

Prepared in cooperation with the National Park Service

Development of Ion-Exchange Collectors for Monitoring Atmospheric Deposition of Inorganic Pollutants in Alaska Parklands



Scientific Investigations Report 2016–5096

Cover photograph: Deployment of ion-exchange collectors near Chatanika, Alaska, March 27, 2012.

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By William G. Brumbaugh, Jesse W. Arms, Greg L. Linder, and Vanessa D. Melton

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U.S. Department of the Interior
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Contents

Abstract.....	1
Introduction.....	2
Purpose and Scope	3
Description of Field Study Sites	4
Materials and Methods.....	6
Snowpack Sampling.....	6
Sampling by Ion-Exchange Collectors	6
Cleaning Procedures.....	7
Chemical Treatment for Analysis	7
Instrumental Analysis	7
<i>Hylocomium splendens</i> Moss Sampling and Analysis.....	8
Quality Assurance.....	8
Ion-Exchange Collector Validation	9
Data Analysis.....	10
Results and Discussion.....	10
2010 and 2011 Studies	10
2012 Study	12
2014 Study	14
Snowpack Samples	14
Ion-Exchange Collectors	14
Ion-Exchange Collector Field Blanks	19
Moss Samples.....	19
Modeling Moss Concentrations from Depositional Loads	29
Summary and Conclusions.....	37
References Cited.....	38
Appendix 1. Dual-Stage Ion-Exchange Collector Column Construction, Extraction, and Analysis.....	42
Appendix 2. Methods of Analysis for Samples of Splendid Feather Moss (<i>Hylocomium splendens</i>) for Trace Metals, Sulfur, and Nitrogen.....	42
Appendix 3. Correlation Tables in Microsoft Excel.....	42

Figures

1. Map showing National Park Service parklands of the Arctic Network in Alaska	2
2. Map showing locations of National Atmospheric Monitoring Program monitoring stations in Alaska.....	3
3. Map showing sampling locations for 2014 field studies	4
4. Photograph showing close-up of the stair-step, splendid feather moss	9
5. Photograph showing ion-exchange collectors deployed on mounting stands near Bettles, Alaska	11
6. Graphs showing comparison of depositional loads of ammonium, nitrate, and sulfate measured in snowpack samples and ion-exchange collectors at four sites in Alaska during the 2012 study.....	12

7.	Graph showing comparison of annual loads of ammonium, nitrate, and sulfate ions measured in snowpack samples and ion-exchange collectors in 2012 at Fairbanks and at two National Atmospheric Deposition Program stations.....	13
8.	Graphs showing comparison of depositional loads in snowpack samples and ion-exchange collectors at eight sites in Alaska during the 2014 study	15
9.	Graph showing comparison of annual depositional loads for selected metals measured by a combination of snowpack samples and ion-exchange collectors at eight sites in Alaska during the 2014 study	18
10.	Box plots showing comparison of nitrate, total nitrogen, total sulfur, and phosphorous concentrations in 1-year and 3-year growth segments of <i>Hylocomium splendens</i> moss samples collected from eight sites of interior Alaska during the 2014 study	24
11.	Box plots showing comparison of calcium, magnesium, potassium, and sodium concentrations in 1-year and 3-year growth segments of <i>Hylocomium splendens</i> moss samples collected from eight sites of interior Alaska during the 2014 study.....	28
12.	Box plots showing comparison of percent ash and concentrations of aluminum, Iron, and manganese in 1-year and 3-year growth segments of <i>Hylocomium splendens</i> moss samples collected from eight sites of interior Alaska during the 2014 study.....	30
13.	Box plots showing comparison of cadmium, cobalt, chromium, and copper concentrations in 1-year and 3-year growth segments of <i>Hylocomium splendens</i> moss samples collected from eight sites of interior Alaska during the 2014 study.....	32
14.	Box plots showing comparison of molybdenum, nickel, lead, and zinc concentrations in 1-year and 3-year growth segments of <i>Hylocomium splendens</i> moss samples collected from eight sites of interior Alaska during the 2014 study	34
15.	Graph showing linear relations (models) between concentrations of phosphorous in moss tissue and nitrate loads based on ion-exchange collector measurements at eight sites in Alaska during 2014	36
16.	Graph showing linear relations between concentrations of total nitrogen in moss tissue and nitrate loads based on ion-exchange collector measurements at eight sites in Alaska during 2014.....	36
17.	Graph showing linear and nonlinear relations between concentrations of total sulfur in moss tissue and annual sulfate loads based on snowpack plus ion-exchange collector measurements at eight sites in Alaska during 2014.....	36
18.	Graph showing linear relations between concentrations of cobalt in moss tissue and annual cobalt loads based on snowpack plus ion-exchange collector measurements at eight sites in Alaska during 2014	36
19.	Graph showing linear relations (models) between concentrations of chromium in moss tissue and annual chromium loads based on snowpack plus ion-exchange collector measurements at eight sites in Alaska during 2014.....	37
20.	Graph showing linear relations (models) between concentrations of nickel in moss tissue and annual nickel loads based on snowpack plus ion-exchange collector measurements at eight sites in Alaska during 2014.....	37
21.	Graph showing linear relations between concentrations of zinc in moss tissue and annual zinc concentrations in snowpack for samples collected in 2014 at eight sites in Alaska	37

Appendix Figures

1–1. Photograph showing dual-stage ion-exchange collector components. Red arrow indicates place where sections are separated for extraction of cations or anions. Polypropylene mesh spacers are shown before they are rolled into cylindrical shape	42
1–2. Photographs showing an ion-exchange collector assembly	42
1–3. Photographs showing an ion-exchange collector funnel assembly	42
1–4. Photographs showing cation extraction process	42

Tables

1. Sampling sites and matrices collected during 2012 and 2014 to determine depositional loads of inorganic atmospheric pollutants	5
2. Concentrations of inorganic constituents measured in snowpack sampled in early April 2014 at eight sites in interior Alaska	16
3. Overwinter depositional loads of inorganic substances estimated from snowpack sampled in early April 2014 at eight sites in interior Alaska	17
4. Spring/summer depositional loads of inorganic constituents estimated from ion-exchange collectors at eight sites in interior Alaska	20
5. Estimated annual depositional loads of inorganic substances at eight sites in interior Alaska, October 2013 to September 2014	22
6. Concentrations of inorganic substances in <i>Hylocomium splendens</i> moss tissue samples collected mid-September 2014 from eight sites in interior Alaska	26

Appendix Tables

1–1. List of supplies to construct ion-exchange collectors	42
2–1. Target determination limits for analysis of moss or lichen tissues by inductively coupled plasma atomic emission spectrophotometry	42
3–1. Results for two-factor analysis of variance for inorganic substances in moss	42
3–2. Relation between concentrations of inorganic substances in 1-year and 3-year <i>Hylocomium splendens</i> moss growth segments	42
3–3. Spearman's rank correlations between inorganic substances in <i>Hylocomium splendens</i> moss and moss ash content	42
3–4. Spearman's rank correlations between nitrogen, phosphorous, and sulfur in moss and nitrogen or sulfur compounds in ion-exchange collectors or snowpack	42
3–5. Spearman's rank correlations between nitrogen, phosphorous, and sulfur in moss, and major cations in ion-exchange collectors or snowpack	42
3–6. Linear models (p -values less than 0.10) between nitrogen, phosphorous, and sulfur in <i>Hylocomium splendens</i> moss and in ion-exchange collectors or snowpack	42
3–7. Spearman's rank correlations between elements in <i>Hylocomium splendens</i> moss and in ion-exchange collectors or snowpack	42
3–8. Linear models having p -values less than 0.10 for trace metals in <i>Hylocomium splendens</i> moss and in ion exchange collectors or snowpack	42

Conversion Factors

[International System of Units to U.S. customary units]

Multiply	By	To obtain
Length		
micrometer (μm)	0.00003937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
kilometer (km)	0.5400	mile, nautical (nmi)
Area		
hectare (ha)	0.003861	square mile (mi^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
Volume		
milliliter (L)	0.03382	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

Datum

Vertical and horizontal coordinate information is referenced to World Geodetic System of 1984 (WGS 84).

Supplemental Information

Temperature in degrees Celsius ($^{\circ}\text{C}$) may be converted to degrees Fahrenheit ($^{\circ}\text{F}$) as $^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$.

Concentrations of chemical constituents in water are given in nanograms per liter (ng/L), micrograms per liter ($\mu\text{g/L}$), milligrams per liter (mg/L), micrograms per liter ($\mu\text{g/g}$), and milligrams per kilogram (mg/kg).

Abbreviations

Al	aluminum
ANOVA	analysis of variance
ARCN	Arctic Network
Ca	calcium
CASTNET	Clean Air Status and Trends Network
Cd	cadmium
Cl	chloride
Co	cobalt
Cr	chromium
Cu	copper
DI	deionized
Fe	iron
<i>H. splendens</i>	<i>Hylocomium splendens</i>
HNO ₃	nitric acid
I	iodine
ICP-MS	inductively coupled plasma mass spectrometry
IEC	ion-exchange collector
ISE	ion-selective electrode
K	potassium
KCl	potassium chloride
KI	potassium iodide
M	molar
Mg	magnesium
Mn	manganese
Mo	molybdenum
N	nitrogen
Na	sodium
NADP	National Atmospheric Deposition Program
NH ₃	ammonia
NH ₄ ⁺	ammonium
Ni	nickel
NO ₂ ⁻	nitrite
NO ₃ ⁻	nitrate
NO ₃ -N	nitrate as nitrogen
NPS	National Park Service
P	phosphorus
Pb	lead
PVC	polyvinyl chloride
RAL	Research Analytical Laboratory

RPD	relative percent difference
S	sulfur
SO ₄ ²⁻	sulfate
SRM	standard reference material
Tot-N	total nitrogen
Tot-P	total phosphorus
Tot-S	total sulfur
U-P	ultrapure
USGS	U.S. Geological Survey
Zn	zinc

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Abstract

Between 2010 and 2014, the U.S. Geological Survey completed a series of laboratory and field experiments designed to develop methodology to support the National Park Service's long-term atmospheric pollutant monitoring efforts in parklands of Arctic Alaska. The goals of this research were to develop passive sampling methods that could be used for long-term monitoring of inorganic pollutants in remote areas of arctic parklands and characterize relations between wet and dry deposition of atmospheric pollutants to that of concentrations accumulated by mosses, specifically the stair-step, splendid feather moss, *Hylocomium splendens*. Mosses and lichens have been used by National Park Service managers as atmospheric pollutant biomonitors since about 1990; however, additional research is needed to better characterize the dynamics of moss bioaccumulation for various classes of atmospheric pollutants. To meet these research goals, the U.S. Geological Survey investigated the use of passive ion-exchange collectors (IECs) that were adapted from the design of Fenn and others (2004). Using a modified IEC configuration, multiple experiments were completed that included the following: (a) preliminary laboratory and development testing of IECs, (b) pilot-scale validation field studies during 2012 with IECs at sites with instrumental monitoring stations, and (c) deployment of IECs in 2014 at sites in Alaska having known or suspected regional sources of atmospheric pollutants where samples of *Hylocomium splendens* moss also could be collected for comparison. The targeted substances primarily included ammonium, nitrate, and sulfate ions, and certain toxicologically important trace metals, including cadmium, cobalt, copper, nickel, lead, and zinc.

Deposition of atmospheric pollutants is comparatively low throughout most of Alaska; consequently, modifications of the original IEC design were needed. The most notable modification was conversion from a single-stage mixed-bed column to a two-stage arrangement. With the modified IEC design, ammonium, nitrate, and sulfate ions were determined with a precision of between 5 and 10 percent relative standard deviation for the low loads that happen in remote areas of

Alaska. Results from 2012 field studies demonstrated that the targeted ions were stable and fully retained on the IEC during field deployment and could be fully recovered by extraction in the laboratory. Importantly, measurements of annual loads determined by combining snowpack and IEC sampling at sites near National Atmospheric Deposition Program monitoring stations was comparable to results obtained by the National Atmospheric Deposition Program.

Field studies completed in 2014 included snowpack and IEC samples to measure depositional loads; the results were compared to concentrations of similar substances in co-located moss samples. Analyses of constituents in snow and IECs included ammonium, nitrate, and sulfate ions; and a suite of trace metals. Constituent measurements in *Hylocomium splendens* moss included total nitrogen, phosphorous, and sulfur, and trace metals. To recover ammonium ions and metal ions from the upper cation-exchange column, a two-step extraction procedure was developed from laboratory spiking experiments. The 2014 studies determined that concentrations of certain metals, nitrogen, and sulfur in tissues of *Hylocomium splendens* moss reflected differences in presumptive deposition from local atmospheric sources. Moss tissues collected from two sites farthest from urban locales had the lowest levels of total nitrogen and sulfur, whereas tissues collected from three of the urban sites had the greatest concentrations of many of the trace metals. Moss tissue concentrations of three trace metals (cobalt, chromium, and nickel) were strongly (positively) Spearman's rank correlated ($p < 0.05$) with annual depositional loads of those metals. In addition, moss sulfur concentrations were positively rank correlated with annual depositional loads of sulfate ($p < 0.07$). Exploratory models indicated linear uptake of the three metals by *Hylocomium splendens* moss and nonlinear uptake of sulfur from sulfate.

Our results provided useful preliminary models for several of the targeted substances; however, our ability to characterize relations between concentrations in moss and loadings for many of the metals was precluded by several factors. The few test sites, small concentration gradients, and generally low concentrations hampered model developments. In addition, the weather was unusually warm throughout Alaska during the

2 Development of Ion-Exchange Collectors for Monitoring Atmospheric Deposition of Inorganic Pollutants

winter of 2013–14, which caused intermittent melting of the snowpack at some of the test sites; consequently, our measurements of overwinter loads based on snowpack samples (obtained in late March) probably underestimated the actual loads. Regardless of these potential limitations, these studies have established a foundation to support further studies that can improve our understanding of how mosses accumulate inorganic substances and ultimately how mosses might be used as biomonitors of atmospheric pollutants; moreover, the successful development and validation of the IECs during this research documents how the methodology can be used for future monitoring efforts in remote regions of Alaska and elsewhere.

Introduction

Protected lands in Alaska managed by the National Park Service (NPS) are under increasing threats from atmospheric pollutants. The Arctic Network (ARCN) park units' enabling legislation (Alaska National Interest Lands Conservation Act of 1980 [Public Law 96–487]) requires that park managers know the condition of natural resources under their stewardship and monitor long-term trends in those resources to fulfill the NPS mission of conserving parks unimpaired. A comprehensive monitoring plan developed by the ARCN calls

for long-term monitoring of ecological conditions in the five ARCN parklands (fig. 1), which includes wet and dry deposition of various pollutants to examine patterns of airborne deposition of sulfur (S) (sulfate [SO_4^{2-}]), nitrogen (N) (nitrate [NO_3^-] and ammonium [NH_4^+] ions), heavy metals, and semi-volatile organic compounds in several NPS lands in Alaska (Lawler and others, 2009). At remote locations, the use of conventional instrumental systems for monitoring deposition and loadings of atmospheric pollutants during extended periods is generally not practical; however, indigenous biotic receptors, such as mosses or lichens, can act as passive samplers that can be used to monitor long-term depositional trends for many atmospheric pollutants. Mosses lack vascular systems and obtain most of their nutrients from precipitation and dry deposition of airborne particles. Tissue concentrations, therefore, should be minimally confounded by uptake of mineral elements from soils and subsequent translocation; accordingly, as part of the terrestrial component of the ARCN comprehensive monitoring plan, the splendid feather moss, *Hylocomium splendens* (*H. splendens*), is being sampled by the NPS as a means to monitor the presence and trends of atmospheric inorganic pollutants (Walton and Stehn, 2014). The use of *H. splendens* in assessing airborne contaminants is fairly well established by studies completed in Europe, especially for certain metals and total N (Tot-N; Rühling and Tyler, 1970; Ross, 1990; Schaugh and others, 1990; Steinnes and others, 1994; Steinnes, 1995; Berg and Steinnes, 1997; Berg and

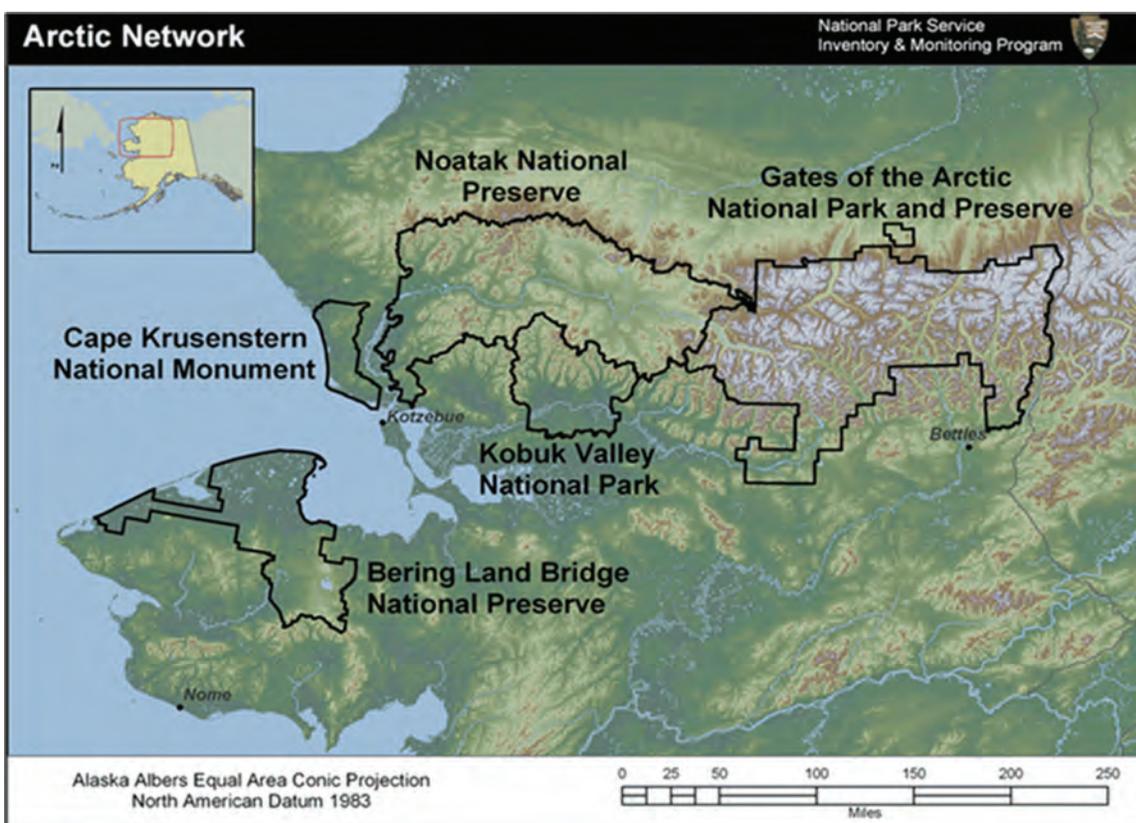


Figure 1. National Park Service parklands of the Arctic Network in Alaska.



Figure 2. Locations of National Atmospheric Monitoring Program monitoring stations in Alaska.

others, 2003, Migaszewski and others, 2009). Recent reviews of moss monitoring programs, however, noted that additional research is needed and comparable data from North America is scarce (Aboal and others, 2010; Harmens and others, 2011; Linder and others, 2013); consequently, considerable uncertainty remains as to exactly how pollutant concentrations in mosses reflect atmospheric exposure and depositional loads, especially for Arctic Alaska where very few studies have been completed.

In support of the ARCN comprehensive monitoring plan, the U.S. Geological Survey (USGS), in cooperation with the NPS, completed a series of laboratory and pilot-scale field studies between 2010 and 2014. The ultimate goal of this ongoing long-term research project is to characterize relations between elemental accumulations in *H. splendens* moss tissue and actual wet and dry depositional loads of various atmospheric contaminants on the Alaskan landscape. Ideally, empirical models then could be developed that allow annual depositional loads to be expressed based on *H. splendens* moss tissue concentrations. To begin, reliable methodology for measuring pollutant deposition and loads that could be used in remote regions of Alaska needed to be validated. For that, specially adapted two-stage ion-exchange collectors (IECs) were developed and tested. The IEC measurements were validated primarily by deploying several of the devices at sites in Alaska with instrumental atmospheric monitoring stations of national

programs (fig. 2) and then comparing results of the two methods. In addition, field-spiked IEC samples were included to assess the stability and recovery of the targeted analytes during IEC deployments. After the validation studies, a large-scale study was completed in 2014 that included measurements of constituents in snowpack, IECs, and *H. splendens* moss tissue samples at eight sites. The discussion of results from the 2014 study is the primary focus of this report.

Purpose and Scope

This report presents methodological procedures and results for chemical measurements of inorganic constituents in snowpack, IECs, and *H. splendens* moss tissues that were collected between 2011 and 2014 from several sites within interior Alaska. The primary objectives of this report are the following: (a) to summarize the developmental status of IECs for use in monitoring atmospheric deposition of inorganic constituents in remote regions of subarctic and Arctic Alaska, (b) to provide baseline deposition data of certain inorganic ionic constituents at a few sites in Alaska, and (c) to summarize preliminary results that may be used to develop empirical models of atmospheric depositional loads based on *H. splendens* moss tissue concentrations.

Description of Field Study Sites

Field experiments included four separate studies; all site locations are summarized in table 1. Between 2010 and early 2011, two short-term (less than 3 months) field tests of IECs were done at a National Atmospheric Deposition Program (NADP) monitoring station near Ashland, Missouri (National Atmospheric Deposition Program, 2014). Those two field tests helped to establish the feasibility of the passive IEC approach and provided valuable practical field experience before attempting to deploy IECs at the more logistically demanding sites in Alaska. The first Alaska field test was done between late July and early October 2011 and included sets of four IECs each deployed at two NADP monitoring stations (Bettles and Poker Creek, fig. 2), and one set was deployed within the city of Fairbanks, Alaska. After that 2011 study, a year-long study was completed in 2012 whereby annual loads were estimated at three sites by combining measurements in snowpack (collected in late March) and IECs (collected in late March to early October). The 2012 study was designed primarily to validate the techniques being used to measure annual depositional loads (snowpack plus IECs). Two of the 2012 sites were co-located with NADP stations at Denali National Park and Poker Creek (fig. 2), which allowed the IEC data to be compared to NADP data for accuracy. The Denali National Park monitoring

station was included because it is the only station in Alaska that measures depositional loads of inorganic constituents from both wet and dry deposition; dry deposition is estimated by using inferential models to integrate data obtained by periodic short-term measurements. A comparison of IEC results to combined wet and dry deposition measured by the NADP at the Denali National Park station was considered an important component because, theoretically, IECs might sample ions both from wet and dry deposition; dry deposition is determined by wet leaching during rain events of ions associated with particulates trapped in the IEC funnel. The extent that IECs actually might sequester some of these ions from dry deposition was unclear, but at least some sequestration of ions from dry deposition by the IECs was indicated from the 2011 study because those IEC results tended to be greater than the corresponding NADP wet deposition data.

