

Spatial trends of precipitation chemistry in the Central Plains region of the United States

Micheal Simpson¹ · Jason A. Hubbart²

Received: 10 October 2015 / Accepted: 29 February 2016 / Published online: 13 April 2016
© Springer-Verlag Berlin Heidelberg 2016

Abstract In the late 1970s, historically high concentrations of anthropogenic air pollutants in the United States prompted the development of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). While much has been learned since program inception, many long-term data sets have yet to be interpreted, the results of which will help guide changing policies. Given the lack of studies in the Central Plains of the Midwestern United States, spatial trends of the past 30 years are presented from ten NADP sites surrounding, and including, Missouri, USA. Concentrations of calcium were highest (0.40 mg/L) and lowest (0.14 mg/L) at north and southeast sites, respectively, with a westward trend of increasing concentration. Ammonium concentrations were highest (0.67 mg/L) at northern NADP locations, with all sites showing an average increase in concentration of 65 % from 1984 to 2014, including south central Iowa which showed an increase of 226 %. Sulfate concentrations were highest for eastern sites (1.70 mg/L), but showed an overall decrease of at least 50 % for all locations since the early 1980s. Nitrate concentrations decreased between 5 and 30 % for each site over the 30-year period. Alkalinity

increased between 10 and 25 % from southern to northern sites, respectively. When grouped into north–south, and east–west regions, significant differences ($p \leq 0.05$) were observed for all constituents, except potassium, between each region. Data syntheses, such as that presented here, advances understanding of long-term precipitation chemistry, thereby improving management strategies intended to mitigate atmospheric chemical deposition.

Keywords National trends network · Central Plains USA · Anthropogenic wet deposition · Atmospheric deposition · Precipitation chemistry · Missouri

Introduction

In 1978, the National Atmospheric Deposition Program (NADP) was initiated to collect wet-only (precipitation) deposition samples and monitor the long-term trends, concentrations, and geographic distributions of the chemical composition of atmospheric precipitation, including acids, nutrients, and base cations (Knapp et al. 1988). The implementation of the NADP was possible due to funding from the National Acid Precipitation Assessment Program (NAPAP), which was charged with the task of supplying improved understanding of acidic precipitation within the continental United States. The NADP comprises five networks, including the National Trends Network (NTN), the Atmospheric Integrated Research Monitoring Network (AIRMoN), the Mercury Deposition Network (MDN), the Atmospheric Mercury Network (AMNet), and the Ammonia Monitoring Network (AMoN), established in October of 1981, October of 1992, January of 1996, October 2009, October 2010, respectively (SAES-422 2014). The NTN remains the largest North American

✉ Jason A. Hubbart
Jason.Hubbart@mail.wvu.edu

Micheal Simpson
mjs5h7@mail.Missouri.edu

¹ Water Resources Program, Department of Soil, Environmental, and Atmospheric Sciences, School of Natural Resources, University of Missouri, 203 ABNR Building, Columbia, MO 65201, USA

² Institute of Water Security and Science, Davis College, Schools of Agriculture and Food, and Natural Resources, West Virginia University, 1098 Agricultural Sciences Building, Morgantown, WV 26506, USA

network that provides long-term records of wet deposition in the United States. Weekly composite samples are collected by site operators and shipped to the Illinois State Water Survey's Central Analytical Laboratory (CAL), located at the University of Illinois, Urbana-Champaign (Martin et al. 2000). Results of analyses are in the public domain and available from the NTN online database (nadp.isws.illinois.edu/data/NTN).

The Midwestern United States has been historically characterized with high emissions of acidic gases, and in particular, oxides of sulfur and nitrogen (Seinfeld and Pandis 1998; Lynch et al. 2000; Butler et al. 2001). The Midwest was previously identified as a major contributor to trans-boundary air pollution during acid rain negotiations between Canada and the United States (Fay et al. 1986; Kvale and Pryor 2006). Damage to Canadian lakes and forests from acid rain precursors have been shown to have a significant economic impact. Acid rain precursors consist primarily of oxidation of sulfur and nitrogen oxides (SO_x and NO_x). Those transformations generally occur slowly resulting in deposition that may occur at great distances from the source (Fay 1983). For example, previous estimates indicated that trans-boundary flow of sulfur emissions from the US into Canada is comprised 75 % of Canadian emissions, whereas the US import is 6 %,

primarily from anthropogenic sources (Galloway and Whelpdale 1980). Sources include biomass burning (Hileman 1990), and biogenic emissions (Guenther et al. 1989), both of which have increased in atmospheric concentration across the Midwestern United States in recent decades. Despite this, since the enactment of several legislative amendments of the Air Quality Act of 1967 (Public Law 90-148), national NO_x and SO_x emissions have decreased by 15 and 33 %, respectively (EPA 2003).

Although many studies of atmospheric wet deposition have been conducted in the Ohio River Valley (Lynch et al. 2000; Pryor et al. 2001; Baumgardner et al. 2002; Kvale and Pryor 2006), the Northeastern US (Martin et al. 2000; Elliot et al. 2007), and the Southeast (Grimshaw and Dolske 2002), there is a lack of such studies in the Central Plains region of the Midwestern United States. Additionally, previous work showed that precipitation amount and ion concentration are inversely proportional (Swank and Crossley 1988). However, few studies have been conducted that establish a clear connection between these two variables. Ultimately, little research has been conducted regarding the long-term trends of precipitation chemistry and atmospheric deposition over the Midwest. Given the implied need, the overarching objective of this investigation was to identify the spatial trends of precipitation

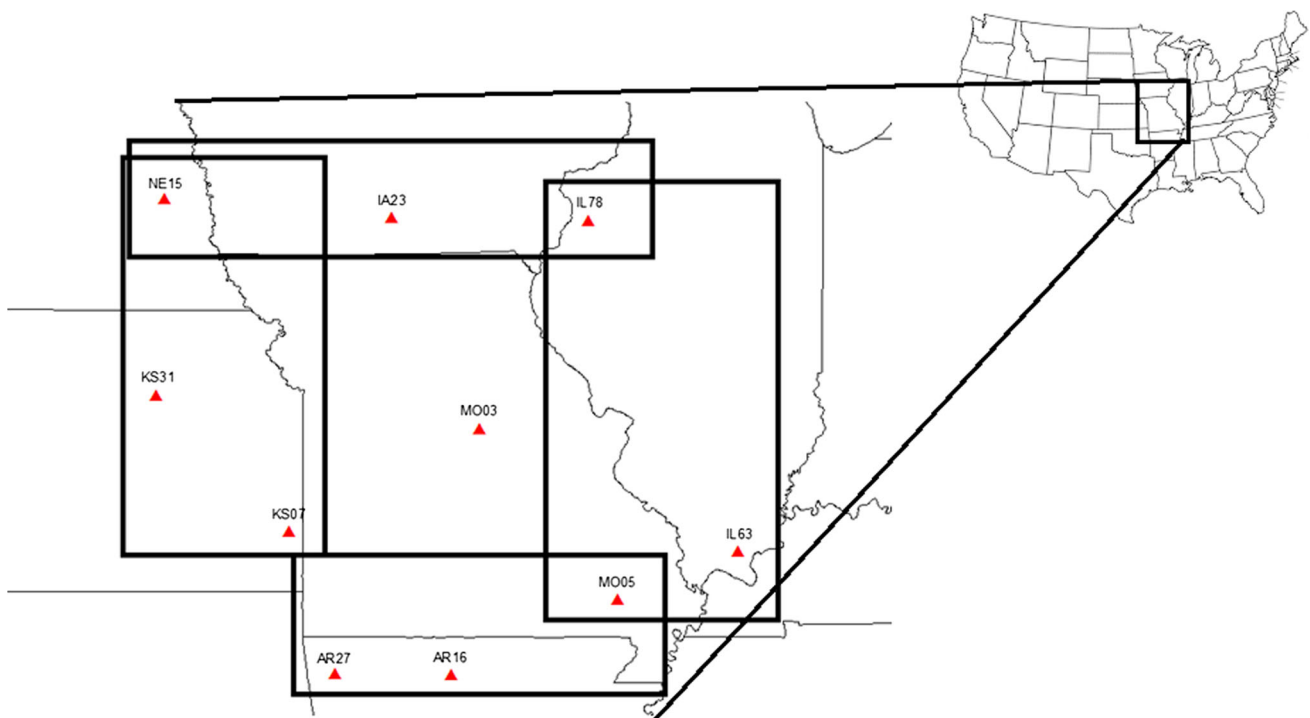


Fig. 1 National Atmospheric Deposition Program study site locations including: Ashland, MO (*MO03*), University Forest, MO (*MO05*), Farlington, KS (*KS07*), Konza Prairie, KS (*KS31*), Mead, NE (*NE15*), McNay Research Center, IA (*IA23*), Monmouth, IL (*IL78*), Dixon Springs, IL (*IL63*), Buffalo Point, AR (*AR16*), and

Fayetteville, AR (*AR27*). Sites were further grouped geographically, indicated by the **bolded black boxes** as northern (*NE15*, *IA23*, *IL78*), eastern (*IL78*, *IL63*, *MO05*), southern (*MO05*, *AR16*, *AR27*), and western (*NE15*, *KS31*, *KS07*)

