Convergence in nitrogen deposition and cryptic isotopic variation across urban and agricultural valleys in northern Utah

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Abstract The extent to which atmospheric nitrogen (N) deposition reflects land use differences and biogenic versus fossil fuel 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 nearby valleys in northern Utah with contrasting land use (highly urban versus intensive agriculture/low-density urban). We predicted greater nitrate (NO₃⁻) versus ammonium (NH⁴⁺) and higher δ¹⁵N of NO₃⁻ and NH⁴⁺ in urban valley sites. Contrary to expectations, annual N deposition (3.5–5.1 kg N ha⁻¹ yr⁻¹) and inorganic N concentrations were similar within and between valleys. Significant summertime decreases in δ¹⁵N of NO₃⁻ possibly reflected increasing biogenic emissions in the agricultural valley. Organic N was a relatively minor component of deposition (~13%). Nearby paired wildland sites had similar bulk deposition N concentrations as the urban and agricultural sites. Weighted bulk deposition δ¹⁵N was similar to natural ecosystems (~0.6 ± 0.7‰). Fine atmospheric particulate matter (PM₂.₅) had consistently high values of bulk δ¹⁵N (15.6 ± 1.4‰), δ¹⁵N in NH⁴⁺ (22.5 ± 1.6‰), and NO₃⁻ (8.8 ± 0.7‰), consistent with equilibrium fractionation with gaseous species. The δ¹⁵N in bulk deposition NH⁴⁺ varied by more than 40‰, and spatial variation in δ¹⁵N within storms exceeded 10‰. Sporadically high values of δ¹⁵N were thus consistent with increased particulate N contributions as well as potential N source variation. Despite large differences in reactive N sources, urban and agricultural landscapes are not always strongly reflected in the composition and fluxes of local N deposition—an important consideration for regional-scale ecosystem models.

1. Introduction

Atmospheric nitrogen (N) deposition 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 over local and regional scales is critical for assessing ecosystem impacts of N as well as for informing environmental policy and regulatory compliance. However, this endeavor is complicated by the presence of numerous biogenic and/or anthropogenic sources—especially agricultural emissions from animal waste or fertilized soils, fossil fuel combustion, and industrial emissions—that have heterogeneous spatial and temporal distributions. Monitoring the chemical composition of precipitation represents a potentially effective strategy for assessing spatial and temporal variations in atmospheric reactive N sources.

In the United States, the National Atmospheric Deposition Program (NADP) uses a network of precipitation sampling sites explicitly located away from urban centers to estimate wet deposition of N at the national scale [Bigelow et al., 2001]. Avoiding urban areas implicitly assumes that local urban emissions impact the chemical composition of precipitation at a given urban site. It is generally assumed that urban areas dominate oxidized N emissions, while agricultural areas dominate reduced N emissions to the atmosphere [Hertel et al., 2012]. However, the impacts and relative importance of urban and agricultural emission hot spots on the spatial and temporal distributions of N deposition remain understudied.

Discrepancies between estimated reactive N emissions and measured deposition fluxes suggest that existing sampling networks have undersampled N deposition associated with urban and agricultural emission hot...
spots [Holland et al., 2005]. Total N deposition is typically higher in urban versus wildland areas [Fenn and Bytnerowicz, 1997; Lovett et al., 2000; Fang et al., 2011; Betze 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 nitrogen oxides (NOx) to the atmosphere [Galloway et al., 2004]. Most NOx oxidizes to nitrate (NO3−) within hours [Beirle et al., 2011] and is subsequently removed by wet or dry deposition over time scales of minutes to days [Hertel et al., 2012]. Several studies documented increased dry deposition and foliar N uptake adjacent to roads due to vehicular NOx emissions [Ammann et al., 1999; Pearson et al., 2000; Redling et al., 2013]. Fertilized agricultural soils also represent a major NOx source, particularly in semiarid climates where low moisture enhances microbial NO production [Davidson and Kingerlee, 1997; Hertel et al., 2012]. The impacts of agricultural NOx on NO3− deposition have received little attention in comparison with fossil fuel combustion.

Ammonium (NH4+) in soluble and particulate forms, in equilibrium with gaseous NH3 emitted to the atmosphere, represents the other primary component of bulk N deposition. Together, these species (NH4) have typical atmospheric residence times of hours to days; particulate NH4+ has lower dry deposition velocities and longer residence times [Hertel et al., 2012]. Agricultural regions with intensive livestock production and fertilizer application are the primary source of global NH3 emissions [Galloway et al., 2004]. However, urban areas increasingly represent a source of NH3 from vehicular fossil fuel combustion [Kean et al., 2000] in addition to smaller sources from industry and other organic wastes (e.g., landfills and sewage treatment plants) [Battye et al., 2003]. Organic N may contribute an important but highly variable component to total deposition [Cape et al., 2011], although relationships between organic N and land use remain poorly characterized.

Despite the strong association between land use and emissions of NOx and NH3 [Hertel et al., 2012], relatively few studies have assessed impacts of intensive urban and agricultural land use on regional-scale (i.e., scales of tens to hundreds of kilometers) patterns of bulk N deposition [Lohse et al., 2008; Tulloss and Cadenasso, 2015]. Previous studies often used forested urban to rural gradients, with natural or low-intensity agricultural landscapes as the end-member [Fenn and Bytnerowicz, 1997; Lovett et al., 2000; Fang et al., 2011; Betze and Groffman, 2013; Rao et al., 2014]. This work documented increased N deposition in proximity to urban centers, usually by measuring N inputs in throughfall from forested canopies. Plant canopies can more effectively scavenge atmospheric dry and fog deposition than a single planar surface (i.e., pavement or bare soil). The presence of a plant canopy typically increases deposition fluxes relative to “bulk deposition,” defined here as wet + dry deposition in the absence of overhanging plants [Fenn and Poth, 2004; Betze and Groffman, 2013; Tulloss and Cadenasso, 2015]. Canopy throughfall deposition measurements clearly demonstrated the potential importance of urban areas as hot spots of dry N deposition.

