National Atmospheric Deposition Program Spring Meeting Asilomar Conference Center Pacific Grove, CA May 6 – 8, 2002

Minutes of the Meeting of the Subcommittee on Network Operations

Attachments

- 1. Meeting agenda
- 2. List of meeting attendees
- 3. Electronic Data Collection in the CAL, Karen Harlin, ISWS
- 4. NED Report
- 5. Site Selection History, Scott Dossett, ISWS
- 6. Administrative and Technical Review of the National Atmospheric Deposition Program, Van Bowersox, ISWS
- 7. Report on N-Con Precipitation Collector, Scott Dossett, ISWS
- 8. Report on N-Con Mercury Collector, Mark Nilles, USGS
- 9. MDN New Sample Train Data, Eric Prestbo, Frontier Geosciences Inc.
- 10. Tracer Dye Fence Post Proximity Study, Scott Dossett, ISWS
- 11. SO₃/SO₄ in AIRMoN Samples, Jane Rothert, ISWS
- 12. USGS External QA Report Natalie Latysh Blind Audit Program
- 13. USGS External QA Report Natalie Latysh Field Blank Program
- 14. USGS External QA Report Natalie Latysh Collocated Program
- 15. USGS External QA Report Natalie Latysh Interlaboratory Comparison Program
- 16. USGS External QA Report Natalie Latysh Intersite Comparison Program
- 17. Site Data Relay in the Brave New World Scott Dossett, ISWS

Network Operations Subcommittee Meeting Final Agenda NADP Spring Business Meeting May 6 – 7, 2002

Monday, May 6

9:15 - 9:30

1:00 – 1:15	Introduction of Attendees and Agenda Overview Approval of August NOS Meeting Minutes	Kristi Morris		
1:15 – 1:30	CAL Review 2002: Report and Response	Karen Harlin		
1:30 - 1:45	NTN & AIRMoN Archive Sample Distribution & Costs	Karen Harlin		
1:45 – 2:00	Electronic Data Collection in the CAL	Karen Harlin		
2:00 - 2:15	ATS External Site Survey/Audit Reports	John Shimshock		
2:15 - 2:45	NED Report	Scott Dossett		
2:45 - 3:15	Break			
3:15 - 3:45	Ad Hoc Committee Report: Recommendations for Current Siting Violations	Joel Frisch		
3:45 - 4:00	Site Selection History	Scott Dossett		
4:00 - 4:30	Ad Hoc Committee Report: Review of NADP Siting Criteria	Chris Lehmann		
4:30	Adjourn			
Tuesday, May 7				
8:00 - 8:45	OTT-Pluvio Phase III rain gage testing	Mary Tumbusch		
8:45 - 9:15	Administrative and Technical Review of the National Atmospheric Deposition Program	Van Bowersox		

9:30 – 9:50	Report on N-Con Mercury Collector	Mark Nilles
9:50 - 10:10	MDN New Sample Train Data	Eric Prestbo
National	Atmospheric Deposition Program – Spring 2001 Int	erim Meeting

Report on N-Con Precipitation Collector

NOS Subcommittee Minutes: Attachment 1

Scott Dossett

10:10 - 10:30	Break	
10:30 - 10:45	Report on MDN Chimney Cap Tests at IL11	Clyde Sweet
10:45 - 11:00	Tracer Dye Fence Post Proximity Study	Scott Dossett
11:00 - 11:30	SO3/SO4 in AIRMoN Samples	Jane Rothert
11:30 - 1:00	Lunch	
1:00 – 1:15	Update on Experiments with Plastic Bag Liners	Karen Harlin
1:15 – 2:15	Discussion on Field Measurements	
2:15 - 2:45	Break	
2:45 - 4:30	USGS External QA Report	Natalie Latysh
4:30 - 4:50	Site Data Relay in the Brave New World	Scott Dossett

Name Archer, Scott F. Artz, Richard Beach, John S. Bowersox, Van Brunette, Bob Dossett, Scott Douglas, Kathy Frisch, Joel Faller, Scott Furiness, Cari Grant, Rich Harlin, Karen Hebert, Eric Jones, Tom Kerchner, Maggie Larson, Bob Latysh, Natalie Lear, Gary Lehmann, Chris Lewis, Preston MacTavish, Dave Morris, Kristi Nilles, Mark Padgett, Pamela Prestbo, Eric Rodger, Bruce Rothert, Jane Schmeltz, David Schroder, LeRoy Sherwell, John Shimshock, John Smith, Luther Snyder, Donald Sweet, Clyde Tonnessen, Kathy Trochta, Jim Tumbusch, Mary Wolfe, Rosemary

Affiliation

USDI-Bureau of Land Management NOAA Air Resources Lab N-Con Systems NADP Program Office Frontier Geoschiences (HAL) ISWS ISWS USGS EPA NC State University **Purdue University** ISWS Harding ESE Advanced Technology Systems, Inc. NOAA/OAR, Air Resources Lab ISWS U.S. Geological Survey U.S. EPA **ISWS Program Office** NYS DEC Air Resources CAPMoN U.S. Fish & Wildlife Service USGS **USDA-Forest Service Frontier Geosciencees** WI DNR ISWS U.S. EPA U.S. Geological Survey MD DNR Advanced Technology Systems, Inc. ManTech Environmental Technology Western Region AES ISWS NPS-University of Montana **WI-DNR USGS-WRD** EPA

Electronic Data Collection in the CAL



Conductivity, pH and Sample Prep

National Atmospheric Deposition Program - Spring 2001 Interim Meeting

NOS Subcommittee Minutes: Attachment 3

Goals of Project

- Electronically collect conductivity and pH data directly from the instruments.
- Provide paperless method for entering lab comments and sample contamination coding.
- Allow more efficient review of QC information.
- Provide a central database to store data for samples other than NTN/AIRMoN.
- Enable export of results to NTN and AIRMoN databases or spreadsheet files for other types of data.

Design Considerations

- System must be unobtrusive and easy to use in a laboratory.
- Data collection system must provide information about sample needed by analyst.
- Control must remain with the analyst rather than the computer.

Sample Initialization

² 10	jects							
_	Code Nam	e Decci	plion	Nanager		Active	Mult. Results	
_	CA Wax	bed Bucket Check Neek	ly check of tap and Barnkead tank wate asched is skats	ar Jane Rothert		r V		
_	CC Leas	hed Lid Checks New I	eached lide	Jane Bothert		ý –	N N	
_	П Мен	Filter Lot Checks New f	ber lots	Jane Rothert		Y	N S	
۲	CF Bagi	Blank Study Test n	epistele base and new bas lots	Leon Rolliet		۲	N	
_	Ing Ison	ne Studi – Éfheck	Create New Sample(s)			19	N	
	New Projec	3						
_			Project Bag Blank, Study					
	on los							
2.4	info mere		Project Code	F				
_	Murcher	CleatNucher	Т		Dist	Action	WellDavide	
•	CF020001	1/02-1 DI		02	5W5	Y	N	
	CF020002	1/02-2 DI	- 100		5WS	Y	N	
	CF020003	1/02/3 DI		<u> </u>	\$₩S	Y	N	
	CF020004	1/02/11 FE25Blank	Start Number 12	3	5WS	Y	N	
	CF020005	1/02-12 FR258lank	-		5WS	۲	N	
	CF020006	1/02-13 FR258lank	No subset of Summing to one	1	5WS	Y	N	
	CF620807	4/02/1 DI	Honder of Sampart to Date	and L.	SWS	N	N	
	CF020008	4/02-2 DI	Clear Number		5WS	N	N	
	CF020009	4/02-3 DI	Cienci Hamber	_	5WS	N	N	
	CF020010	4/02-4 FR25Blank	Multiple Results		\$WS	N	N	
	CF020011	4/02/11 FR25Blank			sws	N	N	
	CF020012	4/02/12 FR25Blank	Description		5WS	N	N	
_			Exit Sample to Dieste	CF020013				
	New Samp		r an sumple of crosse					
				CERTICAL 1	1			
			Last Sample to Create	C- CE CO I S				
			311300	Cancel				
			Wrike	Canoer				

Import directly from field form entry database.

Initialize samples through the sample login screen

Data Collection



Sample Coding

Conductivity and pH

QC Features





- Blank Charts
- Ion Balance
- Built in Data Checks



Export to NTN or AIRMoN Databases Export of other types of data

Additional Features

- Accepts data from FIA, AA, and IC to allow assembly of data from special projects.
- Ad-hoc query screen allows a user to write custom queries.
- Centralized Microsoft SQL Server database allows multiple users to work with the database simultaneously.
- Pre configured reports allow quick printouts of daily activity as a paper backup.

Example of Blank Chart



Samples Collect Tools QC Reanalysis Reports About



| 💼 S..., 🔞 I..., 📴 M... 🖘 T..., 🖳 M..., 🖘 N... 🐄 N...

