deployed at each field site. Samplers will be exchanged at ~6 months to capture an annual wet deposition load. The resin samplers are extracted with 2M KCl (See Fenn et al.). Each set of samplers included a travel blank and a laboratory blank.

Nutrient Concentrations. Nutrient concentrations from water samplers, and filter and resin extracts were analyzed at the Riverside Forest Service Chemistry Laboratory as described in Chapter 2.

Total Annual Deposition Load. By deploying both dry and wet deposition collectors, at each reference stream location, a total annual deposition load will be calculated.

Figure 3.1. Deployment of knife edge surface samplers at Cattle Creek.

3.3. Results

Overall Results.

Across sites, ammonium and nitrate dry deposition were roughly equivalent in magnitude (Table 3.1). Average daily dry ammonium deposition was 1.68 mg-N per day with a maximum of 6.96 mg-N per day and a minimum of 0.14 mg-N per day. Average daily dry nitrate deposition was 1.10 mg-N per day with a maximum of 4.98 mg-N per day and a minimum of 0.01 mg-N per day. Wet deposition was roughly half of dry deposition, making up roughly a third of the overall nitrogen deposition. For the rainy-season (October- May), average daily wet ammonium deposition was 0.66 mg-N per day with a maximum of 2.53 mg-N per day and a minimum of 0.01 mg-N per day. Average daily wet nitrate deposition was 0.56 mg-N per day with a maximum of 1.70 mg-N per day and a minimum of 0.07 mg-N per day.

Across sites, wet phosphate deposition was five times greater than dry deposition (Table 3.1). Average wet phosphate deposition was 0.52 mg-P per day with a maximum of 2.79 mg-P per day and a minimum of 0 mg-P per day. Average dry phosphate deposition was 0.10 mg-P per day with a maximum of 0.84 mg-P per day and a minimum of 0 mg-P per day.

Dry Deposition.

There appears to be a slight seasonal trend in dry deposition with the highest values occurring in the spring and lower values occurring in the fall (Figure 3.2). This appears to hold across sites and for all nutrient species, and appears to be present in both the water surface sampler data as well as the Nylasorb filter data (Figure 3.3.A.). There does not appear to be any spatial trend in dry atmospheric deposition. While there was a lot of variability across sites on any given

sampling day, there were no sites that were consistently higher/lower than any other site for any of the measured nutrient species (Figure 3.2.). Comparison of dry nitrate deposition as measured by water surface sampler to that measured by Nylasorb filter indicates that filters register a higher rate of nitrate deposition as compared to the water surface samplers and that this difference increases with deposition rate (Figure 3.3.A.).

Figure 3.2. Dry deposition as measured using the knife edge water samplers at each of the five reference sites: a) ammonia dry deposition as milligrams of nitrogen per square meter per day, b) nitrate dry deposition as milligrams of nitrogen per square meter per day, c) phosphate dry deposition as milligrams of phosphorus per square meter per day. Error bars represent the standard error between replicate samplers.
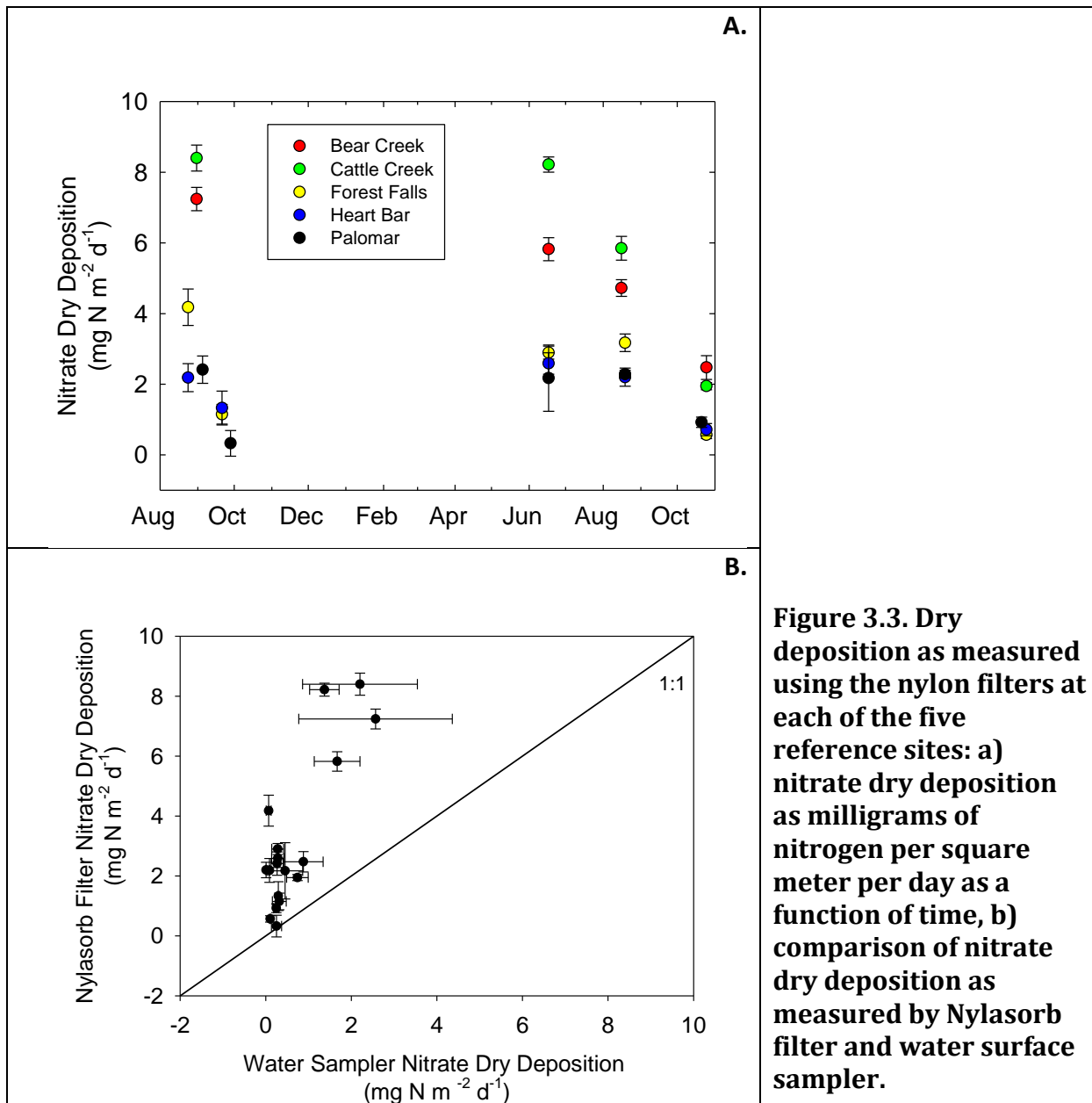
Figure 3.3. Dry deposition as measured using the nylon filters at each of the five reference sites: a) nitrate dry deposition as milligrams of nitrogen per square meter per day as a function of time, b) comparison of nitrate dry deposition as measured by Nylasorb filter and water surface sampler.

Wet Deposition.

There was a large degree of spatial and interannual variability in wet deposition across sites. Palomar Mountain had the largest ammonium deposition of all the sites, consistently for the two years of this study, where it comprised the greatest fraction of the nitrogen wet deposition pool. The two San Gabriel sites had very similar ammonium wet deposition for both years and was slightly higher than the two San Bernardino sites. Nitrate wet deposition was significantly greater in 2012-13 than it was in 2011-12 for all sites with the exception of Heart Bar. The highest nitrate deposition occurred in the San Gabriel sites, Bear and Cattle Creek, where it

comprised the greatest fraction of the nitrogen wet deposition pool. The lowest nitrate wet deposition was at the San Bernardino sites (Forest Falls in 2011-12, and Heart Bar in 2012-13). Wet deposition of phosphate was not consistently higher in either 2011-12 or 2012-13, but variable between sites. The highest phosphate wet deposition was observed at Palomar Mountain in both years, but also fairly high at Bear Creek in 2012-13.

