National Atmospheric Deposition Program Spring Meeting Point Reyes, CA March 23-24, 2004

> Minutes of the Network Operations Subcommittee [NOS] Submitted by Mike Kolian, NOS Secretary

Agenda Items 1:00-5:00 pm Tuesday, March 23

1) <u>Agenda Overview and Approval of Fall 2003 NOS Meeting Minutes</u>, Natalie Latysh Minutes from the 2003 Fall NOS subcommittee meetings in Washington, DC were approved. Natalie made the motion to approve, Scott seconded the motion, no discussion and the motion was passed.

2) <u>USGS External QA findings</u>, Natalie Latysh

Natalie presented the Interlaboratory Comparison Program results for 2003 which is designed to quantify bias and precision of data generated by the CAL. The final results will be posted on the web in the next month - in the interim a summary of the 2003 performance results and findings can be obtained from this presentation (listed below). Many labs are sending in their respective samples late (there are 8 participating labs). It has been suggested that USGS be a little more stern in obtaining the data back from the participating labs. Excel spreadsheets are the data format USGS is requesting. Lab contamination is minimal at the CAL as indicated by few exceedances of the CAL's method detection limit for Ultrapure deionized water samples (blanks). Most of CAL's determinations are within the control limits on the control charts, indicating consistent and acceptable performance. CAL did have a slight problem with K⁺ and Na²⁺. The CAL results are consistent from previous years; slight positive bias for specific conductance, slight negative bias for major ions and pH.

Next, Natalie briefly presented intersite comparison program results for 1998-2003. This program evaluates the target and measured values of pH and specific conductance as performed by the site operators. A total of 11 intersite comparison studies have now been performed. Site operator turnover is a problem but most are involved in the program (~90-95% participation) - site operators are actually required to participate. There is a follow-up with those that fall out of criteria and 92-95% represent the number of successful follow-up regarding measurements. Next, Natalie presented the SHE program 2003 vs blind audit. Conclusions: SHE program shows less variability in bucket - bottle differences than the blind audit program. The SHE program is more representative of bias introduced by sample handling (lower lab variability). Absolute error introduced by sample handling is less than MRL. The actual environmental pH is slightly lower than reported by NTN due to sample handling. Natalie presented the 2003 Field Audit Results. Field audit data indicate low level sample contamination - not environmentally significant to data users. Field exposure tends to buffer H+ concentration and reduce

conductivity. The actual environmental pH is slightly lower than reported by NTN due to sample handling and field exposure and specific conductance is slightly higher than reported by NTN simply due to sample handling and field exposure. USGS is concluding the SHE program does not provide much more information than the field audit program. SHE program will be cancelled in June 2004 and field audit will expand to cover the entire NTN annually starting in 2005.

<u>Proposal to QAGG</u>: USGS is proposing to cancel the SHE program in June 2004 and field audit program will expand to test entire NTN annually starting in 2005. Scott Dossett suggested the following: Look at spacial representation from the field audit program some sites haven't been able to send in a field blank in for 2 years due to lack of rainfall!

Next, Natalie presented the Collocated sampler program for Water Year 2003 (October 2002 - September 2003). This program deploys and operates an exact match of an NADP site in regionally representative areas and in 2003 it was OK00 Salt Plains (US FWS) and WI98 Wildcat Mountain (WI DNR). NM07 and TX22 will be the collocated sites for WY 2004. The collocated program is designed to identify variability introduced by equipment and/or protocol changes and to compare overall system variability to components measured by other external quality assurance programs. The collocated sampler program results for Water Year 2003 were comparable to previous years. Median relative error increased at WI98 between 2002 and 2003 for Na+2, K, and H-ion.

<u>Proposal to QAGG</u>: USGS is proposing to go to two permanent collocated sites instead of two moving or rotating collocated sites. Wear and tear on the equipment during the shipping so they would like to go long-term at a "snow" site and hopefully WI98. This would establish a long-term baseline of collocated variability with present day instruments. Quantify potential bias introduced by upgraded network equipment. NPS is considering funding a third collocated site in the near future (Kristi Morris). USGS QA program has a very useful website: www.btdgs.usgs.gov

For more information about the data and compiled results of these quality assurance programs see attachment 1 (SPRING_04_MASTER_presentation.ppt).

