

Attachment 1, NADP NOS Minutes, Spring 2003

FINAL AGENDA

NADP Spring Business Meeting

Network Operations Subcommittee Meeting

March 25-26, 2003

"NOS"

Tuesday, March 25

1:00-1:10	Agenda Overview and approval of Fall 2002 NOS Meeting Minutes	Mark Nilles
1:15-2:30	External QA findings and future plans	Greg Wetherbee
2:30-3:00	Break	
3:00-3:30	NADP collector dimensions - the future?	Scott Dossett
3:30-3:40	NED report	Scott Dossett
3:40-3:50	Archive sample utilization report and approvals	Karen Harlin
3:50-4:50	ATS External Site Survey/Audit Reports and plans	John Shimshock and Tom Jones
4:50-5:20	Report - NADP siting criteria ad-hoc committee	Chris Lehmann
5:20	Adjourn	

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
NATIONAL TRENDS NETWORK
EXTERNAL QUALITY ASSURANCE PROJECT

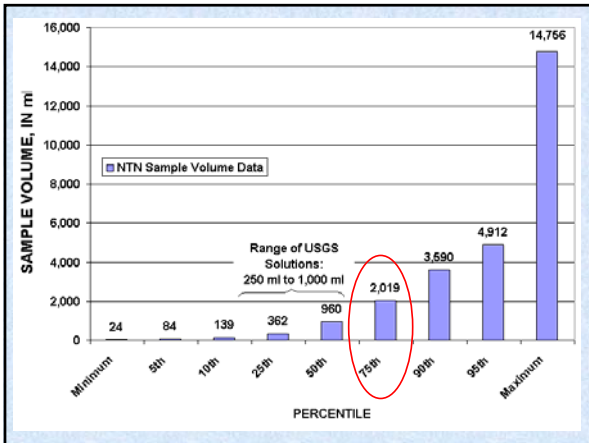
UPDATE FOR SPRING 2003 NADP BUSINESS MEETING

Greg Wetherbee: wetherbe@usgs.gov
Natalie Latysh: nlatysh@usgs.gov



2002 / 2003 External QA Project Changes

- △ NYSDEC joined Interlaboratory Program in 2002
... WELCOME!
- △ Sample Handling Evaluation (SHE) Program Replaced Blind Audit.
... NOT BLIND TO LAB
- △ Sample volumes for SHE and Field Audit now 250, 1,000 and 2,000 ml.
... MORE REPRESENTATIVE



Blind Audit and Field Audit Programs

- ➡ Blind Audit – Intended to measure error and bias from sample handling without field exposure of collection buckets. CAL “blind” to QA samples.
- ➡ Field Audit – Measures error and bias from sample handling and field exposure of collection buckets.

2002 Blind Audit and Field Audit Program Results

- ➡ Preliminary Analysis of 2002 data completed
- ➡ Results are similar to 2000-01
- Nothing new to report...

Collocated-Sampler Program

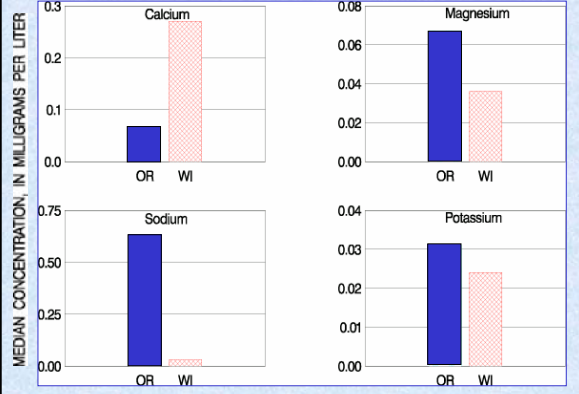
- ➡ Quantify bias and total absolute error of NADP/NTN measurements