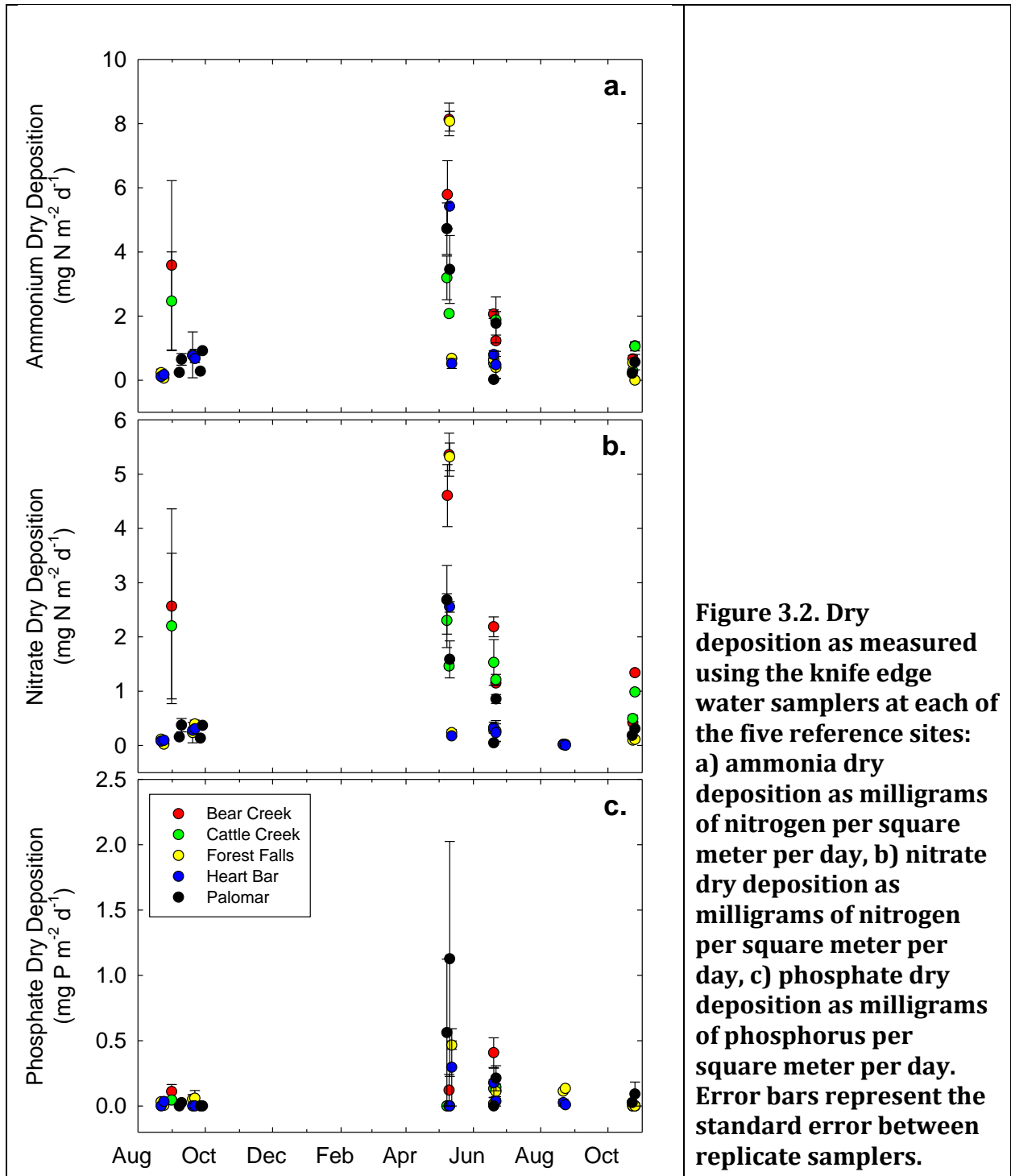**Figure 3.4. Wet deposition as measured using resin samplers at each of the five reference sites: a) ammonia dry deposition as milligrams of nitrogen per square meter per day, b) nitrate dry deposition as milligrams of nitrogen per square meter per day, c) phosphate dry deposition as milligrams of phosphorus per square meter per day. Error bars represent the standard error between replicate samplers.**
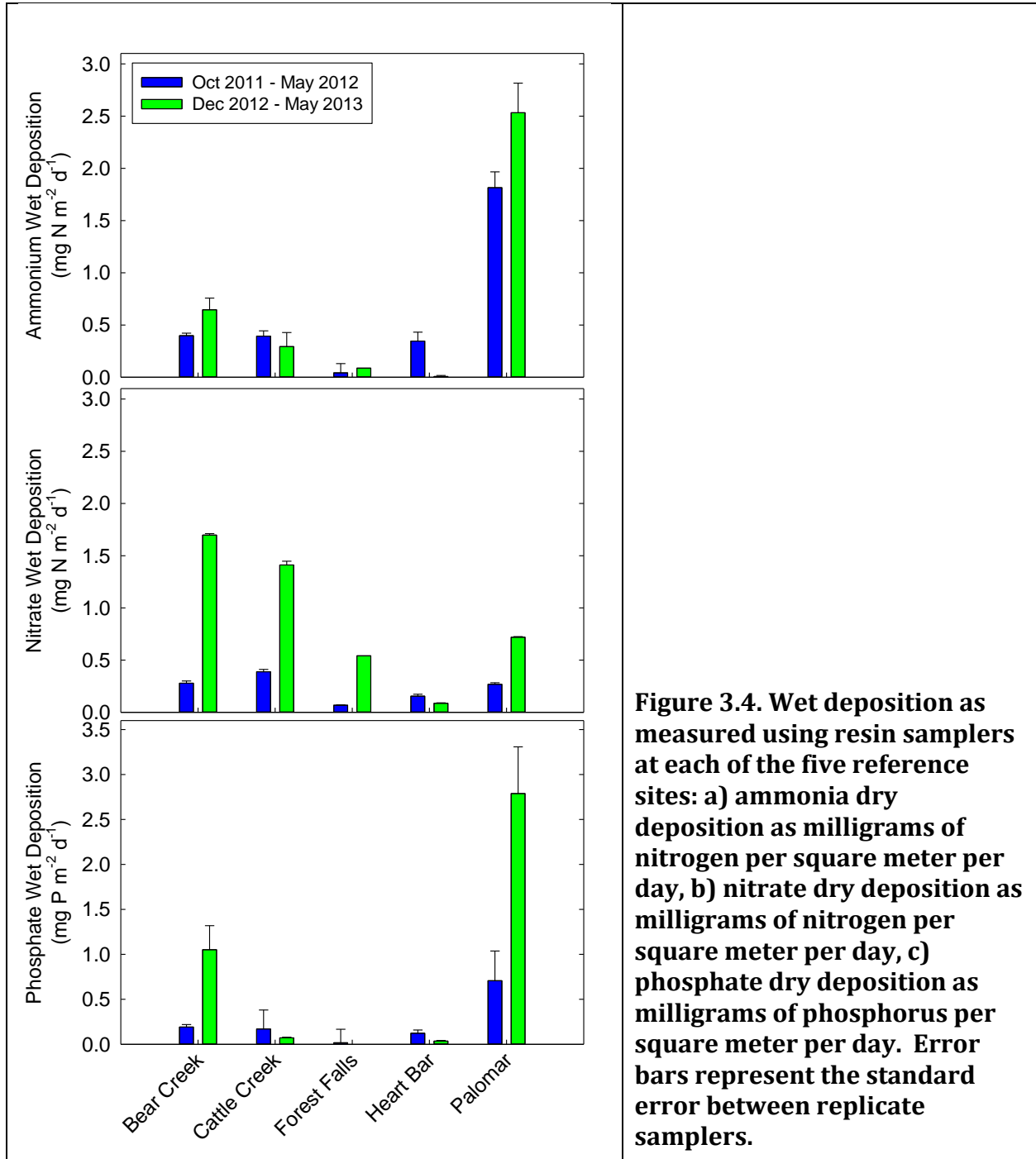
Table 3.1. Wet and Dry Deposition Data. Data are reported as an average for each sampling event and standard error.