3) USGS Quality Assurance Programs MDN, Natalie Laytsh

The QA programs: system blank, field blank, and interlabortory comparison were discussed out in Seattle during a recent visit by USGS to Frontier Geosciences. HAL is working with the USGS on the details that will be required for initiating these QA programs specifically for MDN. For more information on progress and issues see attachment 2 (SPRING_04_MDN_QA.ppt).

4) HAL Report, Bob Brunette

Bob Brunette presented the HAL/MDN update.

MDN HAL Staffing updates: New hire, Connor Christy MMHg and THg analyst, Doug Disney and another MDN research assistant TBA. Kirsi Longley left in December 2003. The MDN sites were presented (82 active US sites, 15 proposed, 7 pending, 8 in Canada, 2 in Mexico and ~30 total Hg sites). Spring 2004 MDN sites BC06 and NB02 shutdown with a couple others shutting down then restarting and about 9 new sites since beginning of 2003. Started two new

sites in Mexico; MX01 and MX02. It is anticipated that these sites will follow the NADP application process and become official. The sites in Mexico are interested in collocating NTN equipment there as well. Site operators for these sites were trained by HAL staff. Filling in several sites in the Gulf of Mexico and in Southern U.S. Hubbard Brook Experimental Forest established an MDN site in February 2004. HAL is increasing their overall capacity in preparation for continued network growth. Total Hg data status update - several Total & Methyl Hg sites established (~30 active sites). MDN 4th quarter 2003 data schedule: preliminary data to users Jan. 21, 2003; Preliminary data to site operators Feb. 13, 2003; End of sponsor review period, Feb. 23, 2003; HAL Transmit Final DB to PO, Feb 27, 2003. Methlymercury and total Hg databases were merged and data will be reported quarterly. MDN Hg data delivery schedule: Preliminary data to MDN operators and site sponsors, April 21, 2004; End of sponsor review period, May 5th, 2004; HAL transmit final dB to PO, May 10, 2004. Bob showed the available Lab quality assurance documents as posted on the web. Bob provided trace metals database update and lab quality assurance updates and time lines. Field QA studies reported. External Audit programs implemented in Nov-Dec 2003. HAL response and clarification to audit recommendations were provided to the review team and was approved by the audit team Jan. 2004. HAL provided clarifications in a handout (see Bob Brunette if interested in a copy). MDN site operations manual will be updated which will need NOS approval - draft is due in May 2004. MDN training video/CD ROM will be updated in June 2004. Training course in Seattle announcement in April 2004 for 3rd week of September 2004. Happens to be very close to NADP Fall annual meeting. ATS/PO have agreed to assist the HAL in developing the course and providing ideas. Course to be held at NOAA's Sand Point (WA18). Trace Metals initiative for the HAL and Program Office, Selenium and Arsenic are not measured accurately with current ICP-MS so there is research associated with a ICP-MS-DRC (direct reaction chamber). A White Paper is planned for supporting Trace Metals. Bob presented the various trace metals wet deposition studies to date. Star Grant for Air Toxics Long Range Transport of Hg, Eric Prestbo representing this in Japan. Mesa Verde study of dry deposition - Eric Prestbo 2004. Indiana dry dep study @ 3 MDN sites -2003-04 - Marty Risch USGS. Lastly, Bob presented upcoming MDN publications.

For detailed information regarding the HAL update see attachment 3 (Spring HAL report 2004.ppt).

5) Road Proximity Study, Scott Dossett

Scott presented road proximity as an issue both in terms of nearby roads and site access roads. Siting criteria (near source criteria). Road proximity study to look at what roads do to influence the program's collectors. Scott provided a brief history of work in this area as well as a picture of the future which includes roads at or near the footprint of the collector. For more information see attachment 4 (ROAD STUDY.ppt)

6) <u>Passive NH3 sampling in the Great Plains - Proposal</u>, Scott Dossett Should NADP measure NH3 at sites located in the Great Plains States? Ogawa sampler is inexpensive and is being published in the literature by researchers such as Joe Scudlark who has done projects using these passive devices in Delaware (Scudlark *et al*, 2003). An intercomparison study was done of passive and active ammonia samplers spaced apart by 3m at a height of 4 m. The study demonstrated the inherit difficulty of accurately measuring ambient