WY02 Collocated-Sampler Program

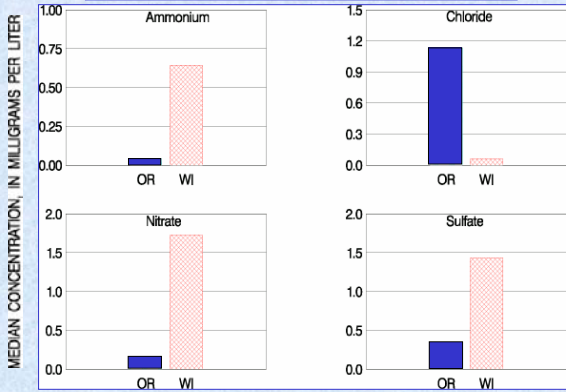
WI98 / 98WI



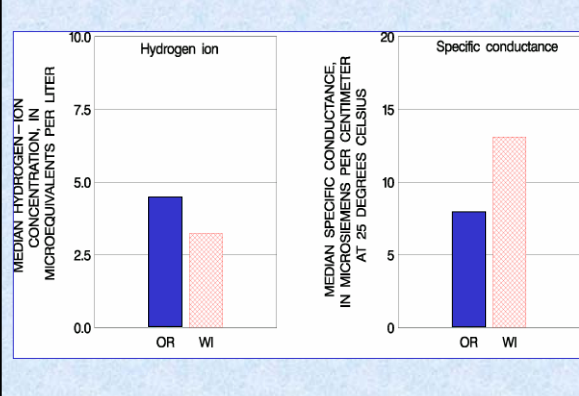
WATER YEAR 2002 COLLOCATED RESULTS



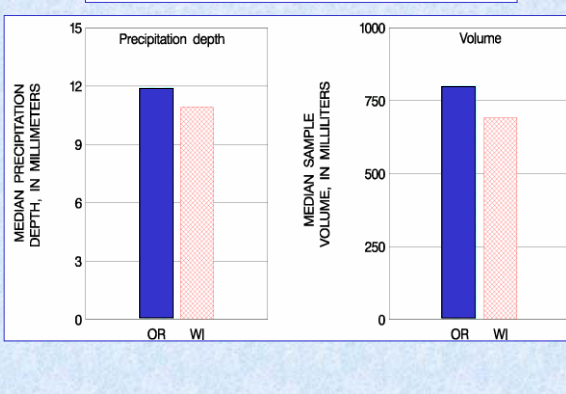
WATER YEAR 2002 COLLOCATED RESULTS



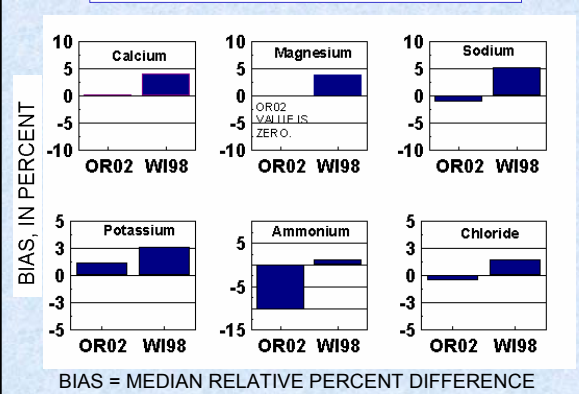
WATER YEAR 2002 COLLOCATED RESULTS



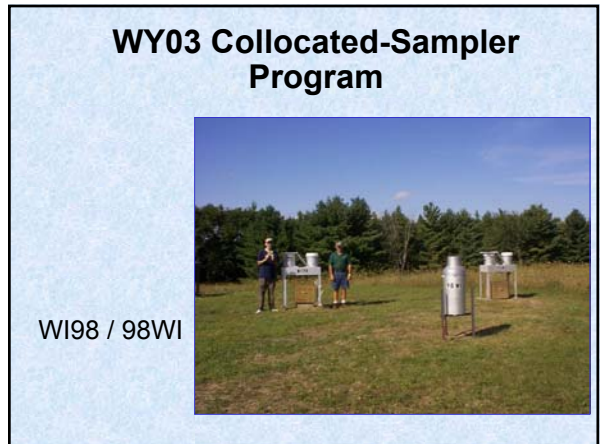
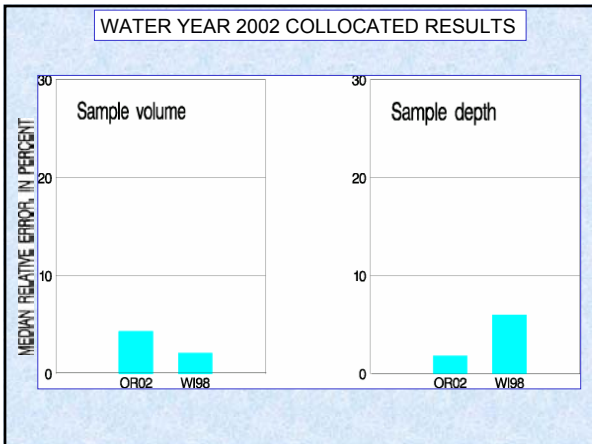
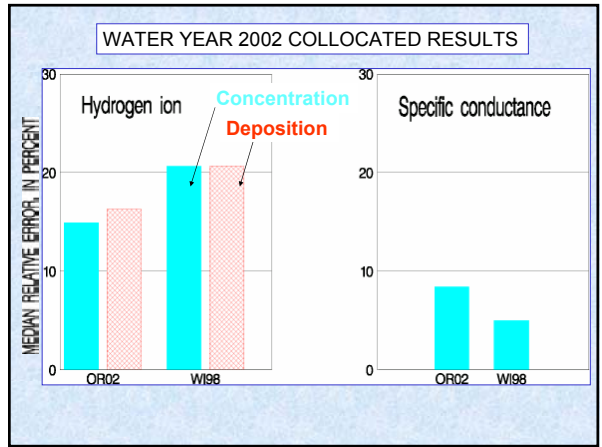
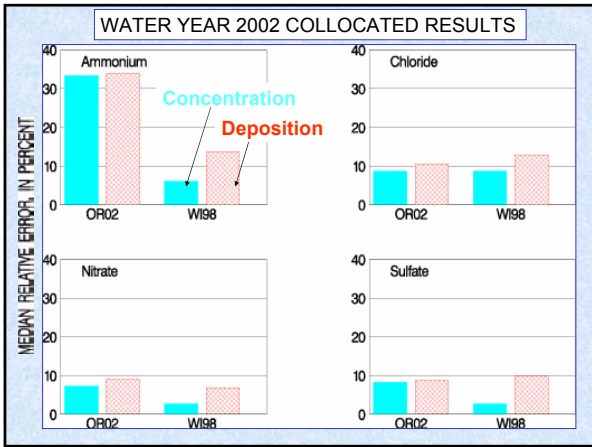
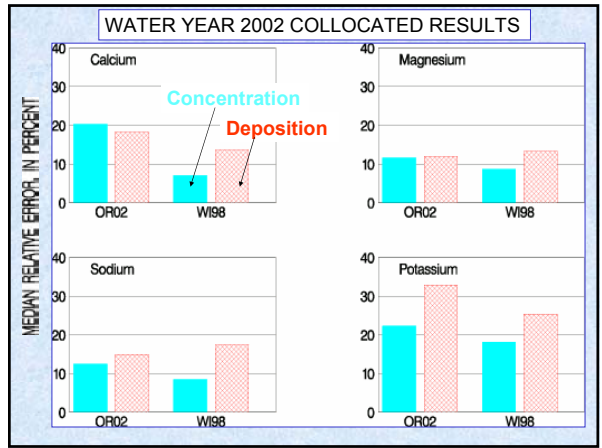
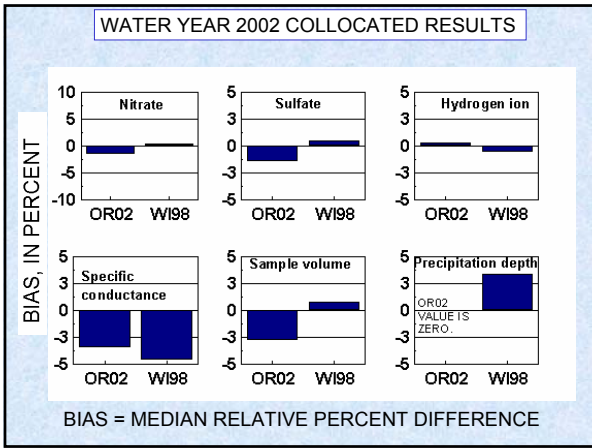
WATER YEAR 2002 COLLOCATED RESULTS



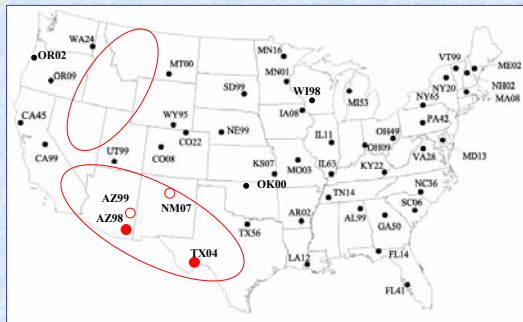
WATER YEAR 2002 COLLOCATED RESULTS



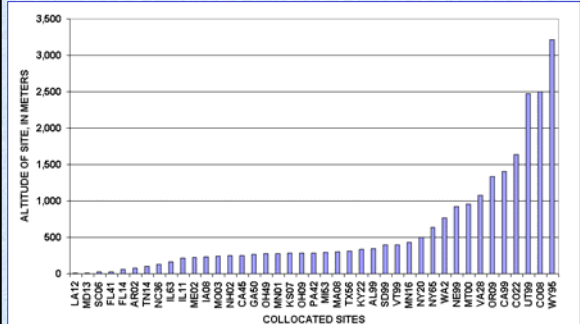
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WY04 Collocated-Sampler Site Selection



Collocated-Sampler Program Site Altitudes



Collocated-Sampler Program

...A Fresh Look

- ? Install several, permanent collocated sites and stop shipping equipment to various locations?
- ? Make the program more research oriented, e.g. site criteria, instrumentation characteristics, etc.?
- ? When NTN equipment is modernized, do we start over with new equipment, or will we collocate old equipment with new?

Interlaboratory Comparison Program

- ➡ Quantify bias and precision of Central Analytical Laboratory (CAL) data
- ➡ Compare CAL performance to other laboratories in USA, Canada, Japan, and Norway

2002 ACCURACY RESULTS FOR CATIONS

	SOLUTION SP98c				
	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Ammonium (mg/L)
NIST Upper Limit	0.018	0.042	0.229	0.068	0.132
NIST Lower Limit	0.014	0.035	0.187	0.055	0.108
CAL Median Values	0.013	0.035	0.211	0.059	0.1
	SOLUTION SP97				
NIST Upper Limit	0.143	0.021	0.027	0.021	0.319
NIST Lower Limit	0.117	0.017	0.022	0.017	0.261
CAL Median Values	0.124	0.017	0.022	0.018	0.28

NIST = Solution concentrations are traceable to NIST standards

2002 ACCURACY RESULTS FOR ANIONS

	SOLUTION SP98c		
	Chloride (mg/L)	Nitrate (mg/L)	Sulfate (mg/L)
NIST Upper Limit	0.257	0.627	2.671
NIST Lower Limit	0.211	0.513	2.185
CAL Median Values	0.228	0.565	2.431
	SOLUTION SP97		
NIST Upper Limit	0.061	1.298	1.254
NIST Lower Limit	0.050	1.062	1.026
CAL Median Values	0.055	1.173	1.13

NIST = Solution concentrations are traceable to NIST standards

Attachment 2a, NADP NOS Minutes, Spring 2003

2002 ACCURACY RESULTS FOR HYDROGEN ION AND SPECIFIC CONDUCTANCE

SOLUTION SP98c		
	Hydrogen Ion ($\mu\text{Eq/L}$)	Conductance ($\mu\text{S/cm}$)
NIST Upper Limit	.	22.495
NIST Lower Limit	.	18.405
CAL Median Values	39.811	22.656

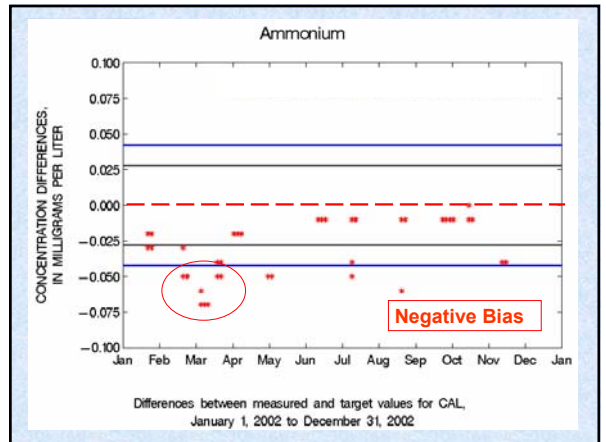
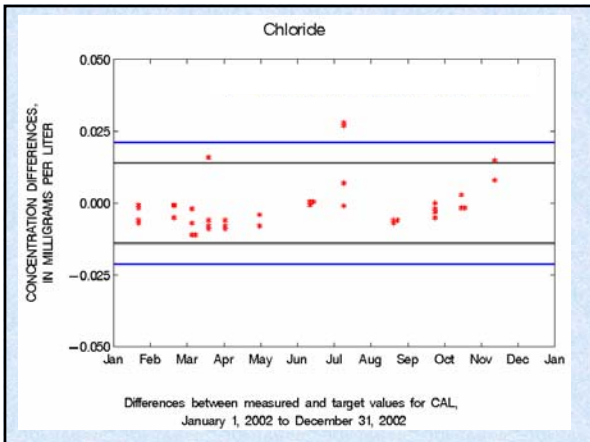
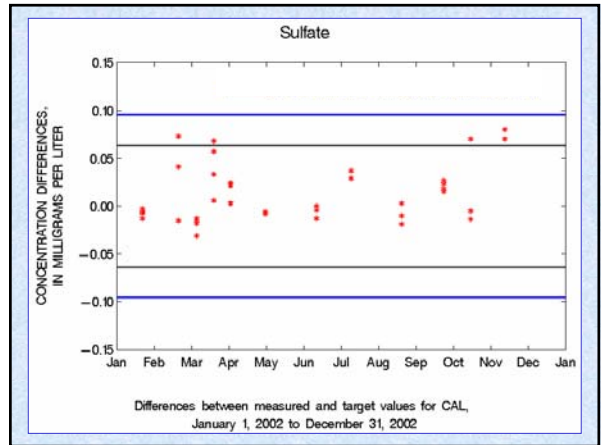
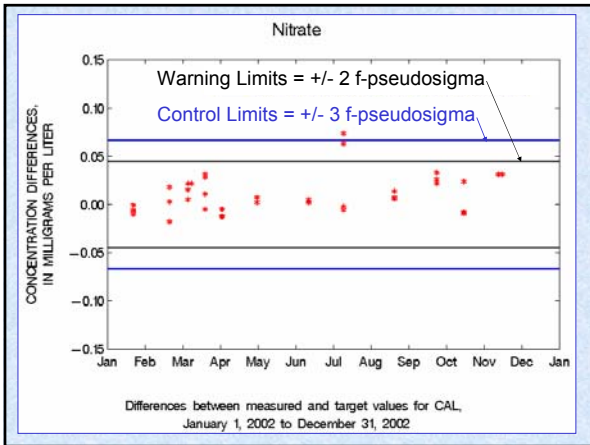
SOLUTION SP97		
	Hydrogen Ion ($\mu\text{Eq/L}$)	Conductance ($\mu\text{S/cm}$)
NIST Upper Limit	.	12.353
NIST Lower Limit	.	10.107
CAL Median Values	17.58	12.15

