Precipitation collector bias and its effects on temporal trends and spatial variability in National Atmospheric Deposition Program/National Trends Network data☆

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ABSTRACT

Precipitation samples have been collected by the National Atmospheric Deposition Program's (NADP) National Trends Network (NTN) using the Aerochem Metrics Model 301 (ACM) collector since 1978. Approximately one-third of the NTN ACM collectors have been replaced with N-CON Systems, Inc. Model ADS 00-120 (NCON) collectors. Concurrent data were collected over 6 years at 12 NTN sites using colocated ACM and NCON collectors in various precipitation regimes. Linear regression models of the colocated data were used to adjust for relative bias between the collectors. Replacement of ACM collectors with NCON collectors resulted in shifts in 10-year seasonal precipitation-weighted mean concentration (PWMC) trend slopes for: cations (-0.001 to -0.007 mgL^{-1}yr^{-1}), anions (-0.009 to -0.028 mgL^{-1}yr^{-1}), and hydrogen ion ($+0.689$ meqL^{-1}yr^{-1}). Larger shifts in NO$_3^-$ and SO$_4^{-2}$ seasonal PWMC trend slopes were observed in the Midwest and Northeast US, where concentrations are generally higher than in other regions. Geospatial analysis of interpolated concentration rasters indicated regions of accentuated variability introduced by incorporation of NCON collectors into the NTN.

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1. Introduction

The National Atmospheric Deposition Program (NADP) National Trends Network (NTN) has produced data of proven quality since 1978 in monitored precipitation chemistry and has evaluated trends in wet-deposition in North America. Changes in wet-deposition chemistry in response to emissions regulations (Lehmann et al. 2005, 2007; Likens et al., 1984), agricultural practices (Li et al., 2016), natural disasters (Wetherbee et al., 2012), and changes in climate (Wetherbee and Mast, 2016) have been explored. Observed trends in wet-deposition chemistry have indicated shifts in the "chemical climate" of the atmosphere from combined effects of changes in emissions, physical and chemical transformations, and climate (Lehmann et al., 2007).

Precipitation-sample collector bias can substantially affect data interpretation including trend analyses and spatial variability. Within long-term monitoring networks like the NTN, collector bias can affect detection of trends in precipitation and atmospheric chemistry. For example, shifts in bias caused by data-collection protocols could impart changes in slopes for temporal trends or artificial variability in spatial patterns, which are not representative of true environmental conditions. Proving sample-collection bias is especially complicated for pollutants contributed to the troposphere by regulated emissions because implementation of emissions controls influence the trends (Lehmann et al., 2007). This study evaluates potential effects on the NTN data records from incorporation of N-CON Systems, Inc. Model ADS 00-120 (NCON)[1] precipitation collectors into the NTN as a replacement for Aerochem Metrics Model 301 (ACM) collectors and to offer algorithms for adjustment of archived ACM data prior to analysis of wet deposition spatial and temporal trends.

1.1. Previous collector studies

Some of the first evaluations of the ACM collector were done at West Point, New York by Graham and Robertson (1987, 1990), who measured small differences in wet-deposition concentrations among 6 colocated ACM collectors within 100 m and a seventh

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[1] Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

ACM collector located 4 km away. The U.S. Geological Survey Precipitation Chemistry Quality Assurance project (PCQA) has estimated overall variability for NTN wet-deposition chemistry and catch efficiency with colocated samplers since October 1988 (Nilles et al., 1994) as part of the PCQA. The PCQA deployed identical ACM collectors to existing NTN sites, which were moved annually, on a water-year (October 1 − September 30) basis, for colocated operation. This program obtained colocated ACM data for different precipitation regimes at four NTN sites annually until 1997 when the program was reduced to 2 colocated sites per year (Gordon et al., 2003), which continued through water year 2006 (Wetherbee et al., 2009). Spatial and temporal analysis of NADP data variability, using the colocated ACM data, was described by Wetherbee et al. (2005).

The PCQA began colocation of dissimilar collectors in 2005 to evaluate performance differences between the ACM and other collectors (Wetherbee et al., 2009). One such instrument was the "deep-bucket" ACM collector made by NADP using an ACM chassis, a larger collection bucket (7 US gal.), and a linear-actuated motor to open the lid. The deep-bucket ACM collector was tested during 2006−08, in an attempt to improve sample catch efficiency and mechanical reliability in severe weather. However, testing of the collector revealed neither improved collection of representative samples nor mechanical robustness (Wetherbee et al., 2010). In a separate study, Wetherbee and Rhodes (2013) determined that the 11-grid ACM sensor for the Mercury Deposition Network (MDN) is more sensitive to light precipitation and opens sooner after precipitation onset than the NTN 7-grid sensor. The grid sensor study was completed as NADP began to evaluate collectors with optical precipitation sensors.

Initially, a prototype collector manufactured by Yankee Environmental Systems, Inc., which included an optical sensor, was tested during 2007−08 as part of the USGS program (Wetherbee et al., 2010). Co-located comparison of ACM and NCON collectors at NADP sites IL11 and VT99 marked the beginning of data collection for this study in water year 2009 (Wetherbee et al., 2013), which continued through water year 2015 (Wetherbee et al., 2009, 2010, 2013, Wetherbee and Martin, 2014; Wetherbee and Mast, 2016).

1.2. NTN's NCON collector retrofit

In 2010, after several years of testing, NADP approved the NCON collector as a replacement for the ACM collectors (http://nadp.sws.uiuc.edu/committees/minutes/fall2010/nos2010fall.pdf). The USGS began to retrofit NTN sites that it supports with NCON collectors in 2010. By the end of 2015, USGS had installed new rain gages and NCON collectors at 75 of the 79 NTN USGS-supported sites, and other agencies installed an additional 17 NCON collectors (Fig. S-1). Installation dates for NCON collector upgrades by USGS and other agencies are shown in Table S-1 (Supplemental Information). This information can be used to evaluate NTN time series data with respect to collector upgrades. Fig. S-1 also identifies a subset of 18 sites with at least 5 years of NCON record at the time of this analysis in 2016. Records from these 18 sites were used for temporal trend analysis ("trend test sites" hereinafter).

1.3. Description of the NCON and ACM collectors

The NCON collector's physical footprint and profile, precipitation sensor, and sample-collection mechanism are different from those of the ACM (Fig. 1). The NCON motor is triggered to move the lid off of the sample-collection bucket to expose the orifice to the atmosphere for sample collection using a Theis Clima precipitation sensor, which counts particles that interfere with an infrared beam.

The ACM motor-actuated lid is triggered by a grid sensor which consists of a heated metal plate and metal grid suspended over the plate by an approximate 2.2 ± 0.3 mm gap. When precipitation droplets physically bridge the gap between the plate and grid, an electrical circuit is completed through the water, which triggers the motor to actuate the lid. The plate then begins a programmed cycle of increased heating to evaporate the droplets off of the plate, which closes the lid after cessation of precipitation. A more detailed description of the ACM and NCON collectors is in the online Supplemental Information.

2. Materials and methods

2.1. Data

The NADP Central Analytical Laboratory (CAL) analyzes all NTN samples for calcium (Ca^{+2}), magnesium (Mg^{+2}), potassium (K^+), sodium (Na^+), ammonium (NH_4^+), Chloride ($Cl^−$), nitrate ($NO_3^−$), sulfate (SO_4^{-2}), bromide ($Br^−$), hydrogen ion (H^+ from pH), and specific conductance. Analysis of all NTN samples by a single laboratory ensures consistency in the data for analysis of trends. The CAL is the sole supplier of network supplies and data quality control to ensure consistent comparability of NADP data. Quality assurance plans and annual quality-assurance reports are on the CAL Web site at: http://nadp.sws.uiuc.edu/cal/cal_publications.html. Independent QA reports published by PCQA are available from the PCQA web site at: https://bqs.usgs.gov/pcqa/.

