



Discussion  
**Authors response**

**1. Introduction**

The objective of our paper, “Spatial patterns of precipitation quantity and chemistry and air temperatures in the Adirondack region of New York,” was to examine spatial patterns of precipitation quantity and chemistry and air temperatures to estimate wet deposition to the Adirondacks and provide input data for regional models (Ito et al., 2002). Soils and surface waters in the Adirondacks have been significantly impacted by acidic deposition (Driscoll et al., 2001). In order to accomplish our objective, we sought to use as much data as possible. We evaluated wet deposition data from two sources, the New York State Atmospheric Deposition Monitoring Network (NYS-ADMN) and the National Atmospheric Deposition Network/National Trends Network (NADP/NTN). The NYS-ADMN included four sites, Whiteface Mountain (WF-ADMN), Nick’s Lake Campground (Nicks), Piseco Lake (Piseco), and Wanakena Ranger School (WRS), and the NADP/NTN included two sites, Huntington Wildlife Forest (HWF) and Whiteface Mountain (WF-NADP), in the Adirondack region. Prior to conducting our analysis, we did a preliminary evaluation to ensure that the databases were consistent, comparable, and complementary (Ito et al., 2002). As a result of this evaluation, we used for our analysis sulfate ( $\text{SO}_4^{2-}$ ) and nitrate ( $\text{NO}_3^-$ ) data from both NYS-ADMN and NADP sites, while we only used ammonium ( $\text{NH}_4^+$ ), hydrogen ion ( $\text{H}^+$ ), calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), potassium ( $\text{K}^+$ ), sodium ( $\text{Na}^+$ ), and chloride ( $\text{Cl}^-$ ) from the two NADP sites. Sistla et al. (2002) took exception to our evaluation of NYS-ADMN data. In response to Sistla et al. (2002), we provide here more details of our comparison of NY-ADMN and NADP/NTN data for the Adirondacks.

**2. Methods**

Annual and quarterly data of the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Cl}^-$  from 1988 to 1999 at four sites, WF-ADMN, Nicks, Piseco, and WRS, were obtained from the NYS-ADMN at: <http://www.dec.state.ny.us/website/dar/baqs/acid->

[rain/index.html](http://www.dec.state.ny.us/website/dar/baqs/acid-rain/index.html). The annual and monthly data from the HWF and WF-NADP were obtained from the NADP/NTN at: <http://nadp.sws.uiuc.edu>. For the NADP/NTN data, quarterly precipitation-weighted ion concentrations were calculated using their monthly precipitation and ion concentrations to make these data comparable with the quarterly data reported for the NYS-ADMN. The concentrations of  $\text{H}^+$  were calculated from the pH values. While Sistla et al. (2002) focused observations only from 1990 to 1999 for the two Whiteface Mountain sites (WF-ADMN and WF-NADP), we evaluated data from 1988 to 1999 for all six sites in the Adirondacks, four sites from the NYS-ADMN network and two sites from the NADP/NTN network (Ito et al., 2002).

As discussed in Ito et al. (2002), the quality of the ion concentration data was first assessed in time-series plots from 1988 to 1999 and the application of analysis of variance for the examination of the differences in the concentrations among the sites, using protected least significant difference for mean separation at the 5% level. We also examined the relationships between sum of cations [ $\text{NH}_4^+ + \text{H}^+ + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+$ ] and the sum of anions [ $\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-$ ] and the relationships between [ $\text{H}^+$ ] and [ $\text{SO}_4^{2-} + \text{NO}_3^-$ ]. Further, as presented by Sistla et al. (2002), predicted values of specific conductance were compared to measured values. Predicted specific conductance was calculated using Eq. (1) (CRC, 1998):

$$\begin{aligned} \text{Predicted specific conductance} \\ = \{73.5 \times [\text{NH}_4^+] + 59.5 \times [\text{Ca}^{2+}] \\ + 53 \times [\text{Mg}^{2+}] + 73.5 \times [\text{K}^+] \\ + 50.1 \times [\text{Na}^+] + 350 \times [\text{H}^+] \\ + 80 \times [\text{SO}_4^{2-}] + 71.4 \times [\text{NO}_3^-] \\ + 76.3 \times [\text{Cl}^-]\} / 1000, \end{aligned} \quad (1)$$

where specific conductance is in  $\mu\text{Scm}^{-1}$  and ion concentrations are in  $\mu\text{eq l}^{-1}$ .

