Field Chemistry Whitepaper

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Let's start with some Field Chemistry History…

- OCTOBER 1984: "The question of lab versus field pH. This question has been discussed…and [we look] for a vigorous discussion of whether the field measurements will be continued…Is it necessary to perform these measurements in the field, and is there value to the measurements?"

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Field Chemistry History, cont.

- MAY 2002: Motion made in NOS to eliminate field pH and specific conductance measurements beginning January 2003. This motion failed to pass. Ad-hoc committee formed to explore issue further.
- JULY 2002: Executive Committee Meeting passed recommendation to the Technical Committee that field chemistry measurements be discontinued beginning January 2003.

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Field Chemistry History, cont.

- SEPTEMBER 2002: Motion made in NOS to eliminate field pH and specific conductance measurements beginning January 2003. This motion failed to pass.
- MARCH 2004: Motion passed by the Joint Subcommittees recommending to Executive Committee to discontinue field chemistry at NTN sites as of January 1, 2005; new sites as of April 1, 2004. Requested that "brochure" be written. (Why we're here today.)

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Field Chemistry History, cont.

- JUNE 2004: Executive Committee accepted recommendation from Joint Subcommittees that field chemistry measurements be eliminated.

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Field Chemistry Whitepaper Discussion Points

- What is the current field chemistry measurement program?
- Why is it advantageous for the NADP to discontinue support for field chemistry measurements?
- Why are field chemistry measurements performed?
- What differences are seen between pH and conductivity measurements made in the field and those made in the laboratory?

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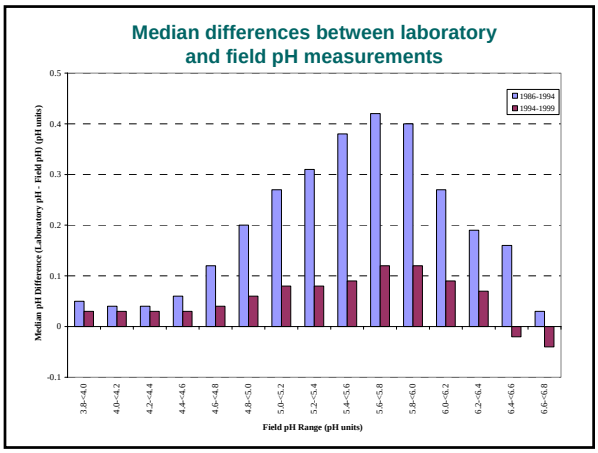

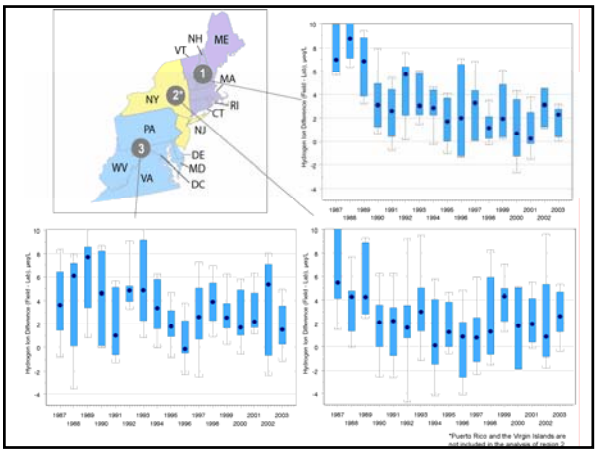

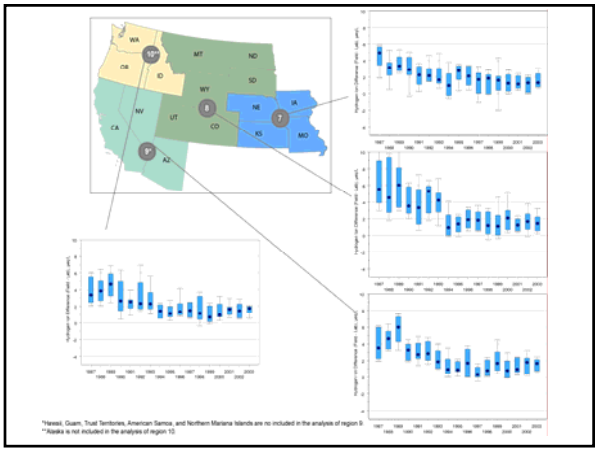

Field Chemistry Whitepaper Discussion Points, cont.