The NTN data-collection and quality assurance (QA) protocols are available in several documents on the NADP Web site. Procedures for operation, maintenance, and sample collection for the NCON and ACM collectors are found on the NADP web site at: http://nadp.sws.uiuc.edu/lib/manualsSOPs.aspx. Field methods for NTN site operation are documented in NADP (2015). Standard operating procedures for NTN sample analysis methods are available at: http://nadp.sws.uiuc.edu/cal/summary_of_procedures.html.

Data from colocated NCON and ACM collectors were obtained for 12 sites in precipitation regimes that commonly receive snow in winter months (Fig. S-2). Not all NADP-monitored precipitation regimes were represented in the study. Site IDs for ACM and NCON collectors are listed in Fig. S-2 and are called "colocated sites" hereinafter. Two colocated sites were operated each water year during 2009−2015, and colocations were moved to 2 different sites each water year, except for sites IL11 and VT99, where data were collected for 3 and 2 water years, respectively. The PCQA colocated sites are not official NTN sites because of their intended short-term operation. Therefore, colocated site data are available by request from the NADP Program office (Mark Rhodes, NADP QA Manager, oral communication, May 2016). Only pairs of samples for the same sampling periods where both samples were of sufficient volume for analysis and assigned Quality Rating codes of "A" or "B" were used.

Data for the trend sites used for this study have been made available online from NADP at: http://nadp.sws.uiuc.edu/data/ntn/. Instrumentation problems, such as power loss, occur infrequently but result in missed weekly samples. Data completeness with respect to sample representation of the total annual measured precipitation depths ranged from 47 to 86 percent with a median of 68 percent for paired samples at each colocated site.

Concentrations less than the CAL's reporting limits were not used for statistical analysis. This censoring practice can bias the data set (Helsel, 2012). However the percentages of concentration values below the detection limits were less than: 1 percent for Ca^{+2}, Mg^{+2}, K^+, and Na^+ and 4 percent for ammonium NH_4^+, and 0 percent for $Cl^−$, $NO_3^−$, SO_4^{-2} and H^+ for 374 weekly sample pairs. Therefore, more rigorous treatment of values below the detection
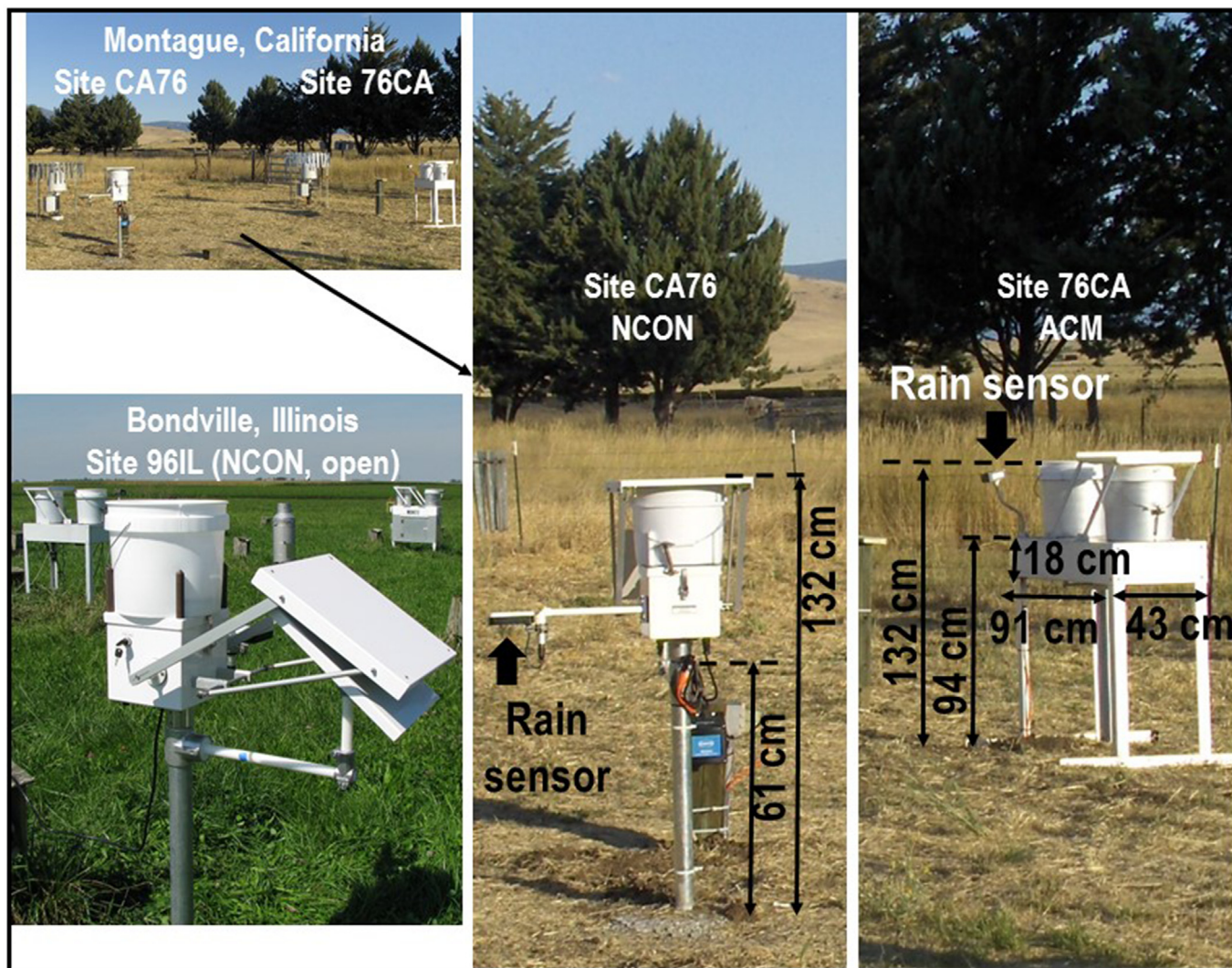
Fig. 1. Examples of colocated Aerochem Metrics Model 301 (ACM) and N-CON Systems, Inc. Model ADS 00-120 (NCON) precipitation collectors operated at National Atmospheric Deposition Program/National Trends Network sites.

limits was deemed unwarranted. Approximately 85 percent of the NTN bromide (Br⁻) data are below detection, and the remainder of the data are near the detection limit. The number of Br⁻ data for collocated sites is limited because Br⁻ became an official NADP analyte in October 2011 shortly after approval of the NCON collector (*http://nadp.sws.uiuc.edu/committees/minutes/fall2011/Joint2011fall. pdf*). Consequently, Br⁻ data are not included in this study.

2.2. Methods

Weekly, monthly, and seasonal precipitation-weighted mean concentrations for each NADP analyte were reviewed by plotting the time series for the 18 trend test sites. Upon visual examination, no obvious shifts or inflections in the time series were coincident with NCON collector start dates. Therefore, autoregressive moving average modeling of the ACM time series records for comparison to the NCON records was deemed unnecessary.

