Four Studies on Effects of Environmental Factors on the Quality of National Atmospheric Deposition Program Measurements

By Gregory A. Wetherbee, Natalie E. Latysh, Christopher M.B. Lehmann, and Mark F. Rhodes

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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
meter (m)	1.094	yard (yd)
	Area	
square meter (m^2)	0.0002471	acre
hectare (ha)	2.471	acre
square centimeter (cm^2)	0.1550	square inch (ft^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
liter (L)	1.057	quart (qt)
cubic centimeter (cm^3)	0.06102	cubic inch (in^3)
	Flow rate	
kilometer per hour (km/h)	0.6214	mile per hour (mi/h)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
	Density	
kilogram per cubic meter (kg/m^3)	0.06242	pound per cubic foot (lb/ft^3)
gram per cubic centimeter (g/cm^3)	62.4220	pound per cubic foot (lb/ft^3)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
°F=(1.8×°C)+32
Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:
°C=(°F-32)/1.8
Vertical coordinate information is referenced to the "North American Vertical Datum of 1988 (NAVD 88)."
Horizontal coordinate information is referenced to the "North American Datum of 1983 (NAD 83)."
Altitude, as used in this report, refers to distance above the vertical datum.
Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).
Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L), micrograms per liter (µg/L), or microequivalents per liter (µEq/L).
Equivalents ratio (milliequivalents / milliequivalents)
Absolute value of x = |x|, where x takes the form of numerical values or algebraic expressions
Maximum probability of rejecting the null hypothesis when it is true (α)
Percent (%)
Water Year = October 1 – September 30 of following year

Abbreviations and Acronyms

Abbreviation	Full name
ACM	AeroChem Metrics Model 301 Precipitation Collector
AIRMoN	Atmospheric Integrated Research Monitoring Network
BBD	Bird and dirt identified in field and laboratory
BCO	Combined contamination identified in field and laboratory
BHC	Handling contamination from field and laboratory
BIC	Insect identified in field and laboratory
BOT	Other contamination identified in field and laboratory
BPC	Plant contamination identified in field and laboratory
BQS	Branch of Quality Systems
Ca^{2+}	Calcium ion
CAL	Central Analytical Laboratory
FBD	Bird droppings identified in field
FCO	Combined contamination identified in field
FFF	Sample not valid due to field protocol failure
FHC	Handling contamination from field
FIC	Insect identified in field
FORF	Field Observer Report Form
FOT	Other contamination identified in field
FPC	Plant contamination identified in field
GIS	Geographic Information System
H^+	Hydrogen ion
HVAC	Heating, Ventilation, and Air Conditioning
LCO	Combined contamination identified in laboratory
LHC	Handling contamination from laboratory
LHH	Horse hair from packaging from old bucket box mailer
LIC	Insect contamination identified in laboratory
LLL	Serious laboratory error
LNT	Sample bottle lid not tight
LOT	Other contamination identified in laboratory
LPC	Plant contamination identified in laboratory
NADP	National Atmospheric Deposition Program
NLCD	National Land Cover Database
NTN	National Trends Network
NWQL	National Water Quality Laboratory
MDN	Mercury Deposition Network
MRLCC	Multi-Resolution Land Cover Database
PCQA	Precipitation Chemistry Quality Assurance Project
PO	Program Office
URL	Universal Resource Locator
USGS	United States Geological Survey

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Abstract

Selected aspects of National Atmospheric Deposition Program / National Trends Network (NADP/NTN) protocols are evaluated in four studies. Meteorological conditions have minor impacts on the error in NADP/NTN sampling. Efficiency of frozen precipitation sample collection is lower than for liquid precipitation samples. Variability of NTN measurements is higher for relatively low-intensity deposition of frozen precipitation than for higher-intensity deposition of liquid precipitation. Urbanization of the landscape surrounding NADP/NTN sites is not affecting trends in wet-deposition chemistry data to a measureable degree. Five NADP siting criteria intended to preserve wet-deposition sample integrity have varying degrees of effectiveness. NADP siting criteria for objects within the 90º cones and trees within the 120º cones projected from the collector bucket to sky are important for protecting sample integrity. Tall vegetation, fences, and other objects located within 5 meters of the collectors are related to the frequency of visible sample contamination, indicating the importance of these factors in NADP siting criteria.

Introduction

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) was initiated in 1978 by the Association of State Agricultural Experiment Stations to monitor long-term atmospheric chemistry and the effects pollutants have on aquatic and terrestrial systems (Nilles, 2000). The number of sites grew from 21 in 1978 to 261 in 2006. As of winter 2009, precipitation was being collected weekly from 251 sites in the United States, including Alaska, Puerto Rico, U.S. Virgin Islands, and Canada (fig. 1). The chronology of the number of sites in the NTN is shown in Figure 2.

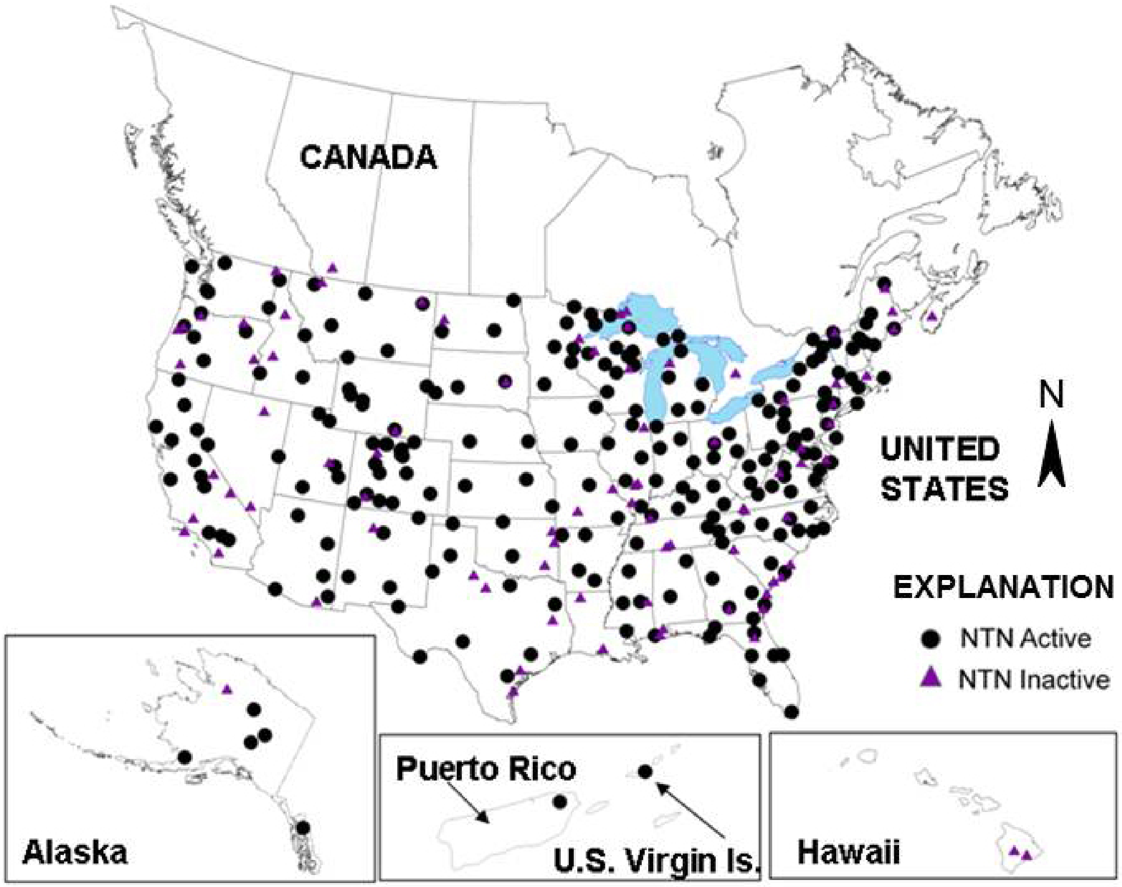


Figure 1. Locations of active (2011) and formerly active National Atmospheric Deposition Program/National Trends Network sites.

The U.S. Geological Survey-Branch of Quality Systems (USGS-BQS) began conducting quality-assurance monitoring for the NADP/NTN in 1978. As of December 2010, the USGS operates three external quality-assurance programs for the NADP/NTN as part of the USGS Precipitation Chemistry Quality Assurance (PCQA) project to assess and document the quality of wet-deposition data for the NADP/NTN. The USGS external quality-assurance consists of field-audits, interlaboratory-comparisons, and a co-located-sampler program (Latysh and Wetherbee, 2005). USGS-BQS works closely with the NADP Program Office (PO) and Central Analytical Laboratory (CAL), located at the Illinois State Water Survey, in Champaign, Illinois. CAL, the contract laboratory for the NADP/NTN, analyzes the weekly precipitation samples collected by the NADP/NTN in addition to providing site operator and instrumentation support and bucket, lid, and bottle washing and deployment. The USGS-BQS works closely with the NADP Program Office (PO) and CAL in designing and implementing PCQA programs. Latysh and others (2005) provide more information about PCQA programs.

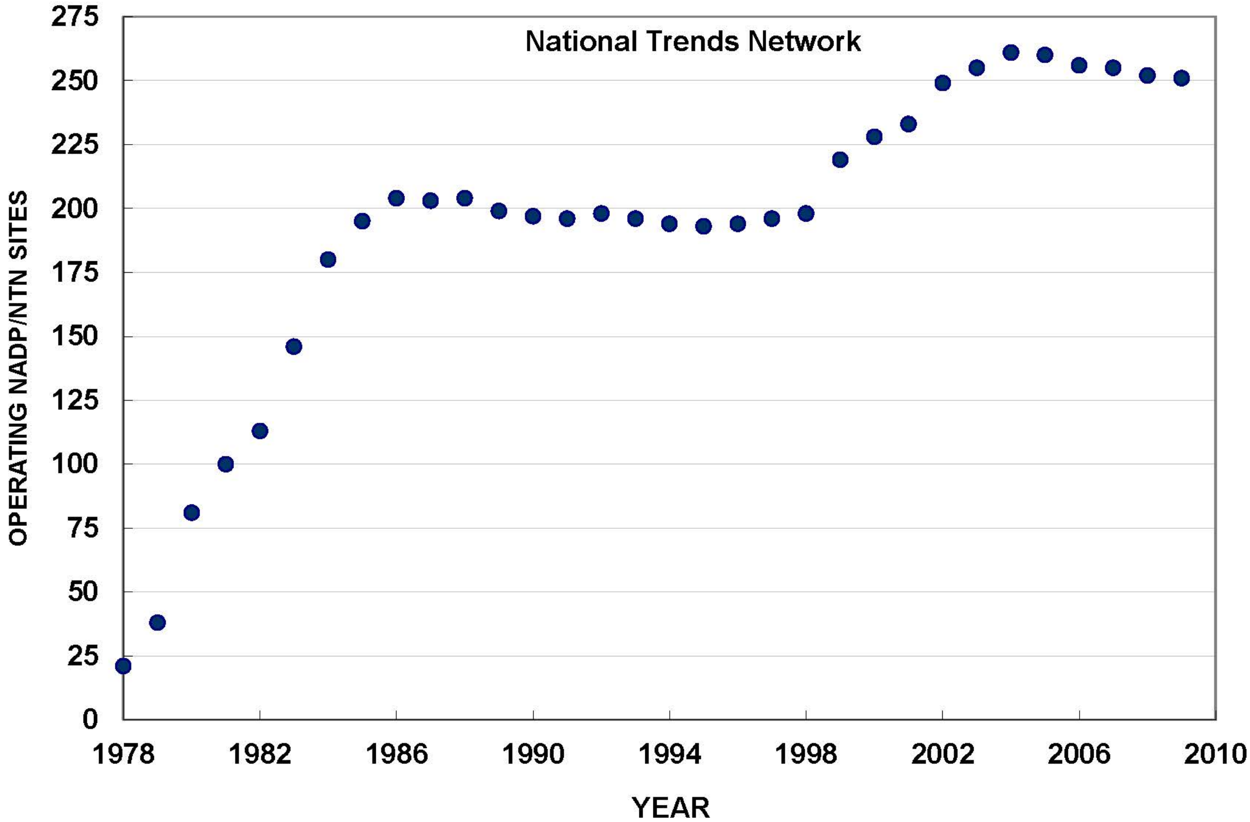


Figure 2. Number of operating National Atmospheric Deposition Program/National Trends Network sites during 1978-2009.

Many technical questions about the integrity and representativeness on NTN measurements have been addressed by PCQA during the past 33 years of network operation (1977–2010). Graham and others (1987 and 1990), See and others (1989), Willoughby and others (1989 and 1990), Gordon and Schroder (1995), and Latysh and Gordon (2004) assessed NTN sample integrity.

Purpose and Scope

The purpose of this report is to evaluate selected aspects of NADP protocols that potentially affect NADP data quality. Results and conclusions included herein have been formally presented at semi-annual NADP business meetings, and summarized in the minutes of those meetings available at Universal Resource Locator (URL) *http://nadp.isws.illinois.edu/committees/minutes.aspx* , but this information has not been available in a citable form.

This report presents the results of four special studies conducted by the PCQA project to evaluate the effects of meteorological conditions, precipitation intensity, site urbanization, and physical monitoring-site characteristics on the quality of NADP data. The special studies were conducted from 2000 to 2010. Data were obtained from a variety of sources, but primarily from NADP/NTN site operators, CAL, PO, and PCQA project personnel.