| site | date | Dry Deposition (mg N/P m^{-2} d^{-1}) | | | | Wet Deposition (mg N/P m^{-2} d^{-1}) | | | |
| | | Static Water Samplers | | | Nylon Filters | | Resin Samplers | | |
		Ammonium	Nitrate	Phosphate	Nitrate	Deployment Period	Ammonium	Nitrate	Phosphate
	October-11					October 2011 - May 2012	0.40 ± 0.02	0.28 ± 0.02	0.19 ± 0.03
	August-12	3.58 ± 2.64	2.57 ± 1.80	0.11 ± 0.05	7.24 ± 0.33				
	December-12					December 12- May 13	0.65 ± 0.11	1.70 ± 0.01	1.05 ± 0.27
	May-13	6.96 ± 1.44	4.98 ± 0.62	0.06 ± 0.11					
	June-13	1.64 ± 0.43	1.67 ± 0.53	0.26 ± 0.17	5.82 ± 0.33				
	August-13				4.72 ± 0.24				
Bear Creek	October-13	0.87 ± 0.22	0.88 ± 0.46	0.00 ± 0.00	2.47 ± 0.34				
	October-11					October 2011 - May 2012	0.39 ± 0.05	0.39 ± 0.02	0.17 ± 0.21
	August-12	2.46 ± 1.54	2.2 ± 0 1.34	0.05 ± 0.02	8.40 ± 0.37				
	December-12					December 12- May 13	0.29 ± 0.13	1.41 ± 0.04	0.07 ± 0.01
	May-13	2.63 ± 0.74	1.88 ± 0.55	0.00 ± 0.00					
	June-13	1.20 ± 0.85	1.37 ± 0.34	0.14 ± 0.08	8.22 ± 0.21				
	August-13				5.85 ± 0.34				
Cattle Creek	October-13	0.68 ± 0.39	0.74 ± 0.25	0.00 ± 0.00	1.95 ± 0.10				
	October-11					October 2011 - May 2012	0.04 ± 0.09	0.07 ± 0.00	0.02 ± 0.15
	August-12	0.15 ± 0.12	0.07 ± 0.06	0.02 ± 0.02	4.18 ± 0.52				
	September-12	0.77 ± 0.53	0.32 ± 0.16	0.06 ± 0.05	1.15 ± 0.28				
	December-12					December 12- May 13	0.09	0.54	0.00 ±
	May-13	4.38 ± 3.70	2.78 ± 2.55	0.23 ± 0.23					
	June-13	0.52 ± 0.28	0.28 ± 0.14	0.06 ± 0.06	2.90 ± 0.19				
	August-13				3.18 ± 0.25				
Forest Falls	October-13	0.27 ± 0.28	0.10 ± 0.01	0.00 ± 0.00	0.57 ± 0.11				
	October-11					October 2011 - May 2012	0.35 ± 0.09	0.15 ± 0.02	0.12 ± 0.04
	August-12	0.14 ± 0.03	0.09 ± 0.01	0.02 ± 0.02	2.19 ± 0.40				
Heart Bar	September-12	0.72 ± 0.06	0.29 ± 0.02	0.00 ± 0.00	1.33 ± 0.48				

site	date	Dry Deposition (mg N/P m^{-2} d^{-1})				Wet Deposition (mg N/P m^{-2} d^{-1})			
		Static Water Samplers			Nylon Filters		Resin Samplers		
		Ammonium	Nitrate	Phosphate	Nitrate	Deployment Period	Ammonium	Nitrate	Phosphate
	December-12					December 12- May 13	0.01 ± 0.01	0.09 ± 0.00	0.04 ± 0.01
	May-13	2.97 ± 2.45	1.36 ± 1.19	0.15 ± 0.26					
	June-13	0.64 ± 0.35	0.28 ± 0.14	0.11 ± 0.11	2.59 ± 0.31				
	August-13		0.01 ± 0.01	0.02 ± 0.02	2.20 ± 0.26				
	October-13				0.72 ± 0.17				
	October-11					October 2011 - May 2012	1.82 ± 0.15	0.27 ± 0.01	0.71 ± 0.33
	September-12	0.45 ± 0.24	0.27 ± 0.14	0.01 ± 0.01	2.41 ± 0.39				
	October-12	0.60 ± 0.32	0.25 ± 0.12	0.00 ± 0.00	0.33 ± 0.36				
	December-12					December 12- May 13	2.53 ± 0.28	0.72 ± 0.01	2.79 ± 0.52
	May-13	4.09 ± 1.13	2.13 ± 0.75	0.84 ± 0.80					
	June-13	0.90 ± 0.91	0.45 ± 0.41	0.11 ± 0.13	2.17 ± 0.94				
	August-13				2.28 ± 0.11				
Palomar	October-13	0.39 ± 0.24	0.25 ± 0.06	0.06 ± 0.07	0.92 ± 0.15				

Overall Dry Deposition Mean	1.68	1.10	0.10	3.21	Overall Wet Deposition Mean	0.66	0.56	0.52
Overall Dry Deposition Maximum	6.96	4.98	0.84	8.40	Overall Wet Deposition Maximum	2.53	1.70	2.79
Overall Dry Deposition Minimum	0.14	0.01	0.00	0.33	Overall Wet Deposition Minimum	0.01	0.07	0.00

3.4. Discussion

Total Annual Deposition.

Wet and dry deposition data were integrated to generate a total annual deposition for ammonium, nitrate and phosphate (Figure 3.5 and Table 3.2). In Southern California there has been an assumption that nitrogen deposition should be dominated by oxidized forms of nitrogen due to domination by automobile exhaust. However, this is not necessarily the case. Water surface sampler deposition data show that in general, ammonium dry deposition is nearly twice as high as nitrate dry deposition. Furthermore, the resin data from Palomar Mountain indicates that ammonium wet deposition is the dominant form of nitrogen during the rainy season and is roughly equivalent to nitrate deposition in the San Bernardino sites. This may be due to the proximity of agricultural activity for these sites, particularly Palomar Mountain. Orange groves, plant nursery operations, and some cattle and dairy activity are significant sources of ambient ammonium.

