

Comparison of precipitation chemistry measurements obtained by the Canadian Air and Precipitation Monitoring Network and National Atmospheric Deposition Program for the period 1995–2004

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Abstract Precipitation chemistry and depth measurements obtained by the Canadian Air and Precipitation Monitoring Network (CAPMoN) and the US National Atmospheric Deposition Program/National Trends Network (NADP/NTN) were compared for the 10-year period 1995–2004. Colocated sets of CAPMoN and NADP instrumentation, consisting of precipitation collectors and rain gauges, were operated simultaneously per standard protocols for each network at Sutton, Ontario and Frelighsburg, Ontario, Canada and at State College, PA, USA. CAPMoN samples

were collected daily, and NADP samples were collected weekly, and samples were analyzed exclusively by each network's laboratory for pH, H⁺, Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺, Cl⁻, NO₃⁻, and SO₄²⁻. Weekly and annual precipitation-weighted mean concentrations for each network were compared. This study is a follow-up to an earlier internetwork comparison for the period 1986–1993, published by Alain Sirois, Robert Vet, and Dennis Lamb in 2000. Median weekly internetwork differences for 1995–2004 data were the same to slightly lower than for data for the previous study period (1986–1993) for all analytes except NO₃⁻, SO₄²⁻, and sample depth. A 1994 NADP sampling protocol change and a 1998 change in the types of filters used to process NADP samples reversed the previously identified negative bias in NADP data for hydrogen-ion and sodium concentrations. Statistically significant biases ($\alpha = 0.10$) for sodium and hydrogen-ion concentrations observed in the 1986–1993 data were not significant for 1995–2004. Weekly CAPMoN measurements generally are higher than weekly NADP measurements due to differences in sample filtration and field instrumentation, not sample evaporation, contamination, or analytical laboratory differences.

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Introduction

The chemical composition of wet deposition is being measured by many networks in North America, primarily by the Canadian Air and Precipitation Monitoring Network (CAPMoN) and the US National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Each network uses its own protocols and instrumentation for precipitation-sample collection, precipitation depth measurement, chemical analysis, and quality assurance. Descriptions of the two networks may be found on the worldwide web at: <http://nadp.sws.uiuc.edu/> and http://www.msc.ec.gc.ca/capmon/index_e.cfm. Because each network uses a different protocol for data collection, it is important to evaluate the comparability of the data obtained by each network for application to continental-scale wet-deposition studies.

The CAPMoN and NADP networks have collaborated by operating co-located monitoring equipment at three sites located at Sutton, Quebec, Canada (CAN4), Frelighsburg, Quebec, Canada (CAN5), and Center County, Pennsylvania, USA (PA15), each denoted by the four-character code in parentheses. The CAN4 collocated site was shut down in 2001, relocated 15 km to the southwest and assigned a new NADP site identifier of CAN5. Data from these two sites for 2001 were combined into a single annual record for this study. The CAN4 site is described by Sirois et al. (2000) as situated in open grassy areas surrounded by mixed forests on all sides. The CAN5-Frelighsburg site is located in rural, southern Quebec province; well removed from industrial and urban activity with some agricultural land use. CAN5 is located at 45°03'06" north latitude and 72°51'42" west longitude at an altitude of 195 m. The PA15 site, located at Pennsylvania State University, is described by Sirois et al. (2000) as situated in a broad valley between two mountain ridges in the Appalachian Mountains at 40°47'18" north latitude and 77°56'48" west longitude at an altitude of 393 m. The PA15 site is located in a 0.03 km², mown grass area in otherwise forested land. During the study period, the trees surrounding the collectors were no taller than the distance between the bases of the trees and the collector. Each collocated site has both CAPMoN

and NADP monitoring instruments for collection of precipitation samples and measurement of precipitation depth.

Data from the CAN4 and PA15 collocated sites were compared by Sirois et al. (2000) for the period September 1986–December 1993 to evaluate the magnitude and bias of differences between network measurements on a weekly, seasonal, and annual basis. That work is referenced extensively herein. This paper is intended to serve as an update and extension of the original analysis, using the 10-year period January 1995–December 2004. Variability in atmospheric chemistry and deposition during 1995–2004 due to changing emissions or climate is not accounted for and assumed not to affect the results.

During 1994, the NADP sampling protocol changed. Prior to 1994, NADP wet deposition samples were sealed and shipped in the collector buckets that had been deployed in the field. Quality assurance data revealed that NADP sample chemistry was altered by contact with the bucket lid o-ring, especially for sodium and hydrogen-ion concentrations (Gordon et al. 1997, NADP website advisory at <http://nadp.sws.uiuc.edu/documentation/advisory.html>, as of 5–10–08). The protocol change enacted in 1994 and in practice today requires that precipitation samples are transferred to a 1-l polyethylene bottle for shipment to the laboratory. Sirois et al. (2000) analyzed data collected prior to the NADP protocol change. The record for 1994 was omitted from this analysis to eliminate any potential variability caused by transition to a new (and current) NADP sample-collection protocol.

Many of the data processing, censoring, and statistical analysis protocols used for this study were obtained from Sirois et al. (2000) to provide a reliable internetwork data comparison between data obtained before and after the 1994 NADP protocol change. The techniques used by Sirois et al. (2000) were not completely duplicated for reasons discussed later. Furthermore, the NADP has included a three-annum assessment of internetwork comparability into its evaluation of attainment of NADP data-quality objectives. Data-analysis methods used for this study are intended to be repeated for ongoing, periodic evaluation of internetwork comparability.

Experimental design and measurement protocols

CAPMoN samples were collected daily if a precipitation event occurred. All precipitation samples were collected in laminated plastic bags with virgin polyethylene interiors and Mylar exteriors. The bags were changed daily at 0800 ± 1 hour regardless of whether precipitation fell within the previous 24 h. The samples were heat-sealed in the bags for shipment to the Environment Canada Laboratory in Downsview, Ontario. CAPMoN samples were collected using a Meteorological Instruments of Canada (MIC) sampler and precipitation depth was measured using the Meteorological Service of Canada (MSC) Type-B rain gage during non-winter months and a Nipher shielded snow gage during winter to optimize snow catch (Sirois et al. 2000). The collector consists of a metal bucket-shaped holder for a sample-collection bag which is covered by a protective lid during dry periods and mechanically removed or replaced when a precipitation sensor signals the onset and cessation of precipitation, respectively. The MSC Type-B rain gage continuously weighs and records the mass of water in a collection vessel open to the sky. The inverted bell-shaped Nipher shield is fitted around the orifice of the gage to dampen wind moving around the gage, thus, enhancing the collection of snow.

CAPMoN samples were analyzed by the MSC laboratory located in Downsview, Ontario, Canada. All CAPMoN data were quality-controlled and validated following the methods described by Vet et al. (1988). A complete description of CAPMoN procedures is found in CAPMoN (1985).

NADP samples were collected in polyvinylchloride (PVC) buckets which were installed in AeroChem Metrics (ACM) Model A-31 wet-dry collectors and covered by a plastic-coated seal. Precipitation depth was measured using an unshielded Belfort Model 5–780 rain gage. The ACM is conceptually similar to the CAPMoN MIC sampler in that it too has a precipitation sensor-activated lid to expose the bucket to the sky during periods of precipitation and then cover the bucket again after precipitation cessation. The sensors on the CAPMoN and NADP collectors both rely on the electrical conductance through

the precipitation that contacts the sensor, but the designs of the two sensors are very different. Like the MSC Type-B rain gage, the NADP Belfort Model 5–780 rain gage is also a weighing-type rain gage fitted with a paper chart recorder.

NADP sample buckets were removed weekly on Tuesdays within minutes of collection of the CAPMoN samples and sealed with a clean PVC lid. After transportation to the field support facility, the site operator weighed the sample for volume determination, removed aliquots for field pH and specific conductance determination, and transferred the remaining sample to a 1-l polyethylene bottle which was shipped for analysis at the NADP Central Analytical Laboratory (CAL) located at the Illinois State Water Survey in Champaign, Illinois. Both the buckets and bottles are reused after cleaning in an industrial deionized water washer. Cleanliness of the buckets and bottles is routinely tested as part of the internal quality assurance program for the CAL (NADP 2002). All NADP data are quality-controlled and validated following the methods described by the NADP CAL Quality Assurance Plan (NADP 2002). With the exception of the common site operator at each colocated site, the CAPMoN and NADP data were collected and samples were handled as if they were generated by independent monitoring networks.

Data analysis methods

Data processing

CAPMoN data used for this analysis were processed and provided by Environment Canada. The daily CAPMoN data were mathematically combined into weekly precipitation-weighted measurements (C^{WM}) to coincide with weekly NADP measurements using the following equation (Sirois et al. 2000):

$$C^{WM} = \left(\frac{\sum_{i=1}^m C_i P_i}{\sum_{i=1}^m P_i} \right) \tag{1}$$

where m is the number of valid daily values in the weekly interval, C_i is the daily concentration of a given ion, and P_i is the daily precipitation depth as

measured by the precipitation gage. Precipitation-weighted mean pH values were calculated by converting daily pH values to hydrogen-ion concentrations and then using Eq. 1 to calculate precipitation-weighted mean hydrogen-ion concentrations, and finally, taking the negative of the base 10 logarithm. All values less than the analytical method detection limits (MDLs) were set to 2/3 of the MDLs to be consistent with Sirois et al. (2000). To limit potential effects of missing data on the inter-comparison, only data for weeks where the valid daily samples represented 95% of the weekly precipitation depth were used, again for consistency with Sirois et al. (2000). The CAPMoN data were reported with qualifiers to identify samples with visible contamination, but the debris type was not specified. Initial attempts to censor the data to remove samples with debris reduced the dataset by a factor of 8. Therefore, neither debris content nor NADP samples were used as a factor to censor CAPMoN data.

