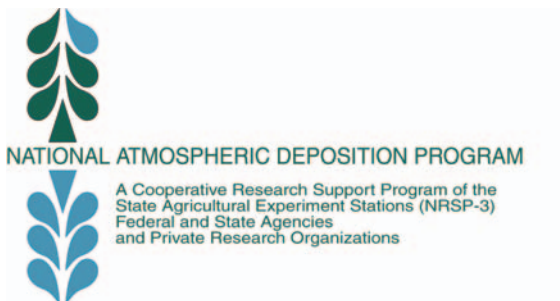
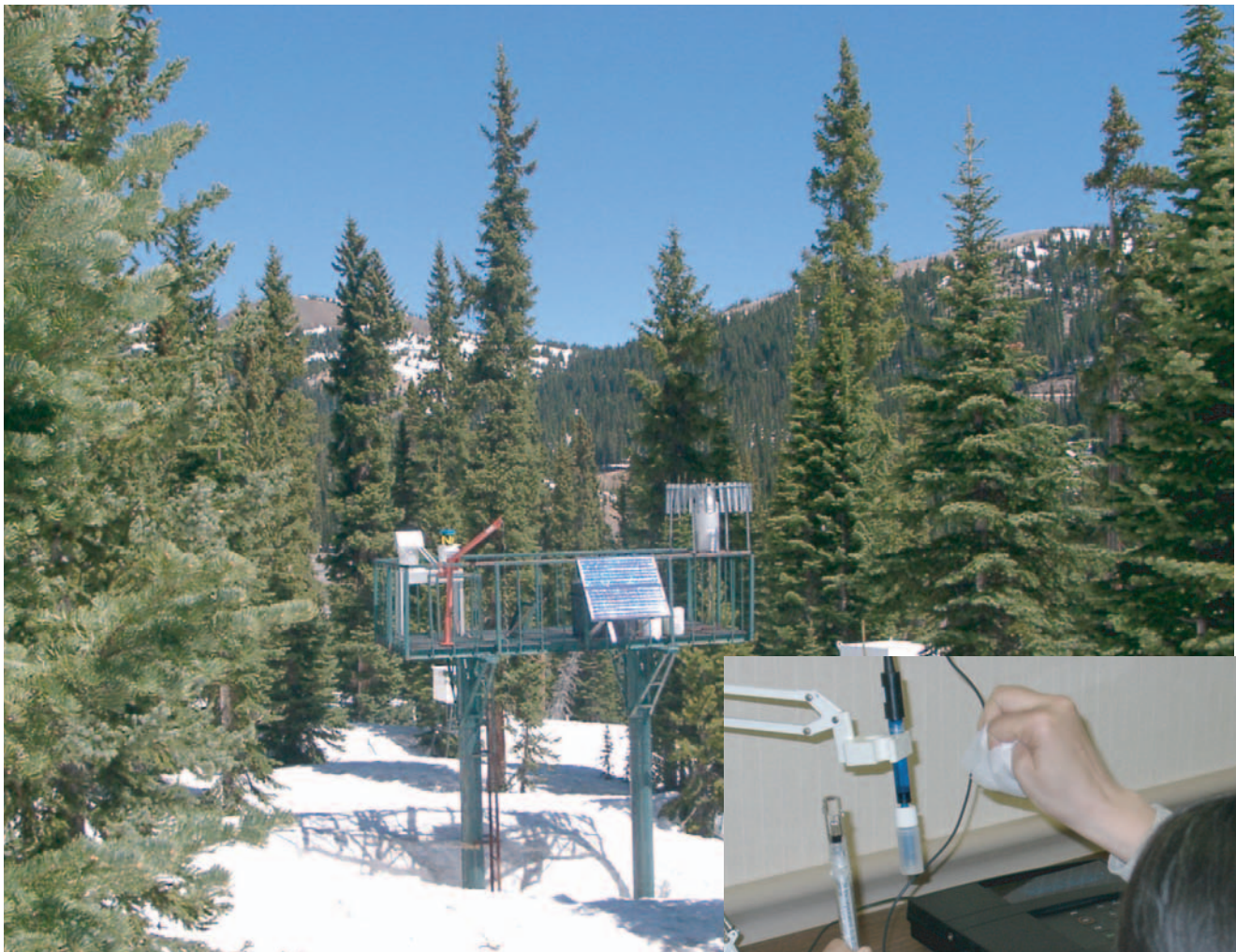


Discontinuation of Support for Field Chemistry Measurements in the National Atmospheric Deposition Program National Trends Network (NADP/NTN)

Christopher Lehmann, NADP Program Office, Illinois State Water Survey, Champaign, IL

Natalie Latysh, Branch of Quality Systems, U.S. Geological Survey, Denver, CO

Cari Furiness, Dept. of Forestry, College of Natural Resources, NC State University, Raleigh, NC



Acknowledgments

The NADP is National Research Support Project-3: A Long-Term Monitoring Program in Support of Research on the Effects of Atmospheric Chemical Deposition. More than 240 sponsors support the NADP, including State Agricultural Experiment Stations; universities; private companies and other nongovernmental organizations; Canadian government agencies; state, local, and tribal government organizations; and federal agencies, including the U.S. Department of Agriculture-Cooperative State Research, Education, and Extension Service (under agreement no. 2002-39138-11964). Any findings or conclusions in this report do not necessarily reflect the views of the U.S. Department of Agriculture or other sponsors.