**3. Results and discussion**

As discussed in Sistla et al. (2002), we acknowledge that there are some procedural differences between the

NYS-ADMN and the NADP/NTN networks. However, for the purpose of examining broad spatial patterns in wet deposition, we felt these differences should be minor and we should be able to use both databases. Indeed the magnitude and temporal patterns in the concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were relatively consistent among all six sites. There was also good agreement in concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  between the co-located NYS-

ADMN and NADP sites at Whiteface Mountain (Ito et al., 2002). In contrast, the time series plots of the concentrations of cations and  $\text{Cl}^-$  showed that there were clear differences in data from the two networks, with some markedly high values at the NYS-ADMN sites relative to those at the two NADP sites (Fig. 1a–f). Annual volume-weighted concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at the NYS-ADMN sites were very high early in

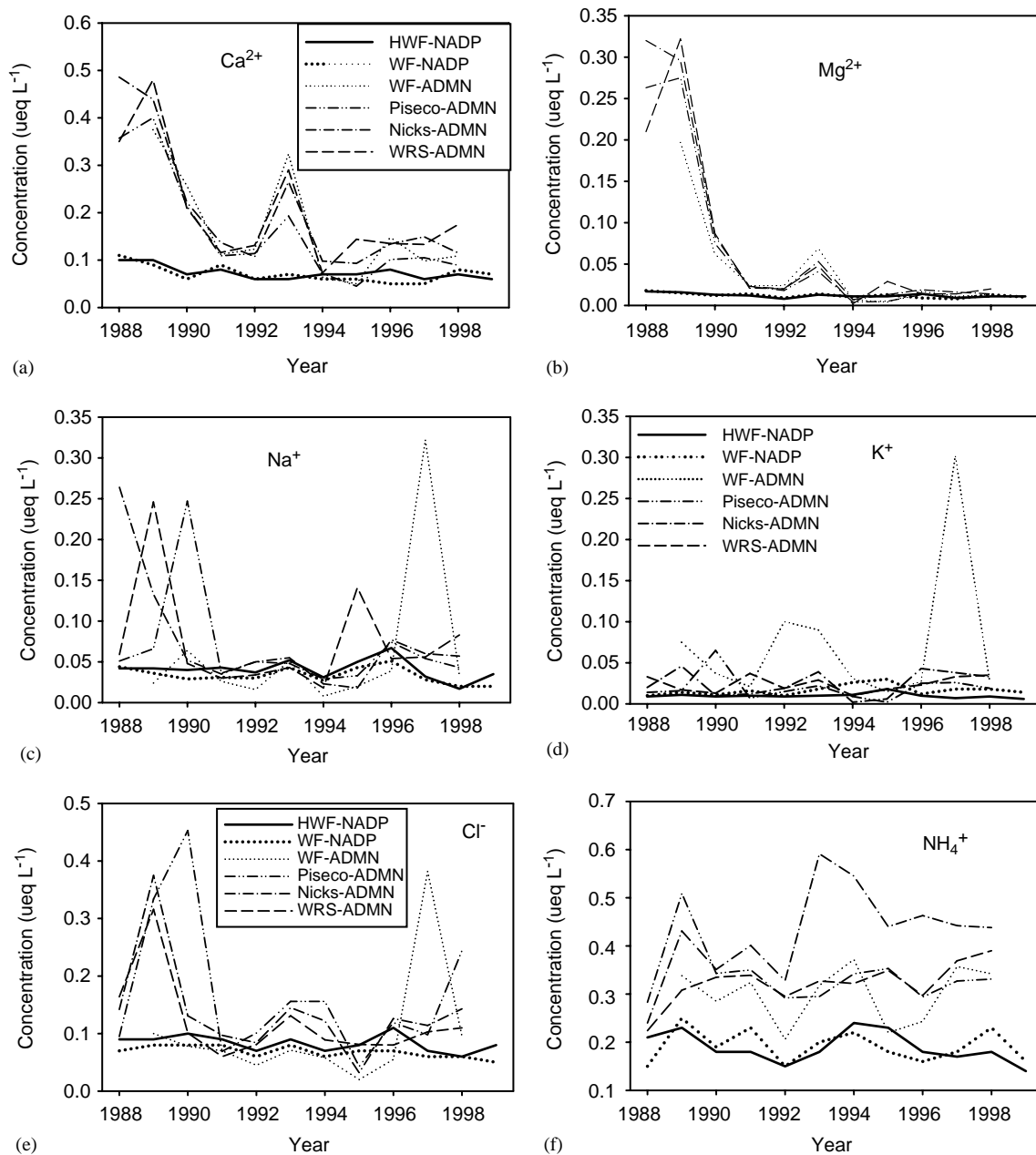


Fig. 1. The concentrations of (a)  $\text{Ca}^{2+}$ , (b)  $\text{Mg}^{2+}$ , (c)  $\text{Na}^+$ , (d)  $\text{K}^+$ , (e)  $\text{Cl}^-$ , and (f)  $\text{NH}_4^+$  from 1988 to 1999 at NADP/NTN and NYS-ADMN sites in the Adirondack region of New York (see text for abbreviations).

the record, compared to the two NADP/NTN sites (Fig. 1a and b). Annual volume-weighted concentrations of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  at the NYS-ADMN sites were sporadically elevated for certain years compared to data from NADP/NTN sites.

A comparison of the sum of cations with the sum of anions for monthly volume-weighted values generally shows an excess of cations at the NYS-ADMN sites ( $R^2 = 0.66$ ,  $[\sum \text{cations}, \mu\text{eq l}^{-1}] = 8.6 + 1.1 \times [\sum \text{anions}, \mu\text{eq l}^{-1}]$ ), compared to the NADP/NTN sites ( $R^2 = 0.97$ ,  $[\sum \text{cations}] = 4.0 + 0.9 \times [\sum \text{anions}]$ ) (Fig. 2a). This cation excess at the NYS-ADMN sites is consistent with elevated concentrations of cations in the time-series plots. The higher scatter in the NYS-ADMN data also resulted in a much lower  $R^2$  (0.66) than the NADP/NTN data ( $R^2 = 0.97$ ).