- Who uses field chemistry data?

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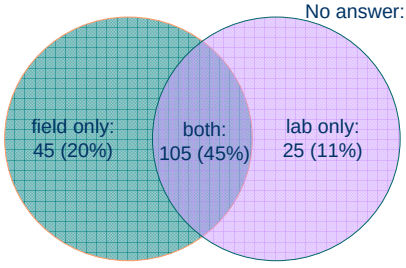
Data user survey: Which NADP-reported pH results do you use?

None: 50 (22%)
No answer: 5 (2%)



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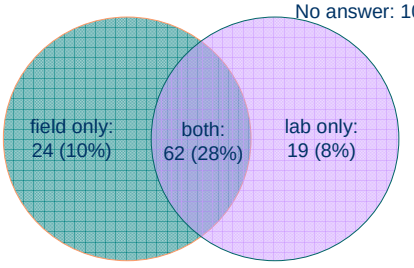
Data user survey: Which reported conductivity results do you use?

None: 115 (50%)
No answer: 10 (4%)



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Field Chemistry Whitepaper Discussion Points, cont.

- Who uses field chemistry data?
- Were other options considered?
- What are the scientific benefits of discontinuing field chemistry measurements?
- Will field chemistry measurements be discontinued completely?
- What are the implications for NADP/NTN site operators?
- How will this affect the data products developed by NADP?

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Field Chemistry Measurement Program: CAL Support

- CAL supplies sites with pH probes, calibration solutions, check samples, training, and instruction manuals as part of general site support
- Sites must provide pH meter, conductivity meter, conductivity cell, and deionized water
- Sites requested to perform weekly field chemistry measurements, but refusal will not generally exclude them from the network
- 8 sites do not currently perform field chemistry measurements

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Field Chemistry Measurement Program: External QA

- USGS supplies sites with verification samples to assess site measurement performance
  - Sites report measured pH & conductivity values
  - >90% of sites met pH & conductivity targets in 2001
  - USGS contacts sites that do not meet targets for follow up
- Site Systems & Performance Surveys assess equipment performance and operator technique

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Field Chemistry Measurement Program: Estimated Costs

- Cost to CAL to provide sites with probes and supplies: ~$2.00 – 3.00 per site-wk
- Cost to sites to provide equipment: ~$2.50 - 3.50 per site-wk
- Site labor to perform field chemistry measurements: ~$5.00 - 15.00 per site-wk
- Cost for USGS intercomparison studies: ~$1.25 – 2.00 per site-wk

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Lab vs. Field Chemistry Measurements

- Paper in press by Latysh and Gordon (Water, Air & Soil Pollution) compared differences in lab and field chemistry at 135 sites from 1986-1999
- 1994 protocol change – O ring problem
- Differences highly correlated with pH, much smaller differences since 1994

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NADP Data User Survey

- Survey sent to 2000+ registered NADP data users June 21, 2002
  - Invitation to take survey E-mailed to users
  - Web site: http://nadp.sws.uiuc.edu/survey/
  - Survey covered use of various NADP data, including field chemistry
- 230 survey responses received as of August 21, 2002
  - http://nadp.sws.uiuc.edu/survey/results.asp

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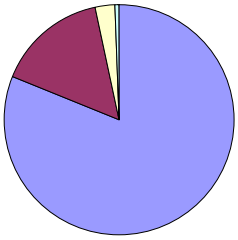
CAL Site Operator Survey



How much time does it usually take you to perform a routine pH analysis?

- 30 or < minutes--81%
- 30 to 45 minutes--15%
- 45 to 60 minutes--3%
- >60 minutes--1%

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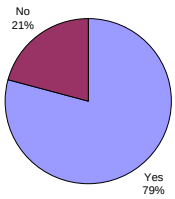
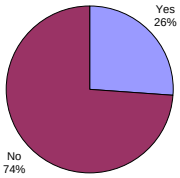
Site Systems and Performance Surveys

Does site follow correct conductivity measurement technique?