The authors gratefully acknowledge the assistance of Pamela Bedient, NADP CAL, Laura Knutson, NADP Program Office, and Timothy Bextel, NADP Program Office, in preparing the figures used in this report. The authors also extend their appreciation for their editorial comments to Eva Kingston, Illinois State Water Survey, and Van Bowersox, NADP Program Office.

About the Cover

Front: Pictured is NADP/NTN monitoring site CO91 at Wolf Creek Pass, Mineral County, Colorado. This site is operated by the U.S. Forest Service (photo courtesy of ATS Chester Engineers). Also pictured is an NADP/NTN site operator measuring precipitation pH (photo courtesy of the NADP CAL).

Inside Back: Monitoring sites in the NADP/NTN.

Back: Hydrogen ion concentrations as pH from measurements made at NADP/NTN field laboratories (top) and at the Central Analytical Laboratory (bottom), 2003.

Introduction

The National Atmospheric Deposition Program (NADP) Network Operations Subcommittee (NOS) has debated the continuance of field measurements of pH and conductivity at National Trends Network (NTN) sites for more than 20 years. The topic was raised again in May 2002, and an ad-hoc committee was tasked with evaluating these measurements.

In September 2002, the ad-hoc committee summarized the reasons for and against continuing field chemistry measurements. In March 2004, NADP subcommittees met in a joint session and recommended that support for field chemistry measurements be discontinued at NTN sites effective January 1, 2005. The NADP Budget Advisory and Executive Committees concurred with this recommendation in June 2004. This report addresses the reasons for discontinuing support for field chemistry measurements and answers the following questions:

- What is the current field site chemistry measurement program?
- Why should the NADP discontinue support for field chemistry measurements?
- Why are field chemistry measurements performed?
- What are the differences between pH and conductivity measurements in the field and in the laboratory?
- Who uses field chemistry data?
- Were other options considered?
- What are the scientific benefits of discontinuing field chemistry measurements?
- Will field chemistry measurements be discontinued completely?
- What are the implications for NADP/NTN site operators?
- How will this change affect NADP/NTN data products?

What is the current field chemistry measurement program?

Field measurements of pH and conductivity have been performed at NTN sites since 1978, and at NADP Atmospheric Integrated Research Monitoring Network (AIRMoN) sites since 1992. A map of current NTN monitoring sites appears inside the back cover. All eight AIRMoN sites and all but eight of the approximately 260 NTN sites currently conduct weekly field chemistry measurements following standard NADP/NTN protocols (Dossett and Bowersox, 1999). Sites are encouraged, but not explicitly required, to conduct field chemistry measurements; nonparticipation does not invalidate samples or preclude NADP/NTN participation.

The NADP's Central Analytical Laboratory (CAL) measures pH and conductivity upon receipt of samples. To support field chemistry measurements, the CAL supplies NTN sites with replacement pH electrodes, calibration solutions, pH buffers, and quality control (QC) check solutions (Rothert et al., 2002).

The CAL also provides training, manuals, and technical support for site personnel. Each

site must supply a pH meter, a conductivity meter, a conductivity cell, deionized water, and personnel to perform measurements.

The U.S. Geological Survey (USGS) supports and administers a site intercomparison program to ensure the quality of NTN field chemistry measurements (<http://nadp.sws.uiuc.edu/QA/>). In this program, the USGS sends a solution of specific pH and conductivity unknown to each site operator to measure and report pH and conductivity values to them. The USGS contacts sites not meeting pH and conductivity targets for follow-up support. Data from the most recent USGS intercomparison study indicate that more than 90 percent of NTN sites met all pH and conductivity targets.

The U.S. Environmental Protection Agency (U.S. EPA) also supports a site survey program to ensure the quality of field chemistry measurements. A survey team under U.S. EPA contract visits each NTN and AIRMoN site to verify that site operators are following standard sample collection and measurement protocols. The survey team provides on-site training to

operators not performing field chemistry measurements correctly.

Why should the NADP discontinue support for field chemistry measurements?

The NADP/NTN has accumulated 25 years of field chemistry data for use in interpreting the relationship between field and laboratory measurements. Discussions at recent NADP meetings have centered on both the program's scientific merits and the financial resources required for field chemistry measurements.

The consensus is that the financial resources allocated to field chemistry measurements could be spent more effectively on field equipment improvements. For example, the NADP wants to replace the existing collector and mechanical raingage at each site with instruments that feature electronic data transfer.

Although such improvements will increase data quality, reporting completeness, and reliability, they will require additional resources. Ending support for field chemistry measurements would free up resources that could be allocated to these improvements.

Why are field chemistry measurements performed?

Sample pH and conductivity measurements are made both at NTN and AIRMoN field sites, typically within 4 hours of sample removal from the precipitation collector, and again at the CAL, typically within 24 hours of sample receipt. Some NADP scientists feel that field site measurements are more representative of conditions when the precipitation occurred than CAL measurements.

As discussed in the next section, laboratory pH values are generally higher than field pH values, indicating a "loss" of acidity. Changes in sample chemistry can occur due to loss and consumption of organic acids, sample contamination, and other factors.