Relative differences between PCQA colocated NCON/ACM sites were calculated by subtracting ACM-sample concentrations from NCON-sample concentrations. Percent differences (PDs), relative to ACM-sample concentrations, were calculated by dividing the relative differences by the ACM-sample concentrations and multiplying

by 100. Median weekly relative concentration differences and PDs were calculated for each analyte (Table 1). Boxplots were used to illustrate weekly PDs for each colocated site (Fig. 2).

R-Project version 3.2.3 was used to conduct regression analysis on paired, weekly ACM (independent or observed) and NCON (dependent or predicted) concentrations from the colocated sites. Model selection was based on approximately normal distribution of residuals with respect to predicted values and whether the model-adjusted ACM record (i.e. predicted NCON record) was consistent with the bias observed in the colocated data for each analyte. Alternative models that used variable transformations and multiple independent variables were evaluated using: (1) minimization of the Akaike Information Criterion (AIC) and Bayesian Information Criterion (BIC) (http://127.0.0.1:24634/library/stats/html/AIC.html, accessed November 30, 2016), and (2) non-multicollinearity of explanatory variables (Variance Inflation Factor [VIF] <10) (Helsel and Hirsch, 1991). Although these diagnostic statistics indicated improved performance for some models using log-transformed variables, resulting predicted values were inconsistent with the colocated data, and thus the more complicated models were not used. All evaluated models are given in the Supplemental Information, Table S-2.

Table 1
Statistics for colocated precipitation collector weekly concentration differences calculated as NCON collector-minus- ACM collector, and percent differences (PD) calculated relative to ACM concentrations.

Parameter	Median relative differences	Standard deviation of differences (N = 374)	Median PD (%)
H ion (μeq L^{-1})	0.000	4.064	0
Spec. Cond. (μS cm^{-1})	0.6	3.0	10
Calcium (mg L^{-1})	0.016	0.179	20
Potassium (mg L^{-1})	0.003	0.064	30
Magnesium (mg L^{-1})	0.003	0.038	20
Sodium (mg L^{-1})	0.005	0.167	20
Ammonium (mg L^{-1})	0.035	0.213	20
Chloride (mg L^{-1})	0.009	0.268	20
Nitrate (mg L^{-1})	0.085	0.440	20
Sulfate (mg L^{-1})	0.051	0.271	20
Sample Volume (mL)	39.9	364.0	0

H ion, hydrogen ion from pH; μeq/L, microequivalents per liter; μS/cm, microsiemens per centimeter; mg/L, milligrams per liter; mL, milliliters; N, number of weekly sample pairs.

The slopes and intercepts determined from the regression models, based on the 12 colocated sites data, were then used to adjust the weekly historical data for the 18 trend test sites for only the portions of their records obtained with ACM collectors. Concentrations for samples obtained using NCON collectors were not adjusted. Seasonal precipitation-weighted mean concentrations were calculated for the adjusted ACM data using the seasons: January—March, April—June, July—September, and October—December. Then, seasonal mean concentrations for the adjusted ACM (predicted NCON) and actual NCON data were combined into a hybrid record consisting of adjusted ACM data and original NCON data for each analyte and each site. A hybrid record is an estimation of the entire record as if an NCON collector was used to collect all of the samples. Original and adjusted hybrid records were plotted together to evaluate any shifts in analyte concentrations.

The Mann-Kendall test was used to estimate trends in the original (ACM plus NCON) and adjusted hybrid records for the 18 trend sites. Changes in estimated trend slopes and intercepts were calculated by subtracting the values for the original record from the values for the hybrid record:

$$\Delta \text{ trend slope} = m_{adj} - m_{org}, \text{ and} \qquad (1)$$

$$\Delta \text{ trend intercept} = b_{adj} - b_{org}, \qquad (2)$$

where: m_{adj} = slope of hybrid record,
m_{org} = slope of original record,
b_{adj} = intercept of hybrid record, and
b_{org} = intercept of original record.

In a separate analysis, the influence of collector bias on the spatial interpolation of precipitation-weighted mean concentrations (PWMC) was investigated using the Spatial Analyst tool in ArcMAP 9.3.1. Prior to spatial analysis, linear models were used to adjust the weekly analyte concentrations for all valid 2000 and 2005 NTN data from sites that met NADP completeness criteria applicable during 2000 and 2005 (http://nadp.sws.uiuc.edu/data/NTN/). Only ACM collectors were used in the NTN during these years. Annual PWMCs were calculated for both the original and adjusted data for each site:

$$\text{Annual PWMC (milligrams per liter)} = \left(\frac{\sum_1^w [(ppt_w \times C_w)]}{\sum_1^w ppt_w} \right) \qquad (3)$$

where:

ppt_w is the weekly precipitation depth associated with weekly composite samples, in centimeters;
C_w is the chemical constituent concentrations, in milligrams per liter, for weekly composite samples; and
w is the number of weeks with samples and associated precipitation depths.

Rasters were calculated for each analyte for both the original and adjusted PWMCs using cubic inverse distance weighting with a 500-km interpolation radius. The original (ACM) concentration rasters were subtracted from the adjusted (estimated NCON) rasters, and the resulting NCON-minus-ACM difference rasters were mapped using the North American 1983 datum and NAD 1983 Albers projection to illustrate regions of relative collector bias in the US.

3. Results and discussion

Median weekly relative NCON-minus-ACM concentration differences (MRDs) and standard deviations of the differences for the 12 colocated sites are listed in Table 1. The MRDs for Mg^{+2}, K$^+$, Na$^+$, and Cl$^-$ were small compared to the CAL's published analytical detection limits (http://nadp.isws.illinois.edu/lib/qaReports.aspx#CAL), but MRDs for Ca^{+2}, NH$_4^+$, NO$_3^-$, and SO$_4^{-2}$ were several times their respective detection limit values. The median H$^+$ MRD is zero with variability of ±4.064 microequivalents per liter (μeq L^{-1}).

Relative concentration differences for H$^+$, Ca^{+2}, NH$_4^+$, NO$_3^-$, and SO$_4^{-2}$ are represented in boxplots for each colocated site in Fig. 2, wherein bias is illustrated by comparison to zero difference lines. The variability for IL11 is larger than the other sites because the data represent approximately 3 water years compared to 1 for the other sites except VT99 (2 years). The bias for Ca^{+2}, NH$_4^+$, NO$_3^-$, and SO$_4^{-2}$ is predominantly positive, indicating that NCON-sample concentrations are generally higher than ACM-sample concentrations as previously reported (Wetherbee et al., 2010, 2012, 2013; Wetherbee and Mast, 2016).

