

Dependence of Daily Aerosol Wet Deposition on Precipitation at Appalachian Mountains Site in the United States

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ABSTRACT

The wet removal of airborne particulates is a significant component of atmospheric deposition in the Eastern United States. This study analyzed the daily wet deposition of major ions at the Canaan Valley site in Appalachian Mountains in Eastern US, for the time interval 2000–2014. The site is part of the Atmospheric Integrated Research Monitoring Network (AIRMoN), and is significantly impacted by acid precipitation, caused largely by anthropogenic sources of SO₂ and NO_x. Results show that the precipitation rate, R, varies mainly in the interval [0.01–100] mm day⁻¹, and the daily wet deposition flux, F, varies about two orders of magnitude for most ions. The largest daily wet depositions are for SO₄²⁻ and NO₃⁻ with extreme values over 30 mg m⁻² day⁻¹. In the case of NH₄⁺, the largest daily wet depositions are over 10 mg m⁻² day⁻¹. Seasonal variations are illustrated by contrasting the winter and summer. In general, there are much larger daily wet deposition fluxes in summer than in winter. For SO₄²⁻ there is more conversion of SO₂ to SO₄²⁻ in the gas phase and in cloud droplets during summer. Similarly, NH₄⁺ has a distinct seasonal variation with a maximum in summer, consistent with larger sources of NH₃ during the growth season. NO₃⁻ has a maximum concentration in precipitation during winter, and a maximum daily wet deposition flux during summer, especially during the most intense rain events. The Na⁺ and Cl⁻ ions have the highest wet deposition in winter due to storms that bring air masses from Atlantic. Analysis shows that precipitation events are effective in wet removal of aerosols providing episodes with some of the highest rates of acid deposition.

Keywords: Wet deposition; Air pollution; Aerosol-cloud interactions; Precipitation; Acid rain.

INTRODUCTION

Atmospheric dry and wet deposition of gases and particulates represent the removal mechanisms of pollution from air. Wet deposition is the removal of atmospheric particles by precipitation and is often divided in two main processes: in-cloud and below-cloud scavenging (Andronache, 2003, 2006; Henzing *et al.*, 2006; Sportisse, 2007; Feng, 2009; Wang *et al.*, 2010). Specific conditions determine the relative importance of each process and, overall, during significant precipitation events, the in-cloud scavenging is dominant. Studies of aerosol wet removal have been reported for numerous regions of the world, particularly based on precipitation chemistry measurements and model simulations (Rasch *et al.*, 2000; Puxbaum *et al.*, 2002; Lehmann *et al.*, 2005; Dentener *et al.*, 2006; Larssen *et al.*, 2006; Croft *et al.*, 2009; Sorooshian *et al.*, 2014). Current research in connection

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with acid rain, air pollution and the impact of aerosols on environment and climate, continue to refine experimental and modelling tools (Monks *et al.*, 2009; Vet *et al.*, 2014).

Wet deposition at mountain sites has specific observational and modelling challenges and is an active area of research. Observations in mountain areas can provide insight into: a) long-range transport of air pollutants; b) impact of acid rain on alpine forests and their response to pollution; c) fog scavenging and aerosol removal from direct cloud impact with terrain slopes; d) role of orographic convection and its effects on precipitation; e) heterogeneous ice nucleation of various aerosol types (Wrzesinsky and Klemm, 2000; Avila and Rodà, 2002; Igawa *et al.*, 2002; Thalmann *et al.*, 2002; Baumgardner *et al.*, 2003; Burkard *et al.*, 2003; Bayraktar and Turalioglu, 2005; Kim *et al.*, 2006; Fischer *et al.*, 2007; Budhavant *et al.*, 2009; Calvo *et al.*, 2012; Pawar *et al.*, 2012; Hallar *et al.*, 2013; Li *et al.*, 2014; Conen *et al.*, 2015; Weiss-Penzias *et al.*, 2015; Sarkar *et al.*, 2015).

In the United States, wet deposition studies have been conducted in relation to the National Atmospheric Deposition Program (NADP), designed to measure atmospheric deposition and assess its effects on the environment. NADP started in 1978 with the goal of providing data on

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the amounts, trends, and geographic distributions of acids, nutrients, and base cations in weekly samples of precipitation. In 1992, the Atmospheric Integrated Research Monitoring Network (AIRMoN) joined the NADP measuring the same chemicals daily rather than weekly. These higher resolution samples increase the ability to evaluate how emissions affect precipitation chemistry using numerical models and can provide insight in cases of isolated precipitation events (Lamb and Bowersox, 2000; Lynch *et al.*, 2000).