Accounting for these changes is important in certain applications, especially for evaluation of total acidic input to sensitive ecosystems. Measurement of conductivity in the field can also give an indication of sample contamination en route to the laboratory.

What are the differences between pH and conductivity measurements in the field and in the laboratory?

Annual isopleth maps of precipitation-weighted mean field pH and laboratory pH values are shown on the back cover for 2003. With improved commercial transport and package handling, sample shipping time from field sites to the CAL has decreased. The median time period between field and laboratory pH and conductivity measurements is currently seven days. Because the NTN collects weekly samples, precipitation samples already may be a week old when collected. Thus, on a temporal basis, field site measurements are not necessarily more representative of field conditions than CAL measurements. As the next section highlights, chemistry differences between field and CAL measurements have decreased over time, partially due to faster shipping times.

Latysh and Gordon (2004) summarized the differences between field versus laboratory pH and conductivity measurements for 135 NTN sites operational between 1987 and 1999. Median differences between laboratory and field pH measurements are shown (Figure 1). The study highlights how these differences have changed due to a sample handling protocol change initiated in 1994. Previously, all precipitation collected in the field was shipped to the CAL in the field bucket minus the portion used to perform field chemistry measurements. After discovery that the bucket seal contaminated the sample during transit, the shipping protocol was changed. The site operator now decants the field sample into a one-liter bottle for shipment to the CAL.

Median differences between laboratory and field pH measurements decreased significantly since this protocol change, and are generally <0.1 pH unit in the 4.5 – 5.4 range, representing typical NTN pH values (Rothert, 2003). Figure 1 also shows that differences between field and laboratory measurements vary with pH.

Figures 2 – 4 are box plots of the differences between field and laboratory hydrogen ion concentrations, aggregated annually across U.S. EPA regions from 1987 to 2003. The box plots used paired field and laboratory pH measurements for all valid (i.e.,

uncontaminated) samples from all sites in the U.S. EPA regions.

Median field minus laboratory hydrogen ion differences in the northeastern United States tend to cluster at +2 microequivalents per liter ($\mu\text{eq/L}$) after the 1994 protocol change. Median differences cluster between +1 and +3 $\mu\text{eq/L}$ in the central United States (Figure 3), and approximately +1 $\mu\text{eq/L}$ in western states (Figure 4).

These analyses allow one to infer the value of a field pH measurement based on the laboratory measurement and location of the site. The 1994 protocol change is evidenced by an abrupt decrease in hydrogen ion differences starting in 1994 in several regions. Although not shown, conductivity differences follow the same general trend as hydrogen ion differences.