_ 8 ×

NED REPORT May 2002 Pacific Grove, CA

- COMPONENT STATI
- RECENT
 IMPROVEMENT
- RECENT PROBLEMS
- SUMMARY OF
 CURRENT
 OPERATION
- PLANS

National Atmospheric Deposition Program – Spring 2002 Interim Meeting NOS Subcommittee Minutes: Attachment 4



COMPONENT STATI- To Fix



RECENT IMPROVEMENTS

• RAINGAGE CLOCKS

- New battery operated rebuild scheme
 - Uses 4 AAAA cells
 - Same profile as existing
 - Winter test at MI53 and NE99 successful
- Repair Vendor
 - Second vendor found!
 - Hard search
 - Mailing units of 6 in specially designed box.

RECENT IMPROVEMENTS

COLLECTOR OPTIONS

- LODA Electronics (our second collector vendor and long standing repair shop) now offers all necessary collector components and options for the NADP wet/dry.
 - Lid heaters
 - Peaked roofs
 - Event recorders (single and dual)

RECENT PROBLEMS

- ISWS Sensor rebuilds
 - Vendor substituted a softer steel for the stainless we require. The sensors rusted and had to be replaced.
- Raingage clock gear (non) return
 - Operators were keeping gears
 - New gear sets cost ~\$90/clock
 - Memos edited, now they switch in field.

SUMMARY OF CURRENT OPERATION

- No sample loss due to lack of components.
- We are doing more motor unit and sensor combined replacements due to:
 - difficult field conditions,
 - component fatigue,
 - concerns about down time.

SUMMARY OF CURRENT OPERATION

- No new parts are entering the system.
- Prospect: repairs will continue to get more expensive and harder to do (ie: clock repair a dying art)

PLANS

- Standard Operating Procedures needed.
- Attempt more data mining to evaluate repairs, sources of failure in order to optimize resource use.

SITE SELECTION HISTORY

Brief History of documents used.

- Consistent themes
- Tension between regionally representativeness and populations limitations
- Changes in level of detail
- How the clients "biased" the meaning of regional
- Is NADP a "rural" network?

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 5

What are "LOCAL" siting criteria?

Objects or areas less than 500 meters from the wet side bucket of the collector.
Vegetive or anthropogenic materials which might unduly influence "site representativeness" or "sample representativeness".

Why 500 meter cut point?

• This is the distance under which operational staff may have good control of management practices either directly or indirectly.



Why 500 meter cut point?

- This is the distance under which operational staff may have good control of management practices either directly or indirectly.
- Beyond 500 meters the airshed gets increasingly well mixed, becoming more "regionally representative".

Why 500 meter cut point?

- This is the distance under which operational staff may have good control of management practices either directly or indirectly.
- Beyond 500 meters the airshed gets increasingly well mixed, becoming more "regionally representative".
- We have information from external audits which describe this area.

From Section 5 of the NTN Site Operations Manual 1999



So....I'll get started

DRAFT DRAFT DRAFT DRAFT DRAFT DRAFT

So....I'll get started

- First step is to discuss data availability and limitations
 - What info do we have?
 - Pictures (current and historic)
 - Should we try to do more operator assisted photo-doc?
 - 5 meter veg and surface types (2001/2002 round)
 - 30 meter sketch
 - 45 spots and areas

What information could we use

- Remote sensing
 - SPOT
 - U2
 - map coverage (from PO)
 - HUGE resolution issues
- Vegetive density index derived from audit or other work
- ????

1978 LOCAL SOURCES

" ... important that local sources not bias a sample...."

4

5 meters- undisturbed land..."no objects"

no objects > 30 degrees on horizon

no concept of 30 meters as site, save NADP instrument (collector and raingage)proximity

100 meter notes about:

- moving sources..air,
- ground water traffic

INSTRUGTION MANUAL NADP/NTN SITE SELECTION AND INSTALLATION

OBJECTIVES

1984

NADP saw NTN coming.

Need to refine populations proximity issues.

Refine the Site Description Questionnaire and needed Site Selection materials.

> A Cooperative Research Program of the State Agricultural Experiment Stations and other Federal, State and Private Research Organizations • IP-7

AM

INSTRUGTION MANUAL NADP/NTN SITE SELECTION AND INSTALLATION REGIONAL SOURCES

" located in and area that typifies a region and minimizes the impact of local sources

1984

"if a region is typified by a certain type of agricultural land use or is in a heavily industrialized region, **the sampler should be located within this region** to provide representation of such extensive pollution sources. Specific sources of concern include industrial operations and suburban/urban area related sources"

RAM

INSTRUGTION MANUAL NADP/NTN SITE SELECTION AND INSTALLATION REGIONAL SOURCES

1984

"general upwind direction...mean annual east-west flow"

10 km --- " industrial operations....power plants..areas whose population approximates 10,000 people

20km --- " same as 10 km IF "upwind"

40km --- " approximate population > 75K AND upwind"

MA

50km --- "Beyond....blend in with the "typical characteristics of the region"

INSTRUCTION MANUAL

LOCAL SOURCES

1984

In general much more detail.

"...point, line or area sources...suitability of a site to serve as a long-term regionally representative station"

20 meter pasture separation (animal density not described)

30 meter vegetated buffer strip and its maintenance

residential structures 30 degree cone of mean winds

45 degree horizon, 30 preferred

100 meters away from parking lots and maintenance yards

NEW 500 meter criteria for feedlots, dairy barns in



ATION
WEIGHTING "HITS"

VIOLATION

30 meter

-grazing

-towers (failing 45)

-cultivation -trees (failing 45)

WEIGHT

5 for each 50
animals estimated, 5 for light seasonal or "open" grazing
15 maximum decreasing by 5
for each 5 meter distance
from collector footprint
50 maximum, 5 for each AOI
50 maximum, 5 for each AOI

WEIGHTING "HITS"

VIOLATION

5 meter

splash sources > 1 meter tall

WEIGHT

25 maximum, 5 for each obstruction with a surface area >10,000 sq cm (10x10x100cm)

wind flow obstructions > 1 meter tall (NOTE" "open fences" excluded)

same as above

vegetation > .6 meters tall

25 maximum, 5 for each AOI

Simple Notification System

- VIOLATION CATEGORY
- Eamples'A' MajorViolation
- 'B' Minor violation>Violation reported < 5 m 11 fromcollector Х 5-29mX>"Tree(s) w/i 45 degree angleX>Row crops within 50 m of collecorSlope >15 degrees w/i xx X>Continue with mΧ or siting reqt's; would need to rate each as " major or minor">>>Report to Data Base could be; This site has 1 or more 'A' and/or 'B'>violations; 04/23/02> orSite has 2 'A' and 3 'B' violations." Site has xxx

THE END----ALMOST















ADMINISTRATIVE AND TECHNICAL REVIEW

NATIONAL RESEARCH SUPPORT PROJECT NO. 3 (NRSP-3)

THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM -A LONG-TERM MONITORING PROGRAM IN SUPPORT OF RESEARCH ON THE EFFECTS OF ATMOSPHERIC CHEMICAL DEPOSITION

November 6 & 7, 2001

National Atmospheric Deposition Program - Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 6

NADP PROGRAM REVIEW TEAM

Dr. John K. Robertson Chair, Program Review Team

Dr. Douglas Burns Ms. Margaret Kerchner Dr. Pamela Padgett Dr. Daniel D. Jones Dr. William McFee Dr. Joseph E. Sickles, II

U.S. Geological Survey
 NOAA Air Resources Laboratory
 USDA-Forest Service
 USDA CSREES
 Department of Agronomy/Purdue University
 U.S. Environmental Protection Agency

Issue 1

Is the NADP satisfactorily achieving the NRSPgoal:

 to provide the scientific research community, resource managers, and policy makers with high quality information on the exposure of managed and natural ecosystems to biologically important chemical deposition and other stressors resulting from changes in the nation's chemical climate?

Recommendations:

 Form a study group whose members will focus on developing the capacity to address total deposition. This study group may make recommendations to the Technical Committee on how NADP could increase attention to and cooperation with CASTNet, AIRMoN-Dry, and other dry deposition networks, and/or how dry deposition sites could be collocated with NADP wet deposition sites without jeopardizing the core, wet deposition monitoring program.

Recommendations: (cont'd)

- Develop a plan of the "ideal" future network of sites for NTN, AIRMoN, and MDN. Provide guidance on how many sites would be sufficient and at what locations. The plan should use spatial statistical analysis.
- Issue consolidated reports of QA/QC activities covering all three networks.

Issue 2

Is the NADP organizational structure efficient and effective in carrying out the mission of the NADP (including the Executive Committee, Budget Advisory Committee, Technical Committee, and Program Office)?

