Ecological Response and Outreach Subcommittee

NADP Spring Subcommittees Meeting
Hampton Inn, 2 Via de Luna Drive
Pensacola, Florida
April 29 & 30, 2008

Draft Meeting Minutes

(revised 8/25/08)

Tuesday, April 29:

a) Status report on outreach letter/invitation to NRSP-3 scientists to attend and participate in NADP meetings – (Andy).

It was suggested that we contact Ray Knighton (USDA) to collect potential topics of interest from the agricultural community. In addition, new SAES representatives are conducting NADP program reviews at the meeting to fulfill agreements. Results from the review, which were made available to the NADP list serve in May would also be useful in drafting outreach letters to the agricultural community.

b) Status report on outreach letter/invitation to local NADP site operators and sponsors – (Andy).

Andy reported that unfortunately due to time constraints on his end, no letters to "local" NADP site operators (with copies to their supervisors) were sent out inviting them to attend and participate in this Spring meeting. The group acknowledged that this outreach effort is probably best made for encouraging site operators to attend the bigger Fall meeting and its scientific symposium. Tom Butler handled our initial effort at this for last fall's meeting in Boulder, CO. Tom reported maybe only a few site operators ended up attending, and even though the Program Office had offered to waive the meeting registration fee, the lack of travel funds in general appeared to be the biggest obstacle in them being able to get to any meeting. It was agreed this is still a worthwhile effort to pursue and Andy committed to working with the Program Office to send out invitation letters for the Fall meeting in Madison with sufficient lead time to take travel arrangements. While no invitation letters were sent out about attending this Spring meeting in Pensacola, Andy committed to renewing this effort for the annual fall in Madison. Finally, it was also noted/clarified; it is the responsibility of the Program Office to notify the site operators and supervisors of the NADP incremental 5-year awards.

c) Status report on revised mercury 1-pager "educational" fact sheet and possible mercury 1-pager "technical" fact sheet – (Pam, Bob Brunette & David Gay).

Mercury one-pager is still on hold because the initiative is still being developed. A decision was made to create 2 separate documents, one that would be more educationally oriented, and a second that be a fact sheet specific to the mercury speciation initiative.

2) Presentation/discussion on using resins to measure precipitation chemistry – (Tracy Dombeck). See addendum for resin column method and research outline.

The use of resin columns as an alternative method for measuring precipitation at NTN sites was based on interest from a previous Kathy Weathers project using resin columns to extract Na, K, Ca, and Mg. As a potential new initiative, tests are being conducted by the CAL on resin column method reproduction using an ion chromatograph over the next 3-4 months. There will be a possible poster presentation at the fall NADP meeting on the comparison and protocols. Discussion followed on potential methods, column efficiency, collection-time periods, and collector designs. The resin initiative would serve as a separate co-located field component. The collector would need to be heated and would need to measure volume. Collector design could potentially be a modified Aerochem collector.

Cation issues such as background levels and recovery (Ca and Mg) were a concern. Constituents such as pH and conductance could not be measured through the process, but other useful analytes such as pesticides may be measured. Potassium may not be a useful extractant since it is a measured analyte. Iodide as an extractant poses problem with IC maintenance, matrix interference and precipitant formation. KI extraction has been useful for measuring Cl, but not very good for phosphate, one of the cation analyzed for the NADP.

Estimate cost to run the alternate resin column method is around $120-140 per month vs. NTN costs ($93 per week). For anions only, the lab cost (upfront) would be up to $2500, however, the constituents measured and extractant cost would factor into it.

It was suggested that they Forest Service experiment forests could serve as test sites. Follow up with Pam Padget and Frank McCormick on the use of forest service sites.

From the CAL, the total nitrogen (TN) method has been re-worked and additional QA has been added. Estimated costs are $20 per sample to run.

3) Other issues and comments?

It was suggested that draft agendas be shared with members that are not on the EROS list serve prior to the fall meeting so that we can coordinate groups on potential combined areas of interest.

<u>Wednesday, April 30</u>:

1) Discussion/Brainstorming Session:
   a) Making the connection between NADP's mission and climate change - how do we do it? – (Tom Butler, Eric Prestbo, Beth Holland or Angela Zahniser)

   The NADP mission as laid out in the Governance Document reads:

   The NADP-

● provides quality-assured data and information in support of research on the exposure of managed and natural ecosystems and cultural resources to acidic compounds, nutrients, mercury, and base cations in precipitation.
● remains one of the nation's premier cooperative research support programs, serving science and education and supporting communication and informed decisions on air quality issues affecting ecosystems and human health.
● seeks to respond to emerging issues and evaluates changes in its measurement systems, including the addition of other chemical and biological species.

In response to the last bullet in the mission statement, the EROS group wanted to brainstorm on ideas of how to address climate change as an emerging issue. Potential linkages identified were: ozone interactions and nitrogen precursors, precipitation and temperature, impacts to mercury emission, and a list of potential collaborators/data networks that we could learn from.