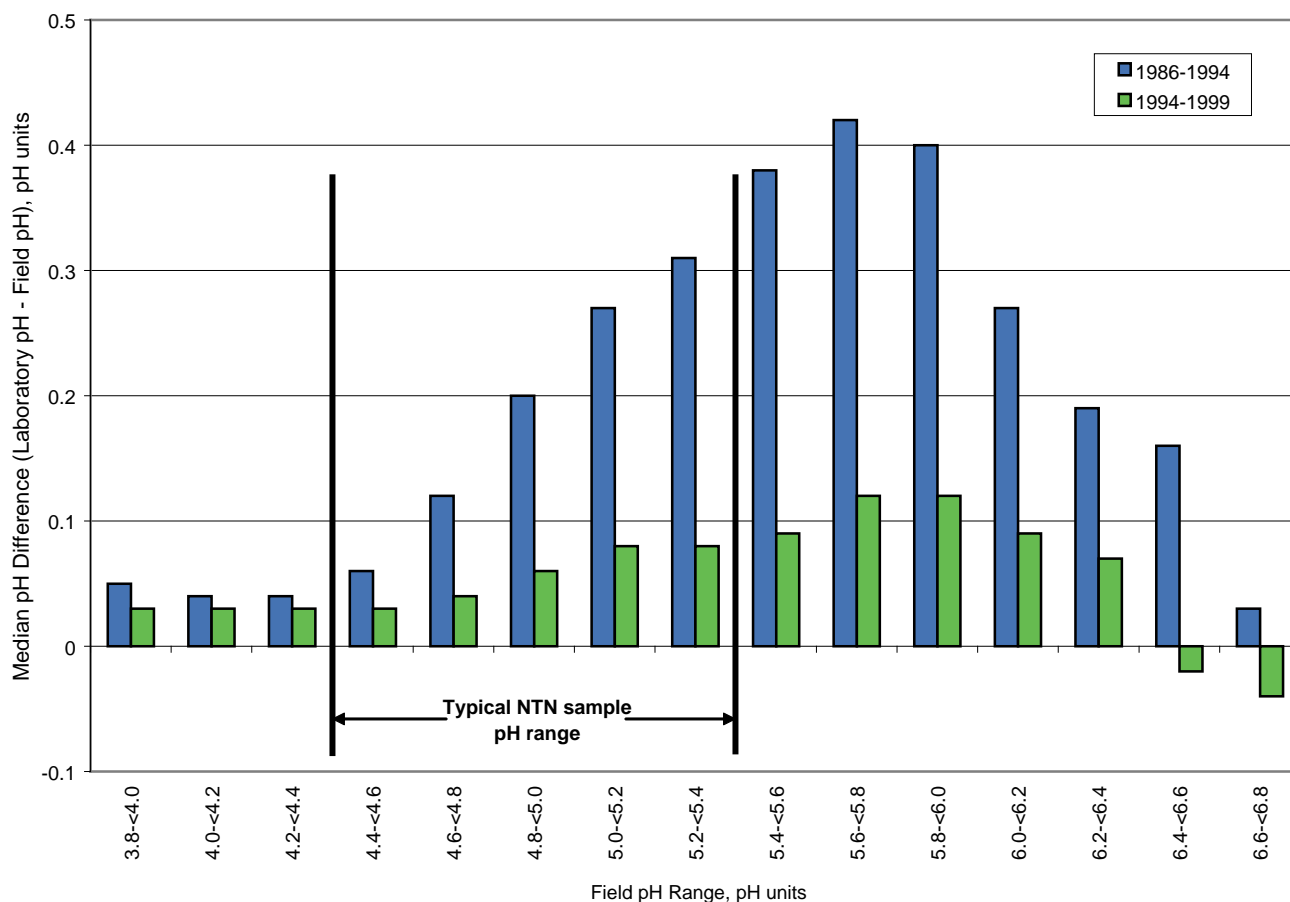
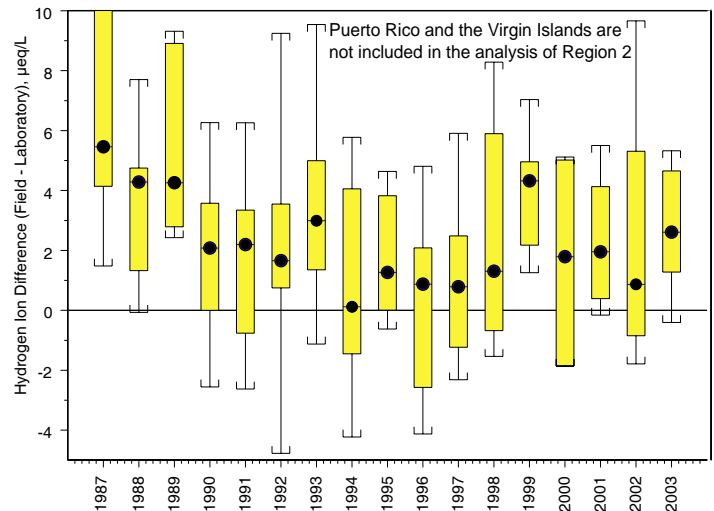
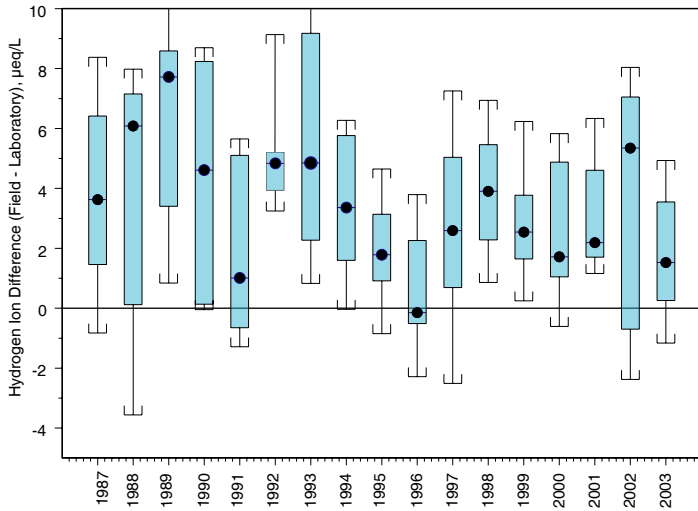
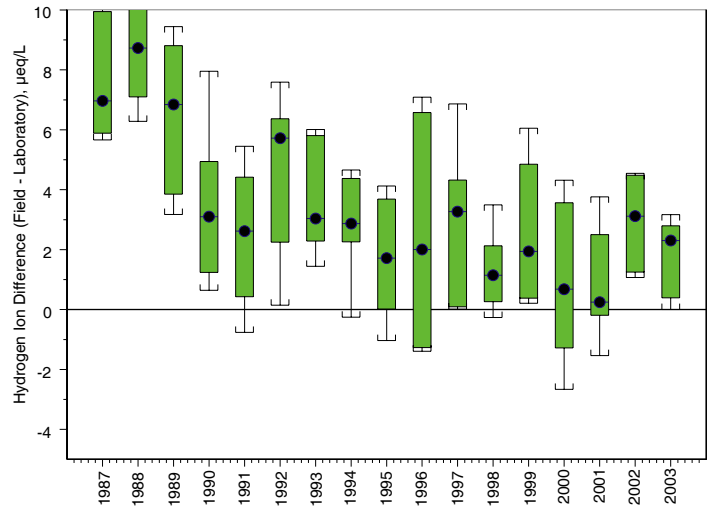
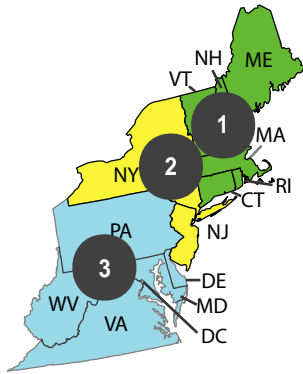