We also examined the relationship between  $\text{H}^+$  and the sum of  $[\text{SO}_4^{2-}$  and  $\text{NO}_3^-]$  as an independent evaluation of the quality of pH data (Fig. 2b). Sistla et al. (2002) suggested that our inferences that pH data from NYS-ADMN should not be used is not valid due to the differences in sampling and analytical techniques between the two networks. While we agree there are some limitations in this technique (i.e., the presence of  $\text{NH}_4^+$ , other cations, and  $\text{Cl}^-$  can all influence pH), the  $R^2$  of the relationship between  $\text{H}^+$  and the sum of  $[\text{SO}_4^{2-}$  and  $\text{NO}_3^-]$  should be an effective indicator of the consistency of the ion concentrations since a strong relationship is expected between these solutes. Indeed the relationship between  $\text{H}^+$  and the sum of  $[\text{SO}_4^{2-}$  and  $\text{NO}_3^-]$  at the two NADP/NTN sites supports this expectation with  $R^2 = 0.89$  with intercept =  $3.2 \mu\text{eq l}^{-1}$ . In contrast, at the four NYS-ADMN sites the relationship between  $\text{H}^+$  and the sum of  $[\text{SO}_4^{2-}$  and  $\text{NO}_3^-]$  was weaker;  $R^2 = 0.65$  with intercept =  $11.1 \mu\text{eq l}^{-1}$ . For the NYS-ADMN sites the  $R^2$ 's were as low as 0.42 with intercept =  $16.6 \mu\text{eq l}^{-1}$  (e.g., Nicks-ADMN) (Fig. 2b), suggesting concern with the quality of some pH values.

Sistla et al. (2002) suggest the use of specific conductance to help evaluate the accuracy of precipitation chemistry data. The  $R^2$  of the relation between the predicted and measured values of specific conductance was 0.94 with intercept = 1.2 at the four NYS-ADMN sites. The  $R^2$  values were between 0.89 and 0.96 with intercept values between 2.1 and  $-0.4$  at individual NYS-ADMN sites (Fig. 2c). There was a clear bias in the NYS-ADMN database with predicted values generally exceeding measured values. The  $R^2$  values were higher at the NADP/NTN sites;  $R^2 = 0.99$  with intercept =  $-0.4$  at the two NADP sites and  $R^2 = 0.99$  at each of the two NADP/NTN sites with intercepts =  $-0.44$  and  $-0.24$  (Fig. 2c). There was no bias in the specific conductance evaluation of the NADP/NTN data. While the check of specific conductance is a helpful tool to assess the accuracy of