NH3 near active sources of NH3. The two passive devices (Willems and Ogawa samplers) had quite good agreement with the annular denuder results. Scott introduced plans to start (midsummer 2004) a one year duration trial of passive NH3 samplers at select NTN sites using the Ogawa Scudlark technique. It would be low cost using existing infrastruction with the CAL performing the analysis. This could be done at 15-20 sites which transect north-south and east-west through the NH3 hotspot in the center of the US. Talking about the bubble in the center of the country where we need the ammonia information. Cannot compare with CASTNET and IMPROVE because these networks do not measure ammonia gas concentration. Mount the 3 inch PVC cannister to the west side of the collector and have a one week exposure - which could be removed every Tuesday by site operator and shipped to CAL in the NTN mailers. For additional information see attachment 5 (NH3 proposal.ppt).

7) Meet the YES TPC 3000, Scott Dosset

Scott presented pictures and went through most of the components of the wet only collector from Yankee Environmental Systems (YES TPC 3000). For pictures see attachment 6 (YES INTRO.ppt).

8) ATS, Chester (name changed) External Site Survey - Changes and Results, Tom Jones Tom Jones gave a summary of the site surveys performed in 2003. ATS performed 104 site surveys in 2003 (72 NTN, 29 MDN, 3 AIRMoN). Results were summarized into three broad categories: 1) equipment performance, 2) site operator performance, and 3) adherence to siting criteria. Few sites (<15%) had major problems with equipment - all problems were addressed during the survey. 8% of the total rain gages checked had to be replaced and PO was contacted. The biggest problem is the maintenance of the Belfort, followed by replacement operator training. Stick gages are not passing simple calibration tests (NOAA and PO). See attached presentation for more details. Treated lumber on the MDN sites will be a problem if they were to go to trace metals. Copper and arsenic are potential contaminants. For site operator performance the pH measurement and field chemistry techniques were the biggest problem the majority of operators did not perform it to protocol (88% of sites had at least one problem). The siting criteria cited most in the surveys were objects over 1m in height within 5m of collector and/or rain gage. 54% of sites (all three networks) are not wholly compliant with all siting criteria. 13% of sites from all three networks had serious problems related to site operator performance all of which were addressed during the survey. For NTN and AIRMoN sites surveyed in 2003, 88% had at least one site operator performance problem related to the techniques used in conducting field chemistry measurements, in particular conducting pH measurements. Overall siting criteria problems for NTN have decreased from previous year indicating perhaps Chris Lehmann and PO are doing a good job of follow-up with sites. For MDN sites siting criteria issues were noted regarding proximity to stationary emission sources, galvanized metal, and treated lumber. These are potential contamination sources for the sample. The overall problems noted for MDN was less favorable than previous year (2002). Tom also mentioned that the 2003 annual site survey report is in draft form now so should be finalized by Fall 2004 meeting. For more information on site survey results see attachment 7 (FINDINGS 2003 SITE SURVEYS PRESENTED SPRING 2004.ppt).

Tom also recapped progress to date on 2004 site surveys - ATS, Chester field crew have done 12 site surveys to date and would like to do a total of 106 NADP sites for 2004. Organ Pipe Cactus

National Monument (AZ06) experienced a 100 year snow storm (February 2004) just prior to the ATS site visit. From the proposed schedule of states there are a potential of 155 NADP sites. This will leave 49 sites to carryover into 2005 site surveys. See attachment 8 (EXTERNAL SITE SURVEYS FOR 2004.ppt).