Meteorological Effects on Measurement Error

Background and Methods

The influence of meteorological characteristics on wet-deposition measurements was evaluated by Raynor and Hayes (1982), Pellett and others (1984), Lynch and others (1989), and Dayan and Lamb (2003). PCQA conducted a study during 2002–2003 using wet-deposition data from co-located pairs of NTN monitoring instruments and a meteorological monitoring station at NADP/NTN site WI98: Wildcat Mountain State Park, near Ontario, Wisconsin. The study was conducted as part of the PCQA Co-Located Sampler program, which is described by Latysh and Wetherbee (2005). The co-located site at WI98 is identified as 98WI. A diagram and photograph of the co-located sites are shown in Figure 3, which consisted of the following instruments:

- 2 - Belfort Model 5-7801 rain gages,
- 2 - AeroChem Metrics Model 301 (ACM) precipitation collectors,
- Campbell Scientific CM6 Tripod Weather Station with an SC32A optically isolated RS232 interface,
- Met One model 034A-L wind set, and
- Campbell Scientific model 101 thermistor probe and model 107 temperature probe.

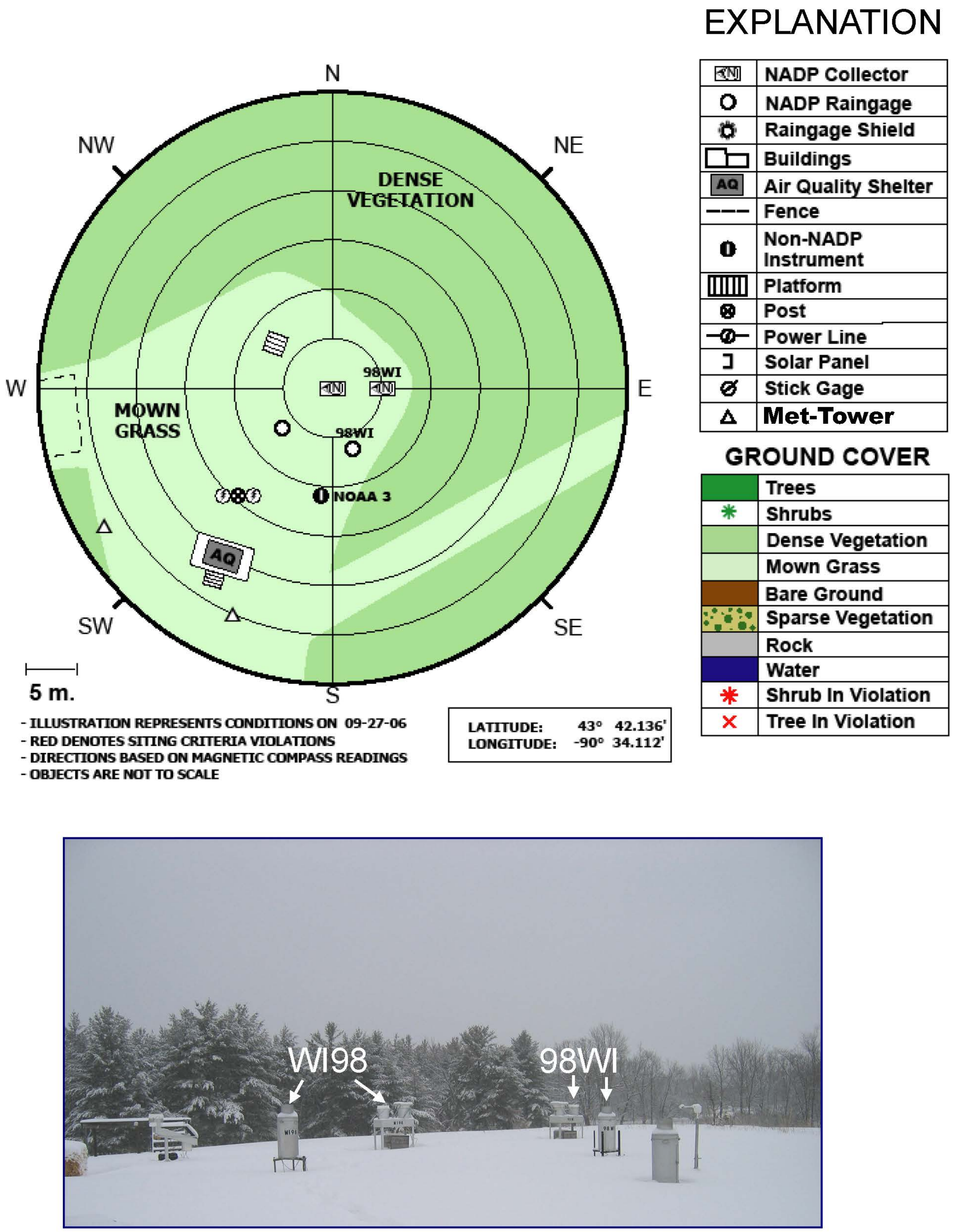
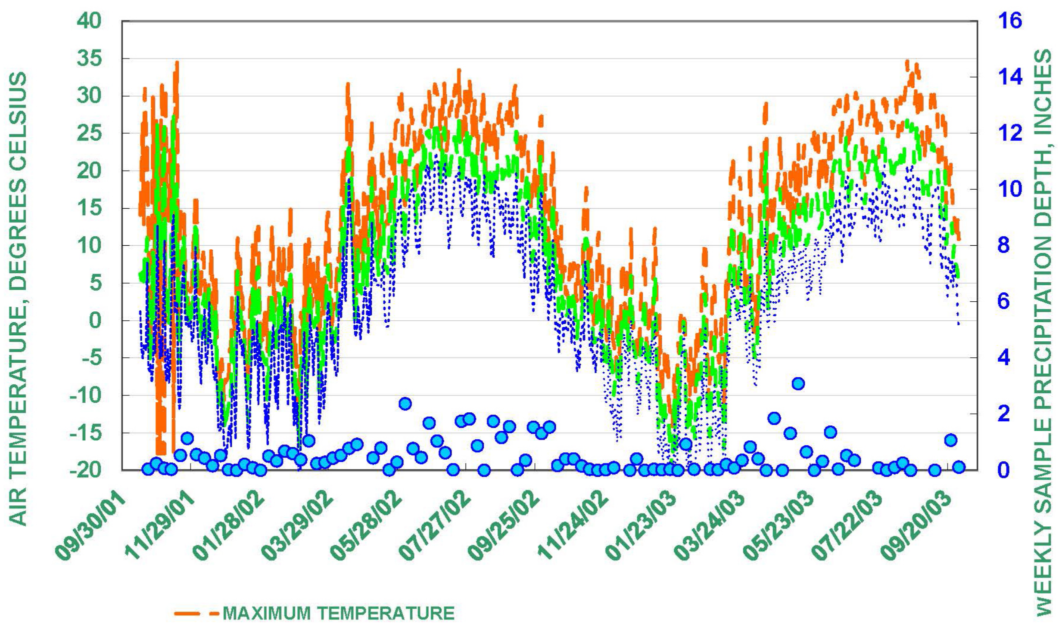


Figure 3. Schematic diagram and photograph of co-located NADP/NTN sites WI98/98WI at Wildcat Mountain State Park near Ontario, WI.

[1] Trade or firm names in this report are for identification purposes only and do not constitute endorsement by the U.S. government.

During water years (October 1 through September 30) 2002–2003, air temperature, wind speed, and wind direction were measured to accompany the co-located-sampler data (fig. 4). Replicate data for precipitation depth and wet-deposition samples for chemical analysis for calcium, magnesium, sodium, potassium, ammonium, chloride, nitrate, sulfate, hydrogen ion, and specific conductance analysis by the CAL were collected at the NTN sites WI98 and 98WI. Solute concentration and specific-conductance differences were calculated for each pair of weekly samples.

Hourly weather data were extracted from the continuous meteorological records for the time periods when the wet-deposition collectors were collecting precipitation. This was accomplished by reading the event-recorder traces on the rain-gage paper charts for the original WI98 site to determine when the collector lids were open. Error associated with manual chart interpretation was not assessed but could be considerable given that trace widths vary depending on the tension on the Belfort pen, the sharpness of its tip, and the amount of ink in the pen. Next, the time intervals when the collectors were open were identified and matched to the hourly meteorological data. For each weekly sample, the minimum, average and maximum of hourly air temperature and wind speed, and the hourly average wind direction and wind-direction standard deviation (sigma-theta) were computed from the data obtained for the periods when the collectors were open. The computed statistics of the weekly meteorological variables were concatenated with the precipitation chemistry differences and evaluated for correlation both graphically and statistically.



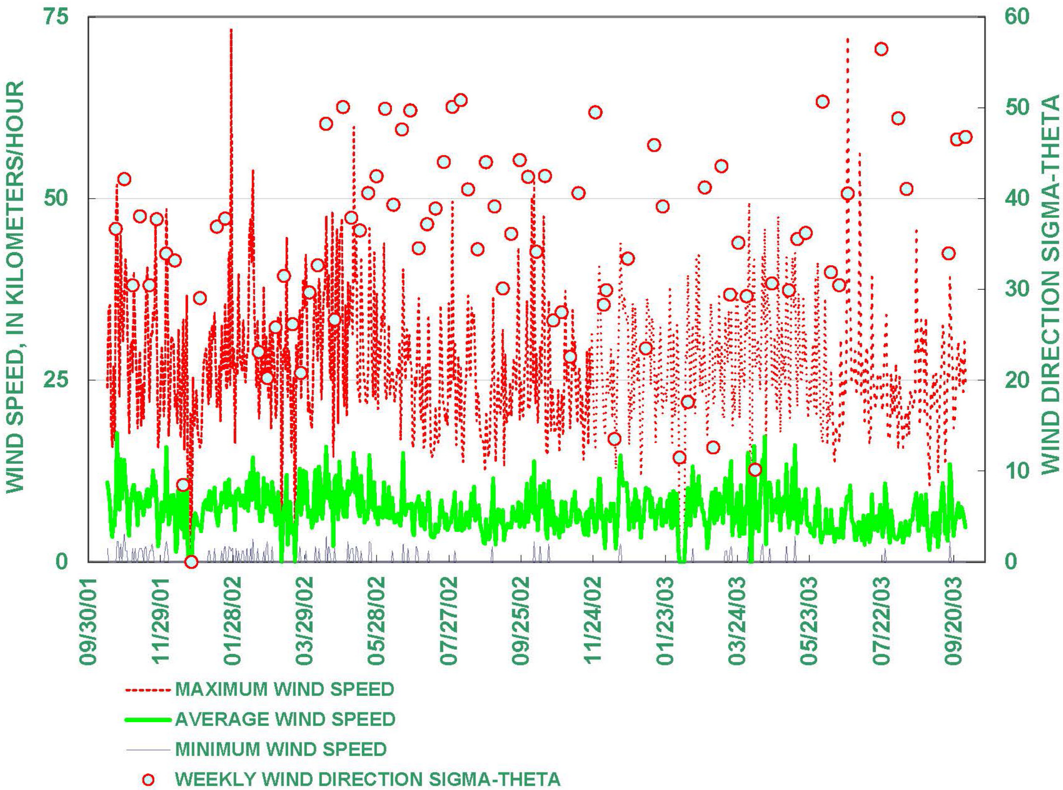


Figure 4. Air temperature, wind speed, weekly wind direction sigma-theta, and weekly NADP/NTN sample and precipitation depth data for co-located NADP/NTN sites WI98 / 98WI: Wildcat Mountain State Park, near Ontario, WI during Water Years 2002–2003.

Results

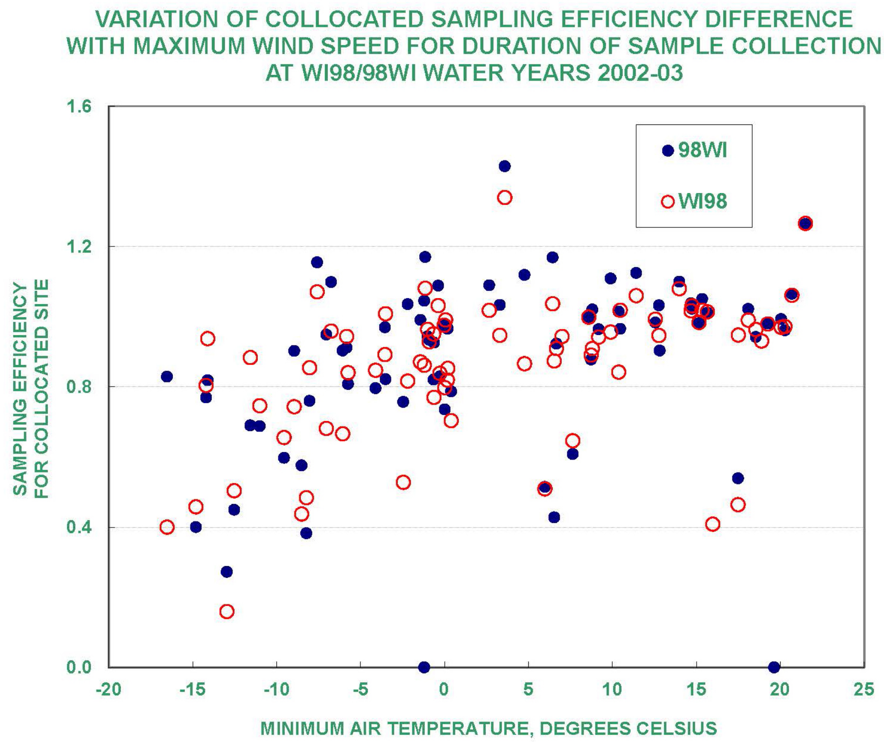
Catch efficiency is the ratio of the precipitation depth measured in the ACM collector to the depth measured by the Belfort rain gage. Catch efficiency was lowest during weeks with colder minimum air temperature and low wind speed (fig. 5). The low catch efficiency occurred during periods of snow or other types of frozen precipitation.