NADP data were provided by the CAL via the NADP Program Office. NADP values less than the MDL were reported as the MDL by CAL, and subsequently, the values were changed to 2/3 of the MDL for comparison to the CAPMoN data. Although the CAPMoN and NADP detection limits are similar, some variability in the computed concentration differences is due to differences in MDLs, especially for magnesium and potassium data. NADP data were reported with many qualifiers, two of which signify atypical equipment operation and contamination with debris of six different types. Data identified as being potentially impacted by equipment failure were eliminated from the analysis, but as stated above, removal of debris-containing samples limited the dataset and was not done.

The CAPMoN and NADP data were merged by weekly sample-collection ending date for the NADP site, which is typically on a Tuesday morning. Weekly CAPMoN-minus-NADP differences in concentrations, precipitation-depth, and sample-depth were calculated. Analysis of the differences included calculation of the following statistics to be as consistent as possible with the previous work of Sirois et al. (2000). These measures are described in detail by Sirois and Vet

(1999) and are only briefly described herein as follows:

- Modified median absolute deviation or M.MAD (Randles and Wolf 1979)—a robust, non-parametric analog of the standard deviation;

$$\begin{aligned}
 & \text{M.MAD} \\
 &= \left(\frac{1}{0.6745} \right) \\
 & \times \text{Median} \left[\left| (C_{\text{CAPMoN}} - C_{\text{NADP}})_i \right| \right] \\
 & - \text{Median} (C_{\text{CAPMoN}} - C_{\text{NADP}})_i \left| \right] \tag{2}
 \end{aligned}$$

where: C_{CAPMoN} = weekly CAPMoN measurement, C_{NADP} = weekly NADP measurement, and the number 0.6745 is included to ensure that the median absolute error term in the numerator is a consistent estimator of the standard deviation of the distribution of x , should that distribution be normal.

- Winsorized standard deviation (Barnett and Lewis 1984)—a robust estimator of the standard deviation calculated by replacing extreme values outside the 1st and 99th percentiles with those respective values and then computing the standard deviation to limit variability due to outliers;
- 90th and 99th Percentiles (P90, P99) of the absolute differences—the positive values of the error term for which 90% and 99% of the probability distribution is included between + and - of that value;
- Nonparametric coefficient of variation (CoV)—calculated as the M.MAD divided by the median CAPMoN value

The M.MAD generally represents the central part of the distribution of the measurement differences. Measurement differences are compared against the M.MAD to evaluate bias. The other statistical measures reflect the broader characteristics of data distributions. All of these measures combined provide an overall description of the

variability of the differences between CAPMoN and NADP measurements (Sirois et al. 2000).

Bias at the central location in the data was characterized by absolute relative bias, calculated as:

Absolute Relative Bias (ARB)

$$= \left(\frac{\text{Median } |C_{\text{CAPMoN}} - C_{\text{NADP}}|}{\text{Median } C_{\text{CAPMoN}}} \right) \times 100, \quad (3)$$

where:

- C_{CAPMoN} weekly precipitation-weighted mean CAPMoN concentration or depth and
- C_{NADP} weekly NADP concentration or depth.

Slight changes in field and laboratory methods, variability in sampling materials (e.g., bags, bottles, etc.), and aging of field equipment can affect the internetwork variability over the duration of operation of long-term monitoring networks. Therefore, time trends of the internetwork differences were evaluated graphically using locally weighted scatterplot smoothing (LOWESS) in SAS (SAS Institute, Inc. 1989) for visual assessment of the moving locations of the quartiles of the differences. The LOWESS plots use a window width of 0.67 and iteration limit of 10. Changes in the relative distance between the LOWESS quartile lines indicate changes in internetwork variability whereby closer lines indicate less variability and vice versa.

Trends in the differences were evaluated with the Seasonal Kendall Test for Trend using the USGS computer program for the Kendall family of trend tests, Kendall.exe (Helsel et al. 2005) available at: <http://pubs.usgs.gov/sir/2005/5275/downloads/>. The Seasonal Kendall test performs the Mann–Kendall trend test for individual seasons of the year, where season length is defined by the user. It then combines the individual results into one overall test for whether the dependent (Y) variable changes in a consistent direction (monotonic trend) over time (Helsel et al. 2005).

Total annual constituent deposition values in units of kilograms per hectare were computed by taking the sum of the products of the week-

ly precipitation-weighted concentrations and the weekly precipitation depths as follows:

$$\text{Deposition}_{\text{Annual}} \text{ (kg/ha)} = \left(\sum_{j=1}^{52} C_j P_j \right) / 100, \quad (4)$$

where 52 is the number of weekly values in the year, C_j is the weekly concentration of a given ion in milligrams per liter, and P_j is the weekly precipitation depth in millimeters as measured by the precipitation gage. As given above, weekly precipitation-weighted concentrations for the CAPMoN instrumentation and weekly NADP concentration data were censored to enhance representativeness of the data and avoid introduction of variability to the internetwork comparison due to missing data. Because the data were censored, the median annual deposition values used for this study for both networks are assumed to underestimate true median annual deposition, and these values should not be used as final estimates of annual deposition. However, these values are perfectly acceptable for comparison of internetwork annual deposition differences, such as presented herein.

Results

Internetwork comparability of weekly data

Scatter plots of the CAPMoN and NADP data (Fig. 1) provide both a qualitative comparison of the networks' data and the ranges of concentration and depth values measured. A 1-to-1 line is shown on each plot for visual comparison of the internetwork data. These scatter plots are similar to those published for pre-1994 data by Sirois et al. (2000). The plots show CAPMoN values to be higher than NADP/NTN values for sample depth and for concentrations of all the measured constituents except sodium.

The plots indicate that CAPMoN pH values generally are lower than NADP pH values. The scatterplot comparison of weekly CAPMoN and NADP precipitation depths indicates a lack of bias because the points plot in an even distribution

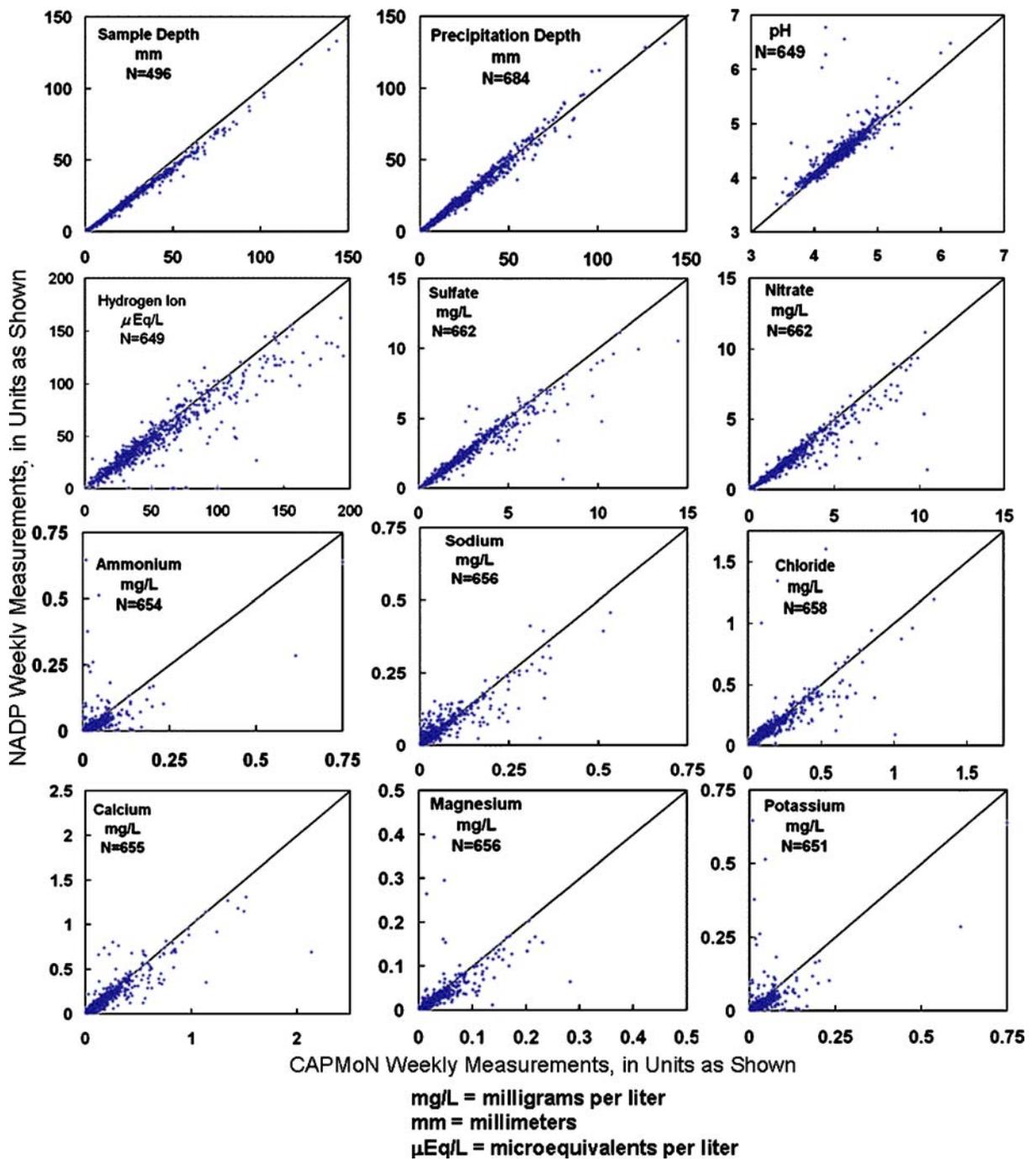


Fig. 1 Scatter plots showing variation of weekly NADP concentration and depth measurements with CAPMoN weekly precipitation-weighted concentration and depth for the period 1995–2004 for three collocated sites combined.