NIST = Solution concentrations are traceable to NIST standards

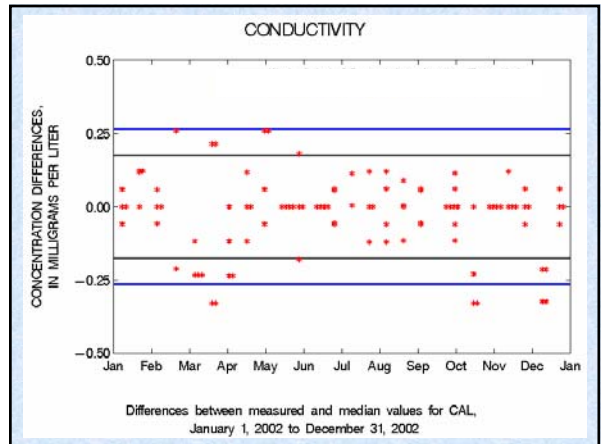
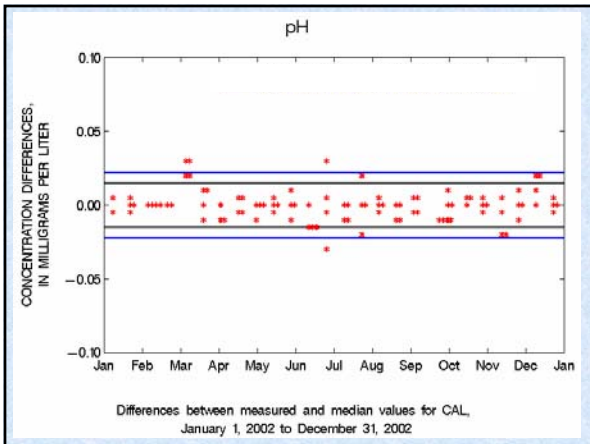
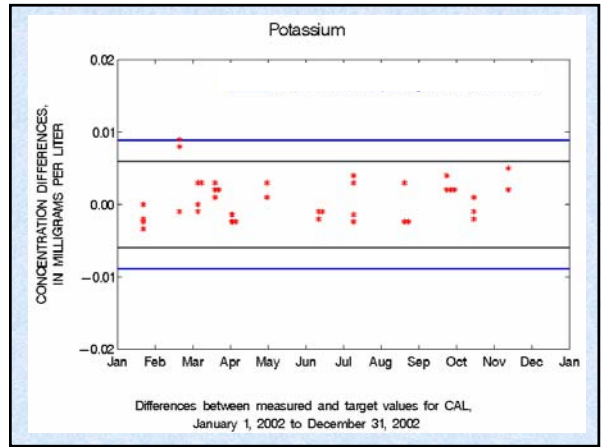
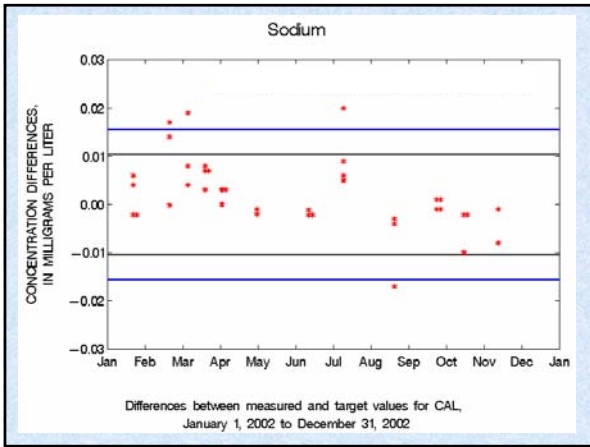
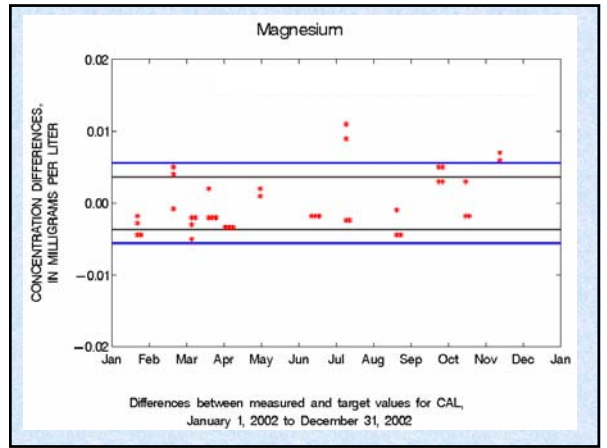
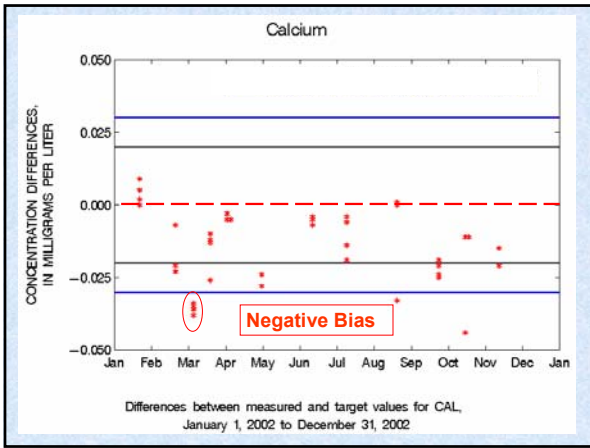
2002 INTERLABORATORY RESULTS FOR CAL

Analyte	Absolute Differences	
	50th Percentile	90th Percentile
Calcium	0.002	0.004
Magnesium	0	0.001
Sodium	0.001	0.008
Potassium	0.001	0.008
Ammonium	0	0.010
Chloride	0.002	0.020
Nitrate	0.003	0.010
Sulfate	0.006	0.018
Hydrogen Ion	0.106	0.898
Specific Conductance	0.113	0.240

Units: Major Ions in mg/L, Hydrogen Ion in $\mu\text{eq/L}$; Specific Conductance in $\mu\text{S/cm}$



Attachment 2a, NADP NOS Minutes, Spring 2003



**2002 STANDARDIZED
NUMBER OF DETECTIONS IN DEIONIZED WATER BLANKS
[N = NONE, 8 BLANKS ANALYZED]**

Analyte	Number of Determinations Greater Than Detection Limit
Calcium	N
Magnesium	N
Sodium	1
Potassium	N
Ammonium	N
Chloride	N
Nitrate	N
Sulfate	N

**2002 Interlaboratory
Comparison Program Summary**



CAL performance in 2002 was consistent with previous 2 years.



Greater than 90 percent of data within control limits for all constituents, except for ammonium. NH_4^+ outside 2001 control limits Feb – Mar.



Negative bias evident for NH_4^+ and Ca^{2+}

Intersite Program

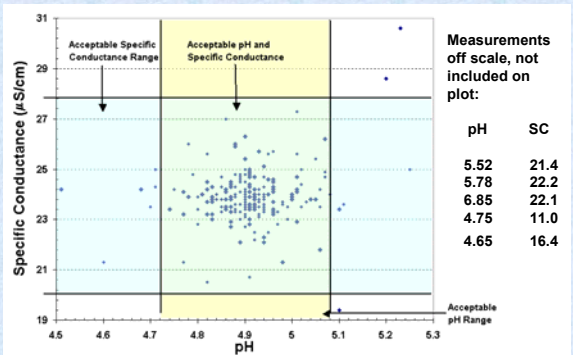


Quantify precision of site operator field measurements of pH and specific conductance



Follow-up with site operators not attaining measurement goals to help improve future data quality

2002 Intersite Results Study 48

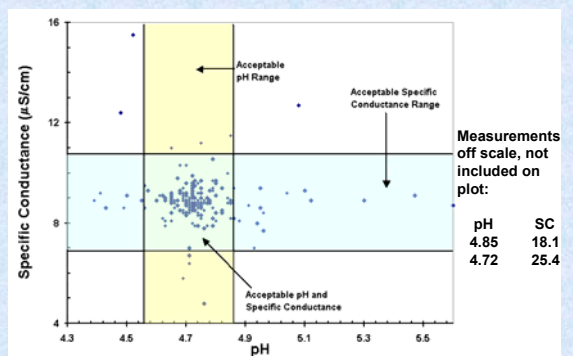


2002 Intersite Results

Spring Study 48

- 212 of 230 (**92.2%**) site operators responded
- pH: **92.4%** in acceptable range
- SC: **97.6%** in acceptable range

2002 Intersite Results Study 49



2002 Intersite Results

Fall Study 49

- 211 of 238 (88.7%) site operators responded
- pH: 87.2% in acceptable range
- SC: 91.5% in acceptable range
- completely inoperable equipment @ 2 sites
- inoperable specific conductance @ 3 sites

2002 Intersite Comparison Program Summary



Site operators continue to show greater than 80 percent attainment of pH and specific conductance goals.