9) CAL Report, Karen Harlin

Karen presented the CAL/Program Office update on the networks. There are 255 sites for NTN (including 2 collocated sites 07NM and 22TX), OK08 discontinued in February 2004. There were 9 new sites in 2003 the growth from 2002 to 2003 was 4%. AIRMoN has 9 active sites (DE99 was converted to a NTN site May 2003). Every Tuesday Morning training aid will be on CD and distributed to new sites. Karen advocated that the site photos should be more interesting for calendar and other outreach purposes. Karen noted that the eFORFs & e-site reports survey was sent out to network sites. NTN sites need a minimum computer capacity so that information can be exchanged electronically - makes managing 255 sites much easier. CAL has new bucket lids the old ones are being recycled in WI. Ammonium was showing up in the blanks with Rutan plastic bags currently in use. New lids/bags are \$0.98 a sample - too expensive! CAL has been looking into replacing the analytical equipment in the lab. IC equipment we be purchased in 2004 to replace aging instrument and to provide backup as well as additional research capabilities. 300 buckets and lids are washed a week. CAL sampling processing is around 13,000 analyses/yr. Jane Rothert has completed and posted the 2001 QA CAL report. 2002 is in preparation right now, available in 2004. ISWS is expanding their building space which will allow more room for shipping and receiving. Greg Dzurisin and Sue Bachman have retired. New personnel have been hired. Outreach is being done primarily through Karen Harlin. American Chemistry Society and Earth Day and testing the pH of rain water and other experiments. Karen also outlined the many research projects that are ongoing at CAL. Trying get total phosphorus instead of just ortho-phosphorus in the samples, 4 and 1 shipping protocol, trace metals, archiving samples, Texas dust event 2004, WMO sample preparation, etc.. CAL is pursuing organic and total nitrogen from precipitation - currently it measures nitrate and ammonium in precipitation. For more information on these topics see attachment 9 (2004SpringCALReportpresentation.ppt).

10) ICP vs AAS Follow-up Report, Karen Harlin

CAL has been using the atomic absorption spectroscopy AAS method since 1978 for base cations. The one in the CAL is over 10 years old, a lot of noise so a ICP-AES was purchased for replacement in 2003. Karen gave an update on work done since the Fall 2003 NOS subcommittee meetings and provided recommendations after she gave the presentation. CAL has been running and will continue to run parallel analysis on the instrumentation. No statistical differences were detected between the two methods. There is a difference but it is so small that it is not significant. For the results, details on the method development, and comparison see attachment 10 (ICP.ppt).

Network Operations Subcommittee [NOS] Agenda Items 8:00-12:00 Wednesday, March 24

NOS subcommittee called to order by Natalie (Chair)

1) Siting Criteria Ad-hoc Committee Report, Chris Lehmann

In 2001, an ad hoc committee was created to review and make recommendations to the NOS subcommittee on the NADP siting criteria which stem back to 1978. The members of the committee include: Chris Lehmann-chair, Scott Dossett, Rick Artz, Marty Risch, Gary Stensland, Mike Kolian, Greg Weatherbee, Preston Lewis, and Bob Larson.

The committee is preparing a white paper to discuss the topics of the siting criteria document with good scientific rationale and design. Chris noted the proposed siting criteria document with the ground rules for comment. Comments can be made through the NADP forums website. The major changes involve site classification (urban, suburban, rural, isolated) and defining and distinguishing siting criteria rules and guidelines. The most contentious issue involves roof-top sampling. The document also contains MDN specific criteria, revisions to regional representativeness, and a remedial action plan section. Many recommendations concerning local siting criteria. Should the snow roof be taken off during the summer? They also make for great sails and lift off the collector which comprises the sample. The only regionally representative criteria related to agriculture would be considering ammonia emissions through SMOKE and other models. Mercury would be captured this way as well. Currently, 22% of sites are not considered regionally representative. Interpolations are done based on 5km from the site so those sites that fall out of the representativeness may fall off annual maps. The committee would like comments on this over the next months and the document finalized and approved by the fall meeting. The proposal is to have people comment on the forum version after its updated based on today's comments.

For more information on what was created by the adhoc committee see the siting criteria document, attachment 11 (SitingCriteria15March04.pdf). To see the siting criteria presentation see attachment 12 (NOS-SitingMarch04.ppt).