Absolute percent differences in solute concentration, specific conductivity, or precipitation amount (gauge and collector) of co-located samplers were calculated as:

$$\text{Absolute Percent Difference} = \left(\left| \frac{(C_o - C_c)}{Average(C_o : C_c)} \right| \right) \times 100, \qquad (1)$$

Where: C_o = Concentration, specific conductance, precipitation depth, or sample volume measurement from original site, and

C_c = Concentration, specific conductance, precipitation depth, or sample volume measurement from co-located site.



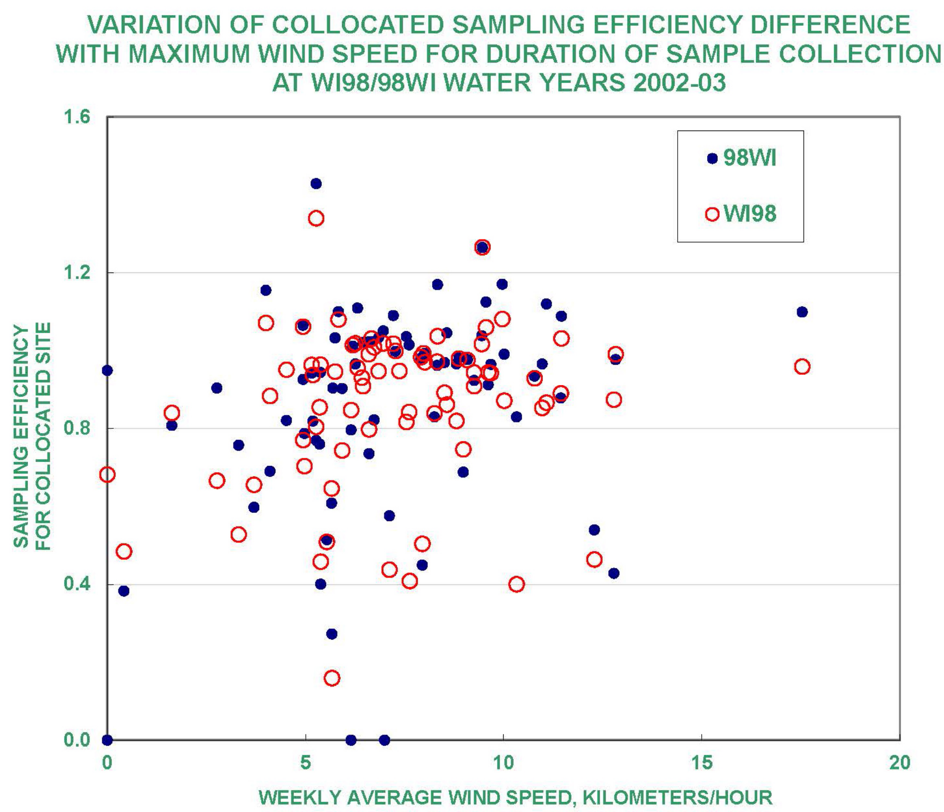
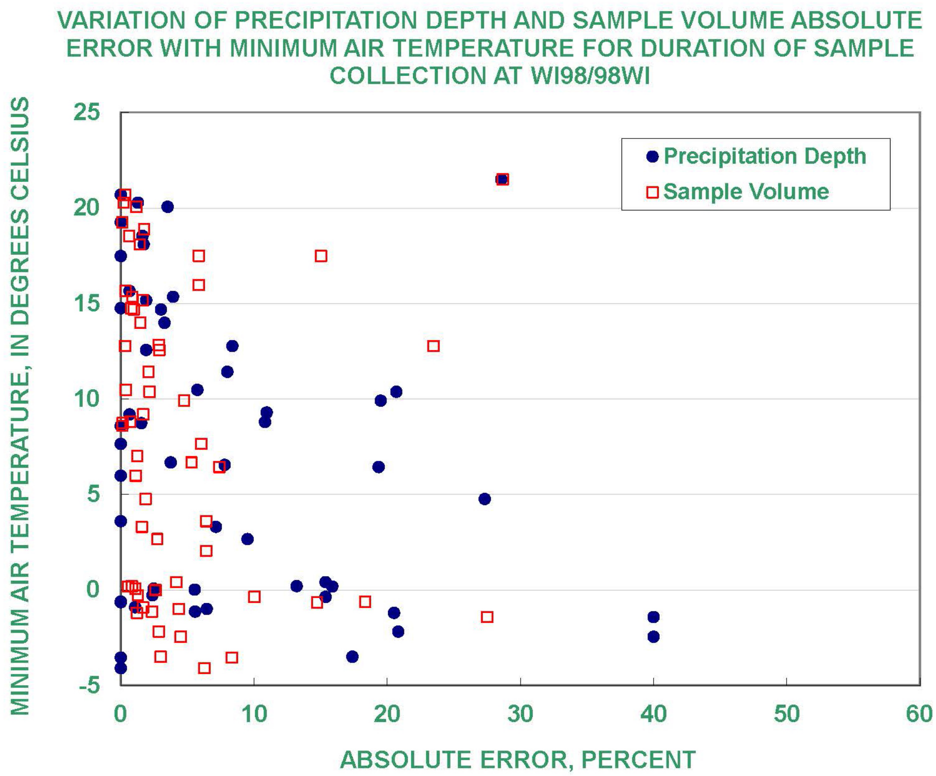


Figure 5. Precipitation-collector catch efficiency ratio related to minimum air temperature and maximum wind speed measured during precipitation collection for weekly NADP/NTN samples from co-located NADP/NTN sites WI98 / 98WI: Wildcat Mountain State Park, near Ontario, WI during Water Years 2002–2003.



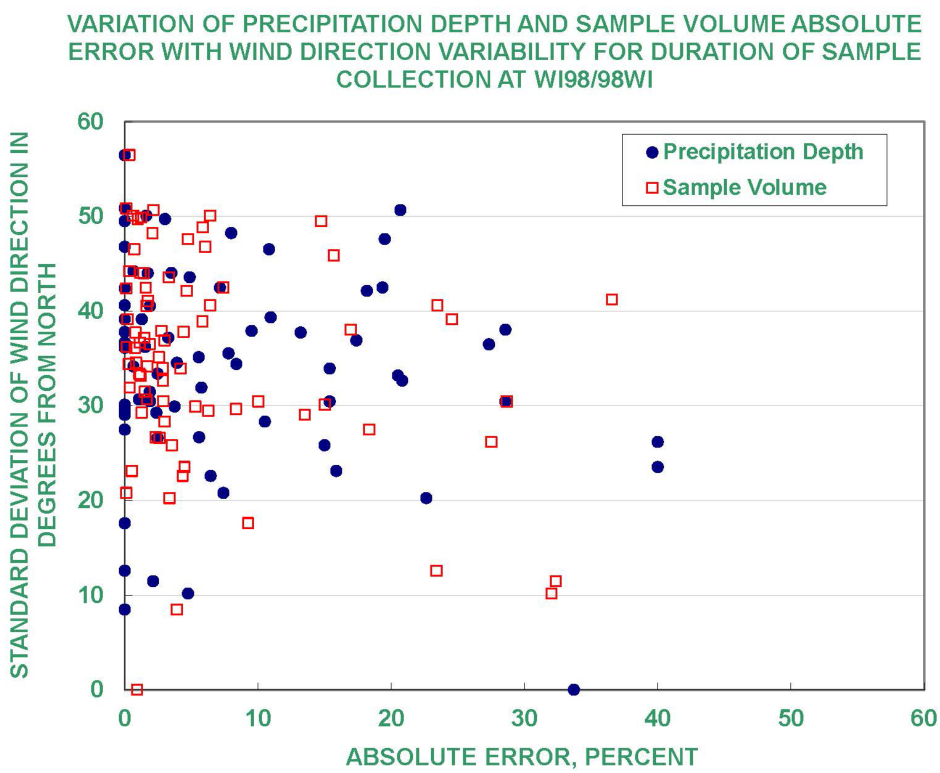


Figure 6. Wet-deposition concentrations and specific conductance related to minimum air temperature and maximum wind speed measured during precipitation collection for weekly NADP/NTN samples from co-located NADP/NTN sites WI98 / 98WI: Wildcat Mountain State Park, near Ontario, WI during Water Years 2002–2003.

Solute concentration differences did not correlate with wind speed or air temperature (fig. 6). These results are consistent with those of Lynch and others (1989), who found that error in their wet-deposition measurements was related to the form of the precipitation (solid versus liquid). However, the results of this study do not support the secondary conclusion of Lynch and others (1989) that error is possibly dependent upon wind speed and direction. This could be due to two different factors. First, a discrepancy exists between the hourly frequency of meteorological data collection and concurrent sample collection for this study because the collector lids can cycle frequently, as much as several times a minute during precipitation events. Many events last less than an hour. Second, relations between error in NADP measurements and wind speed and direction could be site specific.

Conclusions

Although catch efficiency of the ACM collectors is lowest for frozen precipitation samples, that is, collected during periods with colder minimum air temperatures and low wind speed, the variability of the associated precipitation chemistry is independent of these meteorological variables. This conclusion is especially important to the evaluation of NADP/NTN data from sites with extreme winter weather conditions, which commonly have low catch efficiency for most samples throughout the year.

Precipitation Intensity Effects on NTN Samples

Background and Methods

Graham and Robertson (1990) suggest that a large portion of the variability in the NADP/NTN data is due to the characteristics of the precipitation collector, especially the collector's precipitation sensor and its physical "footprint" that provides surfaces for rain splash. Rain splash experiments at the CAL using rhodamine dye indicate that rain drops can splash distances of up to 5.2 meters (Scott Dossett, Illinois State Water Survey, oral and written communications, 2002–2004). Therefore, it is reasonable that sample contamination could increase during intense rainstorms because raindrops can bounce off surfaces near the precipitation collector or into and back out of the collection bucket. In such cases, the representativeness of the precipitation samples is questionable because the samples could be contaminated from rain splashed from nearby surfaces that collect dry deposition, detritus, bird droppings, insects, and other materials between precipitation events.

Low-intensity precipitation could also account for increased error due to the collector sensor design. The collector is opened by precipitation, which completes an electrical circuit between two opposing charged metal surfaces on the face of the sensor (Dossett and Bowersox, 1999) (fig. 7). While some sensors are sensitive to precipitation droplets as small as fog, others are less sensitive and require more precipitation buildup on the sensor to trigger a collector opening. After a collector opens, the sensor’s low-level heating temperature increases to evaporate the precipitation from the sensor surfaces. When precipitation stops, the sensor dries and the electrical circuit is broken. This causes the lid to close. If the sensor doesn't heat up enough to evaporate the precipitation quickly, the collector will stay open longer than necessary. Consequently, some evaporation of the sample or contamination from dry deposition can occur. In some instances, measurable light snowfall will not trigger the collector to open. Data that illustrate this characteristic of the collector are shown in Figure 7. Differences in sensitivity can also be due to the residence time of the sensor in the environment because the sensor surfaces can oxidize with time.

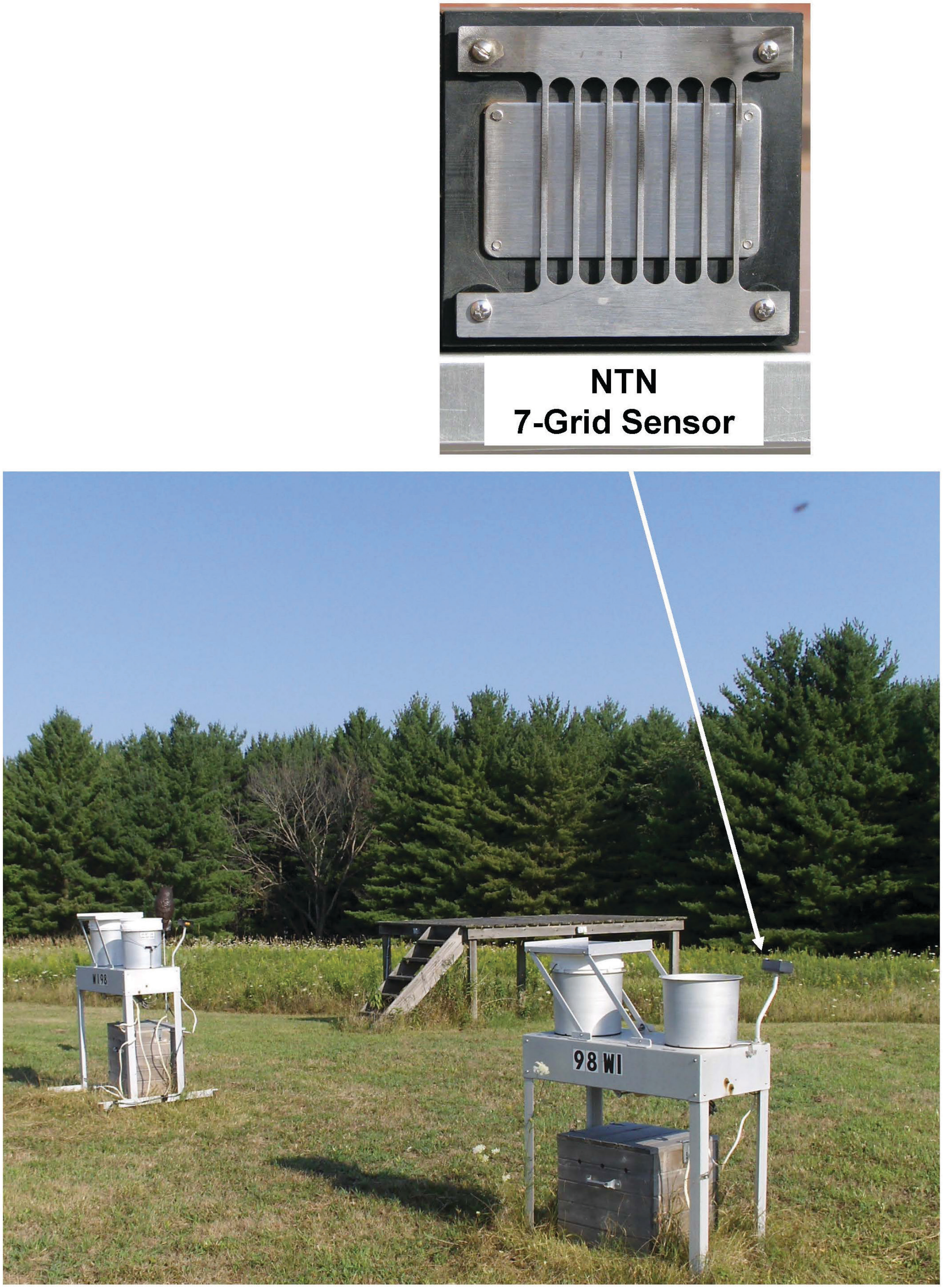


Figure 7. Photographs of NADP grid-type precipitation sensor for the National Trends Network (NTN) and co-located collectors at NADP/NTN sites WI98 / 98WI: Wildcat Mountain State Park, near Ontario, WI.