Across all sites, dry nitrogen and phosphorus deposition was a significant fraction of the total annual atmospheric deposition (Table 3.3), demonstrating the importance of characterizing this fraction when assessing loads of nutrients from the atmosphere.
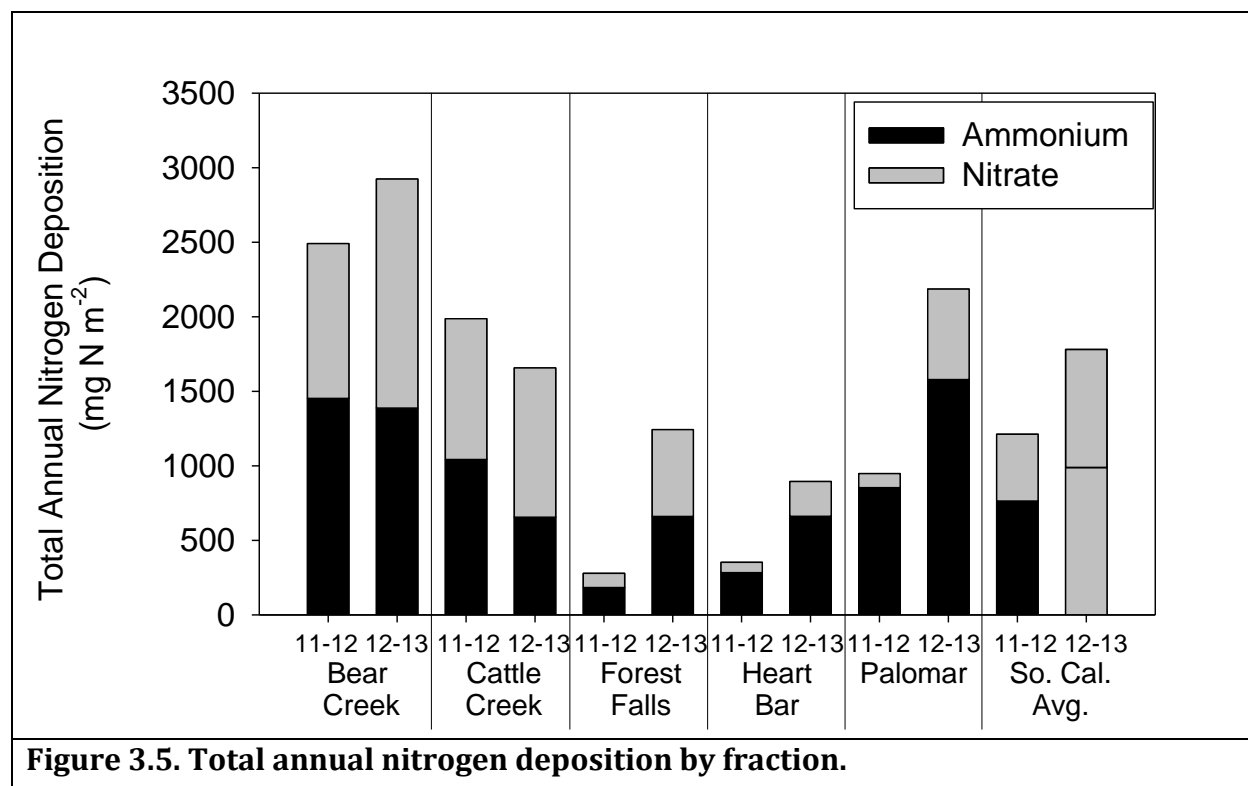

Figure 3.5. Total annual nitrogen deposition by fraction.

Table 3.2. Total annual nitrogen and phosphorus deposition by water year as calculated from wet deposition from resin samplers and dry deposition from water samplers

Site	Water Year	Total Annual Deposition (mg m^{-2})			
		Ammonium	Nitrate	Total N	Phosphate
Bear Creek	Oct 11 - Sep 12	1453	1038	2491	111
	Oct 12 - Sep 13	1388	1536	2924	423
Cattle Creek	Oct 11 - Sep 12	1043	945	1988	79
	Oct 12 - Sep 13	656	1001	1657	43
Forest Falls	Oct 11 - Sep 12	184	95	278	20
	Oct 12 - Sep 13	661	582	1242	37
Heart Bar	Oct 11 - Sep 12	284	69	353	48
	Oct 12 - Sep 13	662	232	895	46
Palomar	Oct 11 - Sep 12	854	94	948	260
	Oct 12 - Sep 13	1579	607	2186	1141
Southern California Average	Oct 11 - Sep 12	764	448	1212	103
	Oct 12 - Sep 13	989	792	1781	338

Table 3.3. Percentage of total annual deposition attributable to dry deposition

Site	Water Year	Total Annual Deposition (mg m^{-2})	
		% N as dry deposition	% P as dry deposition
Bear Creek	Oct 11 - Sep 12	90	37
	Oct 12 - Sep 13	71	9
Cattle Creek	Oct 11 - Sep 12	86	21
	Oct 12 - Sep 13	62	39
Forest Falls	Oct 11 - Sep 12	86	68
	Oct 12 - Sep 13	82	98
Heart Bar	Oct 11 - Sep 12	64	7
	Oct 12 - Sep 13	96	72
Palomar	Oct 11 - Sep 12	30	1
	Oct 12 - Sep 13	46	11
Southern California Average	Oct 11 - Sep 12	71	27
	Oct 12 - Sep 13	71	46

Critical Loads.

Geiser et al. (2010) proposed a critical load for nitrogen deposition that results in changes in lichen species composition at 5 kg-N ha^{-1} y^{-1}. Using that criteria, all of the study sites are significantly above that level (1mg m^{-2} = 0.01 kg ha^{-1}). The Southern California average of

12.12 and 17.81 kg-N ha^{-1} y^{-1} is nearly 2.5 to over 3 times higher than the proposed critical load. Total nitrogen deposition at the two sites in the San Bernardo Mountains, Heart Bar and Forest Falls, varied widely between the 2 water years sampled, but the average of the 2 years suggests that those site are experiencing critical loads likely to shift lichen community structure from oligotrophic (species with low nitrogen tolerance) to nitrophytic species.

4. Utility of Stable Isotope Tracers to Identify Atmospheric Nitrogen-Containing Pollutants in Southern California Reference Streams

4.1. Introduction

The stable isotope signatures of nitrogen (δ^{15}N) and oxygen (δ^{18}O) in nitrate have been used successfully in the past to attribute dissolved nitrate in river water to specific sources. For instance, a comparison of 16 watersheds in the U.S. indicated that the isotopic composition of nitrate differs in forested catchments versus agricultural land (Mayer et al., 2002). The reasons for such differences in N- and O- isotope ratios in nitrate are both the primary source of N and O, and kinetic fractionation in the biogeochemical processes which tend to partition light isotopes (^{14}N and ^{16}O) from heavier ones (^{15}N and ^{18}O) (Kendall, 1998). When soil organic matter is degraded and nitrified, the resulting nitrate δ^{15}N decreases, while the δ^{18}O value depends on the source of water (Mayer et al., 2002). Denitrification generally leads to isotope values increasing at a 2:1 ratio for δ^{15}N and δ^{18}O values (Böttcher et al., 1990). If substrate limitation leads to total conversion of nitrate to dinitrogen gas there is no apparent fractionation (Brandes and Devol, 1997). The highest δ^{18}O values are found in nitrate from atmospheric deposition (Kendall, 1998), while the highest δ^{15}N values have been measured in manure and septic tanks, where ^{14}N is preferentially lost via ammonia volatilization (Heaton, 1986). The ranges of isotope values for different sources tend to overlap, but even then measurements of both stable isotope pairs can often give a unique characterization of nitrate from different sources Kendall, 1998, Figure 4.1.).