Fewer operators participated and fewer met pH and specific conductance goals in the fall than in the spring during 2002.

FY 2002 External QA Project Accomplishments

APPROVED! USGS WRIR – Evaluation of Rain Gages for NADP, By John Gordon

APPROVED! USGS WRIR – 1997-99 QA Results for NADP/NTN, By J. Gordon, N. Latysh, and S. Lindholm

FY 2003 External QA Project Accomplishments

SUBMITTED! Water, Air and Soil Pollution, Investigation of differences between field and laboratory pH measurements, - N. Latysh & J. Gordon

In Review USGS WRIR, 2000-01 QA Results for NADP/NTN, - G. Wetherbee, N. Latysh & J. Gordon

In Review USGS WRIR, Analysis of Collocated Program Results 1988-2001, - G. Wetherbee & N. Latysh

FY 2003 External QA Project Planned Activities

IMPLEMENTED! SHE Program, N. Latysh

In Progress Update Website, - N. Latysh & G. Wetherbee

Started Update USGS WRIR 90-4029 Project Procedures, - N. Latysh & G. Wetherbee

FY 2003 External QA Project Planned Activities

In Progress Quality Assurance Project Plan / Data Quality Objectives, - G. Wetherbee

To Do Create Access Database & Automate Data Handling, - G. Wetherbee & N. Latysh

Attachment 2a, NADP NOS Minutes, Spring 2003

USGS External QA Project

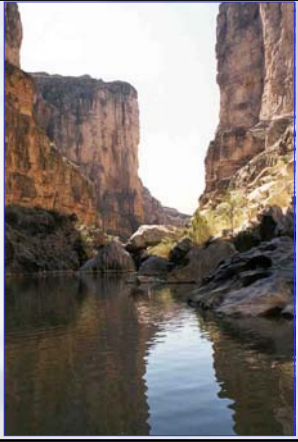
Greg Wetherbee, Chemist
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nlatysh@usgs.gov

Kevin Burke, Hydrologic Aid

<http://bqs.usgs.gov/>

Rio Grande River,
Big Bend National Park



NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
NATIONAL TRENDS NETWORK
EXTERNAL QUALITY ASSURANCE PROJECT

SELECTED RESULTS FROM THE
INTERLABORATORY COMPARISON PROGRAM

Greg Wetherbee: wetherbe@usgs.gov

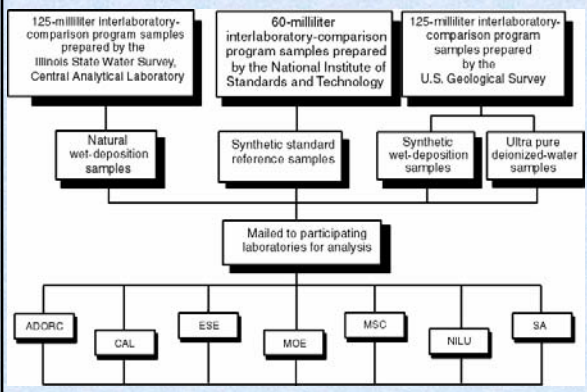
Natalie Latysh: latysh@usgs.gov



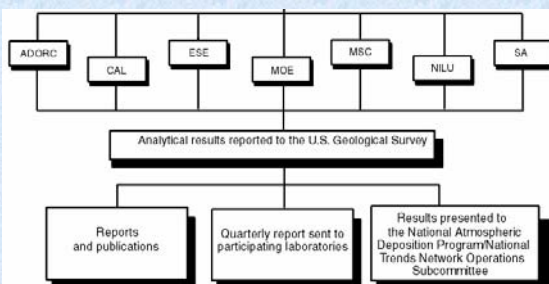
Interlaboratory Comparison Program

- ➡ Quantify bias and precision of data produced by the NADP/NTN Central Analytical Laboratory (CAL)
- ➡ Compare performance of the CAL with other laboratories routinely analyzing low ionic strength samples

USGS INTERLABORATORY COMPARISON PROGRAM



USGS INTERLABORATORY COMPARISON PROGRAM



EXPLANATION OF LABORATORY IDENTIFIERS

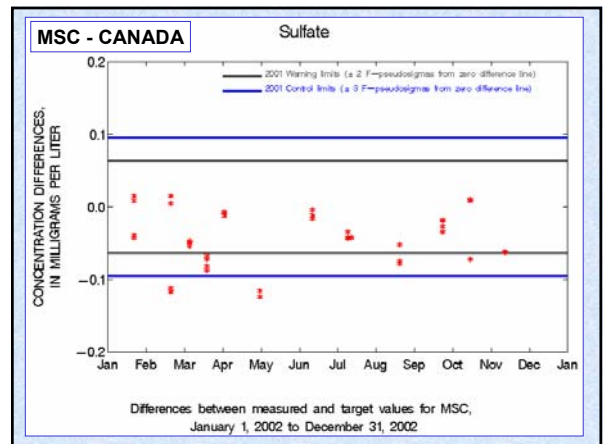
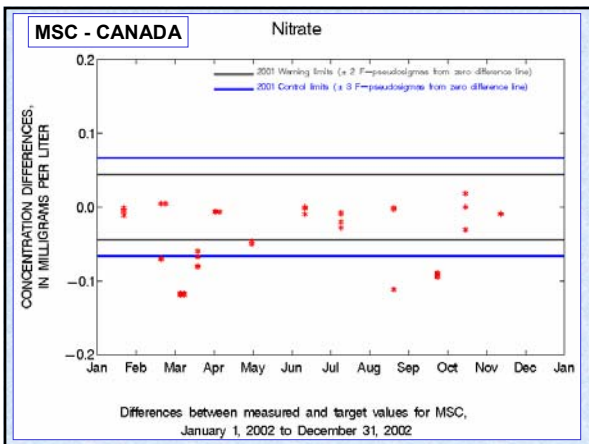
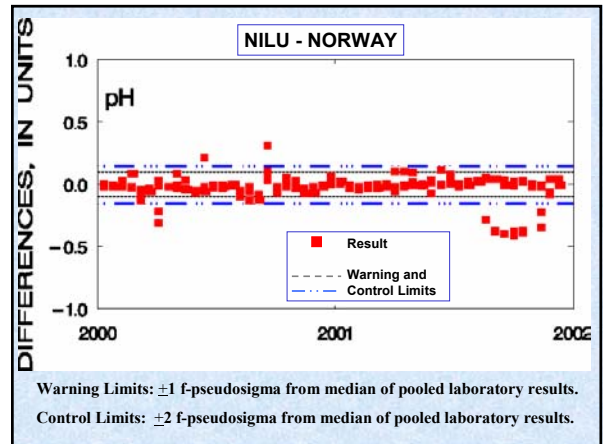
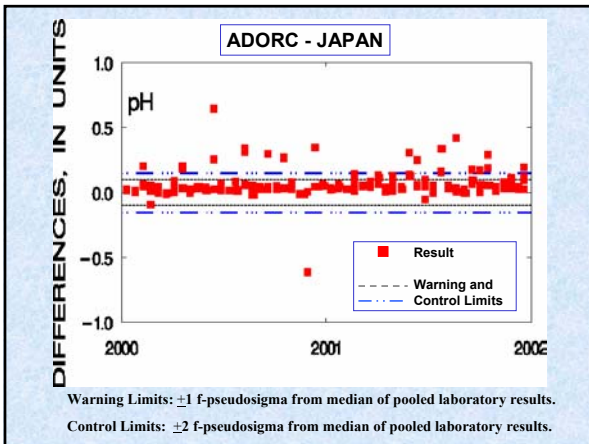
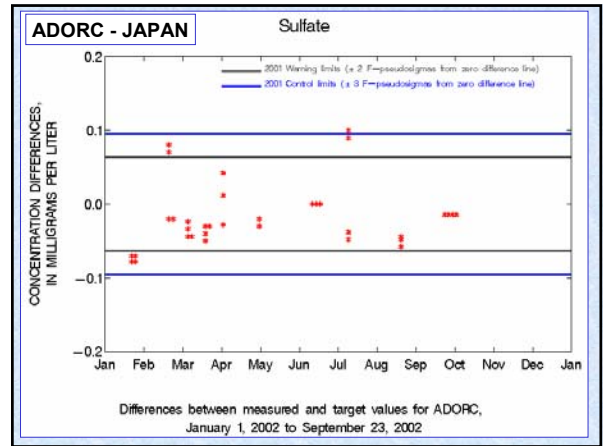
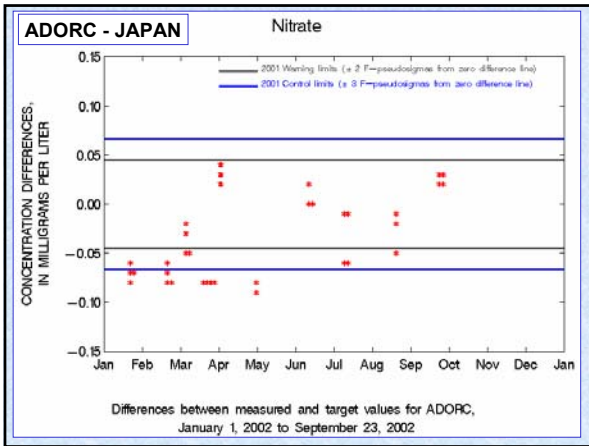
- ADORC = ACID DEPOSITION AND OXIDANT RESEARCH CENTER, JAPAN
- CAL = CENTRAL ANALYTICAL LABORATORY, ILLINOIS, USA
- ESE = ENVIRONMENTAL SCIENCE AND ENGINEERING, INC., FLORIDA, USA
- RENAMED MACTEK IN 2002
- MOE = ONTARIO MINISTRY OF THE ENVIRONMENT, DORSET RESEARCH FACILITY, CANADA
- MSC = METEOROLOGICAL SERVICES OF CANADA, CANADA
- NILU = NORWEGIAN INSTITUTE OF AIR RESEARCH, NORWAY
- NYSDEC = NEW YORK STATE DEPARTMENT OF ENVIRONMENT CENTER, NEW YORK, USA (NEW LAB ADDED IN 2002)
- SA = SHEPARD ANALYTICAL SERVICES, CALIFORNIA, USA

