# Comparison of Wet-Deposition Data for Co-located Canadian Air and Precipitation Monitoring Network and National Atmospheric Deposition Program / National Trends Network Sites, 2005-2011



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University of Illinois, Prairie Research Institute Illinois State Water Survey, NADP Program Office

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## **Conversion Factors**

#### SI to Inch/Pound

Multiply	Ву	To obtain
millimeter (mm)	Depth 0.03937	inch (in.)
liter (L)	Volume 1.057	quart (qt)
	Mass	
milligram (mg)	3.527 x 10 <sup>-5</sup>	ounce, avoirdupois (oz)

## **Abbreviations and Acronyms**

#### The following terms and abbreviations also are used in this report:

Aerochem Metrics precipitation collector
Branch of Quality Systems
Central Analytical Laboratory
site identifier for Sutton, Quebec, Canada
site identifier for Frelighsburg, Quebec, Canada
Canadian Air and Precipitation Monitoring Network
Covariance
Environment Canada
Environment Canada Science and Technology Branch
Illinois State Water Survey
locally weighted scatterplot smoothing
modified median absolute deviation
Meteorological Instruments of Canada precipitation collector
milligrams per liter
millimeters
minimum reporting limit
National Atmospheric Deposition Program
National Trends Network
percent
99th percentile, value greater than 99 percent of all values in a sample
site identifier for Penn State University, Centre County, Pennsylvania
polyvinyl chloride
United States Geological Survey

# Comparison of Wet-Deposition Data for Co-located Canadian Air and Precipitation Monitoring Network and National Atmospheric Deposition Program / National Trends Network Sites, 2005-2011

#### Abstract

Daily Canadian Air and Precipitation Monitoring Network and weekly National Atmospheric Deposition Program / National Trends Network wet-deposition data collected continuously during 2005-2011 at two co-located sites located in Quebec, Canada and Pennsylvania, USA were compared statistically. Data analysis procedures used by Sirois et al. (2000) and Wetherbee et al. (2010) were used to estimate bias and variability between the two networks. Results indicate that the two network data sets continue to be compatible for continental scale studies. In general, CAPMoN values are higher than NADP values. It is speculated that these differences are due to differences in measurement protocols between the two networks. During 2005-2011, variability in co-located CAPMoN-minus-NADP concentration differences remained consistent for calcium, magnesium, sodium, potassium, ammonium, hydrogenion, sample depth, and precipitation depth. Variability decreased for chloride, nitrate, and sulfate after 2008.

### Introduction

Starting in 1986, wet-deposition data were collected on a continuous basis at two co-located sites in Quebec, Canada and Pennsylvania, USA. Daily samples were collected by the Canadian Air and Precipitation Monitoring Network (CAPMoN). Weekly samples were collected by the United States National Atmospheric Deposition Program / National Trends Network (NADP/NTN). Previous studies by Sirois et al. (2000) and Wetherbee et al. (2010) estimated the bias and variability between the two networks using data from these sites. The site in Pennsylvania, USA has been located at Penn State University, Centre County, Pennsylvania, USA (PA15) throughout the entire study period (1986 to present), The site in Quebec, Canada was located in Sutton, Quebec, Canada (CAN4) from 1986 to 2001, and in Frelighsburg, Quebec, Canada (CAN5) from 2001 to 2013.

Each co-located site has both CAPMoN and NADP monitoring instruments for collection of precipitation

samples and measurement of precipitation depth. Each network uses a different protocol for data collection. It is important to evaluate the comparability of the data obtained from each network for application to continental-scale wet-deposition analyses. Descriptions of the two networks may be found on the World Wide Web at: *http://nadp.isws. illinois.edu/* and *http://www.ec.gc.ca/rs-mn*. Variability due to changing emissions and changing climate is not accounted for, and is assumed to not impact the results.

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 inter-network data comparison. NADP has included a three-annum assessment of inter-network comparability as part of its data-quality objective assessment. For this reason, data-analysis methods used for this study are intended to be repeated for ongoing, periodic evaluation of inter-network comparability.

### Methods

#### CAPMoN

CAPMoN samples were collected in laminated plastic bags with virgin polyethylene interiors and Mylar exteriors on a daily basis. Samples were collected at 0800±1 hour regardless of whether precipitation fell within the previous 24-hour period. CAPMoN samples were collected using a Meteorological Instruments of Canada (MIC) sampler. Precipitation depth was measured using the Meteorological Service of Canada (MSC) Type-B raingage during non-winter months and a Nipher shielded snow gage during winter to optimize snow catch (Sirois et al. 2000). Samples were heat sealed in the bags for shipment to the Environment Canada (EC) Laboratory in Downsview, Ontario for analysis. 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).



Figure 1. Co-located wet-deposition monitoring sites CAN5 (Frelighsburg, Quebec, Canada) and PA15 (Penn State University, Centre County, Pennsylvania, USA).