Atmospheric dry deposition is a potentially significant source of "background" nutrients to streams in semi-arid regions and atmospheric nitrate has been shown to have a very unique isotopic signature characterized by high δ^{18}O values (Kendall 1998, Figure 4.1). The purpose of this study component was two-fold. The first part was to measure the dual isotopic composition of nitrate (δ^{15}N and δ^{18}O) accumulated in the water surface samplers to determine the end-member value for this potentially important source. The second part was to measure the dual isotopic composition of nitrate (δ^{15}N and δ^{18}O) in streams located in proximity to the atmospheric samplers to determine if this source signature could be traced into streams. The hypothesis is that atmospheric deposition could potentially be traced directly into streams if it had not been significantly cycled biogeochemically in the system.
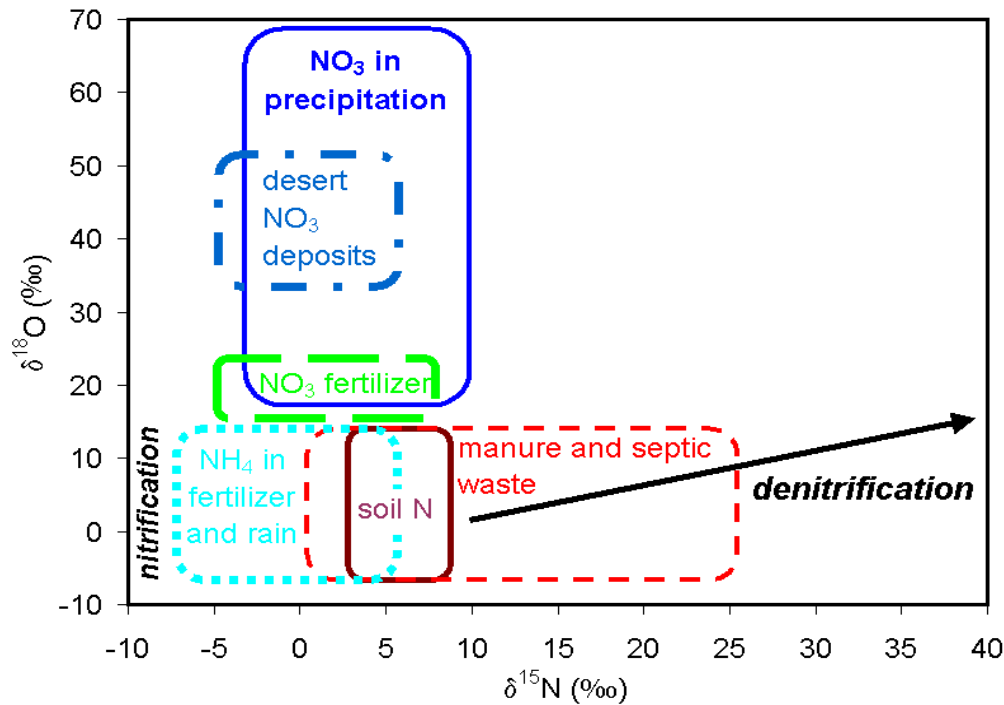
Figure 4.1. Comparison of the isotopic composition of various nitrate sources and processes.

4.2. Methods

Study Design. An additional water sample was collected from each of the passive water surface samplers (described in Chapter 3) to determine the isotopic composition, $\delta^{18}O$ and $\delta^{15}N$ of direct nitrate atmospheric deposition. These samples were compared to the $\delta^{18}O$ and $\delta^{15}N$ of nitrate dissolved in the nearby reference stream (when the stream was flowing). Stream samples were filtered through 0.2 mm filter, and all water samples were frozen until analysis.

Nutrient Concentrations. Nutrient concentrations from water samplers, and filter and resin extracts were analyzed at the Riverside Forest Service Chemistry Laboratory as described in Chapter 2.

Stable Isotope Analysis. Stable isotopic analysis of the $\delta^{18}O$ and $\delta^{15}N$ of dissolved nitrate were conducted at University of California, Davis, Stable Isotope Facility (2011-2012 samples) and by Facility for Isotope Ratio Mass Spectrometry (FIRMS) at University of California, Riverside (2012-2013 samples) by denitrifier assay (Sigman et al. 2001, Casciotti et al. 2002). Isotope ratios were measured on the SerCon Cryoprep trace gas concentration system interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) for analysis of $^{18}O/^{16}O$ and $^{15}N/^{14}N$ of dissolved nitrate (NO_3). Instruments were inspected for physical damage weekly by lab personnel. Calibration, instrument drift, and reproducibility were evaluated with

each run by lab personnel.

The stable isotopic compositions of low-mass (light) elements such as oxygen, hydrogen, carbon, nitrogen, and sulfur are normally reported as "delta" (δ) values in parts per thousand (denoted as ‰) enrichments or depletions relative to a standard of known composition. δ values are calculated by:

$$(\delta \text{ in } ‰) = (R_{sample}/R_{standard} - 1)*1000 \qquad \textit{Eq. 4.1.}$$

where "R" is the ratio of the heavy to light isotope (e.g., $^{18}O/^{16}O$) in the sample or standard respectively. The standard for oxygen is Vienna Standard Mean Ocean Water (VSMOW) and the standard for nitrogen is air.

