

## Convergence in nitrogen deposition and isotopic composition across urban and agricultural valleys in northern Utah

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### Key Points:

- We assessed bulk N deposition and isotopes in urban and agricultural valleys
- N deposition and isotope composition were similar irrespective of land use
- Bulk deposition  $\delta^{15}\text{N}$  was  $-0.6 \pm 0.7\text{\textperthousand}$ , similar to natural ecosystems
- $\delta^{15}\text{N}$  of bulk deposition  $\text{NH}_4^+$  varied by  $40\text{\textperthousand}$ , overlapping  $\delta^{15}\text{N}$  of  $\text{PM}_{2.5}$
- Particulate N contributions likely influence  $\delta^{15}\text{N}$  in bulk deposition

## Abstract

The extent to which atmospheric nitrogen (N) deposition reflects local reactive N sources remains unclear, yet represents a critical uncertainty in ecosystem N budgets. We compared N concentrations and isotopes in precipitation-event bulk (wet + dry) deposition across two nearby valleys in northern Utah with contrasting urban and agricultural land use. We predicted greater nitrate ( $\text{NO}_3^-$ ) vs. ammonium ( $\text{NH}_4^+$ ) and increased  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  in urban valley sites. Contrary to expectations, deposition N fluxes and isotope composition were similar within and between valleys ( $3.5 - 5.1 \text{ kg N ha}^{-1} \text{ y}^{-1}$ ). Organic N was a minor component of bulk N deposition (~13%). Nearby paired wildland sites had similar N concentrations as urban and agricultural sites, suggesting regional convergence in bulk N deposition. However, median bulk N deposition concentrations in our valleys exceeded wet deposition in remote sites monitored by the National Atmospheric Deposition Program (NADP) by more than two-fold. Weighted bulk deposition  $\delta^{15}\text{N}$  measured  $-0.6 \pm 0.7\text{\textperthousand}$ , similar to natural ecosystems. Yet, fine particulate matter ( $\text{PM}_{2.5}$ ) had consistently high values of total  $\delta^{15}\text{N}$  ( $15.6 \pm 1.4\text{\textperthousand}$ ),  $\delta^{15}\text{N}$  in  $\text{NH}_4^+$  ( $22.5 \pm 1.6\text{\textperthousand}$ ), and  $\text{NO}_3^-$  ( $8.8 \pm 0.7\text{\textperthousand}$ ), consistent with equilibrium fractionation with gaseous species.  $\delta^{15}\text{N}$  in bulk deposition  $\text{NH}_4^+$  varied by more than 40%, and spatial variation in  $\delta^{15}\text{N}$  within storms exceeded 10%. Sporadically high bulk deposition  $\delta^{15}\text{N}$  was thus consistent with increased particulate N—not necessarily shifting N sources. Despite differences in reactive N cycling, urban and agricultural land use are not necessarily reflected in the composition of local bulk N deposition—an important consideration for regional-scale biogeochemical models.

## 1 Introduction

Atmospheric deposition of nitrogen (N) derived from anthropogenic sources represents a significant N input to most regions on Earth [Galloway *et al.*, 2004]. Estimating these fluxes and ascertaining their sources is critical for assessing ecosystem impacts of N as well as for informing environmental policy and monitoring regulatory effectiveness and compliance. However, identifying atmospheric reactive N sources and deposition impacts at local and regional scales is complicated by the presence of numerous biogenic and/or anthropogenic sources—especially agricultural emissions from animal waste or fertilizer, fossil fuel combustion, and industrial emissions—that have heterogeneous spatial and temporal distributions. Monitoring the chemical composition of precipitation represents a simple and potentially effective strategy for assessing spatial and temporal variation in atmospheric reactive N sources and environmental impacts. In the United States, the National Atmospheric Deposition Program (NADP) relies on a dispersed network of precipitation sampling sites explicitly located

away from urban centers to estimate wet-only deposition of N at the national scale [Bigelow *et al.*, 2001]. The requirement to avoid urban areas implicitly assumes that local urban emissions will impact the chemical composition of precipitation at a given urban site. Similarly, long-term wet deposition studies often exclude sites with potential local emission influences for ease of interpretation [Lajtha and Jones, 2013]. However, the impacts and relative importance of urban and agricultural emission hotspots on the spatial and temporal distribution of N deposition, particularly the wet deposition component, remain poorly understood.

Discrepancies between estimated reactive N emissions and measured deposition fluxes suggest that existing sampling networks have under-sampled N deposition associated with urban and agricultural emission hotspots [Holland *et al.*, 2005]. Enhanced total N deposition in urban vs. wildland areas has been well documented [Fenn and Bytnerowicz, 1997; Lovett *et al.*, 2000; Fang *et al.*, 2011; Bettez and Groffman, 2013; Rao *et al.*, 2014]. Fossil fuel combustion is concentrated in urban areas [Gurney *et al.*, 2009] and represents the dominant source of NO<sub>x</sub> to the atmosphere [Galloway *et al.*, 2004], most of which oxidizes to nitrate (NO<sub>3</sub><sup>-</sup>) within hours [Beirle *et al.*, 2011] and is removed by wet or dry deposition. Several studies have observed increased dry deposition and foliar N uptake adjacent to roads as a consequence of local vehicular nitrogen oxide (NO<sub>x</sub>) emissions [Ammann *et al.*, 1999; Pearson *et al.*, 2000; Redling *et al.*, 2013]. Ammonium (NH<sub>4</sub><sup>+</sup>) and ammonia (NH<sub>3</sub>) in soluble and particulate forms, in equilibrium with gaseous NH<sub>3</sub> emitted to the atmosphere, represent the other primary component of bulk N deposition. Agricultural regions with intensive livestock production and fertilizer application are the primary source of NH<sub>3</sub> emissions at the global scale [Galloway *et al.*, 2004], although urban areas increasingly represent a source of NH<sub>3</sub> from vehicular fossil fuel combustion [Kean *et al.*, 2000; Felix *et al.*, 2014] in addition to industrial sources and organic

wastes (e.g., landfills and publicly-owned treatment works). In addition, organic N species can contribute an important but highly variable contribution to total deposition [Cape *et al.*, 2011], although relationships between organic N fluxes and land use types remain poorly characterized.

Despite these strong land use patterns in emissions of NO<sub>x</sub> and NH<sub>3</sub>, relatively few studies have assessed impacts of local and regional land-use (i.e., scales of tens – hundreds of km) on bulk N deposition, and little work has compared cities with nearby intensive agricultural regions. Previous studies primarily focused on forested urban to rural gradients, with natural landscapes or low-intensity agricultural regions as the end-member [Fenn and Bytnerowicz, 1997; Lovett *et al.*, 2000; Fang *et al.*, 2011; Bettez and Groffman, 2013; Rao *et al.*, 2014]. This work consistently documented increased N deposition in proximity to urban centers, usually by measuring N inputs in throughfall from forested canopies. Canopies with high leaf area can effectively scavenge atmospheric dry and fog deposition, much of which is subsequently leached from the canopy and captured in funnel collectors during rain events. Thus, canopy throughfall provides a surrogate for total (wet + dry) deposition to forest canopies, and typically yields greater N inputs than “bulk deposition” (wet + dry in the absence of a canopy) sampling in clearings [Fenn and Poth, 2004; Bettez and Groffman, 2013]. Throughfall deposition measurements in forested ecosystems have demonstrated the importance of urban areas as potential hotspots of dry N deposition.