2) 4 in 1 Shipping Protocol, 20-site Experiment Updates, Karen Harlin

Karen gave an update of the shipping protocol trail. Complaints from site operators and funders because of the surcharges associated with shipping the non-standard black box containing the samples going to CAL. The black box mailers are getting pretty beat up. Going to a cardboard which has separation boxes within the main box. Black mailers last about 2 years and are \$70 but its not certain how long the cardboard boxes will last (how often can they be reused?). The cost savings for 100% conversion could be ½ of what the CAL is spending now. The 4 in 1 concept would allow one shipment to contain a 1 month or 4 week supply. Shipping would occur once a month instead of once a week for the black mailer. This method would also reduce the size of the shipped sample considerably. Phase I results indicate no major problems from 6 USGS trial sites or from the CAL. Phase II adds 14 more sites to the trial using the three major shippers -USPS, UPS, and FedEx. CAL added a bar code and logo to identify boxes readily. Phase II has experienced no major problems except inventory supply depletion. CAL is estimating ~\$200/yr/site. CAL is looking into using envelopes for the sample transfer as well. There are cost savings associated with going to envelopes. CAL can continue to add sites at a rate of 5-10 per month through 2004 and more if staff and resources increase. For more details see attachment 13 (4-IN-1March2004.ppt).

3) HAL Review Follow-up, Chris Lehmann

Chris presented the review follow-up recommendations. Major topics include: HAL sample archive program - they are looking for ideas on how to proceed with this archiving whether for measuring trace metals or what type research would be done with them. Also mentioned were network equipment depot (NED) support for MDN, external review of MDN QA reports, SOPs for rain gage chart readings and reporting. HAL is reading rain gage charts in conjunction with recording site operator reading. This essentially creates two readings from one gage. It was recommended by several NOS members that they should use one reading rather than reconcile two. The Program Office uses the site operator readings for all AIRMoN and NTN sites.

Chris Lehmann makes a motion: HAL to create a sample archive program with sample reanalysis procedures. NOS comes up with recommendations for the archive program to be presented at the Fall meeting 2004; Jane seconds the motion. Discussion. Mark Nilles added that a motion shouldn't be made here to make a major change to the statement of work. In order to do this it needs to come from the Executive and Budget Advisory committee members. Reanaylsis is also a concern when archiving samples. Motion by Chris Lehmann retracted, Tom seconds, Motion to create a sample archive program with sample reanalysis procedures was retracted.

Instead, a task group was appointed to create recommendations and determine the need for an MDN sample archive program and to explore sample re-analysis procedures and report back to NOS at the 2004 Fall Technical Meeting. NOS Chair (Natalie Latysh) appointed Jane Rothert, Bob Brunette, Karen Harlin, Clyde Sweet, and David Gay.

Chris Lehmann makes a motion: To write guidelines for annual CAL/HAL QA report and present it to the NOS at the 2004 Fall Technical Meeting. Second by Scott Dossett. No discussion. Motion passes.

Chris Lehmann makes a motion: For a task group consisting of Bob Brunette, Tom Jones, and Scott Dossett to develop site operator procedures and SOPs for calibrating rain gages and maintenance (geared for MDN but with the potential to expand the procedures to NTN and AIRMoN) and to report these findings to NOS at the 2004 Fall Technical Meeting. Second by Bruce Rodger. No dicussion. Motion passes.

Chris Lehmann makes a motion: For NOS chair to pick someone to resolve rain gage chart reading differences between the MDN and NTN and to report to NOS at the 2004 Fall Technical Meeting. Scott Dossett seconds. No discussion. Motion passes.

Chris Lehmann makes a motion: For a committee consisting of Bob Brunette, Tom Jones, and Scott Dossett to also address the undefined sample protocol as recommended in the 2003 HAL external review. Second by Mark. No discussion. Motion passes.

Chris Lehmann makes a motion: For the HAL to present a draft of the revised MDN field operation manual and field SOPs at the 2004 Fall Technical Meeting and a final version to

the Interim Spring Sub-committee Meeting in 2005. Scott seconds. No discussion. Motion passes.

To view the presentation see attachment 14 (HAL-followup-NOS-March04.ppt).