4.3. Results

Atmospheric nitrate deposition had a mean $\delta^{18}O$ of 67.44‰, with a maximum value of 74.79‰ and a minimum of 54.78‰ and a mean $\delta^{15}N$ of -1.82‰, with a maximum value of 5.66‰ and a minimum of -6.74‰. Sites differed in the amount of variability in the isotopic composition, the San Gabriel Mountain sites, Bear and Cattle Creek, had relatively low variability in both the $\delta^{18}O$ and $\delta^{15}N$ compared to the other sites. Palomar Mountain typically had lower $\delta^{18}O$ and $\delta^{15}N$ relative to the rest of the sites. Forest Falls in the San Bernardino Mountains had the widest range in both $\delta^{18}O$ and $\delta^{15}N$ (Figure 4.2).
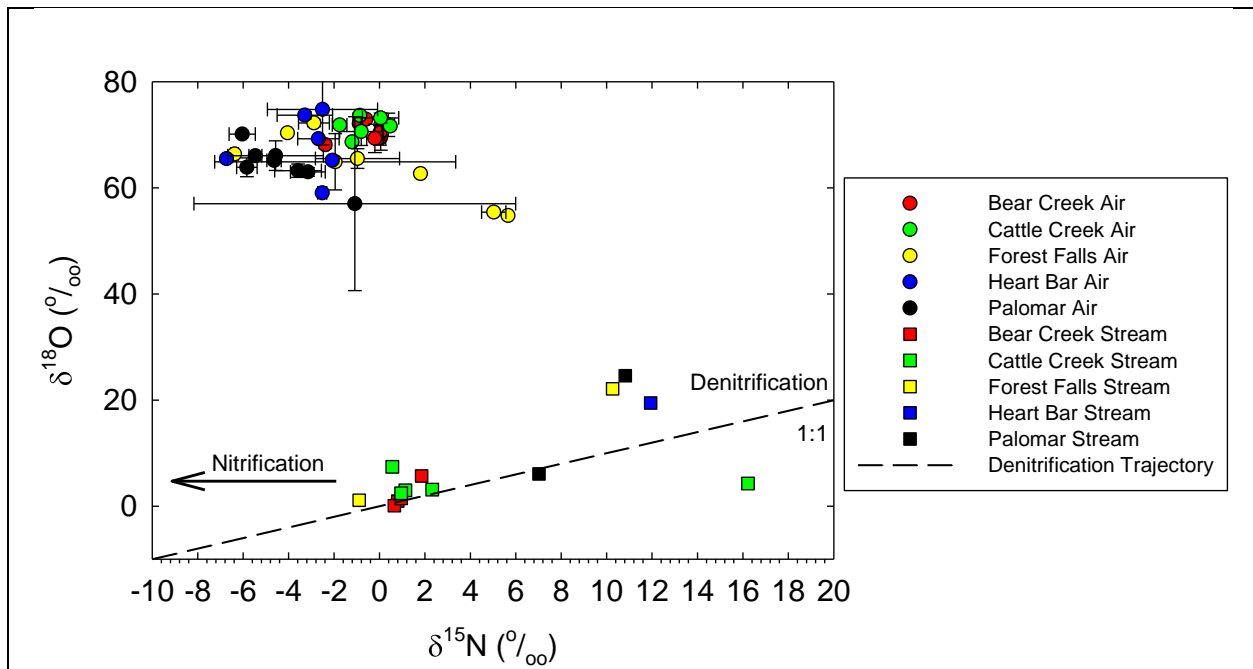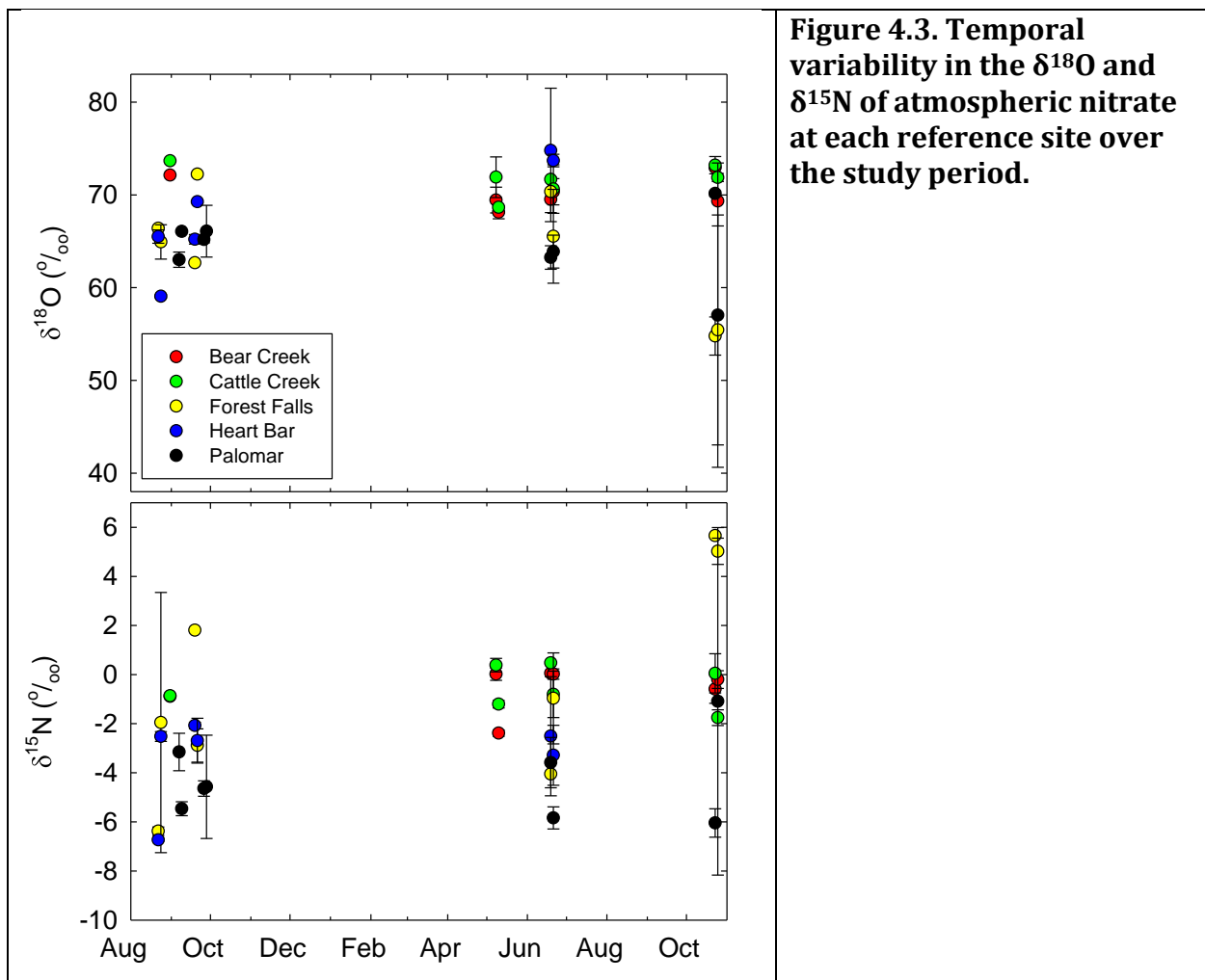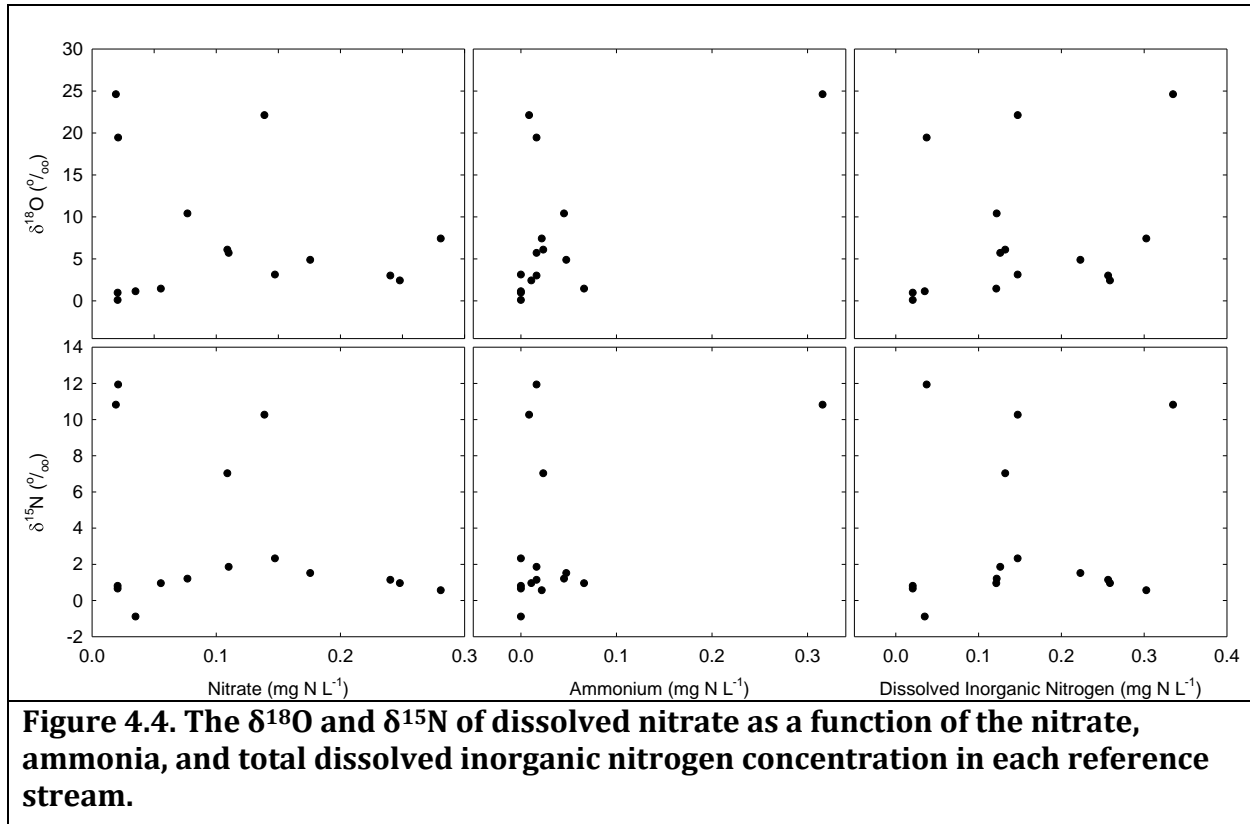

Figure 4.2. The $\delta^{18}O$ and $\delta^{15}N$ of atmospheric nitrate at each reference site compared to co-located reference streams.

Most sites did not demonstrate any significant seasonal variability (Figure 4.3). The San Gabriel Mountain sites, Bear and Cattle Creek, and the Palomar Mountain site did not display any significant seasonal or interannual or seasonal variability. The San Bernardino site did show some temporal variability. Forest Falls did not show significant temporal differences until the final sample event in late September which had significantly lower $\delta^{18}O$ and higher $\delta^{15}N$ values compared to other events. Heart Bar showed a slight increase in $\delta^{18}O$ in the summer of 2013 compared to 2012 but no significant change in $\delta^{15}N$.