Yet, measuring N deposition via canopy throughfall measurements is not practical in heterogeneous and/or sparsely-forested landscapes. First, plants differ substantially in their capacity to adsorb and/or assimilate deposited N [Lovett, 1994; Fenn and Bytnerowicz, 1997; Weathers *et al.*, 2006; He *et al.*, 2007; Sparks, 2009], which can confound attempts to assess relationships between land use and N deposition when vegetation type co-varies. Second, the

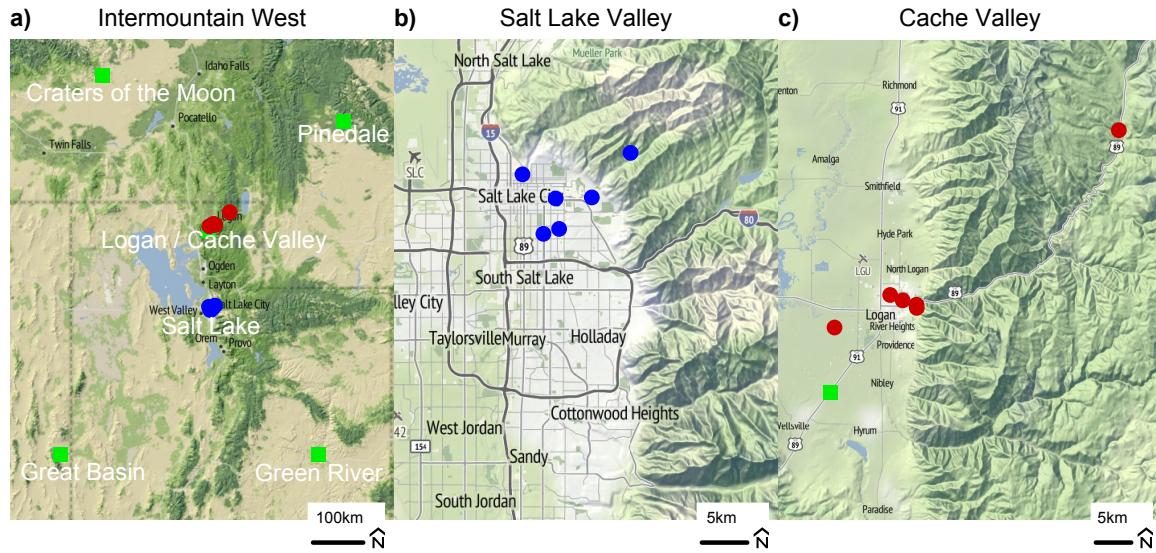
deposition surface provided by a forest canopy is not necessarily representative of the broader landscape. In semi-arid regions, native vegetation is characterized by a patchwork of grasses, shrubs, and bare soil; urban landscapes support a discontinuous and variable canopy of street trees in a landscape dominated by pavement, lawns, and buildings; agricultural areas consist of seasonal or irrigated pastures and row crops, or bare soil. Across this spectrum, bulk deposition measurements provide a comparable metric for assessing regional differences in N deposition [Lewis *et al.*, 1984; Lohse *et al.*, 2008; Liu *et al.*, 2013], especially wet deposition, despite the fact that they underestimate dry deposition to leaf surfaces. Furthermore, they provide a straightforward method to test the hypothesis that local to regional variation (i.e., tens – hundreds of km) in land use affects the chemical composition and fluxes of atmospheric N deposition.

The stable isotope ( $\delta^{15}\text{N}$ ) compositions of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  complement concentration and flux observations, potentially providing insights into spatial and temporal variation in reactive N sources to the atmosphere. Values of  $\delta^{15}\text{N}$  potentially reflect differences in isotope fractionation during the production or emission of atmospheric reactive N. For example,  $\text{NH}_3$  volatilization from animal waste or fertilizer discriminates against  $^{15}\text{N}$ , leading to lower  $\delta^{15}\text{N}$  values in agricultural  $\text{NH}_3$  relative to  $\text{NH}_3$  produced during fossil fuel combustion [Heaton, 1987; Frank *et al.*, 2004; Felix *et al.*, 2013, 2014]. Similarly, variation in  $\delta^{15}\text{N}$  of  $\text{NO}_x$  and  $\text{NO}_3^-$  have been used to distinguish oxidized N contributions from different fossil fuel sources [Elliott *et al.*, 2007; Walters *et al.*, 2015].

However, the capacity of  $\delta^{15}\text{N}$  observations in bulk deposition to record local source influences on N deposition remains largely untested. The origins of atmospheric  $\text{NH}_3$  and  $\text{NO}_3^-$  are of particular interest in the intermountain western United States because of their contribution to the formation of fine atmospheric particulate matter ( $\text{PM}_{2.5}$ ). In this region, winter cold air

pools facilitate the accumulation of PM<sub>2.5</sub> dominated by ammonium nitrate and ammonium sulfate, which represents a major public health concern as well as an ecologically significant N source [Mangelson *et al.*, 1997; Malek *et al.*, 2006; Kelly *et al.*, 2013; Hall *et al.*, 2014]. The isotopic composition of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in PM<sub>2.5</sub> could provide insight into their sources, i.e. from biogenic processes vs. fossil fuel combustion.

Here, we collected bulk deposition samples in rain and snow on a precipitation-event basis at sites spanning two nearby montane valleys in northern Utah, USA, with contrasting land use: the highly urban Salt Lake Valley and the predominantly agricultural Cache Valley (Fig. 1). We asked whether bulk N deposition, N speciation, or N isotope composition would reflect land use differences within and between valleys. We predicted that bulk deposition in the urban Salt Lake Valley would contain more NO<sub>3</sub><sup>-</sup> relative to NH<sub>4</sub><sup>+</sup> in deposition as a consequence of greater vehicular and industrial NO<sub>x</sub> emissions in urban areas. We predicted that bulk deposition in the agricultural Cache Valley would have higher NH<sub>4</sub><sup>+</sup> concentrations due to the prevalence of cattle feedlots and fertilized fields (which volatilize NH<sub>3</sub> that is deposited as NH<sub>4</sub><sup>+</sup> in acidic precipitation), and relatively lower local fossil fuel NO<sub>x</sub> emissions. Similarly, we predicted that δ<sup>15</sup>N in NH<sub>4</sub><sup>+</sup> would be greater in the Salt Lake Valley than in the Cache Valley due to the predominance of fossil fuel vs. agricultural NH<sub>3</sub> sources. To provide further regional context, we compared our measured bulk deposition N concentrations with wet deposition data from several nearby NADP sites.



**Figure 1** Precipitation sampling locations in **a** the geographic context of the intermountain western United States, **b** the Salt Lake Valley, and **c** the Cache Valley. Green squares represent NADP sites, and blue and red circles are sites sampled for the present study. This color scheme is continued in the following figures. Light-grey shaded areas of panels **b** and **c** represent urban land use.

## 2 Materials and Methods

### 2.1 Study area

The study area is characterized by a semi-arid continental climate. The Salt Lake Valley is a major metropolitan area with a population exceeding one million people, whereas the Cache Valley is characterized by concentrated animal agriculture (cattle feedlots and dairies), pasture, and row crops, and has similar populations of cattle and people (approximately 100,000 each; Utah State University Cooperative Extension, unpublished data). In each valley, site locations were chosen to characterize atmospheric inputs to intensively monitored watersheds in the iUTAH hydrologic observatory ([www.iUTAHepscor.org](http://www.iUTAHepscor.org)). Salt Lake Valley sites ( $n = 6$ ) were located within or adjacent to the Red Butte Creek watershed, a focal iUTAH watershed. Five of these sites were located in urban Salt Lake City, and one in Red Butte Canyon Research Natural

Area, an adjacent wildland protected area (Fig. 1b). Cache Valley sites ( $n = 5$ ) were located within the Logan River watershed, another iUTAH focal watershed. Three of these sites were located in the City of Logan (population  $\sim 50,000$ ), one along a roadside in an agricultural landscape with pasture and row crops, and another in Logan River Canyon in the Bear River Mountains east of the Cache Valley. In both valleys, urban sampling sites were located in residential backyards or fenced university properties to prevent tampering with sampling equipment. Two Cache Valley urban sites were relocated to nearby locations in April 2014 due to logistical constraints.