Recommendations:

- Continue efforts to improve communication throughout the organization especially between the Program Office and the Executive Committee.
- Review the present structure and functions of subcommittees, and the composition of the executive and budget committees with the goal of simplifying the organization.

Issue 3

Is NADP sufficiently flexible to adapt its long-term monitoring expertise to future environmental problems, such as nutrient loadings, environmental toxics, and atmospheric deposition in urban areas?

Recommendations:

- Respond flexibly to regional/multi-state and "nontraditional" for deposition data by creating a class of sites whose data is not included in national trends, but collected specifically for these studies.
- Monitor key emerging environmental issues for opportunities to apply NADP's management and scientific skills to the solution of these problems.

Recommendations: (cont'd)

- Become more proactive in its approach to adding new monitoring capabilities such as dry deposition or metals.
- Consider adding a \$1.00 "research tax" to the cost of processing each sample at the CAL/HAL, to allow research by the CAL/HAL and Program Office staff on new methods and procedures, and new analytes.



Is the NADP working towards the accomplishment of its vision? Is there a vision for the future?

Recommendations:

- Produce a white paper on NADP's future role in environmental research.
- Track the implications for chemical analysis of cutting-edge high-throughput technologies that are currently revolutionizing biological research.
- Monitor technology in the areas of publishing, software, and analytical chemistry.

NADP Annual Report 2002-01

National Research Support Project-3 2001 ANNUAL REPORT

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

A Cooperative Research Support Program of the State Agricultural Experiment Stations (NRSP-3) Federal and State Agencies and Private Research Organizations



National Research Support Program-3 Proposal The National Atmospheric Deposition Program A Long Term Monitoring Program in Support of Research on the Effects of Atmospheric Chemical Deposition

This proposal can also be reviewed within the National Information Management and Support System (NIMSS)

Proposal Documents	What is NRSP-3? Additional Information
 Proposal Appendix E. Project Participation Attachment 1. NADP Role in Monitoring Atmospheric Chemical Deposition Attachment 2. Informational and Educational Brochures and Programs Attachment 3. Publications by NADP (NRSP-3) Scientists Attachment 4. NADP (NRSP-3) Cooperators and Technical Committee Attachment 5. Budget Information 	 NRSP-3 Governance NRSP-3 History NRSP-3 Products Administrative and Technical Review Report SAES-422 Multistate Research Activity Accomplishments Report - 2001
Adobe Acrobat Reader is required to view these files. The free Acrobat Reader can be downloaded here:	
Click a link to view the document online. To download a file to your computer for later viewing, right click the document link and select "save link as" (Netscape) or "Save Target as" (Internet Explorer)	

http://nadp.sws.uiuc.edu/nrsp3

NADP Role in Monitoring Atmospheric Chemical Deposition

"The National Atmospheric Deposition Program provides an example of an effective monitoring network where data are delivered because a specific design objective (i.e., loads of air pollutants in wet deposition) was adopted. Many Federal agencies including USGS, NOAA, EPA, NPS, BLM, USDA, TVA, private companies, State, and local government agencies, working in a collaborative partnership, operate this network. Sample collection protocols and quality assurance plans have been established, and the data are considered authoritative by the environmental community."

NADP Role in Monitoring Atmospheric Chemical Deposition

Clean Air Action Plan Federal Partners (U.S. Departments of Agriculture, Interior, Defense, Commerce, Energy, Transportation, Justice; U.S. Environmental Protection Agency, Tennessee Valley Authority). 2000. *Clean Water Action Plan: Coastal Research and Monitoring Strategy*. p27. (http://www.cleanwater.gov/coastalresearch/H2Ofin.pdf)



Northeastern Regional Association of State Agricultural Experiment Station Directors

DEFERRED ON ALL NRSP FUNDING UNTIL ITS SUMMER MEETINGS IN JULY



VOTED TO EXTEND NRSP-3 FOR ONE YEAR

AND

CONSIDER A 4-YEAR RENEWAL IN SPRING OF 2003

Western Association of Agricultural Experiment Station Directors



APPROVED FY03 BUDGET

AND DEFERRED DECISION ON RENEWAL UNTIL ITS SUMMER MEETING IN JULY



Accepted 5-year renewal of NRSP-3. October 2002 - September 2007









[This issue also contains Atmospheric Environment International North America Papers]



PERGAMON An Imprint of Elsevier

"NADP2000 - Ten Years After the Clean Air Act Amendments" Atmospheric Environment, V36 (N10)

Kelly, V.R., G.M. Lovett, K.C. Weathers, and G.E. Likens

"Trends in atmospheric concentration and deposition compared to regional and local pollutant emissions at a rural site in southeastern New York, USA." pp. 1569-1575.

Peters, N.E., T.P. Meyers, and B.T. Aulenbach

"Status and trends in atmospheric deposition and emissions near Atlanta, Georgia, 1986-99." pp. 1577-1588.

Lawrence, G.B.

"Persistent episodic acidification of streams linked to acid rain effects on soil." pp. 1589-1598.

"NADP2000 - Ten Years After the Clean Air Act Amendments" Atmospheric Environment, V36 (N10)

Kamman, N.C. and D.R. Engstrom

"Historical and present fluxes of mercury to Vermont and New Hampshire lakes inferred from ²¹⁰Pb dated sediment cores." pp. 1599-1609.

Schilling, J.S. and M.E. Lehman

"Bioindication of atmospheric heavy metal deposition in the southeastern US using the moss Thuidium delicatulum." pp. 1611-1618.

Grant, R.H. and K.L. Scheeringa

"Estimating climate effects on the atmospheric contribution to the potential available inorganic nitrogen in eastern United States soils." pp. 1619-1630.

"NADP2000 - Ten Years After the Clean Air Act Amendments" Atmospheric Environment, V36 (N10)

Gbondo-Tugbawa, S.S. and C.T. Driscoll

"Evaluation of the effects of future controls on sulfur dioxide and nitrogen oxide emissions on the acid-base status of a northern forest ecosystem." pp. 1631-1643.

Tessier, J.T., R.D. Masters, and D.J. Raynal (short communication)

"Changes in base cation deposition across New York State and adjacent New England following implementation of the 1990 Clean Air Act Amendments." pp. 1645-1648.

Smith, **L**. (technical note)

"Analysis of commented vs uncommented samples from the Clean Air Status and Trends Netwrok (CASTNet)." pp. 1649-1653.

Announcement & Call for Papers

Abstracts Due August 9, 2002 NADP Technical Committee Meeting 10-13 September 2002, Seattle, Washington

The National Atmospheric Deposition Program (NADP) will hold its Annual Technical Committee Meeting on 10-13 September 2002 at the Seattle Center. Rooms are available at the Hampton Inn, 700 5th Avenue North. This marks the 25th year of the NADP, which began as a regional State Agricultural Experiment Station (SAES) project and continues today as SAES National Research Support Project-3 with nearly 250 cooperators (federal, state, local, and tribal agencies; SAES, universities; and non-governmental organizations).

About the NADP: The NADP is recognized internationally for long-term, high-quality measurements of precipitation chemistry. Precipitation is collected at 240 National Trends Network (NTN) sites across the continental United States, Alaska, Hawaii, Puerto Rico, and the Virgin Islands. Data from NTN sites are used to evaluate temporal trends and geographic distributions of atmospheric chemical deposition, as well as to support research on potential impacts of this deposition on terrestrial and aquatic ecosystems. The NADP also includes a 10-site research network, the Atmospheric Integrated Research Monitoring Network (AIRMON), which collects daily samples, evaluates new methodologies, and examines relationships between pollutant sources and deposition. It also includes the Mercury Deposition Network (MDN), which measures total mercury in precipitation at nearly 70 sites in the United States and Canada.

About this meeting: This meeting is intended for people interested in air quality, atmospheric deposition, and the effects of airborne chemicals on cultural and natural resources. The two-day scientific symposium will be on Wednesday and Thursday, 11-12 September. A trip to the Mercury Deposition Network (MDN) Laboratory at Frontier Geosciences, Inc. has been scheduled for Wednesday afternoon. This trip offers an excellent opportunity to see how total and methyl mercury are being measured in precipitation from the MDN, the fastest growing NADP network. Participants may attend an optional field trip to spectacular Mount Rainier National Park on Friday and hear presentations on air quality research in the park and the geological history of Mount Rainier and the Cascades. Annual NADP business, committee, and subcommittee meetings will convene on Tuesday, 10 September.