Figure 4.3. Temporal variability in the $\delta^{18}O$ and $\delta^{15}N$ of atmospheric nitrate at each reference site over the study period.

The dual isotopic composition of nitrate dissolved in headwater streams had a mean $\delta^{18}O$ of 7.28‰, with a maximum value of 24.61‰ and a minimum of 0.09‰ and a mean $\delta^{15}N$ of 4.62‰, with a maximum value of 16.22‰ and a minimum of -0.89‰. Bear Creek, had relatively low variability in both the $\delta^{18}O$ and $\delta^{15}N$ compared to the other sites. Stream nitrate had significantly

lower $\delta^{18}O$ compared to atmospheric nitrate and while there was some overlap in $\delta^{15}N$ values, they were typically higher than atmospheric nitrate (Figure 4.2). There was no significant relationship between stream nitrate, ammonia, or total dissolved inorganic nitrogen and the dual isotopic composition of nitrate in the streams (Figure 4.4).

Figure 4.4. The $\delta^{18}O$ and $\delta^{15}N$ of dissolved nitrate as a function of the nitrate, ammonia, and total dissolved inorganic nitrogen concentration in each reference stream.

4.4. Discussion

The dual isotopic signatures of $\delta^{18}O$ and $\delta^{15}N$ in atmospheric nitrate deposition in Southern California is consistent with literature values for atmospheric nitrate (Kendall 1998, Figure 4.1). While there was some variability in the signature across sites and within sites, there is not a major temporal component overall, which is contrary to findings in other states (Elliott et al. 2009). There may be a slight north-south gradient in the isotopic composition such that sites in the south (Palomar) have lower $\delta^{18}O$ and $\delta^{15}N$ values and sites to the north have higher $\delta^{18}O$ and $\delta^{15}N$ (Figure 4.2). However, distinctiveness of the high $\delta^{18}O$ value for atmospheric nitrate across all sites suggests that the dual isotopic composition of nitrate could be an excellent tracer for direct deposition of atmospheric nitrate into water bodies.

Stream nitrate did not reflect the isotopic composition of atmospheric nitrate, suggesting that

direct deposition of nitrate to streams is minimal. This is not surprising given the relatively small surface area of headwater streams. However, this is not to say that atmospheric deposition is not a significant source of nitrate to streams (Vitousek et al. 1997). Rather, atmospheric deposition of nutrients is more likely indirectly accumulated in streams, by first depositing on the landscape and entering the streams through surface runoff or groundwater. Movement of nutrients through the landscape biogeochemically will alter the isotopic composition of nitrate, in fact most of the stream nitrate sites have an isotopic composition reflective of soil nitrogen; however, values with higher $\delta^{18}O$ and $\delta^{15}N$ may reflect denitrification and values with lighter $\delta^{18}O$ and $\delta^{15}N$ may reflect nitrification (compare Figures 4.1 and 4.2) (Burns et al., 2009). Sites were selected so as to have no upstream anthropogenic sources so stream contamination by wastewater or fertilizer is unlikely. The lack of relationship with nitrogen concentration suggests that much of the isotopic composition is set prior to entering the streams (Figure 4.3), potentially in subsurface flows through the riparian buffer zone (Mayer et al. 2007).

Interestingly, the isotopic signature of atmospheric nitrate may be apparent in near-shore coastal surface waters collected off of Orange County's coast. Figure 4.5 compares the data from this study with surface (collected at 0-5 meters) and deeper (collected at 75-100 meters depth) water samples water samples collected for a different project. Surface ocean waters appear to fall between deep ocean waters and atmospheric nitrate (red triangles, Figure 4.5). This may suggest that direct deposition of nitrate to surface ocean waters may be a significant source of nitrate to near-shore coastal waters.

Figure 4.5. Comparison of Southern California water mass isotopic compositions.
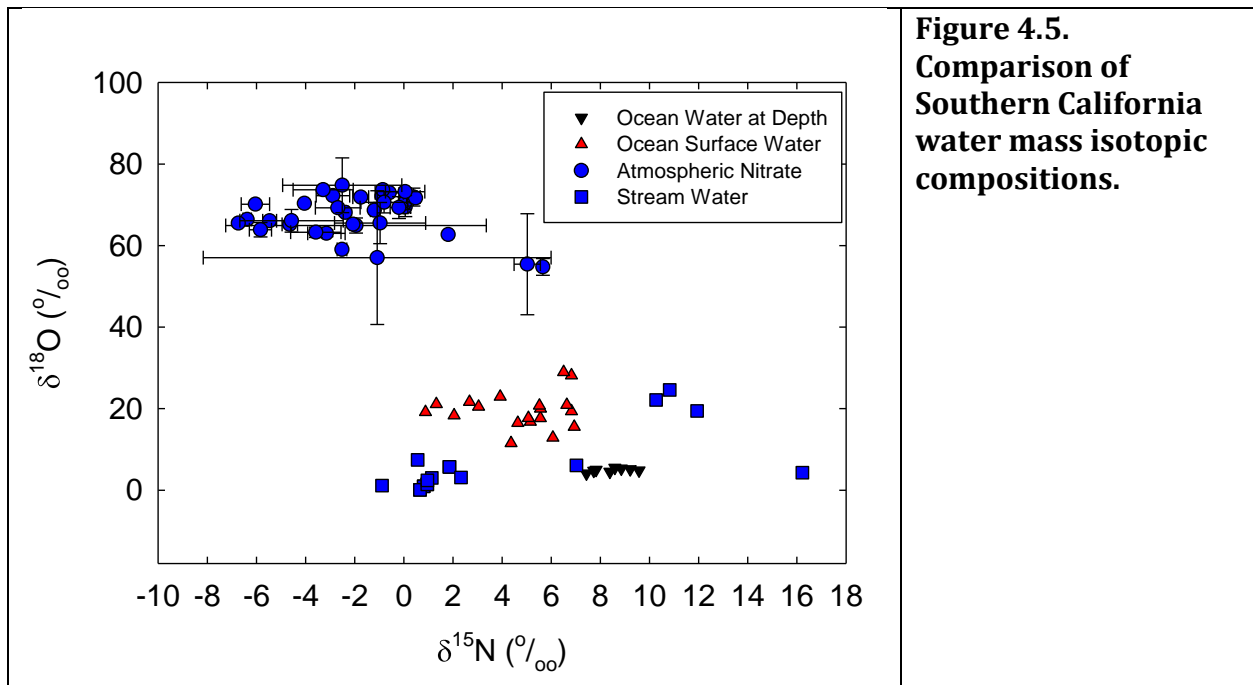
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Appendix 1. Quality Assurance

Table A.1. Data quality objectives for laboratory measurements

Parameter	Accuracy	Precision	Recovery	Target Reporting Limits	Complete ness
Ammonia (as ion)	Standard Reference Materials (SRM, CRM, PT) within 95% CI stated by provider of material	Laboratory duplicate, blind field duplicate, or MS/MSD 10% RPD Laboratory duplicate minimum. Laboratory duplicate, blind field duplicate, or MS/MSD 10% RPD Laboratory duplicate minimum.	Matrix spike 80% to 120% or control limits at ± 3 standard deviations based on actual lab data	0.05 mg/L	90%
Nitrate (as ion)	Standard Reference Materials (SRM, CRM, PT) within 95% CI stated by provider of material	Laboratory duplicate, blind field duplicate, or MS/MSD 10% RPD Laboratory duplicate minimum.	Matrix spike 80% to 120% or control limits at ± 3 standard deviations based on actual lab data	0.05 mg/L	90%
Ortho-Phosphate (as phosphate ion)	Standard Reference Materials (SRM, CRM, PT) within 95% CI stated by provider of material	Laboratory duplicate, blind field duplicate, or MS/MSD 10% RPD Laboratory duplicate minimum.	Matrix spike 80% to 120% or control limits at ± 3 standard deviations based on actual lab data	0.05 mg/L	90%
$\delta^{18}O$ and $\delta^{15}N$ of dissolved nitrate	Standard Reference Materials (SRM, CRM, PT) within 95% CI stated by provider of material	Laboratory duplicate, blind field duplicate, or MS/MSD 10% RPD Laboratory duplicate minimum.	Recovery peak is 80 to 120% of expected value from laboratory concentration data	0.05‰	90%