Investigations described in this report conclude with a 2014 study that included snowpack samples, IECs, and *H. splendens* moss tissues at eight sites in Alaska (table 1; fig. 3). The 2014 study targeted several sites that were expected to reflect local or regional atmospheric depositional sources so that depositional gradients might be measurable. Our goal was to provide a dataset that could be used to evaluate preliminary models, which describe the uptake of ionic constituents from atmospheric deposition by *H. splendens*. Snowpack and

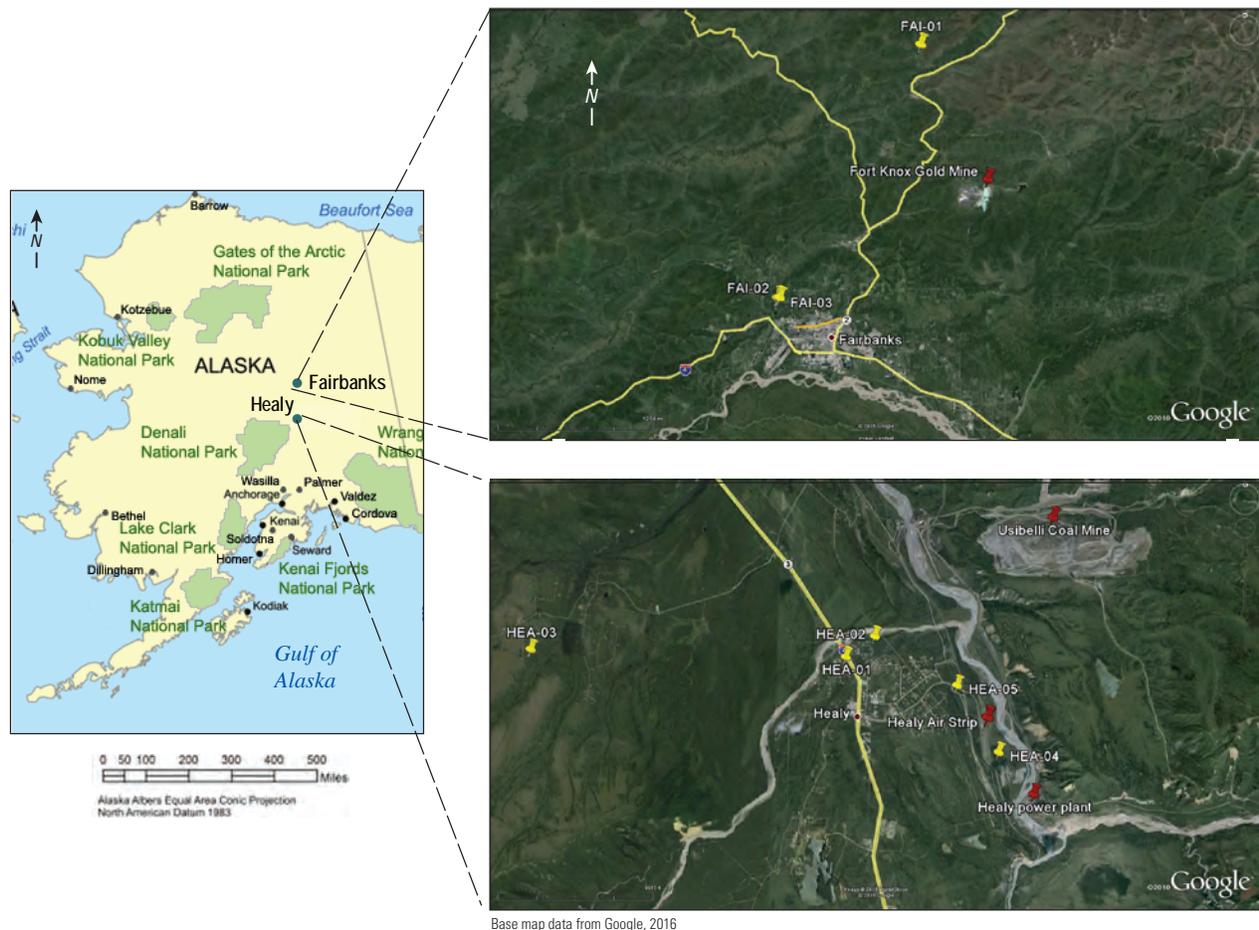


Figure 3. Sampling locations for 2014 field studies.

Table 1. Sampling sites and matrices collected during 2012 and 2014 to determine depositional loads of inorganic atmospheric pollutants.

[IEC, ion-exchange collector; LTER, Long-Term Ecological Research station; NADP, National Atmospheric Deposition Program; UA–F, University of Alaska at Fairbanks; RR, railroad; NPS, National Park Service; ARRC, Alaska Railroad Corporation. Vertical and horizontal coordinate information is referenced to World Geodetic System1984 (WGS 84)]

SITE identifier	Sample type	Latitude (degrees/minutes/seconds)	Longitude (degrees/minutes/seconds)	Description	Land status	Remarks
2012 study						
1	Snow, IEC	65° 09' 21.2"	147° 29' 18.2"	Poker Creek LTER, south of NADP station	UA–F	Bog/meadow.
2A	Snow	64° 51' 12.6"	147° 50' 39.2"	Fairbanks, RR access road, near UA–F	UA–F	Field near highway.
2B	IEC	64° 50' 55.0"	147° 50' 8.6"	Fairbanks, roof of NPS building	NPS	Near major thoroughfare.
3A	Snow, IEC	63° 43' 22.6"	148° 58' 1.6"	Denali National Park, near NADP station	NPS	Clearing near gravel parking lot.
3B	Snow, IEC	63° 43' 23.1"	148° 58' 4.8"	Denali National, near NADP station	NPS	At edge of spruce canopy.
2014 study						
FAI–01	Snow, IEC, moss	65° 9' 26.8"	147° 29' 8.3"	Poker Creek LTER, east of NADP station	UA–F	At edge of spruce canopy.
FAI–02	Snow, IEC, moss	64° 52' 20.7"	147° 51' 44.5"	UA–F campus, northeast edge of "T-field"	UA–F	Spruce forest.
FAI–03	Snow, IEC, moss	64° 52' 19.8"	147° 52' 3.2"	UA–F campus, northwest edge of "T-field"	UA–F	Spruce forest.
HEA–01	Snow, IEC, moss	63° 52' 43.7"	149° 1' 39.1"	Healy near George-Parks Highway	private	Meadow behind motel.
HEA–02	Snow, IEC, moss	63° 52' 57.3"	149° 0' 57.9"	Residence, northeast Healy	private	Mixed meadow/spruce forest.
HEA–03	Snow, IEC, moss	63° 52' 43.9"	149° 9' 11.1"	Residence, 3 kilometers west of Healy	private	Mixed meadow/spruce forest.
HEA–04	Snow, IEC, moss	63° 51' 44.7"	148° 57' 54.2"	Near airstrip, southeast Healy	ARRC	Mixed meadow/spruce forest.
HEA–05	Snow, IEC, moss	63° 52' 27.1"	148° 58' 55.6"	Near gravel road to RR yard, south Healy	ARRC	Mixed meadow/spruce forest.

IEC samples were analyzed for major cations (NH_4^+ , calcium [Ca^{2+}], magnesium [Mg^{2+}], potassium [K^+], and sodium [Na^+]); major anions (chloride [Cl^-], NO_3^- , nitrite [NO_2^-], and SO_4^{2-}); and a suite of trace metals, including cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn). The 1-year and 3-year growth segments of *H. splendens* moss tissue samples were analyzed for NO_3^- , Tot-N, total S (Tot-S), extractable cations and anions, and trace metals. Potential sources at the 2014 sites included emissions from industrial, vehicular, and power generating stations of urban areas in or near Fairbanks or Healy, Alaska. Site selection was limited by the absence of *H. splendens* moss within urban locations where localized loadings might have been greatest. Other targeted pollutant sources included mining operations at an open-pit gold mine south of the Poker Creek station and a surface coal mine near Healy; and a coal-fired power plant, a railroad yard, and a small aircraft airstrip, each near Healy, Alaska.

Materials and Methods

Snowpack Sampling

Snowpack was collected using a 1-meter (m) long by 7.6-centimeter (cm) diameter tube fabricated from a clear polyvinyl chloride (PVC) pipe. The bottom 2.5-cm section of the 1-m tube was cut into a saw-tooth pattern using a table-mounted jig saw, and the outside edge of each “tooth” was beveled and smoothed using a flat file. A 2.5-cm hole was drilled completely through the top end of the tube so that a 1-inch wooden dowel rod could be inserted through the tube to act as a handle during sampling. At the laboratory, the tube and adapter were cleaned with detergent using a large plastic brush, and then the tube was rinsed with a stream of deionized (DI) water (specific resistivity greater than 5 million ohms per centimeter). The bottom one-half of the tube and the adapter were soaked for at least 24 hours in a large cylindrical polyethylene tank filled with ultrapure (U-P) DI water (specific resistivity greater than 18 million ohms per centimeter). For storage and transport, each end of the tube was covered with a thin-walled, wide-mouth 1-liter (L) polyethylene bottle secured in place by a large hose clamp, which in turn was covered by a layer of bubble wrap and finally a large polyethylene bag.

To collect snow, the tube was rotated down into the snowpack using the wooden handle. The snow surrounding the bottom of the tube was cleared away, and a large polycarbonate scoop was inserted underneath the tube. Next, the tube and scoop were lifted from the ground and then tilted to a nearly horizontal position. After collecting a subsample of snowpack in the tube, the snow was transferred to a precleaned 4-L wide-mouth polyethylene jar. To facilitate the transfer of snowpack from the tube to jar, a PVC 4-inch to 3-inch diameter reducing adapter was used as a coupling between the snow tube and the

receiving jar. The scoop, which typically contained a small amount of snow plus some plant fragments, was carefully removed from the tube, and the receiving jar with adapter was attached to the tube. The tube was tilted to the vertical position and tapped with a section of plastic pipe to dislodge the snow from the tube and into the receiving jar. Depending on snow depth (which was measured at each site), a composite of either two or three grabs was transferred to each receiving jar. Upon arrival at each site, the tube was thrust into the snowpack two or three times before sampling to rinse away any residual snow from the previous sampling effort.

Sampling by Ion-Exchange Collectors

Preparation, extraction, and analysis procedures used during 2014 studies for IECs are provided in greater detail in appendix 1, available for download at <http://dx.doi.org/10.3133/sir20165096>. With a few important exceptions, the materials and extraction methods used for IECs prepared for 2010 and 2011 studies followed the procedures described by Fenn (2013). For 2012 and 2014 studies, two-stage IECs were developed and different extraction (elution) solutions were used depending on the column segment and analyte. For the upper (cation) column a 1 molar (M) solution of potassium chloride (KCl) was used for NH_4^+ ions, followed by a 1.6 M solution of nitric acid (HNO_3) to complete elution of cationic metals. For the lower (anion) column, a 1 M solution of potassium iodide (KI) was used following the method of Fenn (2013). About 1 month before scheduled deployment, the IECs were assembled in the laboratory and capped for shipment to the field. All IEC components (funnel, PVC adapters, tubes, plastic mesh, and polyfil fiber) were twice soaked overnight in U-P water before loading the ion-exchange resins. Once on site, four-legged mounting stands were assembled, and then the IEC columns were inserted into mounts after attaching a large plastic funnel to each. A new nylon hair net (typically used by a food handler) was placed over each funnel to reduce entrapment of larger biogenic material, such as leaves and pine cones. The IECs were deployed for about 6 months, beginning in early April 2014. Upon retrieval, the funnel section was removed, and the upper and lower openings were capped.

To prepare columns containing ion-exchange resins, procedures described by Fenn and Poth (2004) and Fenn (2013) were followed with modifications. In anticipation of the need for lower ion-exchange capacities for use in Alaska, 12-inch column lengths were used in place of the 14-inch lengths reported by Fenn (2013), so the volume of ion-exchange resin was reduced accordingly. For preliminary pilot field tests completed with mixed-bed single-stage columns, NH_4^+ background in extracts of “blank” columns (those capped and placed in the field without IEC funnels) was unacceptably high. That observation was previously acknowledged by Fenn and Poth (2004) who indicated that for the mixed-bed approach, blank correction of NH_4^+ background was essential and the background might be problematic when accurate measurements of small loadings were needed. The NH_4^+ background in the blank IEC

tubes presumably resulted as a degradation byproduct from the anion-exchange resin (a quaternary ammine) that happened slowly while the column was exposed to outdoor temperature extremes. Because of the need to quantify extremely small baseline loadings of NH_4^+ for sites in Arctic Alaska, the single-column mixed-bed approach was abandoned. Instead, a two-stage IEC was developed that places the anion-exchange resin in a bottom segment, fully separated from the cation-exchange resin in the upper segment. For these, a 15-cm PVC pipe was used for each of the two column segments. This arrangement was expected to greatly reduce the amount of NH_4^+ “bleeding” from the anion-exchange resin that could be captured by the cation-exchange resin in the upper segment; however, it substantially increased the time and expense needed to prepare and extract the devices. Upon retrieval, the two column segments are separated and extracted independently— NH_4^+ and metal cations in the upper column and anions in the lower column (fig. 1; appendix 1).

Cleaning Procedures

Ensuring that all sampling components were prepared and cleaned consistently was extremely important given the low depositional loads in most of Alaska. After the preliminary experiments, many of the procedural details were revised, including the cleaning methods. To ensure consistency of blank levels for IECs that were to be used for field deployments, only previously unused (new) sections of threaded PVC pipe and polypropylene mesh spacers purchased from a single manufacturing lot were used to prepare columns. We did not do leach tests of PVC components from different manufacturers, but preliminary experiments indicated that those components were not substantial sources of blank background. For the initial cleaning of field-deployed IEC components that must be reused (funnel assemblies and certain connector fittings), only phosphate- and residue-free liquid organic alkaline and acidic detergents were used. After cleaning with the organic detergents, the components are rinsed with copious amounts of DI water and then soaked overnight in a polypropylene tank filled with a fresh volume of U-P DI water. New components were treated only by rinsing and soaking in U-P DI water. Importantly, separate batches of all materials were processed exclusively for use with IECs to ensure that contamination of the anions of interest (Cl^- and NO_3^-) was not introduced by labware that had been processed by a dilute acid treatment that is routinely used for cleaning for trace element analysis.

Chemical Treatment for Analysis

No chemical treatments were necessary before analysis of snow, aside from melting the snowpack sample and filtering a liquid subsample for analysis. After the upper and lower IEC column segments were separated, they were extracted in two steps. The upper and lower columns from the 2012 IECs were

extracted using a 1 M solution of KI, as reported by Fenn and others (2008); however, the extraction of the upper column for IECs deployed in 2014 was modified because sampling for certain metals was also attempted. Presumably, KI was chosen by Fenn and other (2008) for the mixed-bed resin arrangement because the iodine anion (I^-) is most effective for displacing most other anions from the strong anion-exchange resin, whereas K^+ is fairly effective for displacing NH_4^+ from the strong cation-exchange resin; however, K^+ is not particularly effective for displacing most metal cations, and the presence of a large concentration of I^- can be problematic for the determination of metals by inductively coupled plasma mass spectrometry (ICP-MS). Based on a series of laboratory studies involving metals and NH_4^+ spiked onto test columns loaded with strong cation-exchange resin, we determined that a sequential elution beginning with a 1 M solution of KCl, followed by a 1.6 M solution of HNO_3 could be used to recover NH_4^+ (1 M solution of KCl only) and the targeted cationic metals (the latter by analysis of a composite subsample obtained from the 1 M solution of KCl and the 1.6 M solution of HNO_3 extracts).

Instrumental Analysis

Ammonium ion.—The pH of most rainfall is slightly acidic; consequently, ammonia (NH_3) in aerosols and rainfall will be present primarily as the protonated NH_4^+ . Fenn (2013) used a colorimetric procedure to analyze for NH_4^+ , but we used an ion-selective electrode (ISE). The ISE is operationally simpler than colorimetry, and with recent advances in electrode technology, the ISE is theoretically capable of producing comparable detection limits. For analysis of NH_3 or NH_4^+ by an ISE, a small volume of a highly basic (pH of about 12) ionic strength adjustment solution is added to the sample immediately before analysis. The addition of an ionic strength adjustment solution rapidly converts all NH_4^+ to gaseous NH_3 , which is then measured by means of electric current generated within the ISE after diffusion of NH_3 across a gas-permeable membrane on the ISE face and the subsequent rapid acid-base reaction within the electrolyte. When analyzing the 1 M solution of KI extracts obtained from IECs, we determined that a 20-fold dilution of the sample was necessary to avoid instability in the ISE response. Presumably, that instability was caused by interference from iodine gas, which formed in the KI solutions as they became acidic after passing through the cation-exchange resin. In some instances, the ISE response and baseline (zero) values would slowly drift; consequently, regular checks with blanks and a 0.1 milligram per liter (mg/L) standard were necessary to correct measured sample concentrations. For 2014 studies, a 1 M solution of KCl was used instead of KI to elute NH_4^+ from IECs, and this increased the stability for analysis by ISE. Overall, the ISE method has worked satisfactorily and produced detection limits of about 0.005 mg/L.

Anions.—A Dionex ICS-1100 ion chromatograph was used for the analysis for anions (primarily NO_2^- , NO_3^- , and SO_4^{2-}); however, the manufacturer’s standard procedure for

anion determinations was modified for the KI matrix used to extract anions from IECs. After several trials, the specifications that provided the best chromatography was an eluent of 9.0 millimolar sodium carbonate with a flow rate of 1.0 milliliters per minute (mL/min), a suppressor current of 45 milliamps (mA), and an injection loop volume of 25 microliters (μL). Extract samples (as 1 M solution of KI) required a dilution of at least 10-fold to decrease the ionic strength and prevent column and detector overloading. The resulting method had a run time of 18 minutes per sample, which was necessary to elute I⁻ completely off the analytical column. For determining anions in snowpack samples, more conventional operating conditions were used, including a suppressor current of 30 mA and a run time of about 14 minutes. To reduce the detection limit for snowpack, a 250- μL injection loop was used, and calibration standard concentrations were decreased proportionately.

Metal ions.—Metals and other elements were analyzed in IEC extracts and snowpack samples using ICP–MS. All samples were analyzed for trace elements by ICP–MS that was set up and optimized according to manufacturer specifications. Samples were analyzed using quantitative methods using at least four individual standard concentrations for calibration with periodic monitoring of the instrumental response and baseline for each element. Samples were delivered automatically to the instrument by means of a software-controlled autosampler and autodiluter system (Brumbaugh and May, 2008). All extracts were analyzed with at least a 10-fold dilution to reduce concentrations of Cl⁻ and other potential interfering matrix ions. For all analyses, any sample with a concentration exceeding the upper calibration standard for any element was diluted automatically an additional 10-fold in a serial fashion until all concentrations were within the range of the calibration standards. The ICP–MS analysis of snowpack samples was straightforward because the liquid samples could be analyzed directly with no treatment or dilution. Each snowpack sample was simply thawed and shaken, and then a 0.45 micron-filtered subsample of the liquid was pipetted into a secondary sample bottle and acidified to 0.1 percent (volume/volume) HNO₃ with ultrahigh purity HNO₃ for analysis. Analysis of the 1 M solution of KI extracts from IECs for cationic metals—including Cd cation (Cd²⁺), Cu (I) and (II) cations (Cu⁺ and Cu²⁺, respectively), Ni cation (Ni²⁺), Pb cation (Pb²⁺), and Zn cation (Zn²⁺)—was more problematic. Our first attempt to analyze for metals in IECs was from those that had been deployed for 6 months in 2012 at stations in Denali National Park, Poker Creek LTER, and the city of Fairbanks, Alaska. For those 2012 samples, only manganese (Mn), Cu, Ni, Pb, and Zn were detectable (present at least two times greater than field-deployed IEC blank levels). And as was true for the snowpack samples collected from those sites, metals were clearly quantifiable only in the samples from the urban Fairbanks station. Problems encountered during the first IEC analyses for metals were three-fold: (1) concentrations of metals present in precipitation at most locations in Alaska were probably extremely low (note that metals are not

typically measured in wet precipitation); (2) the KI used for the extraction (American Chemical Society grade) contained trace levels of impurities including vanadium, chromium (Cr), Mn, Ni, tin (Sn), and Pb; and (3) obtaining an accurate and stable analytical ICP–MS signal was not possible in a sample of high ionic strength (for example, a 1 M solution of KI) without first diluting the sample by at least 50-fold, which in turn caused method detection limits to increase proportionately. Procedural adjustments for recovering metals from IECs were later investigated through a series of laboratory experiments with metal-spiked IECs, which led to the use of the two-step procedure using first a 1 M solution of KCl, followed by a 1.6 M solution of HNO₃ (appendix 1, available for download at <http://dx.doi.org/10.3133/sir20165096>).

Hylocomium splendens Moss Sampling and Analysis

Samples of *H. splendens* moss were collected in mid-September and only during the 2014 study. At each of the eight sites, about 10 to 15 grams (g) of *H. splendens* moss tissue was sampled from each of three sublocations. Each sublocation included about a 1x1-m area that was within 5–10 m of the IECs. Collections were done manually using powder-free, gloved hands (fig. 4) with care not to disturb the sampling area before each collection. The 24 *H. splendens* moss samples (8 sites times 3 replicates at each site) were shipped to an independent contractor who is an expert botanist and had previous experience in preparing samples of *H. splendens* for analysis according to NPS moss protocols (Walton and Stehn, 2014). The samples were cleaned (foreign material removed), and 1-year and 3-year moss tissue growth segments were isolated to create two separate samples from each site replicate. The 48 cleaned and separated samples of moss tissue were submitted to the Research Analytical Laboratory (RAL) at the University of Minnesota, where they were analyzed according to NPS protocols for percent ash; and concentrations of leachable NO₃⁻ (as N), Tot–N, Tot–S, total phosphorous (Tot–P), and a suite of minor and trace elements. Procedural details used for those analyses are provided in appendix 2, available for download at <http://dx.doi.org/10.3133/sir20165096>.

Quality Assurance

Quality-assurance measures associated with field sampling included spiked IECs, replicate samples (most IECs and *H. splendens* moss samples were collected in triplicate), blank (capped) IECs, field container blanks (snowpack samples), and filtration blanks (snowpack samples). Laboratory quality-control checks for the *H. splendens* moss analyses included blind submission of a freeze-dried aquatic moss standard reference material (SRM) to the RAL, which was analyzed in triplicate. The RAL also completed periodic analyses of calibration check solutions and completed duplicate digestion and



Figure 4. Close-up of the stair-step, splendid feather moss (*Hylacomium splendens*).

analysis of six individual *H. splendens* moss samples. Results for field-spiked IECs, replicated IEC and *H. splendens* moss samples, SRMs, and IEC field blanks are presented in the results and discussion section separately for each study year. During the analysis of snowpack samples and IEC extracts, a blank verification, calibration verification, and a laboratory control solution were determined after every 10 samples. In addition, sample duplicates and postextraction spikes were determined. The target recovery for calibration check solutions was 100 plus or minus (\pm) 10 percent; the target recovery for SRMs and postextraction spikes was 100 ± 25 percent, and the target variation between duplicate analyses was ± 10 relative percent difference (RPD) ($[\text{difference}/\text{mean}] \times 100$ percent). The method detection limit was estimated for each element and analytical run according to the following formula:

$$MDL = 3.3(SD_b^2 + SD_s^2)^{1/2} \quad (1)$$

where

- MDL is the method detection limit,
- SD_b is the standard deviation of three or more preparation blanks, and
- SD_s is the standard deviation of a triplicate analysis of a low concentration sample.

Extracts from blank IECs contained measureable concentrations of certain trace elements, which was not surprising, but the blank concentrations necessarily increased the method detection limits (discussed later in this report). Concentrations of some trace elements presumably were elevated primarily because of impurities in the KI or KCl solutions. Those reagents were purchased as American Chemical Society grade (typically 98+ percent pure); and although higher purity salts are available, the cost for the required quantities was considered prohibitive.

Ion-Exchange Collector Validation

For field validation studies (2010, 2011, and 2012), preliminary weekly reports from the NADP and Clean Air Status and Trends Network (CASTNET) monitoring programs were provided by each of the respective site administrators. The NADP data included concentrations of selected cations and anions (but no trace metals), as well as the precipitation volume collected from a standard area. The CASTNET data included dry deposition loads calculated based on measured fluxes, hourly weather measurements, and inferential models (U.S. Environmental Protection Agency, 2015); thus, from

those weekly data, weekly loads expressed in kilograms per hectare could be calculated. Those data were then compared to loads calculated from IECs or snowpack samples during the same time frame.

Data Analysis

Regression analysis was completed on the 2014 data to describe the relation between the concentrations of the substances in *H. splendens* moss tissue and concentrations of inorganic compounds in snowpack samples, IECs, or both with the objective of developing predictive models. To focus model development, candidate substances in *H. splendens* moss tissue and snowpack samples and (or) IECs were identified by generating information on two aspects: (1) the dynamic range of concentrations across sites; and (2) correlations with the concentrations of inorganic substances in snowpack samples and (or) IECs, or inorganic matter content in *H. splendens* moss (expressed as percent ash).

