Minutes for
Network Operations Subcommittee
Sacramento, CA
October 25-28, 1999

♦ **Introduction**

Introduction given by John Gordon, NOS Chair.

♦ **Approve Minutes from the May 1999 Meeting in Boulder, CO.**

Minutes were approved though the wrong minutes were posted on the web page. The correct minutes will be posted.

Motion #1: Minutes from the 1999 Spring NOS Subcommittee (Boulder, CO) be approved.
Scott Dossett, Mark Niles second Motion carried

♦ **Report to NOS on items forwarded to Executive Committee**

NOS report was accepted from the Spring Meeting with the exception of changing the Executive Committee distribution list. A motion from the Spring meeting was passed that added NOS vice chair and past chair to distribution list. Chairs of subcommittees should keep officers informed. Network design motion was tabled.

♦ **Update on NOS related outcomes from the CAL Audit**

See Attachment #1, CAL Report. Karen Harlin reported on CAL audit, the good items and recommendations. Overall the audit went very well and CAL is producing quality data. The audit only addressed NTN and AIRMoN laboratory functions and CAL data management. Separation of AIRMoN and NTN analysis equipment was not addressed during the audit. CAL does not have a current QA plan; a draft will be out by end of 1999. A final plan to the Executive Com. by Oct. 2000. CAL audit frequency was discussed. CAL recommended an audit every three years. The QA plan for NADP states a laboratory audit will take place every two years.

Motion #2: Audits of CAL to be conducted every three years.

Amendment: *A paper review be conducted within twelve months following a three year audit cycle.*

Mark Niles, Susan Johnson second Motion carried

♦ **Update of the audit/survey program and preliminary results from 1998**

John Shimshock reported on site audits. In 1999, there were 198 sites, two collocated. 199 audits will be conducted by Dec. 1999. He presented results of the 1998 concerns found at the sites. Most sites and operators were performing well. Most siting problems were due to vegetation >1 meter and storage areas/parking lots within 100m. Rain gages had some poor performances regarding weight tests and were recalibrated. All audit results are going to Scott Dossett at CAL for now. When a QA manager is hired for NADP, the results will go to that person.

Motion #3: The Program Office (QA Manager) is to follow up on problems resulting from the ATS site audits, report action on items that can be addressed and document those which can not easily be addressed. Report findings to the subcommittee twice a year.
John Gordon, Joel Frisch second Motion carried

♦ **Update on the raingage study and NCAR experiment**

Laura Hult reported on raingage field trials. Ott Pluvio, Geo Nor, ETI Noah II doing the best in Phase II or field trials. Phase III will involve winter field testing in Boulder, NCAR testing site.

♦ **Aerochem and raingage replacement initiatives**

Mark Nilles discussed sampler specifications need to be "finalized" for now so that two proposals, NOAA initiative and Program Office Request for Proposal can begin funding track.

Motion #4: The modernization specifications of rain gauge and precipitation collector are approved as currently written.

Amendment: *The specifications on the web site are deemed preliminary.*

Van Bowersox, Dennis Lamb second Motion carried

Motion #5: The NOS Subcommittee has 20 days to review sampler specifications and comment to Mark Niles.

Amendment: *The 20-day time limit to comment on specifications was changed to the final subcommittee meeting (October 27, 1999). with the final vote will be taken at that time.*

Joel Frisch, Lee Maull second Motion carried

♦ **NOS subsampling protocol change, is 200 mL adequate for the CAL**

Jane Rothert discussed subsampling changes proposed at Spring meeting. The lab needs at least 200 mL of sample for analysis and 60 mL archive sample. The bottom line is that a sample would need to be at least 250 mL to retrieve a subsample (200 mL for lab and 50 mL for pH and conductance by operator). Jane presented a modified subsampling protocol, see Attachment #3.

Motion #6: Change minimum sample volume sent to CAL from 300 mL to 250 mL to allow for subsampling.

Jane Rothert, Dennis Lamb second Motion carried

♦ **Results from the Decasplitter Study**

See Attachment #4. Jane Rothert presented a study comparing the use of a decasplitter versus hand pouring for obtaining sample splits. She found there was no statistical difference between the two methods. The lab would like to discontinue use because of difficulty using equipment in favor of hand pouring.