The concentration biases are likely due to: 1) NCON collectors opening sooner for nearly all events, more frequently for low intensity events, and closing sooner after event sessions than ACM collectors (Wetherbee et al., 2010); 2) possible contamination splashed from the NCON lid because of a slower opening rate; and 3) possible opening of the NCON collector during a non-precipitation event due to blowing dust or debris, because the sensor is triggered by particle count and not wetness, as is the case for the ACM collector. It is unknown which of these factors is most influential in causing the observed biases. Overall, the NCON opens
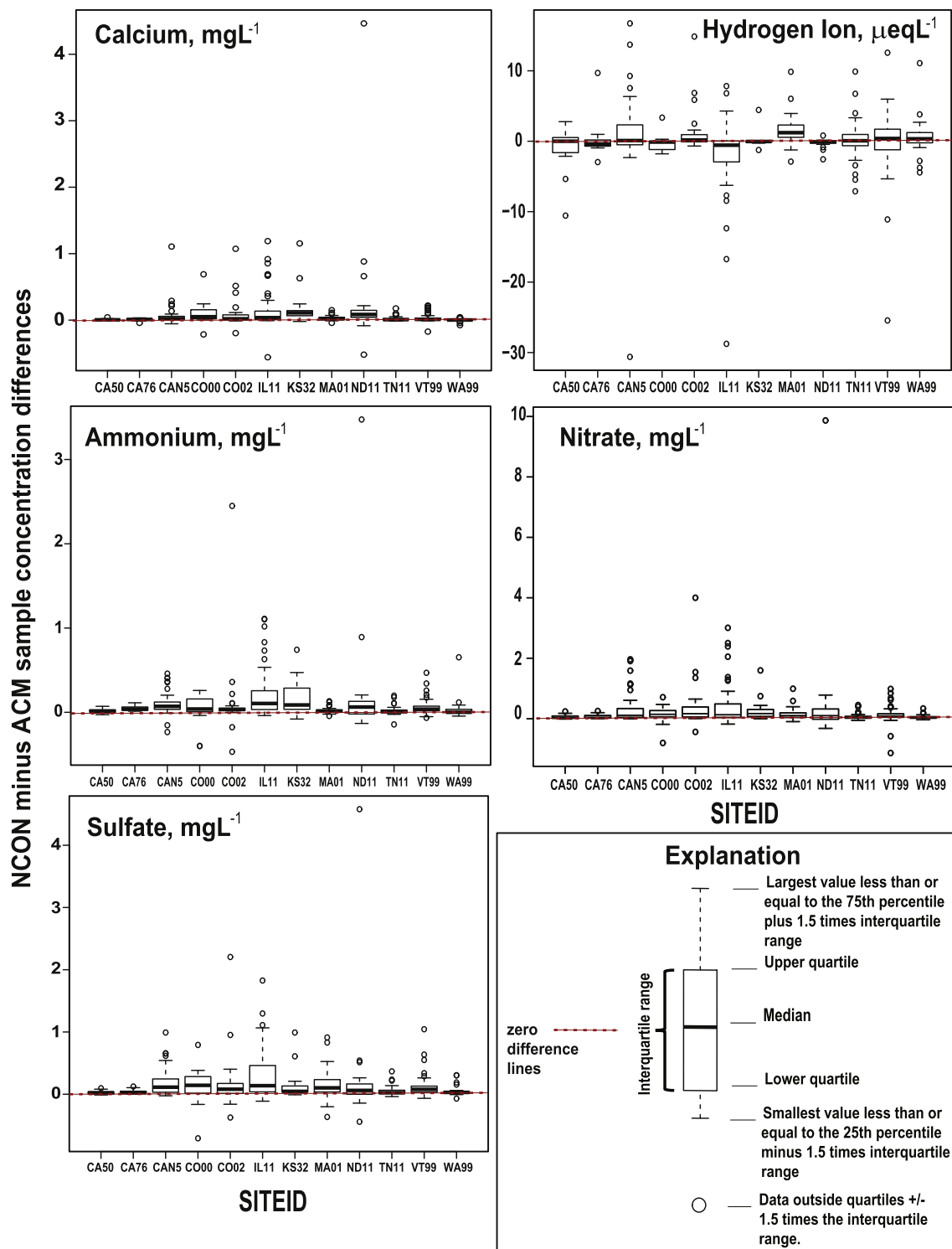
Fig. 2. Calcium, hydrogen ion, ammonium, nitrate, and sulfate concentration differences for weekly precipitation samples collected with colocated Aerochem Metrics Model 301 and N-CON Systems, Inc. Model ADS 00-120 precipitation collectors at National Atmospheric Deposition Program/National Trends Network sites.

sooner, closes sooner, and is exposed to less dry deposition between periods of precipitation than the ACM (Wetherbee et al., 2013).

Generally, the NCON sensor is more sensitive than the ACM sensor in that much less precipitation is required to trigger the NCON's Theis optical sensor than the ACM grid sensor (Wetherbee et al., 2013). Lynch et al. (1989) and Schroeder and Hedley (1986)

showed that precipitation solute concentrations are commonly highest at the onset of wet-deposition events and progressively more dilute throughout the event as a result of initial washout, but notably not always as shown by Colin et al. (1987). The NCON collectors have been shown to be more effective at catching the early onset of events due to the superior sensitivity of their optical precipitation sensors (Wetherbee et al., 2010). Similarly, the NCON
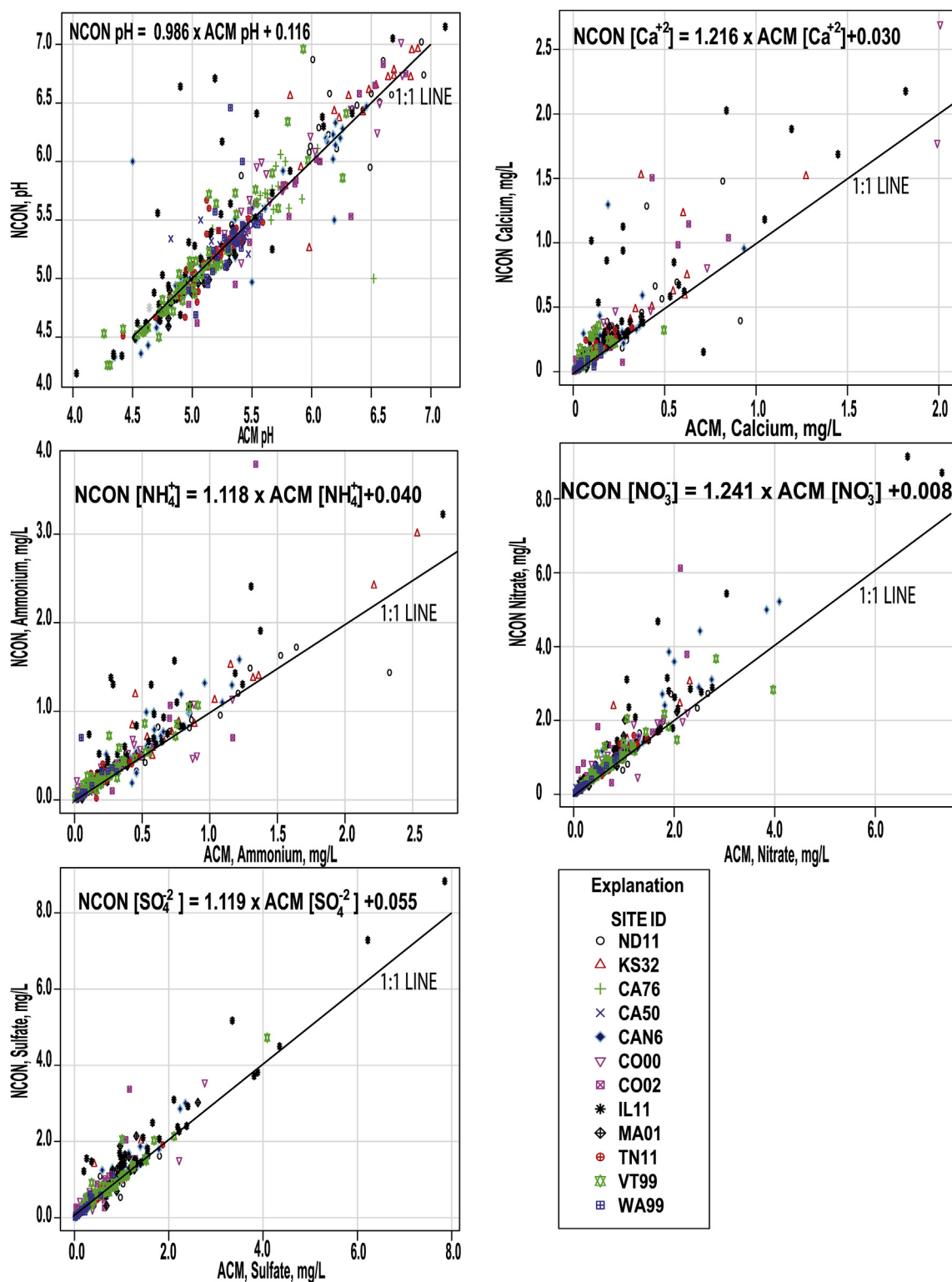
Fig. 3. Paired weekly precipitation concentrations for colocated Aerochem Metrics Model 301 and N-CON Systems, Inc. Model ADS 00-120 precipitation collectors at National Atmospheric Deposition Program/National Trends Network sites and regression equations used to estimate NCON concentrations from measured ACM concentrations.