To identify substances with a high dynamic range, one-way analysis of variance (ANOVA) was used to compare concentrations of various substances (for example, Tot-N, Tot-P, Tot-S, major cations, and metals) in *H. splendens* moss between sites ($\alpha=0.05$). In this analysis, the effect of geographic location on the concentrations of each of the substances was evaluated separately for the 1-year and 3-year growth segments. In addition, the interaction effect (that is, to describe the effect of growth on site differences) was evaluated in a separate analysis using ANOVA with site and growth segment as factors ($\alpha=0.05$). Substances with concentrations that significantly varied between geographic locations (that is, $p<0.05$) were considered to have a high dynamic range and carried forward into subsequent model development. In addition, a simple linear regression was completed for each substance measured in the moss between concentrations in the 1-year growth segments (y variable) and 3-year growth segments (x variable).

As a second step in the process, Spearman's rank correlation analysis was completed to focus model development on substances that were highly correlated between *H. splendens* moss tissue and snowpack samples and (or) IECs, as well as to identify substances in moss that were highly correlated with inorganic matter content in moss (expressed as percent ash). Spearman's rank correlations between the concentrations of substances in *H. splendens* moss tissue and snowpack samples and (or) the IEC were completed on site means ($n=8$), whereas correlations between the concentration of substances in moss and inorganic matter content in moss were completed at the replicate level ($n=24$; 3 replicates per site). Substances that were highly correlated with concentrations of inorganic substances in snowpack samples and (or) IECs or inorganic matter content in *H. splendens* moss tissue (Spearman's rank correlation coefficient $|r_s|>0.7$; $p<0.05$) were carried forward into subsequent model development.

Linear or nonlinear regression analysis was completed to describe the relation between the concentrations of various

substances in moss and concentrations of inorganic substances in snowpack samples and (or) IECs or inorganic matter content in *H. splendens* moss. Predictive models were generated for all substances identified as a result of the ANOVA and Spearman's rank correlation analysis. Linear models were described using the following equation:

$$C_{Moss} = \alpha + \beta C_{Matrix} + \epsilon, \quad (2)$$

whereas nonlinear models were described using the following equation:

$$C_{Moss} = \alpha + \beta * \ln(C_{Matrix}) + \epsilon \quad (3)$$

where

- C is the concentration,
- α is the intercept,
- β is the slope, and
- ϵ is the error term.

Goodness-of-fit for each of the linear and nonlinear models was evaluated based on the coefficient of determination (R^2); models that were statistically significant ($\alpha=0.05$) with an $R^2>0.5$ were considered to be robust predictive models.

Results and Discussion

2010 and 2011 Studies

The goal of studies completed in 2010 and 2011 was to evaluate and adapt the IEC methodology for use in measuring the comparatively low depositional loads of various atmospheric pollutants typical of remote areas in Alaska. Results from these three pilot field studies are discussed briefly in the following paragraphs.

Pilot field test number 1 (Missouri).—Nine single-stage IECs packed with a mixed cation/anion-exchange resin were deployed for 10 weeks between early October and mid-December at the NADP station in Ashland, Mo. Three columns were capped to serve as blanks, whereas the other six had funnels for collection (three for sampling; three were spiked with 50 milligrams [mg] of each anion). Field spike recoveries were 91, 97, and 90 percent for Cl^- , NO_3^- , and SO_4^{2-} , respectively. Results for NH_4^+ were highly variable, in part because levels were greatly elevated in blank IECs; therefore, two-stage IECs were prepared for all subsequent tests. Compared to the weekly NADP data (obtained from the station administrator), measured loadings recovered from the IECs during the 10-week deployment were 68, 133, and 78 percent for Cl^- , NO_3^- , and SO_4^{2-} , respectively. Notably, precipitation amounts during this field test were about one-half of average, totaling only 2.7 inches during the 2-month sampling period. Repeatability (expressed as percent relative standard deviation [RSD]) was 3.5, 8.1, and 2.7 percent for the three unspiked

IECs; and 10.3, 0.8, and 1.0 percent for the spiked IECs for Cl^- , NO_3^- , and SO_4^{2-} , respectively.

Pilot field test number 2 (Missouri).—A total of 10, two-stage IECs containing cation-exchange resin in the upper stage and anion-exchange resin in the lower stage were deployed between early March and early May, once again at the NADP station in Ashland, Mo. As with the first pilot field test, 3 IECs were left capped to serve as blanks, 3 served as samples, and the remaining 4 were used for field spikes. Three of the spiked IECs had 50 mg total (“high” level) each of Cl^- , NO_3^- , SO_4^{2-} , and NH_4^+ added. The fourth spiked IEC had 10 mg total (“low” level) of each anion or cation. After the 10-week deployment, green-brown particulates were visible in each of the collector funnels and within the top and bottom polyfil plugs. The particulates probably consisted mostly of pollen and other biogenic material from the surrounding forest canopy (mostly oak and hickory trees), the dispersion of which was quite evident throughout this locale during the latter part of April and into early May. Upon return to the laboratory, each IEC column was separated into a cation column and an anion column. Moistened cotton swabs were used to remove any visible dust and biogenic material from the top of each column. Recovery of “high” level field spikes averaged 89, 67, 60, and 61 percent, whereas recovery of “low” level field spike was 125, 68, 67, and 69 percent for NH_4^+ , Cl^- , NO_3^- , and SO_4^{2-} , respectively. We hypothesize that the lower field spike recoveries observed for anions was caused by the biogenic particles in the columns, which might have negatively affected the extraction efficiencies as compared to the laboratory

experiments. Presumably, this would be of less concern for most of subarctic and Arctic Alaska where sparse tree cover consists mostly of dwarf black spruce trees. For comparison to the NADP data, results of the unspiked IECs were corrected by dividing by the respective mean field spike recoveries, assuming that the behavior for the spiked ions (sequestration and extraction efficiency) also reflected the behavior of ions collected from precipitation. Using the recovery-adjusted values, IECs had on average 59, 124, 90, and 85 percent of the loadings of NH_4^+ , Cl^- , NO_3^- , and SO_4^{2-} , respectively, compared to the summed weekly NADP data. Importantly, this pilot field test produced very consistent results for the field blanks and much lower NH_4^+ levels compared to the single-stage IECs. Means for the three blanks (in milligrams, with standard deviations in parentheses) were the following: NH_4^+ , 0.040 (0.009); Cl^- , 1.92 (0.01); NO_3^- , 1.07 (0.06); and SO_4^{2-} , 1.54 (0.02). Consistency of the blanks allowed for very low theoretical method detection limits as follows (in milligrams): NH_4^+ , 0.03; Cl^- , 0.27; NO_3^- , 0.17; and SO_4^{2-} , 0.07.

Pilot field test number 3 (Alaska).—For this study (third pilot field test), two-stage IECs were deployed for 10 weeks at three sites in Alaska between mid-July and early October 2011. For deployment at these sites, four-legged free-standing mounting stands were constructed from “economy” fence posts (fig. 5). The deployments included 1 field blank, 1 field spike, and 3 field sample IECs at each site. Site 1 was in the city of Fairbanks, Alaska; site 2 was at NADP station, AK06; and site 3 was near the NADP station, AK01 (table 1). Site 1 was presumed to exhibit greater loadings of the targeted ions

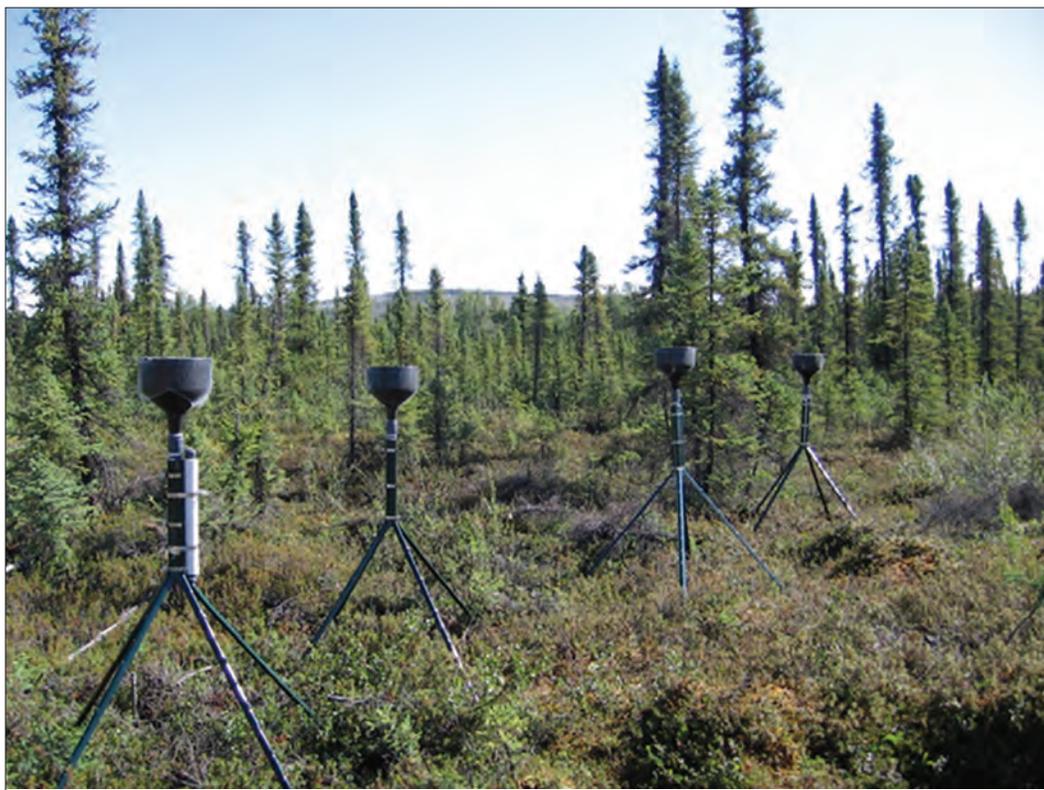


Figure 5. Ion-exchange collectors deployed on mounting stands near Bettles, Alaska.

as compared to the other two sites, which were in relatively remote areas. For each spiked column 50 mg total each of Cl^- , NO_3^- , SO_4^{2-} , and NH_4^+ were added. Two laboratory spikes also were prepared, one receiving 50 mg total and the other receiving 20 mg total of each ion. Mean 10-week depositional loads of NO_3^- , SO_4^{2-} , and NH_4^+ ions measured using IEC samplers deployed at the two NADP stations compared favorably (within about 25 percent) to loads calculated from the weekly wet precipitation samples measured by the NADP. Loadings of these anions as measured by IECs were about 2–3 times greater in the city of Fairbanks, Alaska, compared to the two remote NADP sampling stations. The mean (and standard deviation) spike recovery for NH_4^+ was 75.8 percent (3.0) for the field spikes and 82.1 percent (4.4) for the laboratory spikes. Recovery of Cl^- , NO_3^- , and SO_4^{2-} anions from field-spiked IECs averaged 90, 95, and 97 percent, respectively; and 84, 88, and 87 percent for laboratory-spiked IECs.

Results from the three short-term pilot field tests indicated that the IEC method could be successfully used to support the long-term goals of the research. The four-legged mounting stands worked well for IEC deployment in Alaska, and the modified two-stage design allowed for much lower levels of NH_4^+ to be determined. For the next field study, IEC performance was evaluated during a much longer deployment time for the substances previously investigated, and the measurement of selected trace metals was attempted.

2012 Study

For this investigation, the determination of depositional loads during a full year was attempted by combining measurements from snowpack samples (assumed to represent depositional loads from early October 2001 to late March 2012) and

IECs deployed from late March to early October 2012. At first, we considered the possibility of deploying IECs during two 6-month intervals as a means to measure depositional loadings during the winter and summer seasons. Fenn (2013) has reported use of IECs during the winter to sample ionic constituents from wet snow (as it melts periodically) in the highland regions of the Pacific northwest by mounting a large (4–6 foot long) section of large-diameter black plastic drain pipe directly above the IEC collector funnel; however, for our study it was thought that the dryness of the snow combined with the often high winds typical of Arctic Alaska could contribute to uneven collection and poor retention of the snow in the black pipe retainer before the snow eventually melted and passed through the IEC in the spring. In addition, preparing suitable mounting support for the large-diameter drain pipe would be difficult in areas of permafrost.

As summarized in table 1, sampling for this field test was completed at sites in the city of Fairbanks, Poker Creek LTER (near the NADP station), and in Denali National Park (two adjacent sites near to NADP/CASTNET monitoring station). Snowpack was sampled March 26–29, 2012, roughly 2–3 days before onset of major spring thaw using the methods described in the materials and method section. The IECs were deployed immediately after the collection of snowpack. Notably, at the urban Fairbanks site, the IECs and snowpack samples were not at precisely the same location. And importantly, the IECs at that location were placed on the roof of a two-story building about 10 m above the ground, which evidently greatly reduced the loads of certain metals deposited into those IECs as compared to loads deposited in the snowpack (discussed later in this report). At each test location, 3 IECs, 3 blank IECs, and 1 spiked IEC (50 mg each of NH_4^+ , NO_3^- , and SO_4^{2-}) were deployed. Metals were not spiked in any of the field-deployed IECs, but analysis for metals was attempted in both the snowpack samples and IEC extracts.

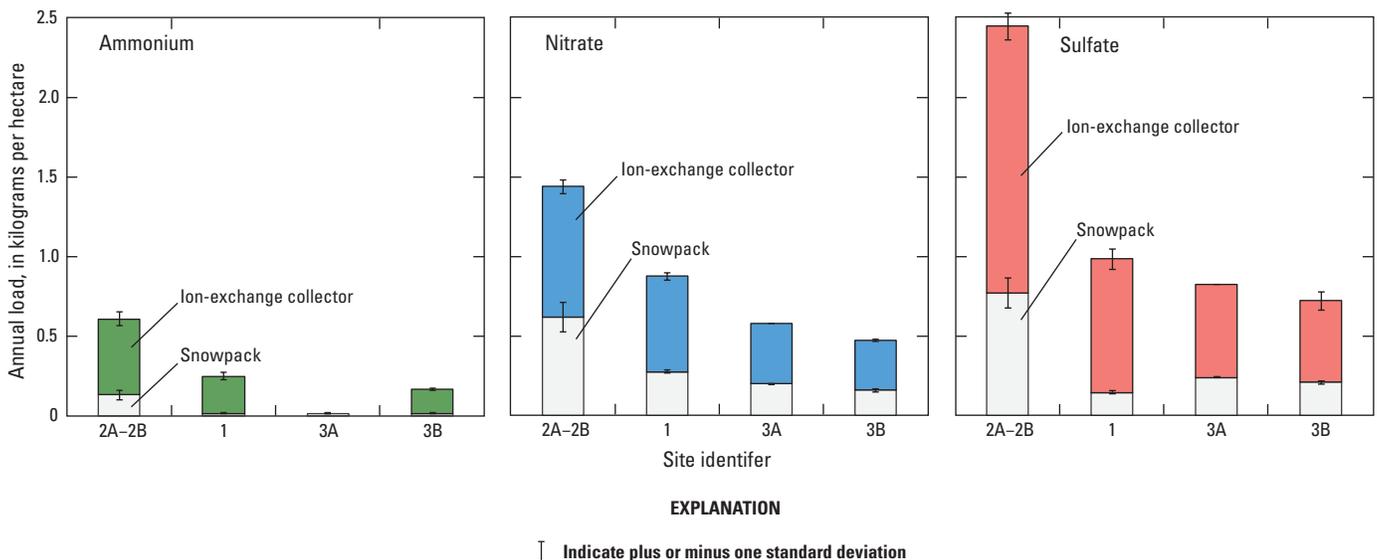


Figure 6. Comparison of depositional loads of ammonium, nitrate, and sulfate measured in snowpack samples (October through March) and ion-exchange collectors (April through September) at four sites in Alaska during the 2012 study.

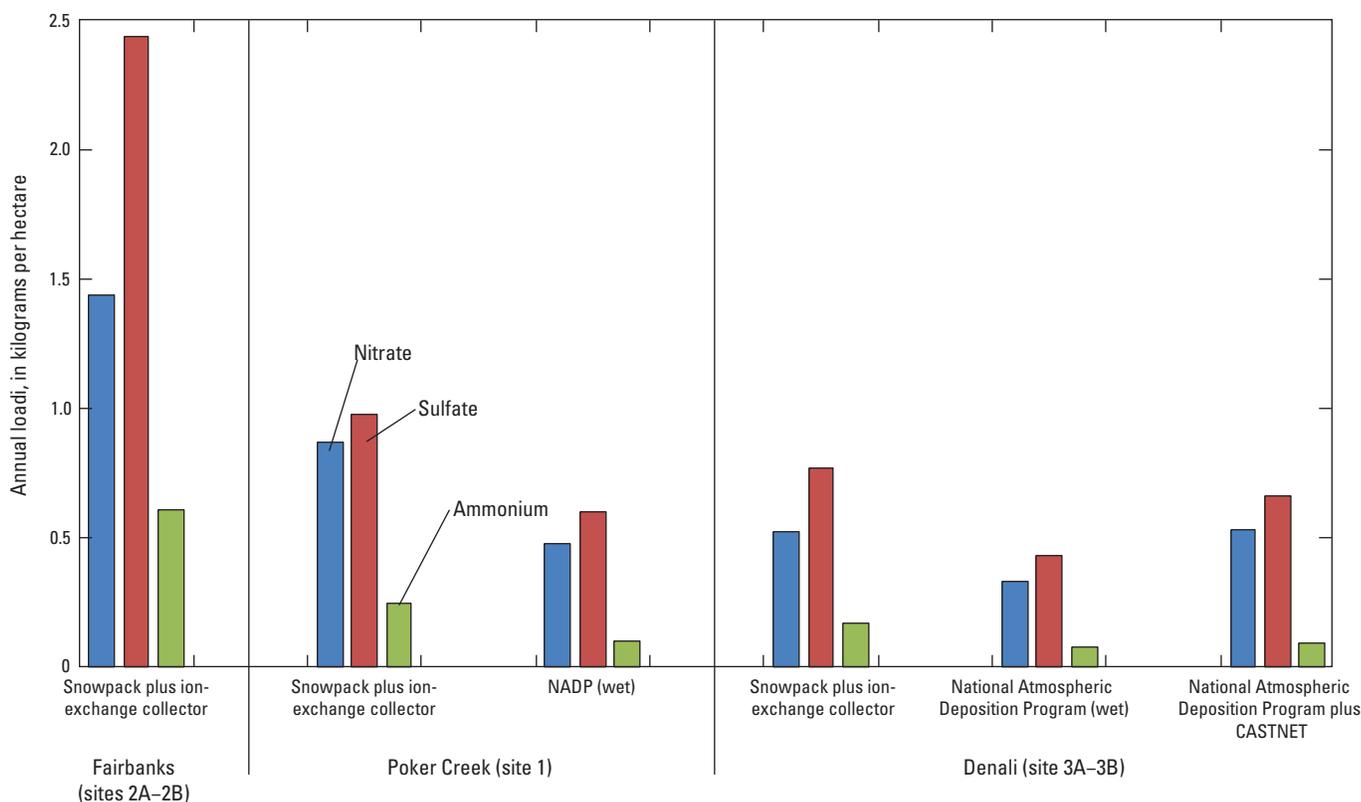


Figure 7. Comparison of annual loads of ammonium, nitrate, and sulfate ions measured in snowpack samples and ion-exchange collectors in 2012 at Fairbanks and at two National Atmospheric Deposition Program stations.

Results for NH_4^+ , NO_3^- , and SO_4^{2-} are depicted graphically in figures 6 and 7. Compared to results from the 10-week pilot of 2011, the snowpack samples collected in March 2012 showed similar trends between anion loadings detected at Fairbanks and the Poker Creek NADP station (once again loads were 2–3 times greater at Fairbanks). Anion deposition in snow was lowest at the two Denali National Park stations and proximity to the spruce forest canopy at site 4 did not seem to greatly affect results as compared to the nearby site 3, which was in a more open area (fig. 6). Unfortunately, a few weeks after the IEC deployment, two of the IECs and mounting stands were damaged by a large animal or animals (probably a moose). Loading of each anion in the snowpack was generally about 30 percent of that collected by IECs between March and October (fig. 6). Annual loadings estimated by these 2011–12 measurements at the Denali National Park stations were comparable to loads calculated from NADP and CASTNET data for wet and dry deposition (fig. 7). The precision among triplicate IECs at each site ranged from 8 to 10 percent RSD for NO_3^- , 2 to 12 percent RSD for SO_4^{2-} , and 5 to 10 percent RSD for NH_4^+ . Recoveries among the four field-spiked IECs averaged 106 ± 7 percent, 105 ± 3 percent, and 101 ± 3 percent for NO_3^- , SO_4^{2-} , and NH_4^+ , respectively. Field IEC blanks ($n=9$) were near detection limits for all three ions.

Most results for metals in snowpack samples collected in 2012 were “nondetects” (typically less than [$<$] 0.1 to $<0.01 \mu\text{g/L}$) except for Cu and Zn in samples obtained from

within the city of Fairbanks. For IECs, Cu and Zn also were clearly detectable (well above blank levels) only from the Fairbanks site, as were Mn and Pb (data not shown). As was true of the snowpack samples, no metals were readily detectable in IEC extracts from the other sites. Results from laboratory experiments, as well as this first attempt to recover metals from field-deployed IECs, indicated that adjustments would be needed to reduce blank levels for metals and at the same time to improve recovery of metals bound to the ion-exchange resins.

The 2011 and 2012 studies demonstrated that measurement of NH_4^+ , NO_3^- , and SO_4^{2-} at the very low atmospheric loadings typical of northern Alaska could be determined with good precision using two-stage passive IECs. Importantly, these studies yielded good agreement between loads estimated by IECs and loads estimated by summing the NADP weekly sample data. Annual load estimates based on snow plus IEC results were greater than, but proportional to, loads estimated from weekly wet precipitation samples collected at each of the two NADP stations (AK01 and AK03); however, loads estimated by snowpack plus IECs agreed more closely with loads estimated by combining weekly NADP plus CASTNET data at the AK01 station, indicating that the IECs effectively sampled these ions from both wet and dry deposition sources (fig. 7).

2014 Study

The 2014 study was designed to assess and produce preliminary empirical models of the uptake of ionic constituents in deposition by the *H. splendens* moss. For that, we targeted six sites that were expected to reflect local or regional atmospheric depositional sources, and two comparatively remote sites, so that overall gradients of depositional loads might be observed (table 1). Potential sources affecting the 2014 sites included emissions from industrial, vehicular, and power generating stations of urban areas in or near Fairbanks or Healy, Alaska; from mining operations at an open-pit gold mine located south of the Poker Creek site and a surface coal mine near Healy; and from a coal-fired power plant, a railroad yard, and (or) a small aircraft airstrip near Healy. Unfortunately, opportunities to select sites within the city of Fairbanks (where localized loadings might have been greatest) were limited by the absence of *H. splendens* moss there; in addition, there were concerns about potential vandalism to the IECs if they were deployed in more populated areas. Our ability to assess overwinter loads from March snowpack samples was also hampered by unusually warm weather throughout Alaska during the winter of 2013–14, which resulted in intermittent melting of snow, especially at test sites near urban areas.

Snowpack and IEC extracts were analyzed for major cations including NH_4^+ , Ca, Mg, K, Na; major anions (Cl^- , NO_3^- , NO_2^- , and SO_4^{2-}); and a suite of trace metals, including Cd, Cu, Ni, Pb, and Zn. The 1-year and 3-year growth segments of moss tissue samples were analyzed for extractable NO_3^- , Tot-N, Tot-S, Tot-P, extractable cations and anions, and 12 trace metals.