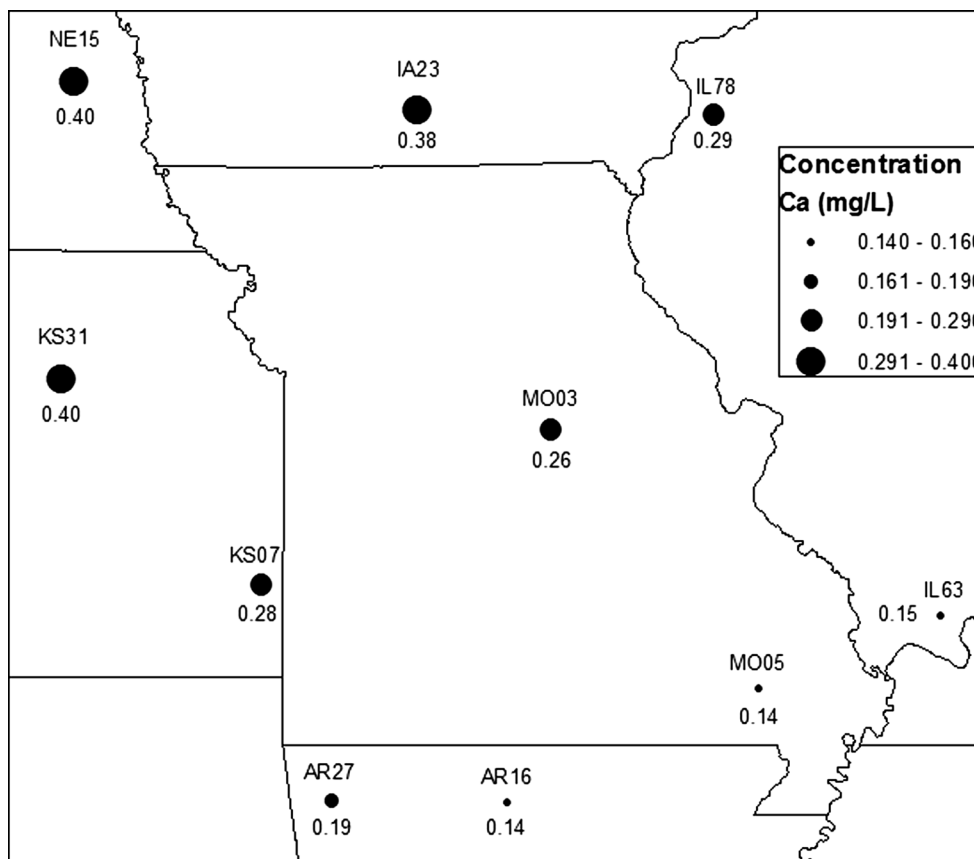


Fig. 2 Average calcium concentrations (mg/L) for each of the ten sites in the current study

chemistry data from ten NADP stations located in six Midwestern United States centralized in and around Missouri (Fig. 1). A sub-objective included comparing geographically grouped inter- and intra-specific differences in pollutant concentrations. This work represents one of few studies utilizing NADP/NTN long-term data to conduct a regional analysis of atmospheric pollutants. This is particularly true for the Central Plains region of the Midwestern United States and in particular, the state of Missouri.

Methods

Data for the current study were obtained from the NTN online database, and included datasets from Ashland, MO (MO03), University Forest, MO (MO05), Farlington, KS (KS07), Konza Prairie, KS (KS31), Mead, NE (NE15), McNay Research Center, IA (IA23), Monmouth, IL (IL78), Dixon Springs, IL (IL63), Buffalo Point, AR (AR16), and Fayetteville, AR (AR27) (Fig. 1). Weekly deposition data were aggregated to annual averaged data and included calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), ammonium (NH₄), nitrate (NO₃), chlorine (Cl),

sulfate (SO₄), and H⁺ (pH) from January 1, 1984 through December 31, 2014. Yearly aggregated data were used instead of weekly data since multiple events are combined by virtue of the weekly sampling regime, and meteorological information typically exhibits considerable variability (Shannon 1999). This approach, therefore, removed any biases associated with different synoptic regimes (Kvale and Pryor 2006), given that the concentration of chemical species in wet deposition is inversely proportional to the precipitation amount (Hansen et al. 1994; Beverland et al. 1998; Garben et al. 2004). To further account for this uncertainty, precipitation-weighted means (mg/L) (Latysh and Wetherbee 2012) were used in place of total wet deposition (kg/ha).

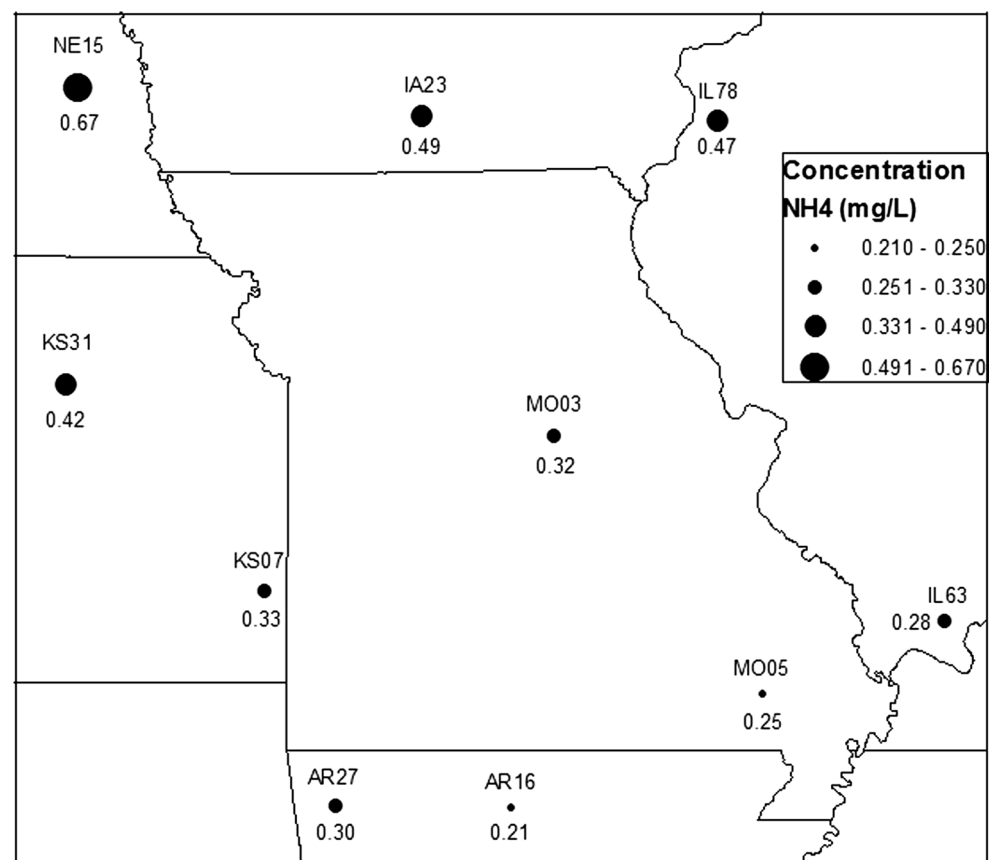
All NADP/NTN collectors are required to use an AeroChem-Metrics wet deposition sampler and Belfort 5-780 Universal recording precipitation gauge. Despite concern of missing light precipitation events by the wet collector due to a delay (i.e. precipitation threshold) in sampler opening (Pryor and Barthelmie 2005), the overall NADP/NTN precision determined from collocated samplers is thought to seldom exceed ±20 % (Nilles et al. 1994). Precipitation is collected when a sensor detects motion of precipitation, which triggers

Table 1 Percent difference of concentration from the beginning of the study (1984 for MO03, MO05, KS31, NE15, IL63, AR16, and AR27, 1985 for IA23 and KS07, and 1986 for IL78) to 2014

Site/constituent	Ca	Mg	K	Na	NH ₄	NO ₃	Cl	SO ₄	H ⁺
MO03	41.25	9.09	2.78	-16.85	84.98	-4.87	-15.94	-47.23	15.38
MO05	42.44	13.16	-40.98	-35.71	57.89	-12.03	-35.42	-45.56	13.17
KS07	83.41	12.00	-20.69	7.89	110.29	-7.17	-9.42	-43.06	20.81
KS31	27.08	-27.08	-21.95	-53.78	36.34	-36.72	-58.86	-49.97	20.52
NE15	19.41	-19.05	-14.71	-29.87	46.99	-22.12	-57.46	-55.16	23.47
IA23	30.98	14.71	145.45	-7.35	226.11	-22.10	-25.56	-51.60	25.57
IL78	43.64	19.23	70.59	29.63	52.04	-30.52	17.05	-61.94	22.83
IL63	5.36	-18.75	3.57	-29.13	16.30	-33.73	-34.23	-54.83	13.21
AR16	11.73	-21.21	8.33	-19.63	18.01	-22.79	-28.24	-43.23	9.34
AR27	-2.32	-32.35	-42.50	-26.61	3.74	-28.54	-20.97	-47.35	9.88

Negative numbers indicate a decrease in concentration since the beginning of the study