- *Ozone and nitrogen precursors*- CMAQ model has been used by EPA (Alice Gilliand) for ozone modeling as a result of climate change out to 2030. Ammonia might also play a significant role as correlations between temperature, precipitation, and ammonia has been noted at several rural sites.
- *Is there a relationship between temperature and ammonia because of manure at rural sites?* Some of the sites have a doubling of concentration in ammonia at one site. NADP doesn't monitor temperature at their sites. This may also be important because longer growing periods would increase the surface area.
- *Change in rainfall*- wet deposition will probably have bigger influence than dry- North Atlantic Oscillation Cycle is often picked up. The importance of long-running stations and how the amount of precipitation might have changed over time. Twenty years just tells you that it is different now than it was in the beginning. Climate change is never one variable. Possibly look at relationships between climate signals and deposition data. Building on empirical relationships that are in the database now.
- *Impacts on mercury emission/re-emissions*- mercury bi-directional flux due to increasing temperature and reemission; re-volatilization because of bedrock and soils with high Hg; increased methylation with wildfires from emissions in wildlife; implications of Hg-Hg0 to reactive gaseous Hg; increases/decreases to global pool; increased precipitation resulting in depositional changes; the role of ozone oxidation of Hg (i.e. oxidation rate increase in Acadia National Park where the highest amounts of Hg concentrations are in ME).
- *Possible collaborators and outreach*-the use of Remote Automated Weather Stations (RAWs) to connect to NADP sites. FACT (Fire air coordination team) subgroup to investigate issue papers for connection between wildfire (Inner Agency Fire Center- funded as a budget line item by BLM out of Boise). Climate Reference Network- Historical Climate Network will be discussed at the Executive Committee meeting. Session of climate change headed by Rick Haeuber at the Fall 2008 meeting. STAR grant climate change and air quality topic, critical loads as a vehicle for climate change connection.

Climate/Deposition Interactions Outline (provided by Gary Lear)-

1 Introduction
- a This information can be used to inform the relationship among deposition and climate
- b Because of the role NADP has played in this area
    - i NADP has a 30-year record where it appears climate has changes
    - ii Will become even more valuable in future years
- a We have a history
- b See governance document for language
- c Seeks to respond to emerging issues and evaluate changes in its measurement system including the addition of other chemical and biological species

2 Role of long-term monitoring
- a Provide validation of models
- b Establishing status and trends
    - i Precipitation chemistry (see Web page for text)
    - ii Correlations between climate change and wet deposition patterns
        - 1 Spatial and temporal
- a Assessing atmospheric response to changes in emissions
    - i Sox, NOx, mercury
- b Inform critical load assessments under future climate scenarios

3 Expected change of climate change on chemical climate
- a Precipitation chemistry
- b Dry deposition and air concentrations
- c Changes in deposition and partitioning of various constituents
    - i Ammonia/ammonium
    - ii Mercury
        - 1 increasing incidence of wildfires
- d Longer growing season influencing dry deposition
- e Changes in emissions
    - i Air conditioning
- f Biotic
    - i insects
    - ii morphology of ecosystems
    - iii productivity
- g Abiotic
    - i fire
    - ii drought
- h Physiology of trees themselves
    - i Foliar/root relationships
- i Static models are only a start
    - i Dynamic models needed
- j Sentinel pathogens
- k Oxygen isotope relationships to temperature

4 Future areas/additional areas for contributions and research of NADP

5 Graphics
   a Emissions vs. deposition /concentrations
6 Invitation to participate
   a NADP has the infrastructure to allow for new studies related to climate change

2.) Kids Corner idea for NADP website:

As an outreach effort, it was suggested that EROS, working with CAL or the Program Office develop an information page for children ages K-8 for the NADP website.

3.) Website update:

Website development priority-Should we hire another part-time staff member to develop and work on the website? Website marketing is important for selling ourselves and promoting ourselves to public officials and the public in general. Suggested action was to bring it up in Executive Meeting as a motion to ask the program office to help.

4.) List of EROS attendees:

Name	**Affiliation**	**Email**
Ryan Nelson	Frontier Geosciences	ryann@frontiergeosciences.com
Maggie Kercher	NOAA	Margaret.Kercher@noaa.gov
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Outline for Resin research.

Resin columns have been evaluated for bulk deposition for sodium, potassium, calcium and magnesium using 1M HCl for extractions (Crabtree and Trudgill, 1981) and throughfall for sulfate, nitrate and chloride using 1M KI as an extractant (Simkin et al., 2003). A study of throughfall in pine forests (Fenn and Poth, 2002) evaluated mixed bed resins for ammonium and nitrate using 2M KCl as the extractant and colorimetric methods for analysis. There has been work done to evaluate both cations and anions using KI as an extractant. The CAL can evaluate their capabilities and reproduce results obtained by the Rachel Carson Analytical Facility, (formerly Institute of Ecosystem Study's IES Analytical Laboratory). They developed and modified an IC method for analyzing chloride, nitrate, and sulfate with 1M KCl used as an extractant.