## 2.2 Precipitation sampling

Snow and rain samples in the Salt Lake Valley were collected on a precipitation event basis, whenever possible, from December 2013 to February 2015 (total  $n = 324$  samples). Samples were collected within 36 h of the end of precipitation events. In cases where samples could not be collected within 36 h of the end of a precipitation event, these samples were discarded and a clean collection bottle was installed to minimize the potential for microbial N immobilization. In the Cache Valley, snow samples were collected from December 2013 through February 2014, and rain samples from April 2014 through February 2015 (total  $n = 168$  samples). Snow was collected from acid-washed high-density polyethylene (HDPE) surfaces mounted on storm boards using acid-washed polyvinylchloride cores as described by Hall et al. [2014]. Rain was collected in HDPE funnels (20 cm diameter) mounted 1 m above the ground on steel posts, installed away from any overhanging vegetation. Funnels were connected via Tygon tubing to HDPE bottles placed inside white plastic cylinders buried beneath the soil. Funnel necks were plugged with polyester fiber to reduce the infiltration of particulate debris, and

Polyester was replaced following rainfall events. Samples from March 2014 often represented a mixture of snow and rain and were separately collected in acid-washed 18.9 l HDPE buckets. After collection, samples were weighed to calculate precipitation amount, filtered through pre-combusted Whatman GF/F filters, and frozen until analysis. Daily time series of precipitation amount were obtained from rain gauges on the University of Utah and Utah State University campuses.

Precipitation samples represented bulk (i.e., wet + dry) deposition given that funnel and storm board surfaces were exposed to the atmosphere between precipitation events. Our protocol contrasted with precipitation sampling at National Atmospheric Deposition Program (NADP) National Trends Network sites, where sampling containers were exposed to the atmosphere only during precipitation events. To further investigate dry deposition contributions to bulk ion loading at our sampling sites, we rinsed the funnel collectors with 18.2 MΩ deionized water for ion analysis after periods of more than two weeks without rain. Given that there were only three such events during the study period, we added the ion fluxes from rinsed samples to ion loads from the subsequent precipitation event for ease of interpretation.

We also compared our observations with five nearby (i.e., within several hundred km) NADP sites in the intermountain western United States (Fig. 1a): Pinedale, WY; Craters of the Moon National Monument, ID; Great Basin National Park, NV; Green River, UT; and Logan, UT. The Logan NADP site was located 10 km southwest of our Logan collection sites in proximity to a US Highway and animal feedlots. Samples from the NADP sites were collected over weekly intervals according to protocols detailed in the NADP National Trends Network operations manual ([http://nadp.sws.uiuc.edu/cal/PDF/NTN\\_Operations\\_Manual\\_v\\_2-2.pdf](http://nadp.sws.uiuc.edu/cal/PDF/NTN_Operations_Manual_v_2-2.pdf)).

### 2.3 Chemical and isotope analysis

All samples were analyzed for ion concentrations ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{F}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ) by ion chromatography (Metrohm Compact IC, Riverview, FL). Analytical precision of ion measurements was assessed using the relative standard deviations of certified standards analyzed as unknowns. Cumulative relative standard deviations measured < 3 % for all ions except for  $\text{F}^-$  (4 %) and  $\text{Mg}^{2+}$  (5 %). Mean reported values of NIST-traceable certified standards differed by < 4 % from measured values calculated using a separate set of NIST-traceable standards. Total dissolved N concentrations were measured on a subset of samples ( $n = 45$ ) with a Shimadzu TOCV analyzer (Columbia, MD). Dissolved organic N (DON) was calculated as the difference between total dissolved N and inorganic N ( $\text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-$ ;  $\text{NO}_2^-$  was typically below detection limit and not discussed further). This approach occasionally yielded negative values ( $n = 6$ ), likely due to compounding analytical variability in the three separate chemical determinations ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and total dissolved N). The most negative DON sample measured  $-0.11 \text{ mg l}^{-1}$ , thus we assigned all samples with DON absolute values <  $0.11 \text{ mg l}^{-1}$  to zero to avoid positively biasing our results, as opposed to simply removing negative values.

A subset of precipitation samples ( $n = 162$ ) was analyzed for nitrogen isotope ratios ( $\delta^{15}\text{N}$ ) of  $\text{NH}_4^+$  using an  $\text{NH}_3$  diffusion method modified from Holmes et al. [1998]. Briefly, 30 ml of sample was added to a 60 ml HDPE bottle along with 1.5 g NaCl (to decrease the osmotic potential of the solution). A glass-fiber filter acidified with  $30 \mu\text{l}$  of 4M  $\text{H}_3\text{PO}_4$  was sandwiched between Teflon tape and added to the bottle. Then, 90 mg of magnesium oxide was added to volatilize  $\text{NH}_3$ , and the bottle was immediately capped and incubated for 7 days on an orbital shaker/incubator at  $40^\circ\text{C}$  to allow  $\text{NH}_3$  to be completely trapped as  $\text{NH}_4^+$  on the acidified filter.

Filters were analyzed for  $\delta^{15}\text{N}$  values (precision  $< 0.2\text{\textperthousand}$ ) by combustion on an elemental analyzer coupled to an isotope ratio mass spectrometer at the Stable Isotope Ratio Facility for Environmental Research facility at the University of Utah (<http://sirfer.utah.edu>). To verify a lack of fractionation during recovery of  $\text{NH}_4^+$  on filter disks, we also analyzed check standards comprised of ammonium sulfate solutions with known  $\delta^{15}\text{N}$  values. We obtained equivalent  $\delta^{15}\text{N}$  values (within  $0.2\text{\textperthousand}$ ) after diffusion of this standard.

Additionally, we analyzed a subset of precipitation samples ( $n = 53$ ) for  $\text{NO}_3^-$  isotopic composition ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) using *Pseudomonas aureofaciens* and the denitrifier method [Casciotti *et al.*, 2002] to generate  $\text{N}_2\text{O}$  for analysis on an isotope ratio mass spectrometer. We used USGS 32 and 34 reference materials (for  $\delta^{15}\text{N}$ ) and USGS 34 and 35 (for  $\delta^{18}\text{O}$ ) to normalize the data to  $\delta$  notation relative to atmospheric  $\text{N}_2$  and VSMOW for N and O, respectively. Mean accuracy was  $0.34\text{\textperthousand}$  for  $\delta^{15}\text{N}$  and  $0.39\text{\textperthousand}$  for  $\delta^{18}\text{O}$ , assessed by comparing the difference between measured vs. known values of USGS 35 (for  $\delta^{15}\text{N}$ ) and USGS 32 (for  $\delta^{18}\text{O}$ ) when these were analyzed as unknowns. Sample precision, determined by standard deviations of several samples analyzed in triplicate, was  $0.08\text{\textperthousand}$  for  $\delta^{15}\text{N}$  and  $0.26\text{\textperthousand}$  for  $\delta^{18}\text{O}$ .