Variability of co-located measurements is mostly attributed to spatial variability in precipitation within the 5 to 30 meter distance between co-located collectors (Wetherbee and others, 2004). Data were obtained for precipitation intensity, wet-deposition concentrations, and precipitation collector-lid openings for four co-located sampler sites to evaluate whether precipitation intensity is related to the overall variability in NADP/NTN measurements. The locations of the four co-located sites are as follows: MN01/01MN, MN16/16MN, NH02/02NH, and WY95/95WY. These sites operated throughout five separate water years and are shown in Figure 8. These co-located sites were selected because they are located in precipitation regimes that receive snow and both frontal and convective rain storms. Site information and periods of record obtained for each of the paired co-located sites used for the precipitation-intensity study are listed in table 1.

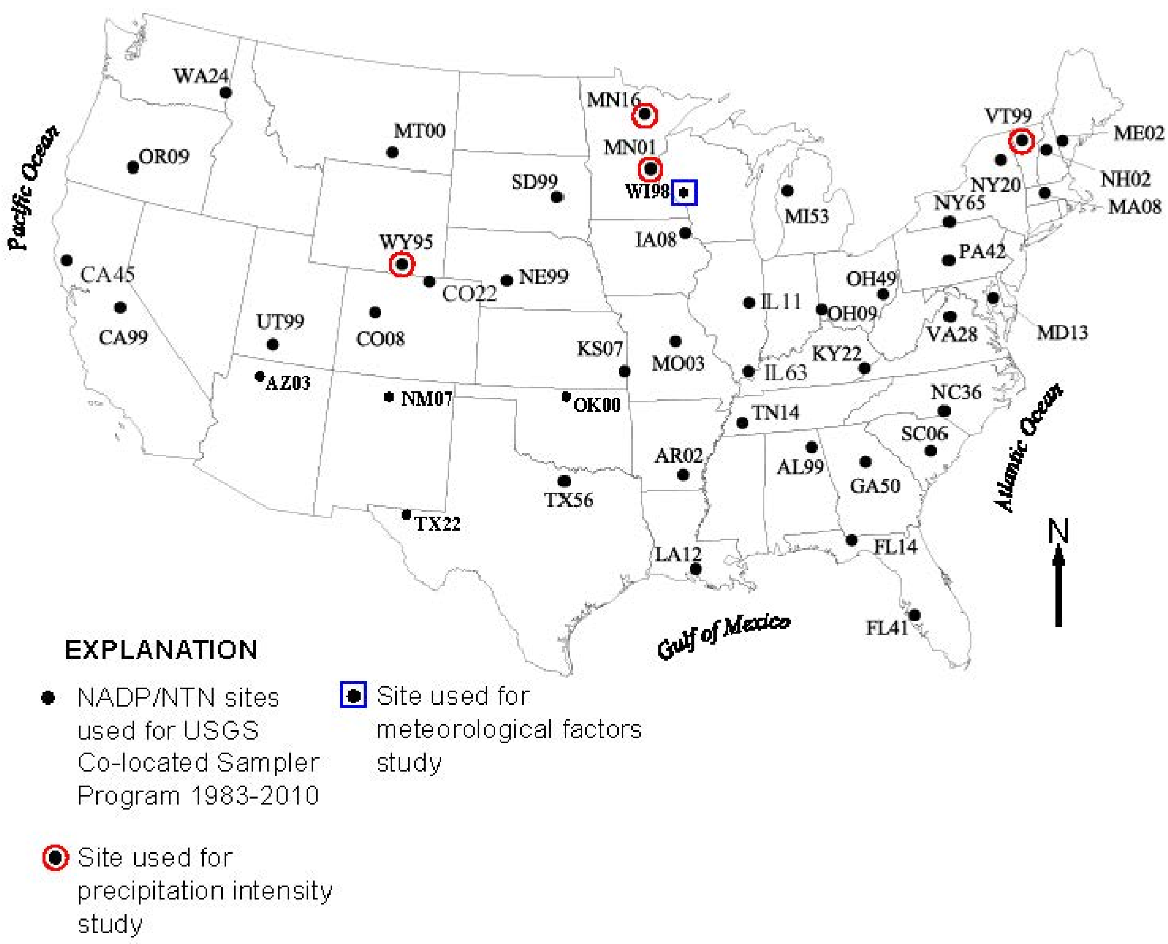


Figure 8. Locations of National Atmospheric Deposition Program / National Trends Network sites used in the USGS Co-located Sampler Study 1983–2010.

Table 1. Information for NADP/NTN co-located sampler sites used to evaluate precipitation intensity effects on data variability.

[Water year, October 1 through September 30; km^2, square kilometers]

Co-located NADP Site IDs	Site Name	Co-located Period of Record (Water Year)	Latitude (degrees north)	Longitude (degrees west)
MN01 / 01MN	Cedar Creek	1999	45.400111	93.212500
MN16 / 16MN	Marcell Experimental Forest	1995	47.531111	93.468611
NH02 / 02NH	Hubbard Brook	2000 & 2001	43.943056	71.703333
WY95 / 95WY	Brooklyn Lake	1998	41.364722	106.240833
	Median Annual Precipitation (centimeters)	**Median Number of weeks with precipitation per year**	**Altitude (meters)**	**Airshed Area (km^2)**
MN01 / 01MN	60.2	42	280	75.1
MN16 / 16MN	78.3	48	431	29.0
NH02 / 02NH	120.2	49	250	11.4
WY95 / 95WY	116.5	47	3,212	14.9

These four sites were selected because abundant quantities of data were collected for these co-located sites, and snow falls at each site during winter months. Figure 3 provides an example of the instrumentation at a typical co-located sampler site.

Photocopies of archived rain-gage charts obtained from the NADP Program Office (Chris Lehmann, Ill. State Water Survey, written communication, 2003) were read manually (approx. resolution of 0.5 hours) to determine the average and maximum precipitation intensities measured during each week. The number of wet-deposition collector openings was also estimated from the event-recorder trace on the rain-gage charts for each weekly sample. An example of a rain-gage chart from co-located sites NH02/02NH is shown in Figure 9. The weekly precipitation intensity data were concatenated with calculated absolute percent errors for weekly measurements of wet-deposition concentrations, specific conductance, precipitation depth, and sample volume.

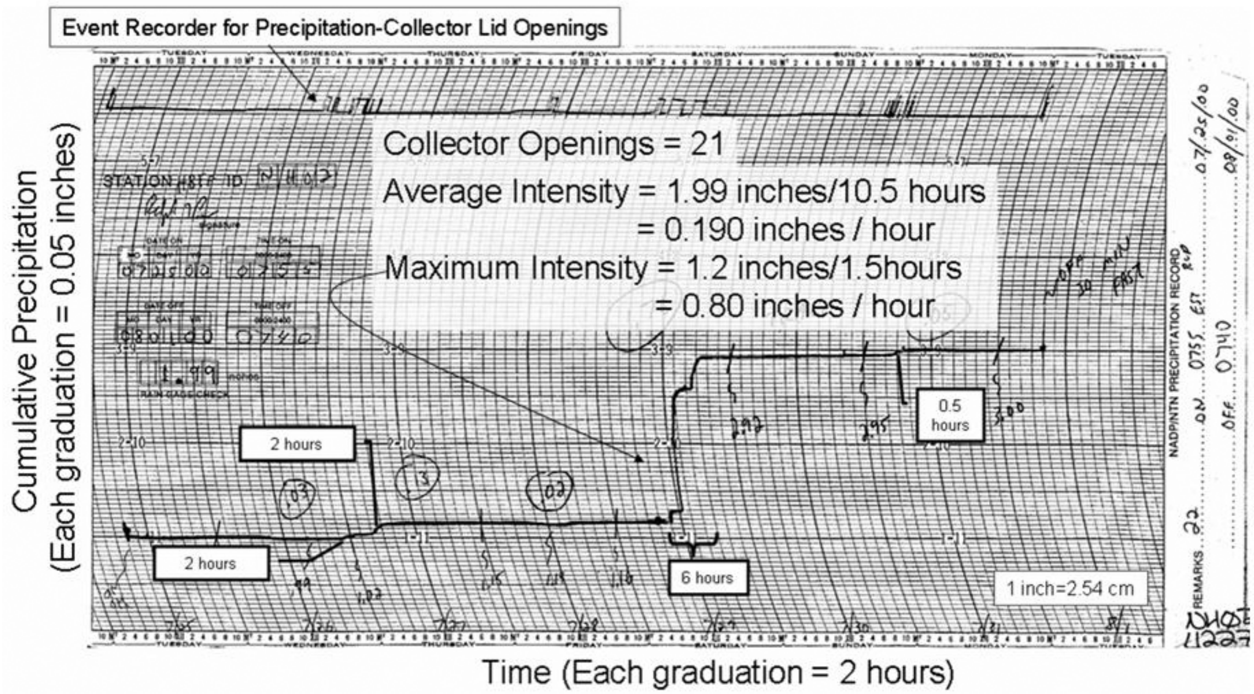


Figure 9. Belfort 5-780 rain-gage chart for NADP/NTN site NH02 at Hubbard Brook Experimental Forest for the week of July 28–August 1, 2000 with example calculations of average and maximum precipitation intensities.

The average precipitation intensity values were calculated as the total precipitation collected for the week divided by the time that precipitation occurred (Figure 9). The maximum precipitation intensity was selected from the portion of the rain-gage trace with the greatest rate of change over less than a four hour period. The precipitation amount recorded during the time period was divided by the time over which it occurred to obtain the maximum precipitation intensity for the week.

Uncertainty in the event recorder and precipitation depth pen traces was not accounted for. Widths of pen traces varied between gages and even between weeks for the same gage. When the ACM cycles its lid, the Belfort gage can mark overlapping event recorder pen traces, which were not accounted for. New NADP electronically recording rain gages collect data with better event-recorder resolution for evaluation of precipitation intensity during sample collection, but those gages were not available when this study was done.

Results

Precipitation intensity data were plotted against catch efficiency and sample-volume absolute percent difference for the four co-located sites combined in Figure 10. There is more variability in catch efficiency and higher absolute percent differences for co-located sample volumes for weeks with relatively low precipitation intensity. Most of the low catch-efficiency data are for weeks with frozen precipitation, which the AeroChem Metrics collector typically under-catches (Lynch and others, 1989, Nilles and others, 1992 and 1994). The results are consistent with data presented by Lamb and Connie (1993), which showed greater variability between co-located wet-deposition collectors for samples with low precipitation depths than for samples from higher precipitation depths.