#### NADP

NADP samples were collected in polyvinylchloride (PVC) buckets which were installed in AeroChem Metrics (ACM) Model A-31 wet-dry collectors. NADP sample buckets were replaced every Tuesday morning. CAPMoN and NADP samples were collected within minutes of one another.

Following transportation to the field support facility, the site operator weighed the sample to determine sample depth, and decanted the sample to a 1-liter polyethylene bottle for shipment to the Central Analytical Laboratory (CAL) located at the Illinois State Water Survey in Champaign, Illinois for analysis.

Both the sample buckets and 1-L bottles are washed in an industrial deionized water washer for re-use. 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, 2011).

The ACM and CAPMoN MIC collectors are similar in that both collectors use a precipitation sensor to control exposure of the wet-side (sample) bucket (Dossett and Bowersox, 1999). Both sensors operate according to electrical conductance, but the designs of the two sensors are very different. With the exception of the common site operator at each co-located site, the CAPMoN and NADP data were collected and samples were handled as if they were generated by independent monitoring networks. The only similarity between the collocated networks at each site is the operator.

NADP precipitation depth was measured using an unshielded Belfort Model 5-780 raingage. Like the MSC Type-B raingage, the NADP Belfort Model 5-780 raingage is also a weighing type raingage fitted with a paper chart recorder. In October 2011, the official NADP raingage at CAN5 was upgraded to an ETI Noah-IV gage.

#### **Data Analysis Methods**

CAPMoN data used for this analysis were processed and provided by personnel from EC. This included calculation of weekly precipitation-weighted concentrations from the daily CAPMoN data. Weekly NADP data were obtained from the NADP Program Office database. Quality assurance data, contaminated samples, and samples obtained during periods of equipment malfunction or uncertain operating conditions were eliminated from this analysis. Censoring and statistical methods used for this report are identical to those described by Wetherbee et al. (2010).

### **Results and Discussion**

Summary statistics for the comparison of the co-located measurement differences are shown in Tables 1 through

4. Results for 2005-2011 median differences (Table 1) are similar to values published by Wetherbee et al. (2010) for 1995-2004. Changes in absolute relative bias between the 1995-2004 and 2005-2011 periods were most notable for potassium, ammonium, and chloride, but modified median absolute deviations for the two periods were very similar for all constituents (Table 2). The 1 percent Winsorized standard deviations were smaller for the 2005-2011 analysis period than for previous periods. This indicates no change in comparability in recent years (Table 2).

A statistically significant bias between network measurements with 90-percent confidence ( $\alpha$ =0.10) was identified for calcium, ammonium, nitrate, sulfate, hydrogen ion, precipitation depth, and sample depth (Table 3).

Ammonium, nitrate, and hydrogen ion are prone to chemical instability. CAPMoN samples are collected and processed daily, and thus might be better preserved than weekly collected NADP samples. CAPMoN's MIC collector's precipitation sensor opens the MIC sooner at precipitation onset than the NADP ACM collector (Sirois et al., 2000). Therefore, the MIC typically collects larger sample depths than the ACM. CAPMoN uses a special snow gage with a Nipher wind shield for winter precipitation-depth measurement. This may explain the greater CAPMoN precipitation depths measured during winter months. Bias due to frozen precipitation characteristics is discussed by Wetherbee et al. (2010).

Time series plots of the weekly differences are shown in Figures 2 through 7. The time series plots include locally weighted scatterplot smoothed lines denoting estimates of the 25<sup>th</sup>, 50<sup>th</sup> (median), and 75<sup>th</sup> percentiles of the differences to illustrate variability over time. Narrowing of the gap between the 25<sup>th</sup> and 75<sup>th</sup> percentiles (interquartile range) indicates less variability in the differences, and vise versa. The interquartile ranges shown in Figures 2 through 7 suggest consistent differences between CAPMoN and NADP measurements over the 2005-2011 period for all parameters, except chloride, nitrate, and sulfate. Variability in chloride, nitrate, and sulfate differences decreased during the 2005 to 2011 study period.

Points plotting higher than the zero difference lines in Figures 2 through 7 indicate higher CAPMoN values, and points plotting below the zero difference lines indicate higher NADP values. The difference values commonly plot above the zero lines, particularly during winter months. Another difference between NADP and CAPMoN is that NADP samples are filtered. CAPMoN samples are not. This might explain at least some of the higher CAPMoN concentration values, particularly for base cations: calcium, magnesium, sodium and potassium. The stability of daily-collected CAPMoN samples is arguably better maintained than weekly-collected NADP samples. This might account for higher CAPMoN concentrations for ammonium, nitrate, and hydrogen ion. **Table 1.** Mean and median CAPMoN-minus-NADP differences for wet-deposition concentrations, precipitation depths, and sample depths measured at co-located CAPMoN/NADP sites in Quebec, Canada and Pennsylvania, USA, 1986-2011.