### 2.3.1 Nitrogen isotope ratios of $\text{PM}_{2.5}$

We sampled  $\text{PM}_{2.5}$  between January and February of 2015 at sites in urban Salt Lake City and near Logan, UT (in the Cache Valley) using calibrated high-volume air samplers at Utah Department of Air Quality (DAQ) sampling stations. Samples were collected over 2 – 5 day intervals, for a total of six Salt Lake City samples and four Logan samples. Salt Lake City samples were collected on  $20\text{ cm} \times 25\text{ cm}$  quartz microfiber filters (2500 QAT-UP, Pallflex Tissuquartz, Port Washington, NY). A subset of Salt Lake City samples and the Logan samples

were collected on Teflon filters on DAQ-operated PM<sub>2.5</sub> samplers. Comparisons of δ<sup>15</sup>N of NH<sub>4</sub><sup>+</sup> extracted from quartz and Teflon filters sampled in Salt Lake City (see details below) showed no significant differences. Prior to sampling, quartz filters were pre-combusted at 500°C for 4 hours and stored in aluminum foil inside sealed plastic bags. Blank filters were co-located inside aerosol samplers but not exposed to gas flow. During PM<sub>2.5</sub> sampling, larger particles were removed with slotted micro-quartz fiber filters (TE-230-QZ, micro-quarts slotted collection substrates, Tisch Environmental, Cleves, OH) on SA-230-F impactor plates (TE-230-QZ, Tisch). After collection, filters and blanks were wrapped in aluminum foil, packed into airtight plastic bags and stored at -20°C. For isotope analysis of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in PM<sub>2.5</sub>, filters were immersed for 24 hours in deionized water and solutions were filtered to 0.45 μm. Values of δ<sup>15</sup>N and δ<sup>18</sup>O of NO<sub>3</sub><sup>-</sup> were determined by the denitrifier method, and δ<sup>15</sup>N of NH<sub>4</sub><sup>+</sup> via diffusion as described above.

Bulk PM<sub>2.5</sub> subsamples collected on quartz filters were also analyzed for total nitrogen content and δ<sup>15</sup>N with an elemental analyzer (NA 1500 NC, Thermo Scientific, Waltham, MA) coupled to an isotope ratio mass spectrometer (DeltaPlus, Thermo Fisher Scientific (Finnigan), Waltham, MA) at the KCCAMS facility of UC Irvine. Data was corrected for the N mass (1.4 ug/cm<sup>2</sup>) and δ<sup>15</sup>N ratios (-6.8‰) of field blanks by isotope mass balance.

## 2.4 Data analysis

We compared bulk ion concentrations between the Salt Lake and Cache Valleys using mixed effects models where sampling sites were treated as random effects to account for within-site correlations. We separately tested for differences among sites in each valley using ANOVA. We did not statistically compare our samples with the NADP data given that they represent two

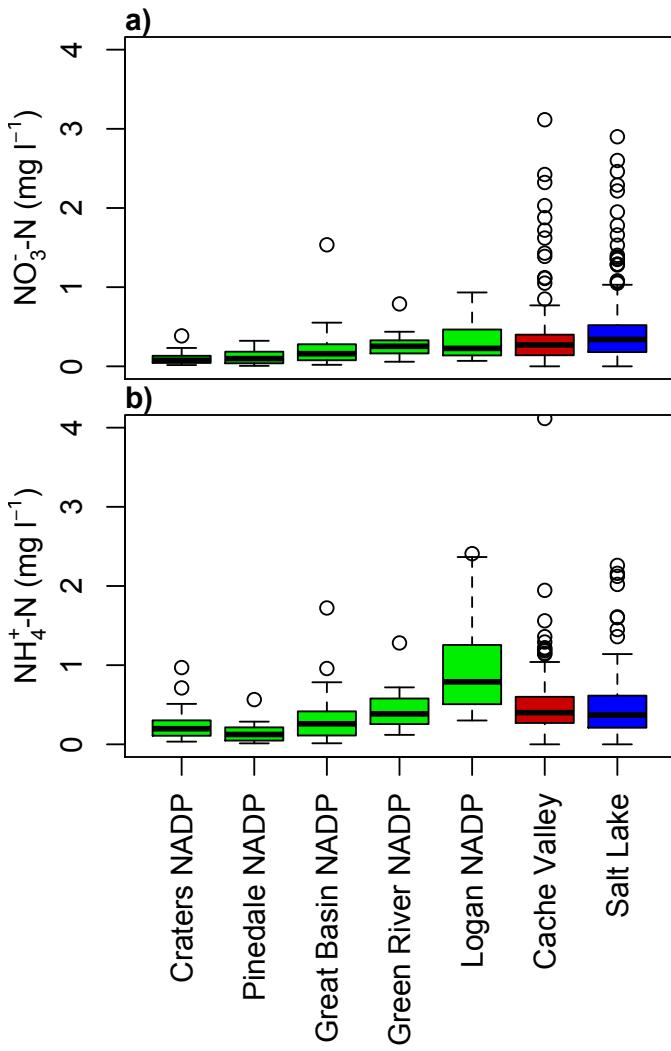
different sample types (i.e., bulk vs. wet deposition), but rather report the NADP data for quantitative and heuristic comparisons. We assessed cumulative bulk N deposition for 2014 at our sites as the product of precipitation amount and total N concentrations; missing values from a particular site were replaced by the means for each event in each valley. We did not have a complete record of bulk deposition chemical composition in the Cache Valley sites from mid February through early April 2014. Bulk deposition N concentrations were statistically equivalent between valleys during the rest of our observation period (December 2013 – February 2015). Therefore, we estimated cumulative bulk N loading for Cache Valley sites during the period of missing data as the product of precipitation amount measured at Utah State University in Logan and mean N concentrations measured during this period in the Salt Lake Valley. Gap-filled data were not used in statistical tests comparing sites or valleys.

We assessed temporal trends in precipitation ion concentrations during 2014 using generalized additive models (GAM) with a Gaussian link function, fitted using the mgcv package in R [Wood, 2006]. We fit ion concentrations as a smooth function of time using regression splines that were penalized according to their “wiggliness” during model fitting to achieve a statistically optimum degree of curvature. Curvature was expressed in terms of degrees of freedom (d.f.) analogous to the order of a polynomial, allowing for fractional d.f. The need to include differing smooth functions of time for different groups of sites (i.e., Salt Lake Valley, Cache Valley, and NADP sites) was assessed by comparing model AIC.3 Data, or a descriptive heading about data

## 4 Results and Discussion

### 4.1 Spatial and temporal patterns in bulk deposition inorganic N concentrations

Contrary to our hypothesis that differences in urban vs. agricultural land use would affect bulk N deposition and N speciation, concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  did not significantly differ between Salt Lake and Cache Valley sampling sites (Fig. 2). Similarly,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations did not significantly differ among sites in a given valley, despite the inclusion of paired wildland sites adjacent to each valley (ANOVA,  $p > 0.05$ ; data not shown). Ammonium concentrations in bulk deposition at the Salt Lake and Cache Valley sites were  $0.45 \pm 0.02$  and  $0.51 \pm 0.04 \text{ mg N l}^{-1}$  (means and standard errors), respectively, whereas  $\text{NO}_3^-$  concentrations were  $0.45 \pm 0.03$  and  $0.39 \pm 0.04 \text{ mg N l}^{-1}$ , respectively (Fig. 2). Median N concentrations in bulk deposition at the Salt Lake and Cache Valley sites were of relatively similar magnitude to median wet deposition N concentrations at the Green River NADP site ( $\text{NO}_3^- = 0.34$ ,  $0.27$ , and  $0.25 \text{ mg N l}^{-1}$ ;  $\text{NH}_4^+ = 0.37$ ,  $0.40$ ,  $0.38 \text{ mg N l}^{-1}$ , respectively; Fig. 2). The Green River site was located 250 – 300 km southeast of these valleys in a relatively remote town with a population of approximately 1000 people. Together, these data suggest regional congruence of bulk deposition N inputs to northern Utah, dominated by the wet deposition component.