sensor detects the cessation of precipitation much sooner than the ACM. However, at arid and windy sites, the NCON can open during dry conditions more frequently than the ACM because blowing snow, detritus, dust, and flying insects can be mistaken by the optical sensor as precipitation, thus allowing dry deposition to

contaminate the samples.

Neutralization of acidity can occur from sample contamination with dust and associated buffering carbonate minerals. This effect was evident in the data in Fig. 3 where most colocated samples with pH > 5.5 were observed from sites in open, windy agricultural
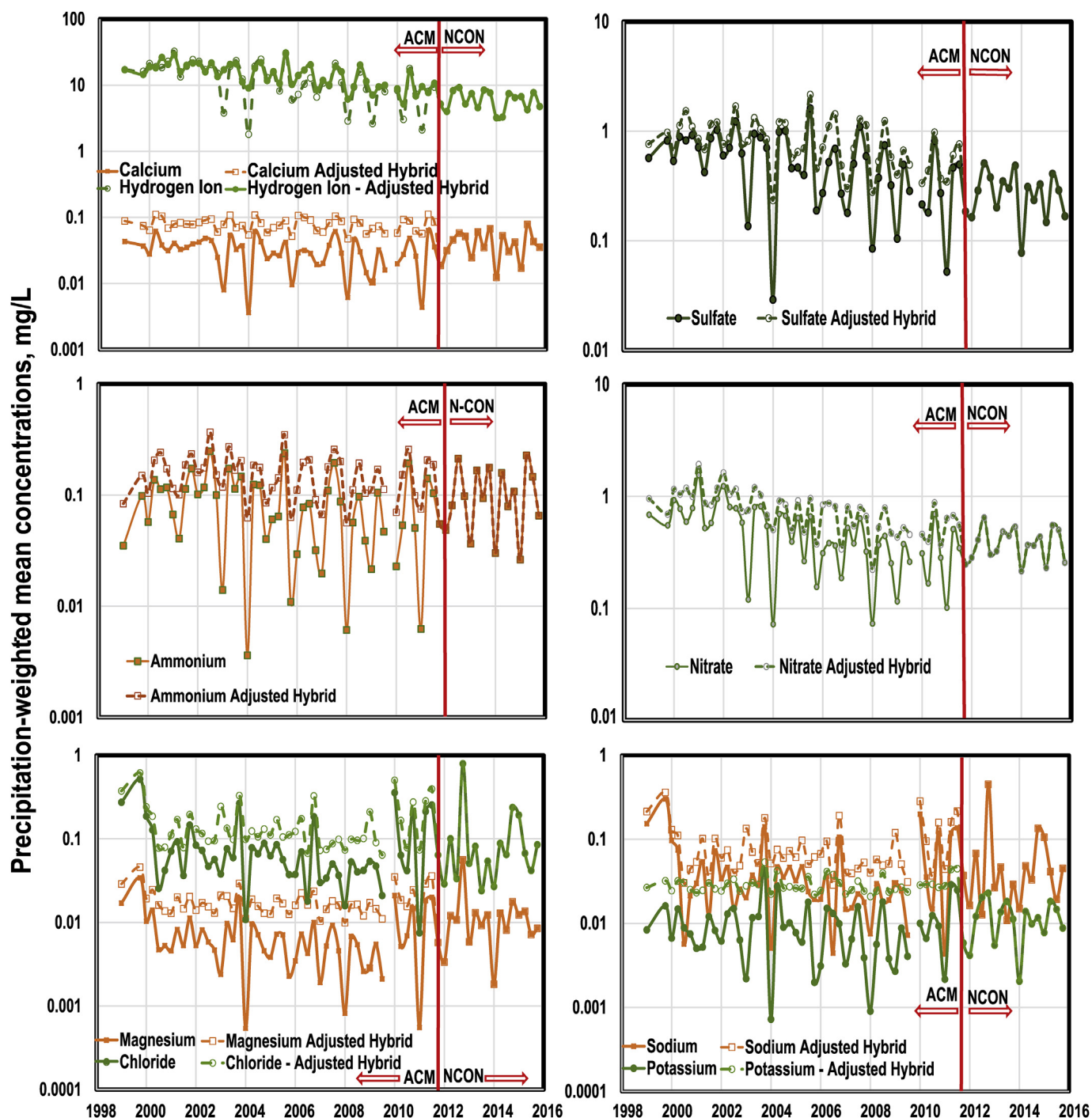
Fig. 4. Time series of calcium, hydrogen ion, sulfate, ammonium, nitrate, magnesium, chloride, sodium, and potassium seasonal precipitation-weighted mean concentrations calculated from weekly original National Trends Network site ME08 records using Aerochem Metrics Model 301 (ACM) and N-CON Systems, Inc. Model ADS 00-120 (NCON) collectors (solid lines) and hybrid records consisting of ACM values adjusted to estimated NCON values and original NCON values (dashed lines). Red lines indicate time of ACM replacement with NCON collector. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

areas (CO00, IL11, KS32, ND11), a windy, high-altitude site (CO02), and two rural forest sites (CAN5, VT99). The bias for H⁺ was seen to be dependent upon geographic location and the acidity of the precipitation. The NCON samples exhibit lower H⁺ concentrations than ACM samples at pH greater than 5.75, but higher H⁺ concentrations at pH below 5.75 (Fig. 3). Precipitation samples with naturally higher pH (>5.5) (compared to all samples) are more susceptible to neutralization of H⁺ (Latysh and Gordon, 2004) than

samples with pH < 5.5.

Multiple linear regression models were calculated using ACM sample volume (mL), precipitation depth (cm), collection efficiency (100 × [sample depth/precipitation gage depth]), and base-10 logarithms of those parameters as additional descriptive variables. Variance inflation factors were less than 2 for all additional variables for all multiple-parameter models. Models using base-10 logarithms of both NCON and ACM concentrations yielded

Table 2

Changes in slopes and intercepts of trends in seasonal precipitation-weighted mean concentrations resulting from model adjustment of measured ACM-collected solute concentrations to estimated NCON-collected concentrations for 18 upgraded National Atmospheric Deposition Program sites. Results for full record trends and 2006-2015 trends are compared.