	This Study (2005-2011)			v	Wetherbee et al., 2010 (1995-2004)			Sirois, Vet, and Lamb, 2000 (1986-1993)		
Analyte (units)	N	Arithmetic Mean Difference	Median Difference	N	Arithmetic Mean Difference	Median Difference	N	Arithmetic Mean Difference	Median Difference	
Calcium (mg/L)	507	0.019	0.011	655	0.019	0.010	494	0.02	< 0.01	
Magnesium (mg/L)	503	0.006	0.003	656	0.004	0.003	497	< 0.01	< 0.01	
Sodium (mg/L)	504	0.011	0.002	656	0.001	0.001	508	-0.02	-0.01	
Potassium (mg/L)	497	0.007	0.003	651	-0.023	0.007	500	< 0.01	< 0.01	
Ammonium (mg/L)	505	0.075	0.053	654	0.027	0.062	541	0.069	0.053	
Chloride (mg/L)	505	0.026	0.011	658	0.016	0.008	528	< 0.01	< 0.01	
Nitrate (mg/L)	510	0.188	0.104	662	0.315	0.147	533	0.210	0.100	
Sulfate (mg/L)	510	0.098	0.055	662	0.221	0.103	532	-0.020	-0.010	
Hydrogen Ion (mg/L)	505	0.621	0.009	649	0.019	0.003	504	0.011	0.008	
Precipitation Depth (mm)	521	1.2	0.8	684	0.8	0.5	711	1.7	1.4	
Sample Depth (mm)	521	2.2	1.9	679	3.1	2.7	696	1.9	1.9	

[mg/L, milligrams per liter; mm, millimeters; N, number of paired weekly samples; <, less than]

**Table 2.** Absolute relative bias, 1 percent Winsorized standard deviations, and modified median absolute deviations for CAPMoNminus-NADP differences in wet-deposition concentrations, precipitation depths, and sample depths measured at co-located CAPMoN/NADP sites in Quebec, Canada and Pennsylvania, USA, 1986-2011.

[%, percent; M.MAD, modified median absolute deviation; mg/L, milligrams per liter; mm, millimeters; <, less than]

This Study (2005-2011)			Wetherbee et al., 2010 (1995-2004)			Sirois, Vet, and Lamb, 2000 (1986-1993)			
Analyte (units)	Absolute Relative Basis (%)	1% Winsorized Standard Deviation	M.MAD (units)	Absolute Relative Basis (%)	1% Winsorized Standard Deviation	M.MAD (units)	Absolute Relative Basis (%)	1% Winsorized Standard Deviation	M.MAD (units)
Calcium (mg/L)	8.3	0.11	0.02	8.2	0.13	0.03	<10.0	0.07	0.03
Magnesium (mg/L)	15.0	0.01	0.004	15.8	0.02	0.004	<50.0	0.01	< 0.01
Sodium (mg/L)	5.9	0.03	0.01	3.2	0.04	0.01	33.3	0.03	0.02
Potassium (mg/L)	16.7	0.04	0.01	35.0	0.30	0.01	<50.0	0.03	< 0.01
Ammonium (mg/L)	14.7	0.10	0.052	16.0	0.19	0.059	16.9	0.11	0.054
Chloride (mg/L)	10.5	0.05	0.02	7.0	0.07	0.02	< 7.7	0.06	0.03
Nitrate (mg/L)	7.7	0.32	0.12	7.6	0.51	0.18	5.0	0.54	0.24
Sulfate (mg/L)	4.1	0.47	0.12	5.0	0.50	0.17	0.5	0.48	0.28
Hydrogen Ion (mg/L)	4.1	0.012	0.005	7.2	0.017	0.007	13.0	0.015	0.008
Precipitation Depth (mm)	4.5	3.3	1.5	2.7	4.3	1.7	7.9	3.7	1.7
Sample Depth (mm)	11.3	2.9	1.4	13.5	2.5	2.1	12.1	3.7	1.0

**Table 3.** Median CAPMoN values and identification of bias per the sign test for CAPMoN-minus-NADP differences for wet-deposition concentrations, precipitation depths, and sample depths measured at co-located CAPMoN/NADP sites in Quebec, Canada and Pennsylvania, USA, 1986-2011.