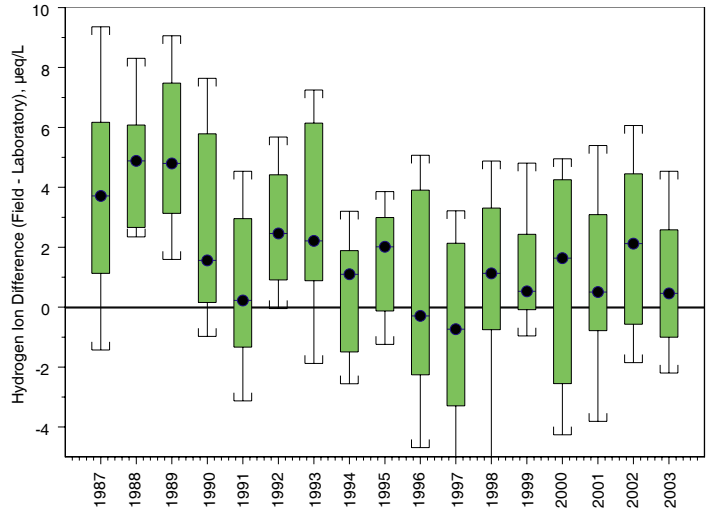
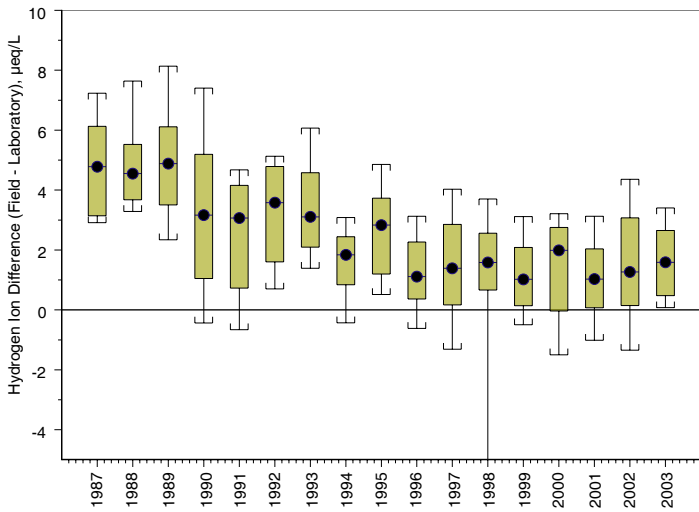
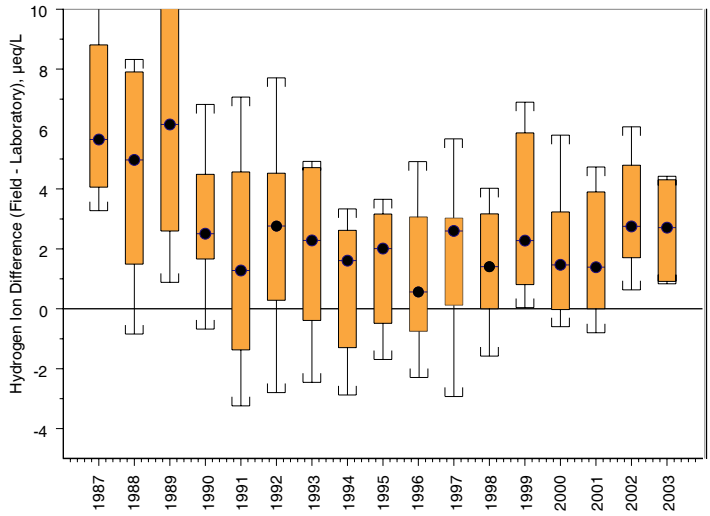
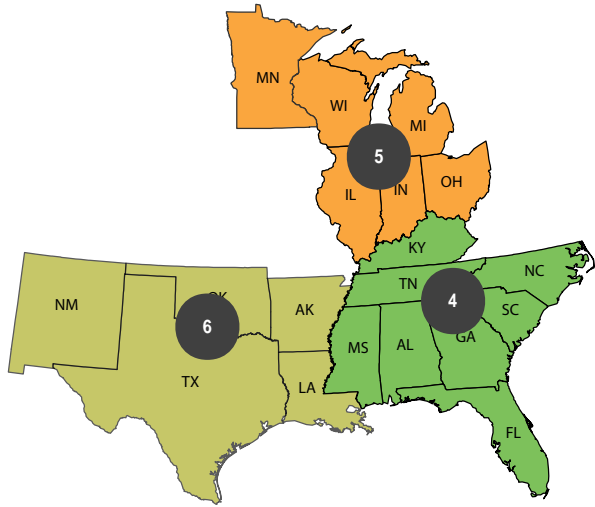
Figure 1. Median differences between laboratory and field pH measurements for specific field pH ranges measured in NADP/NTN precipitation samples, 12/30/1986 – 12/28/1999 (Latysh and Gordon, 2004).



Notes:

Dots represent median annual difference between field and laboratory hydrogen ion concentrations as µeq/L, boxes represent 25th – 75th percentile differences, whiskers represent 10th – 90th percentile differences.