**Figure 2** Concentrations of **a**  $\text{NO}_3^-$  and **b**  $\text{NH}_4^+$  in weekly precipitation samples (NADP sites; green boxes) and event-based bulk deposition samples (Salt Lake and Cache sites from this study, red and blue boxes, respectively). Sites are ordered by increasing mean  $\text{NO}_3^-$  concentrations from left to right. Boxes represent medians and the interquartile range, and data  $> 1.5$  times the range from the box to the whiskers are denoted as outliers (circles).

However, median bulk deposition N concentrations in the Salt Lake and Cache Valleys exceeded wet deposition concentrations at other more remote NADP sites in the region, indicating the importance of regional emissions contributions from northern Utah that had less impact on outlying sites. Salt Lake and Cache Valley bulk deposition inorganic N concentrations

exceeded wet deposition concentrations at the Great Basin NADP site (0.16 and 0.26 mg N l<sup>-1</sup> for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, respectively), and were more than two-fold greater than the Pinedale and Craters of the Moon NADP sites (Fig. 2; NO<sub>3</sub><sup>-</sup> = 0.10 and 0.08 mg N l<sup>-1</sup>; NH<sub>4</sub><sup>+</sup> = 0.12 and 0.20, respectively). Median NO<sub>3</sub><sup>-</sup> concentrations at the Logan NADP site were slightly lower (0.23 mg N l<sup>-1</sup>) than the bulk deposition values measured at the nearby sites sampled in this study (0.27 mg N l<sup>-1</sup>), whereas median NH<sub>4</sub><sup>+</sup> concentrations were approximately two-fold greater than our sites (0.79 vs. 0.40 mg N l<sup>-1</sup>); possible contributing mechanisms are discussed in greater detail below.

Our finding of similar bulk deposition N concentrations across disparate sites in the Salt Lake and Cache Valleys, and their similarities with wet deposition values from the remote Green River site, echoes the results of Lohse et al. [2008]. They found no significant differences in bulk N deposition among wildland and urban sites up- and downwind of Phoenix, AZ. Similarities in boundary layer NO<sub>x</sub> concentrations between the Salt Lake and Cache Valleys, despite their order of magnitude difference in human population, may have contributed to the similarities in bulk NO<sub>3</sub><sup>-</sup> deposition among our study sites. Tropospheric NO<sub>x</sub> typically has a short lifetime (hours) prior to oxidation to NO<sub>3</sub><sup>-</sup> [Beirle et al., 2011]. Mean NO<sub>2</sub> concentrations measured 14 and 11 ppb at sites in the Salt Lake and Cache Valleys, respectively, during 2014 (Utah Department of Air Quality; <http://www.airmonitoring.utah.gov/dataarchive/QL2014-NO2.pdf>). The 25<sup>th</sup> and 75<sup>th</sup> percentiles of NO<sub>2</sub> were 5 and 22 ppb for the Salt Lake site, and 4 and 16 ppb for the Cache Valley site. The difference in mean NO<sub>2</sub> concentrations between the valleys (~ 27 % greater in Salt Lake) was approximately proportional to the difference in median bulk deposition NO<sub>3</sub><sup>-</sup> concentrations between valleys (~ 26 %; Fig. 2), despite the fact that these differences were not statistically significant. Thus, we hypothesize that impacts of local atmospheric and

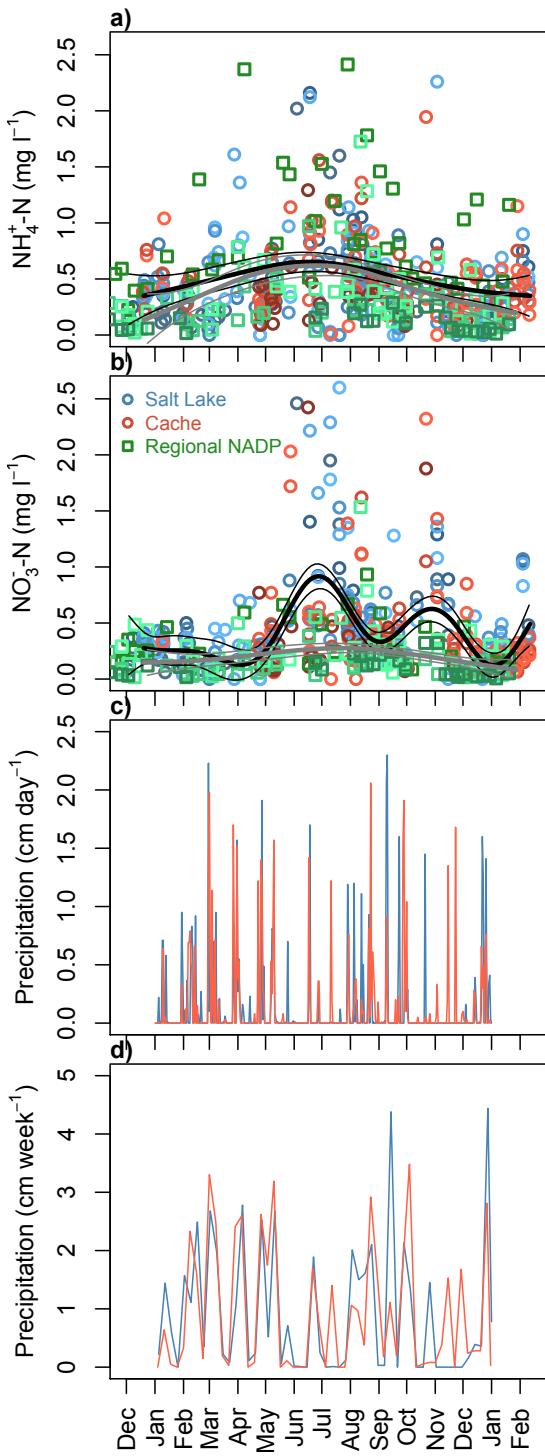
geomorphological characteristics on atmospheric reactive N concentrations and residence times in these valleys may have obscured differences in local emissions rates and sources.