Contributed papers are solicited on all aspects of atmospheric deposition, as well as the meteorology, physics, and chemistry of the atmosphere that influence wet or dry deposition. Both oral and poster presentations are welcome. Send titles and abstracts (up to 200 words), including author(s) name(s), affiliation(s), mailing address(es), and the telephone number and e-mail address of the corresponding author to Kathy Douglas by **9 August 2002.** E-mail (kathy@sws.uiuc.edu)communications are preferred; or, send information to Kathy Douglas, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820 (fax:217/333-0249; phone:217/333-7871). All abstracts will be distributed to meeting participants and other interested individuals.

For questions about the annual meeting: Contact the program chair, Rich Grant, Department of Agronomy, Purdue University, West Lafayette, IN 47907 (phone: 765/494-8048; e-mail: rgrant@purdue.edu). The NADP Internet site includes additional meeting information:

http://nadp.sws.uiuc.edu/
NADP 2002 FALL MEETING

10 -- 12 September 2002

Orcas Room for registration						
	Orcas Room for registration	Fidalgo Room for poster set-up Fidalgo Room for poster remo				
TIME	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY		
0700		Registration Open	Registration Open			
0730	MEETING (1 room - 30 poople)	(continental breakfast)	(continental breakfast)			
0800	MEETING (1 room 30 people)		Scientific Papers Lopez Room			
0830	Shaw Room	Scientific Papers				
0900	(break)	Lopez Room				
0930						
1000	MEETING (1 room-30 people / 1	(break)	(break)			
1020	room15 people)					
1030	(Registration Open)	Scientific Papers Lopez Room	Scientific Papers Lopez Room	FIELD TRIP TO MOUNT RAINIER (box lunches22)		
1100	Shaw and Eidalgo Rooms					
1130	Shaw and Fidaigo Rooms					
1200	LUNCH (on own)	LUNCH (on own)	LUNCH (op owp)			
1230	Lontoin (dir dini)	Editori (dir dini)	Editori (dirowin)			
1300				(000 10100011)		
1330	SUBCOMMITTEE MEETINGS	Scientific Papers	cientific Papers Scientific Papers			
1400		Lopez Room	Lopez Room			
1430						
1500	(break)	(break)	(break)			
1520	TECHNICAL COMMITTEE					
1530	BUSINESS MEETING	Tour of HAL	Tour of HAI Scientific Papers			
1600	Lopez Room	rour orrate	Lopez Room			
1630	Lopozitionii					
1700						
1730						
1800		POSTER SESSION				
1830		and				
1900		RECEPTION/SOCIAL MIXER				
1930		Shaw/Fildalgo Rooms				



Mercury Deposition Network (MDN)



Monitoring Mercury in North American Precipitation





National Atmospheric Deposition Program A Cooperative Research Program of Federal, State, and Private Organizations

1990 Population Density



	NADP Bibliography Search	
Search String:		
Year:	All Years 💌	
Sort by	Match Strength	
	Go	
	Return to NADP Publications	
	Your Comments and Suggestions are always Welcome Return to :[NADP Home] [AIRMoN] [MDN] [Search]	

http://nadp.sws.uiuc.edu/lib/bibsearch.asp

N-CON SAMPLER UPDATE AND DATA ANALYSIS

National Atmospheric Deposition Program - Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 7

WINTERS EVENTS- FREEZE



You can't fool mother nature!

THE BIG FREEZE



So what happened to the NADP style collectors?

FROZEN OPEN



So....what's the difference?

- NADP style collector could be broken free, the ice removed and started up again with the lid mechanism in the correct position.
- The N-CON collector required lid arm readjustment using hand tools to achieve a "hoped for" correct position.



ROTATION OF ADJUSTMENT AT THIS POINT





WINTERS EVENTS-LID FLOP

I suspect caused by freezing of the lid pivot joint. The counterweight was not heavy enough to break the ice and the lid went onto the bucket in this "nose up" attitude. Again a 4 arm collector can not do this!



IMPROVEMENT



CONTINUING ISSUES

There is no provision for an AC powered system with automatic DC backup.

There is no on-board provision for a GFI.

Sensor unit mounting. Nuts too small and MOLEX is positioned in a poor manner making maintenance difficult.





Let's look at some data!

Sample Data Set

- AIRMoN Sampling Protocol (event based)
- 24 January 18 March; 11 Events

	IL98 (control)	IL97	97IL
Collector	Aerochem	N-Con	Aerochem
Sensor	Standard	Optical	(N-Con)

1) Collector exposure time

2) Sample Volume

3) Chemistry

Comparison of Optical Driven ACM with the Standard ACM During a Heavy Rain Event



Date/Time (mm/dd/yy hh:mm)

Collector Exposure Times



Statistic	Sample Depth (inches)			Exposure Time (hh:mm:ss)		Difference per Event	
	NWS Stick Gage	Optical N-Con	Driven ACM	Standard ACM	Driven ACM	Standard ACM	Driven- Standard
Mean	0.65(8)	0.64(9)	0.65(5)	0.62(1)	14:28:02	7:35:52	6:52:10
Std. Error	0.18(2)	0.17(8)	0.17(6)	0.16(8)	2:55:31	1:56:04	1:23:51
Median	0.53(5)	0.52(1)	0.55(4)	0.51(5)	12:56:10	5:27:57	6:45:57
Minimum	0.040	0.053	0.052	0.036	2:38:51	1:35:32	-0:09:58
Maximum	2.220	2.171	2.111	1.987	39:53:00	26:46:26	14:28:49
Sum	7.90(0)	7.79(3)	7.85(4)	7.44(6)	173:36:20	91:10:26	82:25:54
Count	12	12	12	12	12	12	12

Sample Volume Deviation from Independent Aerochem

Sample Volume



Volume-Weighted Mean Concentrations

Volume-Weighted Mean Concentrations



Volume-Weighted Mean Concentrations (Deviation from Independent Aerochem)

Deviation from Independent Aerochem Collector (Volume-Weighted Mean)



Laboratory Hydrogen Ion Concentrations

Laboratory Hydrogen Ion Concentration



Laboratory Hydrogen Ion Deviation from Independent Aerochem

Hydrogen Ion Concentration



Sulfate Ion Concentration

Sulfate



Sulfate Ion Deviation from Independent Aerochem

Sulfate



Equivalent Sulfate Ion Concentration In Volume Differential for IL97/97IL

Sulfate Equivalent Concentration



Volume Deviation from IL98 [mL]

Chloride Ion Concentration



Ammonium Ion Concentration



Ammonium Ion Deviation from Independent Aerochem

Ammonium



Equivalent Ammonium Ion Concentration In Volume Differential for IL97/97IL

Ammonium Equivalent Concentration Deviation



Volume Deviation from IL98 [mL]

Calcium Ion Concentration



Calcium Ion Deviation from Independent Aerochem

Calcium


Equivalent Calcium Ion Concentration In Volume Differential for IL97/97IL

Calcium Equivalent Concentration Deviation

IL97: N-Con Collector O 97IL: Slaved Aerochem



Volume Deviation from IL98 [mL]



Boston Urban Gradient Mercury Deposition Study

Mark Nilles U.S. Geological Survey

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 8

Objectives

- Support the USGS Toxics and NAWQA Programs urban gradient study objectives
 - Hg concentration along an urban gradient for precipitation, surface water, fish tissue and sediment
- Gain knowledge and experience on deploying mercury wet deposition collectors in an urban environment
- Collocate a prototype instrument with MDN
- Test a new sampling train design
- Support continued R&D on new instruments by vendors



Study support

Samplers

N-Con Systems Inc, purchased by USGS Atmospheric Deposition Program

- Site Operation
 - USGS- NAWQA Program
 - MA and NH State agencies
- Sample train design, assembly, cleaning, support
 - Frontier Geosciences Inc.
- Sample analysis

ZUSIGS

 USGS Toxics Program- Trace level mercury lab, Madison, WI

Site locations





Laconia, NH (collocated with NH00)





Manchester, NH





Beverly Airport, MA



Blue Hills Observatory, MA





Acceptance and Installation

- One collector cosmetically damaged in shipment
 - Recommend custom shipping container be designed
- Every collector worked "out of the box"
- Extremely easy installation
 - ◆ 4 sites up and running in 2 days
- No initial startup malfunctions













Initial operation

Heater fan blades melted at 3 sites during very cold weather. This blew the fuse on the collectors. Melting of a wire near the heater caused similar problem on the fourth collector.

N-Con retrofit internal heaters on all collectors

- The lid arms slipped on the motor shaft at two sites resulting in lid arm mis-positioning, blown fuses and some cosmetic damage.
 - Lock-tite applied to these screws
 - N-Con is working on a retrofit with drilled holes to position arm on shaft.

Initial operation

- Two-arm lid attachment system results in uncertain lid positioning, especially with ice/snow
 - N-Con has designed a 4-arm retrofit which should result in certain lid positioning
- Two-arm lid drive system loosens at allen screw attachment points at lid
 - Lock-tite applied to these screws
 - 4-arm retrofit includes better attachment system at lid.