Snowpack Samples

Snowpack samples were collected in triplicate between March 31 and April 3, 2014. Contaminants in snowpack were evaluated in terms of concentrations and loads for use in comparison to moss concentrations. As indicated previously, the snowpack present at the time of our 2014 sampling probably was not representative of the overwinter snowfall, particularly at sites HEA-4 and HEA-5. Two snow-tube grabs were used to collect each composite sample at each site, yet the final volume of melted snow varied by more than a factor of four among the five HEA sites; for example, at sites HEA-4 and HEA-5 the depth of snow was spotty and often less than 20 cm, and average volumes collected were only 0.24 and 0.30 L, respectively. In comparison, snow volumes collected at sites HEA-1 and HEA-2 averaged 0.68 and 0.57 L, and an average of 0.84 L was collected at the more remote site (HEA-3; table 2). The snowpack at the three FAI sites was more substantial and consistent and might have been nearly “intact” as snow depths were about 75 cm and volumes collected ranged from 0.73 to 1.05 L. Partial melting of the snowpack at some of the Healy, Alaska, sites probably caused our results to underestimate overwinter loads of the targeted pollutants there; nevertheless, substantial differences between

sites were evident for several of the pollutant concentrations in the snow.

Concentrations of NH_4^+ , NO_3^- , and SO_4^{2-} , as well as most metals and other elements in snow, were lowest at sites FAI-1 and HEA-3, sites that were assumed to be farthest from any major atmospheric sources (table 2; figs. 8 and 9). One of the replicate snowpack samples collected at the FAI-3 site was probably contaminated by animal waste as evidenced by greatly elevated levels of NH_4^+ , phosphorous (P), and K in that sample as compared to all other samples (table 2); therefore, that replicate was excluded in all subsequent data analyses. Snowpack collected from site HEA-2 had by far the greatest concentrations of NH_4^+ and NO_3^- ions, perhaps as a result of aerial dispersion of ammonium nitrate (NH_4NO_3) being used for rock blasting at the nearby open-pit coal mine or from gravel mining operations that happened in the nearby creek bed during the summer of 2014 (B. Brease, personal commun.). Elevated NH_4^+ concentrations in snowpack samples at that same site might have been affected by contamination from animals; however, there was no visual evidence of animal disturbance where those snowpack samples were collected. In addition, because the NH_4^+ ion was elevated consistently in all three subsamples obtained from that site, contamination from animals seems less likely. The HEA-2 site also had the greatest concentration of SO_4^{2-} in snow; and sites HEA-1, HEA-4, and HEA-5 also had elevated concentrations of SO_4^{2-} compared to the other sites. Those four sites presumably had elevated SO_4^{2-} because of proximity to the coal-burning power plant, as well as numerous residential sources (most residents in the Healy, Alaska, area burn coal for heat).

For many of the metals, concentrations in the snow (table 2) and the estimated overwinter depositional loads (table 3) were consistently greater at the Healy urban sites (HEA-1, HEA-2, HEA-4, HEA-5) as compared to the other four sites. Metals that were elevated at those four sites included aluminum (Al), cobalt (Co), chromium (Cr), Cu, iron (Fe), Mn, molybdenum (Mo), and Ni. The Co was elevated by as much as 10 times in the snow at those four Healy sites as compared to the other four. The Pb was a notable exception as snow from sites FAI-2, FAI-3, and HEA-2 had the greatest concentrations of that metal. Notably, Zn was most elevated in a snow sample collected from site HEA-1. The samples collected from that site were obtained very near to a motel that had a metal roof; consequently, leaching from that roof probably contributed to elevated concentrations of Zn and other metals in the snow at that site (Van Metre and Mahler, 2003). Container blanks and filtration blanks that were collected in association with the snowpack sample analyses revealed no instances of measureable trace elements.

Ion-Exchange Collectors

The IECs were removed from the sampling sites between September 16 and September 20, 2014. Upon retrieval, it was discovered that one of the three IEC replicates (arbitrarily designated as replicate 3) at each of sites FAI-1, FAI-3, and

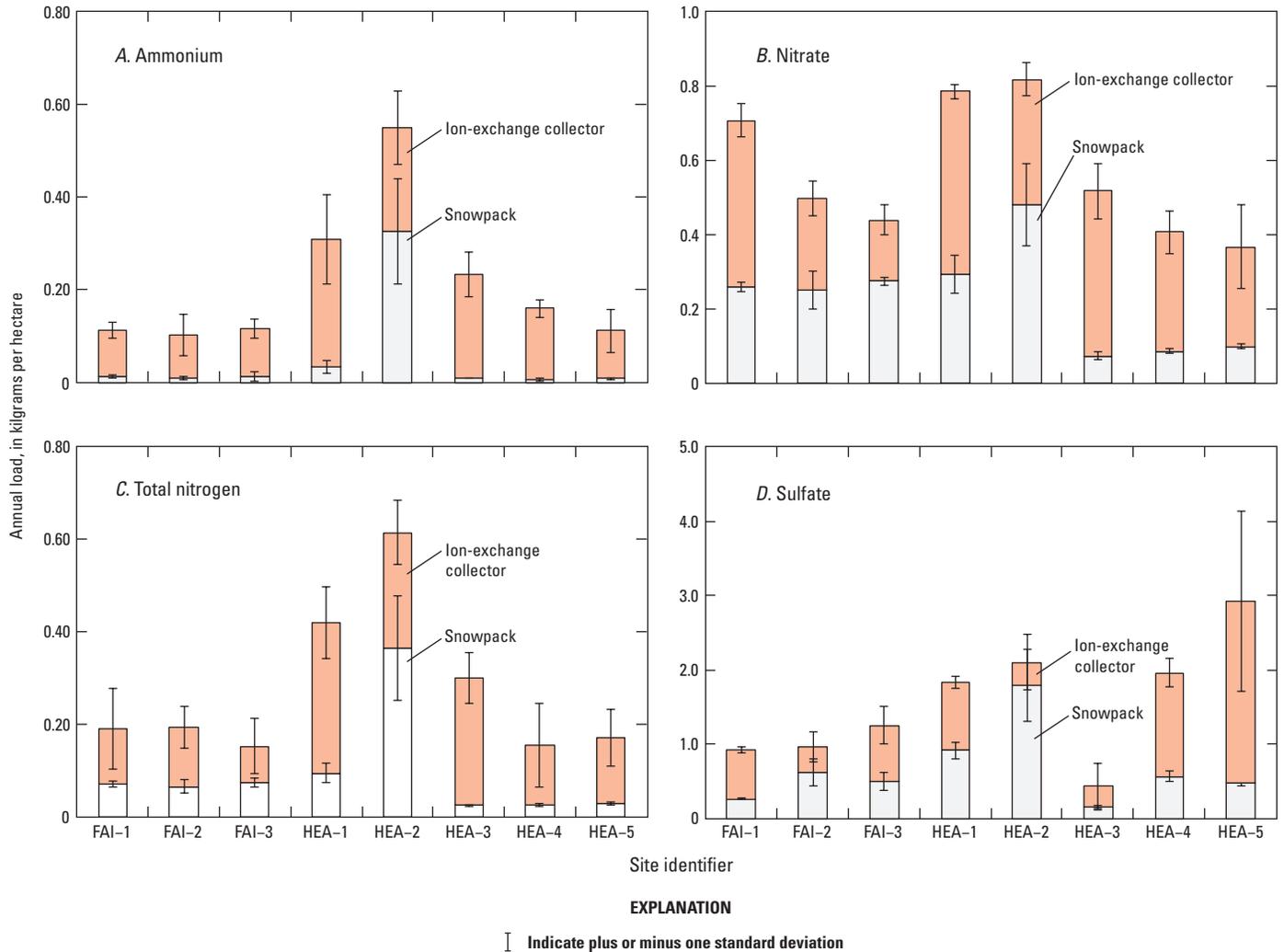


Figure 8. Comparison of depositional loads in snowpack samples (October through March) and ion-exchange collectors (April through September) at eight sites in Alaska during the 2014 study. *A*, ammonium. *B*, nitrate. *C*, total nitrogen. *D*, sulfate.

HEA-4 would not be reliable because of physical damage (for example, a fallen tree limb) or a technical error during deployment (table 4). Recoveries from the three IECs that had been spiked with cations and anions (10 mg for each substance) were the following: NH_4^+ —98, 99, and 100 percent; NO_3^- —85, 90, and 91 percent; and SO_4^{2-} —84, 96, and 98 percent. Recoveries from the one IEC that had been spiked with Cd, Cu, Pb, and Ni (1 mg each) were 100, 108, 91, and 104 percent, respectively; thus, results from the 2014 field-spiked IECs showed that the samplers successfully retained the targeted substances, including selected metals, and that those substances were successfully recovered and quantified by the laboratory extraction procedure. In general, repeatability among triplicate IECs was about ± 20 percent (see next paragraph), which was considered a reasonable target for this sampling method.

Annual loads of NH_4^+ , NO_3^- , Tot-N, and SO_4^{2-} estimated from IECs compared to loads from snow samples are illustrated in figures 8A, 8B, 8C, and 8D, respectively. The NH_4^+

loads were greatest at site HEA-2, which was the only site where snow contributed substantially to the annual load (fig. 8A). The NO_3^- loads were greatest at sites HEA-1, HEA-2, and FAI-1; and NO_3^- in the snow was a substantial contributor to the overall load for most sites (fig. 8B). Loads of Tot-N generally followed the patterns of NH_4^+ , whereby the greatest loads were present at sites HEA-1 and HEA-2; and except for site HEA-2, contributions from snow represented only about 20 percent of the annual loads (fig. 8C). Trends for SO_4^{2-} loads (fig. 8D) were somewhat different than for the N compounds. As was true for N, the greatest SO_4^{2-} contribution from snow was at site HEA-2; however, SO_4^{2-} loads in the IECs were lowest at that site. Sites HEA-4 and HEA-5 had the greatest SO_4^{2-} loads based on IEC measurements, whereas site HEA-3 had the lowest SO_4^{2-} loads for either snowpack or IECs. Overall, these results indicate evidence of an urban N deposition “signal” in the town of Healy, and that winter deposition of NO_3^- and SO_4^{2-} was considerable there, presumably associated with coal-burning emissions.

Table 2. Concentrations of inorganic substances measured in snowpack sampled in early April, 2014, at eight sites in Alaska.

[Rep, replicate number; Vol (L), volume sampled in liters; Tot-N, total nitrogen; mg/L, milligram per liter; NH₄, ammonium; NO₃, nitrate; SO₄, sulfate; P, phosphorus; Ca, calcium; K, potassium; Mg, magnesium; Na, sodium; Al, aluminum, µg/L, microgram per liter; Fe, iron; Mn, manganese; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; Mo, molybdenum; Ni, nickel; Pb, lead; Zn, zinc; <, less than]

Site identifier	Rep	Vol (L)	Tot-N (mg/L)	NH ₄ (mg/L)	NO ₃ (mg/L)	SO ₄ (mg/L)	P (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Al (µg/L)	Fe (µg/L)	Mn (µg/L)	Cd (µg/L)	Co (µg/L)	Cr (µg/L)	Cu (µg/L)	Mo (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)
FAI-1	1	0.9964	0.056	0.007	0.224	0.234	0.003	0.071	0.064	0.021	0.061	2.7	12	7.1	0.01	0.02	0.09	0.05	<0.01	0.02	0.05	1.9
	2	1.0652	0.064	0.017	0.225	0.223	0.003	0.042	0.047	0.016	0.058	2.3	<1	4.5	0.01	0.01	<0.01	0.03	<0.01	0.03	0.06	0.6
	3	1.0746	0.061	0.012	0.231	0.231	0.002	0.063	0.042	0.017	0.059	2.3	<1	7.2	0.01	0.02	0.16	0.05	<0.01	0.03	0.05	0.7
FAI-2	1	0.6941	0.087	0.013	0.340	0.489	0.016	0.193	0.437	0.052	0.064	8.1	<1	27.2	<0.01	0.03	0.02	0.16	0.02	0.43	0.14	3.4
	2	0.9846	0.076	0.014	0.287	0.681	0.030	0.236	0.891	0.096	0.074	11.5	31	50.3	0.01	0.05	0.28	0.25	0.04	0.13	0.18	5.8
	3	0.9109	0.047	0.007	0.184	0.782	0.035	0.237	1.202	0.089	0.113	12.9	17	35.7	0.01	0.06	0.17	0.25	0.03	0.10	0.19	4.3
FAI-3	1	0.8336	0.087	0.024	0.305	0.504	0.018	0.217	0.452	0.056	0.059	9.2	3	28.5	0.01	0.04	0.06	0.15	0.02	0.05	0.11	2.8
	2	0.6707	0.080	0.512 ^a	0.353	0.893	0.357 ^a	0.234	1.542	0.422	0.053	10.6	20	62.6	0.01	0.06	0.20	1.02	0.03	0.41	0.13	4.6
	3	0.6994	0.105	0.026	0.374	0.470	0.009	0.171	0.277	0.043	0.043	7.4	<1	29.6	0.01	0.03	0.18	0.15	0.01	0.06	0.10	2.3
HEA-1	1	0.5845	0.119	0.040	0.392	1.583	0.001	1.286	0.062	0.148	0.153	13.1	13	30.5	0.03	0.37	1.48	0.57	0.03	0.86	0.04	38.9
	2	0.9456	0.119	0.051	0.352	0.735	0.001	0.612	0.035	0.082	0.077	11.7	15	11.9	0.02	0.15	0.19	0.30	0.04	0.23	0.06	3.9
	3	0.524	0.141	0.046	0.464	1.710	0.012	2.999	0.601	0.327	0.809	42.3	54	112.5	0.05	0.68	0.25	3.56	0.12	0.98	0.05	13.1
HEA-2	1	0.4746	0.553	0.471	0.825	3.205	0.014	1.817	0.722	0.253	0.107	82.7	85	83.0	0.04	0.36	0.33	0.67	0.09	0.51	0.16	11.6
	2	0.6988	0.684	0.638	0.831	3.175	0.008	1.571	0.374	0.184	0.100	75.7	94	59.5	0.04	0.30	0.52	0.61	0.12	0.49	0.20	10.2
	3	0.5278	0.482	0.428	0.657	2.202	0.004	1.226	0.210	0.156	0.075	51.7	23	40.3	0.03	0.29	0.34	0.48	0.07	0.38	0.12	6.6
HEA-3	1	0.5933	0.033	0.016	0.094	0.269	0.004	0.173	0.066	0.036	0.066	2.6	14	12.6	0.02	0.07	0.21	0.06	<0.01	0.07	0.04	3.2
	2	1.0209	0.024	0.009	0.078	0.143	0.002	0.098	0.031	0.022	0.054	1.3	2	6.9	0.01	0.03	0.08	0.05	<0.01	0.04	0.01	1.7
	3	0.9203	0.023	0.009	0.070	0.132	0.003	0.086	0.038	0.022	0.056	1.6	5	7.7	<0.01	0.04	0.04	0.04	<0.01	0.05	0.02	1.4
HEA-4	1	0.2514	0.092	0.023	0.329	2.230	0.004	4.145	0.440	0.555	0.164	50.9	79	82.8	0.01	0.52	0.35	0.63	0.15	0.64	0.02	2.8
	2	0.2297	0.076	0.010	0.301	1.859	0.006	3.283	0.466	0.475	0.125	28.4	20	58.1	0.01	0.41	0.19	0.50	0.14	0.54	0.02	1.2
	3	0.2397	0.114	0.046	0.345	2.343	0.010	3.321	0.447	0.537	0.139	38.3	17	65.2	0.01	0.58	0.15	1.53	0.16	0.89	0.02	2.4
HEA-5	1	0.2844	0.101	0.036	0.323	1.569	0.010	1.674	0.363	0.270	0.083	41.9	74	88.3	0.01	0.41	0.19	0.41	0.05	0.44	0.03	3.1
	2	0.2668	0.111	0.036	0.366	1.459	0.008	1.908	0.419	0.274	0.085	44.3	90	89.1	0.01	0.45	0.33	0.45	0.05	0.42	0.03	3.7
	3	0.3359	0.065	0.012	0.243	1.490	0.007	1.977	0.384	0.315	0.096	56.9	80	129.2	0.02	0.46	0.39	0.59	0.05	0.58	0.04	6.4
Reporting limit			0.001	0.001	0.001	0.001	0.1	0.001	0.001	0.001	0.001	0.1	1	0.01								

^a Sample was probably contaminated by animal.

Table 3. Overwinter depositional loads of inorganic substances estimated from snowpack sampled in early April 2014 at eight sites in interior Alaska.

[Rep, replicate number; Vol (L), volume sampled in liters; Tot-N, total nitrogen; kg/ha, kilogram per hectare; NH₄, ammonium; g/ha, gram per hectare; NO₃, nitrate; SO₄, sulfate; P, phosphorus; Ca, calcium; K, potassium; Mg, magnesium; Na, sodium; Al, aluminum ; Fe, iron; Mn, manganese; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; Mo, molybdenum; Ni, nickel; Pb, lead; Zn, zinc; <, less than, --, no data]

Site identifier	Rep	Vol (L)	Tot-N (kg/ha)	NH ₄ (kg/ha)	NO ₃ (kg/ha)	SO ₄ (kg/ha)	P (kg/ha)	Ca (kg/ha)	K (kg/ha)	Mg (kg/ha)	Na (kg/ha)	Al (g/ha)	Fe (g/ha)	Mn (g/ha)	Cd (g/ha)	Co (g/ha)	Cr (g/ha)	Cu (g/ha)	Mo (g/ha)	Ni (g/ha)	Pb (g/ha)	Zn (g/ha)
FAI-1	1	0.062	0.008	0.245	0.256	0.003	0.077	0.070	0.023	0.067	0.061	2.9	14	7.8	0.01	0.10	0.02	0.05	<0.01	0.02	0.05	2.1
	2	0.075	0.020	0.263	0.261	0.003	0.049	0.055	0.019	0.067	0.058	2.7	<1	5.2	0.01	<0.01	0.01	0.04	<0.01	0.04	0.07	0.6
	3	0.072	0.014	0.272	0.273	0.002	0.074	0.049	0.020	0.070	0.059	2.7	<1	8.5	0.01	0.19	0.02	0.06	<0.01	0.04	0.06	0.8
FAI-2	1	0.066	0.010	0.259	0.372	0.012	0.147	0.333	0.040	0.049	0.064	6.1	<1	20.7	<0.01	0.02	0.02	0.12	0.02	0.33	0.11	2.6
	2	0.082	0.016	0.309	0.735	0.032	0.254	0.962	0.103	0.080	0.074	12.4	33	54.3	0.01	0.30	0.05	0.27	0.04	0.14	0.19	6.3
	3	0.047	0.007	0.184	0.781	0.035	0.237	1.201	0.089	0.112	0.113	12.9	17	35.7	0.01	0.17	0.06	0.25	0.03	0.10	0.19	4.3
FAI-3	1	0.080	0.022	0.279	0.461	0.016	0.198	0.414	0.052	0.054	0.059	8.4	3	26.1	0.01	0.05	0.04	0.14	0.02	0.05	0.10	2.5
	2	0.059	-- ^a	0.259	0.657	-- ^a	0.172	1.134	0.311	0.039	0.053	7.8	14	46.0	0.01	0.15	0.04	0.75	0.02	0.30	0.10	3.4
	3	0.080	0.020	0.287	0.361	0.007	0.131	0.213	0.033	0.033	0.043	5.7	<1	22.7	0.01	0.14	0.02	0.12	0.01	0.05	0.08	1.7
HEA-1	1	0.077	0.025	0.251	1.015	0.000	0.825	0.040	0.095	0.098	0.153	8.4	9	19.6	0.02	0.95	0.24	0.37	0.02	0.55	0.03	24.9
	2	0.124	0.053	0.365	0.763	0.001	0.635	0.037	0.085	0.080	0.077	12.1	16	12.3	0.02	0.20	0.16	0.31	0.04	0.24	0.06	4.0
	3	0.081	0.027	0.267	0.983	0.007	1.724	0.346	0.188	0.465	0.809	24.3	31	64.7	0.03	0.14	0.39	2.05	0.07	0.56	0.03	7.5
HEA-2	1	0.288	0.245	0.429	1.669	0.007	0.946	0.376	0.132	0.056	0.107	43.0	44	43.2	0.02	0.17	0.19	0.35	0.05	0.27	0.08	6.0
	2	0.525	0.489	0.637	2.434	0.006	1.205	0.287	0.141	0.076	0.100	58.1	72	45.6	0.03	0.40	0.23	0.47	0.09	0.38	0.15	7.8
	3	0.279	0.248	0.380	1.275	0.002	0.710	0.122	0.090	0.043	0.075	29.9	13	23.4	0.02	0.20	0.17	0.28	0.04	0.22	0.07	3.8
HEA-3	1	0.022	0.010	0.061	0.175	0.003	0.113	0.043	0.023	0.043	0.066	1.7	9	8.2	0.01	0.14	0.05	0.04	<0.01	0.05	0.03	2.1
	2	0.027	0.010	0.087	0.160	0.002	0.110	0.035	0.025	0.061	0.054	1.5	2	7.7	0.01	0.09	0.03	0.06	<0.01	0.04	0.01	1.9
	3	0.023	0.009	0.071	0.133	0.003	0.087	0.038	0.022	0.056	0.056	1.6	5	7.8	<0.01	0.04	0.04	0.04	<0.01	0.05	0.02	1.4
HEA-4	1	0.025	0.006	0.091	0.615	0.001	1.143	0.121	0.153	0.045	0.164	14.0	22	22.8	<0.01	0.10	0.14	0.17	0.04	0.18	0.01	0.8
	2	0.019	0.002	0.076	0.469	0.002	0.827	0.117	0.120	0.031	0.125	7.2	5	14.6	<0.01	0.05	0.10	0.13	0.04	0.14	0.01	0.3
	3	0.030	0.012	0.091	0.616	0.003	0.873	0.118	0.141	0.037	0.139	10.1	5	17.2	<0.01	0.04	0.15	0.40	0.04	0.23	0.01	0.6
HEA-5	1	0.031	0.011	0.101	0.489	0.003	0.522	0.113	0.084	0.026	0.083	13.1	23	27.6	<0.01	0.06	0.13	0.13	0.02	0.14	0.01	1.0
	2	0.032	0.011	0.107	0.427	0.002	0.558	0.122	0.080	0.025	0.085	13.0	26	26.1	<0.01	0.10	0.13	0.13	0.01	0.12	0.01	1.1
	3	0.024	0.005	0.090	0.549	0.003	0.729	0.141	0.116	0.036	0.096	20.9	29	47.6	0.01	0.14	0.17	0.22	0.02	0.21	0.01	2.3
Reporting limit			0.001	0.001	0.001	0.001	0.1	0.001	0.001	0.001	0.001	0.001	0.1	0.01	0.1	0.01						

^a Sample was probably contaminated by animal.