For regions in Eastern US, the precipitation scavenging of particles accounts for a significant part of the total deposition. The wet removal influences the long-range transport of aerosols and their effects on the environment (Butler et al., 2001; Driscoll et al., 2001; Andronache 2004; Butler et al., 2005; Civerolo et al., 2010). Numerous studies at mountain sites in Eastern US were enhanced by additional data collection and documented the detailed behaviour of precipitation chemistry and its impact on high elevation ecosystems (Lynch et al., 2000; Walker et al., 2000; Butler et al., 2001; Driscoll et al., 2001; Collett et al., 2002; Sickles and Grimm, 2003; Baumgardner et al., 2003; Driscoll et al., 2003; Schwab et al., 2004; Butler et al., 2005; Lehmann et al., 2005; Anderson et al., 2006; Fisher et al., 2007; Civerolo et al., 2010). Many previous studies reported wet deposition results aggregated on a weekly, monthly or annual basis, suitable for robust long-term trend characterization. Daily or higher frequency samples can provide insight into the short time variability of wet deposition and possible implications for regions sensitive to acid precipitation. This work presents results based on analysis of wet deposition of measured ions in daily precipitation samples. The goal is to characterize the daily wet deposition of ions at Appalachian Mountains site in Eastern US during precipitation events. Specifically, the study aims to describe the dependence of daily wet deposition flux on precipitation rate, its seasonal variations, and connections with pollution sources.

METHODS

Data analyzed are daily measurements from the Canaan Valley Institute, located in Tucker County in West Virginia at Latitude = 39.0636 N, Longitude = -79.4222 W, and altitude of 988 m a.s.l. (Fig. 1). The sampling site is part of AIRMoN (with site ID: WV99) and data analyzed are from the interval June 2000–December 2014. AIRMoN is a National Oceanic and Atmospheric Administration (NOAA) combined wet deposition, and Clean Air Status and Trends Network (CASTNet) station with daily collections, measurements of acid rain, and deposition of major airborne contaminants. NOAA operates the AIRMoN site within the Canaan Valley Institute's 926-acre research watershed.

Canaan Valley is near the center of the mid-Atlantic highlands region, with one of the largest temperate hardwood forests in the world. These highlands are also the headwaters of the Ohio, Potomac, and Susquehanna rivers, and have the potential to store and transport contaminants via river flow to large regions of the country. The mid-Atlantic highlands are considered to be among the regions in the nation with the highest acid rain pollution (Driscoll *et al.*, 2001; Lehmann *et al.*, 2005).



Fig. 1. Map of Eastern United States with the location of the Canaan Valley sampling site in West Virginia.

Canaan Valley is located at relatively high elevation and has a cooler, moister climate than surrounding areas at lower altitudes. The climate is marked by large day-to-day weather variability caused by transitions between very contrasting air masses. Summer is characterized by moist air flowing north-eastward from the southeast and Gulf of Mexico, with frequent thundershowers. Winter is dominated by intense winds and alternating pulses of cold dry air from Canada and warm moist air from the Gulf of Mexico (Taubman et al., 2006; Davis et al., 2010). Winters are typically cold and snowy, and nearly all snowfall occurs from October through April. Canaan Valley's elevation and geographic location favour significant upslope snow during the winter, particularly during extended periods of north westerly winds. The Valley is frequently impacted by storms that form along the upper East Coast of the United States, resulting in significant precipitation.

Daily measurements are taken when there are precipitation events. Variables measured in daily precipitation samples are: ion concentrations (C), precipitation rate (R), pH of rain water, and conductivity. The ion species analyzed are: Calcium (Ca²⁺), Magnesium (Mg²⁺), Potassium (K⁺), Sodium (Na⁺), Chloride (Cl⁻), Ammonium (NH₄⁺), Nitrate (NO₃⁻), Sulphate (SO₄²⁻), and Phosphate (PO₄³⁻). Analysis presented here includes: a) statistical characteristics of ion concentration in daily precipitation; b) the relationship between the wet deposition flux (F) and rainfall intensity R. The wet deposition flux, F, of a species with concentration C in rainwater, to the ground surface due to precipitation with intensity R is F = CR, expressed in units of mg m⁻² day⁻¹; c) seasonal variations of F, illustrated by contrasting the winter and summer.