Despite the useful information gained from throughfall deposition measurements, this method is less practical in heterogeneous urban and agricultural landscapes. First, plant species differ in their capacity to scavenge atmospheric N [Lovett, 1994; Fenn and Bytnerowicz, 1997; Sparks, 2009], which can confound assessments of land use impacts when vegetation covaries. Second, the deposition surface provided by a forest canopy is not necessarily representative of the broader landscape, especially in semiarid environments with few trees. Bulk deposition measurements provide a comparable metric for assessing regional differences in N deposition [Lewis et al., 1984; Liu et al., 2013], despite their underestimation of dry N deposition to canopies.

The stable isotope (δ15N) compositions of NH4+ and NO3− complement measurements of N concentrations, potentially providing insights into spatial and temporal variations in reactive N sources to the atmosphere. Values of δ15N can reflect differences in sources and/or isotope fractionation during the production or emission of atmospheric reactive N. Atmospheric NH3 from biogenic sources such as urine and manure, and also inorganic fertilizer, often has low δ15N values (e.g., −60−0‰ [Frank et al., 2004; Skinner et al., 2006; Felix et al., 2013, 2014]) as a consequence of kinetic and equilibrium fractionation during NH3 volatilization. This isotopic variation arises both from δ15N values of the source of mineralized NH3, as well as the extent of NH3 volatilization [Hogberg, 1997]. For example, δ15N values in animal waste and fertilizer vary between 2−25‰ and −2−2%, respectively [Bateman and Kelly, 2007; Kendall et al., 2007], but can yield volatilized NH3 that is highly depleted in δ15N, e.g., −56 to −23‰ [Felix et al., 2013]. In contrast to biogenic or fertilizer sources, NH3 released or produced as a by-product of fossil fuel combustion may have relatively higher δ15N values, e.g., −15 to −2% [Felix et al., 2013], given that kinetic fractionation during a phase transition is less likely to be expressed. All else equal, greater values of δ15N of
NH$_4^+$ in atmospheric deposition likely reflect greater contributions of combustion-derived NH$_3$ relative to biogenic/fertilizer NH$_3$.

Variation in $\delta^{15}$N of NO$_x$ and atmospheric NO$_3^-$ has similarly been used to distinguish oxidized N contributions from fossil fuel and biogenic sources [Elliott et al., 2007; Walters et al., 2015]. Median values of $\delta^{15}$N of NO$_x$, from coal combustion ($\sim$10–20‰) are higher than median values of diesel and gasoline combustion ($\sim$20–30‰), which are both higher than median soil NO$_x$ ($\sim$30‰) [Li and Wang, 2008; Walters et al., 2015]. When comparing regions with similar fossil fuel NO$_x$ sources, lower values of $\delta^{15}$N in NO$_3^-$ likely reflect an increasing biogenic emission contribution. In contrast to $\delta^{15}$N, values of $\delta^{18}$O in NO$_3^-$ may be controlled by atmospheric conditions during NO$_x$ oxidation and provide less insight into NO$_x$ sources [Michalski et al., 2003].

The capacity of $\delta^{15}$N observations in bulk deposition to assess and record the influence of local emission sources on ecosystem N inputs remains largely unexplored. The origins of atmospheric NH$_3$ and NO$_3^-$ are of particular interest in the intermountain western United States because of their contribution to the formation of fine atmospheric particulate matter (PM$_{2.5}$). In this region, winter cold air pools facilitate the accumulation of PM$_{2.5}$ dominated by ammonium nitrate and ammonium sulfate, which represents a major public health concern and a significant N source [Mangelson et al., 1997; Malek et al., 2006; Kelly et al., 2013; Hall et al., 2014]. The isotopic compositions of NO$_3^-$ and NH$_4^+$ in PM$_{2.5}$ could provide insight into their sources, i.e., from soil and biogenic processes versus fossil fuel combustion.

Here we collected bulk deposition samples 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 (Figure 1). 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; and agricultural areas consist of seasonal or irrigated pastures and row crops and bare soil for much of the year. We asked: do bulk N deposition, N speciation, or N isotope composition reflect land use differences within and between valleys and over time? We predicted that bulk deposition in the urban Salt Lake Valley would contain more NO$_3^-$ relative to NH$_4^+$ in deposition as a consequence of greater vehicular and industrial NO$_x$ emissions in urban areas. We predicted that bulk deposition in the agricultural Cache Valley would have higher NH$_4^+$ concentrations due to the

![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. The green squares represent the NADP sites, and the blue and red circles are the sites sampled for the present study. This color scheme is continued in the following figures. The light-grey shaded areas of Figures 1b and 1c represent urban land use.](image-url)
prevalence of cattle feedlots and fertilized fields (which volatilize NH$_3$ that is deposited as NH$_4^+$ in acidic precipitation) and lower local fossil fuel NOx emissions. Similarly, we predicted that δ$^{15}$N in NO$_3^-$ and NH$_4^+$ would be higher in the Salt Lake Valley than in the Cache Valley due to increased fossil fuel versus biogenic/fertilizer sources. To provide further context, we compared bulk deposition N concentrations with wet deposition data from several regional NADP sites.