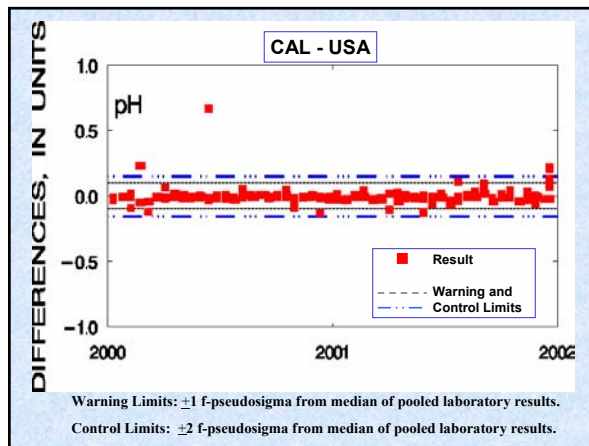
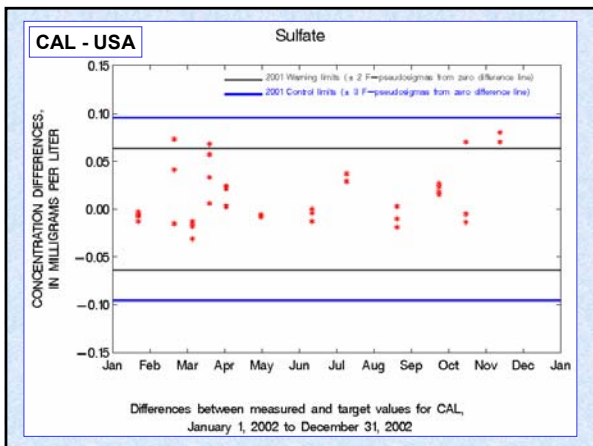
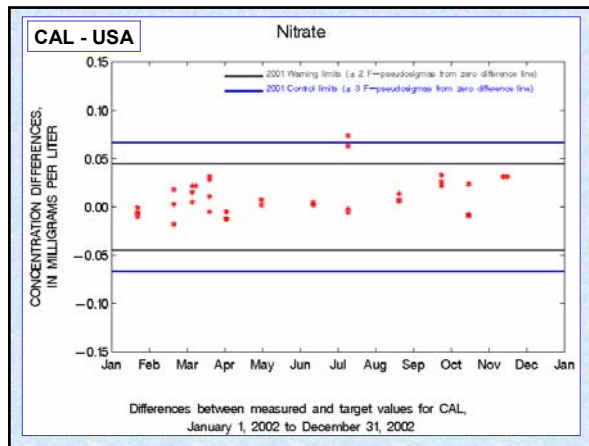
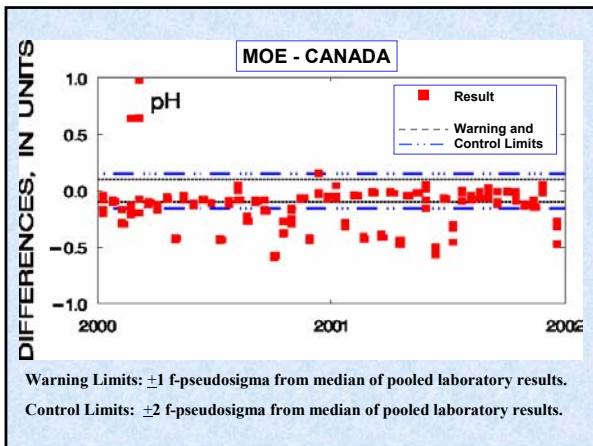
2000 RESULTS FOR CATIONS

LABORATORY	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Ammonium (mg/L)	EXPLANATION
SOLUTION: SP97b						
ADORC	0.107	0.017	0.016	0.012	0.290	VALUE WITHIN NIST RANGE VALUE WITHIN 10% NIST RANGE VALUE >10% OUTSIDE NIST RANGE
CAL	0.128	0.025	0.026	0.016	0.270	
ESE	0.119	0.024	0.018	0.014	0.300	
MOE	0.120	0.025	0.025	0.015	0.290	
MSC	0.128	0.025	0.025	-0.020	0.265	
NILU	0.120	0.020	0.020	0.02	0.260	
SA	0.119	0.024	0.024	0.016	0.290	
SOLUTION: SP98b						
ADORC	0.009	0.026	0.249	0.045	0.120	
CAL	0.013	0.039	0.270	0.055	0.110	
ESE	0.013	0.036	0.248	0.051	0.120	
MOE	-0.020	0.040	0.250	0.055	0.130	
MSC	-	0.039	0.264	0.056	0.117	
NILU	0.010	0.040	0.260	0.040	0.100	
SA	0.010	0.037	0.262	0.052	0.120	

NIST = Solution concentrations are traceable to NIST standards

Attachment 2b, NADP NOS Minutes, Spring 2003





USGS Interlaboratory Comparison Program



Provides a low-cost laboratory quality assurance program for 8 laboratories analyzing low-ionic strength samples.



Provides comparison of data quality for wet-deposition monitoring networks in different countries.



Facilitates meaningful comparison of wet-deposition data between several countries.

NADP field sample
container dimensions

ASPECT RATIO

The Future



New Orleans
March 2003

NADP container dimensions
the future



NADP container dimensions
the future



NADP container dimensions
the future

**What do
snow-rollers
have to do
with NADP?**



NADP container dimensions
the future

**#1 They
occur after
light snow!**



NADP container dimensions
the future

**#2 They require
high wind
speeds and open
areas to mature.**



NADP container dimensions the future

- ◆ Question: What is the ideal aspect ratio (depth/width) for an NADP orifice?

NADP container dimensions the future

- ◆ Question: What is the ideal aspect ratio (depth/width) for an NADP orifice?
- ◆ Question: What is the most practical aspect ratio for an NADP orifice?

NADP container dimensions define the problem

- ◆ 1) Collector subject to loss of snow with wind gusts.

NADP container dimensions define the problem

- ◆ 1) Collector subject to loss of snow with wind gusts.
- ◆ 2) We need a sample volume which sets a reasonable "network sensitivity".

NADP container dimensions define the problem

- ◆ 1) Collector subject to loss of snow with wind gusts.
- ◆ 2) We need a sample volume which sets a reasonable "network sensitivity".
- ◆ 3)?

NADP container dimensions

- ◆ 1) Collector subject to loss of snow with wind gusts.

CURRENT WET COLLECTOR PROBLEMS

PUSHING PLANNING FOR NADP SAMPLE COLLECTION PAST 2000

ARE IMPROVEMENTS INCOMPATIBLE WITH NETWORK UNIFORMITY

THE M.I.M. Syndrome

MADE IN MIAMI

(At least) 3 attributes

1. sensor insensitive to light snow particularly associated with winds
2. collector mainframe/driving mechanism extremely susceptible to icing
3. bucket "aspect ratio"-wind scour
The bucket is too wide for being so short or the bucket is too short for being so wide

From
Albuquerque,
NM 1995

NADP container dimensions

Case1		CASE 1
Date Off = 123097		
EVENT NO.	ER opening accounts for	
1	.40	
2	.14	
3	.15	
SUM	0.69	ER predictive volume = 0.69
Total Precipitation as measured by Belfort = 1.70		Actual sample volume = 0.04
Total Sample Volume = 0.04		
Case2		CASE 2
Date Off = 012098		
EVENT NO.	ER opening accounts for	
1	.08	
2	.09	
3	.09	
4	.57	
5	.33	
6	.13	
7	1.80	
8	.05	
9	.21	
SUM	3.35	ER predictive volume = 3.35
Total Precipitation as measured by Belfort = 4.18		Actual sample volume = 0.61
Total Sample Volume = 0.61		

From
Albu
NM

NADP container dimensions

Case1		CASE 1
Date Off = 123097		
EVENT NO.	ER opening accounts for	
1	.40	
2	.14	
3	.15	
SUM	0.69	ER predictive volume = 0.69
Total Precipitation as measured by Belfort = 1.70		Actual sample volume = 0.04
Total Sample Volume = 0.04		
Case2		CASE 2
Date Off = 012098		
EVENT NO.	ER opening accounts for	
1	.08	
2	.09	
3	.09	
4	.57	
5	.33	
6	.13	
7	1.80	
8	.05	
9	.21	
SUM	3.35	ER predictive volume = 3.35
Total Precipitation as measured by Belfort = 4.18		Actual sample volume = 0.61
Total Sample Volume = 0.61		

From
Albu
NM

NADP container dimensions

CASE CLOSED

BUCKET TOO WIDE OR TOO SHORT

From
Albu
NM

Total Precipitation as measured by Belfort = 4.18
Total Sample Volume = 0.61

NADP container dimensions

define the problem

2) We need a sample volume which sets a reasonable "network sensitivity".