RESULTS AND DISCUSSION

Descriptive Statistics and Long Term Trends of Major Pollutants

Fig. 2 shows the time sequences of SO_4^{2-} and NO_3^{-} annual mean concentrations obtained from the daily precipitation samples at Canaan Valley site for the time interval 2000–2014. The solid line shows the linear trend which is represented by equation y = s + w t, where y and s are in units of (mg L⁻¹) and w is in units of (mg L⁻¹ y⁻¹), and t is time in years starting with t = 1, for year 2000.

There is a significant decrease in SO_4^{2-} concentration in precipitation [Fig. 2(a)] as indicated by the linear trend, which has a coefficient of determination $r^2 = 0.85$. The coefficients in the regression line are: $s = 2.553 \text{ (mg } \text{L}^{-1}\text{)}$ and w = -0.106 (mg L⁻¹ y⁻¹). The 95% confidence interval (CI) of w is (-0.132, -0.079), confirming a significantly downward trend. The decline of SO_4^{2-} concentration in precipitation is caused by the decrease in sulphur dioxide (SO_2) emissions, resulted from the installation of additional scrubbers at many US power plants (Fioletov et al., 2011). For NO_3^{-} , there is a declining trend with a rate slower than the rate of SO_4^{2-} decrease [Fig. 2(b)]. For NO_3^{-} , the linear trend has a coefficient of determination $r^2 = 0.48$, suggesting that there is notable variance not explained by the linear trend. The coefficients in the regression line are: s = 1.708 $(mg L^{-1})$ and $w = -0.046 (mg L^{-1} y^{-1})$. The 95% CI of w is (-0.076, -0.017), indicating that the trend is significantly downward. Similar analysis shows that NH_4^+ has no significant trend in the analyzed data. This is due in part to a lack of significant changes in ammonia (NH₃) emissions, which has major sources in agriculture, from livestock and



Fig. 2. Time series of SO_4^{2-} and NO_3^{-} annual mean concentrations from daily precipitation samples at Canaan Valley site for the time interval 2000–2014. The solid line shows the linear trend.

nitrogen fertilizers, and are dependent on farming practices and meteorological conditions (Lynch and Kerchner, 2005). In contrast to NO_x , there are few regulations relevant to NH₃ emissions, and based on the EPA National Emissions Inventory, NH₃ emissions do not have a downward trend in the region of interest (Pinder *et al.*, 2011).

Table 1 gives a descriptive statistics of ion concentration in precipitation for winter (December, January, February) and summer (June, July, August) at Canaan Valley for the time interval 2000–2014. The Mean, Standard Deviation (SD), and Maximum (Max) are in (mg L⁻¹) units. CV = SD/Mean is the coefficient of variation. The Minimum values are not included because in most cases they are below or close to the detection limit (except for the major pollutants: SO₄^{2–}, NH₄⁺, NO₃[–]). To see if the means for winter and summer are statistically different, the t-test for unequal sample sizes, and unequal variances is used. It is found that for all ion species, except Ca²⁺, the means for winter are significantly different than those for summer at 5% significance level (p values less than 0.05).

The Max values for the mineral ions Ca^{2+} and Mg^{2+} are higher in summer than winter largely due to predominant westerly flow during summer. Such air masses flow above the soil and agricultural areas richer in mineral crust aerosols. Max values of K⁺ are comparable during summer and winter, with possible sources from forest fires during summer and wood burning during winter (Thurston et al., 2011). For Na⁺ and Cl⁻, the higher Max values are in winter. During winter time air masses rich in sea salt aerosols from Atlantic penetrate in Eastern US favoring higher concentrations of Na⁺, and Cl⁻ in precipitation. The Max values of NH4⁺ are higher in summer than in winter, consistent with the regional analysis by Gilliland et al. (2006) where they show that NH₃ emissions are the largest during spring and summer, and this leads to large NH₄⁺ concentrations and wet deposition rates. NO₃⁻ has Max higher in winter than in summer, consistent with results by Sickles II and Shadwick (2007). Clearly, SO₄²⁻ has much higher Max values in summer than in winter, attributed mainly to westerly flow over large SO₂ sources, intense photochemistry during summer, as well as more efficient conversion of SO_2 to SO_4^{2-} in cloud droplets. Also note somehow higher values of PO_4^{3-} in summer than in winter, due to the use of fertilizers in the growth season in agricultural regions upwind from the sampling site.