2. Materials and Methods

2.1. Study Area

The Salt Lake and Cache Valleys are characterized by a similar semiarid continental climate, with mean annual temperature of 11 and 9°C and annual precipitation of 410 and 500 mm, respectively, measured on the valley floors. Precipitation consists mostly of winter snow and spring and fall rains, punctuated by occasional summer storms. The Salt Lake Valley (~25 × 50 km$^2$) is a major metropolitan area with a human population > one million, whereas the Cache Valley (~20 × 60 km$^2$) 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 or >100 km$^{-2}$; Utah State University Cooperative Extension, unpublished data). We assumed that measurements of atmospheric N deposition at sites in these valleys would reflect local (within-valley) emissions as well as an unknown regional contribution. There are no other major urban areas or hot spots of concentrated feedlots/agriculture within hundreds of kilometers of these valleys. In the Salt Lake Valley, within-valley fossil fuel combustion, and dilution and mixing with incoming cleaner air masses, can explain the majority of the temporal variation in carbon dioxide (CO$_2$) concentrations [Strong et al., 2011]. This finding implies that local (as opposed to regional) emissions might also be strongly linked to atmospheric reactive N concentrations in these valleys, especially given the shorter residence times of reactive N relative to CO$_2$.

Montane valleys are an especially useful spatial scale of analysis in this region during winter, where temperature inversions allow mixing of local atmospheric emissions throughout the valleys over time scales of hours to days [Pataki et al., 2005].

In each valley, site locations were chosen to characterize atmospheric inputs to intensively monitored watersheds in the iUTAH hydrologic observatory (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 protected area (Figure 1b). Cache Valley sites (n = 5) were located within the Logan River watershed, another iUTAH focal area. Three sites were located in the City of Logan (population~50,000), one along a roadside in an agricultural landscape with pasture and row crops, and another in Logan River Canyon east of the Cache Valley. We predicted that the deposition sampled in the urban Cache Valley sites would also reflect emissions from the adjacent agricultural landscape, which stretched for 20–30 km to the south, west, and north of Logan. In both valleys, urban sampling sites were located in fenced properties to prevent tampering with equipment. Two Cache Valley urban sites were relocated to nearby locations in April 2014 due to logistical constraints.

In Salt Lake City and the City of Logan, the tree canopy consisted largely of deciduous species native to the eastern United States and represented a relatively small portion of total land cover (~26%) [Nowak et al., 1996]. The wildland sites sampled here had similarly sparse tree cover and were dominated by low-statured (<1 m) herbaceous vegetation and shrubs. The agricultural Logan Valley sites were characterized by annual row crops and pasture.

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 this interval, samples were discarded and a clean collection bottle was installed to minimize the potential for microbial N immobilization. In the Cache Valley, snow and rain samples were collected from December 2013 to February 2014 and from April 2014 to 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 overhanging vegetation. Funnels were
connected via Tygon tubing to HDPE bottles placed inside plastic cylinders buried beneath the soil. Funnel necks were plugged with polyester fiber to reduce infiltration of debris and replaced following rainfall events. Samples from March 2014 often represented a mixture of snow and rain and were separately collected in acid-washed HDPE buckets (18.9 L). After collection, samples were weighed to calculate precipitation amount, filtered through precombusted 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. Values of pH measured on a subset of samples were <6, indicating that NH₃ volatilization was minimal.

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 containers were exposed to the atmosphere only during precipitation events using an automated sampler. 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 2 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 of kilometers) NADP sites in the intermountain western United States (Figure 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 10 km southwest of our Logan collection sites, in close proximity (<100 m) to animal feedlots. Samples from NADP sites were collected over weekly intervals according to protocols detailed in the National Trends Network operations manual (http://nadp.sws.uiuc.edu/cal/PDF/NTN_Operations_Manual_v_2-2.pdf). We analyzed the data corresponding to our period of sample collection (detailed above).

2.3. Chemical and Isotope Analyses

All samples were analyzed for NO₃⁻ and NH₄⁺ concentrations 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 of these standards averaged <3%. Mean-reported values of National Institute of Standards and Technology (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 TOC-V analyzer (Columbia, MD). Dissolved organic N (DON) was calculated as the difference between total dissolved N and inorganic N (NH₄⁺ + NO₃⁻ + NO₂⁻; NO₂⁻ was typically below detection limit and not discussed further). This approach occasionally yielded negative values (n = 6), likely due to compounds contributing to DON variability in the three separate chemical determinations (NH₄⁺, NO₃⁻, and total dissolved N). The most negative DON sample measured −0.11 mg L⁻¹; thus, we assigned all samples with DON absolute values <0.11 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 N isotope ratios (δ¹⁵N) of NH₄⁺ using an NH₃ 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 μL of 4 M H₂PO₄ was sandwiched between Teflon tape and added to the bottle. Then, 90 mg of magnesium oxide was added to volatilize NH₃, and the bottle was immediately capped and incubated for 7 days on an orbital shaker/incubator at 40°C to allow NH₃ to be completely trapped as NH₄⁺ on the acidified filter. Filters were analyzed for δ¹⁵N values (precision <0.2‰) by combustion on an elemental analyzer coupled to an isotope ratio mass spectrometer (Finnigan MAT Delta S, San Jose, CA) 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 NH₄⁺ on filter disks, we also similarly analyzed ammonium sulfate solutions with known δ¹⁵N values. We obtained equivalent δ¹⁵N values (within 0.2‰) after diffusion of these standards.