Initial operation

Solar site - Internal heater drained 4 deep cycle batteries in less than a week.

- Replaced the internal heater with heat tape and sampler has been kept above freezing
- Ordered additional solar panel for next winter



Beverly Airport, MA



Initial Operation - Unresolved Issues

Reports of openings and closing in high winds at two sites but not at other two.

 Suspect small particles are activating optical sensor

Confirmed by manufacturer of sensor

Need to experiment with sensor settings











Data

Only data back from the lab so far is for the system blanks we ran through each collector on day one of operation.
All blanks were 0.07 ng/l or less total Hg
Should have a paper or poster at the fall meeting with environmental data



Summary

- Despite some initial problems, collectors are supporting the study. No new problems reported since late February. All "volunteer" operators are sticking with the study.
- Problems are design related, not reliability related
- Retro-fits (installed and planned) should resolve most major issues. <u>Drive arm retrofit is needed</u> <u>ASAP</u>
- Focused research on optical sensor in various environments is needed







MDN New Sample Train Data

<u>Eric M. Prestbo</u> and Rebecca Turner Frontier Geosciences Inc. ericp@frontiergeosciences.com

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 9



Frontier Geosciences www.frontiergeosciences.con



WHY A NEW SAMPLE TRAIN?

- With new samplers being built and tested time is right to upgrade and improve on the sample train
- Current sample train is made from glass which is:
 - Inexpensive
 - Breaks in the field and during transit
 - Not acceptable for trace metals
 - doesn't seal well at the bottle interface

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 9



Frontier Geosciences www.frontiergeosciences.cor



Some Boundary Conditions for a New Train

- All plastic materials non contaminating for trace metals, methyl mercury or total mercury
- Bigger funnel = better detection limit. However I have concluded that the funnel to bottle ratio must remain nearly the same as current sampler thus 2-liter bottle 5" OD funnel
- Must keep water-air exchange very small like current sample train
- Must be able to oxidize rain right in the bottle

Rugged / easy to field deploy / lab-user friendly National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 9



Frontier Geosciences www.frontiergeosciences.com



Ideal Sample Train Attributes

- Bottle is trace metal clean right off the shelf no laboratory cleaning needed, saving time, water, resources and reducing acid exposure and disposal YES
- Bottles and funnels could be shipped in bulk (12 per shipment) to site to save cost and energy ??
- A single sample bottle/funnel assembly could be returned weekly in small shipper unit to save cost and energy ??
- Funnel assembly would be a single PE-Teflon unit for good performance, simplicity, easy cleaning and rugged – NO
- Bottle would be inexpensive, single-use and thus could be stored indefinitely or if not needed recyclable YES

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 9



Frontier Geosciences www.frontiergeosciences.cor



New Sample Train Specifications

Maximum volume of 2400 ml of water
Funnel opening = 118 cm²
Maximum rainfall amount = 20.3 cm
Maximum flow rate measured = 10.2 cm rain/min.

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 9



Frontier Geosciences www.frontiergeosciences.con



How Much Water is Evaporated During Sample Storage?

400 ml of water – Temperature Range of 15-23 degrees C

	2/6/2001	2/26/2001	Difference	
Scale 1 (g)	810.5	810.0	0.5	
Scale 2 (g)	810.8	810.7	0.1	
			0.4	Mean
			0.1%	Percent

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 9



Frontier Geosciences www.frontiergeosciences.com



Bottle Blank Results and eMDL

Aliquot	ng/aliq
20	0.0539
20	0.0532
20	0.0526
20	0.0490
20	
20	0.0583
20	0.0540
average	0.0535
std. Deviation	0.00299
%RSD	5.6%
eMDL	0.0090
eLOQ	0.0299



Frontier Geosciences www.frontiergeosciences.cor



Method Detection Limit Determination Best estimate of sigma (noise) is slope of [Hg] vs [Hg] Std. Dev.





Frontier Geosciences www.frontiergeosciences.cor



Sample Volume Precision and Storage

Bottles 1-13 sampled rain for 1 week – Bottles 1-6 recovered – bottles 7-13 kept out but closed for another 10 days then recovered

	Total Vol	Total	Total
	(ml)	ng/sample	ng/l
average	76.69	1.23	21.67
st deviation	1.006	0.176	3.129
% RSD	1.3%	14.4%	14.4%

Samples	1 to 6	21.95
Samples	7 to 13	21.42
		97.6%

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 9



Frontier Geosciences www.frontiergeosciences.com



Field Spike Recovery - Accuracy

- 6 samples deployed 3 spiked with 10.7 ng of Hg(II) (no BrCl)
- repeated 2X recovery 92.4% and 91.8%
- 6 Samples deployed collect some rain then spike 3 of the samples with 10.7 ng of Hg(II) (no BrCl)
 Repeated 2X – recovery 105.4% and 81.9%
 Low value of 81.9% - very small rainfall

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 9



Frontier Geosciences www.frontiergeosciences.cor



Some Future Work

- More intercomparisons in the field between standard MDN and new sample train in ACM – both bottle catch and chemistry (Total and MMHg)
- Continued monitoring of off-the-shelf bottle blanks
- More precision and accuracy tests
- Trace metal blanks, precision and accuracy
- Find manufacturer of single-piece funnel assembly
- Develop small bottle/funnel shipper

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 9



Frontier Geosciences www.frontiergeosciences.com





 Objective: To use Rodamine B in a field trial with ambient precipitation to see whether 1 meter and 2 meter posts cause splash onto targets which represent NADP collector wet-side buckets.

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 10

TOOLS

- RODAMINE B
- 27 cm diameter paper filter elements
- PVC pipe material
- Digital camera
- 100 yard ruler


THE SET-UP





POST EVENT







2 METER RESULTS

11-08-01









POST EVENT NOTES

- E, S and SE poles all had splash on them during event. After the event all traces of dye had been washed away except the areas under the targets where the rain did not hit the pole. Under the targets there were obvious signs of dye splash.
- Additionally there were signs of dye on the E, S and SE filter paper during the rein event. Here too, after the event the rain washed almost all evidence of splashed dye.
- Rainfall: 1.01 cm
- Dyed pole height: 2 meter
- Splash distance
 - To South 3 meter
 - To E 4 meters
 - To South 5 meters

RESULTS

- 2 meter pole confirmed splash to 5 meter distant target on 2 occasions
- 1 meter pole splash was not confirmed to 5 meter distant target
- Difficult to get good event, rain rapidly dilutes the dye, event of ~0.25" are optimum.

FUTURE

- Question remains whether repeatable results can be achieved under natural precipitation.
- Technique might be applicable to other potential objects of concern (towers, small buildings)

SULFITE/SULFATE STUDY

Tracie Patten, Jane Rothert, Kaye Surratt

Slide 1:

NTN $SO_4^{2-} > AIRMoN SO_4^{2-}$ during winter months

Slide 2:

AIRMoN Reanalysis shows changes in SO_4^{2-} concentrations, higher concentrations in the winter months in the reanalysis values.

Slide 3:

Example 1

Slide 4:

Example 2

IL11 (Bondville, IL)						
January sample						
0.81 ppm - original						
1.30 ppm - reanalysis						

Slide 5: Experimental parameters

Start Date:	October 1 2001
Start Date.	$D \land 15$ (Decre State)
Site:	PAIS (Penn State)
Sample information:	At least 100 mL of sample shipped to CAL
Sample preparation:	50 mL of sample poured into 60 mL vial and then spiked with 0.25 mL of a fresh 0.03% H ₂ O ₂
H_2O_2 concentration:	$1.4 \text{ ppm H}_2\text{O}_2$
Hold time:	Samples kept at room temperature for one month
	before analysis

Slide 6: Original IC analysis showing SO₃²⁻ peak (unknown)





Reanalysis of the same sample as above showing the unknown or SO_3^{2-} no longer present.









Hydrogen Ion Difference vs. Relative Conductivity Difference



Slide 10:

Hydrogen Ion (Field pH)



Slide 11: Conductivity from pH difference vs Measured Conductivity Difference



Slide 12:





Slide 13:





Slide 14:

NH4⁺ Difference vs NO3⁻ Difference



Conclusion:

AIRMoN SO_4^{2-} during winter months is less than NTN concentrations due to SO_3^{2-} remaining in the AIRMoN samples. AIRMoN reanalysis shows changes in SO_4^{2-} concentrations, higher concentrations in the winter months in the reanalysis values with the difference being greatest in samples containing SO_3^{2-} . Differences in pH after addition of hydrogen peroxide is not explained completely by the oxidation or elimination of organic acids. NH_4^+ converts partly NO_3^- but it doesn't appear to be a stoichiometric conversion.