N is the number of data points of sufficient quality for comparison. *Lines* are drawn at one-to-one ratio for visual comparison

Table 1 Comparison of summary statistics for CAPMoN-minus-NADP weekly concentration and depth-measurement differences for samples obtained at colocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This study (1995–2004)			Sirois et al. (2000) (1986–1993)		
	N	Arithmetic mean difference	Median difference	N	Arithmetic mean difference	Median difference
Calcium	655	0.019	0.010	494	0.02	<0.01
Magnesium	656	<0.01	<0.01	497	<0.01	<0.01
Sodium	656	<0.01	<0.01	508	−0.02	−0.01
Potassium	651	−0.02	<0.01	500	<0.01	<0.01
Ammonium	654	0.030	0.062	541	0.069	0.053
Chloride	658	0.02	<0.01	528	<0.01	<0.01
Nitrate	662	0.32	0.15	533	0.21	0.10
Sulfate	662	0.22	0.10	532	−0.02	−0.01
Hydrogen ion	649	0.019	0.003	504	0.011	0.008
Precipitation depth	684	0.80	0.50	711	1.7	1.4
Sample depth	496	3.2	2.7	696	1.9	1.9

All concentration units in milligrams per liter and depth measurements in millimeters unless otherwise specified
 N number of paired samples from colocated sampling sites

along both sides of the 1-to-1 line. The internet-network comparisons for sodium changed between the pre- and post-1994 periods. While NADP sodium concentrations generally are higher than CAPMoN sodium concentrations, as shown for pre-1994 data by Sirois et al. (2000), the comparison appears to be closer for the 1995–2004 data than for the 1986–1993 data.

Results for the statistical evaluation of inter-network comparability are given in Tables 1, 2, 3,

and 4. Approximately 20% more paired weekly samples were used for the analysis of the 1995–2004 data than for the evaluation of the 1986–1993 data.

Median CAPMoN concentrations are used as a basis of internetwork comparison for both studies for consistency in methodology. Median CAPMoN measurement values are similar between studies. The median CAPMoN concentration values that changed the most between the

Table 2 Comparison of summary statistics for CAPMoN-minus-NADP weekly concentration and depth-measurement differences for samples obtained at colocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This Study (1995–2004)		Sirois et al. (2000) (1986–1993)		Comparison of two studies Percent change ^a between studies for CAPMoN median values
	Median CAPMoN value	Bias at $\alpha = 0.10$ and $>\pm 0.01$ per sign test?	Median CAPMoN value	Bias at $\alpha = 0.10$ and $>\pm 0.01$ per sign test?	
Calcium	0.122		0.100		−22
Magnesium	0.019		0.020		5
Sodium	0.031		0.030	Y	−3
Potassium	0.020		0.020		0
Ammonium	0.387	Y	0.314	Y	−23
Chloride	0.114		0.130		12
Nitrate	1.932	Y	2.010	Y	4
Sulfate	2.044	Y	2.100		3
Hydrogen ion	0.043		0.060	Y	28
Precipitation depth	20.2	Y	17.8	Y	−13
Sample depth	20.6	Y	15.7	Y	−31

Y yes

^aCalculated as: $[(\text{median value})_{2000 \text{ study}} - (\text{median value})_{\text{this study}} / (\text{median value})_{2000 \text{ study}}] \times 100$

Table 3 Comparison of summary statistics for CAPMoN-minus-NADP weekly concentration and depth-measurement differences for samples obtained at colocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This study (1995–2004)			Sirois et al. (2000) (1986–1993)		
	Absolute relative bias (%)	1% Winsorized standard deviation	M.MAD	Absolute relative bias (%)	1% Winsorized standard deviation	M.MAD
Calcium	8.2	0.13	0.03	<10.0	0.07	0.03
Magnesium	15.8	0.02	<0.01	<50.0	0.01	<0.01
Sodium	3.2	0.04	0.01	33.3	0.03	0.02
Potassium	35.0	0.30	0.01	<50.0	0.03	<0.01
Ammonium	16.0	0.19	0.059	16.9	0.11	0.054
Chloride	7.0	0.07	0.02	<7.7	0.06	0.03
Nitrate	7.6	0.51	0.18	5.0	0.54	0.24
Sulfate	5.0	0.50	0.17	0.5	0.48	0.28
Hydrogen ion	7.2	0.017	0.007	13.	0.015	0.008
Precipitation depth	2.7	4.3	1.7	7.9	3.7	1.7
Sample depth	13.5	2.4	2.1	12.1	3.7	1.0

All concentration units in milligrams per liter and depth measurements in millimeters unless otherwise specified

two periods are for calcium (+22%), ammonium (+23%), chloride (−12%), and hydrogen ion (−28%). Median CAPMoN precipitation depth increased between the two periods (+13%) as did sample depth (+27%). Median differences for the 1995–2004 data were the same to slightly lower than for the 1986–1993 data for all analytes except nitrate, sulfate, and sample depth.

Bias typically refers to a disproportionate measurement in one direction compared to the true or accepted value. For this study, bias is quantified relative to the median CAPMoN values to be consistent with the Sirois et al. (2000) and does not imply that CAPMoN data are regarded as more correct than NADP data. Bias in CAPMoN-

minus-NADP measurement differences was evaluated using the Sign test (Kanji 1993) at the $\alpha = 0.10$ (90% confidence) significance level. CAPMoN measurements tended to be higher than NADP measurements for all analytes during 1986–1993 (Sirois et al. 2000). However, the 1994 NADP sampling protocol change appears to have eliminated the bias for sodium and hydrogen-ion concentration for the 1995–2004 data. A small but significant ($\alpha = 0.10$) absolute relative bias for sulfate concentration is indicated for the 1995–2004 data that was not significant during 1986–1993.

Internetwork absolute relative bias was lower for 1995–2004 than for 1986–1993 for all analytes

Table 4 Comparison of summary statistics for CAPMoN-minus-NADP weekly concentration and depth-measurement differences for samples obtained at colocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This study (1995–2004)		Sirois et al. (2000) (1986–1993)	
	P99	CoV (%)	P99	CoV (%)
Calcium	0.351	23.0	0.5	28.6
Magnesium	0.07	<21.0	0.06	<59.0
Sodium	0.12	<32.0	0.26	66.0
Potassium	0.112	35.0	0.2	<59.0
Ammonium	0.803	15.2	0.704	17.2
Chloride	0.28	20.2	0.47	26.0
Nitrate	2.69	9.2	3.04	12.0
Sulfate	2.34	8.4	2.66	13.4
Hydrogen ion	0.077	15.8	0.075	13.4
Precipitation depth	9.4	8.4	22.7	9.5
Sample depth	13.2	10.3	24.6	6.5

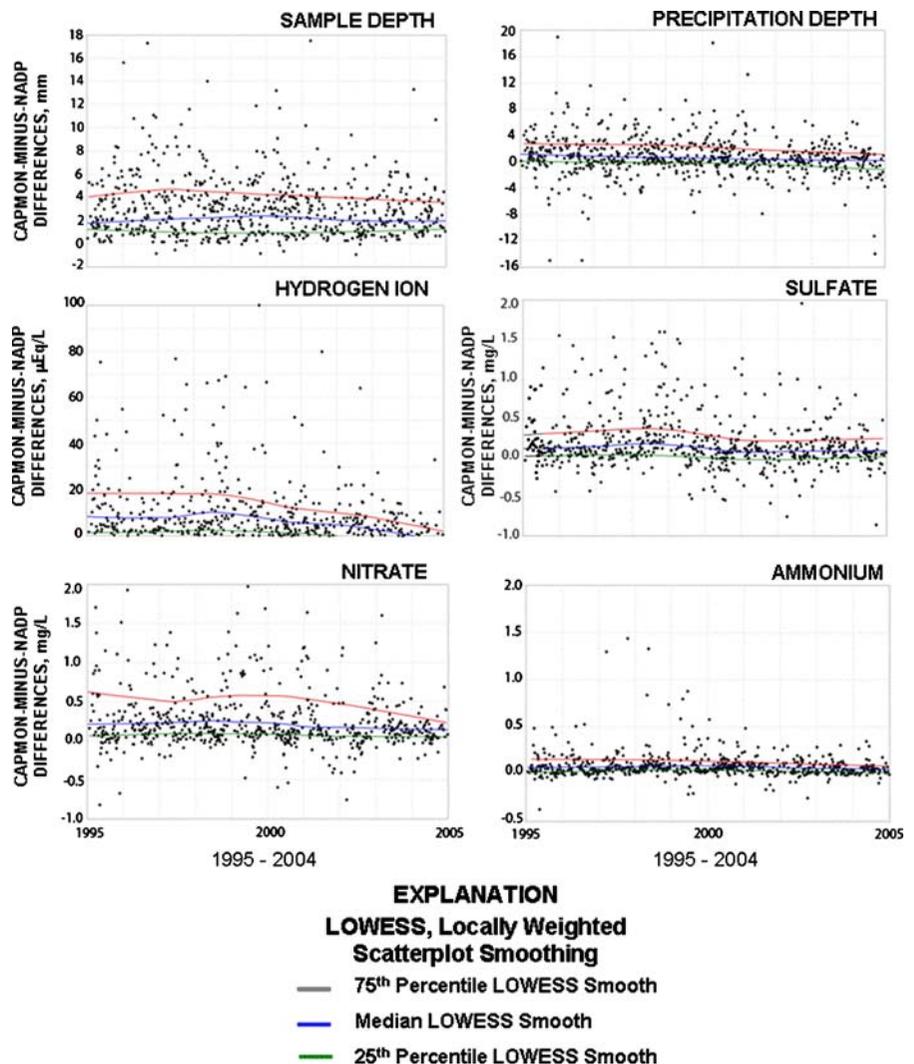
All concentration units in milligrams per liter and depth measurements in millimeters unless otherwise specified