Additionally, we analyzed a subset of precipitation samples (n = 53) for NO₃⁻ isotopic composition (δ¹⁵N and δ¹⁸O) using Pseudomonas aureofaciens and the denitrifier method [Casciotti et al., 2002] to generate N₂O for analysis on an isotope ratio mass spectrometer. We used U.S. Geological Survey (USGS) 32 and 34 reference materials (for δ¹⁵N) and USGS 34 and 35 (for δ¹⁸O) to express the data in δ notation relative to atmospheric N₂.
and Vienna SMOW for N and O, respectively. Mean accuracy was 0.34% for $\delta^{15}\text{N}$ and 0.39‰ for $\delta^{18}\text{O}$, assessed by comparing the difference between measured versus known values of USGS 35 (for $\delta^{15}\text{N}$) and USGS 32 (for $\delta^{18}\text{O}$) analyzed as unknowns. Sample precision, determined by standard deviations of several samples analyzed in triplicate, was 0.08‰ for $\delta^{15}\text{N}$ and 0.26‰ for $\delta^{18}\text{O}$.

### 2.3.1. Nitrogen Isotope Ratios of PM$_{2.5}$

We sampled 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 cm $\times$ 25 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$_{2.5}$ samplers. Comparisons of $\delta^{15}\text{N}$ of NH$_4^+$ extracted from quartz and Teflon filters sampled in Salt Lake City (see details below) showed no significant differences. Prior to sampling, quartz filters were precombusted at 500°C for 4 h 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$_{2.5}$ sampling, larger particles were removed with slotted microquartz fiber filters (TE-230-QZ, microquartz-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 $-20^\circ\text{C}$. For isotope analysis of NO$_3^-$ and NH$_4^+$ in PM$_{2.5}$, filters were immersed for 24 h in deionized water and solutions were filtered to 0.45 $\mu\text{m}$. Values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO$_3^-$ were determined by the denitrifier method and $\delta^{15}\text{N}$ of NH$_4^+$ via diffusion as described above.

Bulk PM$_{2.5}$ subsamples collected on quartz filters were also analyzed for total N content and $\delta^{15}\text{N}$ 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 Keck Carbon Cycle Accelerator Mass Spectrometry Facility of University of California, Irvine. Data were corrected for the N mass (1.4 $\mu\text{g}/\text{cm}^2$) and $\delta^{15}\text{N}$ 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-effect models, where sampling sites were treated as random effects to account for temporal autocorrelations. We separately tested for differences among sites in each valley using analysis of variance (ANOVA). We also binned the data into two seasons (November–March and April–October) to allow for seasonal comparisons between valleys while minimizing excessive post hoc comparisons over finer time scales (i.e., comparing all months). The latter time period represents the predominant growing season in our study area. We did not statistically compare our samples with NADP data given that they represent two different sample types (i.e., bulk versus wet deposition) but rather report NADP data for heuristic comparisons. We assessed cumulative bulk N deposition for 2014 as the product of precipitation amount and measured N concentrations at our sites; 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 to early April 2014. Total bulk deposition N concentrations were statistically equivalent between valleys during the rest of our observation period (December 2013 to 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 (GAMs) with a Gaussian link function, fitted using the mgcv package in R [Wood, 2006]. This method allowed us to test for significant seasonal patterns and also to test whether the two valleys had significantly different temporal patterns in N concentrations or $\delta^{15}\text{N}$—i.e., whether including a separate trend for each valley or site was statistically optimal. 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 Akaike information criterion.
3. Results and Discussion

3.1. Spatial and Temporal Patterns in Bulk Deposition Inorganic N Concentrations

Contrary to our hypothesis that differences in urban versus agricultural land use would affect total bulk N deposition and speciation, fluxes and concentrations of NH$_4^+$ and NO$_3^-$ did not significantly differ between Salt Lake and Cache Valley sampling sites on an annual basis (Figure 2). Ammonium concentrations in bulk deposition at the Salt Lake and Cache Valley sites were 0.45 ± 0.02 and 0.51 ± 0.04 mg N L$^{-1}$ (means and standard errors), respectively, and NO$_3^-$ concentrations were 0.45 ± 0.03 and 0.39 ± 0.04 mg N L$^{-1}$, respectively (Figure 2). However, bulk deposition NO$_3^-$ concentrations (but not NH$_4^+$) differed seasonally between valleys. During the growing season (April–October), NO$_3^-$ was significantly greater at the Salt Lake (0.65 ± 0.10 mg N L$^{-1}$) than the Cache Valley (0.42 ± 0.08 mg N L$^{-1}$) sites ($p < 0.01$). This pattern was predominantly driven by a peak in NO$_3^-$ at the Salt Lake sites during June and July that was not observed at the Cache Valley sites (Figure 3).

Overall, concentrations of NH$_4^+$ and NO$_3^-$ did not significantly differ among sites in a given valley, despite the inclusion of paired wildland sites (ANOVA, $p > 0.05$). Median N concentrations in bulk deposition at the Salt Lake and Cache Valley sites were also of similar magnitude to median wet deposition N concentrations at the Green River NADP site (NO$_3^-$ = 0.34, 0.27, and 0.25 mg N L$^{-1}$ and NH$_4^+$ = 0.37, 0.40, and 0.38 mg N L$^{-1}$, respectively; Figure 2). The Green River site was located 250–300 km southeast of these valleys in a relatively small town (~1000 people). Together, these data suggest regional congruence of bulk deposition N inputs to these northern Utah valleys as well as the nearby landscape, which were dominated by the wet deposition component.