Does site follow correct pH measurement technique?



130 sites surveyed 2002-03

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What field measurements provide

- pH changes from field to laboratory represent unaccounted-for acidic deposition, and may be important factor for sensitive ecosystems
- Chemistry differences indicate solution changes in transit from field to lab, providing a QC check

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Our Conclusions:

- There is continued value to field chemistry measurements
  - Meet the needs of some users
  - Important to some operators
  - Retain a QC tool that might be important as the network goes through equipment and protocol changes

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Our Conclusions:

- However, there is a strong case for limiting field chemistry measurements
  - We know something about the relationship between lab pH and field pH
  - Measurements are not necessary at all sites to assess ecosystem impacts and QC issues
  - Resources allocated for field chemistry measurements could be used for new equipment or allocated towards other field measurements (passive samplers, etc.)
  - Decreased sample handling might improve sample quality

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Potential Scenarios to Consider

- End all field chemistry measurements effective January ??? as originally suggested
- Reduce number of sites that perform field chemistry measurements
  - Maintain a core group of sites (mandatory measurements)
  - Maintain volunteer sites (optional measurements)
- Take no action

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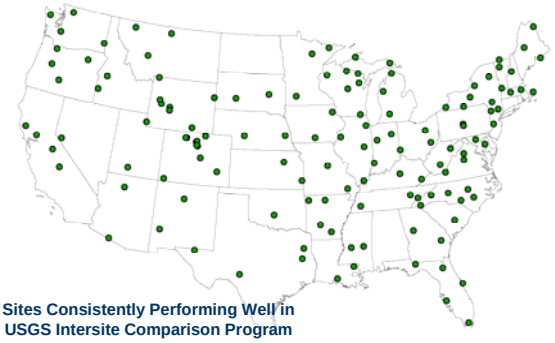
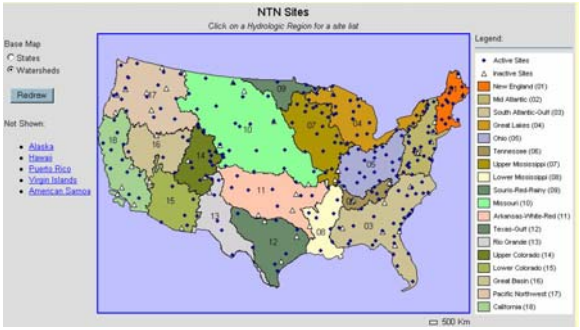
Which sites to choose?



Sites Consistently Performing Well in USGS Intersite Comparison Program

Choose Sites by Hydrologic Region?



Recommendations

- AIRMoN should continue field chemistry measurements indefinitely
- NTN should maintain field chemistry measurements at a core group of ~25-30 sites with full support (probes, solutions, QA programs) until a minimum of 5 years after a new collector design is implemented. At that point, the need for continued measurements should be evaluated

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Recommendations, cont.

- Except for the core group of NTN sites, field chemistry measurements should be voluntary as of January 2005. NOS and Executive Committee should decide if CAL will continue support (solutions, probes)
- There should not be a cost difference between sites performing field chemistry, and those that aren't, as the entire network benefits from the measurements. A cost disparity sets precedent for future field measurements

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Action Plan

- Form ad-hoc committee to choose core group of sites based on long-term network needs
- Standardize equipment and procedures at core group of sites
- Produce brochure for site personnel explaining protocol changes

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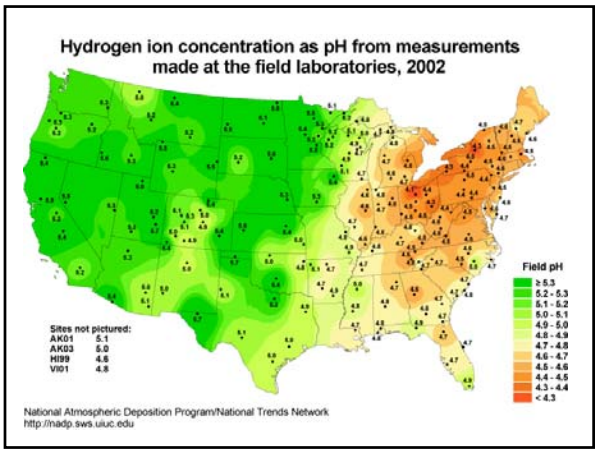