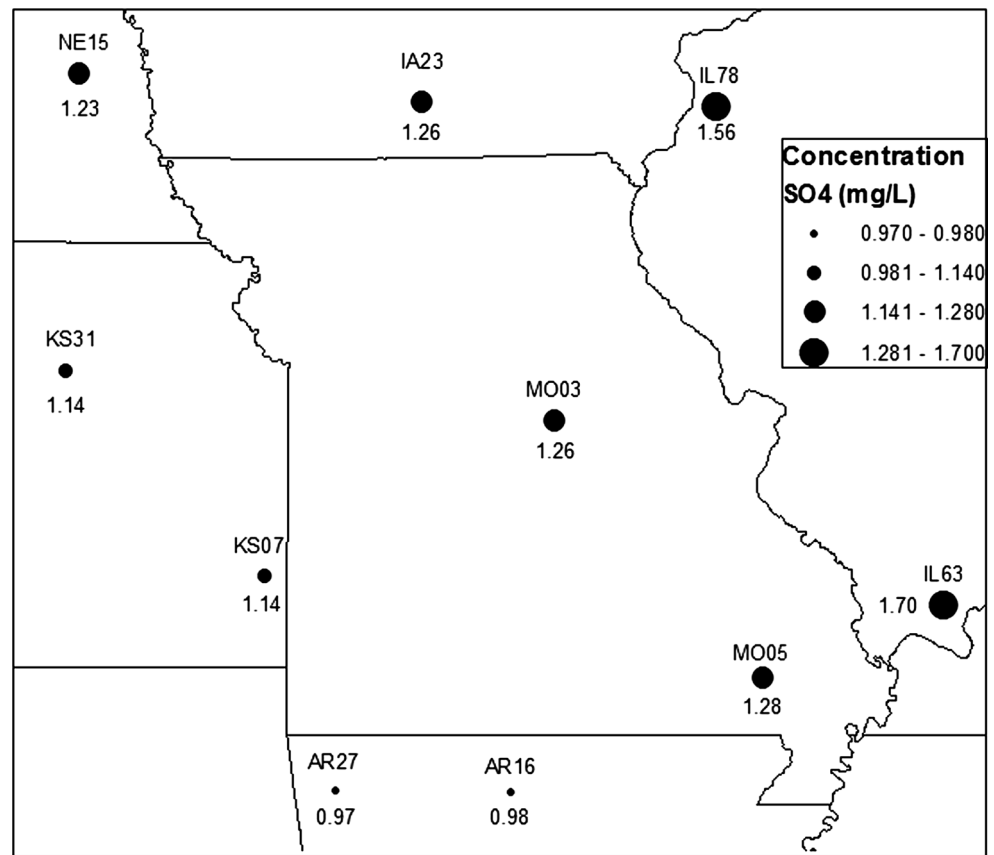
Fig. 3 Average ammonium concentrations (mg/L) for each of the ten sites in the current study



removal of a cover thus allowing precipitation to passively fall in the underlying container. This pre-sterilized container is collected once-weekly by a site operator, precipitation is bottled and shipped (using sterile handling techniques) to the Illinois Survey's Central Analytical Laboratory (CAL), located at the University of Illinois, Urbana-Champaign (Martin et al. 2000). For more information about field and lab methods, the reader is referred to the NTN program website: [http://nadp.](http://nadp.isws.illinois.edu/ntn/)

[isws.illinois.edu/ntn/](http://nadp.isws.illinois.edu/ntn/). The dates for the current study ranged from the beginning of the calendar year 1984 to the end of 2014 (i.e., 30 years), coinciding with the National Ocean and Atmospheric Administration (NOAA) and World Meteorological Organization (WMO) definitions of a climatological study. Three of the sites, KS07, IA23, and IL78, were installed within 2 years after the beginning of calendar year of 1984 with 29-, 29-, and 28-year time-series, respectively. Thus, for

Fig. 4 Average sulfate concentrations (mg/L) for each of the ten sites in the current study



all sites, excluding KS07, IA23, and IL78, the number of years analyzed was 30 ($n = 30$).

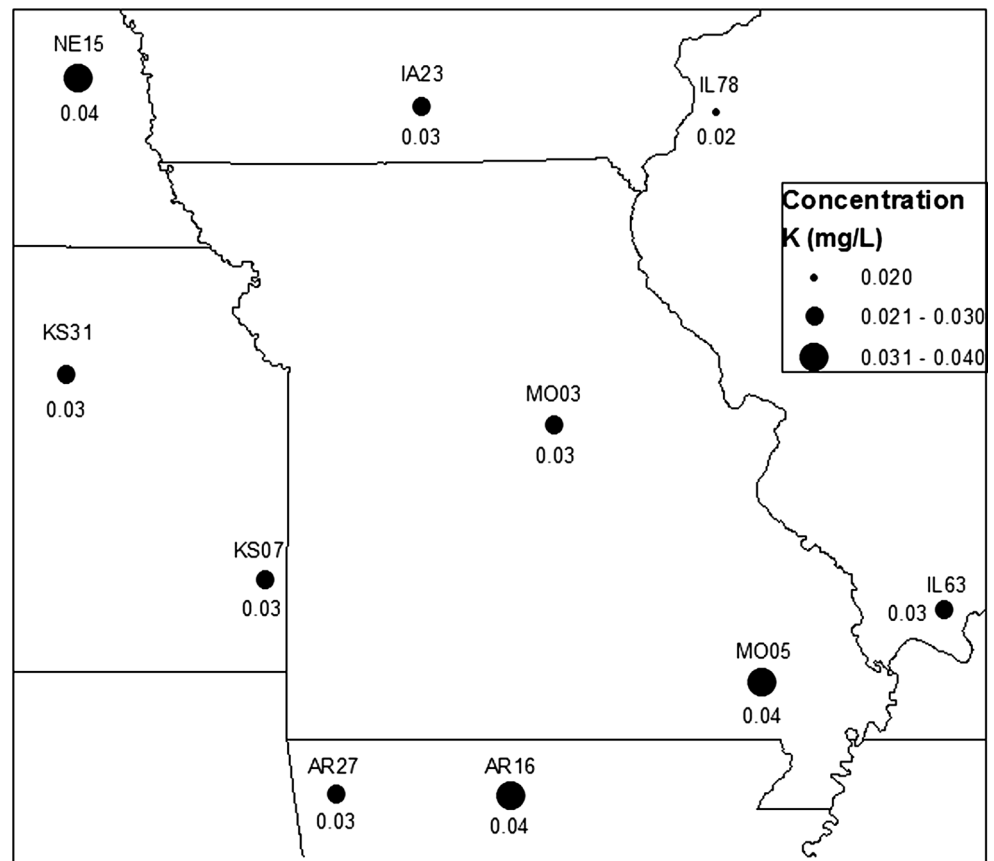
To improve the sensitivity of emission-related trend detection in concentrations, regional averaging was conducted to significantly reduce the effect of small-scale natural spatial variability (Renne et al. 1991; Shannon 1999). Sites were divided between western (NE15, KS31, and KS07), eastern (IL78, IL63, and MO05), northern (IA23, IL78, and NE15) and southern (AR16, AR27, and MO05) regions similar to previous studies (Venkatram et al. 1990; Renne et al. 1991) (Fig. 1). Such an approach reduces potential biases due to climatological variability, in particular, changes in seasonal intensity and frequency of precipitation (Shannon 1999). Data were tested for any violations of linearity using the Anderson–Darling test (Anderson and Darling 1952), collinearity through variance inflation factors (Antanasijevic et al. 2014), and homoscedasticity through the variance (square of the standard deviation). There were no geographic locations (north, south, east, or west) that significantly ($CI = 0.10$) violated these assumptions, allowing for the analyses to proceed without data transformations. Standard descriptive statistics were complemented by analysis of variance (ANOVA) and post hoc Tukey–Kramer multiple comparison tests were implemented to test whether significant

differences existed within and between each constituent group. (Tukey 1953; Kramer 1956; Kleinbaum et al. 2007).

Results and discussion

The highest average concentration of calcium was 0.40 mg/L for both KS31 and NE15, the two western-most sites (Fig. 2). Maximum values over the 30-year period were detected at KS31 (0.68 mg/L) and IA23 (0.67 mg/L), occurring in 2012 and 1988, respectively, whereas site KS31 had the highest standard deviation of calcium concentration (0.11 mg/L). The lowest concentration of calcium was observed at two southeastern sites, MO05 and AR16 (0.14 mg/L) which were also observed to have the smallest average calcium concentrations (0.09 mg/L). For all sites (excepting AR27, Fayetteville, Arkansas), calcium deposition increased over the 30-year period (Table 1). For example, concentration of Ca increased by approximately 85 % at KS07, but only 5 % at IL63, indicating a possible westward trend of increasing calcium concentration in precipitation. While it may not explain a westward trend, it is worth noting that this finding may be linked, in part, to the observation that the o-rings in the buckets used for shipping weekly samples prior to 1994 may have altered

Fig. 5 Average potassium concentrations (mg/L) for each of the ten sites in the current study