However, median bulk deposition N concentrations at the Salt Lake and Cache Valley sites greatly exceeded wet deposition concentrations at several other more remote NADP sites in the region (Figure 2). This contrast supports the importance of local emissions in driving N deposition to the Salt Lake and Cache Valley sites, with impacts that declined with distance. 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$^{-1}$) for NO$_3^-$ and NH$_4^+$, respectively; Figure 2) and were more than twofold greater than the Pinedale and Craters of the Moon NADP sites (NO$_3^-$ = 0.10 and 0.08 mg N L$^{-1}$ and NH$_4^+$ = 0.12 and 0.20, respectively; Figure 2). In contrast to the remote NADP sites, median NO$_3^-$ concentrations at the Logan NADP site (located in the Cache Valley) were only slightly lower (0.23 mg N L$^{-1}$) than the bulk deposition values measured at the nearby sites sampled in this study (0.27 mg N L$^{-1}$), despite the fact that they only reflected wet deposition. This finding suggests a relatively minor year-round contribution of dry deposition to the bulk deposition fluxes that we measured, which
excluded the influence of plant canopies on dry deposition capture. Intriguingly, median Logan NADP wet deposition NH$_4^+$ concentrations were approximately twofold greater than our bulk deposition NH$_4^+$ (0.79 versus 0.40 mg N L$^{-1}$); possible contributing mechanisms are discussed in greater detail below.

To reiterate, we found similar annual bulk deposition N concentrations across disparate sites in the urban Salt Lake and agricultural Cache Valleys, which in turn were similar to wet deposition from the Green River NADP site. This pattern contrasts with previous work in California that documented increasing NO$_3^-$ deposition with proximity to urban versus agricultural emission sources [Tulloss and Cadenasso, 2015]. However, our findings were similar to the results of Lohse et al. [2008], who found no significant differences in N deposition among wildland and urban sites upwind and downwind of Phoenix, AZ. Here overall similarities in NO$_x$ production between the Salt Lake and Cache Valleys, indicated by similar boundary layer NO$_x$ concentrations, may have contributed to patterns in bulk deposition NO$_3^-$ concentrations among our study sites. Tropospheric NO$_x$ typically has a short lifetime (hours) prior to oxidation to NO$_3^-$ [Beirle et al., 2011].

Mean NO$_2$ 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 25th and 75th percentiles of NO$_2$ were 5 and 22 ppb for the

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). (a and b) Nitrate and NH$_4^+$ are shown, respectively. Samples collected in this study spanned from December 2013 to February 2015. The black lines represent the GAM fits for the Salt Lake and Cache Valley bulk deposition samples, and the grey lines represent the GAM fits for the NADP sites. (c) Daily and (d) weekly cumulative precipitations measured near our Salt Lake and Cache Valley sites are shown.
Salt Lake site and 4 and 16 ppb for the Cache Valley site. The difference in mean NO$_2$ concentrations between the valleys (~27% greater in Salt Lake) was very similar to the difference in median bulk deposition NO$_3^-$ concentrations between valleys (~26% greater in Salt Lake; Figure 2), despite the fact that these differences were not statistically significant. Also, the greater peak in summertime NO$_3^-$ concentrations at the Salt Lake relative to the Cache Valley sites (indicated by the greater 75th percentile but similar 25th percentile NO$_2$ value) may have driven the significant summertime increase in bulk deposition NO$_3^-$ at the Salt Lake Valley sites mentioned above.

Bulk deposition NH$_4^+$ concentrations also significantly increased during summer according to the temporal function fit by the GAM (Figure 3a) but did not differ between valleys on a seasonal basis. The similarity in bulk NH$_4^+$ concentrations between valleys was surprising given the large differences between putative urban and agricultural NH$_3$ sources—i.e., the prevalence of feedlots and fertilized agriculture in the Cache Valley, which are thought to dominate NH$_3$ emissions at the global scale [Hertel et al., 2012]. A scale mismatch between the location of NH$_3$ emission hot spots and our measurement sites may have contributed to this result. For example, the median wet deposition NH$_4^+$ concentration at the Logan NADP site (0.79 mg N L$^{-1}$) was approximately double that of the median bulk deposition NH$_4^+$ concentrations at the other Cache Valley sites we measured in this study (0.40 mg N L$^{-1}$), despite their similar median NO$_3^-$ concentrations. The Logan NADP site was located within 1 km of several cattle feedlots, whereas the sites that we sampled were farther away (~10 km) from this particular area.

These patterns suggest that local impacts of agricultural NH$_3$ emissions on wet deposition NH$_4^+$ may be manifested over finer spatial scales (e.g., <10 km) than reflected by valley-scale measurements. Accordingly, the sites we sampled may not have received a strong NH$_3$ influence from animal production despite their close proximity to other agricultural sources and the overall dominance of agricultural land use in the Cache Valley.

In support of this interpretation, other studies observed declining NH$_3$ concentrations or bulk NH$_4^+$ deposition fluxes within hundreds of meters of agricultural point sources [Fowler et al., 1998; Fahey et al., 1999]. Previous work in the Cache Valley showed that atmospheric 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 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 sampling event (total n = 119) in either valley were 0.22 mg N L$^{-1}$ for NH$_4^+$ and 0.13 mg N L$^{-1}$ for NO$_3^-$ but reached as high as 2.26 and 0.94 mg N L$^{-1}$, respectively. For context, mean NH$_4^+$ and NO$_3^-$ concentrations measured 0.48 and 0.42 mg N L$^{-1}$, respectively.

Finally, in addition to patterns in emissions, the removal of atmospheric reactive N by plants [Davidson and Ringerlee, 1997; Sparks, 2009] may also have contributed to variability in bulk deposition values and deviation from expected land use trends. In particular, the presence of greater summer canopy cover from the row crops and pasture in the Cache Valley, compared to the smaller street-tree canopy in the Salt Lake Valley sites, may have facilitated greater net plant uptake of NH$_3$ and NO$_2$ in the former sites. This effect could have a significant impact on atmospheric N concentrations in each airshed, not just in the vicinity of the canopy, given the documented magnitude of foliar N uptake [Sparks, 2009] and a well-mixed atmospheric boundary layer. Disparities in plant canopy cover may have contributed to observed seasonal differences in NO$_2$ concentrations and bulk NO$_3^-$ deposition between valleys, while partially attenuating agricultural NO$_2$ and NH$_3$ emissions to the atmosphere.