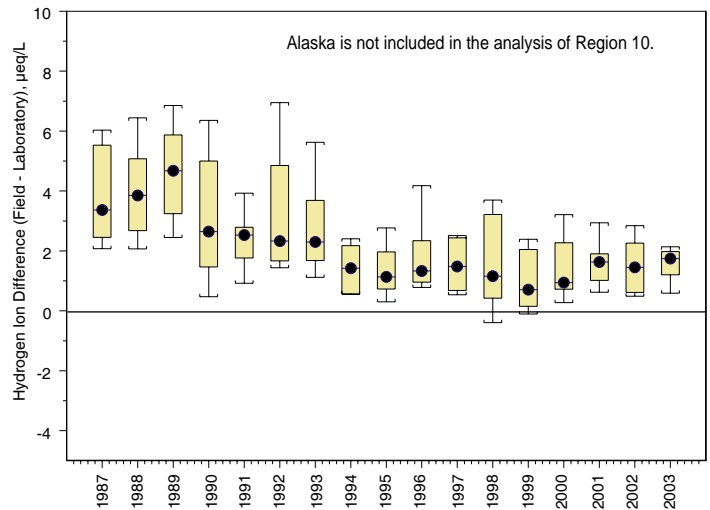
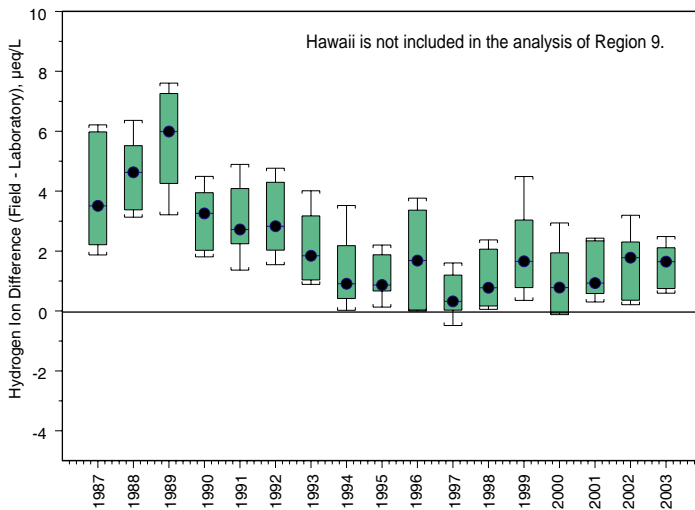
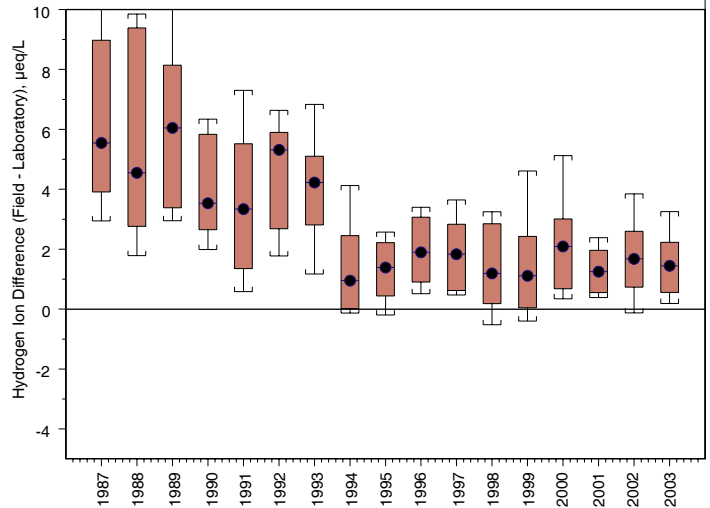
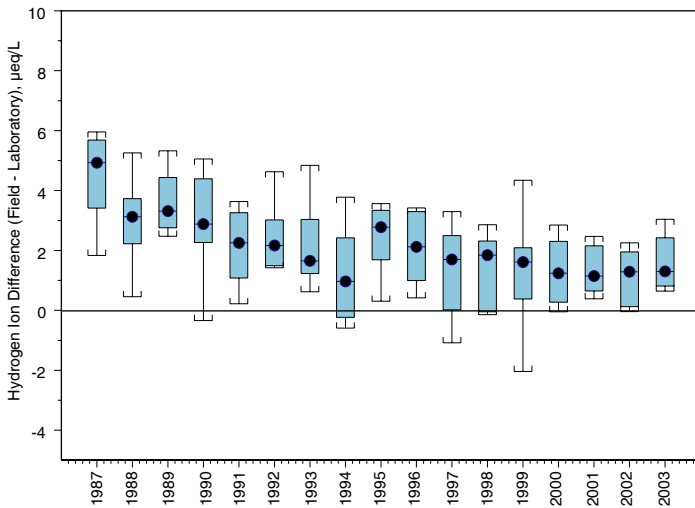
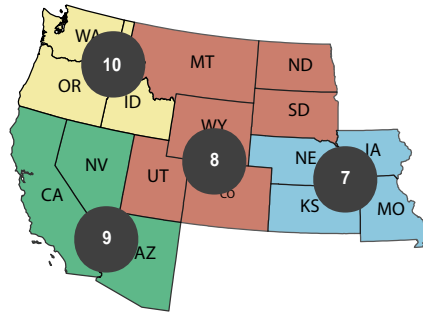
Figure 2. Median hydrogen ion differences for U.S. EPA Regions 1 – 3, 1987 – 2003.