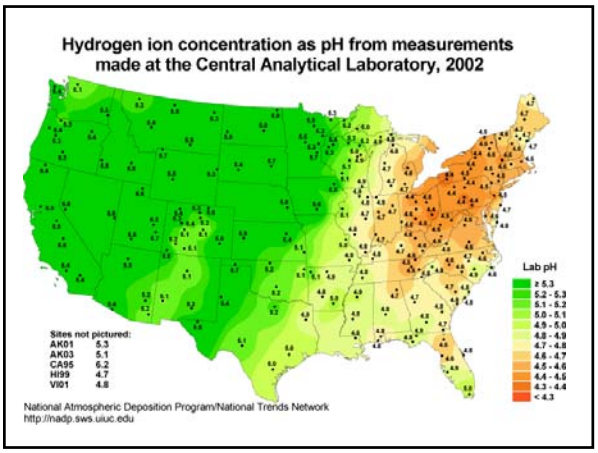

OPTIONAL: Please provide additional comments regarding your use of NADP field chemistry data

- Comparison with own data (12 responses)
- Annual reports (2)
- Watershed loading studies (2)
- Reported to news agencies to provide current information on acid rain status

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Use of Both Field & Lab Chemistry Data

- Data comparison of field vs. lab data; consistency check; quality control (11)
- Comparison with EPA models
- Study pH patterns
- Compare NTN & AIRMoN data
- Use most complete record of data

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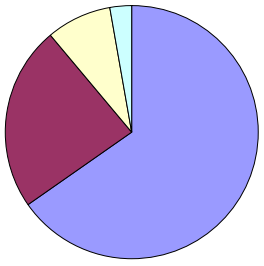
CAL Site Operator Survey



Describe the function of your pH system

- works well most of the time--65%
- OK till probe failure--24%
- OK but takes time--8%
- unsure of data--3%

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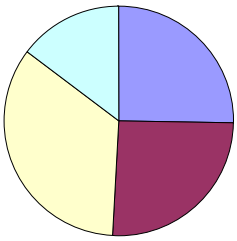
CAL Site Operator Survey



How long does a pH probe usually last?

- no pattern--25%
- > 1 year--25%
- > 2 years--35%
- other--15%

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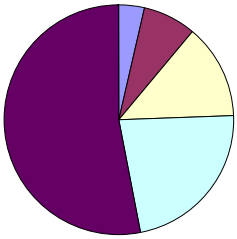
CAL Site Operator Survey



How would you rate the CAL's response when you experience problems? (10=excellent, 1=poor)

- 1-5 scale--3%
- 6-7 scale--8%
- 8 scale--13%
- 9 scale--22%
- 10 scale--56%

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Field Chemistry History, cont.

- SEPTEMBER 2002: Motion made in NOS to eliminate field pH and specific conductance measurements beginning January 2003. This motion failed to pass.
  - Motion passed to produce a report summarizing field and laboratory measurements for NTN for the last 25 years. This report will be mailed to site operators.

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Draft initiative to expand NADP by adopting the capability to measure mercury dry deposition

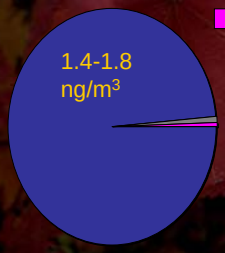
by
Eric Prestbo, Frontier Geosciences
ericp@frontiergeosciences.com
and
Martin Risch, USGS
mrisch@usgs.gov

Table of wet and dry Hg deposition values from Seigneur et al., 2000

Location	Wet Hg ug/m^2/yr	Dry Hg ug/m^2/yr
S.W. PA	15-20	20-30 (RGM sources)
N. MA	20-30	30-66 (RGM sources)
N. MN	5-10	2-5
S. ME	10-15	5-10
S. FL	10-15	10-15