As with inorganic N, annual bulk deposition DON concentrations were also similar between valleys, with means of 0.14 ± 0.04 and 0.14 ± 0.05 mg N L$^{-1}$ 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 DON typically contributed between 17 and 43% (interquartile range) of total precipitation N [Cape et al., 2011]. The data in our present study fell below this range (~13% of total N), lower than these previous estimates. 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.
3.2. Wet Versus Dry Contributions to Bulk N Deposition

The Salt Lake and Cache Valley bulk deposition data showed a greater proportion of extreme NO$_3^-$ and NH$_4^+$ and concentration values that were ≥1.5 times the interquartile range (denoted in Figure 2 as circles) as compared with the NADP data, indicative of dry deposition inputs. Significant temporal differences in NO$_3^-$ concentrations between the Salt Lake/Cache Valley bulk deposition samples and the NADP wet deposition samples were reflected by trends in the GAM smooth functions, which showed two large peaks in June/July and October/November in our bulk deposition samples relative to the NADP samples (Figure 3). These high values, especially for NO$_3^-$, implied the importance of increased summertime dry deposition in both valleys that was not captured by the NADP wet deposition sampling. The significant difference in summertime NO$_3^-$ concentrations between valleys (described above) may have been driven by increased dry deposition in the Salt Lake Valley sites, which showed a pronounced NO$_3^-$ peak in June and July. 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 more uniform (Figure 3), and significant dry NO$_3^-$ deposition to the funnel collector surfaces was only apparent sporadically during summer and late fall.

Intriguingly, winter NO$_3^-$ concentrations were statistically similar between the bulk deposition data obtained in this study and wet deposition data for the remote NADP sites. This suggests that little winter NO$_3^-$ dry deposition was associated with local atmospheric reactive N emissions from the Salt Lake and Cache Valleys, despite the high concentrations of NO$_3^-$-rich 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 midelevation 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 NO$_3^-$ concentrations, summer NH$_4^+$ concentrations were similar between the Salt Lake/Cache Valley sites and the regional NADP sites (Figure 3). However, they diverged in winter, when the Salt Lake and Cache Valley samples had slightly but significantly greater NH$_4^+$ (note the difference between the GAM fits; Figure 3). This difference may imply a greater and more widespread influence of urban and agricultural NH$_3$ emissions on 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], perhaps leading to increased atmospheric NH$_x$ concentrations and NH$_4^+$ deposition relative to wildland areas.

3.3. 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$^{-1}$ yr$^{-1}$ (Figure 4). Bulk deposition rates peaked in July and August, and scaled relatively closely with cumulative precipitation amount, indicating a lack of strong seasonal variation in N inputs (Figure 4). These N deposition rates are modest compared with sites impacted by urban emissions from Los Angeles, CA: ~30–90 kg N ha$^{-1}$ yr$^{-1}$, measured using throughfall deposition under forested canopies [Fenn et al., 2003]. However, cumulative N deposition in our study equaled or exceeded measurements and estimates from many remote wildland sites in the western United States (~1–4 kg N ha$^{-1}$ yr$^{-1}$) [Williams and Tonnesen, 2000; Baron et al., 2011] and was comparable to wet + dry 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$^{-1}$ yr$^{-1}$) from 2011 to 2013, derived by combining sparse measurements with an atmospheric model [Schwede and Lear, 2014]. Our data suggest that local differences in urban versus agricultural land use do not necessarily affect these regional wet-deposition estimates. However, if N deposition was greater at our valley sites proximate to emission sources as compared with more remote montane areas in the region (i.e., tens of kilometers away [Hall et al., 2014]), our data suggest that this current model might overestimate wet deposition.

Although we saw significant evidence for summer dry deposition NO$_3^-$ inputs as described above, our data did not reflect the very high dry deposition N inputs modeled for this region (>12 kg N ha$^{-1}$ yr$^{-1}$; NADP total
deposition maps; http://nadp.isws.illinois.edu/committees/tdep/tdepmaps/preview.aspx#n_wd). This discrepancy likely reflects the fact that the HDPE funnel collectors used here conservatively sampled dry deposition relative to other more complex natural surfaces but also suggests that the model may have overestimated the total area-weighted dry deposition for this region, which has highly variable canopy cover that changes with season, land use type, and landscape position (valley versus montane). Multilayered 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 monolayered surfaces—bare soil, rock, pavement, and rooftops—that represent a substantial portion of urban, agricultural, and wildland landscapes in our semiarid study region during much of the year.

3.4. Stable Isotope Composition of Inorganic N Deposition and PM$_{2.5}$

Contrary to our hypothesis that differences in biogenic and fossil fuel reactive N sources would be reflected in N isotope compositions in the Salt Lake and Cache Valleys, we found no significant differences in $\delta^{15}$N values between valleys for either bulk deposition NH$_4^+$ (Figure 5a) or PM$_{2.5}$ (discussed below). Bulk deposition $\delta^{15}$N of NH$_4^+$ varied widely, between $-17.4$ and $24.1\%_o$ (mean $= -0.8 \pm 0.5\%_o$), but showed no consistent seasonal trend according to the GAM smooth function of $\delta^{15}$N values over time (Figure 5a). We occasionally observed extremely high variability in $\delta^{15}$N of NH$_4^+$ and NH$_3$ concentrations among sites within a valley during a single storm event (exceeding 10$\%_o$ and 1 mg N L$^{-1}$, respectively). This variability is indicated by the vertical distance among points of the same color on a given sampling date in Figure 5. This temporal variability is consistent with fine-scale spatial heterogeneity in NH$_3$ sources as discussed above and variable contributions of particulate N (as discussed below). It also likely reflects spatial and temporal variations in isotope fractionation during scavenging of NH$_3$ from the atmosphere over the course of precipitation events [Heaton, 1987; Heaton et al., 1997; Xiao et al., 2012], which can function analogous to a Rayleigh distillation. Biogenic NH$_3$ is typically thought to have lower $\delta^{15}$N values than fossil fuel NH$_3$, but few measurements have constrained this variation. Importantly, $\delta^{15}$N values of these sources potentially overlap [Frank et al., 2004; Skinner et al., 2006; Felix et al., 2013]. This source