Notes:

Dots represent median annual difference between field and laboratory hydrogen ion concentrations as µeq/L, boxes represent 25th – 75th percentile differences, whiskers represent 10th – 90th percentile differences.

Figure 3. Median hydrogen ion differences for U.S. EPA Regions 4 – 6, 1987 – 2003.



Notes:

Dots represent median annual difference between field and laboratory hydrogen ion concentrations as µeq/L, boxes represent 25th – 75th percentile differences, whiskers represent 10th – 90th percentile differences.

Figure 4. Median hydrogen ion differences for U.S. EPA Regions 7 – 10, 1987 – 2003.

Who uses field chemistry data?

The CAL uses field chemistry measurements to check if solution changes have occurred during transit to the laboratory. Conductance and pH measurements performed at the CAL use QC standards and protocols more stringent than those at field sites (Rothert et al., 2002). Differences between field and laboratory measurements are considered in the CAL's reanalysis protocols. To determine how field chemistry data are used by the NADP/NTN data user community, a survey was sent to more than 2000 registered data users in June 2002. Approximately 230 users replied. Responses to two survey questions are shown.

Survey results indicate that field pH measurements are used by 65 percent of data users and field conductivity measurements by 38 percent of researchers responding.

Responses (percent) to NADP/NTN Data User Survey

Which NADP/NTN-reported pH results do you use?

None	22
Field only	20
Laboratory only	11
Both values	45
No response	2

Which NADP/NTN-reported conductivity results do you use?

None	50
Field only	10
Laboratory only	8
Both values	28
No response	4

Were other options considered?

A proposal limiting field chemistry measurements to a core group of approximately 20 sites was presented to the NADP subcommittees. This proposal was rejected, as there was concern that the time and resources to manage a network of core sites would consume much of the savings from discontinuing field chemistry measurements at all sites.

What are the scientific benefits of discontinuing field chemistry measurements?

Discontinuing field chemistry measurements has several scientific benefits. It will reduce sample handling by site operators, potentially decreasing the chance of contamination during handling. Keeping the entire volume of weekly precipitation samples for laboratory chemistry measurements will increase sample volume available for analysis and archiving. Resources freed from discontinuation of field chemistry measurements will be invested in other programs to modernize the NADP field equipment and other initiatives to improve overall network quality and value to the scientific community.

Will field chemistry measurements be discontinued completely?

All NADP support for NTN field chemistry measurements will be discontinued effective January 1, 2005. Individual site sponsors may continue field chemistry measurements voluntarily, although the data will not be entered into the NADP database. The CAL will no longer provide NTN sites with replacement pH electrodes or field chemistry supplies.

Existing and future AIRMoN sites will continue field chemistry measurements following current protocols with full CAL support. Performing field chemistry measurements of AIRMoN samples, which are collected more frequently (event sampling vs. weekly sampling) has scientific merit that outweighs the additional CAL resources required to support these sites.

What are the implications for NADP/NTN site operators?

All NADP/NTN site operators will continue to collect precipitation samples every week, maintaining sample quality in accordance with NADP/NTN sample collection protocols. Each sample will be sent directly to the CAL after weighing and decanting it from the field bucket to the sample bottle. Site operators will receive revisions to the site operation manual and revised field forms. Sites wishing to perform voluntary field chemistry measurements will receive instructions for aliquot removal based on