Three Atmospheric Mercury Species Contribute to Dry Deposition

- Hg^0 – Elemental Mercury
- RGM – Reactive Gaseous Mercury
- Hg_p – Particulate Bound Mercury



Typical Atm. Mercury Species Abundance

Mercury Dry Deposition Methods

- Litterfall
- Direct Approach – Surrogate Surface
- Indirect Approach – Measure Hg species concentration and meteorological variables, then calculate flux
- Measure Gradients – Modified Bowen-Ratio or Relaxed Eddy Accumulation

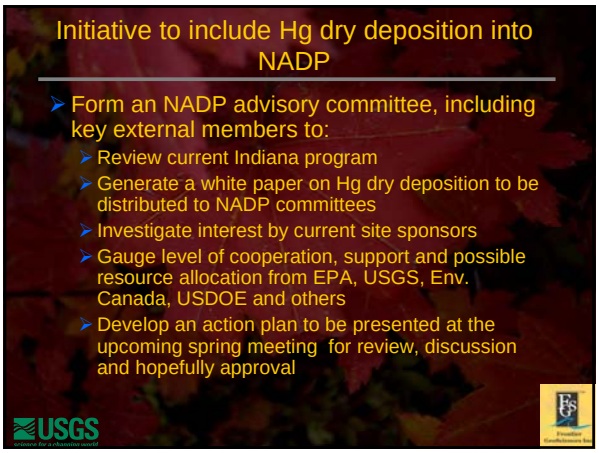
Suggested Dry Deposition National Program

- Litterfall Long-Term Monitoring
  - Start with ecosystem study sites like LTERs where litterfall is already being collected
  - Add interested MDN sites to complement wet deposition
- Measure Atm. Hg species using manual method – apply CASTNet approach
  - Co-locate at MDN and CASTNet sites
  - Pilot Program starting in Indiana
- Continue to support Hg Dry deposition research at super sites, intensives and lab experiments

Indiana Mercury Dry Deposition Study

Martin Risch - USGS and Indiana DEP (2003-2004)

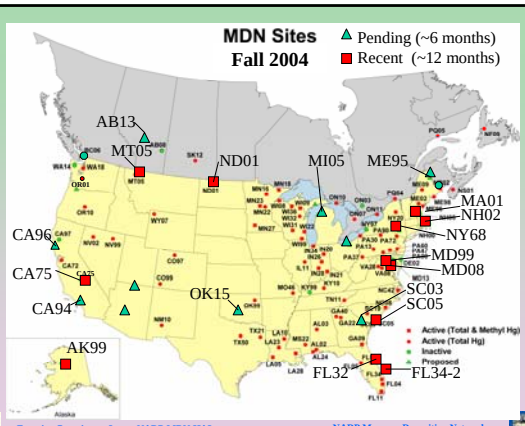
- Detailed SOPs exist for sampling
- Stringent QA plan and QA studies completed
- Infrastructure and equipment is fully developed
- Lab analysis is fully developed with SOPs under review
- Program cost are known


Initiative to include Hg dry deposition into NADP
Form an NADP advisory committee, including key external members to:
Review current Indiana program
Generate a white paper on Hg dry deposition to be distributed to NADP committees
Investigate interest by current site sponsors
Gauge level of cooperation, support and possible resource allocation from EPA, USGS, Env. Canada, USDOE and others
Develop an action plan to be presented at the upcoming spring meeting for review, discussion and hopefully approval
USGS

NADP MDN HAL Report
Fall Technical Meeting

Halifax, Nova Scotia
September 21-23, 2004

Robert C. Brunette
MDN HAL Director



Frontier Geosciences Inc. – NADP MDN HAL
www.Frontiergeosciences.com
NADP Mercury Deposition Network
http://nadp.sws.uiuc.edu/mdn/