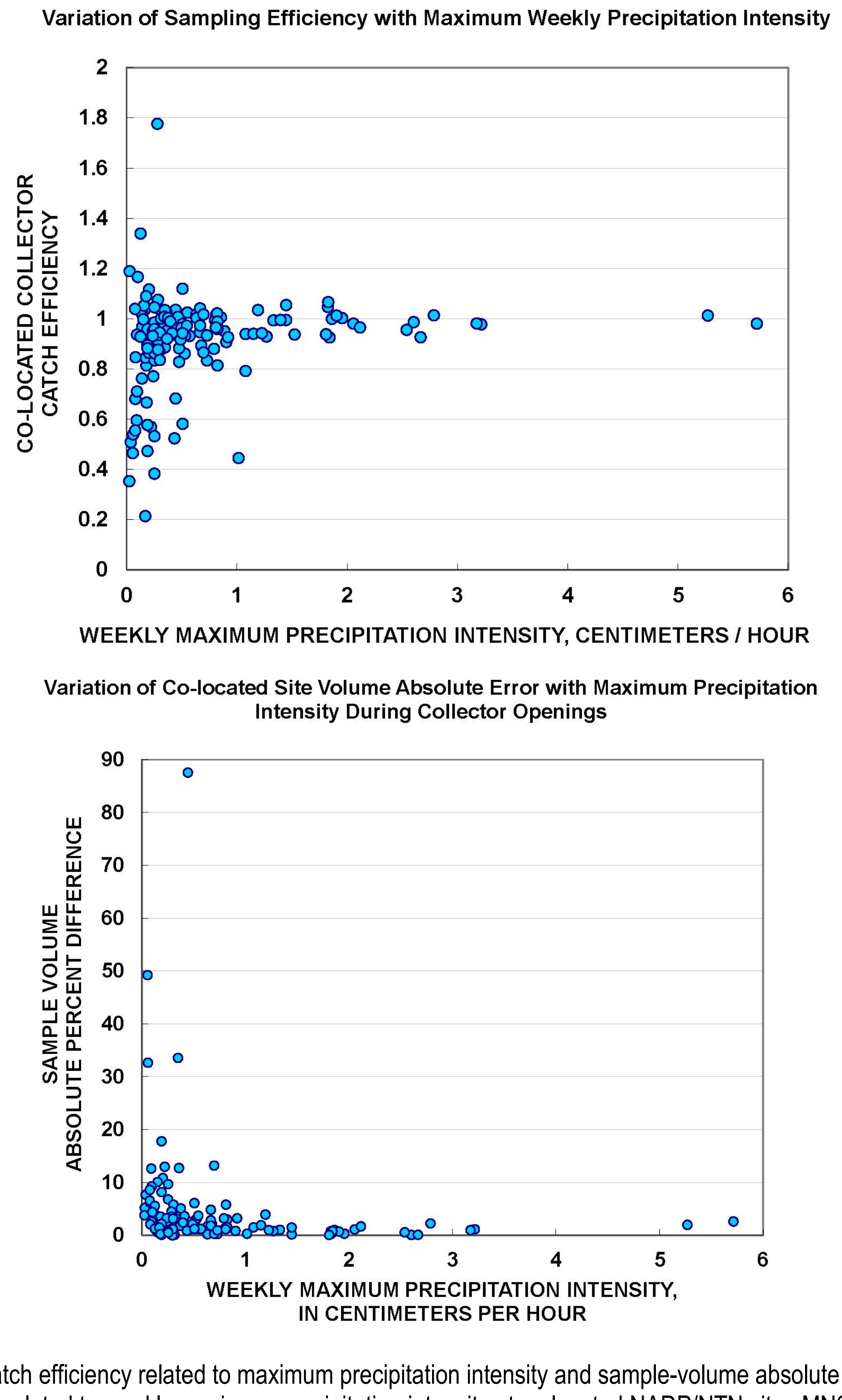


Figure 10. Catch efficiency related to maximum precipitation intensity and sample-volume absolute percent difference related to weekly maximum precipitation intensity at co-located NADP/NTN sites MN01/01MN, MN16/16MN, NH02/02NH, and WY95/95WY.

Absolute percent differences for wet-deposition concentrations of nitrate, sulfate, ammonium, and hydrogen ion from the four co-located sites are plotted against weekly maximum precipitation intensity in Figure 11. The relations in Figure 11 indicate higher variability in NADP/NTN measurements for low-intensity precipitation events than for high-intensity precipitation events.

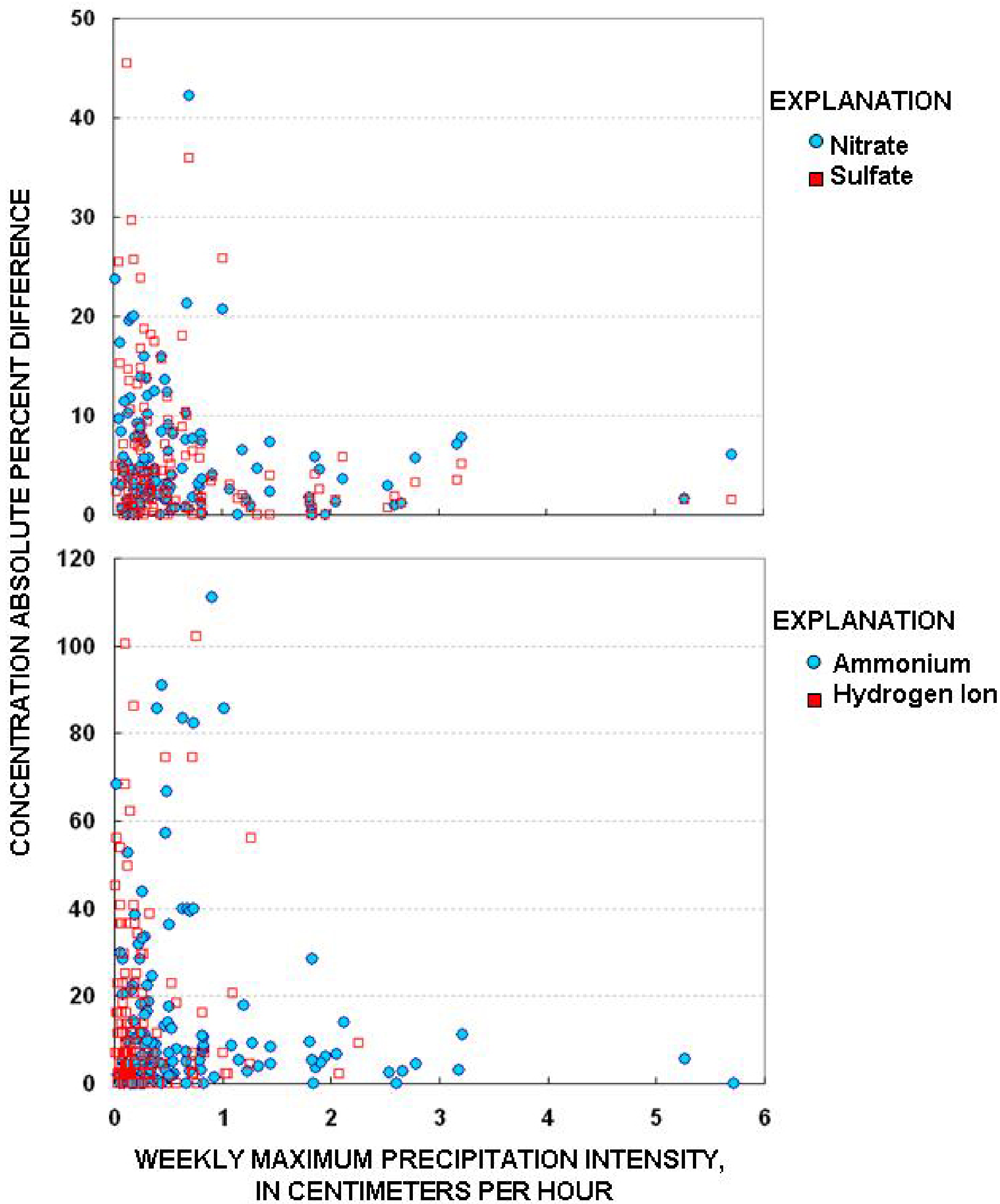


Figure 11. Absolute percent differences for concentrations of sulfate, nitrate, ammonium, and hydrogen-ion in wet-deposition related to weekly maximum precipitation intensity at co-located NADP/NTN sites MN01/01MN, MN16/16MN, NH02/02NH, and WY95/95WY.

Conclusions

Results of the USGS Co-located Sampler Program indicate increased variability in NADP/NTN wet-deposition measurements occurs for low-intensity precipitation events, which are commonly from snow deposition or other types of frozen precipitation events. Therefore, the variability in the measurements is more readily attributed to the capability of the collector's precipitation sensor to detect low-intensity precipitation. These results are consistent with the findings of Tang and others (1987), Lynch and others (1989), and Sirois and others (2000)—three of several studies that conclude winter undercatch of wet-deposition collectors is due to sluggish precipitation sensor response to snow.

Most of the samples for this study and the previous study were collected at low precipitation intensity (that is, <1 cm per hour) and the error in NADP measurements is observed to exponentially increase at lower intensities. For a given site, the proportion of error in annual deposition estimates attributed to low-intensity events was not evaluated. Data in Figures 10 and 11 could be modeled and applied to NADP/NTN electronic precipitation records to estimate error attributed to precipitation intensity.

Site Urbanization Effects on NTN Trends

Background and Methods

The distribution of the human population in the United States is changing, increasing in some areas and decreasing in others. Human activity on the landscape is at least partly responsible for the air pollutants that are removed from the atmosphere by wet deposition. The NTN was originally established exclusively using sites that were expected to provide regionally representative data, but the network has grown to include sites in urban areas and other research-oriented sites that are not considered to measure a regionally representative environmental signal. Samples collected at urban and research sites are suspected to be representative of wet deposition affected by local, anthropogenic emission sources in addition to regionally distributed air pollutants. The NADP Network Operations Subcommittee and the NADP Quality Assurance Advisory Group questioned whether recent urbanization of the lands surrounding NADP/NTN sites affects wet-deposition characteristics at long-term, regionally representative NTN sites; specifically, trends in wet deposition chemistry.

Because nearly all NADP/NTN sites are purposely located away from obvious point sources of air pollution, the analysis focused on trends in ionic composition of wet-deposition that were indicative of urban encroachment. Specific attention was given to evaluation of the site-specific trends in calcium:hydrogen-ion concentration ratios to evaluate whether an "urban scrubber" effect could be detected in the NADP/NTN data. Lovett and others (2000) described the urban scrubber effect as the phenomenon whereby acidic protons in wet deposition are buffered by calcium ion and associated anionic species contained in dust created and suspended by urban activities such as road traffic. Lovett and others (2000) documented this effect by evaluating rural-to-urban transects of bulk deposition measurements in New York. Previous work by Sisterson and Shannon (1990) in Chicago, indicated that urban samples had higher Ca^{2+} and Mg^{2+} concentrations and lower acidity than samples from an upwind suburban site. Butler (1988) discovered that atmospheric dry deposition particle mass was up to 30 percent calcium carbonate ($CaCO_3$), and up to 14 percent dolomite ($CaCO_3$, $MgCO_3$). These inorganic base components in dust are known to buffer acidic precipitation (Hedin and Likens, 1996). Because

Ca^{2+} and H^+ (from pH) concentrations are standard NADP/NTN analytes, they were selected for this study to be indicators of urban encroachment on NADP/NTN sites.

USGS evaluated trends in NADP/NTN wet-deposition chemistry with respect to the percentage of urbanized land surface increase within a 30-mile radius of each NADP/NTN site. Population data were obtained from the U.S. Bureau of Census information available in the ArcMap Geographic Information System (GIS), version 9.2 (ESRI, 2008). Urbanized land surface cover was obtained from the National Land Cover Database (NLCD) 1992–2001 Retrofit Change Product available from Multi-Resolution Land Characteristics Consortium at URL: *http://www.mrlc.gov/change_detection.asp.*

Temporal trends in NADP/NTN precipitation ion-concentration ratios were quantified and mapped using weekly and annual wet-deposition data obtained from the NADP web site at URL: *http://nadp.isws.illinois.edu/*. Trends in wet-deposition were identified and quantified using the Kendall Family of Trends program available from the USGS at URL*: http://pubs.usgs.gov/sir/2005/5275/* (Helsel and others, 2005). The wet-deposition was mapped using the ArcMap version 9.2 GIS (ESRI, 2008) to evaluate spatial patterns for potential correlation of land surface urbanization. Finally, NADP/NTN sites were ranked by percent change in urbanized land area during 1992–2001 within 30-mile radii of the sites to identify sites with the greatest potential to evaluate the effects of urbanization on wet-deposition chemistry.

Results

Figure 12 shows that urbanization of NADP/NTN is generally greater in the Midwestern and Southeastern States and along the East Coast than in Western States. Consequently, the potential for urbanization to affect trends in NADP data is lower in the western portion of the USA than in the eastern portion.

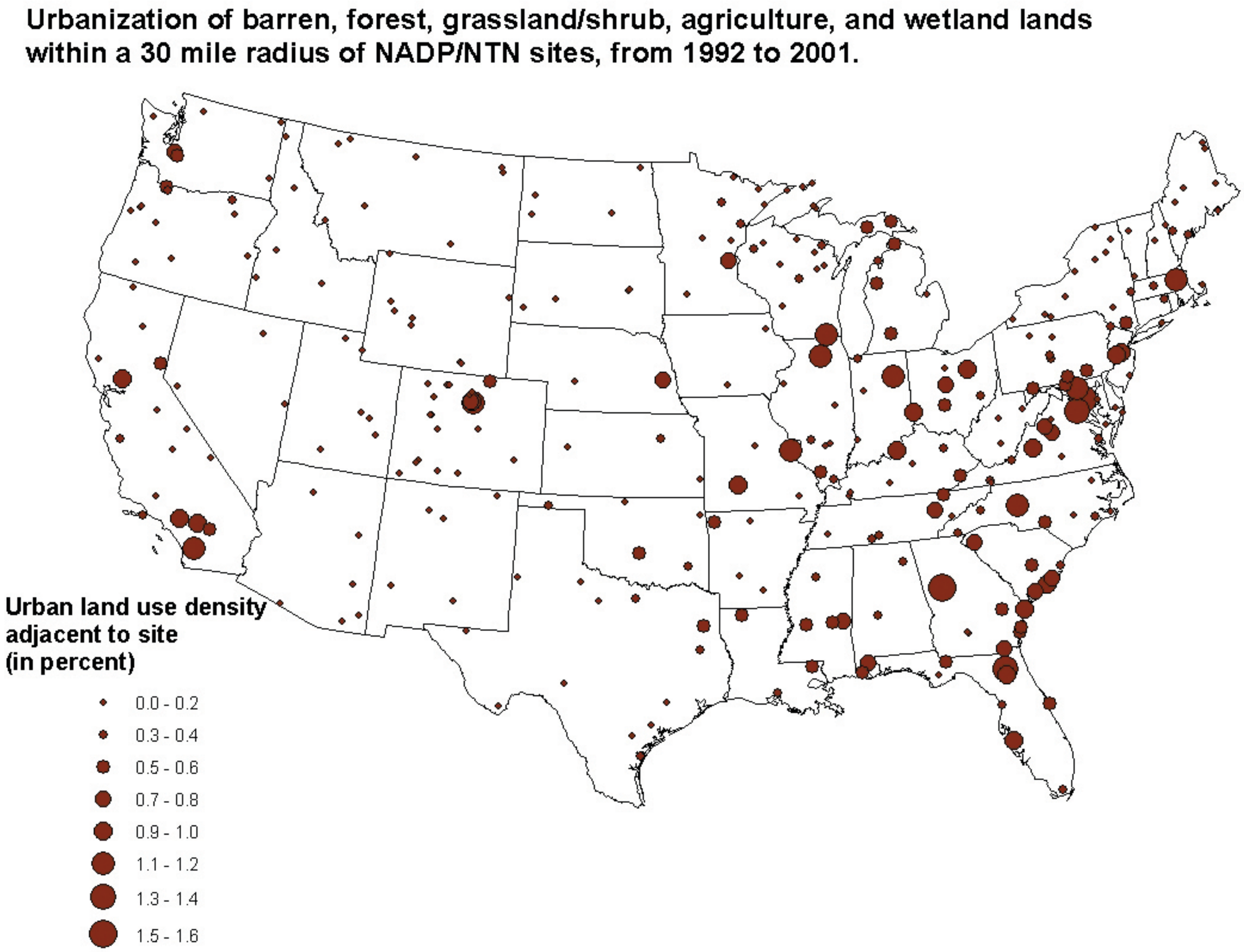


Figure 12. NADP/NTN sites and percent land-use change from non-urban to urban within 30 miles of each site during 1992–2001.