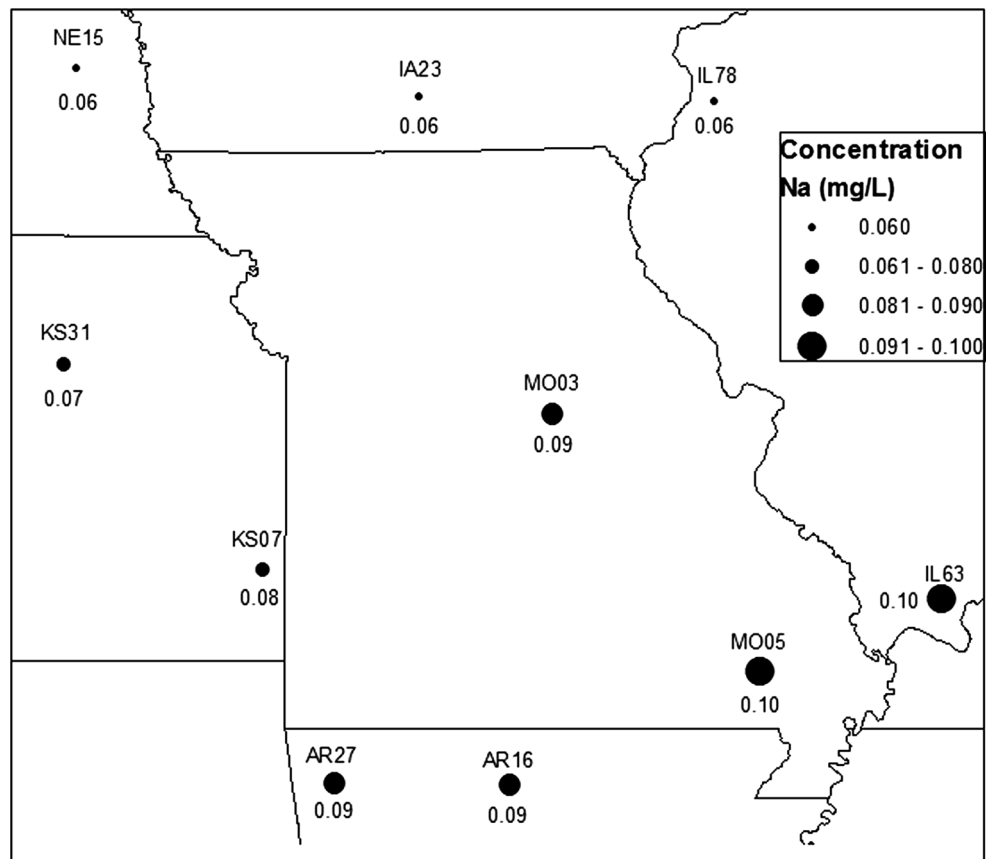
calcium ion concentration, particularly in low-volume samples, as shown by James (1992). A westward increasing trend of calcium concentrations may also be attributable to an increase of annual precipitation in the Midwestern states (Livezey et al. 2007).

The highest average ammonium concentrations were 0.47, 0.49 and 0.67 mg/L for IL78, IA23 and NE15, respectively (Fig. 3). These sites also had the highest maximum ammonium values of 0.61, 0.73, and 0.99 mg/L in 2012, 1988, and 2011, respectively. Conversely, the southern-most sites, AR16, MO05, and AR27, had the lowest average ammonium concentrations of 0.21, 0.25, and 0.30 mg/L, respectively. These trends appear to correspond to regional precipitation regimes. For example, average precipitation at IL78, IA23, and NE15 was approximately, 97, 86, and 71 cm/year, respectively, whereas for AR16, MO05, and AR27, precipitation averaged approximately, 122, 117, and 102 cm/year, respectively. In drier regions, such as observed at northern sites, ammonium ions are more readily volatilized from soil into the atmosphere (Elliot et al. 2007), resulting in more dry deposition relative to wet deposition. This relationship was shown to be related to decreased species diversity and vegetation productivity (Erisman et al. 2007). Additionally, as noted by Nilles and Conley (2001), ammonium

concentrations in precipitation increased in the Northeast between 1981 and 1998, which is postulated to be due in part to the growth in animal husbandry that has spread further into Midwestern states (Pryor et al. 2001). This observation is further validated in that no site recorded a decrease in ammonium concentration over the 30 years period of study (Table 1). In fact, IA23 recorded a 226 % increase in ammonium from 1985 to 2014 whereas AR27 showed the least increase (3.74 %) in ammonium from 1985 to 2014.

The Midwestern United States was previously identified with high emissions of acidic gases, specifically oxides of sulfur (Shannon 1999; Lynch et al. 2000). Results of the current work support previous findings (Table 1; Fig. 4) suggesting that sulfate concentrations remain the highest of the constituents measured by the NADP for each of the ten locations analyzed in the current work (excluding H^+ , a measure of pH). The highest concentrations of Sulfate were 1.81 and 1.56 mg/L from the southern and northern Illinois sites (i.e., IL63 and IL78), respectively. This finding is in general agreement with those of Baumgardner et al. (2002) who showed that Illinois ranked among the highest of states in the United States in terms of nitrate emissions. Higher values of sulfate were previously attributed to increased number of fossil-fuel burning facilities

Fig. 6 Average sodium concentrations (mg/L) for each of the ten sites in the current study



(Grimshaw and Dolske 2002). Notably, while Holland et al. (2004) suggested that mean annual sulfate emissions decreased between 31 and 44 % within the central Ohio Valley region as measured by Clear Air Status and Trends Network (CASTNet) sites between 1990 and 1999, the results presented here show a decrease of only 10 and 5 % from IL78 and IL63, respectively. The difference between study results may be attributable, at least in part, to above average rainfall in Illinois during the latter-half of the 2000s. Additionally, other eastern sites, including MO05 and IA23 recorded annual concentrations of ammonium of 1.28 and 1.26 mg/L, respectively. The southern-most sites, AR16 and AR27, had the lowest concentrations of sulfate (0.98 and 0.97, respectively), consistent with previous studies that showed greater deposition of sulfate in the northern and eastern states (Seinfeld and Pandis 1998; NADP/NTN 2003; Kvale and Pryor 2006). Ultimately, each site reported an average decrease in sulfate concentrations by approximately 50 % over the past 30 years, with IL78 and IL63 recording the largest overall changes (62 and 55 %, respectively) (Fig. 2). Concentration of nitrate was another constituent of great concern, providing impetus for Phase I and Phase II of the Title IV Acid Deposition Control, a division of the Air Quality Act of 1967 and its subsequent amendments (Public Law 101-549,

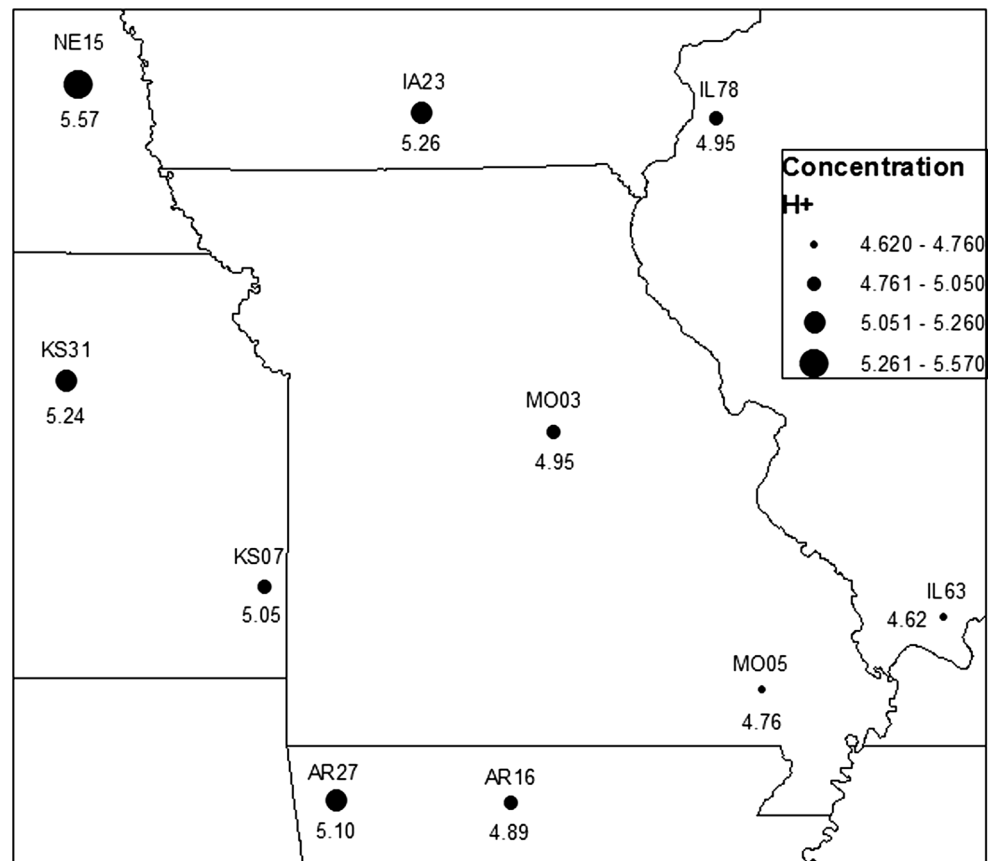
November 15, 1990). As a result, NO_x emissions decreased nationally by 15 % between 1983 and 2002 (EPA 2003).

The current work updates previous findings and includes an additional 12 years of data. During this time, each site reported further decreases in nitrate concentration ranging from 5 % at MO05 to 37 % at KS31. The highest concentration of nitrate was recorded at the northern sites IA23, IL78, and NE15 with values of 1.89, 1.75, and 1.74 mg/L, respectively. The southern sites, AR16 and AR27, recorded the lowest nitrate values of 1.03 and 1.02, respectively (Table 1). These results show a northeastward trend of increasing nitrate concentration, attributable, in part, to either the proximity of combustion plants, lightning, biogenic soil processes, or automobile emissions (Galloway et al. 2003; Elliot et al. 2007).

The average values of both magnesium and potassium did not exceed 0.04 mg/L for any of the ten sites, and did not show any spatial patterns between the 10 sites. There was, however, an observable trend of decreasing average potassium concentrations towards the west, while south eastern sites generally recorded increased concentrations of potassium (Fig. 5).