The coefficient of variation (CV) is shown for comparison between data sets with widely different means. The mean for various ions in Table 1 varies about two orders of magnitude, between 0.01 and 2, and SD has a similar variation. CV shows smaller variations, between 0.7 and 1.5. In general, CV has values around one, indicating that the mean and SD values are comparable. We note that for mineral crust ions and sea salt ions, dominated by natural sources, CV is larger than 1, indicating that SD is larger than the mean. In contrast, for the ions relevant to air pollution (NH₄⁺, NO₃⁻, and SO₄²⁻), drastically influenced by anthropogenic sources, CV is smaller than 1 (with SD smaller than the mean).

Seasonal Variations of Daily Wet Deposition and Dependence on Precipitation Rate

Figs. 3 and 4 show the dependence of daily wet deposition F as a function of precipitation rate R, for winter and summer conditions. At Canaan Valley site, the winter is dominated by snowfall precipitation, while, in summer, the rainfall is the norm. For Ca²⁺, Mg²⁺, and K⁺, F is larger in summer than in winter. This is mainly due to differences in surface cover. Winter is characterized by snow cover with less available sources of mineral aerosols. In contrast, during summer, the ground is characterized by vegetation cover or bare soil and can provide richer sources of mineral particles. For all ions, F increases significantly with the precipitation rate R. For Na⁺, we see larger F values in winter than in summer (the same behavior is seen for Cl⁻, not shown). Given the observed variations of R in the interval [0.01-100] mm day⁻¹, F varies about two orders of magnitude for most ions.

All ions of major interest for air pollution and acid rain, NH_4^+ , NO_3^- and SO_4^{2-} show a significant increase of F with R. The increase is higher during summer than in winter. The largest F values are in summer for the most intense precipitation events. Such events are favored by convective precipitation, mainly from the mesoscale convective systems (MCS) originating in Midwestern regions and moving across the Eastern US, and from frequent thunderstorms.

Table 2 gives the fit parameters of the daily wet deposition flux, F (mg $m^{-2} day^{-1}$), as a function of daily precipitation

Table 1. Descriptive statistics of ion concentration in precipitation for winter (W) and summer (S) at Canaan Valley sampling site in West Virginia, for the time interval 2000–2014. The Mean, Standard Deviation (SD), and Max are in $(mg L^{-1})$ units. CV = SD/Mean is the coefficient of variation.

Variable	Mean		Median		SD		Max		CV	
	W	S	W	S	W	S	W	S	W	S
Ca ²⁺	0.142	0.158	0.084	0.100	0.164	0.186	1.471	1.576	1.153	1.179
Mg^{2+}	0.016	0.021	0.011	0.014	0.015	0.024	0.144	0.266	0.966	1.186
\mathbf{K}^+	0.021	0.026	0.016	0.019	0.017	0.020	0.161	0.165	0.835	0.785
Na^+	0.064	0.031	0.041	0.017	0.069	0.044	0.387	0.355	1.083	1.439
Cl ⁻	0.144	0.103	0.104	0.075	0.138	0.083	0.991	0.502	0.956	0.803
${ m NH_4}^+$	0.296	0.413	0.214	0.352	0.242	0.260	1.229	1.561	0.817	0.629
NO_3^-	1.789	1.393	1.380	1.131	1.417	0.901	7.832	6.344	0.792	0.647
$\mathrm{SO_4}^{2-}$	1.266	2.508	1.063	2.111	0.883	1.959	5.757	11.951	0.697	0.781
PO_4^{3-}	0.010	0.015	0.008	0.010	0.009	0.023	0.108	0.287	0.949	1.526



Fig. 3. Wet deposition flux (F) versus precipitation rate (R) for ions: Ca^{2+} , Mg^{2+} , K^+ , and Na^+ for winter and summer. The lines represent the fit $F = aR^b$.