Blind Audit Program



PRELIMINARY 2001 RESULTS NADP/NTN SPRING MEETING May 6-8, 2002 Monterey, CA

Prepared by Natalie Latysh and John Gordon

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 12



Blind Audit Program



Quantify the contribution of:

- \Rightarrow sample collection,
- ✤ shipping,



and processing (e.g., filtration)

to precipitation chemistry



Overview of the Blind Audit Program





SUBMITTING THE BLIND AUDIT SAMPLES TO THE CAL





Locally Weighted Scatterplot Smoothing was used to depict patterns in blind audit results from 2001

— 75th percentile

— 50th percentile

— 25th percentile

























Boxplots showing the relationship between blind audit sample analytes and paired sample differences

> Upper Quartile Median Lower Quartile



Paired Bucket Sample Concentrations Minus Bottle Sample Concentrations, 2001





Paired Bucket Sample Concentrations Minus Bottle Sample Concentrations





Blind Audit Program: 2001 Paired-Sample Concentration Differences (mg/L)

Analytes	Minimum	25%	Median	75%	Maximum
Calcium	-0.091	-0.009	0.003	0.016	0.380
Magnesium	-0.027	0.000	0.004	0.006	0.020
Sodium	-0.033	-0.001	0.005	0.011	0.070
Potassium	-0.015	-0.002	0.002	0.004	0.023
Ammonium	-0.070	0.000	0.010	0.020	0.100
Chloride	-0.023	0.004	0.010	0.018	0.043
Nitrate	-0.056	0.010	0.021	0.039	0.115
Sulfate	-0.094	0.012	0.031	0.066	0.190
Hydrogen Ion	-12.100	-3.051	-1.229	0.000	3.771
Specific Conductance	-3.800	-0.900	-0.500	0.000	1.800



Boxplots showing the relationship between blind audit sample concentrations and paired sample differences

> Upper Quartile Median Lower Quartile





Target Concentration (mg/L)





Target Concentration (mg/L)


































Target Concentration (**n5**/cm at 25°C)



Results of the Kruskal-Wallis analysis of variance tests to determine the relation between paired blind audit sample differences and the target concentrations used in the blind audit program during 2001



Kruskal-Wallis Test Results for Paired Differences vs. Target Concentration

Analyte	Paired sample	e differences	Statistically significant difference? (a = 0.05)	
	Concentration Basis	Mass Per Bucket Basis	Concentration Basis	Mass Per Bucket Basis
Calcium	0.479	0.657	NO	NO
Magnesium	0.064	0.032	NO	YES
Sodium	0.669	0.605	NO	NO
Potassium	0.139	0.399	NO	NO
Ammonium	0.169	0.151	NO	NO
Chloride	0.129	0.168	NO	NO
Nitrate	0.410	0.036	NO	YES
Sulfate	0.034	0.006	YES	YES
Hydrogen Ion	0.213	0.518	NO	NO
Specific Conductance	0.042	0.010	YES	YES

Boxplots were prepared to show the relationship between paired differences and sample volume for the 250-, 500-, 1000-mL blind audit samples

Upper Quartile

Median

Lower Quartile













science for a changin



Paired Differences (µg)























Results of the Kruskal-Wallis analysis of variance tests to determine if bucket minus bottle differences for the 250-, 500-, and 1,000-mL samples used in the blind-audit program have equivalent distributions



Kruskal-Wallis Test Results for Paired Differences vs. Sample Volume

Analyte	Bucket minus bottle concentrations		Statistically significant difference? (a = 0.05)	
	Concentration Basis	Mass Per Bucket Basis	Concentration Basis	Mass Per Bucket Basis
Calcium	0.756	0.801	NO	NO
Magnesium	0.061	0.010	NO	YES
Sodium	0.128	0.043	NO	YES
Potassium	0.747	0.046	NO	YES
Ammonium	0.879	0.165	NO	NO
Chloride	0.111	0.000	NO	YES
Nitrate	0.033	< 0.0001	YES	YES
Sulfate	0.001	< 0.0001	YES	YES
Hydrogen Ion	0.370	0.700	NO	NO
Specific Conductance	0.968	0.003	NO	YES

Number of Analyte Determinations Greater than the MDL for Ultrapure Deionized-Water Samples During 2000 and 2001

Analyte	2000		2001	
	Bucket portion	Minimally handled bottle portion	Bucket portion	Minimally handled bottle portion
Calcium	10	2	3	2
Magnesium	0	0	10	4
Sodium	2	2	10	4
Potassium	3	0	7	3
Ammonium	2	2	7	1
Chloride	5	1	4	1
Nitrate	5	2	7	3
Sulfate	1	0	4	3

MDL – Method Detection Limit

N = 13 bucket/bottle portions



Summary

- Paired differences between the bucket and bottle portions are small and show little variability for most analytes
- Variability for for the paired differences for most analytes has decreased since 1999
- With the exception of hydrogen ion and specific conductance, all analytes show a slight positive bias resulting from introduction of additional ions in the bucket portion during sample handling and processing
- Results from the Kruskal-Wallis test indicate that paired differences are influenced by sample concentration for sulfate and specific conductance; and paired differences are influenced by sample volume for sulfate and nitrate



Field Blank and Reference Sample Program

PRELIMINARY 2001 RESULTS

NADP/NTN SPRING MEETING May 6-8, 2002 Monterey, CA

Prepared by Natalie Latysh and John Gordon

National Atmospheric Deposition Program - Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 13



Field Blank and Reference Sample Program

Description:

Quantify the contribution of sample collector container surfaces and field exposure to NADP/NTN precipitation chemistry.

A portion of a synthetic precipitation sample is added to a bucket that was exposed for one dry week at the site. The remaining portion serves as the control and is analyzed separately.





Overview of sample submission in 2001:

In 2001, a total of 100 field blank samples were distributed to site operators.

During January through October 2001, 71 field blank samples were submitted for analysis.

Of the 71 field blank samples submitted, 67 yielded complete sets of analyses.





Locally Weighted Scatterplot Smoothing was used to depict patterns in field blank results from January through October 2001

— 75th percentile

— 50th percentile

— 25th percentile


































Boxplots showing the relationship between field blank sample analytes and paired sample differences

> Upper Quartile Median Lower Quartile



Paired Bucket Sample Concentrations Minus Bottle Sample Concentrations





Paired Bucket Sample Concentrations Minus Bottle Sample Concentrations





Field Blank Program:

Paired-Sample Concentration Differences

Analytes	Minimum	25%	Median	75%	Maximum
Calcium	-0.015	0.002	0.006	0.012	0.126
Magnesium	-0.005	0.000	0.001	0.002	0.029
Sodium	-0.007	0.001	0.002	0.004	0.135
Potassium	-0.004	-0.001	0.001	0.002	0.121
Ammonium	-0.130	0.000	0.000	0.010	0.090
Chloride	-0.002	0.006	0.011	0.017	0.123
Nitrate	-0.150	0.000	0.013	0.026	0.100
Sulfate	-0.018	-0.003	0.000	0.014	0.341
Hydrogen Ion	-4.273	-1.423	-0.672	0.000	3.357
Spec Cond	-2.600	-0.400	-0.100	0.100	1.600



Boxplots showing the relationship between field blank sample concentration and paired sample differences

> Upper Quartile Median Lower Quartile





Target Concentration (mg/L)







Target Concentration (mg/L)





Target Concentration (mg/L)











Target Concentration (mg/L)





Target Concentration (mg/L)











Kruskal Wallis test results to determine if sample concentration had an effect on paired sample differences

Analyte	Statistically significant difference? (a = 0.05)		
	Differences units of concentration	Differences units of mass	
Calcium	No	No	
Magnesium	Yes	No	
Sodium	No	No	
Potassium	No	No	
Ammonium	No	No	
Chloride	Yes	No	
Nitrate	Yes	No	
Sulfate	Yes	Yes	
Hydrogen Ion	No	No	
Specific Conductance	Yes	Yes	



Boxplots showing the relationship between paired differences and sample volume for the 250-, 500-, 1000-mL USGS samples

Upper Quartile Median

Lower Quartile









Sample Volume (mL)







Sample Volume (mL)





Sample Volume (mL)













Kruskal Wallis test results to determine if sample volume had an effect on paired sample differences

Analyte	Statistically significant difference? ($\mathbf{a} = 0.05$)		
	Differences units of concentration	Differences units of mass	
Calcium	Yes	No	
Magnesium	Yes	Yes	
Sodium	No	No	
Potassium	No	No	
Ammonium	No	No	
Chloride	Yes	Yes	
Nitrate	Yes	No	
Sulfate	Yes	Yes	
Hydrogen Ion	No	No	
Specific Conductance	No	Yes	



Number of Analyte Determinations Greater than the MDL for Ultrapure Deionized-Water Samples During 2000 and 2001