Data in Figure 13 indicate no relation between statistically significant (α=0.10) 10-year trends in Ca^{2+}:H^+ with increasing change in urban land use during 1990–2000. This implies that the urban scrubber effect is not occurring to a detectable degree at NADP/NTN sites even though land surface urbanization is occurring near these sites. Geographic evaluation of the data in Figure 13 revealed that all of the points with Ca^{2+}:H^+ greater than 0.70 are from sites located in the western and Midwestern regions of the U.S. However, there are many sites in the western and Midwestern regions with Ca^{2+}:H^+ ranging from 0.007 to 0.67 as well. Therefore, the data do not provide a strong indication of geographically specific changes in Ca^{2+}:H^+ ratios during 1992–2001.

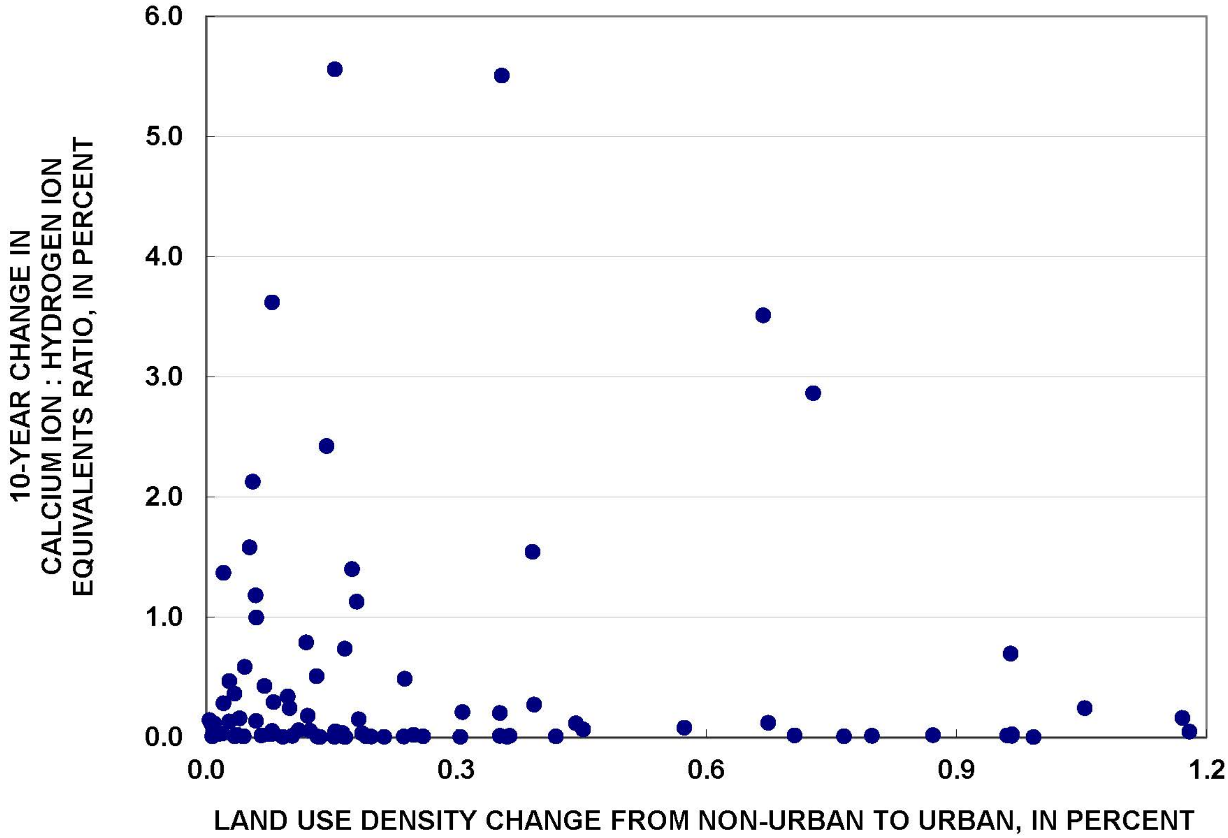


Figure 13. Variation of 10-year change in calcium-ion : hydrogen-ion equivalents ratios for annual precipitation-weighted mean concentrations in NADP/NTN samples during 1992–2001 with urban land-use density change within 30 mile radii of NADP/NTN sites during 1990–2000.

The Ca^{2+}:H^{+} data obtained for calendar years 1990–1999 are spatially represented by iso-contour maps in Figure 14, which shows higher ratios in less populated Western States than in more densely populated and urbanized Eastern States. These maps show one isolated urban area near Davis, California with high Ca^{2+}:H^{+} during 1991 and 1995–1999. High Ca^{2+}:H^{+} ratios are also shown near Las Vegas, Nevada during 1990–1991, 1994, and 1998–1999. By comparison, sites near urban areas in the eastern portion of the country do not have high Ca^{2+}:H^{+} ratios.

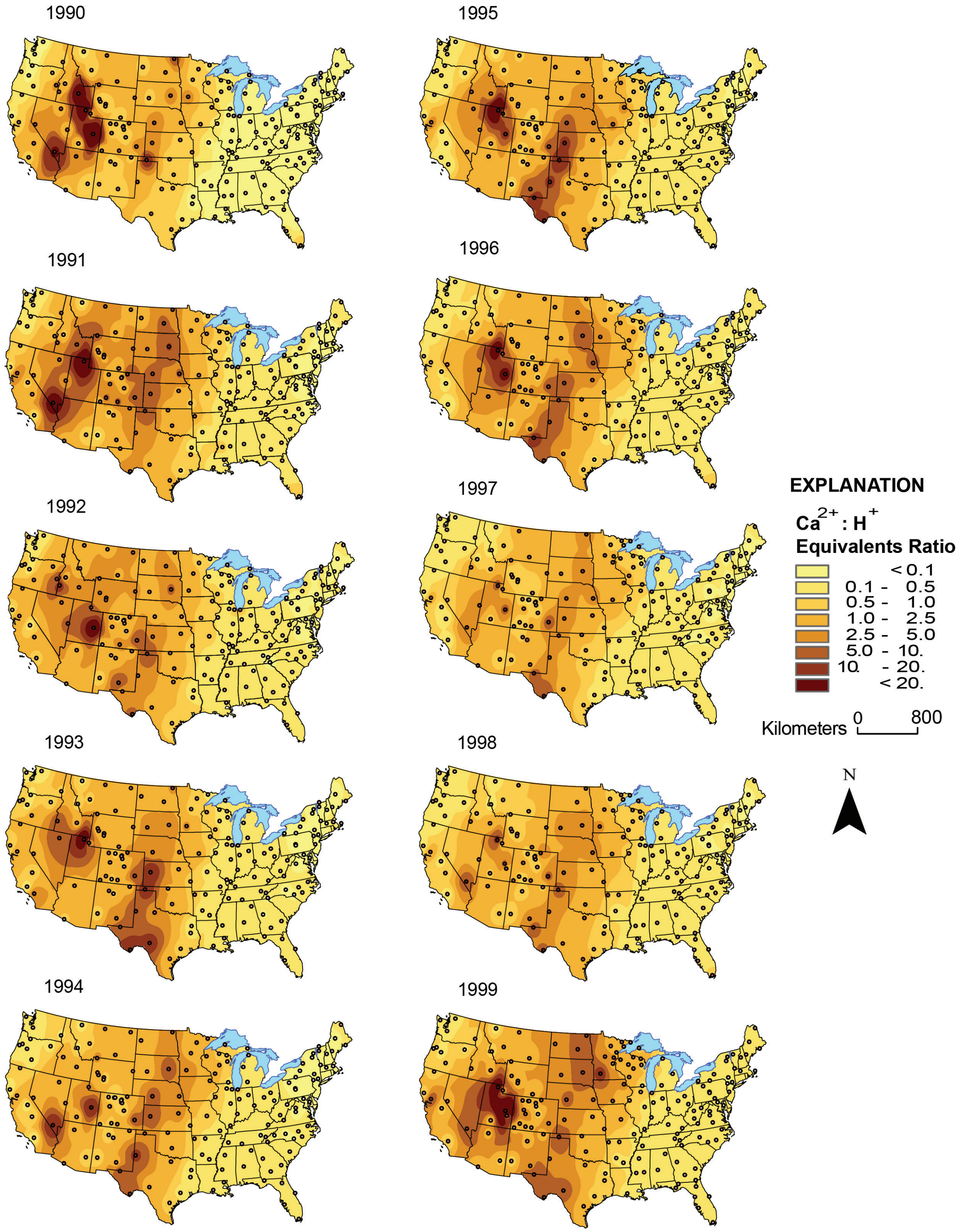


Figure 14. Iso-contour maps of the ratio of calcium-ion : hydrogen-ion for annual precipitation-weighted mean concentrations in NADP/NTN wet-deposition samples across the continental United States during 1990–1999.

Conclusions

Urbanization of the landscape surrounding NADP/NTN sites studied herein is not affecting trends in wet-deposition chemistry data to any measureable degree. Presentation of the results of this study and the above conclusion is not intended to advocate or influence relaxation of NADP siting criteria, which specify that NADP/NTN sites should be located at specific distances from urban or suburban air pollution sources (NADP, 2010).

Relations of Site Characteristics to Sample Integrity

Background and Methods

NADP established specific criteria for the physical characteristics of its network monitoring sites, referred to as “siting criteria” in the NADP Site Selection and Installation Manual (NADP, 2009). The siting criteria for NADP installations are reproduced herein in table 2. Sites in violation of these criteria are requested to remediate conditions to comply with the criteria if and whenever possible.

Table 2. National Atmospheric Deposition Program Site Installation Rules for National Trends Network sites.

[NADP, National Atmospheric Deposition Program; AIRMoN, Atmospheric Integrated Research Monitoring Network; MDN, Mercury Deposition Network; NTN, National Trends Network; m, meters; cm, centimeters; <, less than or equal to; >, greater than or equal to]

Parameter	NADP Network	Description of Criteria
Collector orientation	AIRMoN, MDN, NTN	wet side bucket ± 45° of magnetic west
Sensor orientation	AIRMoN, MDN, NTN	to the north
Distance between collector and rain gage	AIRMoN, MDN, NTN	≥ 5 m, < 30 m
Vertical distance between collector orifice and rain gage orifice	AIRMoN, MDN, NTN	≤ 0.3 m
Vegetation height	AIRMoN, MDN, NTN	≤ 0.6 m within 5 m of instrument base
Vegetation height	AMoN	≤ 0.6 m within 2 m of instrument base
Vertical objects (includes towers, wires, fences), angle of projection from instrumentation	All	≤ 45˚ from top of instrument open to sky
Trees, angle of projection from instrumentation	All	≤ 45˚ from top of instrument open to sky
Buildings, angle of projection from instrumentation	All	≤ 30˚ from top of instrument open to sky
Objects, > 1 m tall, > 5 cm in width or depth	All	≥ 5 m from instrument
> 20% annual precipitation is frozen	AIRMoN, MDN, NTN	wind shield present on rain gage
Wind shield, pivot axis	AIRMoN, MDN, NTN	same height as rain gage orifice
Rooftop installation	All	urban sites only
Rooftop installation, equipment separation from potential emission sources (sewer vents, HVAC systems)	All	maximize separation
Rooftop installation, objects, angle of projection	All	≤ 30˚ from top of instrument

At the NTN's inception, committees to protect sample integrity established most of the siting criteria and the criteria were based on scientific opinion "a priori," and not data analysis or the lack thereof. Graham (1990) compared deposition differences among three co-located ACM collectors in violation of various siting criteria to a control ACM at NTN site NY99. Graham (1990) concluded that observed deposition differences were due to objects within a 45° cone (90° cone from bucket open to sky) from a collector, wind-obstructing objects within five meters of another collector, and proximity of each collector to a nearby highway. The study was limited to one year of co-located data collection at NY99. During 2008, the NADP Quality Assurance Advisory Group suggested re-examination of the siting criteria based on analysis of NADP/NTN data from many sites across the network.

For this study, data from sites with characteristics in violation of NADP siting criteria were evaluated to determine whether a statistically significant relation exists between sample integrity and various types of violations. For example, plant material might be expected to be commonly found in samples from a site that allows vegetation to grow higher and/or closer to the collector than is allowed. Another example is that leaves could be expected to fall into the collector bucket if trees are allowed to grow to a sufficient height in proximity of the collector.