Fig. 4. Wet deposition flux (F) versus precipitation rate (R) for ions: NH_4^+ , NO_3^- , and SO_4^{2-} for winter and summer. The lines represent the fit $F = aR^b$.

rate, R (mm day⁻¹), for winter and summer, expressed as F = aR^b . The fit is obtained using a robust non-linear least-squares fitting technique, employing the least absolute residual (LAR) method. This robust method is less influenced by outliers, and the coefficient of determination r^2 shows that the power fit explains well most of the variance in the data (r^2 values are over 0.9). For each ion species the

parameters a and b are shown with the 95% CI for the two seasons: winter (W), and summer S). To determine whether the fitting parameters a and b are significantly different for the two seasons, the t-test is employed. Results show that the parameter b of the C_a^{2+} fit is not statistically different from winter to summer at 95% confidence level. The same results are found for Cl⁻. For the rest of analyzed ions, the

Table 2. Fit parameters of the daily wet deposition flux, F (mg m⁻² day⁻¹), as a function of daily precipitation rate, R (mm day⁻¹), for winter (W) and summer (S), $F = aR^b$. The parameters a and b are given with the 95% CI.

Variable	a (95% CI)					b (95% CI)				
	W		S		W		S			
Ca ²⁺	0.086	(0.075, 0.097)	0.121	(0.115, 0.126)	0.903	(0.853, 0.953)	0.865	(0.851, 0.878)		
Mg^{2+}	0.012	(0.011, 0.013)	0.018	(0.018, 0.019)	0.894	(0.862, 0.927)	0.824	(0.812, 0.836)		
K^+	0.014	(0.013, 0.015)	0.022	(0.021, 0.023)	1.000	(0.976, 1.023)	0.902	(0.887, 0.917)		
Na^+	0.032	(0.028, 0.035)	0.021	(0.019, 0.023)	1.092	(1.052, 1.132)	0.840	(0.811, 0.869)		
Cl	0.120	(0.113, 0.127)	0.099	(0.096, 0.102)	0.844	(0.822, 0.866)	0.835	(0.826, 0.844)		
$\mathrm{NH_4}^+$	0.265	(0.251, 0.279)	0.349	(0.337, 0.361)	0.831	(0.811, 0.851)	0.974	(0.964, 0.984)		
NO_3^-	2.575	(2.466, 2.685)	1.408	(1.374, 1.442)	0.500	(0.481, 0.519)	0.852	(0.845, 0.860)		
$\mathrm{SO_4}^{2-}$	1.361	(1.308, 1.413)	2.471	(2.367, 2.576)	0.795	(0.780, 0.810)	0.884	(0.871, 0.897)		
PO_4^{3-}	0.007	(0.007, 0.007)	0.012	(0.010, 0.014)	0.999	(0.981, 1.017)	0.905	(0.853, 0.958)		



Fig. 5. Cumulative daily wet deposition for selected ions, for winter and summer.

parameters a and b are statistically different during winter and summer at 95% confidence level, with more pronounced differences for polluting species (SO_4^{2-} , NO_3^{-} , and NH_4^{+}).

The values of parameter a are smaller in winter than summer for most ions, except for Na⁺, Cl⁻, and NO₃⁻. For Na⁺, and Cl⁻, the abundant sea salt in air mass from Atlantic during winter storm explains the exception. For NO₃⁻ the fit shows a much larger b value in summer than in winter, and this leads to a higher value of the parameter a during summer. The coefficient a is higher in summer than in winter for SO₄²⁻, due to more conversion of SO₂ into SO₄²⁻ during summer months. The coefficient b is particularly higher in summer than in winter for NH₄⁺, NO₃⁻, and SO₄²⁻, the ions of major concern for air pollution and acid rain. This feature translates to stronger effects of large precipitation rates on the wet deposition of these ions.