	2000		2001		
Analyte	Field-exposed bucket portion	Minimally handled bottle portion	Field-exposed bucket portion	Minimally handled bottle portion	
Calcium	18	1	15	4	
Magnesium	1	0	4	1	
Sodium	4	0	4	2	
Potassium	0	0	6	2	
Ammonium	8	1	2	1	
Chloride	0	0	18	3	
Nitrate	6	0	9	1	
Sulfate	0	0	6	1	

N = 21 bucket/bottle portions MDL – Method Detection Limit



Blind Audit vs. Field Blank: [Bucket] - [Bottle] [Target] Median Relative Percent Differences

2000 2001 Analyte **BLIND** FIELD **BLIND** FIELD AUDIT BLANK AUDIT BLANK Calcium 0.57 0.35 5.66 2.45 Magnesium 2.17 4.08 4.29 2.04 Sodium 1.76 1.94 2.14 0.83 Potassium 1.20 0.00 2.41 1.67 Ammonium 0.00 2.82 -1.79 0 Chloride 2.15 4.00 1.85 4.00 Nitrate 1.24 1.08 1.37 0.8 1.18 1.03 1.18 Sulfate 0.15 Hydrogen Ion -4.50 -5.71 -4.50 -3.83 Specific Conductance -2.35 -1.22 -1.76 -1.6



* 100

Blind Audit vs. Field Blank:



Median Absolute Percent Differences

	20	000	2001	
Analyte	BLIND	FIELD	BLIND	FIELD
	AUDIT	BLANK	AUDIT	BLANK
Calcium	2.78	6.51	4.00	2.52
Magnesium	3.42	4.08	5.36	2.86
Sodium	2.41	1.94	2.64	0.9
Potassium	3.61	4.35	5.00	4.35
Ammonium	2.82	3.57	2.82	0.00
Chloride	2.22	4.00	2.22	4.00
Nitrate	1.28	1.20	1.38	1.02
Sulfate	1.21	1.25	1.37	0.87
Hydrogen Ion	5.46	6.75	6.37	4.55
Specific Conductance	2.58	5.56	2.59	2.40





Summary

• The number of analyses for the bucket and bottle portions exceeding the MDL for Ultrapure DI samples has increased significantly for chloride, potassium, and sulfate since 2000

• Paired differences between the bucket and bottle portions are influenced by sample concentration for sulfate and specific conductance

• Paired differences between the bucket and bottle portions are influenced by sample volume for magnesium, chloride and sulfate



Collocated Study Results 2000 to 2001

NADP/NTN SPRING MEETING

May 6-8, 2002 Monterey, CA

Prepared by Natalie Latysh and John Gordon

National Atmospheric Deposition Program – Spring 2002 Interim Meeting



NOS Subcommittee Minutes: Attachment 14

Collocated sampler program Objectives

 Estimate overall variability of NADP/NTN
precipitation measurements -- chemistry and physical properties

 Detect changes in variability due to equipment and protocol changes

Compare overall system variability to components measured by other external quality assurance programs



2000-2001 Collocated Sites

2000

CO08/08CO Four Mile Park

 NH02/02NH Hubbard Brook

NH02/02NH Hubbard Brook

2001

• CA99/99CA Yosemite


Collocated Sites 2000 - 2001



science for a changing

Collocated Site at Hubbard Brook, New Hampshire (NH02)



science for a chan

Collocated Site at Hubbard Brook, New Hampshire (NH02)





Collocated Site at Four Mile Park, Colorado (CO08)





Collocated Site at Yosemite National Park, CA (CA99)



science for a chai

Precision Estimates for Collocated Sites:

Difference Between Collectors = $(C_1 - C_2)$

Relative Percent Difference = $\frac{C_1 - C_2}{(C_1 + C_2)/2} * 100$

Absolute Difference Between Collectors = $|C_1 - C_2|$

Absolute Percent Difference=

$$(C_1 + C_2)/2$$

* 100

C₁ - Original Site C₂ - Collocated Site









Science for a changing world











Science for a changing world











1999 Network Median – 0.11









1999 Network Median – 0.049 mg/L







1999 Network Median – 0.22 mg/L







1999 Network Median – 0.024 mg/L







1999 Network Median – 0.019 mg/L









Nitrate Concentration and Deposition Differences

Site Id	MEDIAN RELATIVE CONCENTRATION DIFFERENCE BETWEEN COLLECTORS	MEDIAN ABSOLUTE CONCENTRATION DIFFERENCE BETWEEN COLLECTORS	MEDIAN RELATIVE DEPOSITION DIFFERENCE BETWEEN COLLECTORS	MEDIAN ABSOLUTE DEPOSITION DIFFERENCE BETWEEN COLLECTORS
	mg/L	mg/L	Kg/Hectare	Kg/Hectare
CA99	0.004	0.017	0.017	0.023
CO08	-0.025	0.033	0.003	0.035
NH02-1	-0.021	0.043	-0.110	0.116
NH02-2	-0.014	0.024	-0.020	0.035



Sulfate Concentration and Deposition Differences

Site Id	MEDIAN RELATIVE CONCENTRATION DIFFERENCE BETWEEN COLLECTORS	MEDIAN ABSOLUTE CONCENTRATION DIFFERENCE BETWEEN COLLECTORS	MEDIAN RELATIVE DEPOSITION DIFFERENCE BETWEEN COLLECTORS	MEDIAN ABSOLUTE DEPOSITION DIFFERENCE BETWEEN COLLECTORS
	mg/L	mg/L	Kg/Hectare	Kg/Hectare
CA99	-0.008	0.014	-0.003	0.015
CO08	-0.006	0.015	0.002	0.012
NH02-1	-0.016	0.033	-0.083	0.117
NH02-2	-0.023	0.025	-0.023	0.031



Median Relative Concentration Percent Differences

Analyte	CA99	CO08	NH02-1	NH02-2
Ammonium	0.00	3.64	0.00	0.00
Calcium	8.05	-2.67	-2.02	-4.31
Sulfate	-2.24	-1.68	-1.10	-1.82
Nitrate	0.81	-3.94	-1.93	-1.24
Sample Depth	0.74	4.20	-4.64	-1.37
Sample Volume	0.18	-0.15	-0.69	-1.48





Summary

• CO08 had large median absolute percent differences for deposition for most analytes, reflecting large discrepancies between the collocated raingages

• K, Mg, Ca had the largest median absolute percent differences for units of concentration and deposition

• Median absolute percent differences for units of deposition are greater for the first year of NH02



Interlaboratory Comparison Program

Preliminary Results for 2001

NADP/NTN SPRING MEETING

May 6-8, 2002 Monterey, CA

Prepared by Natalie Latysh and John Gordon

National Atmospheric Deposition Program – Spring 2002 Interim Meeting



NOS Subcommittee Minutes: Attachment 15

Interlaboratory Comparison Program



Quantify bias and precision of data produced by the CAL

Compare performance of the CAL with other laboratories routinely analyzing low ionic strength samples



Samples used in the Interlaboratory Comparison Program during 2001

• Natural wet-deposition samples collected at NADP/NTN sites and bottled by the CAL (i.e. replicate samples)

 NIST (National Institute of Standards and Technology) traceable standard reference samples prepared by High Purity Standards

• Ultrapure deionized-water samples prepared by the USGS

• Synthetic wet-deposition samples prepared by the USGS

Participating Laboratories in the Interlaboratory Comparison Program in 2001

- Illinois State Water Survey, Central Analytical Laboratory (CAL)-Champaign, Illinois
- Environmental Science and Engineering, Inc. (ESE)-Gainesville, Florida
- Shepard Analytical Services (SA)-Semi Valley, California
- Meteorological Service of Canada (MSC)-Ontario, Canada
- Ontario Ministry of the Environment, Water Quality Section (MOE)-Ontario, Canada
- Acid Deposition and Oxidant Research Center (ADORC)-Niigata-shi, Japan

Each laboratory's 50th and 90th percentile differences on replicate samples were summed....

Analyta	CAL		CAL	ESE		ESE
Analyte	ptile 50th	ptile 90th	Sum	ptile 50th	ptile 90th	Sum
Calcium	0.002	0.006	0.008	0.002	0.012	0.014
Chloride	0.002	0.012	0.014	0.003	0.009	0.012



and the labs were
ranked on the basis of the sum
of the 50 th and 90 th percentiles

Lab	Sum	Rank
ADORC	0.001	
CAL	0.001	Tie 1 st
SA	0.001	
ESE	0.002	$-Tie 4^{th}$
MSC	0.002	
MOE	0.005	6



How did the CAL rank out of 6 labs on replicate sample analysis in 2001?