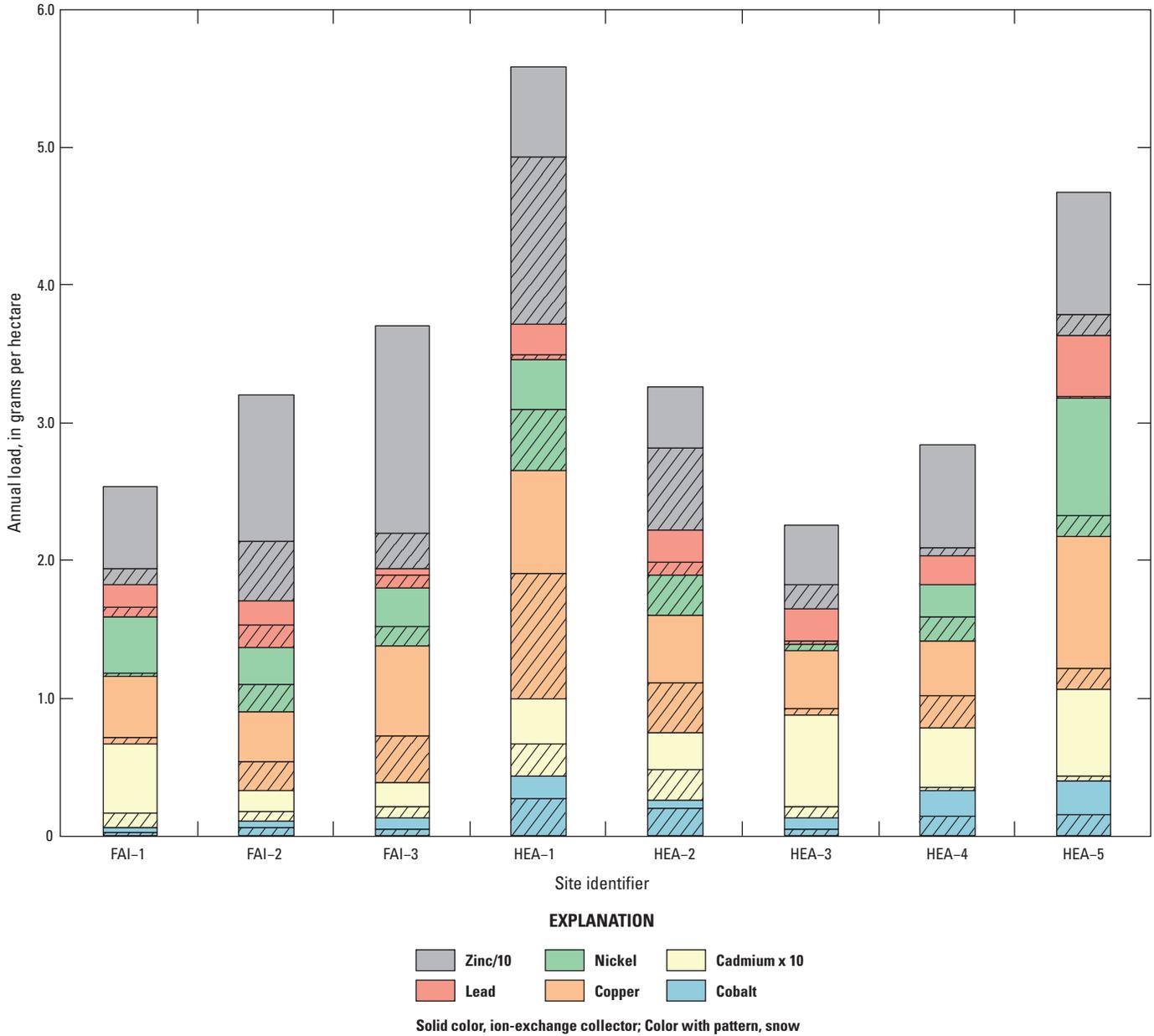


Figure 9. Comparison of annual depositional loads for selected metals measured by a combination of snowpack samples and ion-exchange collectors at eight sites in Alaska during the 2014 study.

Patterns for metal deposition based on IECs generally followed the metal concentrations in snow, but the RPDs between sites were generally not as great. Considering only the IEC results (table 4; fig. 9), Co was highest at sites HEA-1, HEA-4, HEA-5; and Cu, Pb, and Ni were greatest at site HEA-5 (near the railroad yard). Loads for Zn were rather inconsistent between replicate IECs at each site, but sites FAI-2 and FAI-3 (near UA-F in Fairbanks) tended to have higher IEC loads on average than the other sites. Surprisingly, Cd loads based on IECs were greatest at site HEA-3 and FAI-1 (the two more remote sites) but followed closely at sites HEA-4 and HEA-5. Total annual loads of these six trace metals as based

on the combined snow plus IEC measurements produced somewhat different patterns as compared to either snowpack or IECs alone (table 5; fig. 9). The greatest annual metal loads in combination were observed at sites HEA-1 and HEA-5; Cu, Ni, and Zn contributed most to those values. Lowest combined loads for those six metals were measured at the two more remote sites (FAI-1 and HEA-3); however, there was less than a three-fold difference between those two sites and HEA-1 (the site with the greatest combined load). It may be useful to compare potential seasonal differences between metal depositional loads during winter (snowpack) and spring/summer (IECs). For Cd, Cu, or Pb, the contributions to annual

metals loads were usually greater during the warm season (in IECs) than the cold season (in snow), but that trend was less consistent for Co, Ni, or Zn (fig. 9). Notably, the 2014 IECs deployed in the urban Healy, Alaska, locales had much greater loads of Fe and Mn as compared with the 2012 IECs deployed in Fairbanks, whereas the snow concentrations (and loads) for those two metals were comparable between the 2012 Fairbanks site and the 2014 Healy urban locales (data not shown). We hypothesize that the differences between IEC loads for Fe and Mn at urban sites sampled in 2012 and 2014 can be explained by the greater deployment height (above ground level) for the Fairbanks site in 2012. The 2012 IECs in Fairbanks were deployed about 10 meters above ground (on a second story roof); therefore, those IECs probably were exposed to much less dust than those deployed near ground level in 2014.

Ion-Exchange Collector Field Blanks

Maintaining low procedural “background” levels in the IEC field blanks in comparison to concentrations being measured in the sampler IECs proved to be a challenge for some of the metals, particularly for Cr, Fe, Pb, and Ni. Concentrations (and load equivalents) of those four metals in the five field blanks were often greater than the corresponding blank-corrected values of the sampler IECs (table 4). Ideally, all blank values would be less than 10 percent of most sample values; however, even if that target cannot be met, if replicate blanks are consistent, the sample results can be blank-corrected with certainty. In this instance, although Pb was elevated in the extracts of field blanks, those results were consistent, which allows for a reasonable degree of certainty among blank-corrected sample values. Field blank results, however, were less consistent for Cr, Ni, and especially Fe; consequently, sampler IEC loads for those three elements can only be considered qualitative.

Notably, IEC blank levels of many of these same metals tended to be lower for the field studies completed in 2012; however, the extraction with a 1 M solution of KI that was used in 2012 did not quantitatively recover the spiked metals from the IECs. Presumably, the stronger extraction sequence used for 2014 IECs (1 M solution of KCl, 3.2 M solution of HNO₃), which produced good recoveries of spiked metals, also extracted greater amounts of metals from the blank columns. In addition, metal “background” levels tended to be slightly greater in the 1 M solution of KCl reagent as compared with the 1 M solution of KI reagent. Use of a high purity grade of the KCl reagent (for example, “trace metals” grade) should help to reduce blank levels of some of these metals, but operational costs would be greater.

Moss Samples

Moss tissue results for percent ash, concentrations of leachable NO₃⁻ as N (NO₃-N); Tot-N; Tot-S; Tot-P; and Al,

Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, and Zn are presented in table 6. The mean recovery from the BCR 61 moss standard reference material was less than 50 percent for four elements (Al, Cr, Mo, and Na), and the mean recovery for Fe also was low at 67 percent. All other measured elements were within the targeted range of 100±25 percent. The low recoveries observed for Al, Cr, Mo, and Na were probably because of the “partial” digestion method used (appendix 2). The procedure is a partial digestion that does not include hydrofluoric acid and is designed to solubilize only the less refractory solids; consequently, silicate components that may be present as contaminants of the sample are minimally solubilized (Filgueiras and others, 2002). Historical analyses completed at the USGS have indicated that refractory silicate residues of samples often include substantial concentrations of Al, Cr, Mo, and Na; therefore, we do not consider the low results for those four elements, as well as Fe, in the BCR 61 SRM to be of particular concern. Variability between duplicate moss digestions and analyses completed by the RAL varied depending on the analyte. Mean RPDs (duplicate difference/duplicate mean) for the six moss samples analyzed in duplicate ranged from as little as 2–3 percent for Ca, K, Mg, Mn, P, and Zn; to 10–30 percent for Cu, Fe, Co, Cd, Na, Al, Cr, Ni; to 51 percent for Pb and 75 percent for Mo (individual replicate data not shown). The large variation for Pb and Mo was probably partly because of the nearness of some of those concentrations to the reporting limits for those two elements.

Two-factor analysis of variance was completed to determine if there were differences in concentrations of metals and other substances between sites, between growth segments, and to determine the extent that site differences depended on the growth segment analyzed. A separate analysis of variance was subsequently completed to evaluate site differences among moss concentrations for 1-year and 3-year growth segments separately to support posthoc testing (figs. 10–14; appendix table 3–1, available for download at <http://dx.doi.org/10.3133/sir20165096>). Among the 20 variables examined, concentrations of only Ca were not statistically different ($p>0.05$) between any of the eight sampling sites for either growth segment. Among the remaining 19 variables, patterns of relative concentrations between sites were mostly the same for either 1-year or 3-year growth segments, but for some substances the extent that sites differed depended in part on which growth segment was analyzed. Specifically, site differences were not consistent in each growth segment ($p<0.05$) for percent ash and concentrations of Al, Co, Cr, Fe, Mo, and Ni (table 3–1). Regressions between concentrations in the 1-year segments and 3-year segments produced highly significant relations ($p<0.02$) for all substances. Slopes for those regressions were near unity (0.88 to 1.09) for Ca, Mn, Na, K, P, S, Mg, NO₃⁻, and Zn; whereas as slopes for ash and all other metals except Cd were less than 0.60 (appendix table 3–2, available for download at <http://dx.doi.org/10.3133/sir20165096>). Presumably, these findings reflect the fact that at some sites the 3-year segments contained much greater amounts of ash and certain metals as compared to the 1-year segments. Evidently, at sites

Table 4. Spring/summer depositional loads of inorganic constituents estimated from ion-exchange collectors at eight sites in interior Alaska.

[Rep, replicate number; Tot-N, total nitrogen; kg/ha, kilogram per hectare; NH₄, ammonium; NO₃, nitrate; SO₄, sulfate; P, phosphorus; Ca, calcium; K, potassium; Mg, magnesium; Na, sodium; Al, aluminum; g/ha, gram per hectare; Fe, iron; Mn, manganese; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; Mo, molybdenum; Ni, nickel; Pb, lead; Zn, zinc; <, less than; --, no data; All site values are blank corrected using mean of the five ion-exchange collector field blanks]

Site identifier	Rep	TOT-N (kg/ha)	NH ₄ (kg/ha)	NO ₃ (kg/ha)	SO ₄ (kg/ha)	Ca (kg/ha)	Mg (kg/ha)	Na (kg/ha)	Al (g/ha)	Fe (g/ha)	Mn (g/ha)	Cd (g/ha)	Co (g/ha)	Cr (g/ha)	Cu (g/ha)	Mo (g/ha)	Ni (g/ha)	Pb (g/ha)	Zn (g/ha)
FAI-1	1	0.204	0.118	0.494	0.619	0.198	0.049	<0.001	15.3	<10	19	0.07	<0.01	0.1	0.18	0.02	<0.01	<0.1	11.4
	2	0.155	0.082	0.402	0.699	0.386	0.134	0.103	21.6	153	60	0.08	0.06	0.6	0.69	0.04	0.84	0.82	6.5
	3	Missing IEC sample																	
FAI-2	1	0.083	0.046	0.208	0.493	0.652	0.180	0.027	10.7	140	90	<0.01	0.04	1.6	0.35	0.03	0.21	0.16	12.0
	2	0.109	0.077	0.220	0.054	0.566	0.147	0.023	5.1	<10	112	<0.01	0.04	<0.1	0.30	<0.01	0.34	0.29	11.8
	3	0.190	0.154	0.314	0.477	0.444	0.127	0.021	6.9	46	51	0.06	0.06	<0.1	0.45	0.05	0.28	0.07	8.0
FAI-3	1	0.093	0.083	0.125	1.017	0.883	0.336	0.066	9.5	39	245	<0.01	0.13	1.53	0.67	0.01	0.41	<0.1	28.0
	2	0.143	0.124	0.205	0.507	0.550	0.214	0.019	10.6	<10	118	0.06	0.05	<0.1	0.65	<0.01	0.17	0.10	17.1
	3	Missing IEC sample																	
HEA-1	1	0.282	0.215	0.508	1.005	0.476	0.104	0.082	41.7	193	20	0.05	0.18	0.4	0.95	<0.01	0.40	0.16	3.4
	2	0.260	0.199	0.465	0.802	0.473	0.083	0.059	29.0	188	21	0.06	0.15	0.6	0.63	<0.01	0.36	0.23	4.0
	3	0.433	0.410	0.504	0.930	0.523	0.093	0.088	38.2	<10	21	<0.01	0.16	1.3	0.67	0.05	0.31	0.26	12.4
HEA-2	1	0.152	0.112	0.287	0.054	0.356	0.080	0.048	16.9	<10	27	<0.01	0.04	1.4	0.35	0.07	<0.01	0.25	3.2
	2	0.306	0.279	0.395	0.054	0.307	0.061	0.078	13.5	<10	20	0.09	0.06	<0.1	0.90	0.03	<0.01	0.15	4.5
	3	0.294	0.282	0.330	0.827	0.406	0.098	0.043	15.8	86	30	<0.01	0.04	1.3	0.24	0.07	<0.01	0.31	5.6
HEA-3	1	0.199	0.157	0.341	0.054	0.130	0.045	0.039	13.4	<10	16	0.10	<0.01	0.6	0.45	0.01	0.06	0.42	4.0
	2	0.321	0.264	0.514	0.054	0.183	0.047	0.032	13.5	113	19	0.06	0.14	<0.1	0.20	<0.01	0.07	0.23	4.0
	3	0.306	0.254	0.480	0.720	0.140	0.034	0.029	6.1	<10	8	0.04	0.12	<0.1	0.64	0.05	<0.01	0.04	5.0
HEA-4	1	0.190	0.134	0.380	1.588	0.655	0.126	0.051	59.1	200	21	0.06	0.28	1.4	0.52	0.02	0.34	0.29	17.0
	2	0.195	0.173	0.265	1.204	0.550	0.111	0.072	37.1	53	17	0.07	0.10	0.7	0.26	<0.01	0.12	0.12	5.8
	3	Missing IEC sample																	
HEA-5	1	0.118	0.087	0.222	1.452	0.889	0.173	0.070	77.9	208	41	0.07	0.19	0.6	1.14	0.07	0.98	0.52	1.8
	2	0.226	0.168	0.423	1.690	0.890	0.121	0.059	35.5	38	37	0.00	0.15	1.2	0.60	0.07	0.65	0.41	1.8
	3	0.082	0.059	0.161	4.136	3.196	0.637	0.135	69.5	<10	88	0.11	0.38	1.8	1.12	0.10	0.92	0.43	23.1

Table 4. Spring/summer depositional loads of inorganic constituents estimated from ion-exchange collectors at eight sites in interior Alaska.—Continued

[Rep, replicate number; Tot-N, total nitrogen; kg/ha, kilogram per hectare; NH₄⁺, ammonium; NO₃⁻, nitrate; SO₄²⁻, sulfate; P, phosphorus; Ca, calcium; K, potassium; Mg, magnesium; Na, sodium; Al, aluminum; g/ha, gram per hectare; Fe, iron; Mn, manganese; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; Mo, molybdenum; Ni, nickel; Pb, lead; Zn, zinc; <, less than; --, no data. All site values are blank corrected using mean of the five ion-exchange collector field blanks]

Site identifier	Rep	Tot-N (kg/ha)	NH ₄ (kg/ha)	NO ₃ (kg/ha)	SO ₄ (kg/ha)	Ca (kg/ha)	Mg (kg/ha)	Na (kg/ha)	Al (g/ha)	Fe (g/ha)	Mn (g/ha)	Cd (g/ha)	Co (g/ha)	Cr (g/ha)	Cu (g/ha)	Mo (g/ha)	Ni (g/ha)	Pb (g/ha)	Zn (g/ha)
	1	0.022	0.028	<0.001	<0.001	0.071	0.023	0.193	0.4	188	6.8	<0.01	0.11	2.9	0.24	<0.01	1.46	1.8	0.2
	2	0.033	0.042	<0.001	<0.001	0.048	0.019	0.193	1.0	65	5.2	<0.01	0.03	1.4	0.17	<0.01	1.35	1.8	0.2
Field blanks	3	0.030	0.039	<0.001	<0.001	0.067	0.021	0.176	0.3	200	8.5	<0.01	0.09	3.2	0.51	<0.01	0.84	1.8	<0.1
	4	0.026	0.033	<0.001	<0.001	0.040	0.023	0.198	0.1	32	7.1	<0.01	0.00	3.1	0.13	<0.01	0.88	1.7	0.3
	5	0.015	0.019	<0.001	<0.001	0.066	0.024	0.187	0.0	423	8.5	<0.01	0.05	3.9	0.20	<0.01	0.84	2.1	<0.1
Mean of field blanks		0.025	0.032	<0.001	<0.001	0.059	0.022	0.189	0.37	182	7.2	<0.01	0.06	2.9	0.25	<0.01	1.07	1.8	0.2
SD of field blanks		0.006	0.01	--	--	0.01	0	0.01	0.36	138	1.2	--	0.04	0.8	0.14	--	0.27	0.1	0.1
Reporting limit		0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.1	10	0.1	0.01	0.01	0.1	0.01	0.01	0.01	0.01	0.1

where dispersion of airborne dust was a source of metals, the moss had preferentially accumulated certain metals in the older 3-year segments as compared with the new-growth 1-year segments (discussed in more detail later in this report).

The moss tissue results for NO₃⁻-N, Tot-N, Tot-S, and Tot-P are illustrated in figure 10 as box and whisker plots for each of the eight sites. Leachable NO₃⁻ tended to be greater at sites FAI-1, FAI-2, and HEA-5, as compared to FAI-3 and the other four HEA sites (fig. 10A), and that pattern was similar for either 1-year or 3-year segments but only for 1-year growth segments were the differences statistically significant (*p*<0.05). For Tot-S or Tot-P, no sites were significantly different from one another for 1-year growth segments; but for the 3-year segments, the sites fell into two groups for Tot-S (fig. 10C) and into three groups for Tot-P (fig. 10D). Presumably, the absence of significant site differences in Tot-S or Tot-N accumulated by mosses collected from all six of the urban-influenced sites reflects a broader (less localized) dispersion of nitrates and sulfates originating from multiple atmospheric sources. Also, Tot-P and leachable NO₃⁻ might have been most elevated at site FAI-2 because of closer proximity of that site to the university experimental agricultural fields. There could be several factors why differences between sites were often less pronounced in the 1-year growth segments, but one factor might have been that the smaller sample mass available for the 1-year growth segments adversely affected the precision of those measurements.

Trends for moss concentrations across the eight sites varied among the major alkali and alkaline earth cationic metals (Ca, K, Na, and Mg) are presented in figure 11. For Ca there were no significant differences among any sites for either 1-year or 3-year moss segments; and for some reason, variability was unusually high for Ca among replicate moss samples obtained from site FAI-1 (fig. 11A). Considering only the 3-year growth segments, Mg concentrations were lowest at sites FAI-3 and HEA-3 (fig. 11B), whereas concentrations of Na and K were lowest at the two most remote sites, FAI-1 and HEA-3 (figs. 11C and 11D). The K concentration of moss from site HEA-1 (next to the motel on George-Parks highway) also was comparatively low, yet Na was comparatively high at that site and at site HEA-5. Elevated Na in moss from sites HEA-1 and HEA-5 might have reflected uptake from dispersal of deicing salt applications to nearby roadways. And perhaps the lower K concentrations observed in moss at site HEA-1 happened indirectly as a result of decreased K uptake caused by competitive uptake of Na. Variable spatial trends observed for these major cation analyses seem to suggest that contributions originating from underlying substrates might have influenced some of the moss results, and that factor might have been more important at sampling locations where the underlying layer of peat moss was relatively thin (Linder and others, 2013).

Results for percent ash and concentrations of Al, Fe, and Mn in the moss samples are presented in figure 12. On average, the ash content of the moss tissue samples ranged from about 2 to 6 percent; however, variation of moss ash content

F (g/ha)	Mn (g/ha)	Cd (g/ha)	Co (g/ha)	Cr (g/ha)	Cu (g/ha)	Mo (g/ha)	Ni (g/ha)	Pb (g/ha)	Zn (g/ha)
<10	27	0.08	0.01	0.16	0.24	0.02	<0.01	<0.01	13.4
153	65	0.09	0.07	0.57	0.72	0.04	0.88	0.89	7.1
Missing IEC sample									
153	46	0.086	0.04	0.36	0.48	0.03	0.88	0.89	10.3
0	19	0.006	0.033	0.206	0.240	0.011	0	0	3.1
140	110	<0.01	0.06	1.60	0.47	0.05	0.54	0.27	14.5
<10	167	0.00	0.10	0.22	0.57	0.03	0.48	0.48	18.0
63	86	0.07	0.12	<0.1	0.70	0.08	0.38	0.26	12.4
102	121	0.04	0.09	0.91	0.58	0.05	0.47	0.34	15.0
39	34	0.03	0.02	0.69	0.09	0.02	0.07	0.10	2.3
41	272	<0.01	0.16	1.58	0.81	0.03	0.45	0.10	30.6
<10	164	0.07	0.10	<0.1	1.40	0.01	0.47	0.20	20.5
Missing IEC sample									
41	218	0.066	0.13	1.58	1.11	0.02	0.46	0.15	25.5
0	54	0	0.034	0	0.296	0.009	0.008	0.052	5.0
201	40	0.07	0.42	1.36	1.31	0.01	0.95	0.18	28.3
204	34	0.08	0.31	0.82	0.94	0.03	0.60	0.30	8.0
29	86	0.02	0.55	1.46	2.72	0.12	0.87	0.29	19.9
145	53.0	0.06	0.43	1.21	1.66	0.05	0.81	0.26	18.7
82	23.2	0.02	0.10	0.28	0.77	0.05	0.15	0.05	8.3
49	71	0.01	0.23	1.61	0.70	0.12	0.12	0.33	9.2
29	65	0.12	0.29	0.12	1.37	0.12	0.22	0.30	12.3
99	54	0.01	0.21	1.51	0.52	0.11	0.01	0.38	9.4
59.0	63.2	0.05	0.24	1.08	0.86	0.12	0.11	0.34	10.3
29.4	7.0	0.05	0.04	0.68	0.37	0.00	0.09	0.03	1.4
<10	24	0.12	0.04	0.72	0.49	0.01	0.10	0.45	6.0
116	26	0.07	0.17	<0.1	0.25	<0.01	0.11	0.25	6.0
<10	15	0.04	0.16	<0.1	0.68	0.05	<0.01	0.06	6.4
115.6	22.0	0.07	0.12	0.72	0.47	0.03	0.11	0.25	6.1
0.0	4.7	0.03	0.06	0.00	0.18	0.02	0.01	0.16	0.2
222	43	0.06	0.42	1.53	0.70	0.06	0.52	0.29	17.7
58	32	0.07	0.20	0.73	0.39	0.03	0.26	0.12	6.1
Missing IEC sample									
140	37	0.07	0.31	1.13	0.54	0.05	0.39	0.21	11.9
82	6	0.01	0.11	0.40	0.15	0.01	0.13	0.09	5.8
231	69	0.07	0.32	0.68	1.27	0.09	1.12	0.53	2.8
64	63	0.01	0.28	1.34	0.73	0.09	0.77	0.42	2.9
<10	136	0.12	0.55	1.94	1.34	0.11	1.13	0.45	25.4
147.4	89.0	0.07	0.38	1.32	1.11	0.10	1.01	0.46	10.4
83.5	33.0	0.05	0.12	0.51	0.27	0.01	0.17	0.05	10.7
10	0.1	0.01	0.01	0.1	0.01	0.01	0.01	0.01	0.1