except nitrate and sulfate and for sample depth (Tables 3 and 4). The largest changes in absolute relative bias were observed for magnesium, sodium, potassium, and hydrogen-ion concentrations. It is unclear which factors are influencing the changes in absolute relative bias, but the 1994 NADP sampling protocol change and the subsequent change of sample filters during 1998 are two events that are suspected to have reduced sodium contamination of NADP samples. Since 1998, it has been standard NADP protocol to filter all samples using 0.45 – μm Gelman™ polyethersulfone filters. Prior to 1998, Millipore™ HAWP (hydrophilic mixed cellulose esters) filters were used, and sodium contamination from

the filters was a recurring problem. There is no sodium contamination with the Gelman filters. All parameters approximate the target concentrations for standard reference materials. Gordon et al. (1999) documented that the NADP protocol changes played a role in reducing bias in NADP data for sodium and hydrogen-ion concentrations. Note that only NADP filters its samples prior to chemical analysis and CAPMoN does not.

Winsorized standard deviations of the between-network differences for 1995–2004 are generally higher than for the 1986–1993 data. Winsorized standard deviation increased by a factor of 10 for potassium concentration (Tables 3 and 4), but potassium is present in low concentrations in

Fig. 2 Locally weighted scatterplot smoothing of distribution quartiles for CAPMoN-minus-NADP colocated measurements of *sample depth*, *precipitation depth*, and concentrations of *hydrogen ion* (from pH), *sulfate*, *nitrate*, and *ammonium* at sites CAN4, CAN5, and PA15 over the 10-year period 1995–2004



precipitation; thus, small absolute increases in concentration translate into large percent increases. M.MAD values for 1995–2004 were slightly lower than for 1986–1993 for all analytes except ammonium and for sample depth. Comparison of the coefficients of variation for the two time periods indicate overall lower relative variability in the internetwork differences for all analytes except hydrogen ion and sample depth for the 1995–2004 data. This is consistent with what is known about the variability of wet-deposition measurements, whereby variability generally tends to decrease with increasing sample depth and decreasing concentration (Sirois et al. 2000; Wetherbee et al. 2004, 2006). The fact that the Winsorized standard deviations of the differences increased but the M.MAD generally decreased in 1995–2004 relative to 1986–1993 suggests that variability of the differences is increasing while bias is remaining constant. This characteristic of the between-

network differences could be attributed to aging instrumentation that is losing sensitivity to detection of precipitation due to wear.

Trends in weekly differences

LOWESS in SAS (SAS Institute, Inc. 1989) was used to identify trends in weekly internetwork differences during 1995–2004 as shown in Figs. 2 and 3. LOWESS is described by Cleveland (1985) and is useful for observing nonlinearities in trends (Lynch et al. 1996). The LOWESS method, which does not assume a functional relation between concentration and time, was used with a window width of 0.67 with an iteration limit of 10 to generate the plots in Figs. 2 and 3. LOWESS lines were drawn approximately through the upper and lower quartiles of the distribution of each analyte (75th and 25th percentiles, respectively) and through the median of the distribution. The

Fig. 3 Locally weighted scatterplot smoothing of distribution quartiles for CAPMoN-minus-NADP colocated measurements of sodium, chloride, calcium, magnesium, and potassium at sites CAN4, CAN5, and PA15 over the 10-year period 1995–2004

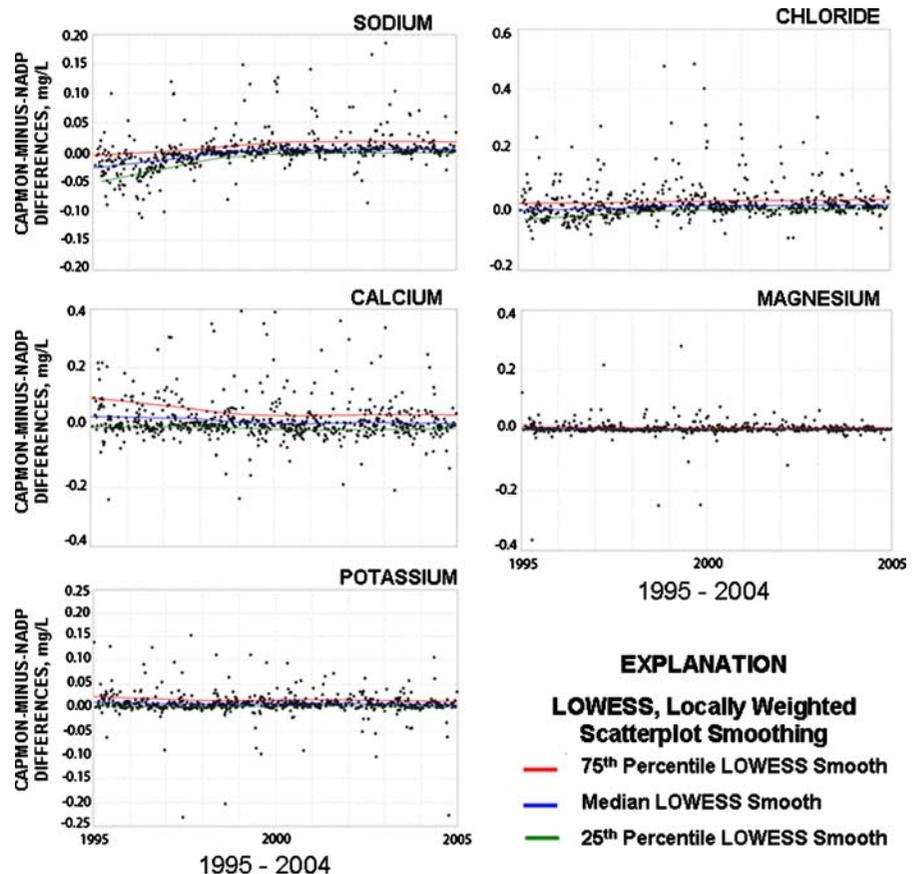


Table 5 Seasonal Kendall Trend Test results for natural log of CAPMoN-minus-NADP measurement differences during 1995–2004 for colocated sites CAN4, CAN5, and PA15

Analyte	<i>Tau</i>	<i>S</i>	<i>Z</i>	<i>p</i>	Estimated trend slope	Estimated trend intercept	10-year percent change
Calcium	0.052	28	0.698	0.4854	0.0193	-3.95	17
Magnesium	-0.072	-39	-0.989	0.3226	-0.0258	-5.16	-23
Sodium	-0.156	-84	-2.149	<i>0.0317</i>	-0.0926	-4.20	-80
Potassium	0.054	29	0.728	0.4664	0.0087	-4.87	8
Ammonium	-0.128	-69	-1.756	<i>0.0790</i>	-0.0396	-2.53	-35
Chloride	-0.078	-42	-1.061	0.2885	-0.0213	-3.90	-19
Nitrate	-0.176	-95	-2.428	<i>0.0152</i>	-0.0383	-1.54	-34
Sulfate	-0.185	-100	-2.556	<i>0.0106</i>	-0.0699	-1.63	-61
Hydrogen ion	-0.159	-86	-2.195	<i>0.0282</i>	-0.0571	1.88	-50
Precipitation depth	-0.174	-94	-2.401	<i>0.0163</i>	-0.0670	0.61	-58
Sample depth	-0.100	-54	-1.368	0.1712	-0.0223	1.08	-20