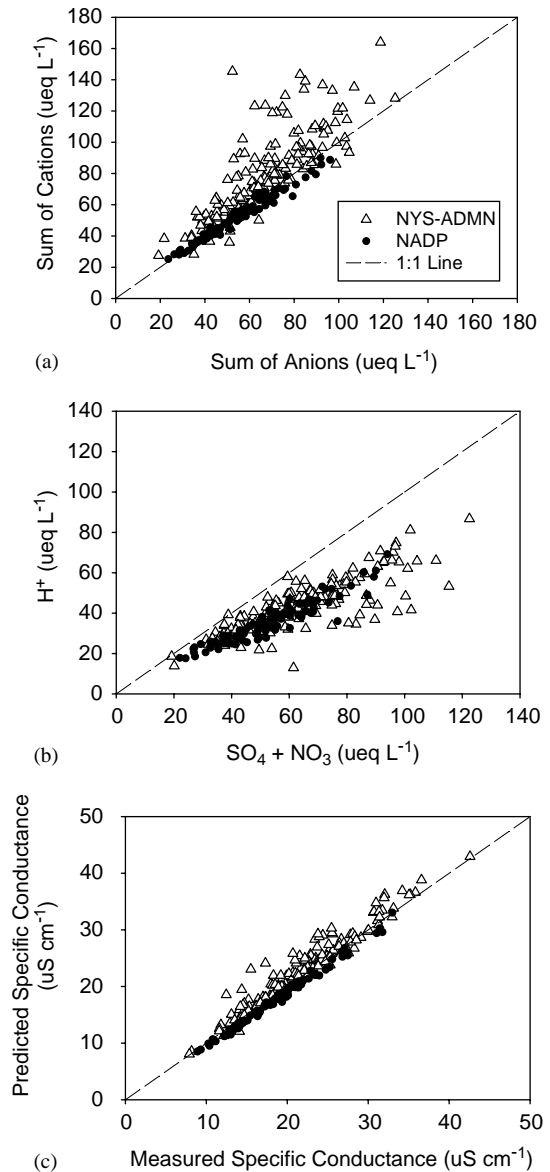


Fig. 2. The plot of the relationships between (a) the sum of cations and the sum of anions, (b) between  $\text{H}^+$  and the sum of  $[\text{SO}_4^{2-}$  and  $\text{NO}_3^-]$ , and (c) between the predicted and measured specific conductance at NADP/NTN and NYS-ADMN sites in the Adirondack region of New York (see text for abbreviations).

solution chemistry data, it has limitations for precipitation samples. The equivalent conductance of  $\text{H}^+$  is much greater than other solutes (see Eq. (1)). In low pH precipitation samples,  $\text{H}^+$  predominately contributes to specific conductance values (Sawyer and McCarty, 1978). The mean of the contribution of  $\text{H}^+$  to the predicted specific conductivity was 67.8% at the

six sites, or 66.8% at the NYS-ADMN sites and 69.7% at the NADP/NTN sites. The high contribution of  $H^+$  to specific conductance suggests that this measure is largely a check of the accuracy of pH and would not be particularly effective for the evaluation of other ions.

As a result of these analyses, we have concerns with the accuracy of some of the NYS-ADMN data. To err on the side of caution, we choose not to use any data for a solute for which we had any concerns over its accuracy. It is not appropriate for us to conduct a critical review of the NYS-ADMN database. However, we strongly urge Sistla and colleagues to conduct such an assessment. Also, appropriate metadata should be provided. Sistla et al. (2002) indicate that the NYS-ADMN sites have been sharing samples with the Adirondack Lakes Survey Corporation (ALSC) and the NADP for duplicate analysis. Providing the results of these duplicate analyses would be useful. Sistla et al. (2002) also indicate that the NYS-ADMN is “also phasing in” an ion balance check with each deposition sample”. We would suggest it would be important for the NYS-ADMN to do ion balance check for all ongoing and completed analyses.

We certainly recognize the importance of both the NADP/NTN and the NYS-ADMN networks in providing data for evaluating precipitation chemistry in the Adirondacks. We would encourage the NYS-ADMN network to include a rigorous procedure for Quality Control and Quality Assurance to ensure the integrity of the analyses of the temporal and spatial patterns of precipitation chemistry in New York State. Only after these steps are taken will the NYS-ADMN database reach its full potential as

a resource to the scientific and public policy communities.

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