Recent MDN Site Start-Ups

- NH02 - Hubbard Brook – 02/10/04
- SC05 - Cape Romaine NWR – 03/09/04
- NY68 - Biscuit Brook – 03/16/04
- AK99 - Ambler – 05/18/04
- MD99 - University Of Maryland – 06/08/04
- MD08 – Piney Res. – 07/06/04
- VT99 - Underhill – 08/03/04
- SC99 - Savannah River – 08/10/04
- HD01 - Huejutla - 08/10/04

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NADP Mercury Deposition Network
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Pending MDN Site Starts

- OK15
- CA94
- AB13
- CA96
- SC03
- ME95
- MI05
- ME95
- CA99
- N. Arizona
- Ohio
- S. Arizona

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NADP Mercury Deposition Network
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MDN Sites in Mexico –

In partnership with the Instituto Mexicano de Tecnologia del Agua

Frontier Geosciences Inc. – NADP MDN HAL
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http://nadp.sws.uiuc.edu/mdn/

Mexico MDN Sites

- HD01 Official MDN Site
- Puerto Angel Site – PO Revisions
- Mexico Sites – Remote
- Shipping Cost and Logistics – Quarterly
- MDN Field Spike Experiments
  - Field Sample Bottle Hg Spikes
  - Lab Sample Bottle Hg Spikes

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HAL Capacity And Preparation For Network Growth

- HAL Total Hg Wet Dep MDN Samples To Date: ~ 24,000
- HAL Methyl Hg Wet Dep MDN Samples To Date: ~ 4,500
- Currently - 6.0 FTE Dedicated MDN HAL
- 2 Additional FTE MDN Dedicated Staff Expected – Feb 04
- 5 Additional Frontier Staff Trained In Support Positions
- Purchase Equipment To Support 10 New Sites – Winter 04

MDN HAL Data Base Update

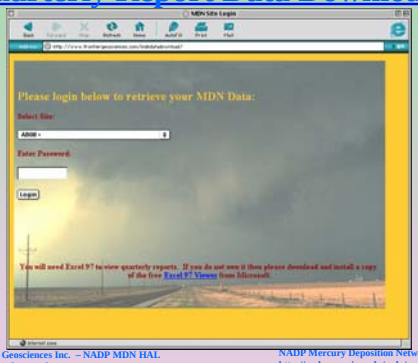
- MMHg Data Base Merged W/Total Hg DB:
  - > Incorporated Into MDN Total Hg DB - 2002
  - > Quality Code System Incorporated - 2002
  - > MMHg Data Follows All Aspects Of THg Data
  - > All MMHg Data Posted On MDN Download Site
  - > MMHg Data Now Reported Quarterly w/THg
- Trace Metals Data Base –

  To be adapted from newly developed Frontier LIM system

HAL MDN Total And Methyl Hg Data Status

- **MDN 2nd Qtr 2004 (Total and Methyl Hg)**
  - Preliminary Data to Operators: Aug 16, 2004
  - Preliminary Data to Site Sponsors: Sept 1, 2004
  - End Of Sponsor Review Period: Sept 10, 2004
  - HAL Transmitted DB to PO: Sept 10, 2003
- **MDN 3rd Qtr 2004 (Total and Methyl Hg)**
  - Preliminary Data to Operators: Oct 14, 2004
  - Preliminary Data To Site Sponsors: Oct 28, 2004
  - End Of Sponsor Review Period: Nov 7, 2004
  - HAL Transmit Final DB to PO: Nov 7. 2004

MDN E-Cabinet Preliminary Quarterly Report Data Download



MDN Field QA Studies

- MDN Co-located ACM Study – WI08
- MDN HAL WA18:
  - Duplicate MDN ACM Co-located Study
  - MDN ACM Vs. NCONN Vs MICB
  - PE Rainwater Sample Collection For USGS
  - Pb210 Isotope Study – Correlation To Hg
  - Trace Metals
  - Particulate Bound And Gas Phase Mercury
- Co-located ACM vs. MICB @ WI31 WDNR
- MDN Co-located Ground vs. FAMS - FL34

USGS MDN External Audit Program

- External Laboratory PE Sample – Full Scale
  - Single Blind
  - Implemented Nov-Dec 2003
- External System Blank – Full Scale
  - Single Blind
  - Implemented Nov-Dec 2003
- HAL To Continue 3 Lab Rainwater Comparison