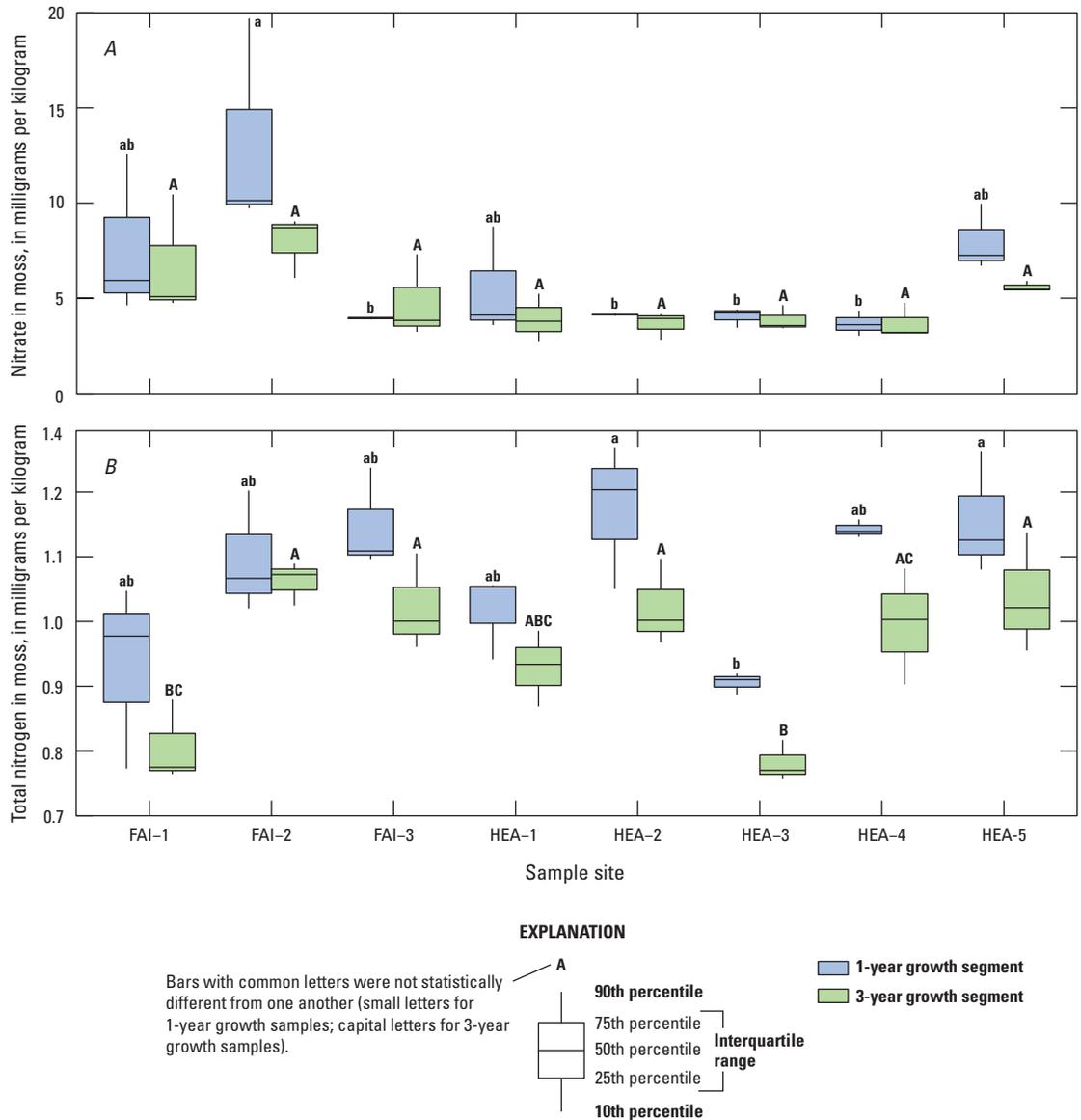


Figure 10. Comparison of nitrate, total nitrogen, total sulfur, and phosphorous concentrations in 1-year and 3-year growth segments of *Hylocomium splendens* moss samples collected from eight sites of interior Alaska during the 2014 study.

within a site and the range between sites was much greater in 3-year growth segments than in the 1-year segments (fig. 12A). In particular, 3-year growth segments of moss samples from sites HEA-1, HEA-4, and HEA-5 had substantially greater ash content than all other samples. Presumably, elevated ash content was influenced mostly by particulate deposition (dust), probably from gravel roads or parking lots near to those sites. Also, the 3-year segments might have had greater ash content compared to the younger 1-year growth segments because 3-year segments have additional nodes nearer to the ground that could adsorb and retain more fine dust particles; accordingly, concentrations of Al and Fe, which are two of the most abundant metallic elements present in most soils, tracked closely with ash content (fig. 12A, 12B, and 12C). And, like

the ash content, the concentrations of those two metals in the 3-year moss segments were much greater at sites HEA-1, HEA-4, and HEA-5 as compared to the other five sites. For Mn (fig. 12D), concentrations in the 1-year growth segments closely matched those in the 3-year segments; however, differences between sites did not fit any particular pattern with respect to urban location. The greatest Mn concentrations, for example, were observed in moss from one of the more remote sites (HEA-3), but Mn was also elevated in moss from the HEA-1 site (next to the motel on George-Parks highway); furthermore, the Mn concentrations were lowest in moss samples obtained from sites HEA-4 and HEA-5, which generally had the greatest concentrations of most other metals. And for some

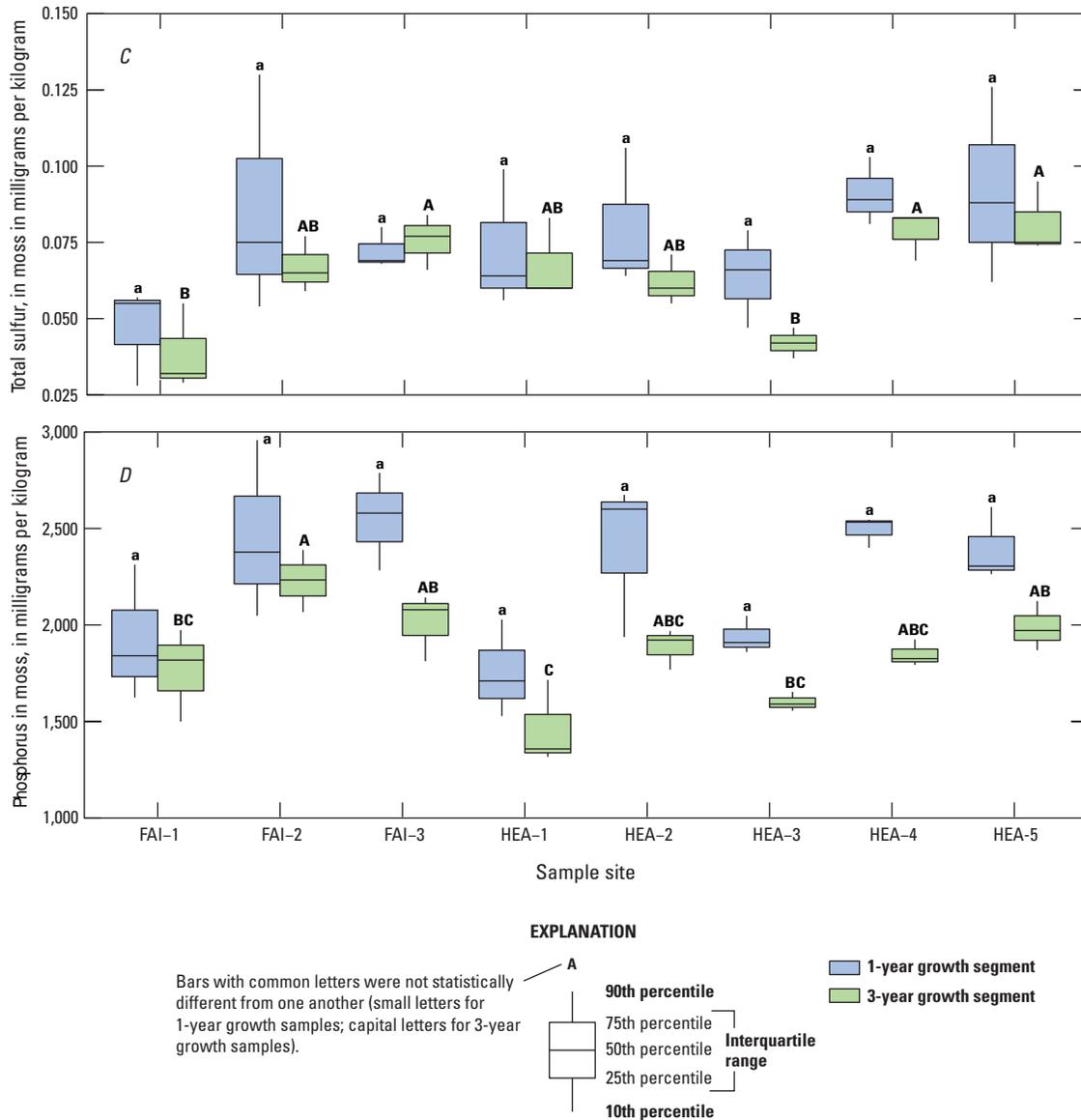


Figure 10. Comparison of nitrate, total nitrogen, total sulfur, and phosphorus concentrations in 1-year and 3-year growth segments of *Hylocomium splendens* moss samples collected from eight sites of interior Alaska during the 2014 study.—Continued

reason, variability was much less between replicate samples for Mn for those two sites as compared to the others.

Moss tissue concentrations of eight trace metals are depicted in figures 13 and 14. Considering primarily results of the 3-year growth segments, trends between moss concentrations at the eight sites were fairly consistent for most of the trace metals; for example, moss at sites HEA-1, HEA-4, and HEA-5 had greater concentrations of Co, Cr, Cu, Mo, Ni, and Pb as compared to the other five sites ($p < 0.05$); and in most instances the other five sites were not statistically distinguishable from one another (fig. 14). Two exceptions were Cd and Zn. For Cd, only moss from HEA-4 had substantially greater concentrations than the other sites (fig. 13A); and for Zn, only

moss from HEA-1 had substantially greater concentrations than the rest (fig. 14D).

Interestingly, the 1-year growth segments consistently had greater concentrations as compared to the 3-year segments for N, S, and P (figs. 10A, 10B, 10C, and 10D), as well as Mg and K (figs. 11B and 11C), but the opposite pattern was observed for ash, Al, Fe (figs. 12A, 12B, and 12C), Na (fig. 11D), and most trace metals (figs. 13 and 14). In contrast, the Ca concentrations of each of the two growth segments were very closely matched (fig. 11A). Simple linear regressions between concentrations of substances in the 1-year segments (y variable) to that of the 3-year segments (x variable) produced slopes of less than 0.60 for percent ash and most of the trace metals, which presumably reflected greater accumulation

Table 6. Concentrations of inorganic substances in *Hylocomium splendens* moss tissue samples collected mid-September 2014 from eight sites in interior Alaska.

[Rep, replicate number; Segment, growth segment; Tot-N, total nitrogen; %, percent; NO₃-N, nitrate and nitrogen; mg/kg, milligrams per kilogram (dry weight basis); P, phosphorus; Ca, calcium; K, potassium; Mg, magnesium; Na, sodium; Al, aluminum, µg/L, micrograms per liter; Fe, iron; Mn, manganese; Cd, cadmium; Co, cobalt; Cr, chromium; Cu, copper; Mo, molybdenum; Ni, nickel; Pb, lead; Zn, zinc; --, no data; NA, not analyzed because of insufficient sample mass]

Site identifier	Rep	Segment (years)	Ash (%)	Tot-N (%)	NO ₃ -N (mg/kg)	Tot-S (%)	P (mg/kg)	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)	Al (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Mo (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
FAI-1	1	1	2.55	0.98	4.62	0.057	1,840	4,010	5,920	1,360	29	156	210	790	0.08	0.15	0.85	3.40	0.06	0.85	0.53	32
	1	3	2.77	0.76	5.08	0.032	1,500	4,360	4,930	1,280	37	435	320	940	0.11	0.32	1.35	3.12	0.08	1.77	0.59	38
	2	1	3.85	1.05	5.94	0.055	2,310	10,100	6,970	1,640	36	197	210	290	0.32	0.18	0.77	3.48	0.01	0.78	0.92	53
	2	3	3.38	0.88	10.45	0.055	1,970	10,280	6,600	1,500	44	309	340	380	0.30	0.25	1.26	2.98	0.01	1.41	0.88	59
	3	1	2.16	0.77	12.56	0.028	1,620	3,440	4,860	1,270	36	283	330	560	0.13	0.23	1.02	2.40	0.01	1.02	0.97	39
	3	3	1.94	0.77	4.75	0.029	1,820	2,880	5,250	1,390	39	169	270	550	0.13	0.29	1.89	4.48	0.12	2.04	0.70	34
FAI-2	1	1	3.30	1.02	19.70	0.054	2,050	5,120	7,540	1,290	64	357	460	410	0.09	0.25	1.49	4.05	0.05	1.46	1.15	46
	1	3	1.93	1.09	8.71	0.059	2,390	4,450	8,380	1,430	57	161	190	290	0.09	0.14	1.20	3.78	0.15	0.73	0.48	37
	2	1	3.18	1.07	9.72	0.075	2,380	4,740	8,530	1,310	62	146	180	290	0.08	0.21	0.82	3.75	0.10	0.52	0.32	40
	2	3	3.63	1.02	9.04	0.065	2,070	5,600	7,430	1,270	60	396	480	480	0.09	0.34	1.42	3.86	0.19	1.25	1.15	52
	3	1	2.98	1.20	10.13	0.130	2,960	4,450	9,700	1,500	66	107	150	520	0.07	0.22	0.73	3.82	0.04	0.45	1.06	48
	3	3	4.38	1.07	6.06	0.077	2,230	5,030	8,270	1,270	80	431	540	500	0.11	0.37	2.06	4.02	0.10	2.12	1.37	47
FAI-3	1	1	3.41	1.24	4.01	0.068	2,790	3,760	9,670	1,360	67	162	270	450	0.06	0.14	1.22	3.99	0.06	0.78	0.39	50
	1	3	3.82	1.11	7.31	0.084	2,140	4,770	8,090	1,210	69	439	630	670	0.14	0.31	1.85	3.97	0.16	2.11	1.13	71
	2	1	3.13	1.11	3.96	0.080	2,280	3,340	8,520	1,410	31	81	160	300	0.07	0.13	0.91	3.04	0.08	0.52	0.31	32
	2	3	3.53	0.96	3.83	0.077	1,810	3,990	7,100	1,240	66	418	400	370	0.09	0.23	1.49	3.25	0.04	1.71	0.77	41
	3	1	2.95	1.10	3.89	0.069	2,580	4,100	8,280	1,370	50	132	150	300	0.10	0.12	1.02	3.39	0.06	0.85	0.43	39
	3	3	3.59	1.00	3.24	0.066	2,080	4,790	7,590	1,220	62	402	510	490	0.09	0.27	1.72	3.40	0.05	1.62	0.87	46
HEA-1	1	1	4.66	1.05	8.76	0.056	2,030	4,090	5,720	1,690	105	641	950	760	0.14	0.53	3.51	5.43	0.14	2.72	1.39	104
	1	3	6.38	0.99	2.71	0.060	1,720	4,350	5,440	1,610	90	1,120	1,870	760	0.20	0.83	6.33	5.81	0.35	4.53	1.68	112
	2	1	3.39	1.06	3.59	0.099	1,710	4,010	4,950	1,610	73	680	950	770	0.15	0.53	2.55	5.01	0.02	2.22	1.09	98
	2	3	6.13	0.87	3.79	0.060	1,360	4,070	4,280	1,460	85	1,151	1,750	760	0.13	0.78	4.58	5.43	0.17	4.23	2.29	98
	3	1	4.37	0.94	4.12	0.064	1,530	4,040	4,630	1,550	73	495	840	910	0.14	0.50	2.04	4.71	0.08	2.14	1.11	94
	3	3	8.84	0.93	5.23	0.083	1,320	4,130	4,430	1,540	70	1,012	2,360	990	0.22	0.96	5.57	5.62	0.37	5.38	2.56	95

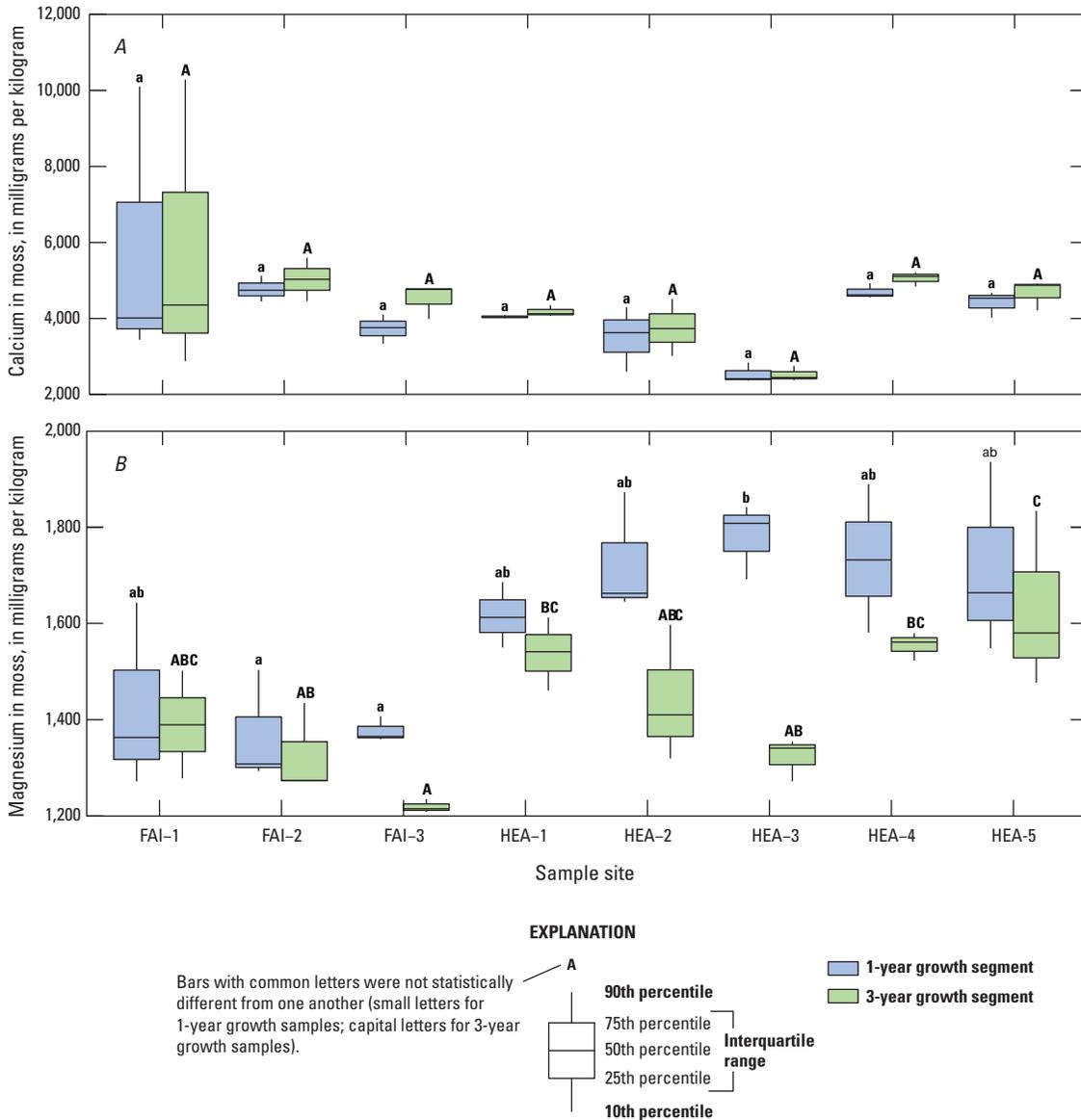


Figure 11. Comparison of calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) concentrations in 1-year and 3-year growth segments of *Hylocomium splendens* moss samples collected from eight sites of interior Alaska during the 2014 study.

of dust particles in the older (and nearer to the ground) growth segments.

Moss tissue concentrations of most of the trace metals were strongly (positively) correlated ($p < 0.05$) with the ash content of the moss, particularly for 3-year growth segments (appendix table 3–3, available for download at <http://dx.doi.org/10.3133/sir20165096>). Those included Co, Cu, Cr, Mo, Ni, and Pb, as well Al and Fe (discussed previously). Such results indicate that accumulation of those metals by the

mosses likely was derived substantially from airborne dust, probably associated with nearby gravel roads or other disturbances, such as gravel mining or mine blasting operations; accordingly, the ash content and concentrations of most metals were greatest in moss tissues obtained from sites HEA–1, HEA–4, and HEA–5; and, except for Mn and Cd, were lowest in moss from HEA–3 (a presumed reference site).

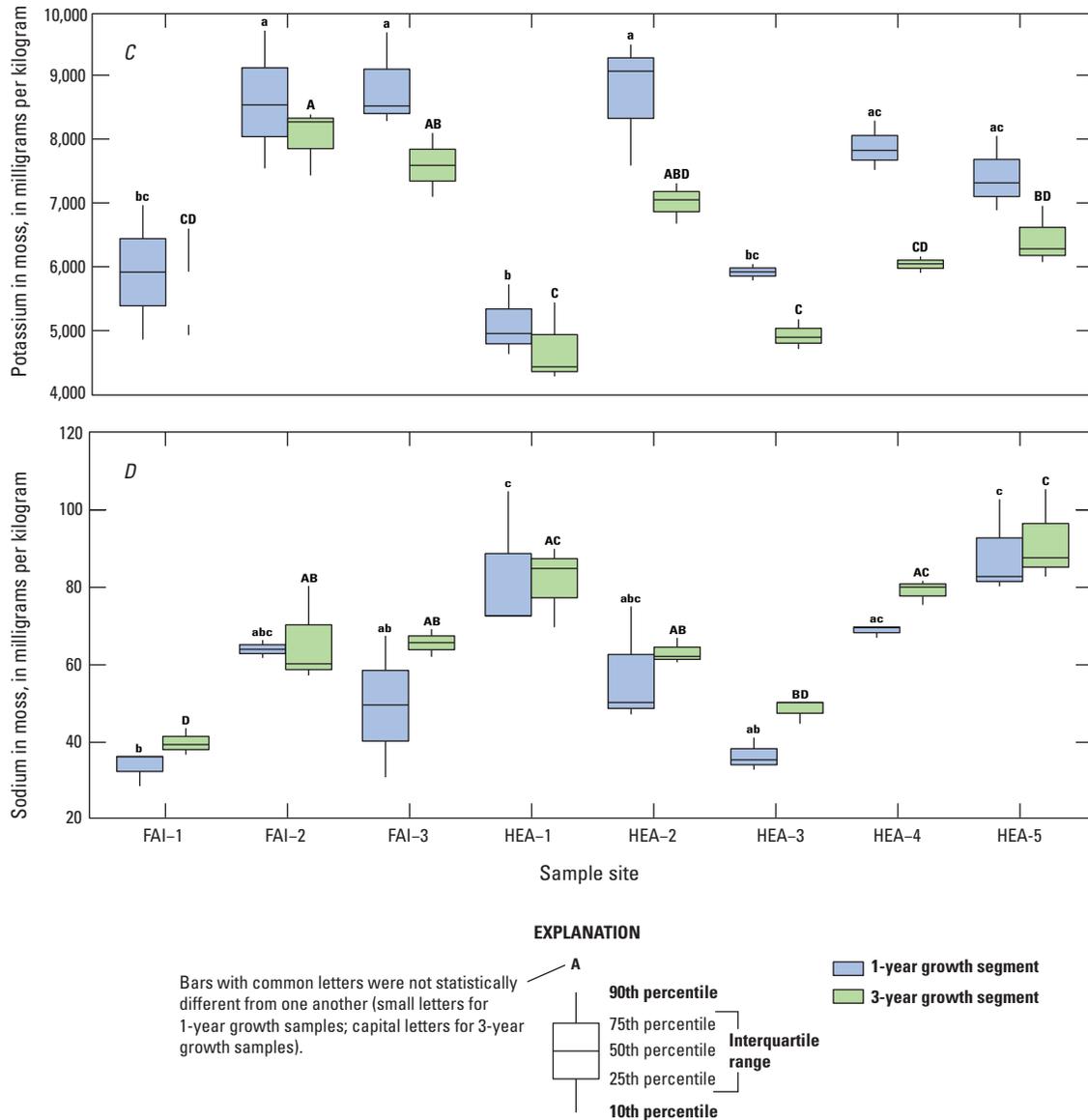


Figure 11. Comparison of calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) concentrations in 1-year and 3-year growth segments of *Hylocomium splendens* moss samples collected from eight sites of interior Alaska during the 2014 study.—Continued

Modeling Moss Concentrations from Depositional Loads

Spearman’s rank correlation analysis was done between moss tissue concentrations (1-year or 3-year) and (a) snowpack concentrations, (b) overwinter loads based on snowpack, (c) spring-summer loads based on IECs, or (d) annual loads based on snowpack plus IECs. Preliminary regression models were then plotted between moss concentrations and

depositional parameters for those correlations that were significant ($p < 0.05$).