Motion #7: Discontinue use of the USGS deca-splitter in favor of hand pouring spilt samples for the USGS Intercomparison Study.

Rick Artz, Scott Dossett second Motion carried

Further discussion led to subsampling protocol again and resulted in this motion.

Motion #8: A line item from the NTN Subsampling Procedures be removed (never take more than 100 grams for subsample) and replaced with shaking a sample (according to written procedure) before pouring subsamples and limit subsample volume to 250 mL.

Amendment: *Add shaking protocol to other appropriate areas in NTN Subsampling Procedures document such as the example situation listed in procedure.*

Mark Mesarch, Scott Dossett second Motion carried

- **Design of the upcoming Ott raingage field study**

Mark Nilles reported on design of upcoming field study. USGS purchased 6 Ott raingages because of extra resources and Ott was looking good in previous studies. Equipment Committee will come up with draft field study plan for where the gages should go. Asking NOS for input for potential field trail sites and what kind of data downloading should be utilized. Five will be next to a Belfort and one doubled up at one collocated. The gages are outfitted with data loggers. Comments and suggestions should be given to Mark Nilles.

- **LODA sensor ACM sensor comparison results-are they equivalent for the CAL?**

Scott Dossett reported on status of new equipment that fits the Aerochem 301. A new sensor has been developed and testing data was presented.

Motion #9: NOS endorses the use of LODA sensors as equivalent to Aerochem and be used in the field.

Scott Dossett, Mark Niles second Motion carried

- **Update on network Growth Issues- what planning and decision have been made since the spring meeting?**

Van reported on CAL status to handle >50 samples. Analytically there is no problem except for staff, hence more money. Maybe an additional IC if more than an increased fifty samples. Space problems for shipping and receiving also. Can AIRMoN be separated? Yes, but need money for an additional IC, $50,000. Could have better information if a target number is defined.

- **Collocated site for FY2000**

John Gordon reported on site picked for collocation sites NH02 and CO08. The collocated year runs from October 1999 to September 2000.

- **Comparison of Pittman and standard Aerochem motorbox and statistical analysis of motorbox opening times**

Scott Dossett reported on statistics. High output motorbox opens in 11 seconds and standard Aerochem opens in 7 seconds.

Motion #10: NOS endorses the use of Pittman High Output Motorbox as equivalent to Aerochem Metrics motorbox and is to be used in the field.

Scott Dossett, second Motion carried

- **An Analysis of Field Blank and Reference Sample Data**

John Gordon reported on field blank samples. See Attachment #5 for results. Twenty five percent of sites reported no field blanks because they had no dry weeks.

- **Developing NOS standard guidelines to clarify requirements of the NOS Chair, Vice Chair, and Secretary**

John Gordon discussed the need to clarify the arrangement of subcommittee officers and their duties. Guidelines will be presented at Spring 2000 meeting.

Motion #11: Committee of past two NOS chairs and current chair shall author a statement of NOS Subcommittee officer duties and bring forth to NOS committee.

Joel Frisch, Scott Dossett second Motion carried

- **Discussion of collector raingage specifications**

NOS subcommittee again discussed the raingage specifications after a few days for review. Specifications to be added include ability to function without power, anti icing component, lightening protection and decrease snow scouring.

Motion #12: The collector and rain gage specifications be accepted with the added comments as discussed in NOS Subcommittee.
Scott Dossett, Joel Frisch second Motion carried

- **Election of new officers**

Motion #13: John Shimshock be elected as NOS Subcommittee Secretary for one year.
Scott Dossett, Rick Artz second Motion carried

Attachment Summary

1. CAL Audit Report Karen Harlin
2. Infrastructure needs for the NADP: Timeline, Progress, functional specifications and rationale for new sampling equipment Mark Nilles
3. NTN Subsampling procedures Jane Rothert
4. USGS Decaspilt vs. poured Interlaboratory Comparison Sample Study Jane Rothert
5. Field Blank Analysis and Reference Sample Data

Sept 1999 CAL Audit Report

POSITIVE FEEDBACK

- "The CAL operates smoothly and effectively turning out quality data to support both networks. The staff is knowledgeable, well trained, and has an enthusiasm for doing its tasks that is contagious. Many employees have been with the program for many years, speaking to their dedication to the program and to the quality of the work environment provided by management."

