



Considerations for Long-Term Monitoring of Airborne Contaminants and Ecological Effects in the Southeast Alaska Network

Natural Resource Report NPS/SEAN/NRR—2016/1238



ON THE COVER

Visible haze emissions from cruise ships trapped under a temperature inversion in Skagway, Alaska near the Klondike Gold Rush National Historical Park

Photograph by: Rick Graw, USFS

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Natural Resource Report NPS/SEAN/NRR—2016/1238

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Executive Summary

The National Park Service (NPS) Inventory and Monitoring (I&M) Program supports NPS units with basic natural resource information to assist in science-based stewardship activities. NPS units are grouped into 32 Inventory and Monitoring Networks by geographic proximity and similarity of ecological conditions. As one of the 32 Inventory and Monitoring Networks, the Southeast Alaska Network (SEAN) supports three NPS units: Glacier Bay National Park and Preserve (GLBA), Klondike Gold Rush National Historical Park (KLGO), and Sitka National Historical Park (SITK), encompassing nearly 3.3 million acres of parklands and approximately 4% of the total area managed by the NPS.

One focus of the NPS Inventory and Monitoring Program is the long-term monitoring of a select suite of environmental parameters or resources, termed Vital Signs, as indicators of resource condition or Park health. Within each Network, a suite of Vital Signs has been selected to suit the unique information needs of Network Parks. While air quality is fairly pristine in Southeast Alaska's National Parks, localized areas of air pollution and long-range atmospheric transport of pollutants have the potential to affect fragile ecosystems. In response, Airborne Contaminants were selected as one of 12 core Vital Signs for monitoring the condition of SEAN Parks (Note: "airborne contaminants" has been defined to include all potential airborne or atmospheric pollutants, including airborne toxics such as mercury and criteria pollutants such as nitrogen or sulfur compounds). By establishing baseline conditions and then monitoring a group of pertinent measures or indicators into the future, broad shifts in the extent and magnitude of primary airborne contaminants of concern can be detected and used to inform the stewardship of park resources.

The first step in defining baseline conditions in the SEAN was implemented by Schirokauer et al. (2014) who completed an inventory of ambient air quality, wet deposition loads, lichen tissue contaminant concentrations, and lichen community composition during the summers of 2008 and 2009. Their report established baseline conditions, developed standard operating procedures (SOPs) for field methods, and presented several recommendations for further data analysis. This report builds upon this initial work by advancing several of the recommended analyses to inform final monitoring design choices.

This report is organized into five chapters which summarize prior airborne contaminant investigations conducted in the SEAN park units (Chapter 1), incorporate new data analyses to inform future sampling designs (Chapters 2-4), and offer recommendations for a long-term monitoring program (Chapter 5), each of which we briefly summarize below.

Chapter 1: We introduce background information and provide a brief summary of prior work to set the stage for our analyses.

Chapter 2: We summarized ten years (2004-2013) of wet deposition data from the Juneau National Atmospheric Deposition Network (NADP) site (AK02), as recommended by Schirokauer et al. (2014), to assess seasonal variation in deposition of airborne contaminants, including primary combustion products. We then validate the assumption that enhanced deposition of nitrogen and

sulfur compounds are associated with the summer tourist season, which is an important consideration for the development of a final sampling design for contaminant deposition.

Chapter 3: We summarize mercury deposition from March 2010 to May 2013 from a former NADP Mercury Deposition Network (MDN) site located at Bartlett Cove in GLBA and compare results with three other stations in Alaska and six sites in the Pacific Northwest (NW) to better understand variation among sites and assess the value of continued station operation. Bartlett Cove typically recorded the second lowest mercury deposition and the overall lowest precipitation-weighted mean mercury concentration out of the other nine stations. On the weekly time scale, Bartlett Cove had the second lowest mercury concentration out of the dataset. We also illustrate the concept of “mercury washout” and relationship of rainfall depth with mercury concentration. With our limited dataset, it was not feasible to directly assess the degree of correlation among stations on an ecologically-relevant time scale (e.g., seasonal or annual).