HAL/PO Meeting – April 2004

- Follow-Up To Point Reyes, Spring 2004
- Documented HAL and PO Data Coding
- PO Synchronizing Codes For Data Base
- MDN MMHg Final Data Base
- Rain Gauge Reading Synchronization w/PO
- Sample Bottle Cap Weight Differences

MDN HAL 2003 Audit – 1 Year Progress Report

- ***59%*** of HAL Audit Items ***"Fully Resolved"***
- ***40%*** are ***"In-Progress"***
- ***26 "In Progress" Audit Items***
  - **HAL (11):** **#18, #19, #35, #36, #38, #39, #44, #47, #48, #49, #55**
  - **HAL, PO (8):** **#3, #8b, #34, #40, #50 #56, #57, #59**
  - **Ad Hoc (2):** **#2, #24**
  - **HAL, USGS, NOS (1):** **#4b**
  - **PO, NED (1):** **#23**
  - **PO QA Manager (1):** **#6**
  - **PO, NOS (1):** **#33**
  - **PO (1):** **#62**

Dec 2004 – All but 4 audit items expected to be "Fully Resolved"

March 2005 – 4 remaining audit items to NOS/DMAS

HAL Site Operator Training Course

- Seattle, Washington Hg Analytical Lab
- October 13-14, 2004
- 15 MDN Site Operators To Attend
- Field Course Held @ NOAA Sand Point
- MDN Course Will Follow CAL Training

Recent Progress On HAL Audit Items

- Duplicate Data Entry - Lab Analysis Data
  - Microsoft Access Based Lab Data Sheet
  - Utilizes Same Double Entry System In MDN DB
  - New Data Sheet To Be Applied In 4th Quarter 2004
  - Methyl Lab Data Sheet To Follow In 1st Qtr 2005

HAL/PO Trace Metals Initiative

Trace Metals In Wet Deposition Research Completed:

- Frontier ICP-MS Based Analysis Validation Study Complete
- Eliminates Need For HG-AFS For Se & As
- One Digestion & Analysis For Full Suite Of Metals
- Routine Lab Production Digestion & Analysis Technique
- 10-40 x Decrease In Reporting Limit For 9 Top Trace Metals
- Trace Metals Field and Analytical Techniques Ready For Use
- Presentation and Poster @ Fall Technical Meeting

Trace Metals Wet Deposition Studies To Date

- SFBADPS – 1 Year Study @ 1 MDN and 2 Quasi MDN Sites
- City Of Sacramento TMDL Study – Short Term Event Based Study
- Venice Lagoon Wet Deposition Study – Short Term Event Based Study
- MPCA – 1 Year Study @ 4 MN MDN Sites
- PO/HAL – 9 Month Study @ IL11
- MEDEP – 1 Year Study @ ME96
- USGS – 1 Year Study @ IN20, IN21, IN28
- HAL Sponsored - WA18 Trace Metals Study – 5 year record
- PSU – 2 Year Study @ PA13 and PA30 – Will Continue Through 2004
- PSU - PA47 and PA72 – Started June 2003
- LADEQ - 4 LA MDN Sites – Expected Start Date Sept 2003

MDN - Storm Event Based Sampling

- Tropical Storm – Event Based Hg Sampling
  - Ops received extra glassware to support effort
  - Email and Phone calls made to prepare site ops
  - Compilation Of Results From 2002-2004 Pending
- Storms Captured 2004: Bonnie, Charlie, Ivan

Upcoming MDN Publications

- MDN Total Hg Overview - 1996-2003
- MDN MMHg Paper – 8 year record of data
- MDN Trace Metals Paper – 4 year study

Issue: Precipitation Amount Differences at Co-Located Sites

At its 26 March 2003 meeting, the Network Operations Subcommittee (NOS) resolved:

"the Program Office report one reading for precipitation amounts for NTN and MDN co-located sites when the same raingage is used for both networks."