NADP container dimensions

2) We need a sample volume which sets a reasonable "network sensitivity".

What is "network sensitivity"?

NADP container dimensions

2) We need a sample volume which sets a reasonable "network sensitivity".

What is "network sensitivity"?

The minimum precipitation amount which, when converted to sample volume, yields sufficient liquid to perform all mandated chemical analyze.

NADP container dimensions

2) Orifice size analysis

NADP container dimensions

2) Orifice size analysis

Orifice Size (radius-cm/diameter-inches)	Container depth (inches)	Aspect ratio (depth/orifice)	Sample (mL) gained per 0.01" precip *	Precipitation for 35 mL sample volume (inches)	Volume based on "network sensitivity" of 0.02" *
14.7/11.5 NADP bucket	9.5	0.8	17.24	0.02	35
10.2/8.0 8" PVC	16	2.0	8.30	0.04	17
15.7/12.4 CAPMON	19.6	1.6	19.65	0.02	39
12.7/10.0 10" PVC	20	2.0	12.86	0.03	26

Literature search

Literature search

- ◆ NWS on-line and ISWS/UI archives

Literature search

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 - Why was the 8" orifice of the NWS standard gage selected?

Literature search

- ◆ NWS on-line and ISWS/UI archives
 - Why was the 8" orifice of the NWS standard gage selected?

NO INFORMATION AVAILABLE

Literature search

◆ NWS on-line and ISWS/UI archives

- What is the "ideal" orifice size?
 - ◆ Krutyka, 1953 discusses minimum orifice requirement to collect representative precipitation amount sample.....~4 inches diameter, no depth figures given

Literature search

◆ NWS on-line and ISWS/UI archives

- ◆ What is the "ideal" orifice size?
 - ◆ Krutyka, 1953
 - ◆ Goodison, et al "WMO Solid Precipitation Intercomparison /measurement Experiment 1998"

Literature search

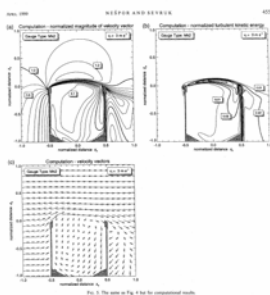
◆ NWS on-line and ISWS/UI archives

- ◆ What is the "ideal" orifice size?
 - ◆ Krutyka, 1953
 - ◆ Goodison, et al "WMO Solid Precipitation Intercomparison Measurement Experiment 1998"
 - Reports typical information about wet losses, evaporative, shielding, country differences
 - (DFIR recommended as secondary standard)

Literature search

◆ NWS on-line and ISWS/UI archives

- ◆ What is the "ideal" orifice size?
 - ◆ Krutyka, 1953
 - ◆ Goodison, 1998
 - ◆ Nespor and Sevruk, 1999



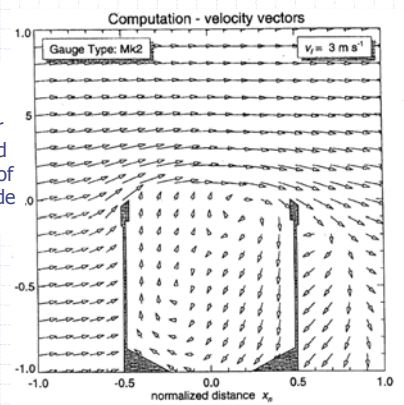
Similarly, the particle acceleration a_x and a_y in the horizontal x and y directions are

$$a_x = -\frac{1}{\rho} \frac{\partial \rho}{\partial x} - \frac{1}{\rho} \frac{\partial \rho}{\partial y} \frac{dy}{dx} - \frac{1}{\rho} \frac{\partial \rho}{\partial z} \frac{dz}{dx} \quad (6)$$

$$a_y = -\frac{1}{\rho} \frac{\partial \rho}{\partial x} \frac{dx}{dy} - \frac{1}{\rho} \frac{\partial \rho}{\partial y} - \frac{1}{\rho} \frac{\partial \rho}{\partial z} \frac{dz}{dy} \quad (7)$$

where u_x and u_y are the velocity components of the particle and the air, corresponding to the horizontal directions x and y , respectively.

The particle drag coefficient C_D depends mainly on Re (equivalent air), when the particle reaches its terminal



Experimental work on turbulence over gage orifice and modeled work of turbulence inside gage.

Literature search

- ◆ NWS on-line and ISWS/UI archives
- ◆ What is the "ideal" orifice size?
 - Krutyka, 1953
 - Goodison, 1998
 - Nespor and Sevrak, 1999

Summary: classic raingage literature is most developed regarding the loss of liquid or frozen precipitation due to wind influences, surface wetting losses, evaporation, loss to heated orifices. **Specific study of loss from open cylinder by wind scouring not found.**

ACTION?

Summary

- 1) NADP experience is conclusive: sample loss due to wind scour from accumulated snow in the 3.5 gallon field container negatively impacts the network.
- 2) Sample volume considerations are an important concern regarding how wide the orifice of a new container should be.
- 3) The width of the the container dictates the depth and hence aspect ratio. This is of particular importance in over all collector design.

NADP container dimensions

2) Orifice size analysis

Orifice Size (radius-cm/ diameter-inches)	Container depth (inches)	Aspect ratio (depth/orifice)	Sample (mL) gained per 0.01" precip *	Precipitation for 35 mL sample volume (inches)	Volume based on "network sensitivity" of 0.02" *
14.7/ 11.5 NADP bucket	9.5	0.8	17.24	0.02	35
10.2/ 8.0 8" PVC	16	2.0	8.30	0.04	17
15.7/ 12.4 CAPMON	19.6	1.6	19.65	0.02	39
12.7/ 10.0 10" PVC	20	2.0	12.86	0.03	26

Recommendations

- ◆ NOS appoint an ad-hoc committee to formulate protocol for and address precipitation collector design issues concerning the implementation of a 10" diameter orifice, 2.0 aspect ratio bag container/field sample collection holder for use on the NTN program. This committee should issue a report (detailing where possible hardware and procedural design) at the October 2003 annual meeting.

Network Equipment Depot Update to NOS New Orleans 2003

- Parts status
- Shipping
- News Items

Parts Status

PART	AVAILABLE	REPLACED (12 mos)
motor boxes	45	122
sensors	54	142
event recorders	39	37
gage clocks	77	137
gage mechanisms	51	17
		====
		455
motor boxes	42	96
sensors	58	99
event recorders	52	55
gage clocks	72	121
gages	65	20
		====
		391

Network growth ~ 5% (335/318)
accounts for 20 additional

Parts Status

HYBRID CLOCKS GOING OUT TO ALL SITES
REQUESTING CLOCKS (limited by supply in a few cases)

51 finished (goal of 50 this year)

100 battery packs finished

TO DATE

51 to sites

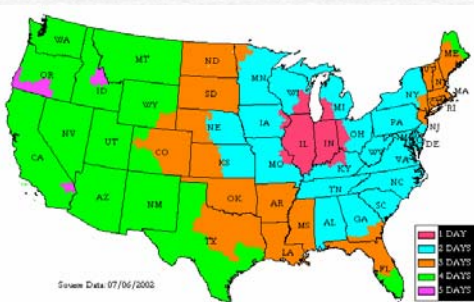
5 of these returned (battery problems causing slow downs)

continuing questions about battery packs (documentation needs to be expanded, life expectancy unknown)

SHIPPING CHANGE

- The change to 3rd Day Select UPS has not had a noticeable effect on the number of samples lost during collector malfunction. The overwhelming factors dictating speed of repair are:
 - Operator weekly checks and prompt communication
 - Uncertainty in diagnosis
 - Good CAL review of incoming data
 - Climate at site (is it conducive to mechanical work?)
 - Parts availability

Regular UPS ground to red and blue
Third Day select to rest



NEWS ITEMS

- We are barely holding our own with provision of motor boxes and sensors to sites. There are aspects of the relationship of the motor box and sensor mechanism related to switching which we do not understand and can not predict.

NEWS ITEMS

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- We are **not** gaining ground due to attempted improvements in repair technique.

NEWS ITEMS

- We are barely holding our own with provision of motor boxes and sensors to sites. There are aspects of the relationship of the motor box and sensor mechanism related to switching which we do not understand and can not predict.
 - We are **not** gaining ground due to attempted improvements in repair technique.
- Improvement + entropy = stasis**

NEWS ITEMS

- 10/02 trip to IN22- review (underground power supply)
- NED IS UNDER FUNDED**

Current system funded at \$2/week. At current revenue (330x2x52) and current part consumption (455) We are funded approximately \$75 per repair(34320/455)*. Although repairs are highly variable, shipping costs alone consume about 10 to 15% of this revenue. Average component repair (BEST Inc.) for 1st quarter 2003 is ~ \$103.25 with a range of \$75 to \$165.