Data were obtained for the period 2003–2007 from the CAL database for 44 sites with specific siting criteria violations and 15 sites with no siting criteria violations as identified by site surveys conducted by EEMS, Inc. during 2007–2008. EEMS, Inc. is contracted by the NADP Program Office to conduct annual site surveys at approximately 100 NADP sites annually. The sites used for this study are listed in table 3. Control sites were used multiple times for comparison to sites with siting criteria violations. For each comparison, the same number of sites was used for the control group and the group of sites with siting-criteria violations. Conditions observed for site surveys conducted during 2007–2008 were assumed to be applicable to the study period.

Table 3. Matrix of sites used to evaluate independence of National Atmospheric Deposition Program (NADP) siting criteria violations and visible sample contamination for wet-deposition samples collected during 2003–2007.

[NADP, National Atmospheric Deposition Program; >, greater than or equal to]

		NADP Sites with Siting Criteria Violations				
		*1	*2	*3	*4	*5
NADP Sites with no siting criteria violations (control sites)	* Siting criteria violation for randomly selected control site	Vegetation≥0.6 meters tall within 5 meters of collector	Object(s) within 45-degree cone open to sky from collector	Fence(s) within 5 meters of collector	Trees in 30-degree cone open to sky from collector	1-meter tall objects within 5 meters of collector
ND08	*1,2,3,4,5*	ID11	AR16	AZ99	IN22	AR27
AZ97	*1,2,3,4,5*	ND11	CO96	NC25	MN08	AZ03
OH71	*1,2,3,4,5*	NV05	GA09	NY08	MN32	CO10
TX02	*1,2,3,4,5*	SD04	ME98	NY29	MS19	CO97
NE15	*2,3,4,5*		MS30	OK99	NH02	CT15
SC06	*3,4,5*		NC34	TX10	OK17	GA33
WA98	*2,4,5*		WI37	TX16	PA18	IN41
SC11	*4,5*			UT98	PA42	KS31
AL10	*4,5*				SC05	ME00
NY20	*4,5*				UT99	MN16
TX04	*4,5*				VT99	MN18
WY99	*2*					MN99
NC35	*5*					NY20
KS32	*5*					TX22
NC36	*5*					

NADP data are reviewed and assigned qualifiers to identify imperfect samples that are potentially contaminated, visibly contaminated with foreign objects, or confirmed as chemically contaminated. Other qualifiers provide information on collector performance, potential breaches of sample integrity (for example, "lid not tight" when the sample bottle lid is loose and/or leaking), and sufficiency of sample volume available for chemical analysis. The qualifiers provide a means for screening data to limit variability due to extraneous effects. For this study, only weekly samples with sufficient volume for chemical analysis were used for this study (a.k.a. "W-coded" samples). Samples identified as having trace volumes and samples that required dilution to obtain sufficient volume for analysis were censored from the data set to remove potential variability attributed to dilution. Duplicate samples which are run for internal quality assurance were also censored.

The final data set contained 10,877 weekly, W-coded samples. Of the 10,877 samples, 5,927 samples (55 percent) were qualified by contamination codes indicating specific contamination types observed in the samples or some other imperfection that could affect sample integrity. Of these 5,927 samples, the CAL assigned a screening level code of "C" to 910 samples, indicating that the samples were chemically contaminated per the laboratory's data screening protocols (NADP/CAL, 2008). CAL's sample limitation codes (for example, "C" codes) and contamination codes (for example, "NON", "BHC", "FHC", "LLL", and others) are data fields in CAL's database, but these codes are not available to data users who accesses the data from the NADP website. The percentages of each of the contamination types represented in the data set are listed in table 4.

Table 4. Summary of contamination codes for National Atmospheric Deposition Program / Central Analytical Laboratory data selected to evaluate independence of visible sample contamination and siting criteria.

[Shading identifies contamination types in more than 5 percent of all samples]

Contamination code	Contamination code description	Percentage of 10,877 samples assigned contamination code
BBD	Bird and dirt identified in field and laboratory	0.13
BCO	Combined contamination identified in field and laboratory	10.94
BHC	Handling contamination from field and laboratory	0.02
BIC	Insect identified in field and laboratory	3.36
BOT	Other contamination identified in field and laboratory	0.01
BPC	Plant contamination identified in field and laboratory	11.71
FBD	Bird droppings identified in field	0.48
FCO	Combined contamination identified in field	2.67
FFF	Sample not valid due to field protocol failure	0.21
FHC	Handling contamination from field	0.21
FIC	Insect identified in field	5.60
FOT	Other contamination identified in field	0.06
FPC	Plant contamination identified in field	7.60
LCO	Combined contamination identified in laboratory	0.30
LHC	Handling contamination from laboratory	0.13
LHH	Horse hair from packaging from old bucket box mailer	0.01
LIC	Insect contamination identified in laboratory	1.21
LLL	Serious laboratory error	0.02
LNT	Sample bottle lid not tight	1.74
LOT	Other contamination identified in laboratory	0.80
LPC	Plant contamination identified in laboratory	7.25

Rothert and others (2009) showed that it is typically not possible for a person to distinguish between different types of visible contamination in NADP / NTN samples even though site operators and CAL technicians are required to record their observations of the different types of materials present. Therefore for this study, a sample was visibly contaminated if it was assigned any contamination code other than the codes: "NON" (not contaminated), "BHC", "FHC", "LHC", "LLL", and "LNT" (table 4). These codes are assigned to samples in the CAL database, but they are not available to data users in data obtainable from the World Wide Web. For the selected data set, 61 percent of the samples from sites with siting criteria violations were assigned contamination codes indicating visible contamination. By comparison, 52 percent of the samples from the control sites were assigned contamination codes indicating visible contamination.

A follow-up comparison of visible sample-contamination data for NTN sites during the same 2003–2007 study period was done to determine whether sites with common physical characteristics are more prone to having low or high numbers of visibly contaminated samples. Data from the CAL database were evaluated for NTN sites with complete data records for the study period. Sites were ranked by the number of samples with visible contamination. Site characteristics, including siting criteria violations, were obtained from EEMS site-survey database and from site photographs viewed on the NADP web site.

Results

Independence of siting criteria violations and visible sample contamination was tested using 2-by-2 contingency tables based on the Chi-Square distribution using SAS statistical software (SAS, 2008). The null hypothesis for the frequency analysis is: "Visible sample contamination is independent of siting criteria violations." Statistical confidence associated with incorrectly rejecting the null hypothesis when true was evaluated at the $\alpha=0.05$ significance level (95 percent confidence). Results for the frequency analysis for the entire data set are listed in table 5.

Results in table 5 indicate a lack of significant ($\alpha=0.05$) independence between visible sample contamination and objects located too close to the NADP/NTN collectors. For sites with objects within the 90^o cone open to sky, 68 percent of the samples contain visible contamination, whereas for sites with no siting criteria violations, 46 percent of the samples had visible contamination. Sites with trees within a 120^o cone open to sky had a higher percentage of visibly contaminated samples than sites with no siting criteria violations.

Table 5. Frequency of visible contamination in wet-deposition samples for sites with selected National Atmospheric Deposition Program siting criteria violations: (1) object(s) in 90° cone open to sky; (2) trees within 120° cone open to sky; (3) vegetation greater than or equal to 0.6 meters tall within 5 meters of collector; (4) fence within 5 meters of collector; and (5) 1-meter tall objects within 5 meters of collector.

[N, sample count; Chi-Square p-values = probability of incorrectly deciding that contamination is not independent of violation; >, greater than or equal to; m, meters]

Siting criteria violations	Weekly samples (N)	Visibly contaminated? Yes (percent)	Visibly contaminated? No (percent)	Chi-Square p-values
Object(s) in 90° cone from collector open to sky?				
YES	1,390	68	32	<0.0001
NO	1,149	46	54	
Trees in 120° cone from collector open to sky?				
YES	2,499	61	39	< .0001
NO	1,925	52	48	
Vegetation > 0.6m tall within 5m of collector?				
YES	574	38	62	.0392
NO	620	44	56	
Fence(s) within 5m of collector?				
YES	1,221	47	53	.9537
NO	1,294	47	53	
1m tall objects within 5m of collector?				
YES	2,785	47	53	.0141
NO	2,507	51	49	

Shading denotes lack of statistically significant (α=0.05) independence of siting criteria violation type(s) and visible contamination.

Visible sample contamination is not significantly (α=0.05) independent of vegetation at least 0.6 m tall within 5 m of the collector. However, in this case, a lower percentage of samples were contaminated for sites with this siting criterion violation than for those that violated the 90° cone criterion. The intent of the siting criterion for vegetation to be less than 0.6 m tall is to limit plant detritus, pollen, and insect contamination in NADP/NTN samples. However, the results indicate that contamination occurs less frequently when this criterion is not met. Similarly, the results also indicate that the presence of fences within 5 m of the collectors is independent of visible sample contamination. The vegetation and fences can be effective in shielding the collectors from wind, which can be beneficial for precipitation sample collection.

Some contamination sources are more important during specific seasons or may be introduced for specific precipitation types. For example, insect and plant contamination is more common during

May–October than during November–April (fig. 15). Therefore, the data set was analyzed by season and precipitation type. To simplify the analysis, seasons were defined by three-month periods: winter, December–February; spring, March–May; summer, June–August; and fall, September–November. Results of the seasonal frequency analysis are listed in table 6.

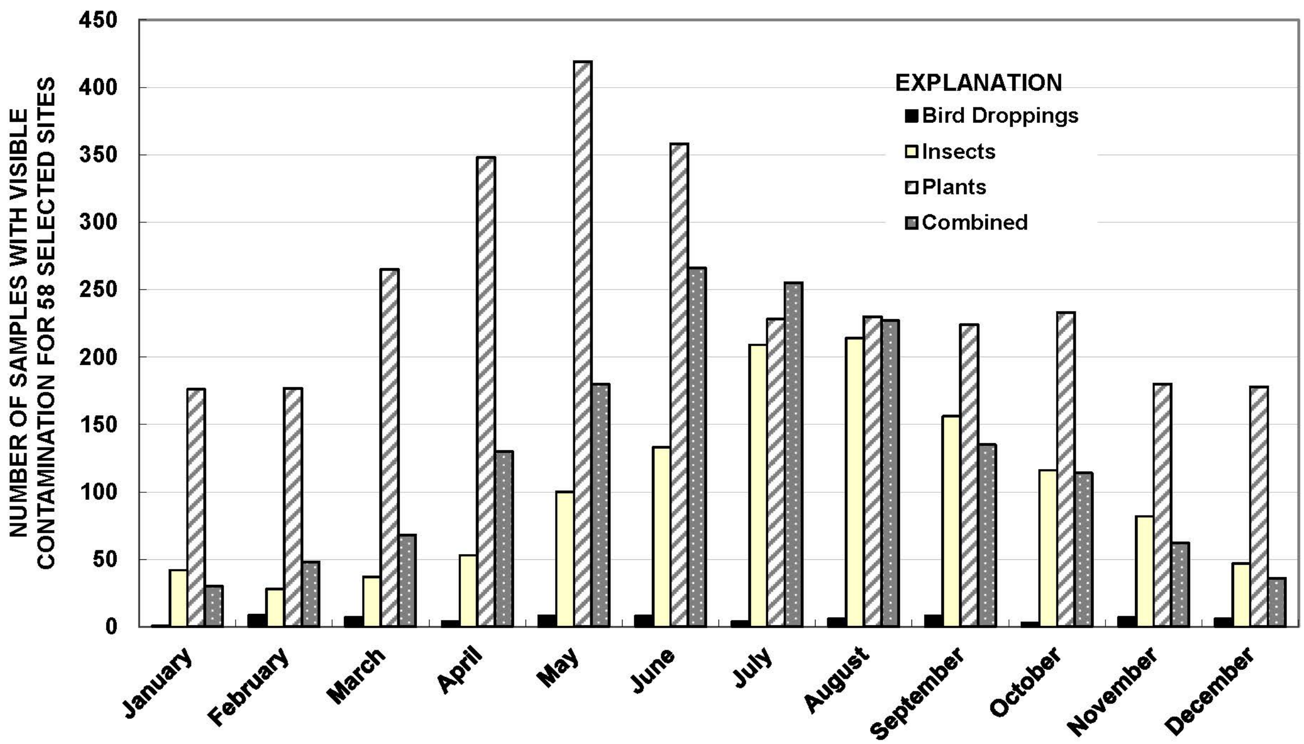


Figure 15. Monthly frequency of contamination types in National Atmospheric Deposition Program / National Trends Network wet-deposition samples from 58 sites during 2003–2007 for all sample types.

Precipitation type is recorded by the site operators on the FORFs by assigning codes to each day with precipitation: "R", rain; "S", snow; "M", mixed (that is, liquid and frozen precipitation); and "U", undefined. For this study, weekly samples with only rain or only snow codes were categorized as such, and weekly samples containing both rain and snow and/or mixed codes were categorized as having mixed precipitation types. Results of the precipitation type analysis are listed in table 7.

Results indicate that visible sample contamination is not significantly (α=0.05) independent of objects within the 90^{o} cone open to sky and trees within the 120^{o} cone open to sky from the collector during all seasons (table 6). Sites with no siting criteria violations tend to have a lower percentage of contaminated samples than sites with violations, especially during fall and winter when plant debris (leaves, needles, seeds) falls from vegetation.

For sites with objects within the 90^{o} cones, visible sample contamination occurs for rain and snow, but not for mixed precipitation types (table 7). For sites with trees in the 120^{o} cones, visible sample contamination occurs during weeks with rain, but not for weeks with snow or mixed precipitation.