I. Where to start.
   A. Develop/Modify IC method on CAL's back-up Dionex 500 instrument.
   B. Evaluate CAL's capabilities to prepare, extract, and analyze resin column extracts.
      1. Analyze excess samples previously extracted by their lab group.
      2. Compare columns prepared by their group with columns prepared at CAL using monthly composite with excess deposition from pre determined sites and CAL's internally prepared QC solutions.
      3. Use NWRI samples to analyze for TN extracted in columns.(???extract)
      4. Load ½ of KW group prepared columns and ½ of CAL prepared columns with CAL's in-house prepared QC solutions.
   C. Time frame for this work 3-4 months, goal poster at NADP Fall Meeting.

II. What additional work can be done to evaluate resins as throughfall and or wet deposition collection devices.
   A. Additional Lab studies
      1. Additional resins/extractants for a variety of analytes.
      2. Stability of resins, temperatures, moisture
      3. methods of extraction, i.e. sonicating shaking
      4. extractants more instrument friendly
   B. Additional field studies
      1. Evaluate strength and stability of resins in freezing and drying conditions.
      2. Collector design.
      3. Length of collection periods.
   C. Comparative study between wet collectors and resin collectors.

III. What new things could NADP learn.
   A. Monitoring in remote/heterogeneous terrain where saturation density is low so better resolution.
   B. May improve evaluation of nitrogen deposition (better ammonium stability)
   C. May allow expansion of analytes in future, pesticides, trace species.
   D. May allow for increased sampling duration.

Method

Analysis: Nitrogen compounds are oxidized in-line to nitrate using an alkaline persulfate digestion at 90°C with additional energy supplied by ultraviolet light. After digestion, the nitrate is then passed through a cadmium column, quantitatively reducing it to nitrite. The nitrite is then reacted with sulfanilamide, under acidic conditions, to form a diazonium ion. This ion is coupled with N-(1-naphthyl)ethylenediamine dihydrochloride (NED) to produce a pink dye that absorbs at 540 nm and is proportional to the total nitrogen concentration. This method will recover nearly all forms of nitrogen, including nitrate and nitrite, thus it is termed total nitrogen. Nitrate and nitrite are not recovered in the conventional Kjeldahl nitrogen method.

Equipment: The total nitrogen method is applied using a Lachat Quik-Chem Flow Injection Analyzer 8000+ Series, an eight channel proportioning pump, Lachat Sample Preparation Module A30X11 with UV-254 nm light, Lachat Total Nitrogen Reaction Manifold including a cadmium reduction column, peek bubble trap), Lachat's Omnion Software V 3.0, and Lachat's XYZ Autosampler.

Method Range: 0.024 – 2.00 mg N/L: Six standards prepared from potassium nitrate and calculated as KNO_3-N were prepared to construct calibration curve from 0.00 – 2.00 mg N/L.

Method Detection Limit: Calculated as 0.010 mg/L N (based on multiple analyses of the 0.050 mg/L N standard.

Quality Control: Nine different quality control standards (QCS) are used to verify the method's accuracy and precision. The CAL prepares in-house synthetic "Faux Rain" quality control standards that are used on all instruments. In addition, seven other QCS are prepared weekly and analyzed to validate the method and check the persulfate digestion and cadmium reduction column efficiency. The nine QCS are listed below.

Quality Control Standard	**Compound**	**Concentration (mg/L N)**	**Recovery (%)**	**Standard Deviation**	**n**
Standard E	KNO_3	0.05	106.5	0.003	13
CAL's synthetic "Faux Rain" 25th percentile concentration laboratory control standard (FR25)	KNO_3	0.204	99.2	0.008	13

CAL's synthetic "Faux Rain" 75th percentile concentration laboratory control standard (FR75)	KNO_3	0.779	95.3	0.024	13
Standard B	KNO_3	1	100	0.011	13
Sulfanilamide Digestion Check Standard (typical recovery for this compound by this method is 80.5%)		2	81.3	0.113	13
Urea		1	97.5	0.012	4
NWRI Water Science & Technology Environment Canada PT 0091 # 6		Target: 0.477 Mean: 0.487	97.3	0.012	7
NWRI Water Science & Technology Environment Canada PT 0091 #9		Target: 0.270 Mean: 0.267	96.8	0.010	5
Cadmium Reduction Column Check Standard	NO_2	1	98.1	0.030	4

Reference:
-QuikChem® Method 10-107-04-3-A, Lachat Instruments, Milwaukee, WI 53218