The similarities in bulk  $\text{NH}_4^+$  concentrations between valleys were also surprising given the large differences in urban vs. agricultural  $\text{NH}_3$  sources, i.e. the prevalence of feedlots and fertilized agriculture in the Cache Valley. A scale mismatch between the location of  $\text{NH}_3$  emissions hotspots and our measurement sites may have contributed to this result. For example, median wet deposition  $\text{NH}_4^+$  concentrations at the Logan NADP site ( $0.79 \text{ mg N l}^{-1}$ ) were approximately double those of the bulk deposition  $\text{NH}_4^+$  concentrations at the other Cache Valley sites we measured in this study ( $0.40 \text{ mg N l}^{-1}$ ), despite having similar median  $\text{NO}_3^-$  concentrations. The Logan NADP site was located within 1 km of several cattle operations, whereas the sites that we sampled were farther away ( $\sim 10 \text{ km}$ ) from this particular area. This pattern suggests that impacts of agricultural  $\text{NH}_3$  emissions on wet deposition  $\text{NH}_4^+$  may be manifested over finer spatial scales (e.g.  $< 10 \text{ km}$ ) than reflected by valley-scale measurements. Accordingly, the sites we sampled may not have received a strong agricultural  $\text{NH}_3$  influence despite their close proximity to agricultural sources and the overall dominance of agricultural land use in the Cache Valley. In support of this interpretation, Fahey et al. [1999] found a sharp decline in bulk  $\text{NH}_4^+$  deposition to regional background levels within 2 km of an agricultural point source in the northeastern United States. Previous work in the Cache Valley documented that atmospheric  $\text{NH}_3$  concentrations varied approximately 2.5-fold between rural and urban sites separated by approximately 15 km (R. Martin et al., Utah State University, unpublished data), further implying highly localized emissions. Spatial heterogeneity in atmospheric reactive N concentrations was also indicated by high spatial variation in deposition inorganic N concentrations among sites in a given valley for a given storm event. The mean within-valley

standard deviations for a given storm event were  $0.22 \text{ mg N l}^{-1}$  for  $\text{NH}_4^+$  and  $0.13 \text{ mg N l}^{-1}$  for  $\text{NO}_3^-$ , but reached as high as  $2.26$  and  $0.94 \text{ mg N l}^{-1}$ , respectively.

#### 4.2 Wet vs. dry contributions to bulk inorganic N deposition

The Salt Lake and Cache Valley bulk deposition data showed a greater proportion of extreme  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentration values that were  $\geq 1.5$  times the interquartile range (denoted in Fig. 2 as circles) as compared with the NADP data, indicative of dry deposition inputs. Temporal differences in  $\text{NO}_3^-$  concentrations between the Salt Lake/Cache Valley bulk deposition samples and the NADP wet deposition samples were reflected by the GAM smooth functions, which showed two large peaks in June/July and October/November in the bulk deposition samples (Fig. 3). These high values, especially for  $\text{NO}_3^-$ , implied the importance of increased summertime dry deposition that was not captured by the NADP sites. In polluted southern California airsheds with highly seasonal precipitation inputs, dry deposition to forested canopies represents a dominant form of N inputs [Bytnerowicz and Fenn, 1996; Fenn and Bytnerowicz, 1997; Fenn and Poth, 2004]. In our study area, the temporal distribution of precipitation is typically more uniform (Fig. 3), and significant dry  $\text{NO}_3^-$  deposition to the funnel collector surfaces was only apparent during summer and late fall.



**Figure 3** Inorganic N concentrations in event-based bulk deposition samples from sites in the Salt Lake Valley (blue circles; six sites) and Cache Valley (red circles; five sites) and weekly wet deposition samples from regional NADP sites (green squares; five sites). Nitrate and  $\text{NH}_4^+$  are shown in panels **a** and **b**, respectively. Samples collected in this study spanned December 2013 to February 2015. The black lines represent the GAM model fits for the Salt

Lake and Cache Valley bulk deposition samples, and the grey lines represent the GAM model fits for the NADP sites. Daily and weekly cumulative precipitation measured near our Salt Lake and Cache Valley sites are shown in panels c) and d).

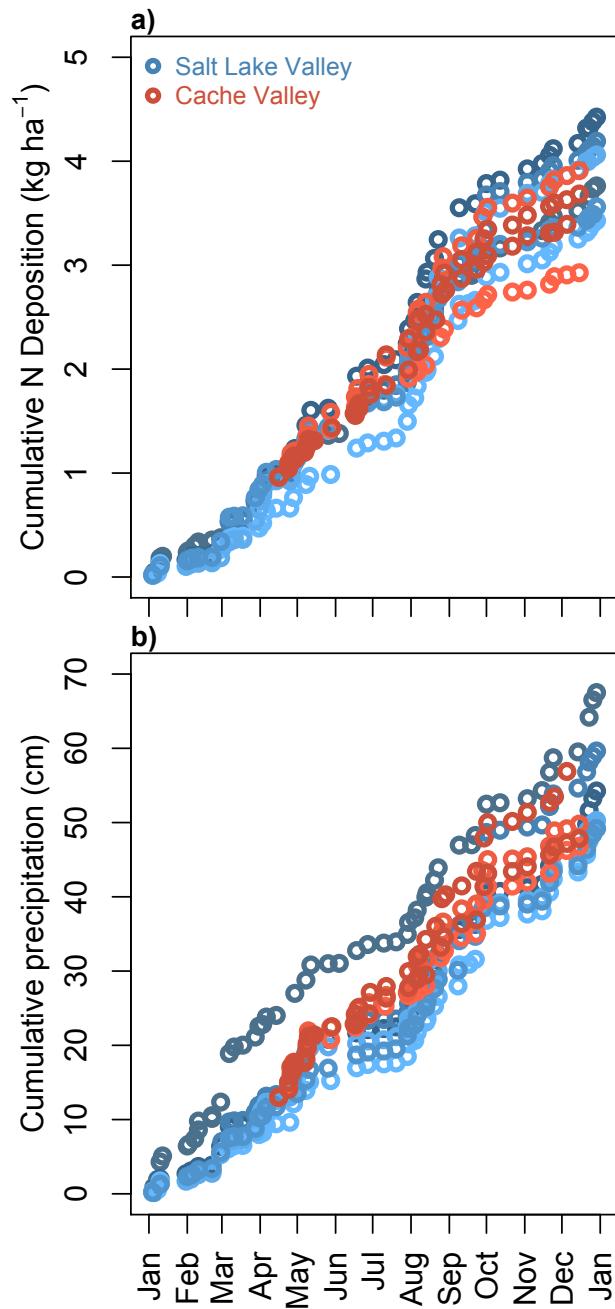
Intriguingly, winter inorganic N concentrations were much more similar between the bulk deposition data obtained in this study and wet deposition data for the remote NADP sites. This comparison suggests that little winter  $\text{NO}_3^-$  dry deposition was associated with local atmospheric reactive N emissions from the Salt Lake and Cache Valleys, despite the presence of  $\text{NO}_3^-$ -rich  $\text{PM}_{2.5}$  aerosols in these valleys [Mangelson *et al.*, 1997; Kelly *et al.*, 2013]. Previous work in the Salt Lake Valley showed that dry deposition of N to snow was highly variable in space and time [Hall *et al.*, 2014]. Dry deposition increased during periods of persistent cold air pools, and dry deposition N inputs peaked at mid-elevation montane sites as opposed to the valley floor [Hall *et al.*, 2014], where most of the sites sampled in the present study were located. Our present data provide additional evidence that winter dry N deposition may be spatially limited or sporadic in the study area.

In contrast to the temporal patterns in  $\text{NO}_3^-$  concentrations, summer  $\text{NH}_4^+$  concentrations were similar between the Salt Lake/Cache Valley sites and the regional NADP sites (Fig. 3). However, they diverged in winter, when the Salt Lake and Cache Valley samples had slightly but significantly greater  $\text{NH}_4^+$  (Fig. 3; note the difference between the GAM smooth functions). This difference may imply a greater and more widespread influence of urban and agricultural  $\text{NH}_3$  emissions on  $\text{NH}_4^+$  deposition during winter, possibly due to seasonal variation in atmospheric conditions. Stable atmospheric conditions often prevail in montane valleys in the intermountain western United States during winter [Lareau *et al.*, 2013], leading to increased atmospheric  $\text{NH}_x$  concentrations and  $\text{NH}_4^+$  deposition relative to wildland areas.