* NED technician not included

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Presentation to NADP-NOS at Spring 2003 Meeting in New Orleans by Karen Harlin
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NADP NTN and AIRMoN Archival Sample Status (updated March 14, 2003)

Below is a summary of recent activities relating to archival sample disposition:

1) Samples to be purged from CAL archives (NTN >5yrs old and AIRMoN > 2yrs old)

Dr. Tyler Coplen, U.S. Geological Survey, Reston, VA 20192, 703-648-5862,
tbcoplen@usgs.gov

This request for 1999 AIRMoN archival samples collected at two sites collocated with NTN (OH09, PA15) was approved via email ballot December 2002. Samples will be sent in April 2003. Dr. Coplen has previously received archival samples from these stations. His research involves testing the hypothesis that daily composited and weekly samples have the same $^{18}\text{O}/^2\text{H}$ signal.

Brian Scott, Aquatic Ecosystem Protection Research Branch, National Water Research Institute, Canada Centre for Inland Waters Burlington, Ontario L7R 4A6, 905-336-4934,
brian.scott@cciw.ca

A request to receive a limited number of additional samples was approved via email ballot December 2002. Dr. Scott has not yet specified the sites of interest. He has received 1997-1998 AIRMoN archival samples from DE02, MD15, and NY67. He plans to measure perfluoroalkanoic acids and their sulfonated analogs, and haloacetic acids (such as trifluoroacetic acid, monochloroacetic acid, dichloroacetic acid and trichloroacetic acid) in monthly pooled samples from these sites. He has published an article on haloacetic acids in Canadian lake water and precipitation (*Environmental Science and Technology*, 34:4266-4272). He wants to extend his analysis to urban U.S. sites and is interested in samples from NTN sites near urban areas. He is also receiving CAPMoN samples.

Dr. Jeffrey Welker, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO 80523-1499, 970-491-179, jwelker@nrel.colostate.edu

All 1999 AIRMoN and 1996 NTN samples that were not sent to other researchers were approved for use by Dr. Welker and James White in a December 2002 email vote. NTN samples from 1996 were sent in February 2003. AIRMoN samples will be shipped in April. Welker and White have a NSF-funded study to determine spatial and temporal patterns of the isotopic (d^{18}O and dD) characteristics of precipitation. These samples will be used to strengthen their analysis during a year that is intermediate between El Nino and La Nina climate phases. Their findings have been presented at the Fall 2002 NADP meeting and the December 2002 AGU meeting.

Dr. Emi Ito, Dept. Geology & Geophysics and Limnological Research Center, University of Minnesota, Minneapolis, MN 55455, 612-624-7881, eito@umn.edu

1996 archival NTN samples from 8 sites (IA08, LA12, MT07, NE15, NY52, NC03, WI25, PR20) were approved for Dr. Ito, however, her instrument is down and she approved sending them to Dr. Welker for 1996. These samples were shipped to Welker and White in February 2003. Dr. Ito's research seeks to obtain a modern calibration of the hydrogen and oxygen isotopic ratios of meteoric water at selected NADP sites over a 5-

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year period. By constructing time series records of the data at these sites, she hopes to establish the relationship between isotopic ratios in precipitation and in lacustrine carbonates, soil carbonates, aquatic cellulose, etc. She has received archival samples from 8-25 sites since 1993. Dr. Ito has approval for up to 25 stations through 1997.

Stephen Monroe, Hydrologic Technician, USGS Water Resources Division, Flagstaff, AZ 86002, 928-556-7141, samonroe@usgs.gov
NTN 1996 archival samples and active archival samples from 1997 to 2001 from AZ03 were sent to Dr. Monroe in February 2003. His request for access to active and expired archival samples for a site in northern Arizona (AZ03) was approved by the executive committee in July 2003. His research is titled "Hydrogeologic Assessment of South Rim Area, Grand Canyon National Park." The project's objectives are 1) determine if local or regional recharge contribute to selected south rim springs issuing from the regional limestone aquifers and 2) develop baseline water-chemistry information for selected springs. Samples will be measured for tritium, carbon 13/12, oxygen 18/16, and hydrogen 2/1. The results of these analyses will be used to define isotopic characteristics of precipitation at the south rim of the Grand Canyon. These data will be used to complement well and spring data from this region to address groundwater flow path and residence time questions.

Dr. Madhav Machavaram, E.O. Lawrence Berkeley National Laboratory, Berkeley, CA 94720, 510-486-5026, MVMachavaram@lbl.gov
A request for 1996 NTN samples from selected Midwestern sites (CA-67, CA-95, OR-10, WA-99, CO-99, OK-00, TX-10, TX-56, FL-03, MI-26) and future samples from these sites as archives become available was approved by an email vote December 2002. Samples from these stations will be used to study the stable isotope variations in North American precipitation which are mainly due to the El Nino effect on the climate. Dr. Machavaram has received NTN active archive samples from nine sites and presented preliminary results at the 2002 NADP fall meeting. He is using use ^{18}O and ^2H measurements to identify water body or land surface sources of water vapor producing the clouds and precipitation at these sites. By determining water vapor sources over space and time, Dr. Machavaram hopes to improve our understanding of hydrologic cycling in the southern Great Plains and how changes in the cycle influence climate (Note: Dr. Welker also requested these sites, therefore, they were split and sent to both researchers)

(2) Active Archival Samples

(NTN <5 yrs old; AIRMoN < 2 yrs old; up to 30 mL is available since a minimum volume of 30 mL must be retained in CAL archives)

Dr. Madhav Machavaram, E.O. Lawrence Berkeley National Laboratory, Berkeley, CA 94720, 510-486-5026, MVMachavaram@lbl.gov
The CAL has sent Dr. Machavaram subsamples for Jan. 1999-Sept. 2000 archival samples from nine NTN sites (AR03, CA42, KS32, LA30, OK00, OK29, TX10, TX56, & UT99). He has been approved for samples through 2002. Additional sample shipments are pending until the end of the mandatory one-year holding period. He will use ^{18}O and

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^2H measurements to identify water body or land surface sources of water vapor producing the clouds and precipitation at these sites. By determining water vapor sources over space and time, Dr. Machavaram hopes to improve our understanding of hydrologic cycling in the southern Great Plains and how changes in the cycle influence climate.

Dr. Tyler Coplen, U.S. Geological Survey, Reston, VA 20192, 703-648-5862, tbcoplen@usgs.gov
Received 1999 NTN samples collected at NTN & AIRMoN collocated sites (OH09, PA15). See Section (1) above for details.

Dr. Jeff Welker, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO 80523-1499, 970-491-179, jwelker@nrel.colostate.edu
In January 2003 Dr. Welker received NTN subsamples from six priority sites (CO02, AZ99, WA14, VT99, FL11, CA99) from 1989-2001. Jim White and Dr. Welker received approval for the active archive samples for 16 sites in July 2002 (AR03, AZ99, CA99, CO02, FL11, IL63, MA13, MT00, NC35, NV05, NY10, TX03, VT99, WA14, WI36, and WY99). Shipments of the remaining sites are pending. These samples are needed to partially complete a component of their NSF project which includes the annual temperature, ^{18}O , & D relationships between 1989 and 2001. They have been working with Bob Larson to develop isotopic maps for the entire U.S. and presented their research at the 2002 NADP fall meeting. Dr. Welker has previously received samples from WI36 and three Oregon sites (02-Alesea, 10-Andrews Forest, and 18-Starkey). Welker (CSU), Ehleringer (U-Utah), Berry (Stanford), Bowling (U-Utah), McDowell (Oregon State), and Bond (Oregon State) are conducting studies in northern Wisconsin and across Oregon addressing carbon and water cycling in deciduous and evergreen forests. They will document the isotopic relationship between the oxygen of precipitation and the oxygen of CO_2 . These measurements will help partition the net flux of CO_2 and understand the fundamental linkages between the water and carbon cycle.

Dr. Carol Kendall, USGS, National Research Program, Menlo Park, CA, 650-329-4576, ckendall@usgs.gov
Dr. Kendall received approval in September 2002 to obtain samples from 100 NTN sites from calendar year 2000. She is interested in determining the temporal and spatial variations in the $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ of nitrate (selected samples will be analyzed for $\delta^{15}\text{N}$ of ammonium) in precipitation. Analysis of these isotopes may help to differentiate among the different types of atmospherically derived nitrate and ammonium, and quantify atmospheric deposition of nitrogen to land and water. The CAL is working with Dr. Kendall to define sites and protocols for volume weighted sample preparation from ~100 sites. Work should begin this spring.

**(3) Incoming excess sample for NTN
(Volume greater than required by CAL, collected by special request only)**

Dr. Mark Castro, Associate Professor, Appalachian Laboratory, University of Maryland Center for Environmental Science, Frostburg, MD 21532-2307, 301-689-7163, castro@al.umces.edu.

Samples from MD03, MD13, PA00, VW18, VA28, and NC35 from 2002 were shipped to Dr. Castro in September and December 2002 and March 2003. This request was approved in July 2002. These samples will be used for his research on total nitrogen (organic and inorganic) in precipitation in the Chesapeake Bay watershed.

Dr. Eugene Perry, Professor of Geology, Northern Illinois Univ., DeKalb, IL, t60ecp1@wpo.cso.niu.edu

Samples from IL46 and MO43 (downwind and upwind respectively from St. Louis) were shipped to Dr. Perry in December 2002. This request was approved May 2001. Dr. Perry will check the feasibility of a newly discovered isotopic parameter that may help make it possible to distinguish sources of sulfate pollution. This research is based on a recent report that atmospheric oxidation of sulfur produces sulfate with an oxygen isotope signature that distinguishes it from virtually all mineral sulfate. This signature (non mass-dependent isotope fraction) can only be determined by measuring the relative abundance of all three stable isotopes of oxygen (^{16}O , ^{17}O , and ^{18}O).