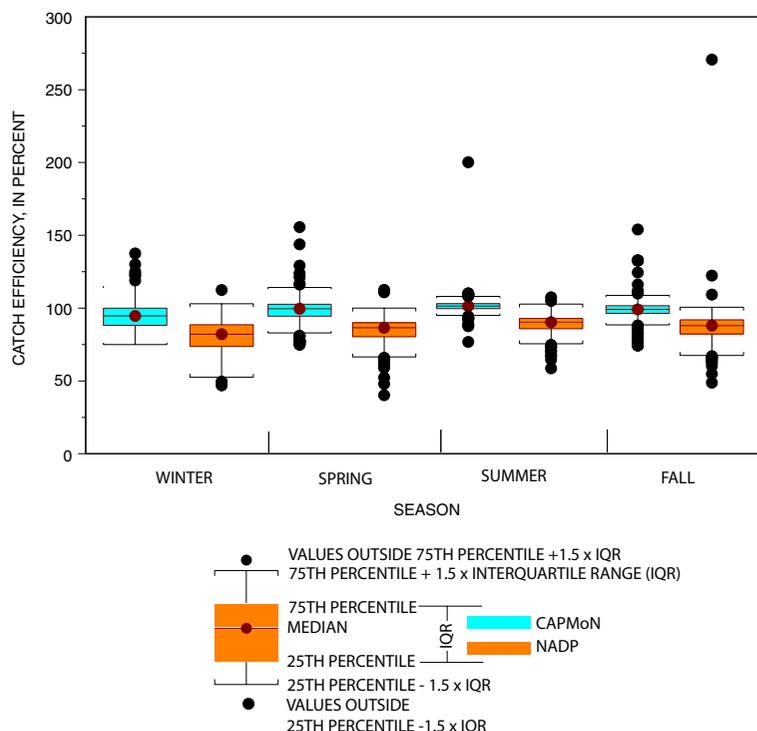
Italicized entries denote significant trends at $\alpha = 0.10$; Analysis parameters: 12 seasons per year over the 10-year period 1995–2004; Null hypothesis: No trend (slope = 0)

Tau Kendall’s Tau = $S/n \times (n-1) \times 0.5$ statistic; *S* Kendall’s *S* statistic = sum of the S_i series over all seasons; *Z* Seasonal Kendall test statistic; *p* probability of rejecting the null hypothesis when true

distance between the upper and lower quartile lines approximates the inter-quartile range and illustrates the relative variability in the internet-network differences over time. The plots are scaled to enhance resolution of the LOWESS lines. Less than 1% of the data points fall outside the maxima and minima of the graphs.

The LOWESS graphs in Figs. 2 and 3 indicate that internetwork variability as determined by CAPMoN-minus-NADP weekly differences decreased and became less positively biased over the 10-year period for calcium, ammonium, nitrate, sulfate, hydrogen-ion concentrations, and for sample and precipitation depths. Internetwork

Fig. 4 Comparison of *boxplots* of precipitation collector catch efficiency distributions by season for CAPMoN and NADP data at sites CAN4, CAN5, and PA15 over the 10-year period 1995–2004, whereby sample depth for both networks is divided by the CAPMoN precipitation gage depth and converted to a percentage



variability decreased and became less negatively biased for weekly sodium and chloride concentrations, possibly due to NADP 1994 sampling- and 1998 filtering-protocol changes. Internetwork variability for weekly magnesium and potassium concentrations appears relatively unchanged over the 10-year period per the LOWESS graphs.

Results for the Seasonal Kendall trend analysis for the weekly CAPMoN-minus-NADP measurement differences are given in Table 5 to complement the qualitative, visual depictions given by the LOWESS graphs. The *p* values and 10-year percent change values are shaded in Table 5 to denote statistically significant trends with 90% confidence ($\alpha = 0.10$).

All of the trends identified as statistically significant in Table 5 have a negative slope, which indicates improved internetwork comparability. As such, the results in Table 5 indicate that internetwork comparability improved for sodium, ammonium, nitrate, sulfate, and hydrogen-ion concentrations and for precipitation depth measurement. The estimated trend for internetwork sodium concentration difference has the highest absolute 10-year percent change (−80%). The 10-year percent change for hydrogen-ion concentration is −50%. The marked improvements in internetwork comparability for sodium and hydrogen-ion concentrations are attributed, at least in part, to the NADP sampling and filtration protocol changes in 1994 and 1998, respectively.

Effect of precipitation type on internetwork comparability

Weekly collector catch efficiency values, calculated as the ratio of sample depth to precipitation gage depth, indicate that CAPMoN and NADP collectors tend to under catch frozen precipitation because median catch efficiencies for both networks are slightly lower in fall and winter than in spring and summer (Fig. 4). Sample depth has been shown to affect the comparability of the CAPMoN and NADP data (Sirois et al. 2000). NADP data include a flag to identify whether rain, snow or a mixture of precipitation types, comprise each weekly sample. The variations of M.MAD values with precipitation type for weekly precipitation-weighted measure-

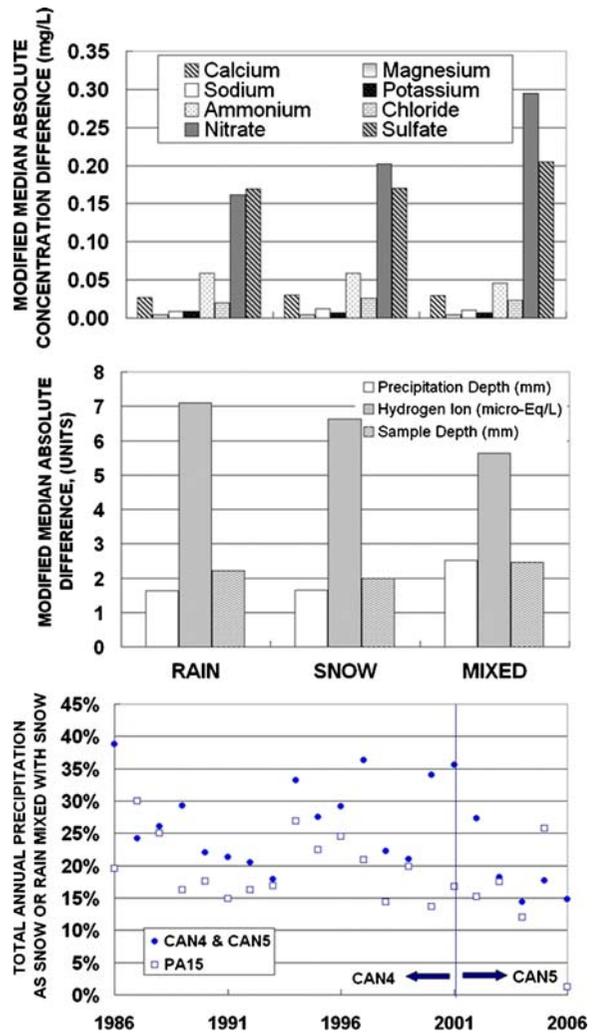


Fig. 5 Graphical comparison of CAPMoN-minus-NADP modified median absolute differences for weekly, collocated measurements of precipitation-weighted analyte concentrations, sample depth, and precipitation depth obtained for different precipitation types and at sites CAN4, CAN5, and PA15 over the 10-year period 1995–2004

ments of each constituent are illustrated in Fig. 5. The M.MAD data in Fig. 5 indicate that variability in the nitrate- and sulfate-concentration and precipitation-depth differences are greater for samples containing frozen precipitation than for rain samples, whereas variability in hydrogen-ion concentration differences tends to be lower for samples containing frozen precipitation. CAPMoN’s method of collecting, cooling, and analyzing hydrogen-ion concentration on a daily basis is likely to yield lower pH than measured in

Table 6 Comparison of summary statistics for CAPMoN-minus-NADP annual deposition differences for samples obtained at collocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This study (1995–2004)			Sirois et al. (2000) (1986–1993)		
	<i>N</i>	Arithmetic mean difference	Median difference	<i>N</i>	Arithmetic mean difference	Median difference
Calcium	20	0.294	0.287	14	0.319	0.279
Magnesium	20	0.054	0.047	14	0.041	0.040
Sodium	20	0.061	0.109	14	−0.076	−0.053
Potassium	20	−0.006	0.034	14	0.031	0.077
Ammonium	20	1.086	1.010	14	1.097	1.070
Chloride	20	0.260	0.300	14	0.130	0.112
Nitrate	20	4.958	4.157	14	3.946	3.807
Sulfate	20	3.592	3.982	14	3.048	3.747
Hydrogen Ion	20	0.089	0.104	14	0.149	0.142

All units in kilograms per hectare

N number of paired annual deposition values from collocated sampling sites

Table 7 Comparison of summary statistics for CAPMoN-minus-NADP annual deposition differences for samples obtained at collocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This study (1995–2004)		Sirois et al. (2000) (1986–1993)	
	Median CAPMoN deposition value	Bias at $\alpha = 0.10$ and $> \pm 0.01$ per sign test?	Median CAPMoN deposition value	Bias at $\alpha = 0.10$ and $> \pm 0.01$ per sign test?
Calcium	1.150	Y	1.352	Y
Magnesium	0.182	Y	0.220	Y
Sodium	0.356		0.500	
Potassium	0.210	Y	0.223	
Ammonium	3.588	Y	3.800	Y
Chloride	1.036	Y	1.448	Y
Nitrate	18.193	Y	21.668	Y
Sulfate	19.327		26.621	Y
Hydrogen ion	0.411	Y	0.736	Y

All units in kilograms per hectare

Y yes

Table 8 Comparison of summary statistics for CAPMoN-minus-NADP annual deposition differences for samples obtained at collocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This study (1995–2004)			Sirois et al. (2000) (1986–1993)		
	Absolute relative bias (%)	Standard deviation	M.MAD	Absolute relative bias (%)	Standard deviation	M.MAD
Calcium	25.0	0.145	0.240	20.6	0.275	0.283
Magnesium	25.8	0.022	0.037	18.2	0.037	0.038
Sodium	30.6	0.112	0.133	10.6	0.143	0.117
Potassium	16.2	0.168	0.086	34.5	0.120	0.068
Ammonium	28.1	0.561	0.840	28.2	0.470	0.507
Chloride	29.0	0.140	0.146	7.7	0.103	0.115
Nitrate	22.8	1.823	3.099	17.6	1.252	0.769
Sulfate	20.6	2.287	3.712	14.1	2.265	2.592
Hydrogen ion	25.3	0.054	0.078	19.3	0.044	0.045

All units in kilograms per hectare

weekly NADP samples because weekly sampling typically exposes the sample to its container walls longer and allows for potential degradation of organic acids and buffering by introduced particulates under variable temperature conditions.