Nitrogen, phosphorous, and sulfur in moss compared to substances measured in snow or IECs.—Spearman’s rank correlations between concentrations of Tot-N, NO₃-N, Tot-P, and Tot-S in moss, with loads of NH₄⁺, NO₃⁻, phosphate (PO₄³⁻; measured as P), or SO₄²⁻ ions based on measurements in snow, IEC (excluding P), or the summation of snow plus IEC are summarized in appendix table 3–4 (available for download at

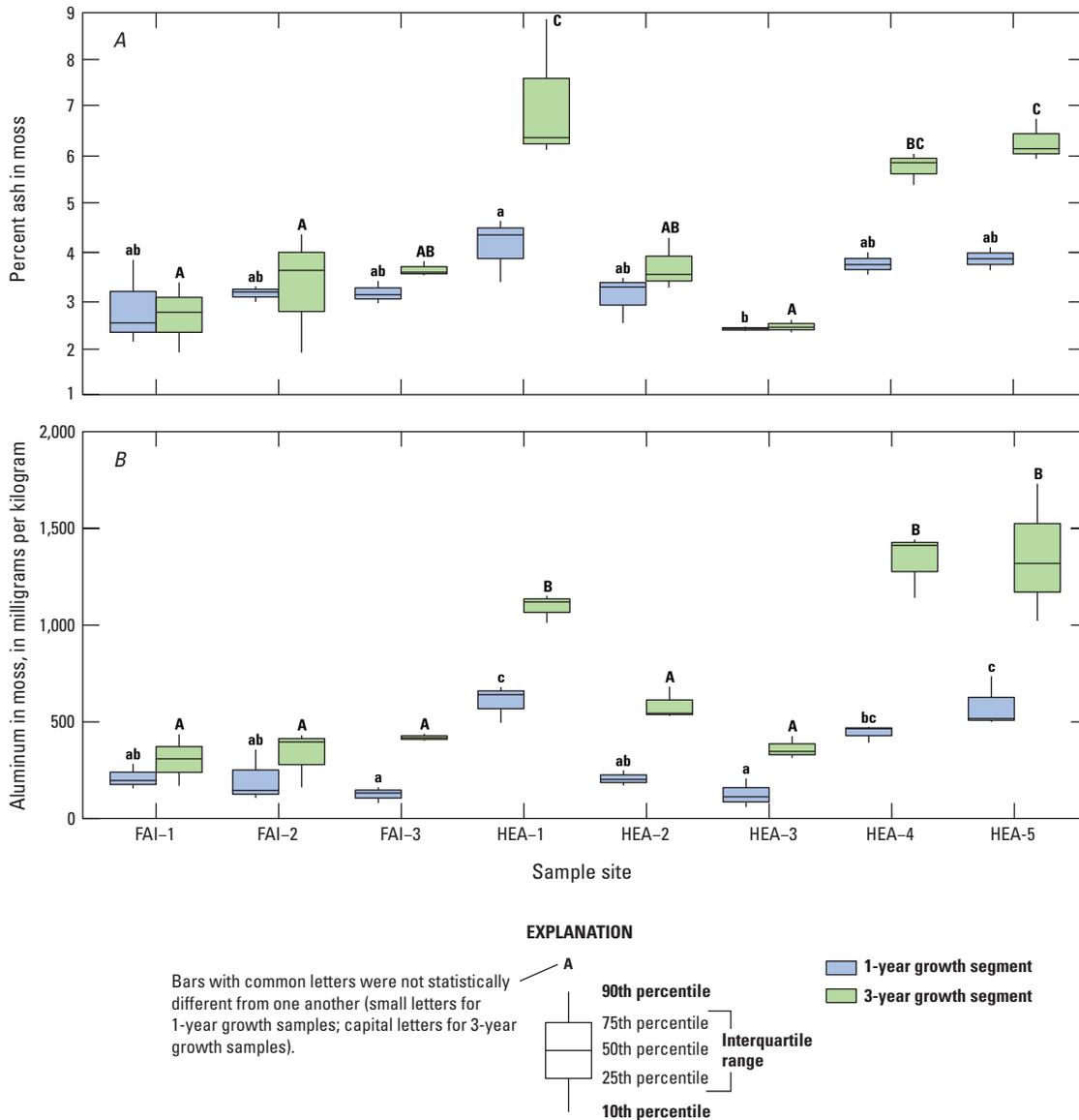


Figure 12. Comparison of percent ash and concentrations of aluminum, (Al), Iron (Fe), and manganese (Mn) in 1-year and 3-year growth segments of *Hylocomium splendens* moss samples collected from eight sites of interior Alaska during the 2014 study.

<http://dx.doi.org/10.3133/sir20165096>). The Tot-N and Tot-P concentrations in moss produced some unexpected results; for example, Tot-N and Tot-P concentrations in moss were strongly positively correlated with the concentrations of NO_3^- or P in snow (as might be predicted); however, conversely, those elements were often strongly negatively correlated with warm season NO_3^- loads estimated from the IECs (figs. 15 and 16). Those correspondences were driven mostly by data from the two sites farthest from urban locales (FAI-1 and HEA-3), which exhibited the lowest concentrations of N

and P in moss and NO_3^- in snow but among the greatest NO_3^- loads based on IECs (P or PO_4^{3-} was not measurable in IEC extracts); consequently, data from additional site locations would be needed to confirm these seemingly unusual results. Notably, the differences between sites for NO_3^- concentrations in snow were small in comparison to the differences based on IECs, and the positive relations between N in moss and NO_3^- in snow were stronger for 1-year growth segments than for 3-year growth segments. The possibility that variation in N or P concentrations in moss might have been associated with

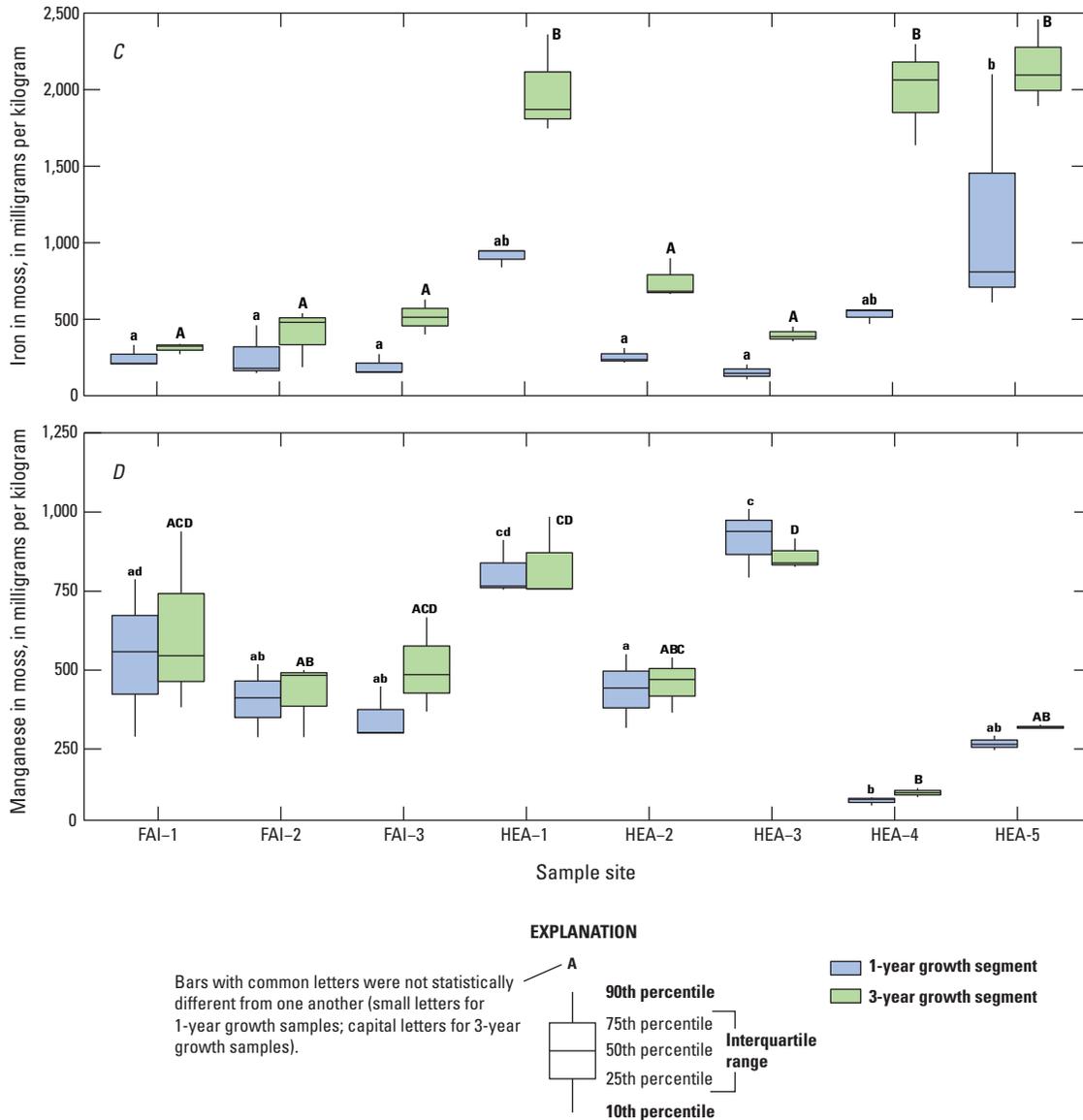


Figure 12. Comparison of percent ash and concentrations of aluminum, (Al), Iron (Fe), and manganese (Mn) in 1-year and 3-year growth segments of *Hylocomium splendens* moss samples collected from eight sites of interior Alaska during the 2014 study.—Continued

variation in ash content; that is, greater ash content might have effectively diluted the measured N or P content of the sample. Spearman’s rank correlations, however, do not support that notion as relations between moss Tot–N and ash content were weakly positive, and there was no correlation between Tot–P in moss and ash content.

The substantial rank correlations ($p < 0.10$) between Tot–P, Tot–N, and Tot–S in moss and major cations (Ca, K, and Mg) in snowpack or IECs are summarized in appendix table 3–5 (available for download at <http://dx.doi.org/10.3133/sir20165096>).

Notably, K could not be measured in IEC extracts because a 1 M solution of KCl was used as an extractant. Moss concentrations of each of these three elements were positively correlated with concentrations of one or more of the major cations in snow, loads derived from IECs (assumed as deposition during spring and summer), or both. The Tot–P in moss was most strongly correlated with K concentrations in snowpack and, to a lesser degree, Mg loads based on IECs. The Tot–N in moss was correlated with Ca and Mg in either snow or IECs and K in snow (relation of K also with spring

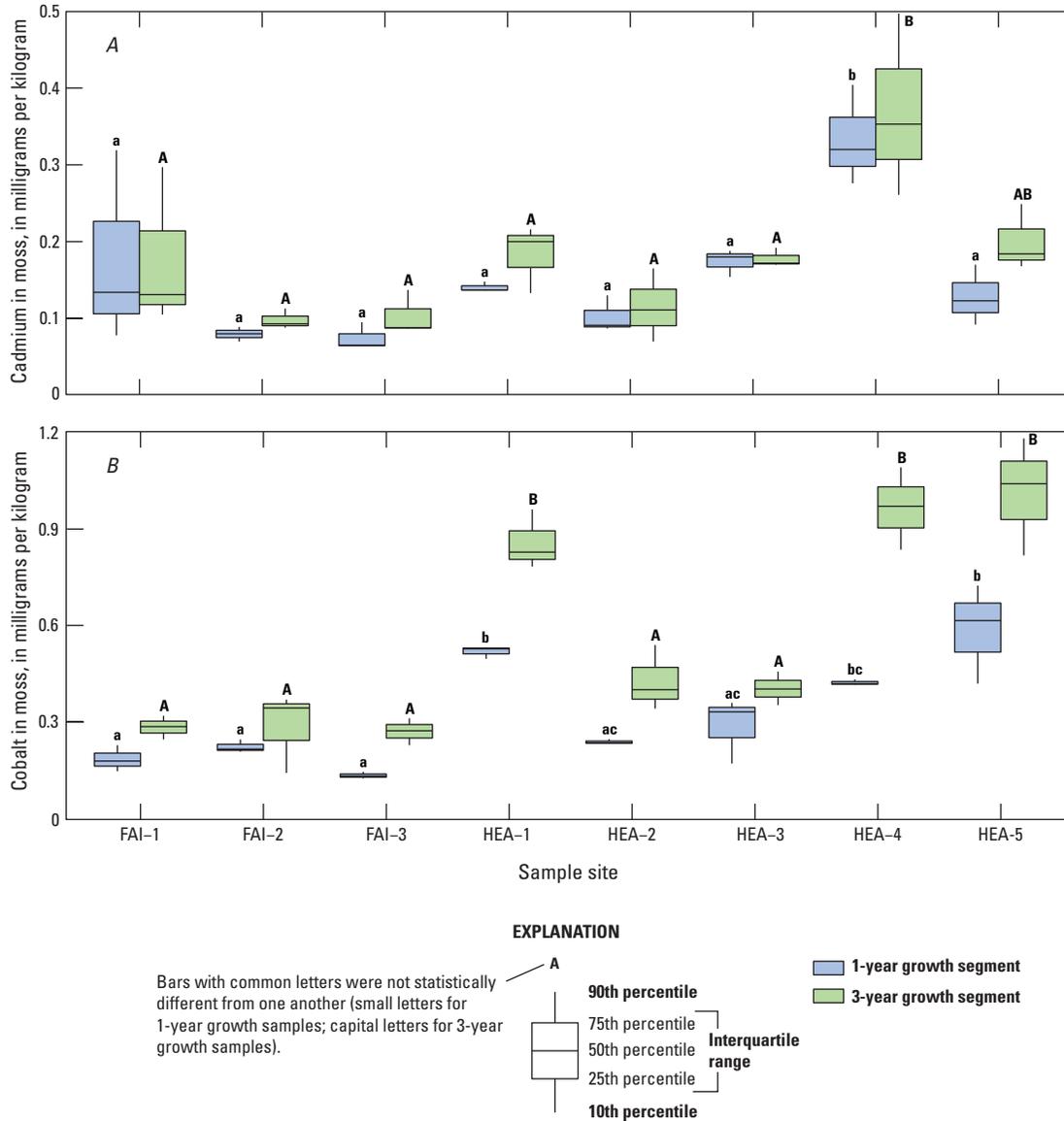


Figure 13. Comparison of cadmium (Cd), cobalt (Co), chromium (Cr), and copper (Cu) concentrations in 1-year and 3-year growth segments of *Hylocomium splendens* moss samples collected from eight sites of interior Alaska during the 2014 study.

summer deposition might be assumed), whereas Tot-S was correlated with Ca and Mg, in either snow or IECs, but not K. Correlations for N and S were driven mostly by the two sites farthest from urban locales (FAI-1 and HEA-3), which exhibited the lowest concentrations of N and S in moss and, correspondingly, the lowest loads of Ca and Mg (based on snowpack plus IECs). Perhaps such relations indirectly reflect use of Ca salts (which often contain considerable amounts of Mg) for ice and dust control on roads in urban areas, which

somehow affected uptake of N compounds by the moss. The Tot-N in moss was not correlated with deposition of NH_4^+ , but oddly, leachable NO_3^- in moss was (weakly) negatively correlated with NH_4^+ loads. The reason for the latter observation is puzzling.

Results for exploratory linear model calculations for N, P, and S are presented in appendix table 3-6 (available for download at <http://dx.doi.org/10.3133/sir20165096>). As indicate previously, N and P concentrations in moss were strongly

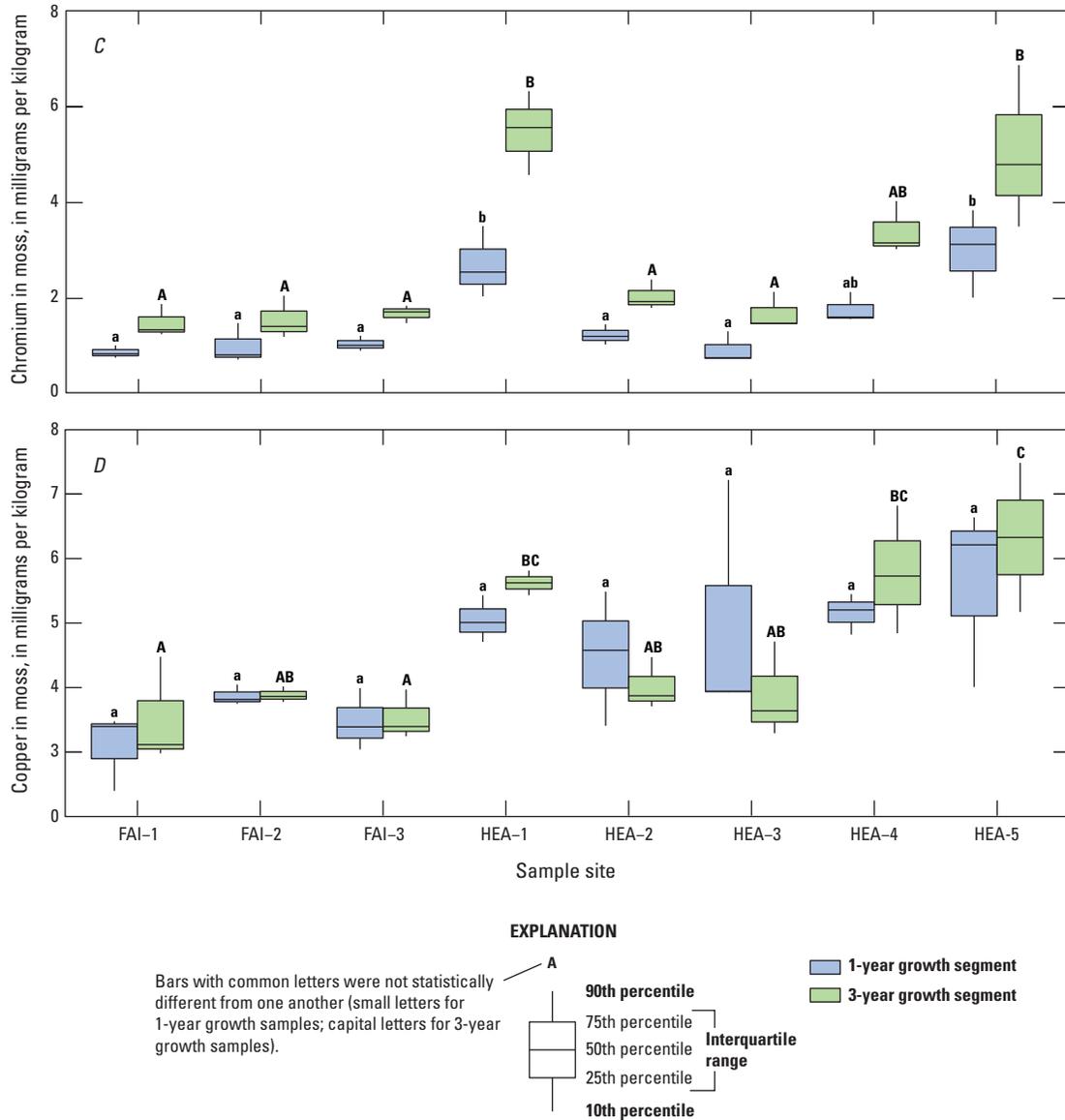


Figure 13. Comparison of cadmium (Cd), cobalt (Co), chromium (Cr), and copper (Cu) concentrations in 1-year and 3-year growth segments of *Hylocomium splendens* moss samples collected from eight sites of interior Alaska during the 2014 study.—Continued

(positively) correlated with the concentrations of NO_3^- or P in snowpack (as might be predicted); however, conversely, those elements were often strongly negatively correlated with warm season NO_3^- loads estimated from the IECs (figs. 15 and 16). Relations between Tot-S in moss tissues and SO_4^{2-} in either snowpack or IECs also were fairly strong; however, a nonlinear model provided the best fit to those data (fig. 17).

Metals and other elements.—Spearman’s rank correlations between moss concentrations and loads based on

snowpack, IECs, or the summation of snowpack plus IECs are in appendix table 3–7 (available for download at <http://dx.doi.org/10.3133/sir20165096>). For annual loads based on snow plus IEC measurements, the following elements were significantly correlated ($p < 0.05$) with moss tissue concentrations (in order of increasing p values; moss growth segment in parentheses): Fe (1 year), Cr (1 year), Co (1 and 3 year), Zn (3 year), Cr (3 year), Al (1 and 3 year), Fe (3 year), and Ni (1 year); however, among those six metals, only the

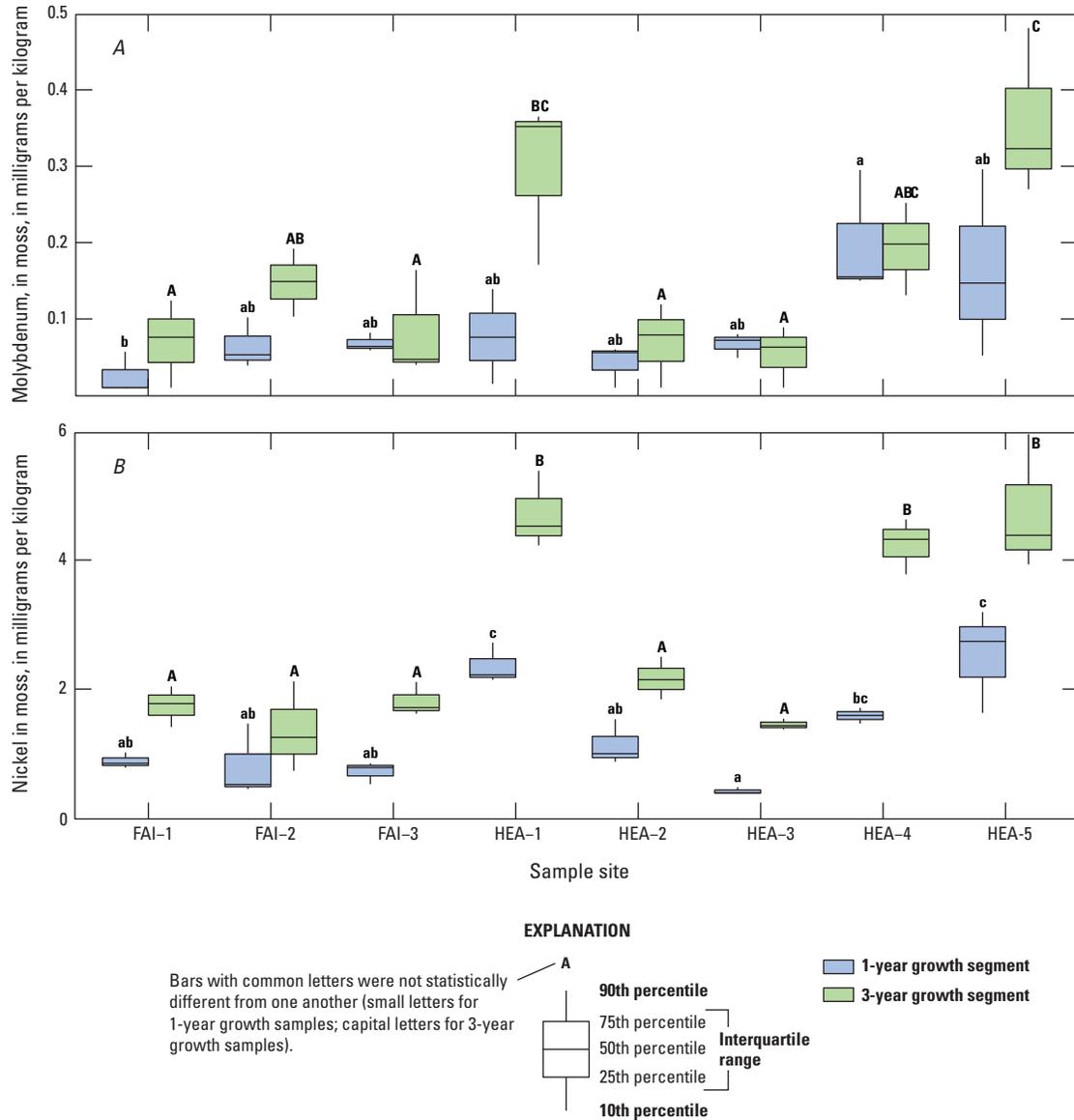


Figure 14. Comparison of molybdenum (Mo), nickel (Ni), lead (Pb), and zinc (Zn) concentrations in 1-year and 3-year growth segments of *Hylocomium splendens* moss samples collected from eight sites of interior Alaska during the 2014 study.

