Determination of annual loads of inorganic atmospheric contaminants in northern Alaska by measurement in snowpack and passive ion collectors

W. Brumbaugh[1], S. Earhart[2], G. Linder[3], and P. Neitlich[4]

[1] U.S. Geological Survey, Columbia, MO; [2] Five Rivers Services, LLC, Columbia, MO; [3] U.S. Geological Survey, Brooks, OR; [4] National Park Service, Winthrop, WA

Presented at the 33rd annual meeting of the Society of Environmental Toxicology and Chemistry, Long Beach, CA, November 11-15, 2012

ABSTRACT

Protected lands in Alaska managed by the U.S. National Park Service (NPS) are under increasing threats from atmospheric contaminants. At remote locations the use of conventional systems for monitoring deposition of atmospheric contaminants over extended time intervals is generally not practical; consequently, sampling methods that require minimal maintenance and no power for operation are needed for use in monitoring these areas. We determined annual loads of ammonium, nitrate, and sulfate at three sites in northern Alaska, based on two types of sample collections at each site: (1) winter snowpack sampled just before onset of thaw in late March and (2) ion-exchange collectors (IECs) for passive, integrative sampling from wet and dry precipitation between March and October. At each site, snow samples were collected in triplicate and three IECs were deployed. Two-stage IECs were developed for this study, which produced much lower ammonium ion concentrations in field blanks as compared to a single-stage design investigated previously. For a 10-week, 2011 pilot study we obtained close agreement between loadings estimated by IECs and National Atmospheric Deposition Program (NADP) weekly wet precipitation samples. Annual loads estimated for 2011-2012 based on the snowpack and IECs were comparable to historical values reported by the NADP at stations in northern Alaska (2012 NADP data pending). Our studies demonstrate that measurement of ammonium, nitrate, and sulfate at the very low atmospheric loadings typical of remote locations in northern Alaska can be determined using the 2-stage IECs with precision of between 5 and 10% RSD. Comparison of 2012 total annual loads estimated by snowpack plus IECs to that of NADP wet deposition data is pending, as well as analyses of IEC extracts for a suite of trace elements.

INTRODUCTION

Background

Passive sampling for selected ionic pollutants using specially adapted, ion-exchange collectors (IECs) shows promise for monitoring loads of ionic contaminants from both wet and dry deposition (Fenn and Poth 2004; Simkin et al. 2004). However, the methodology has not been demonstrated in arctic environments and the very low concentrations of ionic contaminants that are typically present in precipitation of pristine regions of northern Alaska presents increased challenges for this technique.

Objectives

- Develop passive sampling methodology for determining annual loads of selected atmospheric pollutants in remote regions of Alaska.
- Evaluate IEC precision based on replicate variation and IEC accuracy based on comparison to data obtained at National Atmospheric Deposition (NADP) monitoring stations and by recovery of spikes added to IECS at time of deployment
- Combine measurements in 2011 snow pack with 2012 IEC data to determine annual loads at each of three sites.

MATERIALS AND METHODS

Sampling

- 2011: 10-week IEC pilot (Fairbanks plus 2 NADP stations)
- 2012: Snowpack + 6-month IEC (Fairbanks plus 2 NADP stations)

Snow

- Sampled March 2012, 2-3 days before onset of major spring thaw
- 7.6-cm diameter snow tube fabricated from clear PVC pipe
- Composite of 2-3 grabs; 3 composite samples from each site

Ion Exchange Collectors (IECs)

- 2-stage column s from 2.5-cm diameter PVC pipe; 3 per site
- Fitted w/ large black (UV-resistant) HDPE funnel
- Upper column : high-purity cation exchange resin
  - NH_4^+ & metal cations
- Lower column : high purity anion exchange resin
  - Cl^-, NO_2^- + NO_3^-, SO_4^{2-}, PO_4^{3-}

Analysis

Snow

- Direct analysis of melt by ICP-MS and Ion Chromatography (IC)

IECs

- Extraction w/ high-purity 1M KI
- Extracts diluted 20X for analysis by ISE, IC, & ICP-MS

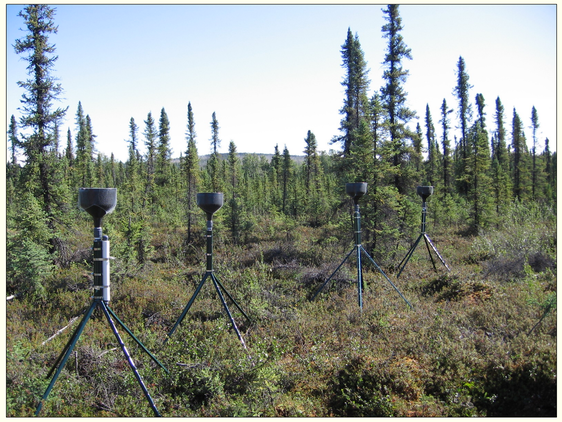
PHOTOS

A. 2-stage IEC components B. Loading resins into IECs
C. Snow sampling D. Deploying IECs in late March, 2012
E. IECs on 4-legged mounts in northern Alaska

A. B.

C. D.

E.