- "..... the QA Specialist, independent of the CAL management function, has brought about many improvements in QA procedures, most notable being widespread use of control charts by the analysts..."

- "Over the years the CAL has developed a sophisticated computer system to assist in all aspects of their work.... CAL has completed an intensive internal review to make sure their systems are ready for Y2K."

- "....the CAL is currently operating in control under a virtually complete set of SOPs which describe each function in detail. This documentation represents an outstanding effort of the CAL staff. Not only are the SOPs in place, but older copies indicate annotations of changes."

- "The team notes a well educated, dedicated staff. Management is doing an excellent job with cross training." "One of the great strengths of the CAL is the experienced

and dedicated staff."

- "All of the analytical staff placed significant effort on maintaining cleanliness and order in their analytical space."

- In laboratory areas "Housekeeping practices are excellent."

- Safety showers, eyewash stations, fire extinguishers and fume hoods were readily available.

- "Chemical storage appears to be adequate and well managed. Chemicals were properly dated and stored."

- "Good" sample management.

- Well kept logbooks for each instrument.

- "CAL has continued to upgrade instrumentation and data interface programs."

- "Excellent" analytical procedures!!!

- "CAL continues to participate and do well in interlaboratory comparisons."

IMPROVEMENTS AND RECOMMENDATIONS

❖ QA Documentation

The CAL does not have an up to date QA plan in place. Recommendations are:

1. Decide on the approach they will take to document QA
2. Prepare the drafts in an accepted (e.g. EPA guidelines), consistent format
3. Get review and approval as required
4. Implement the plans

An internally reviewed final draft is submitted to the NADP Executive Committee for adoption by October 1, 2000.

A CAL QAP dated 1991 mirrored Ch. 3 of the NADP QAP (June 30, 1991). This umbrella document is past due for revision. A major revision of the CAL QAP was delayed until the arrival of a PO QA Manager who would be charged with updating the NADP QAP. This timing would avoid discrepancies in the two plans.

The audit team requested a current CAL QAP; a Draft Revision of the 1991 plan (Sept 99) was provided to the team prior to the audit. The auditors recommend that the CAL proceed with the preparation of a final QAP in the absence of an updated NADP QAP.

❖ SOPs

SOPs with a recent single date are indicative of a lack of ongoing review and maintenance and should be avoided. The committee was concerned that the SOP updates were in sink with the biannual audits rather than ongoing as needed.

The 1993 audit report indicated that improvements in document control, review, and consistent content were needed. In 1998/99 the CAL adopted the USEPA Standard Operating Procedure (SOP) format for all CAL laboratory and operations SOPs. During the past year, all SOPs have been revised to accommodate this new format. SOPs will continue to be reviewed, added, deleted, and revised as needed on an ongoing basis.

❖ Staffing

Relieve supervisory analysts from some laboratory duties

New analyst in training for AIRMoN will assume some workload of supervisory analyst

❖ Laboratory Facilities

Shared space in the Flow Injection Analysis (FIA) and Atomic Absorption Spectroscopy (AAS) laboratory areas

No control over possible cross-contamination from the co-inhabitant's reagents, samples, and procedures. Cleanliness of the other tenants space.

FIA: An unventilated digestion oven may introduce contaminants into the laboratory air.

Chemical storage under shelves and in hoods, may also pose contaminants and should be investigated or removed from the laboratory.

The CAL has shared laboratory space with other researchers since 1978. Internal blanks and control samples do not indicate any evidence of contamination.

A request is still pending with the State of Illinois Capital Development Board for a new laboratory facility. If constructed, the CAL would be able to design laboratories to their specifications.

❖ Temperature control

Concern with lack of temperature control in laboratory areas. Recommended establishing a route for amending facilities and making this known to the analytical staff.

All laboratories currently have an individually controlled wall-mounted thermostat. The sample preparation laboratory and the IC laboratory have independent heat and cooling units for additional control. The AAS laboratory has an auxiliary air conditioner. No action is needed.

❖ Safety Program

Cease the disposal of used reagents and chemicals into the sewer system.