Sodium and chlorine decreased from 7 to 53 % at each site over the 30-year period, with the exception of KS07 which showed a sodium concentration increase of 7.89 %

Fig. 7 Average hydrogen ion concentrations for each of the ten sites in the current study



and IL78, which recorded an increase of chlorine concentration of 17.05 %. There was a southward increasing trend of sodium concentration, presumably related to the proximity to the Gulf of Mexico (i.e., the sea; Fig. 6). Additionally, the greatest decrease in sodium over the 30-year period was at KS31 (53.78 %) while the least decrease in sodium was at IA23 (7.35 %). An increase in the alkalinity of precipitation was detected for each site, ranging from 10 % (AR16 and AR27), to 25 % at IA23. The most acidic rain, based on lowest average pH, was recorded at MO05 and IL63, two southeastern locations, with values of 4.76 and 4.62, respectively. MO03 and AR16 were the only two sites with pH values below 5.00 (4.95 and 4.89, respectively). Additionally, there was an observable eastward decreasing trend in pH across the study area (Fig. 7).

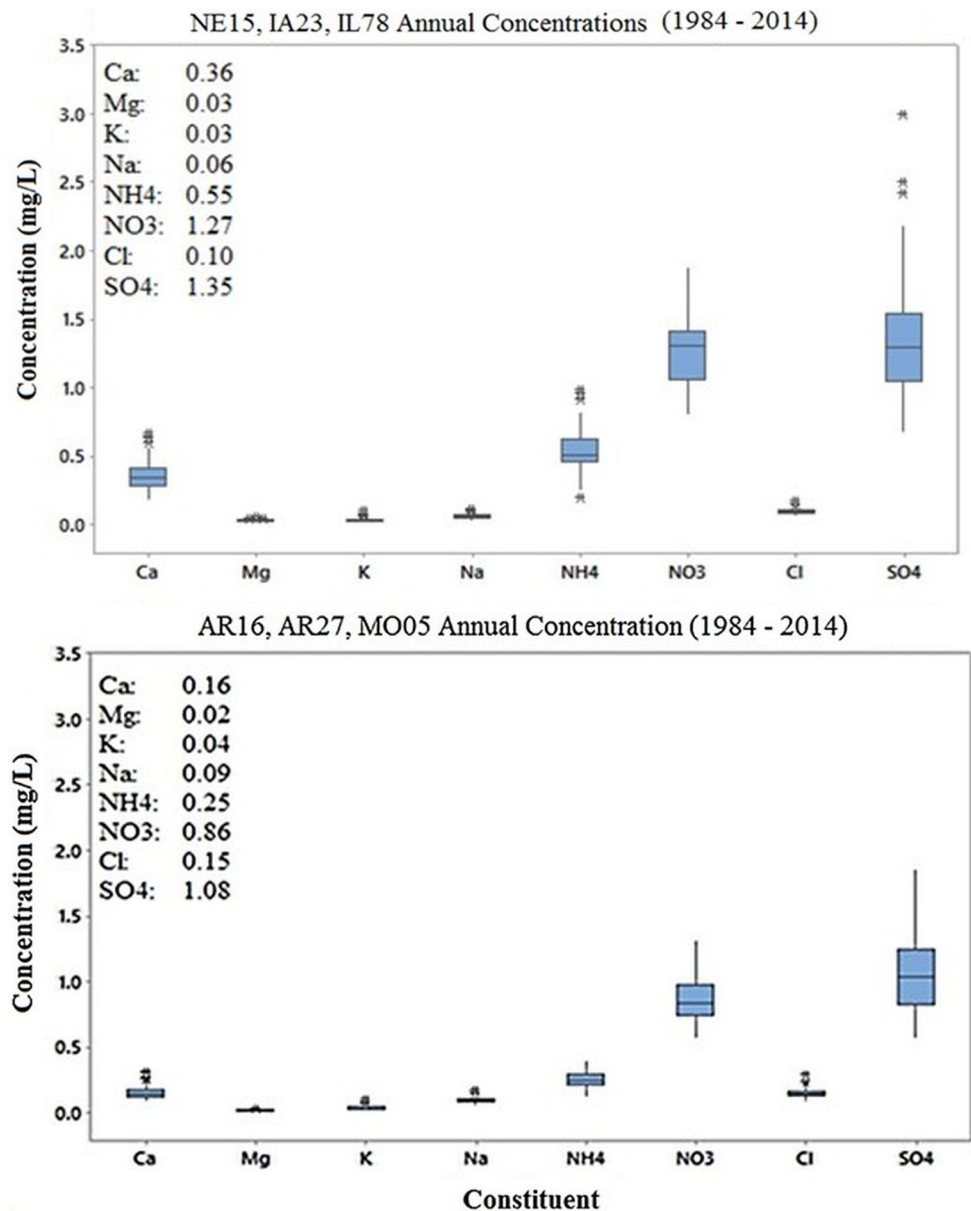
Geographically grouped sites: inter-specific differences

Northern sites (Fig. 1) had higher annual average concentrations of calcium (0.36 mg/L), magnesium (0.03 mg/L), ammonium (0.55 mg/L), nitrate (1.27 mg/L), and sulfate (1.35 mg/L) with a difference of means of 0.202, 0.001, 0.293, 0.411, and 0.270 mg/L, respectively (Fig. 8). Conversely, the southern sites had higher concentrations of

potassium (0.04 mg/L), sodium (0.09 mg/L), and chlorine (0.15 mg/L) with a difference of means of 0.004, 0.032, and 0.054 mg/L, respectively. The mean H⁺ concentrations in the north and south were 5.364 and 4.917 mg/L, respectively. This produced a difference of means of 0.348, resulting in a significant difference in hydrogen ions between the north and south regions ($p < 0.001$), in addition to all other constituents measured with the exception of potassium ($p = 0.091$). Magnesium ($p = 0.007$) and nitrate ($p = 0.010$) showed slightly significant p values, whereas calcium, sodium, ammonium, chlorine, and sulfate all showed highly significant differences ($p < 0.001$) for eastern-western comparisons. Potassium also varied spatially insignificantly ($p = 0.442$), indicating K concentrations are not variable over the Midwest.

Resultant trends are consistent with the findings of Parungo et al. (1990) and Ceron et al. (2002) who showed that coastal regions exhibit higher concentrations of sodium and chlorine. Lloyd (2010) also concluded that fluxes of sodium in the northern part of the Midwest were generally low (5–10 g Na ha⁻¹ week⁻¹), whereas areas closer to the coastline had sodium deposition in excess of 40 g ha⁻¹ week⁻¹. This correlates well with the results presented in that the southern sites (i.e., sites closer to the ocean) had higher concentrations of sodium and chloride.

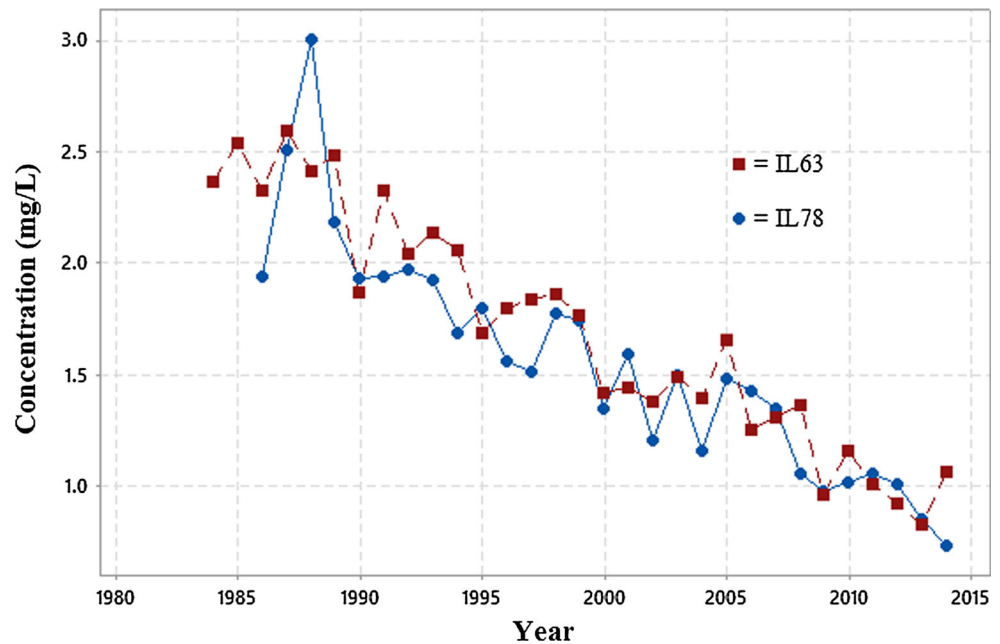
Fig. 8 Box-and-whisker plots for calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), ammonium (NH₄), nitrate (NO₃), chloride (Cl), and sulfate (SO₄) for Northern (NE15, IA23, and IL78) and Southern (AR16, AR27, and MO05) geographically grouped sites. Average ion concentrations are in mg/L. Stars indicate outliers for each NADP stations data



Results from Grimshaw and Dolske (2002) showed sodium concentrations in Florida to be between 14.5 and 19.5 $\mu\text{eq/L}$. Results presented here indicate continental sodium concentrations of 3.32 and 5.23 $\mu\text{eq/L}$ for northern and southern sites, respectively. Thus, Lloyd (2010) found sodium concentrations in coastal regions to be approximately four times greater than inland regions, which is consistent with the results presented here and those provided by Grimshaw and Dolske (2002). Lloyd (2010) further showed that sodium and chloride fluxes are not efficiently assimilated by rain, thereby resulting in significant differences between geographic locations.