Differences:

Most HAL/operator differences are less than 0.05 inches over the week

- P. O. Recommendations to HAL (page 4):
  - continue to read every precipitation chart.
  - read daily amounts to the nearest 0.01 inches rather than 0.005 inches
  - only enter differences when they differ from operator by more than 0.02 inches.
  - Verify zero precipitation amounts (used for QC).

Program Office Recommendations

- P. O. Recommendations to CAL (page 4):
  - document the criteria that result in the re-reading of precipitation charts.
  - clarify the criteria for changing site operator readings
  - edit operator depths when CAL and operator differences are more than 0.02 inches.
  - Zero precipitation amounts shall be verified, since dry samples are used for QC purposes..

Program Office Procedures

If NTN and MDN do not agree, the Program Office will:

- Check dates and times for errors and reconciled
- Check all records where
  - MDN or NTN (or both) values are missing.
  - Either lab reports zero precipitation and other lab reports 0.01 inches or more
  - Check only important (large) differences (see conditions, page 4)
- Include a reconciled_PPT field, for all differences

How far are NTN sites away from towns?

Why is it important or IS IT?

The way I read the current siting criteria document, there is no rule for the placement of sites near urban, industrial, housing or otherwise developed areas, save the 500m and 100m road and parking lot type rules. Of course the 1m object within 5m height rule and the 45 degree "clear to sky" rule may also come into play..this means we'd require them to be 500' from a 500' stack.

Given that (with mixed success) the program has attempted to locate sites “a priori” in areas of mixed airsheds, this represents a MAJOR change in network philosophy. We'd essentially be changing from stated rule of 10km separation to a stated rule of 100m separation.

SO… what does the network look like?

Proximity numbers not available in current PO database.

CAL SITEINFO database used

CAL QUESTIONAIRE

- 253 records
- My guess is that the data or good to 10 or 15%.

Nearest Town or Village to the NADP/NTN Site

Site ID: _____

Site Name: _____

Operator Name: _____

Please, complete the following form using a highway map. Remember that the direction needed is FROM the nearest town TO the site, the site is the unknown.

1. Nearest town/village of 1000 or more population

   _____

2. Nearest town/village of any size that one can find on a road atlas or state highway map.

   _____

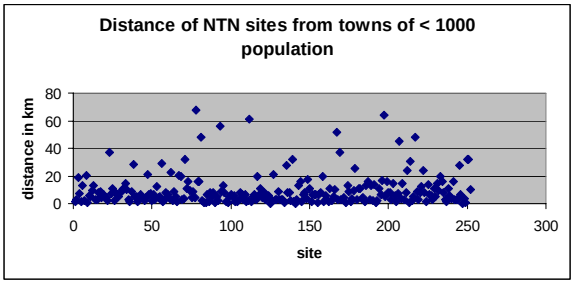
3. Direction FROM town/village (listed in #2) TO the sampler (N, NE, E, etc.) _____

4. Distance from town/village to sampler in a straight line or "as the crow flies" _____

Sketch of site including nearest town, sampler, any physical features (rivers, lakes, etc.) And any man-made features (highways, railroads, structures,

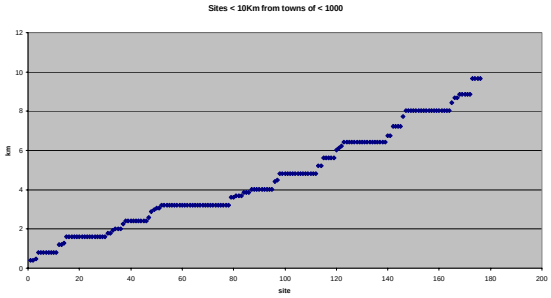
Average NTN network distance from the site to a town with pop. <1000 people (YES we asked the question this way) was 9.419.

The distribution of distances however shows quite a clustering below 10km and many long distance sites (see File 1 attached).



SO.... I trimmed everything out of the spreadsheet which was greater than 10kM.

Of the sites < 10kM from a town < 1000 people (177!) the average distance was 4.4 km.
(See File 2 attached.



I'd like to see use have some RULE for proximity to developed areas and suggest it be set at 5kM.