Analyte (unit)	Full record				2006−2015 portion of record				
	Value of maximum trend slope changes (unit $L^{-1}yr^{-1}$)	Maximum trend intercept changes (unit $L^{-1}yr^{-1}$)	Trend significance changes		Value of maximum trend slope changes (unit $L^{-1}yr^{-1}$)	Maximum trend intercept changes (unit $L^{-1}yr^{-1}$)	Trend significance changes		Largest 10-year changes in seasonal mean concentrations[a] (unit L^{-1})
			I − S (N sites)	S − I (N sites)			I − S (N sites)	S − I (N sites)	
Ca^{+2} (mg)	−0.006	+0.124	8	2	−0.007	+0.105	11	0	−0.070
Mg^{+2} (mg)	−0.003	+0.214	6	3	−0.004	+0.268	11	1	−0.040
Na^+ (mg)	−0.003	+0.111	7	2	−0.005	+0.095	9	1	−0.050
K^+ (mg)	−0.002	+0.083	10	3	−0.001	+0.030	7	3	−0.010
NH_4^+ (mg)	−0.006	+0.208	6	3	−0.006	+0.149	8	1	−0.060
Cl^- (mg)	−0.005	+0.174	6	1	−0.009	+0.274	11	0	−0.090
NO_3^- (mg)	−0.040	+0.963	3	1	−0.016	+0.895	11	1	−0.160
SO_4^{-2} (mg)	−0.036	+0.974	0	0	−0.028	+1.020	4	0	−0.280
H^+ (µeq)	+0.183	+2.880	0	1	+0.689	+9.990	1	1	+6.890

mg, milligrams, Ca^{+2}, calcium; Mg^{+2}, magnesium; Na^+, sodium; K^+, potassium; NH_4^+, ammonium; Cl^-, chloride; NO_3^-, nitrate; SO_4^{-2}, sulfate; H^+, hydrogen ion; µeq, micro-equivalents; unit $L^{-1}yr^{-1}$, mg or µeq per liter per year; N, number out of 18 sites; I − S, change from insignificant to significant trend at 0.05 significance level; S − I, change from significant to insignificant trend at 0.05 significance level; unit L^{-1}, mg or µeq per liter.

[a] Greatest slope change multiplied by 10 years.

predicted values with residuals that more closely approximated normality. However, even with application of bias correction factors to adjust the antilogarithms of the predicted values, the models using log-transformed data did not produce estimated NCON concentrations that were consistent with the positive bias exhibited in the colocated data. Therefore, log-transformed models are presented in the supplemental information, but they were not used for subsequent analysis of collector bias. Instead, the least complex statistical models relating the colocated concentrations were found to be most appropriate for adjustment of the data for collector bias.

The models in Table S-3 were selected to adjust weekly ACM-sample concentrations for the 18 trend test sites to create the hybrid records consisting of adjusted ACM and measured NCON sample data. Scatter plots and fitted regression lines for the selected models are shown in Fig. 3. All of the model slopes are highly significant ($p < 0.0001$), and the intercepts are all significant at the $\alpha = 0.02$ significance level, except for NO_3^- and pH. The adjusted R-square for the selected K^+ model is low (0.1942), owing to the high variability of the K^+ concentrations, which are typically low (e.g. less than 5 times the detection limit). Examples of time series for seasonal PWMCs are compared for original and hybrid records for site ME08 in Fig. 4.

The Seasonal Mann-Kendall test was used to estimate trends in seasonal PWMCs for the 18 trend test sites for both the original and hybrid records for each site. Changes in trend slopes and intercepts were calculated by subtracting the estimated parameters for the original and hybrid records (original minus hybrid) for both the full periods of record and the 10-year period of 2006−2015 (Table 2). The hybrid record trends exhibited more negative slopes than the original trend slopes for nearly all of the seasonal PWMCs for both the full-record and 10-year trends, but trend slopes increased for H^+. Although adjustment of the original ACM values to estimated NCON values changed the magnitudes of the trends only slightly, the adjustment affected the calculated statistical significance of the trends. Twice as many statistically insignificant trends became statistically significant compared to those that switched from

statistically significant to insignificant (Table 2). The hybrid records are less variable than the unadjusted, original records (Fig. 4) because the models adjust the ACM data to the mean of the ACM/NCON paired data, which may cause the observed changes in trend significance for hybrid records compared to the original records.

The largest 10-year (2006-2015) changes in seasonal PWMCs among the 18 trend test sites are given in Table 2. The ACM collectors were replaced by the NCON collectors at approximately the midpoint of this period (2010). It was assumed that one-half of the maximum shift over the 10-year period occurred prior to collector change out. Therefore, the maximum shifts in NTN PWMCs that can be attributed to ACM replacement with NCON collectors are estimated by one-half of the largest 10-year changes given in Table 2. For example, the largest 10-year change in seasonal SO_4^{-2} PWMC (-0.280 mg L^{-1}) that can be attributed to ACM replacements with NCON collectors is approximately -0.140 mg L^{-1}.

Slope changes were mapped for both full record and 2006-2015 trends for analysis of any spatial patterns among the 18 trend test sites (Fig. 5). Regional patterns in full record trend slope changes were observed for NO_3^- and SO_4^{-2}. Larger (more negative) changes occurred for sites in the Midwest and Northeast, where NO_3^- and SO_4^{-2} concentration are high relative to the rest of the network (NADP, 2015).

Spatial variability in national PWMC maps that is introduced by NCON collector bias was evaluated using NADP data for 2000 and 2005, relatively dry and average precipitation years, respectively. As stated in the methods above, PWMCs for each site were interpolated to calculate rasters for both original and model-adjusted values, and then the rasters were subtracted to create PWMC difference maps for each analyte (Figs. 6−7). The maps for both years use the same color-coding scale for Ca^{+2}, NH_4^+, NO_3^-, and SO_4^{-2}, but not for H^+ and precipitation depth.