Internetwork comparability of annual deposition data

The results given in Tables 6, 7, 8, and 9 indicate that median CAPMoN-minus-NADP annual deposition differences are all positive for this study (1995–2004), indicating that CAPMoN deposition values are higher than NADP deposition values. The same was true for the 1986–1993 study except for sodium deposition. As indicated previously, the 1994 and 1998 NADP sampling and filtration protocol changes have improved the sodium concentration measurements in NADP samples, which have reversed the internetwork comparability for sodium deposition. This shift in annual sodium deposition difference is consistent with the trend analysis results for the weekly measurement differences (see Table 5 and Fig. 3). Like the 1986–1993 study, the 1995–2004 annual deposition values for calcium, magnesium, potassium, ammonium, chloride, nitrate, and hydrogen ion were identified as significantly ($\alpha = 0.10$) biased per the Sign test. In addition, the bias previously identified for sulfate deposition in 1986–1993 is not significant for 1995–2004 data.

Table 9 Comparison of summary statistics for CAPMoN-minus-NADP annual deposition differences for samples obtained at collocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This study (1995–2004)		Sirois et al. (2000) (1986–1993)	
	P90	CoV (%)	P90	CoV (%)
Calcium	0.449	20.9	0.550	21.0
Magnesium	0.069	20.3	0.063	17.4
Sodium	0.211	37.3	0.291	23.4
Potassium	0.181	40.9	0.248	30.6
Ammonium	1.524	23.4	0.829	13.3
Chloride	0.344	14.1	0.175	7.9
Nitrate	4.801	17.0	2.160	3.6
Sulfate	6.644	19.2	4.404	9.7
Hydrogen ion	0.141	19.0	0.087	6.2

All units in kilograms per hectare

Median CAPMoN annual deposition values given in Tables 6 and 7 are lower for 1995–2004 than for 1986–1993. Sirois et al. (2000) showed that variability in the differences tends to decrease with decreasing concentration and increasing sample depth and vice versa. In simple terms, larger samples tend to be more dilute, and the variability of laboratory analyses of low concentrations inherently is relatively low compared to analysis of high concentrations. There is less variability in the measurement of precipitation-gage and sample depths for larger precipitation volumes (storms or events) as compared to the variability for smaller volumes. To determine whether this relation for the weekly measurements was applicable to annual deposition measurements, the 1995–2004 annual CAPMoN-minus-NADP deposition differences were plotted against the CAPMoN annual deposition and total annual precipitation depth values (not shown), and no relations between the internetwork annual deposition differences and the magnitude of annual deposition or precipitation depth were observed.

Standard deviation values in Table 8 are higher for the 1995–2004 annual deposition differences than for the 1986–1993 annual deposition differences for potassium, ammonium, chloride, nitrate, sulfate, and hydrogen ion. The cause(s) for the apparent increase in internetwork variability for annual deposition of these analytes are unknown.

Data in Fig. 5 show that internetwork median absolute concentration differences for chloride, nitrate, and sulfate tend to be larger for paired weekly samples that include frozen precipitation. However, the percentage of total annual precipitation that was frozen at each site tended to decrease with time during 1995–2004 from approximately 25% to 15%. Therefore, frequency of frozen precipitation can be ruled out as a potential cause for the increased internetwork variability in deposition.

Annual precipitation-weighted mean concentrations

Scatter plots of the annual precipitation-weighted mean concentrations and depths for the 1995–2004 data are shown in Fig. 6, and statistical

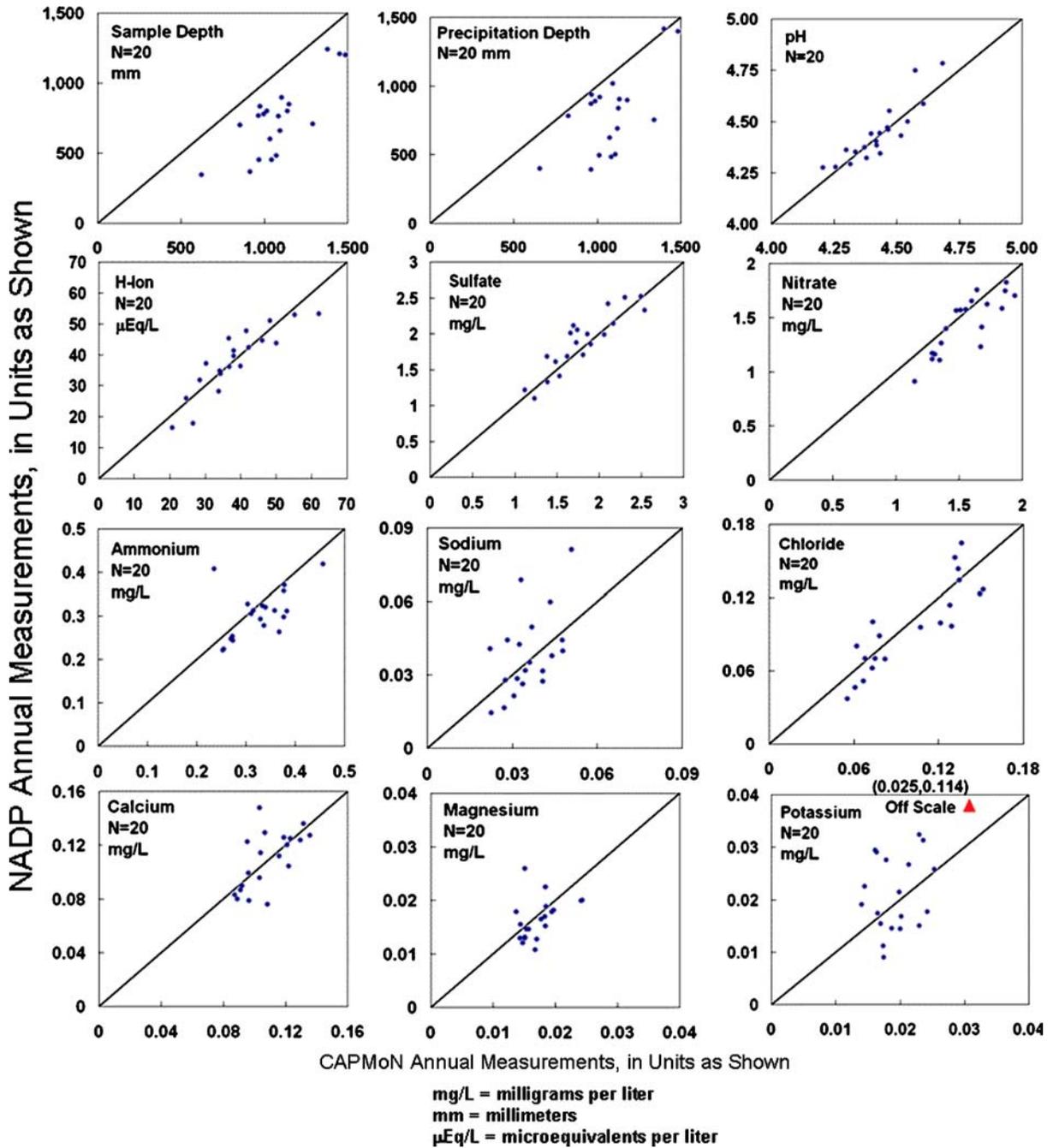


Fig. 6 Scatter plots showing variation of NADP annual precipitation-weighted mean concentrations and total annual depths with CAPMoN annual precipitation-weighted mean concentrations and total annual depths for three

colocated sites combined. *N* is the number of annual paired data points. *Lines* are drawn at one-to-one ratio for visual comparison

results for these data are given in Tables 10, 11, 12, and 13. Although significant ($\alpha = 0.10$) biases are observed for ammonium, nitrate, precipitation

depth, and sample depth, comparison of the scatter plots in Fig. 6 to those published for 1986–1993 data (not shown herein) by Sirois et al. (2000)

Table 10 Comparison of summary statistics for CAPMoN-minus-NADP annual precipitation-weighted mean concentration differences, total annual precipitation depth, and

total annual sample depth for samples obtained at collocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This study (1995–2004)			Sirois et al. (2000) (1986–1993)		
	N	Arithmetic mean difference	Median difference	N	Arithmetic mean difference	Median difference
Calcium	20	<−0.01	<0.01	14	0.02	0.020
Magnesium	20	<0.01	<0.01	14	<0.01	<0.01
Sodium	20	<−0.01	0.014	14	−0.01	−0.010
Potassium	20	<−0.01	<−0.01	14	<0.01	0.010
Ammonium	20	0.022	0.026	14	0.076	0.066
Chloride	20	<0.01	0.01	14	<0.01	<0.01
Nitrate	20	0.12	0.117	14	0.21	0.230
Sulfate	20	−0.08	−0.096	14	0.11	0.130
Hydrogen ion	20	0.0004	0.0002	14	0.0097	0.0090
Precipitation depth	20	276.	245.	14	91.0	97.5
Sample depth	20	338.	292.	14	152.9	164.9

All concentration units in milligrams per liter and depth measurements in millimeters unless otherwise specified
N number of paired samples from collocated sampling sites

indicate that the biases for these measurements have been reduced. Sirois et al. (2000) illustrated strong biases for sodium concentration and pH that are not observed for the 1995–2004 data in Fig. 6. After elimination of the median differences as estimators of the biases, the standard deviation, M.MAD, P90, and CoV results were calculated.