Figure 4. (a) Cumulative N deposition and (b) precipitation measured during 2014 at sites in the Salt Lake Valley (blue circles; six sites) and Cache Valley (red circles; five sites).
variability, along with the spatial heterogeneity of biogenic NH₃ emissions and highly localized deposition described above, may have obscured isotopic differences between valleys despite their probable differences in NH₃ sources.

In contrast to NH₄⁺, δ¹⁵N of NO₃⁻ differed between valleys on a seasonal basis (Figure 5b). Values of δ¹⁵N of NO₃⁻ in bulk deposition were significantly lower (p < 0.01) in the Cache Valley (−4.5 ± 0.8‰) than in the Salt Lake Valley (−1.3 ± 0.5‰) during the growing season (April–October) as assessed with ANOVA, despite the fact that a single GAM function for both valleys adequately described the overall annual trend. This summertime decrease is consistent with an increased summertime biogenic NOx contribution from fertilized Cache Valley agricultural soils, as NOx derived from soil microbes tends to have lower δ¹⁵N values than most fossil fuel sources [Li and Wang, 2008; Walters et al., 2015]. On an annual basis, δ¹⁵N of NO₃⁻ measured 0.0 ± 0.5‰ and was statistically equivalent between valleys. Considering both valleys together, δ¹⁵N of NO₃⁻ showed a significant seasonal trend (indicated by the GAM fit) with lower values during the growing season (Figure 5b).

Freyer [1991] found a similar ~5‰ summertime decline in δ¹⁵N of NO₃⁻ in European precipitation and speculated that temperature-dependent isotope exchange reactions among atmospheric NOy species and decreased contributions of particulate NO₃⁻ could also be responsible for seasonal patterns in δ¹⁵N of NO₃⁻, in addition to potential changes in NOx sources. Values of δ¹⁸O in bulk deposition NO₃⁻ varied between 63.7 and 92.6‰ (mean 73.2 ± 0.9‰) and also displayed a significant seasonal trend of lower values during the growing season (Figure 5c). This pattern is consistent with seasonal variation in atmospheric HNO₃ formation pathways [Michalski et al., 2003] and does not necessarily imply variation in NOx sources to the atmosphere.

Mean δ¹⁵N values in bulk PM$_{2.5}$ (15.6 ± 1.4‰) and the NO₃⁻ (8.8 ± 0.7‰) and NH₄⁺ (22.5 ± 1.7‰) components of PM$_{2.5}$ were significantly greater (p < 0.0001) than bulk deposition δ¹⁵N of NO₃⁻ and NH₄⁺.

Figure 5. Values of δ¹⁵N in (a) NH₄⁺ and (b and c) NO₃⁻ in a subset of precipitation samples from the Salt Lake Valley (blue circles) and Cache Valley (red circles).
studies consistently found ammonium nitrate and total PM2.5 mass increase during winter [Hand et al., 2012]. Thus, one plausible interpretation of the occasionally high δ15N values for biogenic or fossil fuel NH3 sources described above. A variable contribution of δ15N-enriched particulate NO3− frequently exceeded 0‰, greater than many previous estimates of δ15N values for biogenic or fossil fuel NH3 sources described above. A variable contribution of δ15N-enriched particulates thus provides a plausible explanation for sporadically high δ15N values of deposition NH4+, an interpretation that appears to have received little attention in the literature. This interpretation is bolstered by contrasting our results with wet deposition δ15N 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 δ15N of NH4+ values <0‰ for precipitation samples with no dry deposition component. These studies were also located in areas impacted by mixtures of urban and agricultural NH3 sources, as were our study sites; consequently, the large positive δ15N deviations we observed in some samples could be parsimoniously explained by a variable contribution of dry particulate NH4+ deposition collected in our bulk samplers, which was not sampled in these wet deposition studies. Similarly, values of δ15N in bulk deposition NO3− occasionally reached as high as 8.7‰, similar to the mean values in PM2.5 (8.8 ± 0.7‰; Figure 6). Therefore, our bulk deposition NO3− δ15N values could also potentially be interpreted as a variable mixture of δ15N-enriched particulate NO3− and δ15N-depleted gaseous HNO3, in addition to a mixture of isotopically variable NO3− sources as discussed above. Overall, the mass- and volume-weighted isotopic compositions and standard errors of δ15N in NH4+ and NO3− in bulk deposition measured −1.6 ± 0.4 and 0.8 ± 0.5‰, respectively. Given that volume-weighted mean concentrations of NH4-N and NO3-N measured 0.34 ± 0.01 and 0.24 ± 0.01 mg N L−1, respectively, weighted δ15N of total inorganic N measured −0.6 ± 0.7‰. Because relatively few comprehensive studies of the isotope composition of bulk N deposition have been conducted, these measurements provide a useful reference for future studies. (Figure 6). The NH4+ component of PM2.5 had especially high δ15N values. These measured 24.1 ± 2.3 and 20.1 ± 1.6‰ in the Salt Lake and Cache Valley sites, respectively, but differences were not statistically significant. Values of δ15N of NO3− in PM2.5 were much lower than NH4+ of PM2.5 but were still significantly greater than δ15N of NO3− observed in bulk deposition (Figure 6). In the Salt Lake and Cache Valleys, δ15N of NO3− in PM2.5 measured 9.5 ± 1.0 and 7.7 ± 0.5, respectively, and did not significantly differ. Values of δ18O in NO3− of PM2.5 measured 81.6 ± 2.7‰, similar to bulk deposition. Annual mean concentrations of PM2.5 were similar at monitoring sites in both study valleys during 2013 and 2014 (Utah Department of Air Quality; http://www.airmonitoring.utah.gov/dataarchive/).