The maps show regions where relatively prominent PWMC differences occur, both positive and negative, indicated by warm and cool colors, respectively. It is in these regions where the NADP's annual PWMC and deposition maps have been most affected since
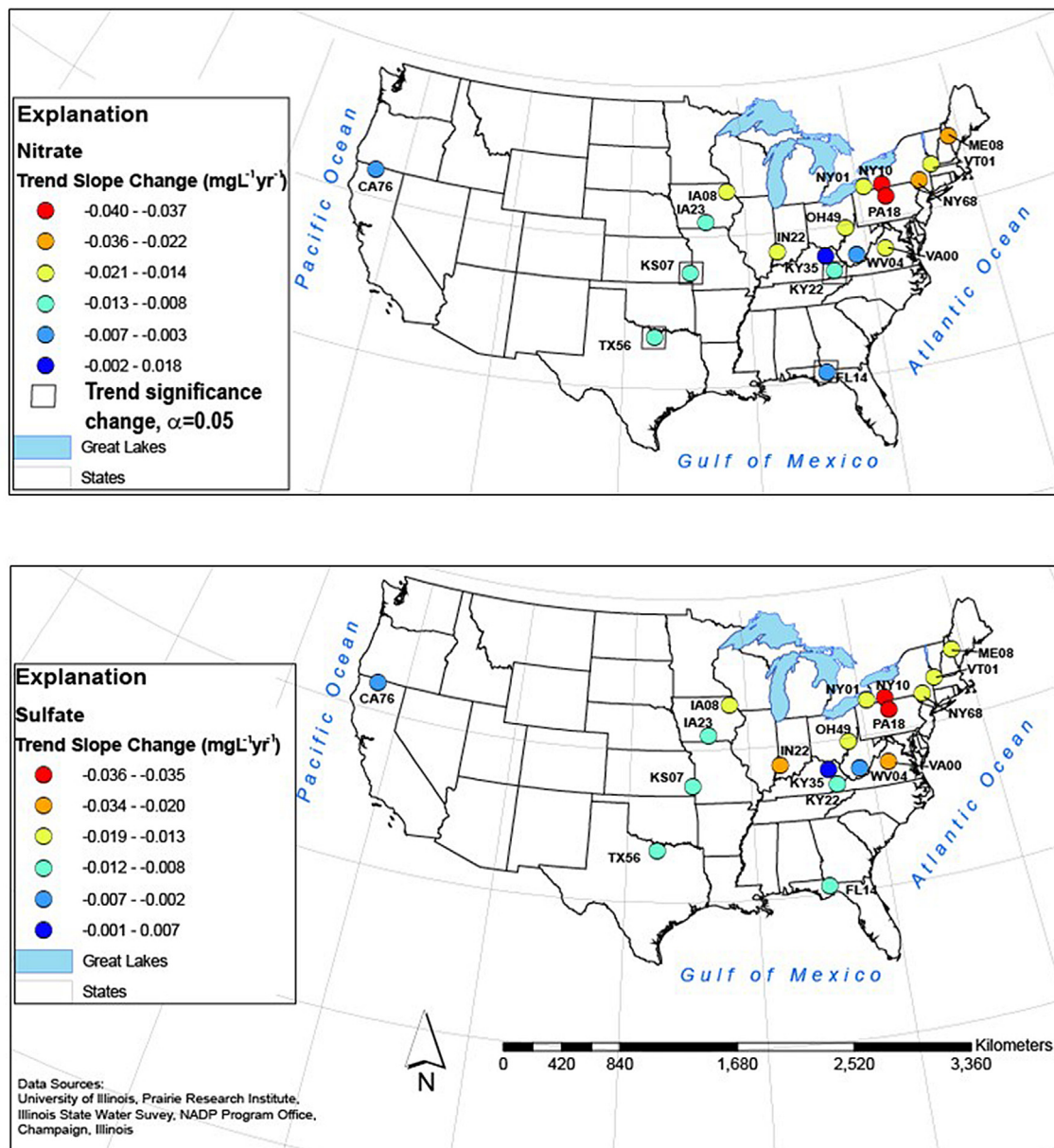
Fig. 5. Spatial distribution of Seasonal Kendall trend changes resulting from regression-model adjustment of full, original weekly nitrate and sulfate concentrations for precipitation samples collected with Aerochem Metrics Model 301 collectors at National Trends Network sites. Periods of record range from 16 (ME08) to 37 (OH49) years among 18 sites with at least last 5 years of record collected using N-CON System, Inc. Model ADS 00-120 collectors.

approximately 2012 by replacement of ACM collectors with NCON collectors. The 2000 and 2005 maps show similar regions of H^+, and SO_4^{-2} PWMC differences in the Midwest and Northeast, and similar regions of Ca^{+2} PWMC differences in the Plains and Southwest. For NH_4^+, PWMC differences are greatest in the Plains for 2000 but more prominent in the Southwest for 2005. The maps indicate similar PWMC differences for NO_3^- for 2000 and 2005 in the Plains and Great Lakes regions plus a region of higher differences in the Southwest for 2005. Annual precipitation depth did not have an obvious effect on spatial PWMC differences, but this was not explored quantitatively.

4. Conclusions

Precipitation samples collected by the NADP/NTN using NCON collectors usually exhibit higher concentrations of official NADP

analytes than samples from ACM collectors. However, samples from NCON collectors commonly are characterized by higher pH than ACM samples at NTN sites with relatively high pH (pH > 5.5). Linear regression models were fit to weekly paired data from colocated ACM and NCON collectors for NTN analytes. Comparison of original and model-adjusted records revealed that retrofit of ACM precipitation collectors with NCON collectors at NADP/NTN sites resulted in small shifts in 10-year seasonal PWMC trend slopes (-0.001 to -0.007 mgL^{-1}yr^{-1} for cations, -0.009 to -0.028 mgL^{-1}yr^{-1} for anions, and $+0.689$ meqL^{-1}yr^{-1} for hydrogen ion). Spatial analysis of the annual NCON-minus-ACM differences indicated larger shifts in NO_3^- and SO_4^{-2} seasonal PWMC trend slopes in the Midwest and Northeast regions, where concentrations were generally higher than other regions in the US.

Geospatial comparison of interpolated concentration rasters created from original (ACM) and model-estimated (NCON) data
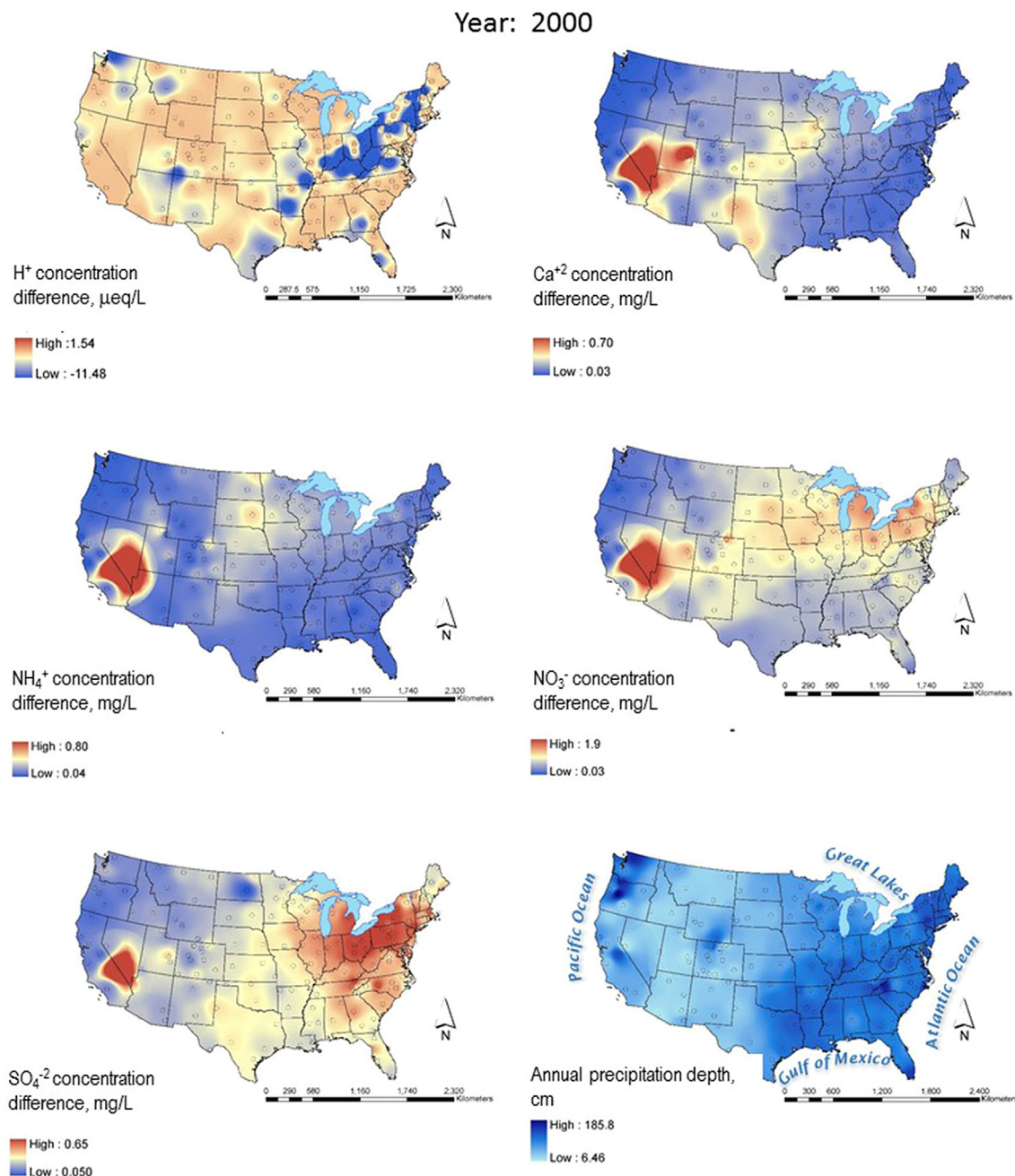
Year: 2000