All Accuracy, Precision, and Recovery metrics were met as planned for the final data products (Table A.1). Analytical runs that did not meet the criteria were discarded and the samples reanalyzed. Generally, loss of accuracy and precision during a run was caused by mechanical problems with the instrument. Ammonia was the most problematic of the elements primarily because of the large variation in sample concentrations which occasionally resulted in bleed-over of off-scale samples into near low concentration samples near detection limits. An upgrade in instrumentation in 2013 improved consistency of the analytical runs and fewer reruns. The reporting limits of 0.05mg/L were maintained through the chemical analysis. The upgraded instrument enabled the reporting limits to be lowered to 0.01 mg/L, but for consistency across all samples, the 0.05 value was maintained. Most of the ortho-phosphate values were very low resulting in a significant portion of non-detects. This was expected given the nature of the study. Phosphate is not a typically air-borne pollutant except during high winds and dusty conditions.

The completeness criteria was near 100% for all filter and resin samples. The analytical completeness for the water (KSS) samplers was near 100% for nitrate and phosphate, but less than 95% for ammonia due to low sample volumes collecting during the last sampling period. As noted in the report, environmental factors (freezing and evaporation) cause problems sample collection.

The completeness for the stable isotope analysis of atmospheric deposition was 64%. The low completeness was due to evaporation from the sampling dishes. Sampling for nutrient deposition was prioritized and required significantly less sample volume (10mL) compared to sampling for nitrate stable isotope analysis (40mL). Sampling for isotope analysis only occurred when sample volumes permitted. Similarly, completeness for stream water nitrate isotopic analysis was 47%, due to low flows in headwater streams. For Bear and Cattle Creek in the San Gabriel Mountains, flows were perennial and thus isotopic analysis is >90%; however for low flow creeks in the San Bernardino and Palomar Mountain sites, drying events prevented sampling for isotopic analysis.

Table A.2. Document and record retention, archival, and disposition information.

	Identify Type Needed	Retention	Archival	Disposition
Sample Collection and Field Records	Hardcopy and electronic	Life of the project*	20 years	Hardcopy discarded after 20 years, database maintained by PSW
Chain of custody for samples	Hardcopy and electronic	Life of project	20 years	Hardcopy discarded after 20 years, database maintained by PSW
Analytical Records	Electronic and hardcopy	Life of the project	Hardcopy for 20 years at Riverside	Hardcopy discarded after 20 years, database maintained by PSW
Data Records	Electronic—raw, quality assured, and analyses	Life of project	20 years	Quality assured database maintained by PSW Raw data maintained for life of project Analyses maintained in publications

All data are retained in hard copy form, Access database, and excel products. Hard copies are retained in the laboratory file cabinets. The Access database is maintained electronically and backed up on the Forest Service's "O" drive. Excel files are maintained on the laboratory computer, the PI's computer and backed up on the "O" drive. Retention and Archival will be followed as detailed in Table A.2.

Quality Control

Matrix: water
Analytical Parameter(s): Conventional Constituents
Analytical Method/SOP Reference: Field Sampling

QC Type	Information Provided	Frequency	Acceptance Limits
BLANKS			
Field Equipment Blank	Contamination in sampling equipment	2 times per sampling season	Non-detect
Field Blank	Transport, storage, and field handling contamination	5%	Non-detect
Bottle Blank	Contamination of sampling containers	5%	Non-detect
CALIBRATION CHECKS			
Field Equipment Calibration	Calibration drift and memory effect of field instruments	Every sampling trip	
Standard Reference Sample	Field Instrument Accuracy	Every sampling trip	+/-10% Conductivity or +/- 0.5pH units
REPLICATES			
Field Duplicate	Precision of all steps after acquisition	5%	+/- 10%

Bottle blank is deionized water in bottle at time of shipment.
Field blank is deionized water in bottle taken to field, left for 2 weeks, brought back for shipment.
Field duplicate requires taking an additional sample at a station.
Field equipment blank is deionized water passed through sampling equipment and collected as a normal sample.
Field equipment blanks are collected at the beginning and the end of the sampling season.
Standard reference sample is either an independent pH 7 buffer or 46.7μS.

All field collection QC procedures were followed as prescribed. There were no instruments deployed. No contamination due to transport or storage was detected for water. Duplicate samples collected from the same KSS were within the 10% limit. Samples collected from the 2 separate KSS deployed were often outside the 10% limit, but that was expected.

Matrix: water
Analytical Parameter(s): Conventional Constituents, nitrate, ammonium, phosphate

| Analytical Method/SOP Reference: |
| Continuous flow analyzer and ion |
| chromatograph |

QC Type	Information Provided	Frequency	Acceptance Limits
BLANKS			
Reagent blank	Contaminated reagent	5%	Non-detect
Analytical Instrument Blank	Contamination of analytical instrument	5%	Non-detect
SPIKES			
Analysis matrix spike	Instrument bias	5%	80-120% Recovery
CALIBRATION CHECK SAMPLES			
Span check	Calibration drift and memory effect	Every batch of samples	+/- 10%
Standard Reference Sample	Instrument Accuracy	5%	+/- 10%
REPLICATES & SPLITS			
Laboratory splits	Inter-laboratory precision	5%	+/- 10%
Analysis replicates	Instrument precision	Beginning and end of every sample batch	+/- 10%

Reagent blanks and instrument blanks were conducted with every run. Analytical runs were either postponed or discarded when data was outside of the acceptable limits. Testing for spike recovery was conducted at the beginning of a series of analytical runs, typically 20% of the runs. Calibration of standards and reference samples were evaluated with every sample batch. Runs that were outside of the 10% range were discarded, although this rarely happened. Replicate samples and SRS were used every 12th sample. The laboratory standard is +/- 5% for acceptable limit. Runs that exceeded the 5% limit were reanalyzed. This occurred roughly 10% of the time with the original instrument and never with the upgraded instrument.

Matrix: water
Analytical Parameter(s): $\delta^{18}O$ and $\delta^{15}N$ of dissolved nitrate
Analytical Method/SOP Reference: Denitrifier method and trace gas ion ratio mass spectrometer

QC Type	Information Provided	Frequency	Acceptance Limits
BLANKS			
Analytical Instrument Blank	Contamination of analytical instrument	5%	Non-detect
CALIBRATION CHECK SAMPLES			
Span check	Calibration drift and memory effect	Every batch of samples	+/- 10%
Standard Reference Samples	Instrument Accuracy	10%	+/- 10%
REPLICATES & SPLITS			
Laboratory splits	Inter-laboratory precision	5%	+/- 10%
Analysis replicates	Instrument precision	Beginning and end of every sample batch	+/- 10%

Instrument blanks and laboratory control standards were conducted with every run. Analytical runs were either postponed or discarded when data was outside of the acceptable limits. Calibration of standards and reference samples were evaluated with every sample batch with check standards run after every 10th sample. Blanks were run at the beginning and end of each sample run. Analysis replicates were run every 10th sample as well and were always within the +/- 10% acceptance limit. Runs that were outside of the 10% range for control standards and replicates were discarded, although this rarely happened. Two laboratories were used for sample analysis; however, both laboratories used the same IAEA and NIST standards for instrument calibration and quality control checks and met all inter-laboratory comparison requirements.