CAL complies with all university and state chemical hygiene disposal plans. Hazardous materials are disposed per the University's chemical waste pick-up system. A CAL analyst is the Bldg representative for the UI waste disposal program and is familiar with the procedures.

❖ **Safety Program** (con't)

No well-defined safety protocol appeared to the available and accepted by the CAL staff.
Written safety plans are needed at the bench level and should be lab specific.

Each analyst has a copy of the current safety plan. Mark Peden is the ISWS Chemical Hygiene Officer and Chair of the Safety Committee. A CAL analyst is a member of the ISWS safety committee. Committee minutes are on the ISWS web page. Safety training, coordinated through university, occurs on a regular basis. Management will ensure that all CAL staff have a current copy of the safety manual and ensure that new staff are notified of this plan.

Increased safety requirements for safety glasses, lab coats, and gloves for analysts and casual visitors.

Door signs are being ordered for hazardous laboratory areas "Eye Protection Required". The safety committee was informed of this report and is reviewing procedures.

AAS vents do not have maintenance logs.

These logs are available.

Fire extinguishers should be available in the laboratories as well as the hallways and of sufficient size. Records of validity checks were missing.

The local Fire Dept performs this review annually. An inspection was performed in Oct.

❖ **Safety Program** (con't)

Lists of chemicals in each lab should be listed outside each lab and filed with the fire dept.

Under evaluation.

MSDS sheets on file in Bldg 9 were not current (1994 was most recent) and were incomplete (gases unavailable).

The CAL will file MSDS sheets in each laboratory, rather than depend on a central location.

Helium tank too close to AAS.

The tank was 3 feet behind the AA, mounted to a wall behind the instrument. A safety hazard is unlikely, however, the tank has been moved.

Determine the safe minimum low pressure setting for use of acetylene

This is determined by the manufacturer to be 50 psi. The analyst uses that cut-off point.

Determine a better method for moving acetylene tanks in place.

Under evaluation.

❖ **Safety Program** (con't)

Working alone in the laboratory policy needs to be better defined.

The ISWS safety committee addressed this issue and determined that someone working alone shall notify at least one person where they are working and how long they will be there. This is also covered in the Lab Safety Plan.

Prohibit food and drink in the labs.

Some analyst's office areas are located in their laboratory. The ISWS policy has been that food is allowed on their desk if that is their work area.

❖ **Sample Management**

Evaluate computerized schedules and sample tracking systems for laboratory and data management systems.

Sample tracking using an Access database or within a LIM system is being investigated.

❖ Laboratory Protocols

Would like to see an extract of the operator's manuals with a maintenance calendar. There is no plan in place that covers training for new operators or the maintenance of current skills.

This is currently incorporated into most SOPs. As SOPs are updated additional required maintenance will be included. The updated CAL QAP will also address training.

❖ Laboratory Instrumentation and Equipment

Forecast the periodic replacement of all instrumentation and computers.

The focus for 1999 was on computer hardware and software due to Y2K issues. Laboratory equipment needs are currently under evaluation.

❖ Analytical Procedures

Calibration check standards were not in within the range of the FR25 and FR75.

Only IC check samples were run and plotted. All should be run and plotted in addition to the FR samples.

These issues vary with the methods utilized, however, they are being reviewed and procedural modifications may be recommended. Check sample data were available for all procedures, however, some analyst do not plot the results. This is under review.

Adopt a clear policy on rounding analytical values at the bench.

The instrument software may dictate the level of rounding available to the analyst. CAL procedures will be reviewed.

Add calibration standards closer to the MDL.

This is under review.

Review the calibration ranges to ensure that they continue to reflect the sample population.

This is under review.

❖ Data Management

Hire data support staff to enable the CAL to meet program goals for data deliverables to the PO.

Interviews have concluded. Expected date of hire Nov. 99.

Reevaluate data validation and verification programs to better utilize artificial intelligence.

Evaluate the use of list of samples that don't meet specific criteria rather than lists of all samples.

Updating data review and validation programs has been discussed. In light of the data back log, this issue is targeted for review after the new data specialist is hired.

Evaluate the need to ensure that hardcopy FORFs and FOFs are edited to reflect all edits.