The high δ15N values of PM2.5 are consistent with an ~33‰ equilibrium fractionation between gaseous NH3 and particulate NH4+ and ~21‰ for ammonium nitrate relative to nitric acid vapor [Heaton et al., 1997]. These fractionations lead to much greater δ15N in PM2.5 relative to gaseous precursors. Individual PM2.5 samples varied between 17.3 and 31.4‰ in δ15N of NH4+ and overlapped with the most enriched values of δ15N of NH4+ in bulk deposition (Figure 6). The bulk deposition δ15N values >10‰ exceed most previous wet deposition measurements [Heaton, 1987; Fukuzaki and Hayasaka, 2009; Jia and Chen, 2010; Xiao et al., 2012]. Concentrations of the ammonium sulfate portion of PM2.5 remain relatively consistent throughout the year in our study area, despite the fact that ammonium nitrate and total PM2.5 mass increase during winter [Hand et al., 2012]. Therefore, our bulk deposition NO3− δ15N values could also potentially be interpreted as a variable mixture of δ15N-enriched particulate NO3− and δ15N-depleted gaseous HNO3, in addition to a mixture of isotopically variable NO3− sources as discussed above. Overall, the mass- and volume-weighted isotopic compositions and standard errors of δ15N in NH4+ and NO3− in bulk deposition measured −1.6 ± 0.4 and 0.8 ± 0.5‰, respectively. Given that volume-weighted mean concentrations of NH4-N and NO3-N measured 0.34 ± 0.01 and 0.24 ± 0.01 mg N L−1, respectively, weighted δ15N of total inorganic N measured −0.6 ± 0.7‰. Because relatively few comprehensive studies of the isotope composition of bulk N deposition have been conducted, these measurements provide a useful reference for future studies. (Figure 6). The NH4+ component of PM2.5 had especially high δ15N values. These measured 24.1 ± 2.3 and 20.1 ± 1.6‰ in the Salt Lake and Cache Valley sites, respectively, but differences were not statistically significant. Values of δ15N of NO3− in PM2.5 were much lower than NH4+ of PM2.5 but were still significantly greater than δ15N of NO3− observed in bulk deposition (Figure 6). In the Salt Lake and Cache Valleys, δ15N of NO3− in PM2.5 measured 9.5 ± 1.0 and 7.7 ± 0.5, respectively, and did not significantly differ. Values of δ18O in NO3− of PM2.5 measured 81.6 ± 2.7‰, similar to bulk deposition. Annual mean concentrations of PM2.5 were similar at monitoring sites in both study valleys during 2013 and 2014 (Utah Department of Air Quality; http://www.airmonitoring.utah.gov/dataarchive/).
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]. It is uncertain whether concentrated urban or agricultural N emissions might alter the isotope composition of deposition measured in more remote ecosystems. Previous studies in natural ecosystems had a median δ^{15}N value of ~1.3‰ [Houlton and Bai, 2009], similar to our present data. These similarities imply that local urban or agricultural influences do not necessarily impart a significant isotopic signature to bulk deposition N inputs on an annual basis.

4. Conclusions

Despite the strong impacts of land use on NOx and NH3 emissions documented elsewhere [Galloway et al., 2004; Hertel et al., 2012], we conclude that substantial valley-scale differences in urban versus agricultural land use in northern Utah were not strongly manifested in the mean speciation, isotope composition, or fluxes of bulk atmospheric N deposition to our funnel collectors on an annual basis. Differences between valleys were only apparent during summer, when bulk deposition NO_{3}^{-} concentrations increased at the Salt Lake Valley sites, and δ^{15}N of NO_{3}^{-} was lower at the Cache Valley sites. Our data suggest that relatively coarse regional estimates of these parameters may suffice for use in ecosystem-scale N cycling models, although they may miss hot spots of NH3 emissions that are deposited very close to the source. Although median-measured bulk deposition N concentrations exceeded wet deposition concentrations from several remote NADP sites in the region, they were similar to wet deposition from another regional NADP site. 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 estimating total deposition to nonvegetated surfaces—soil, rocks, pavement, and rooftops—that represent a substantial portion of wildland, urban, and agricultural landscapes in the intermountain western United States, especially during fall and winter.

Values of δ^{15}N in atmospheric deposition are complex to interpret because they not only represent a mixture of reactive N sources varying in δ^{15}N but also a variable mixture of phases (gas, particulate, and aqueous) impacted by large isotope fractionations. Our data highlight the potential importance of the latter phenomenon. We found large differences between δ^{15}N of bulk deposition and PM_{2.5}, suggesting that temporal variation in particulate contributions to bulk N deposition could potentially obscure initial isotope differences among biological versus fossil fuel reactive N sources. Even where source δ^{15}N values differ, spatial and temporal heterogeneities in particulate contributions could decrease the power to detect these differences. Thus, we recommend caution when interpreting atmospheric δ^{15}N measurements solely in terms of mixtures of sources. This is especially important when sampling schemes may selectively capture gaseous versus particulate N as opposed to the entire atmospheric reactive N pool, thus leading to physical isotope fractionation.

References