Dr. Carol Maddox, College of Veterinary Medicine, Univ. of Illinois, 217-265-0399, maddox@uiuc.edu

Dr. Maddox has received pooled samples from 20 states west of the Mississippi to determine the potential of detecting *Bacillus anthracis* (anthrax) and other microbes in precipitation. Results are pending.

(4) Pending Archival Samples Requests for Committee Approval

Dr. Dean Malvick, Department of Crop Sciences, Univ. of Illinois, 217-265-5166, dmalvick@uiuc.edu, and **Dr. Carol Maddox**, Univ. of Illinois, College of Veterinary Medicine

Dr. Malvick requests the use of NADP samples to test the concept of monitoring precipitation for plant and animal pathogens. He proposes monitoring two fungal pathogens in the central US. He will work with Dr. Maddox who will monitor 1 or 2 bacterial animal pathogens. They are preparing a proposal to USDA-CSREES. Details on the number of samples and sites of interest are not yet available.

Dr. Ivan Krapac, Geochemist, Illinois State Geological Survey, Champaign, IL, 217-333-6442, krapac@isgs.uiuc.edu

Dr. Krapac has requested current excess volume precipitation samples from Midwestern sites downwind of large feedlots. He is preparing a proposal to USDA to evaluate the use of precipitation and particulate samples to monitor the distribution of antibiotics in air downwind of large feedlots. Details on the number of samples and the sites of interest are not yet available.

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**ATS External Site Survey
Audit Reports**

Tom Jones and John Shimshock

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**All data to the Program office is
completed thru February 2003**

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Plans for 2003 remaining audits include

Arizona, Arkansas, Delaware, Idaho, Indiana,
Iowa, Kentucky, Maryland, Michigan,
Minnesota, New Mexico, Oregon,
Pennsylvania, South Carolina, Tennessee,
Wisconsin

Ontario, Canada

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**For 2003
ATS is looking to audit 110 sites**

From the proposed schedule of sites we have a potential
for 115 sites

Including the sites audited for this year **ATS** is looking
for 95 sites to complete the target of 110 sites

This schedule will be flexible to accommodate new sites that
come on line for this year

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**ATS has audited as of today 15 sites
for 2003**

9 NTN

5 MDN

1 AIRMoN

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Geographic locations of these sites

Florida
Mississippi
Puerto Rico
US Virgin Islands

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This effort has taken the following to accomplish

2,585 Driving miles

13,176 Flying miles

150 Gallons of gasoline

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Of the 9 NTN all are revisited sites

Of the 5 MDN sites, 4 are revisited sites, and
1 new site

The 1 AIRMoN site is a new site

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Recurring problems for revisited sites:

Replacement operator training

Vegetation control

Maintenance of backup batteries

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ATS has looked at 4 AIRMoN sites to date

Issue found for the AIRMoN sites

Accuracy for the 8 inch stick gage

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The protocol for checking the stick gage was developed and approved at a joint meeting held at the ISWS complex in January 2002.

This protocol was tested by the ISWS at the Bondville IL11 site. The error for this test was set for + / - 0.01".

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The test protocol

Equipment:

- 2 plastic volumetric flasks 500 ml class B accuracy, ASTM E288.
- 1 plastic volumetric flask 1000 ml class B accuracy, ASTM E288
- 2 plastic wash bottle 100 ml
- 3 plastic utility funnel (to fit 500 ml Volumetric Flask)
- 6 one-gallon plastic water bottles

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The test protocol

Method:

Fill all Volumetric Flasks to calibration mark with tap water, use funnel and wash bottle to reach mark. Fill both 1 gal bottles with tap water.

Empty and shake out the overflow can, and measuring tube. Dry the measuring stick.

Fill the measuring tube with 500 ml of water from one volumetric flask. Have the operator measure the depth with the measuring stick. Value should equal 0.61 inches on stick. Empty the measuring tube into the overflow can. Shake out the measuring tube and dry the measuring stick. Fill the measuring tube with 1000 ml of water from the 1000 ml volumetric flask. Have the operator measure the depth with the measuring stick. Value should equal 1.21 inches on the stick. Dry the measuring stick. Add the remaining 500 ml of water from the last volumetric flask and have the operator measure the depth. Value should equal 1.82 inches on the stick. Empty the measuring tube into the overflow can. Observe the overflow can for leakage. Report if leaking. Have the operator transfer a portion of the overflow can to the measuring tube and measure the depth, record this value. Discard the water from the measuring tube. Transfer the remaining depth from the overflow can and have operator measure. Add both values obtained value should be 2.43 inches of water. Return the water to the overflow can and add the 2 two gallons of water to the 8" can and 2" tube. Place a paper towel under the can and tube.

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The test protocol

Wait a minimum of one half hour. Observe overflow can and tube for leaks. Paper towel should not be damp. If damp or wet, overflow can or tube is leaking.

Empty overflow can and measuring tube, shake dry. Assemble stick gage for sampling.

Known errors:

500 ml volumetric flasks will deliver 500 ml +/- 0.4 ml the 1000 ml 0.6 +/- this translates into an error of 0.002 inches of water. Another error will be the transfer of water from the flasks into the measuring tube.

Error bar should be +/- 0.01" which would be +/- 8 ml of water.

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Data

SITE	500 ML		1000 ML		1500 ML		TRANSFER	
	ERROR	+/-	ERROR	+/-	ERROR	+/-	ERROR	+/-
IL11	0.61	0.00	1.22	0.01	1.82	0.00	2.42	-0.01
VT99	0.63	0.02	1.26	0.05	1.89	0.07	2.50	0.07
WV99	0.62	0.01	1.25	0.04	1.87	0.05	2.49	0.06
FL18	0.62	0.01	1.25	0.04	1.88	0.06	2.49	0.06
	0.61		1.21		1.82		2.43	

At VT99, WV99, and FL18 the problem might lie in the stick and/or the 2" tube

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Review of Some of the Findings From the External Site Visit Program for 2002

John Shimshock and Tom Jones

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Sites visited in calendar year 2002 = 90

Includes

- 67 NTN sites
- 20 MDN sites
- 3 AIRMoN sites

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Exclude Sites That Were "Rain Outs" And Other Storm Related Cancellations (Ice)

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Yields Total of 81 Sites

- 58 NTN sites
- 20 MDN sites
- 3 AIRMoN sites

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Segregate this list by "old" versus "new" sites

"Old" At least one prior visit by **ATS** (began visiting NTN sites in 1998)

"New" Initial visit to the site by **ATS** (includes most MDN sites and all AIRMoN sites Also includes a relocated site – VA28)

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By our definition, collocated sites count as two or more sites

(e.g., IL11 – Bondville – would currently count as three sites)

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Total of 47 “**Old**” sites
(not segregated by network)

Total of 34 “**New**” sites
(not segregated by network)

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Without looking at any statistical analyses, **ATS** suspected (gut feeling) that the “New” sites seemed to have more site related and equipment related problems (on average) than “Old” sites

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Selected the following parameters for the statistical analysis:

Siting Criteria

- Objects > 1 meter height within a 5-meter radius of the precipitation collector and Belfort rain gauge

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Selected the following parameters for the statistical analysis:

- 45 degree rule violated – precipitation collector and Belfort rain gauge
- Vegetation height > 0.6 meters height within a 5 meter radius of precipitation collector

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Selected the following parameters for the statistical analysis:

- Δ precipitation collector orifice height and Belfort rain gauge orifice height >12”

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Footnotes:
 Current NADP Siting Criteria excludes the Belfort rain gauge for the first two parameters

Selected parameters are common to all networks

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NADP "QA Group" currently examining the siting criteria – may ultimately determine that some parameters may not truly be a criterion (i.e., "thou shall / thou shall not") but rather a "desirable" attribute - Would suspect, though, that the parameters previously listed may ultimately be determined to be "criteria"

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Interested in examining whether or not the Site Operator attempts to maintain sample integrity when changing the bucket or bottle

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Also interested in examining the results of the audit of the Belfort rain gauge

- 0 to 4-inch range only (failures at the 1", 2", 3" or 4" depths)
- Rain gauge hysteresis problem – request replacement gauge

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Results (percentages)

PARAMETER	OLD	NEW	LOSER
Objects > 1 meter height – precipitation collector (35)	66%	34%	"Old"
Objects > 1 meter height – Belfort rain gauge (30)	59%	43%	Draw
45 degree rule violated - precipitation collector (13)	46%	54%	Draw
45 degree rule violated - Belfort rain gauge (9)	33%	67%	"New"
Vegetation height > 0.6m - precipitation collector (25)	48%	52%	Draw
Δ Orifice heights > 12" (8)	50%	50%	Draw
Sample integrity not maintained by the Site Operator (7)	43%	57%	Draw
Belfort rain gauge failures (24)	38%	67%	"New"
Belfort rain gauge hysteresis (2)	100%	0%	Draw

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Interpretations

Attempt to stay in the "No Spin Zone" (Bill O'Reilly)

In general, the "New" sites seem to have as many site related problems as the "Old" sites – Perhaps suggest that site related problems at "Old" sites are very difficult to correct

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Interpretations

In general, the "New" sites seem to have more Belfort rain gauge problems than the "Old" sites

Perhaps suggest that periodic servicing of the gauges is improving overall gauge performance