The observation of higher ammonium concentrations in the northern sites is consistent with the findings of Nilles and Conley (2001) who noted greater ammonium deposition in the Midwest due to increased animal husbandry. Converting the results presented here from mg/L to $\mu\text{eq/L}$ resulted in average ammonium concentrations for northern and southern sites to be 30.30 and 19.59 $\mu\text{eq/L}$, respectively. These results are somewhat lower than results found by Martin et al. (2000) who reported ammonium concentrations of 30–40 $\mu\text{eq/L}$ for a forested ecosystem in New Hampshire. The discrepancy in concentrations may be attributable to weather systems that propagate over oceanic

Fig. 9 Sulfate concentrations in mg/L for IL78 (circles) and IL63 (squares) from 1984 and 1986 to 2014, respectively



waters and thus tend to exhibit lower concentrations of ammonia. For example, Junge and Gustafson (1958) and Brezonik et al. (1983) found ammonium concentrations in Florida to be 0.04 and 0.07 mg/L, respectively. A more recent study by Grimshaw and Dolske (2002) showed the average ammonium concentration in Florida to be, approximately 0.108 mg/L.

Sulfate concentrations have been noted to be decreasing since Phase I of Title IV of the Clean Air Act Amendments (Lynch et al. 2000; EPA 2003; Kvale and Pryor 2006; Table 1). Results from the current work corroborate this observation in that the largest decreasing trends in sulfate occur from 1980 to 2014 coinciding with that period of time (Fig. 9). While this observed trend is prevalent, most researchers have conducted their analyses based on deposition of sulfate rather than measuring concentrations independent of precipitation amounts. Martin et al. (2000) provided one of the few studies where results show sulfate concentrations between, approximately, 30 and 60 $\mu\text{eq/L}$. In the current work, the Eastern sites (IL78, IL63, and MO05; Fig. 10) showed the highest concentrations of sulfate (83.870 $\mu\text{eq/L}$), whereas results from southern sites (MO05, AR16 and AR27) more closely resembled the results presented in Martin et al. (2000) (59.665 $\mu\text{eq/L}$). Differences between study results could be due to, at least in part, to geographic location and land-use. For example, Martin et al. (2000) conducted their study in a forested ecosystem, similar to the NADP sites located at Ashland, MO (MO03), University Forest, MO (MO05), and Buffalo Point, AR (AR16).

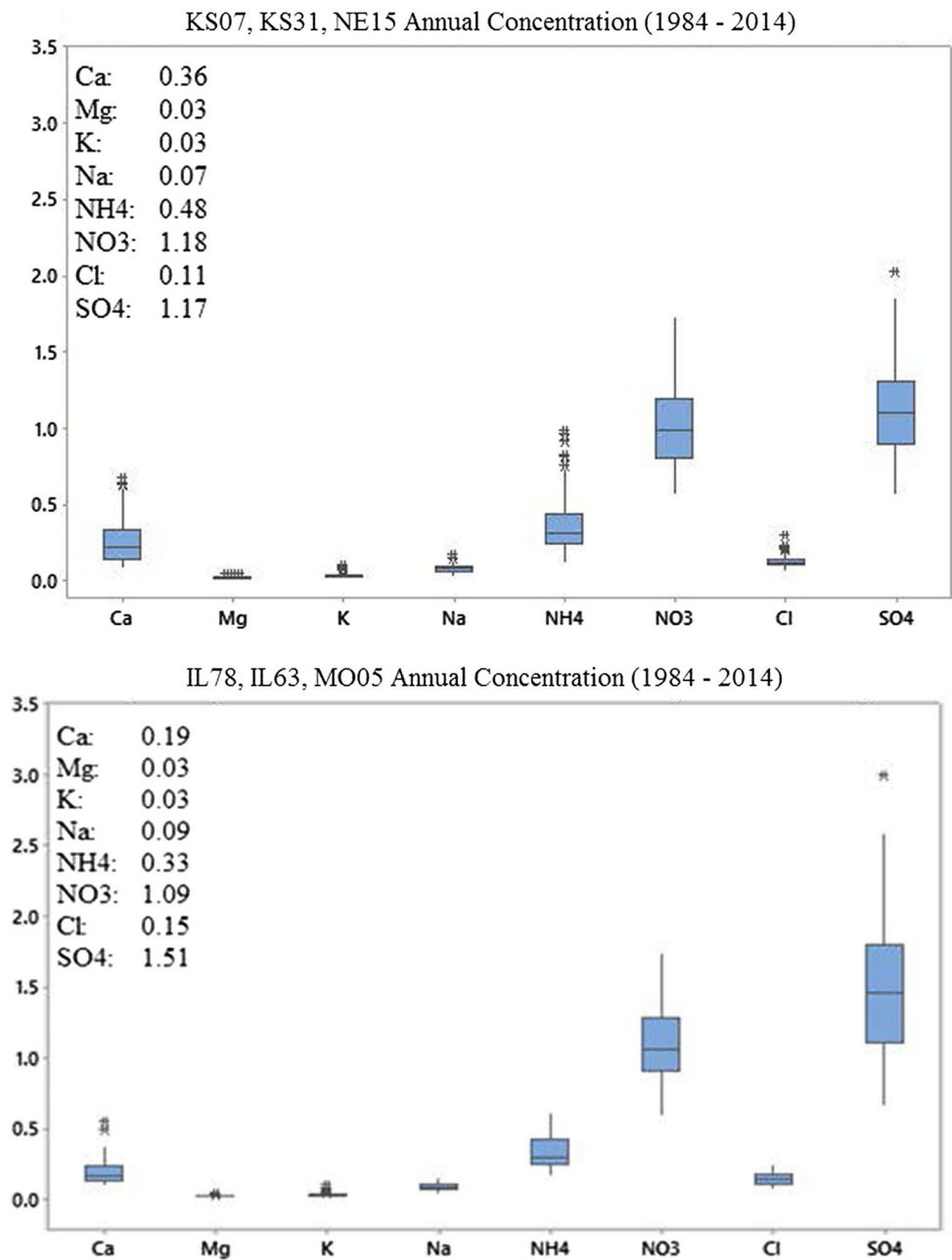
For all sites, with the exception of IL63, there was a positive correlation between mean annual temperature and concentration of calcium (Table 2), whereas all NADP

sites showed a positive correlation for hydrogen ions and ammonium. Conversely, there was a negative correlation between mean annual temperature and sodium concentration between all 10 sites. The Ashland, Missouri site (MO03) was the only location where chlorine was not negatively correlated to mean annual temperature. There was, however, a variable but negative correlation between ion concentration and precipitation amount (Table 3), similar to that reported by Swank and Crossley (1988). Conversely, as the amount of precipitation recorded by an NADP station increased, the pH of the precipitation tended to increase as well (Table 3). While the mechanics of these observations are beyond the scope of the current work, future studies should include comparisons of precipitation amount to concentration over larger domains to better explain relationships observed in the current work.

Geographically grouped sites: intra-specific differences

The only constituent that did not produce a significant p value ($CI = 0.05$) for the western sites (KS31, NE15, and KS07) was sulfate ($p = 0.277$). Concentrations of calcium were significantly different ($p < 0.001$) between KS07 and NE15, and KS07 and KS31. Potassium, sodium, and H^+ concentrations showed significant differences between both KS31 and NE15 ($p = 0.002$, 0.004, and 0.001, respectively), and KS07 and NE15 ($p = 0.010$, $p < 0.001$, and $p < 0.001$, respectively). The p value for the two Kansas locations for sodium and H^+ was slightly non-significant at 0.071 and 0.066. Ammonium, nitrate, and chlorine deposition were all significantly different for the three possible

Fig. 10 Descriptive statistic plots for calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), ammonium (NH₄), nitrate (NO₃), chloride (Cl), and sulfate (SO₄) for Western (KS07, KS31, and NE15) and Eastern (IL78, IL63, and MO05) geographically grouped sites. Averages ion concentrations are in mg/L



pair-wise groupings between the western sites of Konza Prairie (KS31), Mead (NE15), and Farlington (KS07). Ammonium deposition has been noted to be highest in the Midwest and variable across relatively small domains (as shown here), mostly due to food production and chemical N fertilizer applications (Du et al. 2014). Concentrations of ammonia have also been shown to comprise a significant fraction of the total nitrogen flux to forested ecosystems (Lindberg et al. 1990; Langford and Fehsenfeld 1992). In the current work, the highest average concentrations of ammonium were at Mead, Nebraska, an agriculturally dominant location. This finding may be related to the

relatively high pH at NE15 (pH = 5.57; Table 1) which, when reacted with the soil, may act as a sink of ammonium (Menzi et al. 1998).