As with inorganic N, bulk deposition DON concentrations were also similar between valleys, with means of  $0.14 \pm 0.04$  and  $0.14 \pm 0.05$  mg N l<sup>-1</sup> in the Salt Lake and Cache Valley sites, respectively. However, 49 % of the samples measured had DON concentrations below the conservative detection limit we adopted here. A global meta-analysis found that organic N typically contributed between 17 – 43 % (inter-quartile range) of total precipitation N [Cape *et al.*, 2011]. The data in our present study fell below this range (~13 % of total N). Thus, we found no evidence that anthropogenic emissions from these valleys increased DON contributions to bulk deposition. If anything, background DON contributions may have been diluted by inorganic N from regional anthropogenic emissions.

#### 4.3 Bulk N deposition totals

Cumulative bulk N deposition was similar between valleys but was variable among sites, ranging between 3.5 and 5.1 kg N ha<sup>-1</sup> y<sup>-1</sup> (Fig. 4). Bulk deposition rates peaked in July and August, and scaled relatively closely with cumulative precipitation amount (Fig. 4). These N deposition rates are modest compared with sites impacted by urban emissions from Los Angeles, CA but exceed measurements and estimates from many wildland sites in the western United States [Williams and Tonnesen, 2000; Fenn *et al.*, 2003; Baron *et al.*, 2011], and are comparable to bulk deposition measurements from the Phoenix, AZ metropolitan area [Lohse *et al.*, 2008]. The bulk N deposition totals we measured here were similar to modeled wet deposition estimates for our study region ( $4 - 6$  kg N ha<sup>-1</sup> y<sup>-1</sup>) from 2011 to 2013, derived by combining sparse measurements with an atmospheric model [Schwede and Lear, 2014]. Importantly, our data suggest that local land use differences do not significantly affect these regional wet-deposition estimates.

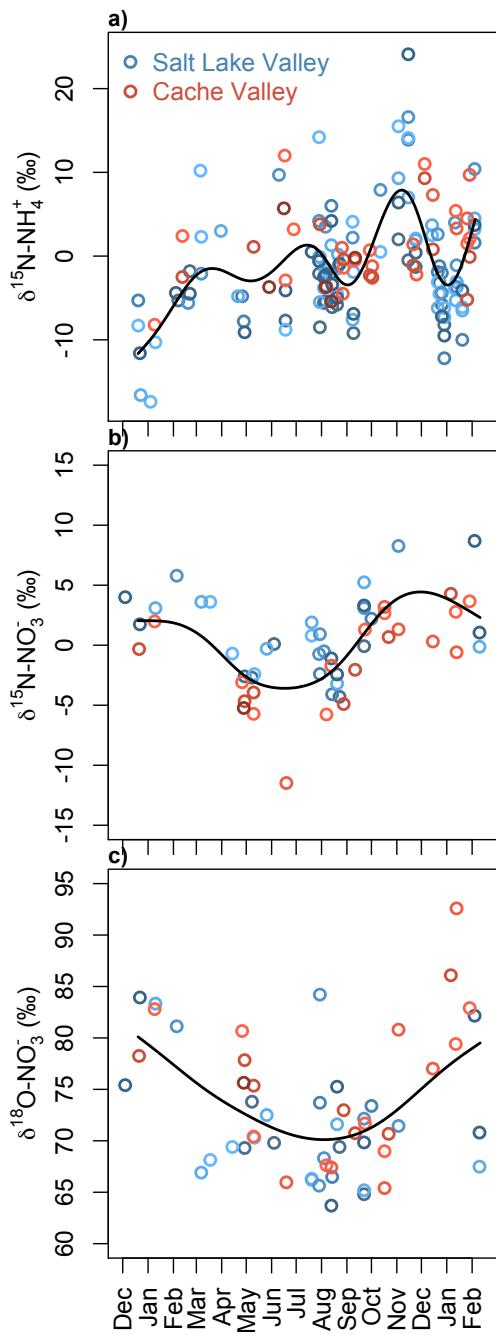


**Figure 4** Cumulative N deposition **a** and precipitation **b** measured during 2014 at sites in the Salt Lake Valley (blue circles, six sites) and Cache Valley (red circles, five sites), where different shades of each color represent different sites within a valley.

Although we saw evidence for summer dry deposition  $\text{NO}_3^-$  inputs as described above, our data did not reflect the very high dry deposition N inputs modeled for this region ( $> 12 \text{ kg N ha}^{-1} \text{ y}^{-1}$ ; NADP total deposition maps, [http://nadp.isws.illinois.edu/committees/tdep/tdepmaps/preview.aspx#n\\_wd](http://nadp.isws.illinois.edu/committees/tdep/tdepmaps/preview.aspx#n_wd)). Plant canopies likely would have scavenged much more dry N deposition from the atmosphere than our funnel collectors [Fenn and Poth, 2004; Sparks, 2009], but we suggest that our bulk deposition estimates provide a useful metric for assessing total deposition to the relatively uniform surfaces—pavement, rooftops, and bare soil and rock—that represent a substantial portion of urban and wildland landscapes in our semi-arid study region.

#### 4.4 Stable isotope composition of inorganic N deposition and $\text{PM}_{2.5}$

Contrary to our hypothesis that biogenic vs. fossil fuel reactive N sources would be reflected in the N isotope composition of bulk deposition, we found no systematic differences in  $\delta^{15}\text{N}$  values of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , or in  $\text{NO}_3^-$  or  $\text{NH}_4^+$  of  $\text{PM}_{2.5}$ , between the Salt Lake and Cache Valleys. Rather,  $\delta^{15}\text{N}$  values fluctuated significantly over time as indicated by the GAM smooth functions (Fig. 5). Little seasonality was apparent in  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$ , which varied between -17.4 and 24.1‰ (mean =  $-0.8 \pm 0.5\text{‰}$ ). We occasionally observed extremely high variability in  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  and  $\text{NH}_4^+$  concentrations among sites within a valley during a single storm event (exceeding 10‰ and  $1 \text{ mg N l}^{-1}$ , respectively). This variability is consistent both with fine-scale spatial heterogeneity in  $\text{NH}_3$  sources as discussed above, and partitioning between gaseous  $\text{NH}_3$  and particulate  $\text{NH}_4^+$  ( $\text{NH}_x$ ). It also likely reflects spatial variation in isotope fractionation during scavenging of  $\text{NH}_x$  from the atmosphere during precipitation events [Heaton, 1987; Xiao *et al.*, 2012], which can function analogous to a Rayleigh distillation.



**Figure 5** Values of  $\delta^{15}\text{N}$  in **a**  $\text{NH}_4^+$  and **b**  $\text{NO}_3^-$  in a subset of precipitation samples from the Salt Lake Valley (blue circles) and Cache Valley (red circles), where different shades of each color represent different sites within a valley. Nitrogen isotope ratios did not significantly differ between valleys.