The CAL will meet with the PO data staff to review this policy.

Decasplit vs. Poured Interlaboratory Comparison Sample Study

Currently the decasplitter, furnished by the USGS, is used to split approximately 2 liters of a mixed NTN sample (2 different NTN samples are mixed in a 2 litter bottle) into two sets of ten 125 mL bottles. These samples are then placed in plastic bags and shipped to John Gordon at the USGS in Denver, CO. The decasplitter is designed to split 1 liter of sample into 10 equal parts but is hard to handle and clean and is susceptible to contamination. The CAL would like to evaluate the use of poured aliquots versus the decasplitter to see if pouring the samples would also result in ten samples of equal concentrations. This study is designed to look at the difference between poured aliquots and the decasplitter.

As much as possible, the same protocols will be used to prepare and divide the samples. Instead of ten125-mL samples as is done when preparing the samples for the USGS intercomparison studies, ten 60-mL samples will be prepared using the decasplitter. Another ten 60-mL samples using the same solutions will be prepared as poured aliquots. Four different matrices of solutions will be used, generating a total of eighty 60-mL samples. Only forty of these samples will be used in this study unless more data is needed.

The four solutions used will consist of the following:

1) 2 samples of approximately 750-mL each from 2 NTN sites east of the Mississippi River (East Coast sites)(EC)
2) 2 samples of approximately 750-mL each from 2 NTN sites west of the Mississippi River (West Coast sites)(WC)
3) 2 samples of approximately 750-mL each one from a site east of the Mississippi River and one from a site west of the Mississippi River (Mixed)
4) Exactly1 liter of FR25 and 1 liter of FR75 (FR)

Solutions #1, #2, and #3 will be chosen from routine NTN samples that are of sufficient volume to have about 750 mL remaining in the shipping bottle after pH and conductivity aliquots and two filtered NTN samples have been removed. The two samples will then be filtered and poured into a 2-L bottle. The contents of the bottle will be thoroughly mixed by inverting the bottle and while inverted, shaken briskly with a horizontal motion for 5 - 10 seconds. The bottle will then be turned upright. This inversion and shaking procedure will be repeated ten times(1). The bottle containing the mixed samples will then be allowed to sit for at least 24 hours. Immediately before subsampling from the 2-L bottle, the above mixing procedure will be repeated.

(1) Elementary Quantitative Analysis, Theory and Practice, Second Edition, W.J. Blaedel and V.W. Meloche, Harper and Row, Publishers, pg 257, 1963.

After 24 hours or more and thoroughly mixing, the samples will be handled in one of two ways. A small portion of the sample will be used to purge the decasplitter to remove any residual water left over after cleaning it. Approximately 750 mL of the sample will then be poured into the decasplitter for subsampling into ten 60-mL polyethylene bottles. The remaining 750 mL of the mixed sample will be poured into ten 60-mL bottles with the cap replaced on the 2-liter bottle and the bottle inverted and shaken briskly with a horizontal motion for 5 - 10 seconds between each bottle. Solution #4 will be the control solution in this study and will be made from the simulated rain samples prepared at the CAL. One liter of each 99FR25 and 99FR75 will be measured and added to a 2-L bottle. The sample will be split as above after sitting and mixing for at least 24 hours.

The 60-mL bottles will then be placed in plastic bags which will be labeled with the site ID's from the original samples and with the date on of the samples. The bag will also be clearly marked as to whether these aliquots came through the decasplitter or were poured aliquots. Samples will be grouped by decasplitter or poured aliquot and by solution number (#1, #2, #3, or #4). There will be a total of eight bags of ten 60-mL bottles of sample, each bag marked with site, sample, and subsampling information and sample type (real precipitation sample or control). These bags will then be given to Jane Rothert for distribution to the labs as internal blind samples.

Rothert, upon receipt of the first set of bagged samples, will remove 5 of them and label them as SWS5, SWS6, SWS7, SWS8, or SWS9, using polyethylene tape. Field Observer Report Forms (FORF) for each bottle will be prepared using the SWS code assigned to each bottle as the station ID. The date on/off will be used to identify which samples were processed which week. The FORF will contain sufficient information to identify the sample and subsampling method. Five of these blind samples will be put into the analysis queue each week for eight (8) weeks. These five samples will be processed as internal blind samples.