Calcium, sodium, nitrate, chlorine, and H⁺ showed a significant difference ($p < 0.001$) between the eastern sites IL63 and IL78, as well as IL78 and MO05. Magnesium and ammonium deposition were also significantly different between all three sites. Potassium and sulfate concentrations were spatially similar for the two Illinois locations, with p values of 0.804 and 0.467 mg/L, respectively. Despite results indicating significant differences of sulfate, nitrate, and ammonium between IL63, IL78, and MO05,

Table 2 Correlation coefficient value between ion concentrations and mean annual temperature from the beginning of the study (1984 for MO03, MO05, KS31, NE15, IL63, AR16, and AR27, 1985 for IA23 and KS07, and 1986 for IL78) to 2014

Site/constituent	Ca	Mg	K	Na	NH ₄	NO ₃	Cl	SO ₄	H+
MO03	0.09	0.17	-0.13	-0.03	0.09	-0.13	0.23	-0.23	0.16
MO05	0.30	0.21	-0.01	-0.21	0.27	0.03	-0.21	-0.12	0.21
KS07	0.15	0.06	0.19	-0.14	0.18	-0.07	-0.13	-0.21	0.16
KS31	0.24	-0.04	-0.17	-0.20	0.08	0.07	-0.16	-0.06	0.03
NE15	0.26	-0.02	-0.06	-0.18	0.37	0.01	-0.26	-0.28	0.46
IA23	0.23	0.16	-0.12	-0.19	0.28	0.33	-0.10	0.23	0.02
IL78	0.40	0.36	0.01	-0.28	0.17	0.07	-0.21	-0.01	0.10
IL63	-0.20	-0.23	-0.13	-0.40	0.03	-0.18	-0.33	-0.28	0.26
AR16	0.00	-0.18	-0.22	-0.15	0.10	-0.14	-0.05	-0.23	0.13
AR27	0.15	-0.11	-0.15	-0.23	0.18	-0.08	-0.20	-0.19	0.26

Table 3 Correlation coefficient value between ion concentrations and mean annual precipitation from the beginning of the study (1984 for MO03, MO05, KS31, NE15, IL63, AR16, and AR27, 1985 for IA23 and KS07, and 1986 for IL78) to 2014

Site/constituent	Ca	Mg	K	Na	NH ₄	NO ₃	Cl	SO ₄	H+	Precip
MO03	-0.45	-0.46	-0.29	-0.33	-0.14	-0.34	-0.37	0.23	0.54	1040.68
MO05	0.01	0.03	0.25	0.41	-0.02	-0.22	0.40	-0.16	0.15	1230.36
KS07	-0.59	-0.39	-0.24	-0.02	-0.44	-0.64	-0.05	-0.37	0.01	1150.74
KS31	-0.41	-0.24	-0.15	-0.06	-0.22	-0.34	-0.07	-0.09	-0.10	830.59
NE15	-0.40	-0.22	-0.14	-0.27	-0.35	-0.58	-0.13	-0.33	0.11	700.71
IA23	-0.56	-0.43	0.18	-0.22	-0.28	-0.63	-0.19	-0.41	0.15	900.71
IL78	-0.49	-0.51	-0.26	-0.24	-0.14	-0.51	-0.27	-0.44	0.28	860.98
IL63	-0.21	-0.10	-0.13	0.06	-0.09	-0.39	0.02	-0.36	0.27	1340.45
AR16	0.17	0.21	0.23	0.21	0.07	-0.27	0.23	-0.25	0.29	1080.18
AR27	-0.32	-0.01	-0.08	0.21	-0.40	-0.32	0.28	-0.04	-0.14	1130.01

Precip average precipitation over the study period for each station (mm)

Kvale and Pryor (2006) suggested these ions may have a common source linked to synoptic-scale climate systems that propagate over the Ohio River Valley region. Results show a positive correlation between mean annual temperature and concentration of ammonium (Table 2), consistent with the findings of Ciezka et al. (2015).

Unlike the eastern grouped sites, magnesium, sodium, nitrate, and chlorine were not significantly different ($p < 0.05$) among the northern sites (NE15, IA23, and IL78). Conversely, hydrogen ions were found to be significantly different between all site combinations ($p < 0.006$). Ammonium concentrations were significantly different between NE15 and IA23, and NE15 and IL78 ($p < 0.001$), but were statistically insignificant between the two northeastern sites (IL78 and IA23; $p = 0.850$). Calcium, potassium, and sulfate ions were found to be different ($p < 0.05$) for the pairing of sites with Monmouth (i.e., IL78 with NE15 and IA23), the northeastern-most location. The differences in these constituents may be due, in part, to anthropogenic dusts and fertilizer application in agricultural fields (Ciezka et al. 2015). It is of interest to note that fertilizers containing these ions, including potassium chloride, are also capable of degassing

potassium back into the atmosphere when not absorbed into the soil (Du et al. 2014).

No significant differences were recorded between any of the sites for sodium coinciding with the results of Lloyd (2010) who showed that sodium concentrations tend to be highly variable inland of coastal regions, since the southern sites are nearest the ocean. The current work shows sodium and chlorine concentrations were highest at the southern locations, including IL63, consistent with findings from Parungo et al. (1990) and Ceron et al. (2002). Conversely, ammonium concentrations were significantly different for each pairing of sites ($p < 0.001$). Chlorine concentrations were found to be significantly different for MO05 and AR15 ($p = 0.039$). Calcium, potassium, and hydrogen ions were significantly different between AR27 and AR16, and MO05 and AR27. Conversely, magnesium, nitrate, and sulfate concentrations were different between the combination of sites which included University Forest (i.e., MO05 and AR27, and MO05 and AR16).

Cautions pertaining to the results of the current work include the potential for o-rings in the buckets used for shipping to alter the calcium concentrations, particularly in low-volume samples (James 1992). It was previously

showed that from 1979 to 1987, concentrations of Ca, Mg, Na, K, SO₄, Cl, and pH were affected by the o-rings from a blind audit sampling program conducted by the United States Geological Survey (USGS), thus skewing sample results during that time. In addition, given potential under catch problems due to inaccurate precipitation sensor sensitivity thresholds (see “Introduction”), future research might include different or additional precipitation devices to identify the accuracy limitations of currently used precipitation apparatus opening and closing to eliminate possible under catch issues (Martin et al. 2000).

Conclusions

Historically high concentrations of anthropogenic air pollutants in the Midwestern United States prompted a climatological (i.e., 30-year) study of several constituents as measured by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Spatial trends were assessed for ten NADP sites including: Ashland, MO (MO03), University Forest, MO (MO05), Farlington, KS (KS07), Konza Prairie, KS (KS31), Mead, NE (NE15), McNay Research Center, IA (IA23), Monmouth, IL (IL78), Dixon Springs, IL (IL63), Buffalo Point, AR (AR16), and Fayetteville, AR (AR27). Each site was analyzed based on standard descriptive statistics in addition to percent increase or decrease from the beginning (January 1, 1984) to the end of the study (December 31, 2014). Yearly aggregated concentrations were used to alleviate variability in synoptic-scale weather (Shannon 1999). The highest and lowest concentration levels of Ca were recorded at KS31 and NE15, and MO05 and AR16, the two western-most and southeast sites with values of 0.40 and 0.14 mg/L, respectively. The highest ammonium concentrations were recorded at the northern sites: IL78, IA23, and NE15, with NE15 being the largest of 0.67 mg/L, presumably, at least in part attributed to increased animal feedlots since the 1980s (Pryor et al. 2001). None of the 10 sites recorded a decrease in ammonium over the 30-year study, consistent with the findings of Nilles and Conley (2001) who observed that NH₄ concentrations in precipitation have increased between 1981 and 1998 in the northeast. In some instances, such as at IA23, a 226 % increase in ammonium concentration was observed from 1985 to 2014. Sulfate concentrations were highest in the eastern sites of IL63 and IL78, consistent with the findings of Baumgardner et al. (2002). Each site ($n = 10$) recorded a decrease of sulfate values by at least 50 % during the 30-year period. Additionally, nitrate concentrations decreased 5–30 % for each site. An increase in alkalinity was observed at each site, ranging from 10 % (AR16 and AR27) to 25 % (IA23). The

lowest average pH values were recorded at the southeast locations of MO05 (4.76) and IL63 (4.62).

In addition to individual site statistics, each site was grouped into either a northern-southern, or eastern-western region showing a significant difference ($p < 0.001$) for each ion, excluding potassium ($p = 0.092$ and $p = 0.442$ for north–south and east–west regions, respectively, and thus significant ($CI = 0.05$) spatial heterogeneity of several important atmospheric wet-deposition constituents within the Midwestern United States. Results presented here immediately improve the understanding of differences and similarities in spatial precipitation chemistry, allowing for improved management plans and policy in the Midwestern US, as well as inter-site precipitation trends that are continentally (and globally) connected.

Acknowledgments The NADP is National Research Support Project-3: A Long-Term Monitoring Program in Support of Research on the Effects of Atmospheric Chemical Deposition. More than 240 sponsors support the NADP, including State Agricultural Experiment Stations; universities; private companies and other nongovernmental organizations; Canadian government agencies; state, local, and tribal government organizations; and federal agencies, including the U.S. Department of Agriculture-Cooperative State Research, Education, and Extension Service (under Agreement No. 2002-39138-11964). Any findings or conclusions presented in this article may not reflect the views of the U.S. Department of Agriculture or other NADP sponsors. The authors gratefully acknowledge resources of the Interdisciplinary Hydrology Laboratory (<http://www.forth2o.net>) that made this analysis possible, and multiple reviewers whose thoughtful feedback greatly improved the article.