	This S1 (2005-2	tudy 011)	Wetherbee e (1995-2	et al., 2010 004)	Sirois, Vet, and Lamb, 2000 (1986-1993)		
Analyte (units)	Median CAPMoN Concentration Value	Bias at α=0.10 & >+/-0.01 per Sign Test?	Median CAPMoN Concentration Value	Bias at α=0.10 & >+/-0.01 per Sign Test?	Median CAPMoN Concentration Value	Bias at α=0.10 & >+/-0.01 per Sign Test?	
Calcium (mg/L)	0.132	Yes	0.122	No	0.100	No	
Magnesium (mg/L)	0.020	No	0.019	No	0.020	No	
Sodium (mg/L)	0.034	No	0.031	No	0.030	Yes	
Potassium (mg/L)	0.018	No	0.020	No	0.020	No	
Ammonium (mg/L)	0.360	Yes	0.387	Yes	0.314	Yes	
Chloride (mg/L)	0.105	No	0.114	No	0.130	No	
Nitrate (mg/L)	1.342	Yes	1.932	Yes	2.010	Yes	
Sulfate (mg/L)	1.350	Yes	2.044	Yes	2.100	No	
Hydrogen Ion (mg/L)	0.023	Yes	0.043	No	0.060	Yes	
Precipitation Depth (mm)	18.6	Yes	20.2	Yes	17.8	Yes	
Sample Depth (mm)	16.8	Yes	20.0	Yes	15.7	Yes	

[mg/L, milligrams per liter; mm, millimeters; %, percent; Bias, bias between CAPMoN and NADP measurements at the a statistical significance level and median relative difference exceeds +/- 0.01 units; >, greater than]

**Table 4.** Coefficient of variation and 99th percentile of CAPMoN-minus-NADP differences for wet-deposition concentrations,precipitation depths, and sample depths measured at co-located CAPMoN/NADP sites in Quebec, Canada and Pennsylvania, USA,1986-2011.

[P99%, 99th percentile of CAPMoN-minus-NADP absolute difference; CoV (%), coefficient of variation calculated as modified median absolute deviation divided by the median CAPMoN value, in percent; mg/L, milligrams per liter; mm, millimeters; <, less than]

	This Study (2005-2011)		Wetherbe (199	e et al., 2010 5-2004)	Sirois, Vet, and Lamb, 2000 (1986-1993)		
Analyte (units)	<b>P99</b> %	<b>CoV</b> (%)	<b>P99%</b>	<b>CoV</b> (%)	P99%	<b>CoV</b> (%)	
Calcium (mg/L)	0.35	18.9	0.35	23.0	0.5	28.6	
Magnesium (mg/L)	0.06	20.0	0.07	21.1	0.06	<59.0	
Sodium (mg/L)	0.12	17.6	0.12	32.3	0.26	66.0	
Potassium (mg/L)	0.14	33.3	0.11	35.0	0.2	<59.0	
Ammonium (mg/L)	0.45	14.4	0.80	15.2	0.704	17.2	
Chloride (mg/L)	0.27	18.1	0.28	20.2	0.47	26.0	
Nitrate (mg/L)	1.69	9.0	2.69	9.2	3.04	12.0	
Sulfate (mg/L)	1.48	8.8	2.34	8.4	2.66	13.4	
Hydrogen Ion (mg/L)	0.02	21.1	0.08	15.8	0.075	13.4	
Precipitation Depth (mm)	8.0	8.0	9.4	8.4	22.7	9.5	
Sample Depth (mm)	9.7	8.3	11.9	10.5	24.6	6.5	



**Figure 2.** Time series of CAPMoN-minus-NADP calcium and magnesium concentration differences and locally weighted scatterplot smoothed quartiles of the differences during 2005-2011.



**Figure 3.** Time series of CAPMoN-minus-NADP sodium and potassium concentration differences and locally weighted scatterplot smoothed quartiles of the differences during 2005-2011.



**Figure 4.** Time series of CAPMoN-minus-NADP ammonium and chloride concentration differences and locally weighted scatterplot smoothed quartiles of the differences during 2005-2011.







**Figure 6.** Time series of CAPMoN-minus-NADP hydrogenion concentration differences and locally weighted scatterplot smoothed quartiles of the differences during 2005-2011.



Figure 7. Time series of CAPMoN-minus-NADP precipitation-depth and sample-depth differences and locally weighted scatterplot smoothed quartiles of the differences during 2005-2011.

### Conclusions

Results presented herein indicate consistent and comparable results for the CAPMoN and NADP wet-deposition networks. As such, merging data from the two networks for continental scale studies is appropriate. Biases quantified for CAPMoN versus NADP measurements were consistent between the 2005-2011 and 1996-2004 periods for the two co-located CAPMoN/NADP sites in Quebec and Pennsylvania.

In general, CAPMoN values are commonly higher than NADP values. This is due to differences in precipitation sensors, sample containers, sampling frequency, and sample-processing protocols, especially during winter months. Over the 2005-2011 period, the variability in co-located CAPMoN-minus-NADP concentration differences remained consistent for calcium, magnesium, sodium, potassium, ammonium, hydrogen-ion, sample depth and precipitation depth. Variability decreased for chloride, nitrate, and sulfate differences after 2008.

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