Summary of CAL's Rankings:

> $1^{st} - 2$ $2^{nd} - 1$ $3^{rd} - 3$ $4^{th} - 1$ $5^{th} - 3$

Analyte	Rank
Ammonium	tie 3 rd
Calcium	3
Chloride	5
Hydrogen Ion	1
Magnesium	tie 1 st
Nitrate	5
Potassium	5
Sodium	tie 4 th
Sulfate	3
Specific Conductance	2




































USGS

































science for a changin

Number of Analyte Determinations Greater than the MDL for Ultrapure Deionized-Water Samples During 2001

Analyte	ADORC	CAL	ESE	MOE	MSC	SA
Calcium	1					
Magnesium		1				
Sodium				1		
Potassium						
Ammonium	1			1	1	
Chloride				1		
Nitrate						
Sulfate						

N = 8 samples per laboratory MDL - Method Detection Limit





Summary

• The CAL performed well in the Interlaboratory Comparison Program in 2001

Finished in top 3 out of 6 laboratories in the replicate analysis for 6 of the 10 analytes

• Very few outliers on the control charts

• Only had 1 analysis exceed the MDL for magnesium in the Ultrapure DI samples



Intersite Comparison Program 2000-2001

National Atmospheric Deposition Program – Spring 2002 Interim Meeting NOS Subcommittee Minutes: Attachment 16

Intersite Comparison Program



Onsite pH measurements are considered to be more accurate of initial precipitation chemistry than subsequent laboratory measurements

Intersite-Comparison Program is designed to assess the accuracy of onsite pH and specific conductance measurements

A synthetic precipitation sample prepared by the USGS is mailed to all site operators, who are asked to determine the pH and specific conductance

If measurements are outside of the acceptable range, the operator is asked to participate in a follow-up study and perform pH and specific conductance measurements on additional samples

Intersite Comparison Program

- Four Intersite Comparison studies were conducted during spring and fall of 2000-2001
- High participation indicates that site operators show willingness and interest in the study

and the second sec
and the second s
A STARLEY AND A ST
Sales and the second
And the second
STATISTICS AND A VIEW
The subscription of the second s
STEP TANK NOW
R. L. C. BRANCH MARKED MARK
A DECEMBER OF A
And the second se
 Second and second and the second s
the second s
A REAL PROPERTY AND A REAL
A PERSON AND A PER
of the standard standard standard standards
A STATE OF THE AREA STATE AND A STATE OF THE AREA STATE
AN AND MANY AND
NUT INTEREST SHIT IN CALL AND INTEREST AND AND
·····································
the second second second second
and the second states of the second states and the
A STATE OF A STATE OF A STATE OF A STATE
and the second
The second s
NAME AND ADDRESS OF A DOCUMENT OF A DOCUMENTA OF A DOCUMENT
A DELAS
A REAL PROPERTY OF A REAL PROPERTY.
A DESCRIPTION OF THE OWNER OF THE
ALC AND A REAL AND A
and the second s
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
A CONTRACT OF THE OWNER OF THE OWNER OF
and the second se

<u>Study</u>	Active Sites	<u>Responses</u>
44	218	213
45	219	211
46	220	206
47	223	212



pH Values from Previous Intersite Comparison Studies



Network Median pH (1999) – 4.84



Network Median Specific Conductance (1999) – 12.9 μ S/cm

% Met pH Goal
% Met Specific Conductance Goal



100

90

Intersite Comparison Study Number

Sites that did not meet Intersite Comparison goals during 2000 and 2001



- Failed 3 of 4 pH measurements
- Failed 2 of 4 specific conductance measurements
- Failed 3 of 4 specific conductance measurements

VI01

Variability of pH measurements correlated with pH of the sample



Variability of specific conductance measurements correlated with specific conductance of the sample



Median SC
of all30.6538.326.115.7observations

Intersite Comparison Program Follow-up

Evaluation of Site Operator's Performance

 $\mathbf{Z}\text{-}\mathbf{score} = \frac{\mathbf{x} - \mathbf{x}}{\mathbf{fps}}\mathbf{\underline{m}}$

where x = individual observation

 $\underline{\mathbf{x}}_{\mathbf{m}}$ = median of all observations

fps = **f**-**pseudosigma of all observations**

 $\frac{(75^{th}-25^{th} \text{ percentile})}{1.349}$

• Z-values account for deviation from accuracy limits, based on difficulty of measuring pH at specific hydrogen ion concentrations

• Cumulative z-values are considered for three previous intersite-comparison studies in assigning site operators, who failed to meet accuracy goals, into four categories



Intersite Comparison Program

Follow-up



Intersite Comparison Program

Please visit our website:

http://btdqs.usgs.gov/precip/project_overview/index.htm



DATA RELAY IN THE BRAVE NEW WORLD

National Atmospheric Deposition Program – Spring 2002 Interim Meeting

NOS Subcommittee Minutes: Attachment 17

SITE TRIUMVIRATE







IN THE BRAVE NEW WORLD BAD STUFF HAPPENS

Current wind speed at Bondville is 0 m/s...hold it...can that be true??

OPTIONS

- Remote relay only
- On-site relay only
- Combination of the above
- ????????



GOES At 1453Z on April 26, a GOES-10 frame break was observed with 5 scans lost attributed to loss of signal synchronization at CDA. At 0135Z on April 28, a GOES-10 frame break was observed with 4 scans lost attributed to hi BER at CDA, reasons unknown.

REMOTE RELAY



Lots of manufacturers offer prepackaged systems using GOES or other satellite platforms.

Cell phone and local radio transmission also are possibilities.

Will a mixture of remote relay techniques be necessary?

How to relay data to operator?

LET'S GO SHOPPING AT CAMPBELL SCIENTIFIC!

- CR10X
- Keyboard for same
- Optical isolated RS 232
- High Data Rate GOES with box, data cables solar power, batteries

\$1119.00 \$260.00 \$145.00

\$3536.00 \$5060

Source Campbell 2002 price sheet, some quantity discounts may apply
WHAT A SMALL BAND OF PITTSBURGHIAN'S CAN DO FOR YOU

Routine repairs will include:



- Grounding and surge protector checks
- YAG antenna orientation and performance checks
- Calibration of tipping bucket rain gage
- Inspection of power for platform AC or Solar/ battery
- Phone line check if applicable
- House keeping for the site
 - Observation of security rules at dams, reservoirs and locks.

Reporting of DCP repairs

- Report within 24 hours via e-mail, phone call, fax transmission to designated individual
- Use reporting method that district has designed

OR

- Provide a report jointly developed with the district to provide all necessary information and data on a DCP repair
- ATS will NOT leave the platform without assuring that:
 - > DCP is operating properly
 - > All associated hardware if functioning and calibrated e.g. tipping bucket rain gage, incremental shaft encoder, temperature measurement etc.
 - > All latches on instruments are fastened and all gates and doors are locked.
 - > ATS can also provide a first line of electronic repair on DCP hardware

On-site relay

- CASTNET- remote phone line query, hardcopy back-up
- IMPROVE- flash memory, ???

- What does NADP require?
- What type of technology will site operators be accustomed to?

On-site relay



LET'S GO SHOPPING AT CAMPBELL SCIENTIFIC!

- CR10X
- · Keyboard for same
- NEMA 4 shelter power supply
- Optical isolated RS 232
- 4 MB storage module

– or

- PCMCIA adapter
- CF cartridge

\$1119.00

- \$ 260.00
- \$ 420
- \$145.00

\$ 435

\$???? \$ 20.00

\$ 30.00

~\$2500.00

CyberTracker

The most efficient way to gather large quantities of data for field observations, even by non-literate users, at a level of detail not possible before.

The CyberTracker field computer is designed to be quick and easy to use in the field, even by non-literate users. A userfriendly interface developed for PalmOS computers allows field workers to record more than 300 observations per day. The Palm or Visor can be linked to a GPS.

The CyberTracker software allows users with no programming skills to:

•Design and edit a database.

•Use the Screen Writer to customise a screen sequences.

Gather data with the CyberTracker field computer (with optional GPS and barcode scanner).

 View data with the CyberTracker Geographic Information System.

Export data, e.g. to Excel or ArcView, for advanced analysis.



ONSET Engineering

HOBO H08 OEM

4-Channel Data Logger The HOBO® H08 OEM 4-Channel External logger and 4-Channel External-IP (independent power) are available to qualified* OEMs to build customized loggers. OEMs can add their own sensors and use Onset's "Educator" software to customize the header information and specify measurement units for each channel. Endusers can use standard BoxCar® Pro software for PC's to launch loggers, readout loggers, plot data, and export data files to popular spreadsheet packages.



COSTS ARE NOT COMPOUNDING

- Some type of on-site data relay will be needed due to inevitable problems with remote relay and associated costs.
- On-site relay should be designed to Pentium desktop standard
- All systems must compartmentalize components for field replacement.