Comparison of the Fig. 6 graphs to their counterparts published by Sirois et al. (2000) indicates that overall internetwork comparability improved for annual precipitation-weighted mean values during 1995–2004 except for total annual precipitation and sample depth measurements. Results in Tables 10, 11, 12, and 13 support this

Table 11 Comparison of summary statistics for CAPMoN-minus-NADP annual precipitation-weighted mean concentration differences, total annual precipitation depth, and

total annual sample depth for samples obtained at collocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This study (1995–2004)		Sirois et al. (2000) (1986–1993)		Comparison of two studies Percent change ^a between studies for CAPMoN median values
	Median CAPMoN value	Bias at $\alpha = 0.10$ and $>\pm 0.01$ per sign test?	Median CAPMoN value	Bias at $\alpha = 0.10$ and $>\pm 0.01$ per sign test?	
Calcium	0.109		0.120		9
Magnesium	0.017		0.020		15
Sodium	0.034		0.040	Y	15
Potassium	0.019		0.020		5
Ammonium	0.331	Y	0.343	Y	3
Chloride	0.095		0.130		27
Nitrate	1.577	Y	1.920	Y	18
Sulfate	1.736		2.240		23
Hydrogen ion	0.0374		0.0608	Y	38
Precipitation depth	1089.	Y	1113	Y	2
Sample depth	1059.	Y	1033	Y	−3

All concentration units in milligrams per liter and depth measurements in millimeters unless otherwise specified
 Y yes

^aCalculated as: $[(\text{median value})_{2000 \text{ study}} - (\text{median value})_{\text{this study}} / (\text{median value})_{2000 \text{ study}}] \times 100$

Table 12 Comparison of summary statistics for CAPMoN-minus-NADP annual precipitation-weighted mean concentration differences, total annual precipitation depth, and

total annual sample depth for samples obtained at collocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This study (1995–2004)			Sirois et al. (2000) (1986–1993)		
	Absolute relative bias (%)	Standard deviation	M.MAD	Absolute relative bias (%)	Standard deviation	M.MAD
Calcium	2.8	0.01	0.01	16.7	0.02	<0.01
Magnesium	11.8	<0.01	<0.01	<50	<0.01	<0.01
Sodium	41.2	0.01	0.01	25	0.01	0.01
Potassium	5.3	0.02	0.01	50	0.01	<0.01
Ammonium	7.9	0.044	0.027	19.2	0.038	0.033
Chloride	11.6	0.01	0.02	<7.7	0.01	0.01
Nitrate	7.4	0.08	0.18	12	0.09	0.11
Sulfate	5.5	0.09	0.22	5.8	0.15	0.11
Hydrogen ion	0.6	0.0029	0.0051	14.8	0.0038	0.0033
Precipitation depth	22.5	111.0	265.3	8.8	77.2	77.4
Sample depth	27.6	99.2	170.2	16.0	69.1	57.2

All concentration units in milligrams per liter and depth measurements in millimeters unless otherwise specified

conclusion. Not only were the median CAPMoN annual precipitation-weighted mean analyte concentrations values lower for 1995–2004 but both the arithmetic mean and median differences were also lower for 1995–2004 than for 1986–1993 for all analytes except sodium. Biases for sodium and hydrogen-ion concentrations found to be statistically significant ($\alpha = 0.10$) by the Sign test for 1986–1993 were not significant for 1995–2004.

The plots in Fig. 6 that compare CAPMoN and NADP total annual precipitation depth and sample depth illustrate the effects of the different rain gages and sample collectors, respectively. The

CAPMoN MIC collector sensor tends to open the collector earlier at the beginning of precipitation events than does the sensor for the NADP ACM collector, which allows the CAPMoN MIC collector to catch more precipitation than the NADP ACM (Landis and Keeler 1997). The CAPMoN rain gage is fitted with a Nipher shield during winter to dampen wind turbulence and enhance snow catch, but the NADP Belfort rain gages at the CAN4/CAN5 and PA15 sites do not have wind shields, which largely explains why precipitation depth values are higher for the CAPMoN data than for the NADP data.

Table 13 Comparison of summary statistics for CAPMoN-minus-NADP annual precipitation-weighted mean concentration differences, total annual precipitation depth, and

total annual sample depth for samples obtained at collocated sites during the 1986–1993 and 1995–2004 periods of record

Analyte	This study (1995–2004)		Sirois et al. (2000) (1986–1993)	
	P90	CoV (%)	P90	CoV (%)
Calcium	0.03	8	0.05	<8.3
Magnesium	0.01	<18	<0.01	<50
Sodium	0.03	26	0.03	25
Potassium	0.01	53	0.03	<50
Ammonium	0.065	8	0.079	9.7
Chloride	0.04	19	0.03	11.8
Nitrate	0.22	12	0.14	5.8
Sulfate	0.28	13	0.30	5
Hydrogen ion	0.0086	14	0.0072	5.5
Precipitation depth	350.5	24	134.9	7.0
Sample depth	295.6	16	134.1	5.5

All concentration units in milligrams per liter and depth measurements in millimeters unless otherwise specified

Despite lower median CAPMoN annual precipitation-weighted concentrations during 1995–2004, absolute relative bias was lower during the period than for 1986–1993 for all analytes except sodium and chloride. Internetwork variability with respect to annual precipitation-weighted mean concentrations is similar for the two time periods with the greatest increase in the standard deviation of the differences shown for precipitation and sample depth measurements. The CoV estimates increased most for chloride, nitrate, sulfate, and hydrogen-ion concentrations and for precipitation and sample-depth measurements between the two time periods. The P90 values for nitrate and hydrogen-ion concentrations are higher for 1995–2004 than for 1986–1993, and especially so for the precipitation and sample-depth measurements. This indicates increased internetwork variability in these parameters at the extreme ends of the data distributions.

Discussion

Some characteristics of the 1995–2004 internetwork data pertaining specifically to sodium and hydrogen-ion concentrations are revealed in every way that the data are compared, be it weekly measurements, annual precipitation-weighted means, or annual deposition values.

These characteristics are:

- A shift occurred in internetwork comparability of weekly and annual precipitation-weighted mean sodium concentrations. CAPMoN weekly sodium concentration data were slightly positively biased during 1995–2004, whereas the NADP sodium concentrations were strongly biased positive during 1986–1993.
- Internetwork comparability of hydrogen-ion concentration data improved during 1995–2004. Weekly and annual internetwork hydrogen-ion concentration comparability was not statistically significantly biased during 1995–2004 like it was during 1986–1993.

These characteristics are suspected to be at least partly attributed to the following factors:

- The 1994 NADP sampling protocol change that eliminated shipping samples in buckets in favor of decanting to reusable 1-l polyethylene bottles for shipment. This change reduced the hydrogen-ion (pH) and sodium concentrations (Gordon et al. 1997).
- The 1998 NADP CAL filter change, which has been documented to have reduced sodium contamination in NADP samples (Gordon et al. 2003).

Many long-term monitoring networks face similar challenges in maintaining uniform operation and consistent performance of instrumentation throughout the network. The NADP has done this for over 30 years. A site-audit team ensures that the NADP field equipment is kept in the best possible condition by testing and calibrating the equipment at each site approximately once every 3 years. During the period of 1995–2004, the CAN4 site was audited three times (1996, 1998, 2000), CAN5 was audited once (2002), and PA15 was audited four times (1995, 1998, 2001, 2004). Similarly, CAPMoN sites are inspected twice each year by regional inspector(s) to ensure that the site operator and instruments conform to network requirements. Nevertheless, it is reasonable to expect some loss of instrument performance over time. For example, the collector precipitation sensors, which trigger collector lid opening for precipitation collection, could become less sensitive, resulting in under-catch of precipitation from late openings at the onset of precipitation or by staying open after the conclusion of precipitation to allow evaporation and/or contamination with dry deposition. Data are available to evaluate changes in collector response over the duration of field deployment, but that evaluation is beyond the scope of this study.

Sirois et al. (2000) present several physical factors that could affect the internetwork comparability, including higher catch efficiency for the MIC-B collector and superior precipitation catch for the snow-shielded Canadian standard precipitation gage (Goodison et al. 1989; Vet 1991). Sirois et al. (2000) also address analytical laboratory bias and sample contamination with dry

particles as potential sources of variability and bias, but they provide evidence for discounting these sources as having minor, if any effect on inter-network comparability. The reader is referred to that paper where those issues are expertly treated.