Table 6. Seasonal frequency of visible contamination in wet-deposition samples for sites with selected National Atmospheric Deposition Program siting criteria violations: (1) object(s) in 90° cone open to sky; (2) trees within 120° cone open to sky; (3) vegetation greater than or equal to 0.6 meters tall within 5 meters of collector; (4) fence within 5 meters of collector; and (5) 1-meter tall objects within 5 meters of collector.

[V. Contam., visibly contaminated; N, sample count; %, percent; spring, March–May; summer, June–August; fall, September–November; winter, December–February; Chi-Square p-values = probability of incorrectly deciding that contamination is not independent of violation; ≥, greater than or equal to; m, meters.]

	Spring				Summer			
		V. Contam.?				V. Contam.?		
Siting Criteria Violation	Weekly Samples (N)	Yes (%)	No (%)	Chi-Square p-values	Weekly Samples (N)	Yes (%)	No (%)	Chi-Square p-values
Object in 90° cone open to sky?								
YES	351	77	23	<0.0001	378	78	22	0.0069
NO	314	48	52		323	69	31	
Trees in 120° cone open to sky?								
YES	621	65	35	.0055	684	78	22	< .0001
NO	496	57	43		551	68	32	
Vegetation ≥ 0.6m tall within 5m?								
YES	172	35	65	.0143	162	67	33	.7659
NO	160	48	52		187	66	34	
Fence(s) within 5m?								
YES	294	59	41	.0054	339	59	41	.0103
NO	349	48	52		360	68	32	
1-m Objects within 5m?								
YES	713	49	51	.0003	765	67	33	.1614
NO	653	59	42		728	64	36	

	Fall				Winter			
		V. Contam.?				V. Contam.?		
Siting Criteria Violation	Weekly Samples (N)	Yes (%)	No (%)	Chi-Square p-values	Weekly Samples (N)	Yes (%)	No (%)	Chi-Square p-values
Object in 90° cone open to sky?								
YES	327	60	40	<0.0001	334	52	48	<0.0001
NO	288	32	68		224	18	82	
Trees in 120° cone open to sky?								
YES	615	58	42	.0003	579	40	60	.0056
NO	470	47	53		408	31	69	
Vegetation ≥ 0.6m tall within 5m?								
YES	131	31	69	.2869	109	9	91	.3459
NO	159	36	64		114	13	87	
Fence(s) within 5m?								
YES	307	44	56	.5712	281	25	75	.9593
NO	314	41	59		271	25	75	
1-m tall objects within 5m?								
YES	691	43	57	.3994	616	25	75	.1726
NO	590	46	54		536	29	71	

Table 7. Frequency of visible contamination in wet-deposition samples based on precipitation type for sites with selected National Atmospheric Deposition Program siting criteria violations: (1) object(s) in 90° cone open to sky; (2) trees within 120° cone open to sky; (3) vegetation greater than or equal to 0.6 meters tall within 5 meters of collector; (4) fence within 5 meters of collector; and (5) 1-meter tall objects within 5 meters of collector.

[N, sample count; %, percent; Chi-Square p-values = probability of deciding that contamination is not independent of violation when it is; >, greater than or equal to; m, meters; shading denotes statistically significant (α=0.05) lack of independence between presence of visible contamination and siting criteria violation.]

	Precipitation Types Composited in Weekly Samples											
	Rain				Snow				Mixed			
		Visibly Contam-inated?				Visibly Contam-inated?				Visibly Contam-inated?		
Siting Criteria Violations	Weekly Samples (N)	Yes (%)	No (%)	Chi-Square p-values	Weekly Samples (N)	Yes (%)	No (%)	Chi-Square p-values	Weekly Samples (N)	Yes (%)	No (%)	Chi-Square p-values
Object in 90° cone open to sky?												
YES	1046	70	30	<0.0001	163	67	33	<0.0001	125	44	56	0.0238
NO	830	54	46		119	6	94		105	30	70	
Trees in 120° cone open to sky?												
YES	1751	71	29	< .0001	310	11	89	< .0001	388	44	56	.0391
NO	1552	57	43		123	31	69		171	35	65	
Vegetation > 0.6m tall within 5m?												
YES	347	49	51	.3077	71	17	83	.0080	113	25	75	.4023
NO	458	53	47		65	3	97		62	31	69	
Fence(s) within 5m?												
YES	996	50	50	.0049	75	28	72	.0012	131	36	64	.0969
NO	933	57	43		119	10	90		136	26	74	
1-m tall objects within 5m?												
YES	1741	56	44	.4955	522	26	74	.0001	439	37	63	.3313
NO	2079	55	45		139	11	89		202	33	67	

For sites where vegetation is at least 0.6 m tall within 5 m of the collector, visible sample contamination is significantly (α=0.05) independent of the siting criteria violations except during spring (table 6). During spring, the frequency of visibly contaminated samples is not independent on the presence of tall vegetation, whereby sites with such violations tend to have fewer visibly contaminated samples. Visible sample contamination is not significantly (α=0.05) independent on tall vegetation near the collectors during weeks with snow, but not for weeks with rain or mixed precipitation types (table 7). Sites with no siting criteria violations had a lower (14 percent) frequency of visible sample contamination than sites with the 0.6 m tall vegetation violations during snow periods. The results imply that tall vegetation near the collectors could have unintended benefits that enhance sample integrity even though the vegetation violates a siting criterion.

Visible pollen in NADP/NTN samples can cause the sample to be classified as contaminated with plant material. However, pollen in the samples results from washout, whereby precipitation physically removes materials suspended in air. Therefore, it can be argued that pollen is a naturally washed out material and such wet-deposition components should not be characterized as contaminants in NADP/NTN samples. Ignoring pollen in the samples could allow more samples to be classified as valid, particularly in areas with abundant vegetation.

Visible contamination in the wet-deposition samples is not significantly (α=0.05) independent of the presence of fences within 5 m of the collector during spring and summer. Visibly contaminated samples occur more frequently at sites with no siting criteria violations in spring than summer. During fall and winter, the presence of fences is independent of visible sample contamination. Results in table 7 indicate that visible contamination is not significantly (α=0.05) independent of fences within 5 m of the collectors for weeks with only rain. Sites without fences had a slightly higher frequency of contaminated samples. During weeks with only snow, visible contamination is not significantly (α=0.05) independent of the presence of fences. Sites with fences tended to have 18 percent more contaminated samples during weeks with only snow.

Visible sample contamination is independent of the presence of 1-m tall objects within 5 m of the collector for all seasons except spring, during which sites with no siting criteria violations had a higher frequency of sample contamination (table 6). On the other hand, these same sites had a lower frequency of sample contamination than sites in violation due to 1-m tall objects during weeks with snow (table 7). Although these mixed results are statistically significant, identification of potential physical causes for them cannot avoid speculation given the available data.

Results of the follow-up evaluation of common physical characteristics among sites with both few and many visibly contaminated samples are supportive of the frequency analysis. The 20 sites with the lowest number of samples with visible contamination in order of fewest to most are: TX04 (36 samples), NY96, NM01, AZ97, WY02, CA45, MT00, MD08, MI51, MT07, WV18, CO93, FL32, MT96, WY98, ME04, AZ06, CO18, UT08, and AZ03 (69 samples). The 20 sites with the highest numbers of samples with visible contamination in order of fewest to most are: NC03 (178 samples), VI01, IL63, OH17, WV04, WV05, AR02, VA99, VA24, SC05, TN00, NY99, AL99, MS19, SC06, CO96, VT01, TN11, MN16, and AR03 (229 samples). Regional comparison of these two groups revealed that 14 of the 20 sites with the lowest visible sample contamination are located in the Western US, and 19 of the 20 sites with the most visible sample contamination are not located in the Western US.

Site photographs were evaluated to identify which sites had substantial stands of trees within approximately 100 m of the collector, and which sites were in more open areas with few or no trees. Eighty percent of the sites with the highest visible sample contamination are located within 100 m of trees, whereas 25 percent of the sites with the lowest visible sample contamination are near trees. Seventy percent of the sites with the highest visible sample contamination are in violation of the criterion of no trees allowed within the 120^o cone open to sky from the collector. By comparison, 10 percent of the sites with the lowest visible sample contamination are in violation of the same criterion. Thirty-five percent of the sites with the highest visible sample contamination are in violation of the criterion for no objects within the 90^o cone open to sky from the collector, but none of the sites with the lowest visible sample contamination violate this criterion.

Sites within both groups of low and high visible sample contamination are similarly in violation with respect to siting criteria for fences within 5 m of the collector (1 to 2 sites per group) and 1-m tall objects within 5 m of the collector (6 sites per group). Both groups of sites are similarly located away from agricultural operations. Five of 20 sites with the lowest visible sample contamination were in violation of the criterion for no vegetation taller than 0.6 m within 5 m of the collector, compared to one of 20 sites for the group with the highest sample contamination. Sixty-five percent of the sites with the highest visible sample contamination are maintained by mowing vegetation around the collectors. By comparison, ten percent of the sites with the lowest visible sample contamination are mowed. These results are another indication that allowing vegetation to grow tall around the collector without mowing is associated with fewer visibly contaminated samples.

Conclusions

NADP siting criteria for NTN sites were originally established at the inception of the program (circa 1978) without the benefit of data to support their effectiveness. The effectiveness of five NADP siting criteria intended to preserve wet-deposition sample integrity were evaluated using the hypothesis that samples from sites in violation of such criteria tend to have a higher frequency of visible contamination. Frequency analyses using two-by-two contingency tables based on the Chi-Square distribution were used to statistically evaluate the independence of siting criteria violations and visible sample contamination.

The results obtained are as follows:

Objects within the 90^o cones projected from the collectors open to sky are not independent of visible sample contamination. This siting criterion is verified as useful in protecting sample integrity, and mitigation of these violations is likely to enhance data quality. This conclusion is supportive of Graham's (1990) co-located sampler study,

Trees within the 120^o cones projected from the collectors open to sky are not independent of visible sample contamination. This siting criterion is verified as useful in protecting sample integrity. Mitigation of these violations by removing or pruning trees will likely enhance data quality.

Vegetation at least 0.6m tall within 5m of the collectors is not independent of visible sample contamination, especially during spring and summer months when the frequency of visible plant contamination in the samples is highest. However, contrary to the intent of the criterion, tall vegetation near the collector is beneficial to sample integrity because samples from sites with no siting criteria violations had a higher frequency of visible sample contamination than sites in violation due to tall vegetation near the collectors.

The presence of fences within 5m of the collectors is not independent of visible sample contamination, especially during spring and summer months. During spring, sites with fences have a slightly higher frequency of visibly contaminated samples, but the reverse is true during summer. Because fences within 5m of the collector are associated with both positive and negative effects on sample integrity, this criterion is not important.

Objects at least 1m tall within 5m of the collectors are not independent of visible sample contamination, especially during spring. Only during weeks with rain in summer did sites with these objects have a higher frequency of visibly contaminated samples than sites with no siting criteria violations. This siting criterion is potentially useful in protecting sample integrity; especially during rainy seasons. This result is consistent with Graham's (1990) co-located sampler study.

Trees in proximity of the collectors are associated with visible sample contamination. The effects of trees on sample contamination are regionally variable. Fewer visibly contaminated samples are observed for sites in the Western US than sites in the Midwest, South, and East Coast.

Summary

The ability of NADP/NTN wet-deposition collectors to obtain complete samples that are representative of the precipitation chemistry is evaluated by catch efficiency; the ratio of sample volume collected to the precipitation depth measured by the rain gage. Catch efficiency is reduced for frozen precipitation samples collected during periods with colder minimum air temperatures and low wind speed, but the variability of precipitation chemistry measurements is independent of these meteorological conditions.

NADP CAL personnel have shown that rain splash creates a potential for NADP/NTN sample contamination. However, results of the USGS Co-located Sampler Program indicate no such effects for relatively high precipitation intensity. Instead, increased variability in NADP/NTN wet-deposition measurements occurs for low-intensity precipitation events, which commonly include frozen precipitation types. Therefore, variability in NADP/NTN measurements is more readily attributed to the capability of the precipitation collector sensor to detect low-intensity precipitation.

The NTN was originally established using sites assumed to provide regionally representative data, but the network has grown to include sites in urban areas. Meanwhile, there has been recent urbanization of the lands surrounding NADP/NTN sites. Concern about potential effects of urbanization of the land surface on trends in NADP/NTN data for long-term, regionally representative NTN sites were addressed by analysis of wet-deposition chemical characteristics over space and time. Urbanization of the landscape surrounding NADP/NTN sites is not affecting trends in wet-deposition chemistry data to a measureable degree.

NADP established criteria for required physical characteristics of NTN sites at the inception of the program (circa 1978). The criteria were modified slightly throughout the 33-years of network operations, but always without the benefit of data to support the effectiveness of the criteria. The effectiveness of five NADP siting criteria intended to preserve wet-deposition sample integrity were evaluated using a statistical analysis of the frequency of visible sample contamination for sites in violation of siting criteria and sites with no siting criteria.

Results confirm that criteria mandating the absence of : (1) objects within the 90^o cones projected from the collectors open to sky, and (2) trees within the 120^o cones projected from the collectors open to sky are beneficial to protecting sample integrity. The third criterion evaluated mandates the absence of vegetation at least 0.6m tall within 5m of the collectors. This criterion is actually counterproductive because results herein indicate that tall vegetation close to the collector is associated with a reduced frequency of sample contamination. Finally, criteria for (4) fences within 5m of the collectors, and (5) objects at least 1m tall within 5m of the collectors, are only beneficial seasonally, and their usefulness is questionable. Violations of siting criteria are subject to remediation actions, which can be costly, and they can cast doubt on data quality. This evaluation of their effectiveness is available for NADP consideration for modification of siting criteria to potentially reduce costs and increase confidence in the data.

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