When all 40 samples have been analyzed and the results have gone through routine NTN reanalysis screening, a statistical evaluation of the data will be done by the CAL and the USGS staff. A decision will then be made as to whether use of the decasplitter can be discontinued and replaced with poured aliquots for subsampling.

Statistical Comparison of Decasplitter Samples and Poured Samples

F test (variances of two normal populations are equal at 95%), one-tailed test, F = 6.39 = critical value

Sample ID	*Ca*	*Mg*	*K*	*Na*	*NH_4*	*NO_3*	*Cl*	*SO_4*	*Cond*	*H*
FL99/TX10	1.7	1.5	2.7	4.7	1.5	2.1	0.0	1.1	3.4	2.1
NY65/SC06	1.7	0.0	1.0	15.0(P)	14.0(D)	1.4	0.0	7.5(D)	1.8	2.8
OR98/OK00	19.6(D)	0.0	8.8(D)	9.2(D)	3.4	6.0	1.0	2.3	106.0(P)	2.
FR25/FR75	26.4(P)	4.0	4.0	3.8	1.7	1.5	1.5	3.5	1.1	1.2

Note: D = decasplit samples
P = poured samples
The letters in parentheses indicate which type of sample has the lower variance.
F = v1/v2 where v1 > v2

t-test or rank sum test: Is t > 2.13 at 4 degrees of freedom and, therefore, statistically different?

Sample ID	*Ca*	*Mg*	*K*	*Na*	*NH4*	*NO3*	*Cl*	*SO4*	*COND*	*H*
FL99/TX10	no	no	no	yes	no	no	yes	no	no	no
NY65/SC06	no	no	no	no	no	no	no	no	no	no
OR98/OK00	no	no	no	no	no	no	no	yes	no	no
FR25/FR75	no	yes	no	no	no	yes	no	no	no	no

Note: t = difference between the means of two groups/standard error of the difference between the means.

1998 Field Blank Program Results
-- by Target Concentration

Analyte	Bucket minus bottle differences significance levels (p-value) by sample target concentration	Statistically significant (a=0.05) differences by concentration
Sodium	0.410	No
Calcium	0.233	No
Hydrogen Ion	0.224	No
Sulfate	0.198	No
Magnesium	0.148	No
Potassium	0.107	No
Nitrate	0.026	Yes
Specific Conductance	0.001	Yes
Chloride	0.000	Yes
Ammonium	0.000	Yes

Results of the Kruskal-Wallis analysis of variance test to determine the relation between paired field-blank sample differences and the sample target concentrations

preliminary 1998 data

1998 Field Blank Program Results --by sample volume

Analyte	Bucket minus bottle concentrations attained significance (p-value) levels on a concentration basis	Statistically significant (a=0.05) differences determined between 250-, 500- and 1,000- mL USGS samples
Ammonium	0.943	No
Specific Conductance	0.828	No
Hydrogen Ion	0.819	No
Potassium	0.550	No
Calcium	0.291	No
Sodium	0.035	Yes
Nitrate	0.031	Yes
Magnesium	0.003	Yes
Chloride	0.000	Yes
Sulfate	0.000	Yes

Results of the Kruskal-Wallis analysis of variance test to determine if bucket minus bottle differences for the 250-, 500-, and 1,000- mL samples have equivalent distributions on a concentration basis

preliminary 1998 data

1998 Field Blank Program Results
-- by sample volume, on a mass basis

Analyte	Bucket minus bottle concentrations attained significance (p-value) levels on a mass per bucket basis	Statistically significant (a=0.05) differences determined between 250-, 500- and 1,000- mL USGS samples
Potassium	0.923	No
Nitrate	0.813	No
Ammonium	0.501	No
Hydrogen Ion	0.423	No
Sodium	0.379	No
Chloride	0..287	No
Specific Conductance	0.195	No
Calcium	0.155	No
Magnesium	0.050	Yes
Sulfate	0.010	Yes

Results of the Kruskal-Wallis analysis of variance test to determine if bucket minus bottle differences for the 250-, 500-, and 1,000- mL samples have equivalent distributions on a mass per bucket basis

preliminary 1998 data