concentrations of Co, Cr, and Fe were consistently correlated with snowpack and IEC loads. Concentrations of Cu, Pb, and Zn in moss tissue were significantly correlated with the same metal in snowpack (as a concentration or as a load), but none were correlated with load based on IECs. The relation for Zn was influenced greatly by elevated Zn concentrations in snowpack samples obtained from one site (HEA-1), the samples from which were probably elevated because of leaching of Zn from the metal roof of the motel near the sampling

site. Yet, for Zn at least, accumulation by mosses from the snow melt was evidently an important route of uptake at that site. Patterns for Pb in moss tissues were enigmatic when compared separately to snowpack or IECs. Moss Pb concentrations (1 year or 3 year) were always negatively correlated with Pb in snowpack (as a load or a concentration) but always positively (albeit weakly) correlated with loads based on IECs (spring through fall). Perhaps these trends were artificially biased because of low Pb concentrations and relatively small

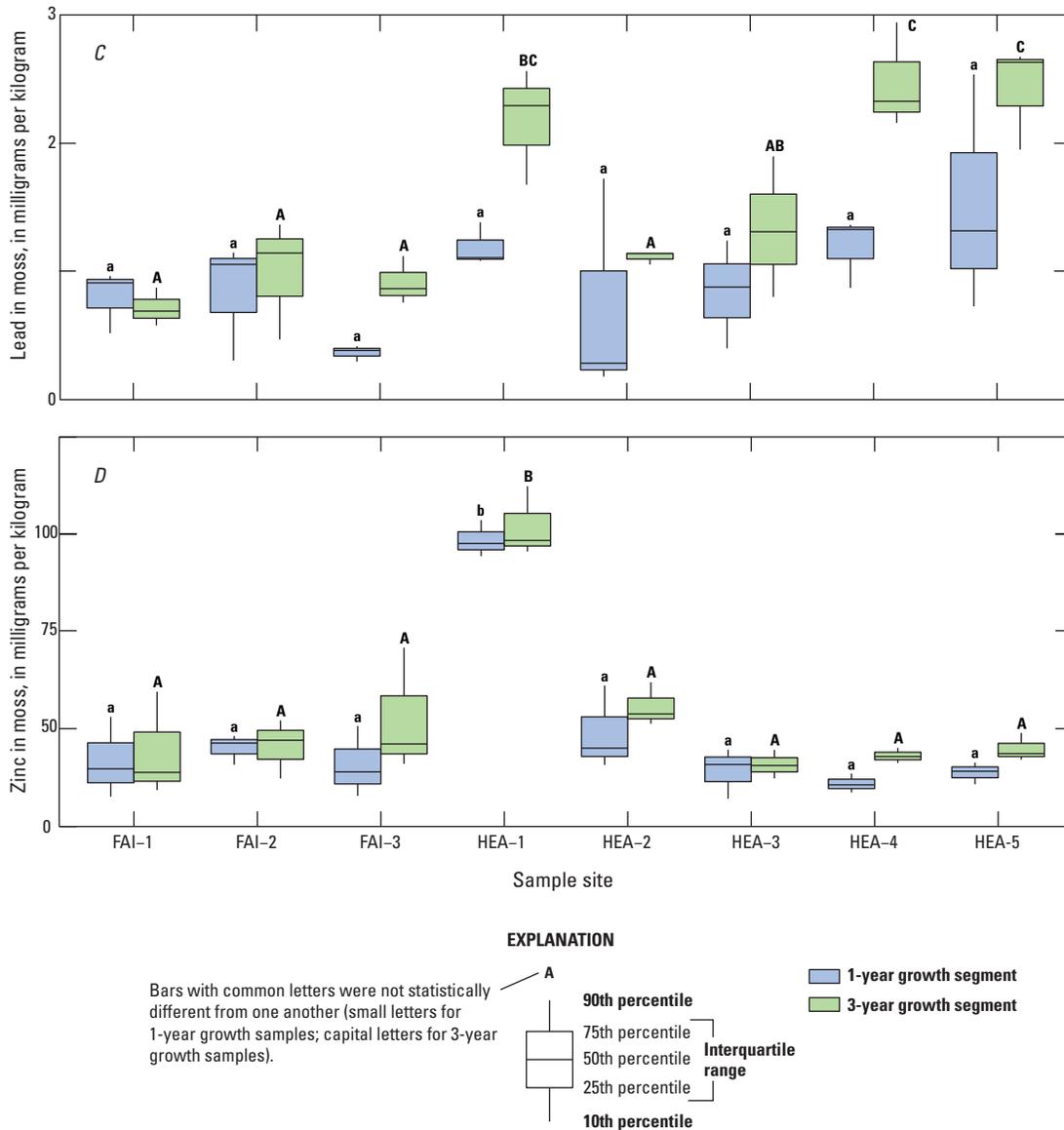


Figure 14. Comparison of molybdenum (Mo), nickel (Ni), lead (Pb), and zinc (Zn) concentrations in 1-year and 3-year growth segments of *Hylocomium splendens* moss samples collected from eight sites of interior Alaska during the 2014 study.—Continued

gradients across sites, but it also might reflect important seasonal differences for Pb deposition in this region. Considering primarily IEC results, moss tissue metal concentrations were most strongly (positively) correlated with depositional loads for Al, Co, Cr, Fe, and Ni. Those metal concentrations in moss were also strongly correlated with the ash content of the moss samples, indicating that dry deposition (airborne dust) was the major source of those substances.

Results for exploratory linear model calculations for metals in moss with depositional loads are presented in appendix table 3–8 (available for download at <http://dx.doi.org/10.3133/sir20165096>). Preliminary models indicated a highly linear uptake of Co, Cr, and Ni by *H. splendens* moss as compared to measures of deposition, and for those metals, the relations were substantial based on sampling of either snowpack or IECs; however, models based on snowpack were stronger when expressed in terms of the concentration rather than the

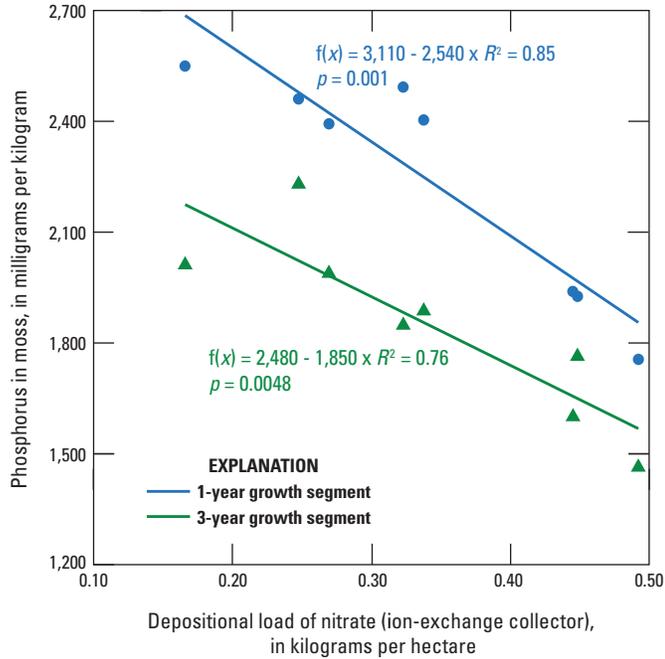


Figure 15. Linear relations (models) between concentrations of phosphorous in moss tissue (1- or 3-year growth segments) and nitrate loads based on ion-exchange collector measurements at eight sites in Alaska during 2014.

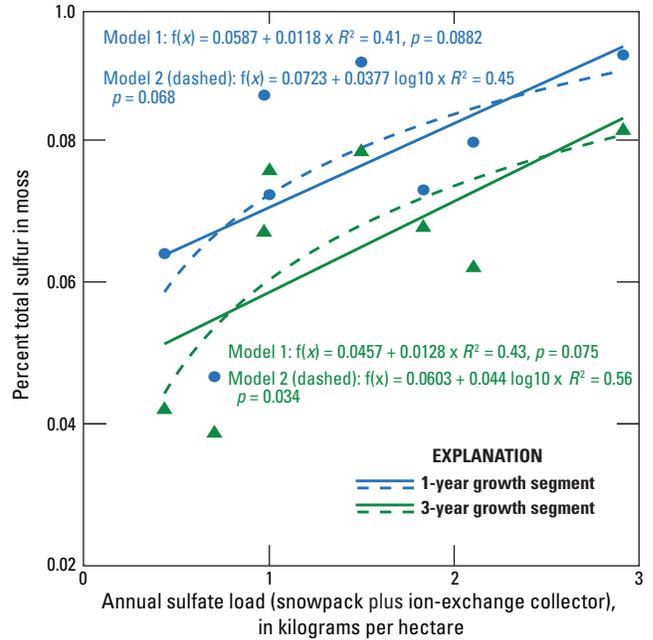


Figure 17. Linear and nonlinear relations (models) between concentrations of total sulfur in moss tissue (1- or 3-year growth segments) and annual sulfate loads based on snowpack plus ion-exchange collector measurements at eight sites in Alaska during 2014.

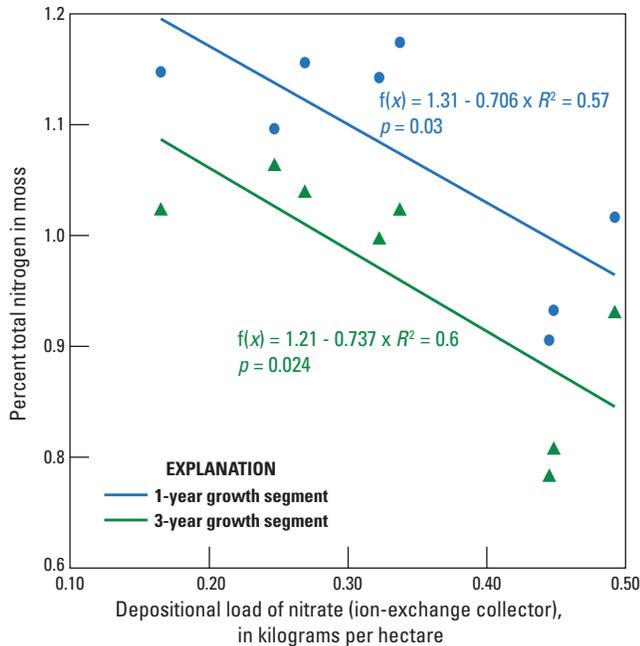


Figure 16. Linear relations (models) between concentrations of total nitrogen in moss tissue (1- or 3-year growth segments) and nitrate loads based on ion-exchange collector measurements at eight sites in Alaska during 2014.

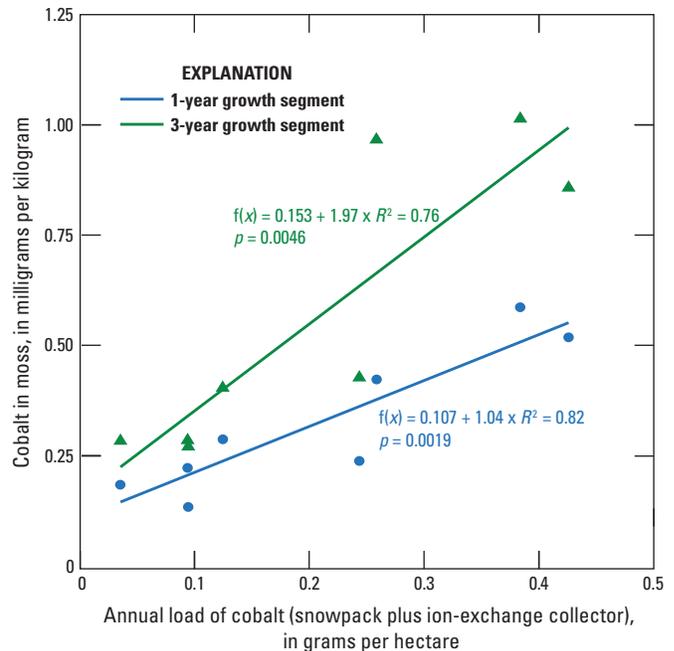


Figure 18. Linear relations (models) between concentrations of cobalt in moss tissue (1- or 3-year growth segments) and annual cobalt loads based on snowpack plus ion-exchange collector measurements at eight sites in Alaska during 2014.

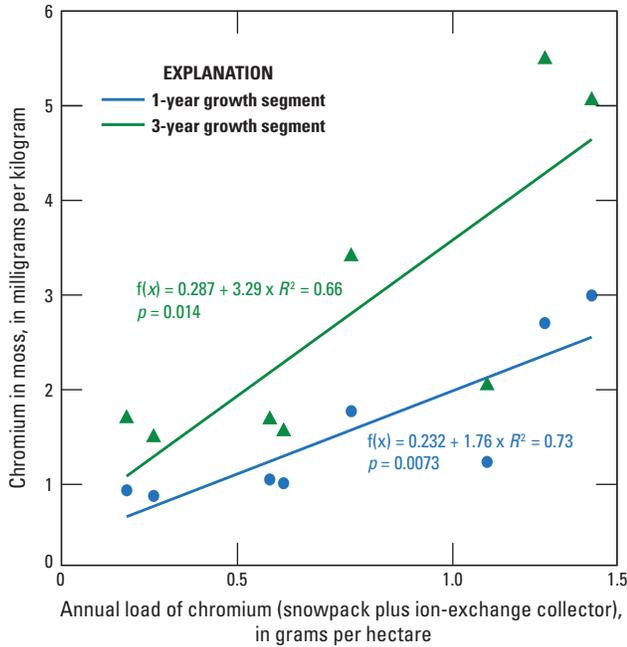


Figure 19. Linear relations (models) between concentrations of chromium in moss tissue (1- or 3-year growth segments) and annual chromium loads based on snowpack plus ion-exchange collector measurements at eight sites in Alaska during 2014.

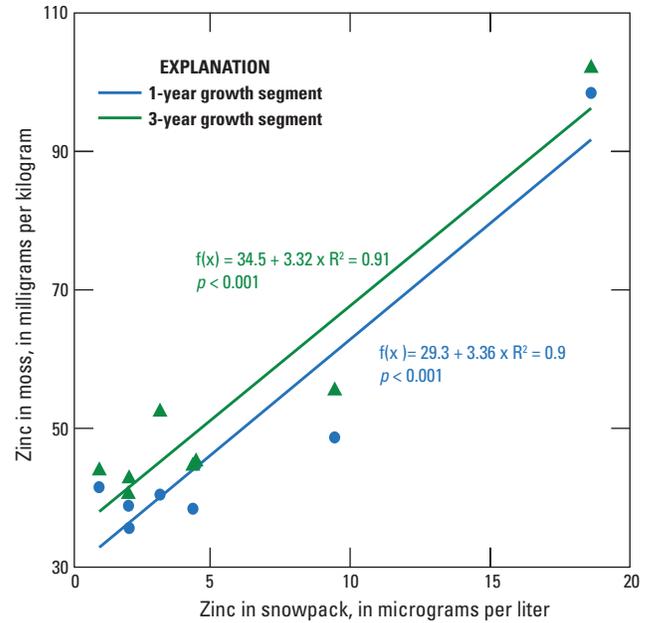


Figure 21. Linear relations (models) between concentrations of zinc in moss tissue (1- or 3-year growth segments) and annual zinc concentrations in snowpack for samples collected in 2014 at eight sites in Alaska.

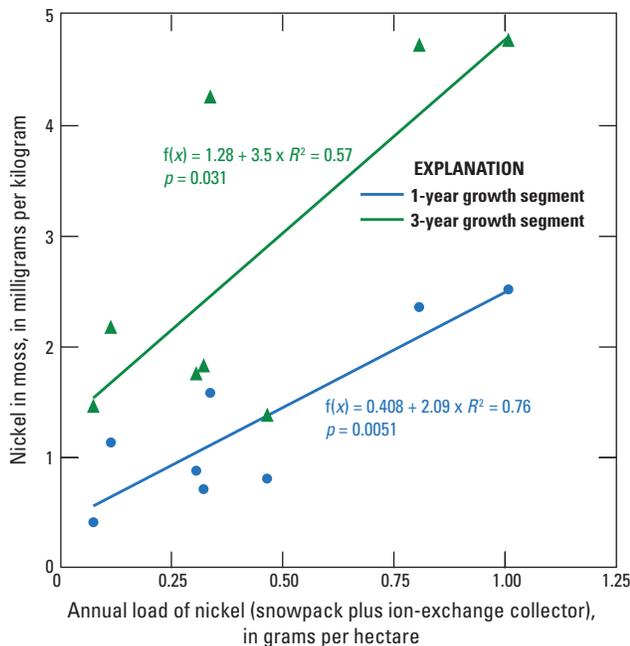


Figure 20. Linear relations (models) between concentrations of nickel in moss tissue (1- or 3-year growth segments) and annual nickel loads based on snowpack plus ion-exchange collector measurements at eight sites in Alaska during 2014.

load. There were substantial correlations between moss concentration and deposition for some of the other metals, including Al, Cd, Fe, and Zn; however, linear models for those were significant ($p < 0.05$) only when based on IECs (Al, Cd, and Fe) or in snowpack (Zn), but not both. Most of the successful models were about equally significant for either 1- or 3-year moss growth segments, and slopes of the models were similar for each of the segments (figs. 18, 19, and 20 for Co, Cr, and Ni, respectively; fig. 21 for Zn in snowpack).

Summary and Conclusions

Results from the 2014 study determined that concentrations of certain metals and sulfur in tissues of the splendid feather moss, *Hylocomium splendens*, that were collected from two different regions of interior Alaska reflected differences in presumptive deposition from local atmospheric sources as measured by ion-exchange collectors (IECs) and snowpack samples. Moss tissues collected from two sites farthest from urban locales had the lowest levels of total nitrogen and sulfur, and moss tissues collected from three of the urban sites had the greatest concentrations of many of the trace metals. Moss concentrations of aluminum, cobalt, chromium, iron, and nickel were strongly (positively) correlated with depositional loads of those metals. Most metal concentrations in moss were positively correlated with the ash content of the moss samples, indicating that dry deposition (airborne dust) was probably the

major source of those substances. Moss tissue zinc concentrations were strongly correlated with zinc concentrations in snow, but not with zinc loads based on IECs; however, that relation was influenced mostly by elevated zinc at a single site. There also was a positive correlation between total sulfur in moss and annual depositional load of sulfate ($p < 0.10$), and between total sulfur in moss and the ash content of moss, but there was no correlation between nitrogen or phosphorous in moss and ash content of moss. For some reason, nitrogen and phosphorous concentrations in moss were strongly positively correlated with the concentrations of nitrate or phosphorous in snow (as might be predicted); however, conversely, those elements were often strongly negatively correlated with warm season nitrate loads estimated from the IECs. The net result (based on snow plus IEC as a combined load), was that there was no correlation between total nitrogen in moss and the presumptive annual depositional loads of either ammonium or nitrate.

Exploratory models indicated a highly linear uptake of cobalt, chromium, and nickel by *Hylocomium splendens* moss as compared to measures of depositional loads; and for those metals the relations were statistically significant ($p < 0.05$) based on sampling of either snowpack or IECs. However, models based on snowpack were improved (smaller p values) when expressed in terms of the concentration rather than the load. There were positive correlations between moss concentration and deposition for other metals, including aluminum, cadmium, iron, and zinc; however, linear models for those were significant ($p < 0.05$) when based on IECs (aluminum, cadmium, and iron) or in snowpack (zinc), but not both. Evaluations of 1- or 3-year moss growth segments separately showed that for the successful models, the slopes and statistical significance were similar between the two segment types. Simple linear regressions between concentrations of substances in the 1-year segments (y variable) to that of the 3-year segments (x variable) produced slopes of less than 0.60 for percent ash and most of the trace metals, which presumably reflects greater accumulation of dust particles in the older (as nearer to the ground) growth segments. Interestingly, total nitrogen, sulfur, and phosphorous concentrations were consistently greater in the one-year growth segments of moss tissue, but the opposite pattern was observed for most of the trace metals. A relation between total sulfur in moss tissues and sulfate deposition in either snow or the IECs was evident as well, but a nonlinear model provided a better fit to those data.

The 2014 study provided useful preliminary models for some of the targeted substances; however, our ability to characterize relations between concentrations in moss and loadings for many of the metals was probably inhibited by relatively small gradients and the small number of test sites. Unfortunately for our study, the winter of 2013–14 in interior Alaska was unusually warm with several rainfall events so the snowpack was greatly reduced at many of our sites when we sampled the snow. Consequently, overwinter depositional loads were probably underestimated, especially at the sites in Healy, which might have reduced the magnitude of the load

differences between the more remote sites and the urban sites. That might also explain why moss models based on snow concentrations were often more successful than those based on snow loadings because actual loads measured from snowpack probably were inexact. Alternative methods for measuring over-winter deposition are being considered for future studies.

Despite the aforementioned limitations, these studies have established a foundational basis to support further studies that can improve our understanding of how mosses accumulate inorganic substances and ultimately how mosses might be used as biomonitors of atmospheric pollutants; moreover, the successful development and validation of the IECs accomplished during this research documents the utility of the methodology for use with future monitoring efforts in remote regions of Alaska and elsewhere.

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Appendixes 1-3

Appendix 1. Dual-Stage Ion-Exchange Collector Column Construction, Extraction, and Analysis

Appendix 1 is available for download as an Adobe Acrobat file at <http://dx.doi.org/10.3133/sir20165096>.

Figure 1–1. Photograph showing dual-stage ion-exchange collector components. Red arrow indicates place where sections are separated for extraction of cations or anions. Polypropylene mesh spacers are shown before they are rolled into cylindrical shape.

Figure 1–2. Photographs showing an ion-exchange collector assembly.

Figure 1–3. Photographs showing an ion-exchange collector funnel assembly.

Figure 1–4. Photographs showing cation extraction process.

Table 1–1. List of supplies to construct ion-exchange collectors.

Appendix 2. Methods of Analysis for Samples of Splendid Feather Moss (*Hylocomium splendens*) for Trace Metals, Sulfur, and Nitrogen

Appendix 2 is available for download as an Adobe Acrobat file at <http://dx.doi.org/10.3133/sir20165096>.

Table 2–1. Target determination limits for analysis of moss or lichen tissues by inductively coupled plasma atomic emission spectrophotometry.

Appendix 3. Correlation Tables in Microsoft Excel

Appendix tables 3–1 through 3–8 are available for download as Microsoft Excel files at <http://dx.doi.org/10.3133/sir20165096>.

Table 3–1. Results for two-factor analysis of variance (site and growth segment) for inorganic substances in moss.

Table 3–2. Relation between concentrations of inorganic substances in 1-year (as y variable) and 3-year (as x-variable) *Hylocomium splendens* moss growth segments (ordered by goodness of fit; R^2).

Table 3–3. Spearman's rank correlations between inorganic substances in *Hylocomium splendens* moss and moss ash content (ordered by p -value, smallest to largest).

Table 3–4. Spearman's rank correlations between nitrogen, phosphorous, and sulfur in moss and nitrogen or sulfur compounds in ion-exchange collectors or snowpack (ordered by p -value, smallest to largest).

Table 3–5. Spearman's rank correlations (p -values less than 0.05) between nitrogen, phosphorous, and sulfur in moss, and major cations in ion-exchange collectors or snowpack (arranged by *Hylocomium splendens* moss substance, then by p -value, smallest to largest).

Table 3–6. Linear models (p -values less than 0.10) between nitrogen, phosphorous, and sulfur in *Hylocomium splendens* moss and in ion-exchange collectors or snowpack (ordered by p -value, smallest to largest).

Table 3–7. Spearman's rank correlations (p -values less than 0.05) between elements in *Hylocomium splendens* moss and in ion-exchange collectors or snowpack (ordered alphabetically by element).

Table 3–8. Linear models having p -values less than 0.10 for trace metals in *Hylocomium splendens* moss and in ion exchange collectors or snowpack (ordered alphabetically by element).

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