Sample evaporation

Sirois et al. (2000) also hypothesize that sample evaporation from the NADP buckets could be a potential source of bias for inter-network comparability. To address this, the US Geological Survey (USGS) conducted an experiment in Arvada, Colorado during 2006 to investigate potential NADP sample evaporation and to develop an algorithm to adjust concentrations for sample evaporation loss. Results of the USGS pilot study indicate that NADP sample evaporation can range from 3% to 33% but averages only 8%, which is small. Even so, evaporation is expected to make the samples more concentrated. NADP samples are more prone to evaporative concentration than CAPMoN samples due to the weekly frequency of NADP sample collection, yet CAPMoN precipitation-weighted weekly concentrations typically are higher than weekly NADP concentrations. Therefore, sample evaporation is not likely to affect the comparability of the NADP and CAPMoN data. The evaporation study results are available online from the USGS at: http://bqs.usgs.gov/precip/frontpage_special2.htm.

Sample contamination

Contamination of the wet-deposition samples attributed to solutes adsorbed to the bags and buckets used for sample collection was assessed using blank data obtained from Environment Canada for CAPMoN sample bags deployed to the CAN4, CAN5, and PA15 sites during dry periods (D. MacTavish, Environment Canada, written communication) and from the USGS for NADP field-audit samples for buckets deployed during dry weeks. The bags were collected from the field, sealed, and shipped to the MSC laboratory for analysis. MSC rinsed the bags with deionized water and these bag-blank samples were analyzed for solute concentrations. The USGS field-audit

quality assurance program for NADP involves shipping bottles of synthetic precipitation solutions to each of the NADP/NTN sites, and after a dry week, the site operators pour 75% of the field-audit solutions into the dry collection bucket while reserving the remaining 25% in the original bottle. After 24 h residence time, the bucket sample is contained in a standard NADP 1-l polyethylene sample bottle, and the bucket sample and original bottle sample are shipped together to the CAL for separate analysis. The calculated positive bucket sample-minus-bottle sample concentration differences are considered to represent sample contamination.

Both the CAPMoN bag-blank and USGS field-audit data were analyzed to determine the maximum probable sample contamination due to field exposure, sample handling, shipping, and analysis. The maximum probable sample contamination was considered to be represented by the 90% upper confidence limits (UCL) on the 90th percentiles of the contamination concentrations determined for each set of samples. The 90% UCL on the 90th percentile is the maximum contamination expected in 90% of the samples with 90% confidence. Contamination concentrations obtained for the CAPMoN and NADP dry bucket rinse samples were multiplied by the approximate 100 and 188 mL rinse volume, respectively, to compute the estimated contamination mass for each analyte (Table 14).

The maximum probable contamination levels for the CAPMoN and NADP samples are compared in Table 14. The field-audit program began in 1997 and field-audit data were available for 1997–2003 at the beginning of the study. These data indicate that contamination attributed to field exposure, sample handling, shipping, and analysis is higher in NADP samples than in CAPMoN samples. Therefore, sample contamination does not explain why CAPMoN weekly composite concentrations are higher than NADP weekly concentrations.

Because sample evaporation and contamination do not explain the concentration differences between CAPMoN and NADP data, sample preparation, collector characteristics, and sampling frequency must be the dominant factors contributing to the observed differences. As

Table 14 Maximum probable contamination attributed to sample containers represented by the 90-percent upper confidence limits for the 90th percentiles of dry period container rinseate concentrations for Canadian Air and Precipitation Monitoring Network (CAPMoN) during

1994–2004 at sites CAN4, CAN5, and PA15 and National Atmospheric Deposition Program (NADP) during 1997–2003 at all sites participating in the U.S. Geological Survey Field Audit quality assurance program

Analyte	CAPMoN maximum probable contamination mass ^a (µg/bag)	NADP maximum probable contamination mass ^b (µg/bucket)
Calcium	2.7	13.
Magnesium	0.5	1.5
Sodium	1.0	3.4
Potassium	0.9	3.4
Ammonium	3.0	7.5
Chloride	1.6	7.5
Nitrate	3.8	14.
Sulfate	3.7	11.

^aComputed from the maximum probable contamination concentrations for CAPMoN dry bag 100 mL rinseate samples and (data provided by D. MacTavish, Environment Canada) and converting to mass

^bComputed from the maximum probable contamination concentrations obtained from USGS field audit contamination concentrations estimated for approximate 188 mL rinseate samples and converting to mass

mentioned earlier, only NADP samples are filtered using a 0.45-µ m polyetherulfone filter, prior to analysis. Filtration removes particulate and colloidal materials from NADP samples that remain in the CAPMoN samples. This difference alone might account for a large portion of the differences observed between CAPMoN and NADP concentrations.

Both the NADP and MSC analytical laboratories participate in an external interlaboratory-comparison quality assurance program administered by the USGS, whereby both laboratories analyze aliquots of four identical sample solutions on a bimonthly basis. The data are compared in control charts and by comparing the median absolute differences between laboratory-reported values and the most probable values for each analyte. Both laboratories reported very similar results for the USGS interlaboratory-comparison program samples during 1995–2004, and no consistent bias was identified for either laboratory (Gordon et al. 1999, 2003; Wetherbee et al. 2004, 2005, 2006). Therefore, any inter-network bias identified herein is not attributed to laboratory sample analysis.

The MIC precipitation sensor is more sensitive than that of the ACM, and the MIC sensor opens the collector earlier than the ACM sensor (Landis and Keeler 1997). Wet deposition concentrations can often be higher at the onset of precipitation

events than later in the events (Schroeder et al. 1987). Also, as Sirois et al. (2000) point out, nutrient constituents such as nitrate and ammonium could be consumed or altered by microorganisms in the precipitation samples, which might explain why samples left in NADP collector for a week could have lower concentrations than CAPMoN samples collected within 24 h. Willoughby et al. (1990) concluded that samples left in an NADP bucket on a collector for 1 week had stable nitrate concentrations, but ammonium was not evaluated in that study.

Summary and conclusions

This study of CAPMoN and NADP inter-network comparability was done as a follow-up to earlier work by Sirois et al. (2000). The new results contained herein are for the period 1995–2004 and are intended to be used in conjunction with the results of the earlier work, which applies to the period 1986–1993. Both networks continue to maintain production of high-quality data. It is recognized that the comparability of these important long-term monitoring networks needs to be reevaluated and updated periodically for continental-scale studies of pollutant wet deposition in North America. Results presented herein indicate that data from the two networks can be

combined to obtain reliable integrated datasets for such studies. The comparability of the networks is improving and is expected to continue to improve as NADP modernizes its rain gages and precipitation collectors and as both networks work together to improve measurement capabilities.

The results suggest that the CAPMoN sensor, which provides greater precipitation catch efficiency, is allowing sampling of higher chemically concentrated precipitation at the onset of precipitation events and during light precipitation events. More frequent collection of CAPMoN samples likely provides better preservation of pH and other ions, which could account for a portion of the observed CAPMoN and NADP-measured deposition differences. Windshields on the CAPMoN snow gages likely play a role in increasing the differences between CAPMoN and NADP deposition measurements.

Positive relative bias in CAPMoN concentration measurements can largely be attributed to the fact that NADP samples are filtered, whereas CAPMoN samples are not. Sample evaporation and container contamination are unlikely to account for variability or bias in internetwork concentration comparability.

This study produced the following specific results:

- Median weekly precipitation-weighted CAPMoN ion concentrations are similar between the 1986–1993 and 1995–2004 studies. The median weekly CAPMoN concentration values that changed the most between the two periods are for calcium (+22%), ammonium (+23%), chloride (–12%), and hydrogen ion (–28%). Median weekly CAPMoN precipitation depth increased between the two periods (+13%) as did sample depth (+27%).
- Weekly CAPMoN measurements tended to be higher than weekly NADP measurements for all analytes during 1986–1993, except for sodium and sulfate. A small but significant ($\alpha = 0.10$) bias for sulfate concentration is indicated for the 1995–2004 data that was not significant during 1986–1993.
- The variability of between-network differences decreased for all weekly measurements except hydrogen-ion concentration and sample depth during 1995–2004. Significant decreasing trends in internetwork differences (improved internetwork comparability) for weekly sodium, ammonium, nitrate, sulfate, and hydrogen-ion concentrations and for weekly precipitation depth differences were identified.
- Variability in the weekly sodium- and sulfate-concentration and precipitation-depth differences are greater for samples containing frozen precipitation than for rain samples, whereas variability in weekly hydrogen-ion concentration differences tends to be lower for samples containing frozen precipitation.
- The NADP 1994 sample preparation and 1998 filtration protocol changes have reversed and improved internetwork comparability for annual sodium deposition. For the 1995–2004 period, annual deposition values for calcium, magnesium, potassium, ammonium, chloride, nitrate, and hydrogen ion were significantly ($\alpha = 0.10$) biased, with CAPMoN annual deposition values higher than NADP values. In addition, the bias previously identified for annual sulfate deposition in 1986–1993 was not significant for 1995–2004 data. Large biases for sodium and calcium concentrations and pH identified by Sirois et al. (2000) are not observed for the 1995–2004 data.
- Biases for sodium and hydrogen-ion concentrations found to be statistically significant ($\alpha = 0.10$) by the Sign test for 1986–1993 were not significant for 1995–2004.
- Cause(s) for the apparent increases in internetwork variability for annual deposition of potassium, ammonium, chloride, nitrate, sulfate, and hydrogen ion are unknown.
- Significant ($\alpha = 0.10$) biases observed for ammonium, nitrate, precipitation depth, and sample depth for 1986–1993 measurements identified by Sirois et al. (2000; not shown herein) were reduced during 1995–2004.
- Internetwork variability, with respect to annual precipitation-weighted mean concentrations, is similar for the two time periods with the greatest increase in variability shown for precipitation and sample-depth measurements.

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