RESULTS

Figure 1. Comparison between anion loads based on passive IEC sampling and weekly NADP wet precipitation samples for 10-week pilot tests conducted at 3 sites in Alaska during summer 2011. Note: there is no NADP station in Fairbanks.

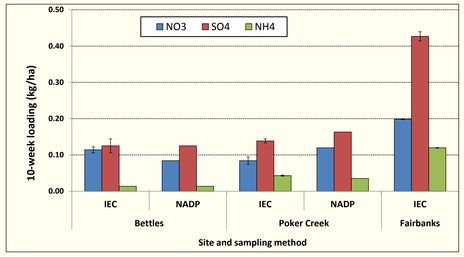


Figure 2. Loading of selected anions in 2011-2012 snowpack at 3 sites in Alaska. Site "Denali-1" located in open area; "Denali-2" next to forest canopy.

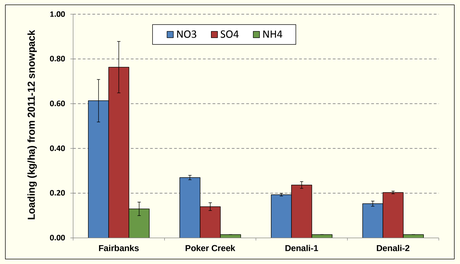
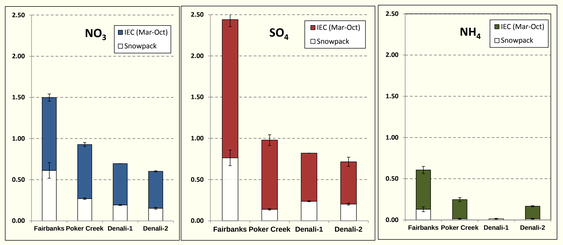


Figure 3. Annual loads (Oct 2011 - Oct 2012) of selected ionic contaminants at 3 sites in Alaska as measured by combination of snowpack and IEC samplers. Site "Denali-1" located in open area; "Denali-2" next to forest canopy. Note: 2 of 3 IECs deployed at Denali-1 were destroyed by moose.



DISCUSSION

- 10-week pilot test in 2011: Close agreement between depositional loadings of nitrate, sulfate, and ammonium ions as calculated from weekly wet precipitation samples measured by the National Atmospheric Deposition Program (NADP) and co-located IEC samplers deployed at two Alaskan NADP sites (Bettles and Poker Creek; Fig. 1). Loadings of these anions as measured by IECs were about 2-3 times greater in the city of Fairbanks compared to the two remote NADP sampling sites.
- Snowpack samples collected in March 2012 showed similar trends between anion loadings at Fairbanks (2-3 times greater) and the Poker Creek NADP site (Fig. 2) compared to results from the 10-week pilot of 2011 (Fig. 1).
- Anion deposition in snow at the two Denali sites was not greatly affected by proximity to forest canopy (Fig 2.).
- Loading of each anion in snow pack was generally about 30% of that collected by IECs between March and October (Fig. 3).
- Annual loadings estimated by these 2012 data are comparable to historical loads reported by NADP in wet deposition (2012 NADP data pending).
- Precision among triplicate IECs ranged from 8 to 10 %RSD for NO_3; 2 to 12% RSD for SO_4 ; and 5 to 10% RSD for NH_4
- Recoveries among 4 field-spiked IECs averaged 106 ± 7%; 105 ± 3% ; and 101 ± 3% for NO_3, SO_4, and NH_4, respectively.
- Field IEC blanks (n=9) were near detection limits for all 3 ions.

CONCLUSIONS

Our studies demonstrate that measurement of ammonium, nitrate, and sulfate at the very low atmospheric loadings typical of northern Alaska can be determined with good precision using 2-stage passive ion-exchange collectors (IECs). The 2011 pilot study indicated close agreement between IECs and NADP weekly sampling. Compilation of 2012 NADP results for comparison to the total annual loads estimated by snowpack and IECs is ongoing, as well as analyses of IEC extracts for a suite of trace elements. Dry deposition of these ions is assumed to be sampled by IECs, but that contribution has yet to be evaluated.

ACKNOWLEDGMENTS

Funding for this project was provided in part by National Park Service. For their excellent technical assistance we thank Andrea Blakesley, Paul Atkinson, Jim Lawler, and Zachary Richter (NPS); Jamie Hollingsworth and Brian Charlton (Univ. Alaska @ Fairbanks); and Mike Walther, Tom May, Vanessa Melton-Silvey, and Jesse Arms (USGS). Preliminary data from National Atmospheric Deposition Program (NRSP-3) obtained from NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820.

REFERENCES

1. Fenn, M.E. and Poth, M.A. 2004. Monitoring nitrogen deposition in through-fall using ion-exchange resin columns: a field test in the San Bernadino Mountains. *J. Environ. Qual*. 33:2007-2014.
2. Simkin, S.M, Lewis, D.N., Weathers, K.C., Lovett, G.M., Schwarz, K. 2004. Determination of sulfate, nitrate, and chloride in through-fall using ion-exchange resins. *Water Air Soil Pollut.* 2004. 153:343-354.