To compare the effect of wet deposition in winter and summer we calculate the cumulative F for each season. Thus, for a species of concentration C in precipitation, we calculate the daily F_i, sort the data in ascending order, and calculate the Cumulative F as a sum of all daily F_i. The sum extends over the total number of cases, N (the number of days with significant precipitation from the samples available in the data set). The plot of Cumulative F versus the number of cases is shown in Fig. 5 for selected ions, for winter and summer. The plot for NH_4^+ for example, shows that during summer, there is more Cumulative F than in winter. This is due to predominant: a) higher values of NH₄⁺ concentration in rainwater; b) higher precipitation rate; and c) more frequent precipitation events in summer than in winter. Similar arguments are valid for NO3-, and SO_4^{2-} . The NO_3^{-} differences between the two seasons are mainly due to more precipitation events in summer than in winter. For SO₄²⁻, large differences exist, and summer is marked by enhanced SO₂ oxidation, and in-cloud conversion to SO_4^{2-} . Fig 5(d) shows the behavior for Ca^{2+} (the plot is also representative qualitatively for Mg^{2+} and K^+). In this case, there is a smaller increase of Ca²⁺ sources in summer

versus winter, and the main differences are dominated by the role of higher frequency of precipitation events in summer.

Concerning the precipitation pH, the daily average values in summer are slightly lower than in winter. Thus, during summer months, at this site, the precipitation is more acidic than during winter time. There is no significant dependence of pH on the rainfall rate. A more dramatic difference in precipitation regime is seen between winter and summer. For summer, both the Mean and Max values of R are higher than the corresponding values in winter. Also, the frequency of precipitation events is higher in summer than in winter. These results indicate that the highest wet deposition cases in summer months can be significantly driven by conditions leading to strong convective precipitation events.

CONCLUSIONS

This study analyzed the daily wet deposition of chemical ions relevant for acid rain for the time interval 2000–2014. The daily samples were measured during precipitation events at Canaan Valley site in Appalachian Mountains in Eastern US. The site is part of the Atmospheric Integrated Research Monitoring Network (AIRMoN), and is representative for mid-Atlantic highlands region. It is significantly impacted by acid precipitation, caused largely by major anthropogenic regional sources of SO₂ and NO_x. Over the whole time interval, the concentrations of SO₄^{2–} and NO₃⁻ show a significant downtrend, due to the effective long term emission control of SO₂ and NO_x.

Concerning the variations of daily wet deposition, F, with the precipitation rate, R, results show that precipitation rate R varies mainly in the interval [0.01-100] mm day⁻¹, and the daily wet deposition F varies about two orders of magnitude for most ions. The largest daily wet depositions are found for SO₄²⁻ and NO₃⁻ with extreme values over 30 mg m⁻² day⁻¹. The NH₄⁺ wet deposition fluxes have episodes over 10 mg m⁻² day⁻¹. For the mineral ions, Ca²⁺ has the largest wet deposition while Mg²⁺ has smaller fluxes.

Seasonal variations of the daily wet deposition are significant for most ions. In general there are much larger daily wet deposition fluxes in summer than in winter. For SO_4^{2-} there is a more efficient conversion of SO_2 to SO_4^{2-} in the gas phase and in-cloud droplets during summer. Similarly, NH₄⁺ is impacted by sources of NH₃, which are stronger during the growth season, leading to higher NH₄⁺ concentrations and wet deposition rates during summer. In the case of NO_3^- , the highest concentrations in precipitation are during winter. The large wet deposition fluxes during summer are in part due to increased precipitation rates. For mineral aerosols (Ca^{2+}, Mg^{2+}) the larger fluxes in summer versus winter are caused mainly by precipitation differences. A notable exception is shown by the Na^+ and Cl^- ions which have more significant wet deposition in winter due to storms that bring air masses from Atlantic.

The analysis shows that there are more frequent precipitation events in summer than in winter, and that summer has higher precipitation rates than winter. Mesoscale convective systems originating in Midwestern regions of US move across the Appalachian Mountains, and the convection is enhanced by terrain slopes and by the summer unstable conditions, leading to frequent thunderstorms. In the cases of storms moving from the east side of mountains, the terrain is also favorable for enhanced convection, leading to enhanced precipitation. The study shows that for Canaan Valley, the summer convective precipitation events are effective in wet removal of aerosols, leading to the highest rates of deposition, with potential implications for the effects of pollution on vegetation, soil and streams.

ACKNOWLEDGMENTS

We acknowledge the use of data from the National Oceanic and Atmospheric Administration (NOAA), United States Environmental Protection Agency (USEPA), and from the National Atmospheric Deposition Program, (NRSP-3). 2007. NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820.

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Received for review, May 15, 2015 Revised, August 6, 2015 Accepted, September 10, 2015