4) NED Update, Scott Dossett

Scott gave NED update and went through the money problems the Program Office is experiencing. Motor boxes and sensors are flying off the inventory shelf as well as other mechanical parts. May be giving under representative numbers due to increasing MDN network requirements. Probably stuck with the current precipitation collector for 5 more years - to complete the necessary phase III testing, implementation, etc. NED has identified a new vendor RIES LAB who is investigating the components and repair history in order to make adjustments and reconfiguring the sensor heater and thermistor. AC systems are experiencing repeat failures at sites from installations done up to 25 years ago. Independent of the rain gage and collector there are other infrastructure problems and issues. Complaints: NED is under funded with only one technician there is a ramp up in repairs over the recent years. Hypothetical question to Scott Dossett: If you had an infusion of funds what would you do first? The collector - collector sensor then the motor box development would be the priority. For more information on the NED situation see attachment 15 (NED.ppt).

5) Bag Sampling Update, Scott Dossett

Scott presented bag sampling in an effort to determine feasibility of: getting rid of bucket washing, shipping cost savings, maintaining a material more appropriate for target compounds. Yankee sampler allows various bucket sizes (7 gal). The sensitivity of the network is to analyze samples down to 0.01 of an inch of precipitation and the bags may endanger the sensitivity of the network. Bag availability is the difficult issue right now. Scott is comparing the bag on the Yankee with standard Aerochem, N-CON, and regular Yankee sampler. Procedure: Install bag, Protect with lid, install elastic retainer, bag and evacuate.

Discussion: change at the CAPMON and New York State use bags right now both cite reasonable success using bags and their respective protocols. Its on the procedure of extracting the sample and cutting the bag to decant the sample. NY bucket is 5 gallon. They pull a sample when there is enough volume to analyze with a glove. Could do blank tests using the NY and CAPMON methods to determine if there is any contamination occurring or what is introduced during extraction of using the bag. One problem Scott points out is availability of the bags - manufacturer is not flexible, bags must be purchased in large units. Others include field testing of this procedure (requires resources) and small samples sizes would pose a problem (hard to remove from bag). It would be nice to have the change in collector and bag sampling occur at the same time. When there is a change there is a step function in the data so having these changes occurring in parallel would be ideal. For more information on this study see attachment 16 (BAG SAMPLING.ppt).

6) PO Collector Shootout, Scott Dossett

Scott gave an update on the backyard testing on the different collectors. The study will last into May 2004. Collector options critique as per NADP NOS design document. Contestants: current ACM collector, Yankee YES TCP 3000, N-CON Systems ADS 100, and MIC A100. Design criteria based on Infrastructure Committee - Rick Artz, Rona Birnbaum, Van Bowersox, Gary

Lear, Mark Nilles, Al Riebau, Eric Prestbo. Design criteria (range, accuracy, sensitivity, resolution, false reporting, temperature limits, wind limits, reliability, maintenance, splash free, integration, collector orifice, container materials, multiple collector, cover operation, electrical power, height, data reporting, grounds maintenance) were evaluated for each of the collectors in order to rank them against each other. 1 being the highest mark for a design criteria category. Yankee actually came out with the highest score 12 out of 15 possible. Performance in ice and snow? ISWS "Backyard" test site only received moderate snowfall. Although, riming and collection of snow and ice on leading edge of N-CON collector lid would perhaps allow it to fall into sample bucket as it opens and closes. Only the N-CON sampler failed to open during a light snow event - not as sensitive as the others. For collecting rain, the Aerochem sampler was consistently capturing less than the stick gage and the others were fairly close and consistent in measurement, perhaps with a positive bias. Yankee collector was ranking better in chemical analysis because it has less splash than the others. It had consistently lower concentrations than the rest of the samplers. The chemical analysis is showing the positive bias with regard to concentrations of the main analytes. The YES sampler was consistently lower in bias than the NCON. Scott would pick the Yankee for the network if we had to decide today about continuing with the phase III testing. For more details on this study and chemical analysis performance see attachment 17 (COLLECTOR STUDY.ppt).

7) <u>Uniform NADP Site Selection Guide</u>, Scott Dossett

Scott noted the need to get a uniform program wide siting manual. Currently, only NTN has a formal manual. Streamline the Q&A document for easy use. Scott Dossett, Chris Lehmann, and David Gay are the crew working on this issue. Need to get committee approval after finalizing modifications to siting document. Site selection and installation manual is woefully bad right now as well. The next order of business is updating the site installation manual. Uniform site selection guide form has been changed and updated - this is posted on the web and is still being revised. For further information see attachment 18 (SITE SELECTION PAPERWARE.ppt).