The occasionally high values of  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  in bulk deposition (Fig. 5a) may have reflected increasing contributions of particulate  $\text{NH}_4^+$  to bulk deposition. Values of  $\delta^{15}\text{N}$  in bulk  $\text{PM}_{2.5}$  were greater ( $15.6 \pm 1.4\text{\textperthousand}$ ) than most bulk deposition samples, and  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  from both valleys were even more enriched, averaging  $24.1 \pm 2.3$  and  $20.1 \pm 1.6\text{\textperthousand}$  in the Salt Lake and Cache Valley sites, respectively. These high  $\delta^{15}\text{N}$  values are consistent with a  $\sim 33\text{\textperthousand}$  equilibrium fractionation between gaseous  $\text{NH}_3$  and particulate  $\text{NH}_4^+$  [Heaton *et al.*, 1997], leading to much greater  $\delta^{15}\text{N}$  in  $\text{PM}_{2.5}$  relative to precursor compounds. Individual  $\text{PM}_{2.5}$  samples varied between 17.3 and  $31.4\text{\textperthousand}$  in  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$ , and overlapped with the most enriched values of  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  in bulk deposition (Fig. 5). Thus, any isotope variation in  $\text{NH}_3$  associated with volatilization of agricultural  $\text{NH}_3$  vs. thermogenic (i.e., combustion or industrial) sources may have been obscured in our bulk deposition samples due to the presence of a variable component of particulate  $\text{NH}_4^+$ . This interpretation is bolstered by contrasting our results with wet deposition  $\delta^{15}\text{N}$  data from China, Japan, and South Africa [Heaton, 1987; Fukuzaki and Hayasaka, 2009; Jia and Chen, 2010; Xiao *et al.*, 2012]. These studies consistently found  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  values  $< 0\text{\textperthousand}$  for precipitation samples with no dry deposition component. These studies were also located in areas impacted by mixtures of urban and agricultural  $\text{NH}_3$  sources, as were our study sites; consequently, the large positive  $\delta^{15}\text{N}$  deviations we observed in some samples could be explained by a variable contribution of dry particulate  $\text{NH}_4^+$  deposition collected in our bulk samplers, which was not sampled in these wet deposition studies.

Values of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  in bulk deposition  $\text{NO}_3^-$  showed clearer seasonal trends than  $\text{NH}_4^+$  and less variation among sites within a given storm (Fig. 5b,c). Values of  $\delta^{15}\text{N}$  in bulk deposition  $\text{NO}_3^-$  varied between -11.5 and  $8.7\text{\textperthousand}$  (mean  $0.0 \pm 0.5\text{\textperthousand}$ ) and decreased during summer relative to winter (Fig. 5b). Values of  $\delta^{18}\text{O}$  in bulk deposition  $\text{NO}_3^-$  varied between 63.7

and 92.6 ‰ (mean  $73.2 \pm 0.9$  ‰) and also decreased during summer relative to winter (Fig. 5c).

Freyer et al. [1991] found a similar ~ 5‰ summertime decline in  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  in European precipitation, and speculated that temperature-dependent isotope exchange reactions among atmospheric  $\text{NO}_y$  species, decreased contributions of particulate  $\text{NO}_3^-$ , or an increased contribution of biogenic  $\text{NO}_x$  sources could be responsible. Here, we found that  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  in  $\text{PM}_{2.5}$  measured  $8.8 \pm 0.7$  ‰ and  $\delta^{18}\text{O}$  was  $81.6 \pm 2.7$  ‰. The former were equivalent to the highest observed  $\delta^{15}\text{N}$  values in bulk deposition. Therefore, our bulk deposition  $\text{NO}_3^- \delta^{15}\text{N}$  values could also potentially be interpreted as a variable mixture of  $\delta^{15}\text{N}$ -enriched particulate  $\text{NO}_3^-$  and  $\delta^{15}\text{N}$ -depleted gaseous  $\text{HNO}_3$ , in addition to a mixture of isotopically variable  $\text{NO}_3^-$  sources.

Overall, the mass and volume-weighted isotopic composition and standard errors of  $\delta^{15}\text{N}$  in  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in bulk deposition measured  $-1.6 \pm 0.4$  and  $0.8 \pm 0.5$  ‰, respectively. Given that volume-weighted mean concentrations of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  measured  $0.34 \pm 0.01$  and  $0.24 \pm 0.01 \text{ mg N l}^{-1}$ , respectively, weighted  $\delta^{15}\text{N}$  of total inorganic N measured  $-0.6 \pm 0.7$  ‰. Because relatively few comprehensive studies of the isotope composition of bulk N deposition have been conducted, these measurements provide a useful constraint for ecosystem-scale N isotope models. For example, N isotope mass balance has been used to estimate the importance of denitrification at the global scale, requiring an estimate of the N isotope composition of atmospheric deposition inputs [Houlton and Bai, 2009]. Previous studies in natural ecosystems had a median  $\delta^{15}\text{N}$  value of  $-1.3$  ‰ (ibid.), similar to our present data. These similarities imply that local urban or agricultural influences do not necessarily impart a significant isotopic signature to N in bulk deposition.

## 5 Conclusions

Despite the strong impacts of land use on NO<sub>x</sub> and NH<sub>3</sub> emissions documented elsewhere [Galloway *et al.*, 2004], we conclude that valley-scale differences in urban vs. agricultural land-use in northern Utah were not manifested in the speciation, isotope composition, or fluxes of bulk atmospheric N deposition to our funnel collectors. Although median measured bulk deposition N concentrations exceeded wet deposition concentrations from several remote NADP sites in the region, they were similar to another remote NADP site. This finding is important in the context of atmospheric deposition measurement networks such as NADP, where local land use characteristics are often implicitly assumed to impact wet deposition fluxes [Bigelow *et al.*, 2001]. The observed decoupling between local differences in reactive N emissions and a similar composition of bulk N deposition between valleys may have reflected 1) the importance of differing atmospheric and geomorphological characteristics in controlling boundary-layer N concentrations and residence times; 2) fine-scale emissions and deposition hotspots not captured by our sampling sites; 3) low dry deposition capture by our sampling apparatus. It is well known that plant canopies scavenge gaseous and particulate reactive N to a greater extent than the funnels we used to collect bulk deposition [Fenn and Poth, 2004; Sparks, 2009; Bettez and Groffman, 2013]. However, our bulk deposition estimates likely provide a useful metric for assessing total deposition to the relatively uniform surfaces—bare soil, rocks, pavement, and rooftops—that represent a substantial portion of wildland and urban landscapes in the intermountain western United States.

Values of  $\delta^{15}\text{N}$  in bulk deposition may represent a useful metric for quantifying the contribution of particulate vs. gaseous NH<sub>4</sub><sup>+</sup>, and perhaps NO<sub>3</sub><sup>-</sup>, to bulk deposition. However, large equilibrium fractionations between gas and particle phases, evident when comparing  $\delta^{15}\text{N}$

in  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in bulk deposition with  $\text{PM}_{2.5}$ , may mask any initial isotope differences among biological vs. fossil fuel reactive N sources. Thus, we recommend caution when interpreting atmospheric  $\delta^{15}\text{N}$  measurements solely in terms of partitioning among sources. This is especially important when sampling schemes may selectively capture gaseous vs. particulate N as opposed to the entire atmospheric reactive N pool, thus leading to physical isotope fractionation.

### Acknowledgments and Data

Upon manuscript acceptance all data will be publicly available on line from the iUTAH Modeling and Data Federation at [data.iutahepscor.org/mdf](http://data.iutahepscor.org/mdf). We thank the NADP program for providing their data on line. S. Chakraborty and D. Fernandez provided analytical assistance, and D. Eiriksson, E. Schulze, D. Tarboton, B. Greene, D. Epstein, S. Jackson, J. Turner, A. Armstrong, and H. Quinn assisted with sample collection. J. Wessling, D. Zhang, and X. Xu contributed to sample analysis. We also thank Utah Department of Air Quality staff, especially S. Arens, for assistance with  $\text{PM}_{2.5}$  collection, and B. Schichtel from the US National Park Service for use of a high-volume sampler. This research was supported by NSF EPSCoR grant IIA 1208732 awarded to Utah State University as part of the State of Utah Research Infrastructure Improvement Award, and by NSF grant DBI-1337947 to the University of Utah. Any opinions, findings, and conclusions or recommendations expressed are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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