Fig. 6. Year 2000 National Trends Network annual precipitation-weighted mean concentration differences calculated by raster subtraction (b minus a); where raster (a) generated from original, weekly samples collected with Aerochem Metrics Model 301 (ACM) collectors, and raster (b) generated from the same values adjusted to estimated N-CON Systems, Inc. Model ADS 00-120 (NCON) collector concentrations, using linear models of colocated ACM and NCON data. Interpolated 2000 total annual precipitation depth map shown for reference.

indicated regions of increased variability introduced by incorporation of NCON collectors into the NTN. Regions of increased spatial variability are analyte specific. In general, spatial variability is increased by collector bias in regions where analyte concentrations are relatively high. Spatial variability of interpolated PWMCs has increased for: H^+ (from pH), Ca^{+2}, and SO_4^{-2} in the Midwest and Northeast; NH_4^+ in the Plains and Southwest, and NO_3^- in the Plains, Great Lakes, and Southwest.

After more NCON data are collected, a more rigorous analysis that includes data from NCON sites in the Plains, Southeast, Rocky Mountains, and West Coast is needed. A sample size of

approximately 50 sites with at least 5 years of NCON record and as many years or more of ACM record could be used to calculate upper confidence limits on a high percentile (e.g. 95th percentile) of trend slope changes to better estimate the maximum expected shift in PWMCs from upgraded NCON sites.

The following method for trend analysis is suggested, but not necessarily endorsed by NADP: 1) Adjust ACM data records to obtain estimated NCON results using models in Table S-3; 2) Perform trend analyses on both the adjusted and unadjusted data; 3) Present the two trend slopes as a range; 4) Identify changes in trend significance and treat changes from insignificant to
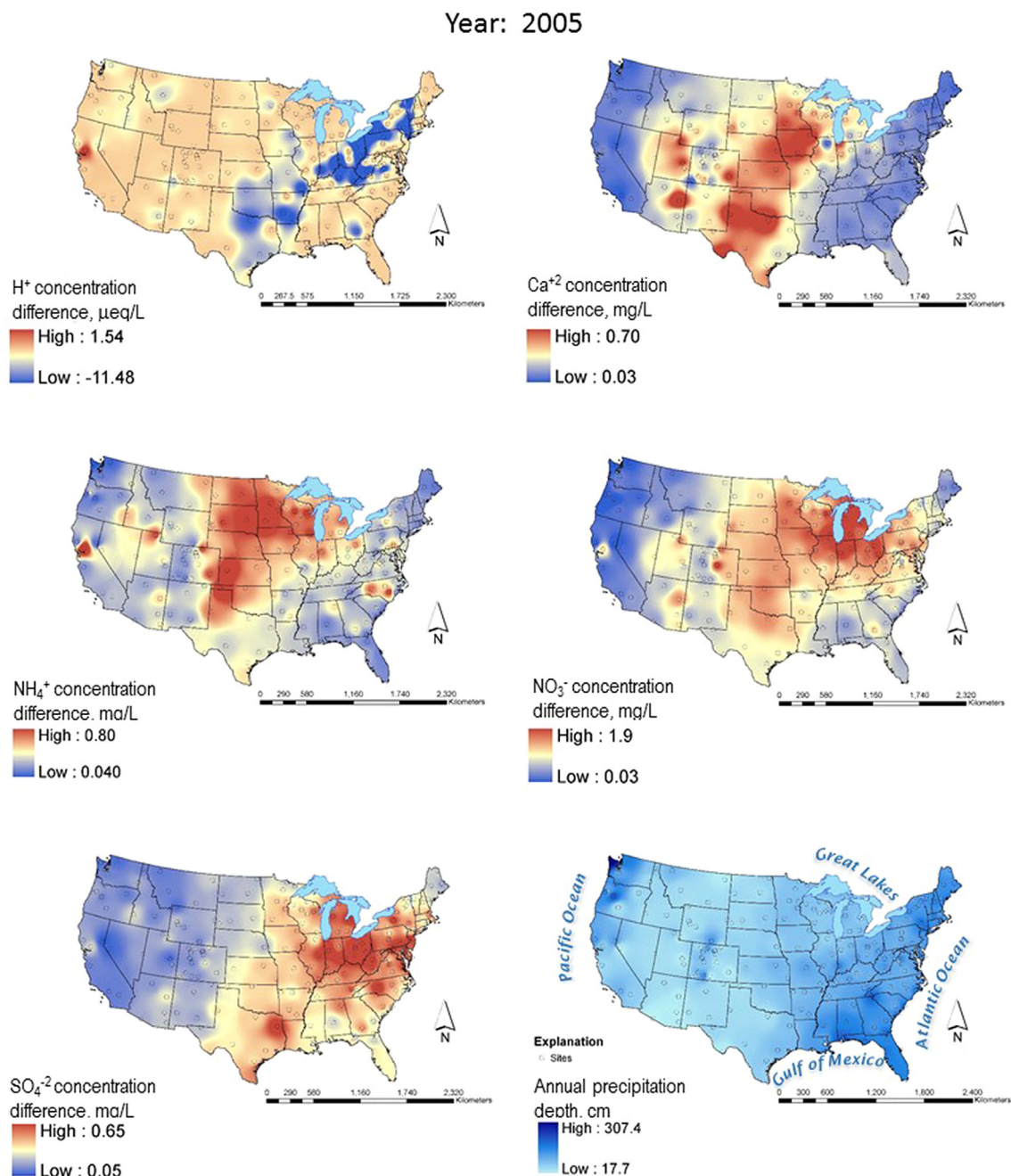
Year: 2005

Fig. 7. Year 2005 National Trends Network annual precipitation-weighted mean concentration differences calculated by raster subtraction (b minus a); where raster (a) generated from original, weekly samples collected with Aerochem Metrics Model 301 (ACM) collectors, and raster (b) generated from the same values adjusted to estimated N-CON Systems, Inc. Model ADS 00-120 (NCON) collector concentrations, using linear models of colocated ACM and NCON data. Interpolated 2005 total annual precipitation depth map shown for reference.

significant with caution. A method for spatial analysis (e.g. annual deposition maps) is also offered for consideration: 1) Adjust ACM data records to obtain estimated NCON results; 2) Perform the spatial interpolation twice using (a) both actual NCON records and the adjusted ACM data combined and (b) the original NADP data with no adjustment (Note: both rasters must use data for exactly the same sites); 3) Subtract the rasters obtained (a minus b) and inspect the resulting difference map for irregularities (e.g. area in Southwest USA in Fig. 6); 4) Present the spatial analysis product that appears most representative, stating that different rasters are obtained using adjusted and unadjusted NADP data.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.12.036.

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Further reading

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