References

- Anderson TW, Darling DA (1952) Asymptotic theory of certain goodness-of-fit criteria based on stochastic processes. *Ann Math Stat* 23:193–212
- Antanasijevic D, Pocajt V, Peric-Grujic A, Ristic M (2014) Modelling of dissolved oxygen in the Danube River using artificial neural networks and Monte Carlo simulation uncertainty analysis. *J Hydrol* 519:1895–1907
- Baumgardner RE, Larvery TF, Rogers CM, Isil SS (2002) Estimates of the atmospheric deposition of sulfur and nitrogen species: clean air status and trends network, 1990–2000. *Environ Sci Technol* 36:2614–2629
- Beverland I, Crowther J, Srinivas M, Heal M (1998) The influence of meteorology and atmospheric transport patterns on the chemical composition of rainfall in southern England. *Atmos Environ* 32:1039–1048
- Brezonik PL, Hendry Jr CD, Edgerton ES, Schultze RL, Crisman TL (1983) Acidity, nutrients, and minerals in atmospheric precipitation over Florida: deposition patterns, mechanisms, and ecological effects. EPA-600/3-83-004, Environmental Research Laboratory, Corvallis, OR, USA, p 203
- Butler T, Likens G, Stunder B (2001) Regional-scale impacts of Phase I of the Clean Air Act Amendments in the USA: the relation between emissions and concentrations, both wet and dry. *Atmos Environ* 35:1015–1028
- Ceron RMB, Padilla HG, Belmont RD, Torres MCB, Garcia RM, Baez AP (2002) Rainwater chemical composition at the end of

- the mid-summer drought in the Caribbean shore of the Yucatan Peninsula. *Atmos Environ* 36:2367–2374
- Ciezka M, Modelska M, Gorka M, Torjanowska-Olichwer A, Widory A (2015) Chemical and isotopic interpretation of major ion compositions from precipitation: a one-year temporal monitoring study in Wroclaw, SW Poland. *J Atmos Chem* 73:61–80
- Du E, de Vries W, Galloway JN, Hu X, Fang J (2014) Changes in wet nitrogen deposition in the United States between 1985 and 2012. *Environ Res Lett* 9:1–8
- Elliot EM, Kendall C, Wankel SD, Burns DA, Boyer EW, Harlin K, Bain DJ, Butler TJ (2007) Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the Midwestern and northeastern United States. *Environ Sci Technol* 41:7661–7667
- Environmental Protection Agency (2003) Latest findings on national air quality: 2002 status and trends. Office of Air Quality and Standards, Air Quality Strategies and Standards Division. Research Triangle Park, NC
- Erismann JW, Bleeker A, Galloway J, Sutton MS (2007) Reduced nitrogen in ecology and the environment. *Environ Pollut* 150:140–149
- Fay JA (1983) Long range transport of acid rain precursors. MIT Energy Laboratory, Cambridge, MA 02139, MIT-EL 83-005
- Fay JA, Kumar S, Golomb D (1986) US-Canada transboundary flows of acid deposition precursors. In: Transactions of the APCA specialty conference on the meteorology of acid deposition, pp 36–44
- Galloway JN, Whelpdale DM (1980) An atmospheric sulfur budget for eastern North America. *Atmos Environ* 14:409–417
- Galloway JN, Aber JD, Erismann JW, Seitzinger SP, Howarth RW, Cowling EB, Cosby BJ (2003) The nitrogen cascade. *Bioscience* 53:341–356
- Garben B, Motelay-Massei A, Blanchoud H, Ollivon D (2004) A single law to describe atmospheric nitrogen bulk deposition versus rainfall amount: inputs at the Siene River Watershed scale. *Water Air Soil Pollut* 155:339–354
- Grimshaw HJ, Dolske DA (2002) Rainfall concentrations and wet atmospheric deposition of phosphorous and other constituents in Florida, USA. *Water Air Soil Pollut* 137:117–140
- Guenther AB, Lamb BK, Westberg HH (1989) U.S. National biogenic sulfur emissions inventory. In: Saltzman ES, Cooper WJ (eds) Biogenic sulfur in the environment. American Chemical Society Symposium Series No. 393, Washington DC, pp 14–30
- Hansen K, Draaijers G, Wilfred P, Gundersen P, van Leeuwen N (1994) Concentration variations in rain and canopy throughfall collected sequentially during individual rain events. *Atmos Environ* 28:1673–1684
- Hileman B (1990) Biomass burning: environment hurt more than thought. *Chem Eng News* 26:4–5
- Holland DM, Caragea P, Smith RL (2004) Regional trends in rural sulfur concentrations. *Atmos Environ* 28:1673–1684
- James KO (1992) 1990 quality assurance report, NADP/NTN deposition monitoring laboratory operations, Central Analytical Laboratory, January 1991 through December 1991. National Atmospheric Deposition Program. National Trends Network Coordinator's Office, Natural Resources Ecology Laboratory, Colorado State University, Fort Collins, p 83
- Junge GE, Gustafson PE (1958) On the distribution of sea salt over the United States and its removal by precipitation. *Tellus* 9:164–173
- Kleinbaum D, Kupper L, Nizam A, Muller K (2007) Applied regression analysis and other multivariable methods, 5th edn. Mass: Duxbury Press, Boston, p 928
- Knapp WW, Bowersox VC, Chevone BI, Krupa SV, Lynch JA, McFee WW (1988) Precipitation chemistry in the United States: Summary of ion concentration variability 1979–1984. USDA Cooperative State Research Service, Washington, DC
- Kramer CY (1956) Extensions of the multiple range test to group means with unequal numbers of replications. *Biometrics* 12:307–310
- Kvale KF, Pryor C (2006) Precipitation composition in the Ohio River Valley: spatial variability and temporal trends. *Water Air Soil Pollut* 170:143–160
- Langford AO, Fehsenfeld FC (1992) Natural vegetation as a source or sink for atmospheric ammonia: a case study. *Nature* 553:581–583
- Latysh NE, Wetherbee GA (2012) Improved mapping of National Atmospheric Deposition Program wet-deposition in complex terrain using PRISM-gridded data sets. *Environ Monit Assess* 184:913–928
- Lindberg SE, Bredmeier M, Schaeffer DA, Qi L (1990) Atmospheric concentrations and deposition of nitrogen and major ions in conifer forests of the United States and Federal Republic of Germany. *Atmos Environ* 24:2207–2220
- Livezey R, Vinnikov K, Timofeyeva M (2007) Estimation and extrapolation of climate normal and climate trends. *J Appl Meteorol Climatol* 46:1759–1776
- Lloyd PJ (2010) Changes in the wet precipitation of sodium and chloride over the continental United States, 1984–2006. *Atmos Environ* 44:3196–3206
- Lynch JA, Bowersox VC, Grimm JW (2000) Changes in sulfate deposition in eastern USA following implementation of Phase I of Title IV of the Clean Air Act Amendments of 1990. *Atmos Environ* 34:1665–1680
- Martin CW, Likens GE, Buso DC (2000) Comparison of long-term precipitation chemistry measurements at the Hubbard Brook experimental forest, New Hampshire. *Water Air Soil Pollut* 120:359–379
- Menzi H, Katz PE, Fahrni M, Neftel A, Frick R (1998) A simple empirical model based on regression analysis to estimate ammonia emissions after manure applications. *Atmos Environ* 32:301–307
- National Atmospheric Deposition Program (NRSP-3)/National Trends Network (2003) NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL, 61820
- Nilles M, Conley B (2001) Changes in the chemistry of precipitation in the United States, 1981–1998. *Water Air Soil Pollut* 130:409–414
- Nilles M, Gordon J, Schroder L (1994) The precision of wet atmospheric deposition data from national atmospheric program/national trends network sites determined with collocated samplers. *Atmos Environ* 28:1121–1128
- Parungo F, Nagamoto C, Hoyt S, Bravo H (1990) The investigation of air quality and acid rain over the Gulf of Mexico. *Atmos Environ* 24:109–123
- Pryor SC, Barthelmie RJ (2005) Liquid and chemical fluxes in precipitation, throughfall and stemflow: observations from a deciduous forest and a red pine plantation in the Midwestern USA. *Air Water Soil Pollut* 163:203–227
- Pryor SC, Barthelmie RJ, Sørensen L, Jensen B (2001) Ammonia concentrations and fluxes over a forest in the Midwestern USA. *Atmos Environ* 35:5645–5656
- Renne DS, Brachet WR, Shannon JD, Sisterson DS, Olsen AR (1991) Analysis of source-receptor relationships for sulfur compounds using spatial and trend techniques. In: Proceedings of the 9th symposium on turbulence and diffusion. American Meteorological Society, Boston, pp 106–109
- Seinfeld J, Pandis S (1998) Atmospheric chemistry and physics: from air pollution to climate change. Wiley-Interscience, New York, p 1232

- Shannon JD (1999) Regions trends in wet deposition of sulfate in the United States and SO₂ emissions from 1980 through 1995. *Atmos Environ* 33:807–816
- State Agricultural Experiment Stations (SAES) -422 Mutistate Research Activity Accomplishments Report (2014) NRSP-3, The National Atmospheric Deposition Program—a long-term program in support of research on the effects of atmospheric chemical deposition
- Swank W, Crossley DA (1988) Forest Hydrology and Ecology at Coweeta. In: *Ecological studies*, vol 66. Springer, New York, p 469
- Tukey JW (1953) The problem of multiple comparisons (Unpublished manuscript). In: *The collected works of John W. Tukey VIII. Multiple comparisons*. Chapman and Hall, New York, p 300
- Venkatram A, McNaughton D, Karamchandani PK, Shannon JD, Fernau M, Sisterson DL (1990) NAPAP SOS/T8, Relationships between atmospheric emissions and deposition/air quality. National Acid Precipitation Assessment Program, Washington, DC