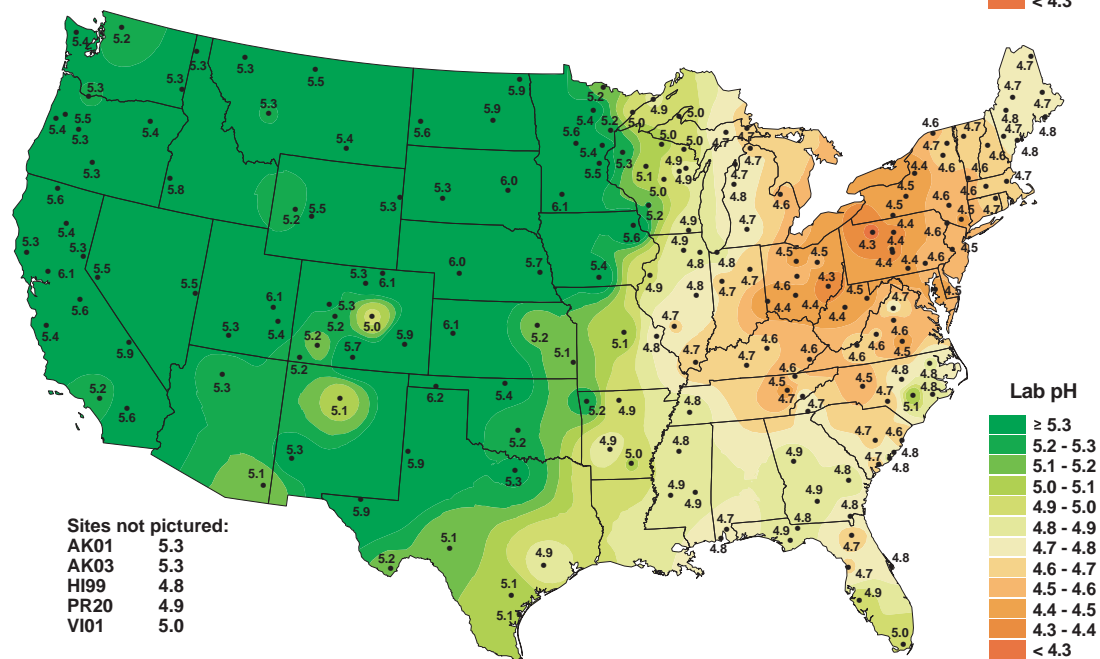
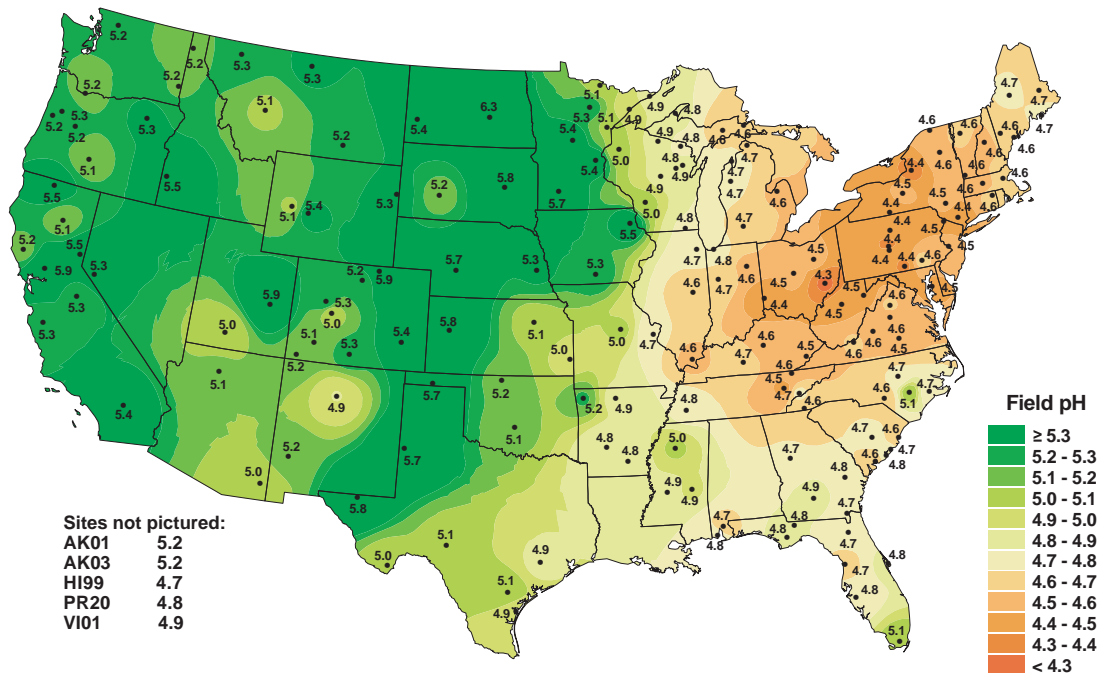
established NADP/NTN sub-sampling protocols that ensure sample integrity.

How will this change affect NADP/NTN data products?

There will be no effect on isopleth maps developed and published in NADP printed annual summaries. Field measurements of pH and conductivity are not used currently to develop these maps. Isopleth maps of field pH and hydrogen ion deposition are only available electronically, and the 2004 maps will be the last ones prepared and added to the set available on the NADP Web site. The 1978–2004 field chemistry measurements will continue to be available for download from the NADP Web site (<http://nadp.sws.uiuc.edu>). Voluntary field chemistry measurements after January 1, 2005 will not be reported to the NADP or be available on the NADP Web site.

References

- Dossett, S.R., and V.C. Bowersox. 1999. *National Trends Network Site Operation Manual*. NADP Manual 1999-01. National Atmospheric Deposition Program Office at the Illinois State Water Survey, Champaign, IL. <http://nadp.sws.uiuc.edu/lib/manuals/opman.pdf>
- Latysh, N., and J. Gordon. 2004. Investigation of differences between field and laboratory pH measurements of National Atmospheric Deposition Program/National Trends Network precipitation samples. *Water, Air, and Soil Pollution* **154**(1-4): 249-270.
- Rothert, J. 2003. *Quality Assurance Report: Laboratory Operations, 2001*. NADP QA Report 2003-01. Central Analytical Laboratory at the Illinois State Water Survey, Champaign, IL. <http://nadp.sws.uiuc.edu/lib/qa/qa2001.pdf>
- Rothert, J., K. Harlin, and K. Douglas. 2002. *Quality Assurance Plan: Central Analytical Laboratory*. NADP CAL QA Plan 2002-01. Central Analytical Laboratory at the Illinois State Water Survey, Champaign, IL. <http://nadp.sws.uiuc.edu/lib/qaplans/qapCal2002.pdf>



Hydrogen ion concentrations as pH from measurements made at NADP/NTN field laboratories (top) and at the Central Analytical Laboratory (bottom), 2003.

The NADP Program Office is located at the Illinois State Water Survey, and affiliated agency of the University of Illinois and a Division of the Illinois Department of Natural Resources. All NADP data and information are available from the NADP Internet site:

<http://nadp.sws.uiuc.edu>

For further information, special data requests, or to obtain copies of this publication, contact the NADP Program Office, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820.

e-mail: nadp@sws.uiuc.edu