Chapter 4: We compare WRF/Chem (Weather Research and Forecasting model, coupled with Chemistry; Grell et al. 2005) simulations of cruise ship emissions (Mölders et al. 2014) during the 2008 and 2009 tourist seasons (May 15-September 15) to ambient air quality measurements from the three SEAN parks. This estimated the contribution of cruise ship emissions towards ambient NO₂, NO_x, HNO₃, and SO₂ concentrations to help inform monitoring program design. Agreement among simulated cruise ship emission contributions and ambient concentrations of NO₂, and SO₂ were highest (up to $r_s=0.73$) at sites in KLGO (particularly Dyea and Chilkoot Sainly Hill), suggesting that cruise ships may be an important emission source to consider when developing a final sampling design for long-term airborne contaminants monitoring in this Park. GLBA sites also showed some agreement ($r_s\approx 0.50$) among simulated cruise ship emissions and observed airborne contaminant concentrations, with little to no agreement in SITK ($r_s<0.29$), suggesting that cruise ships may be a less important emission source to consider when developing sampling designs for these parks.

Chapter 5: We present recommendations for a scalable monitoring design that includes 1) an efficient surveillance program using lichen tissue chemistry, 2) direct assessment of wet deposition and ambient air quality where potential problems are identified, and 3) continuous monitoring of mercury deposition. We also identify opportunities to expand the scope of the program to include adjacent lands. Key partnership opportunities include monitoring air quality and contaminant deposition adjacent to the Skagway harbor with the Municipality of Skagway and participation in ongoing biomonitoring of local and regional patterns of air quality using lichen communities with the U.S. Forest Service.

Appendix A: As a reference, we include pertinent research and background information on the airborne contaminants that are currently of concern in the SEAN.

Appendix B: Additional graphical results from comparisons among modeled and observed ambient atmospheric contaminants concentrations in Chapter 4 are presented.

Appendix C: Detailed cost estimates for our long-term monitoring design are provided.

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Acronyms and Abbreviations

Acronym or Abbreviation	Description
ADEC	Alaska Department of Environmental Conservation
AIS	Automated Information System
AQRVs	Air Quality Related Values
CAL	Central Analytical Laboratory
DDTs	Dichlorodiphenyl Polychloro-ethanes and –ethylenes
DENA	Denali National Park and Preserve
FIA	Forest Inventory and Analysis
GAAT	Gates of the Arctic National Park and Preserve
GLBA	Glacier Bay National Park and Preserve
HAL	Mercury Analytical Laboratory
I&M	Inventory and Monitoring Program
IER	Ion Exchange Resin tube sampler
KLGO	Klondike Gold Rush National Historical Park
MDN	Mercury Deposition Network
NAAQS	National Ambient Air Quality Standard
NADP	National Atmospheric Deposition Network
NOAA	National Oceanic and Atmospheric Administration
NOAT	Noatak National Preserve
NPS	National Park Service
NTN	National Trends Network
NW	Northwest
OD	Open Deposition IER sampler
PCBs	Polychlorinated Biphenyls
POI	Period of Interest
POP	Persistent Organic Pollutant
PWM	Precipitation-Weighted Mean concentration
QA/QC	Quality Assurance/Quality Control
SEAN	Southeast Alaska Network
SITK	Sitka National Historical Park
SOC	Semi-volatile Organic Compounds
SOP	Standard Operating Procedure
TD	Throughfall deposition IER sampler
TNF	Tongass National Forest
UAS	University of Alaska Southeast
US EPA	U.S. Environmental Protection Agency
USFS	U.S. Forest Service
USGS	U.S. Geological Survey

Acronym or Abbreviation	Description
WACAP	Western Airborne Contaminants Assessment Project
WRF/Chem	Weather Research and Forecasting Model with Chemistry
H ⁺	Rainfall pH ion
Cl ⁻	Chloride anion
H ₂ SO ₄	Sulfuric acid
H ₂ O	Water
Hg	Mercury
HNO ₃	Nitric acid
K ⁺	Potassium cation
Mg ²⁺	Magnesium cation
MeHg	Methylmercury
Na ⁺	Sodium cation
NH ₃	Ammonia gas
NH ₄ ⁺	Ammonium ion
NO	Nitric oxide, nitrogen monoxide
NO ₂	Nitrogen dioxide
NO ₃ ⁻	Nitrate ion
NO _x	Nitrogen oxides (NO+NO ₂)
PM _{2.5} or PM ₁₀	Particulate Matter with diameter of 2.5µm or 10µm
SO ₂	Sulfur dioxide
SO ₄ ²⁻	Sulfate ion

Chapter 1 – Background and Setting

Introduction

Long-term monitoring of natural resources is fundamental in fulfilling the National Park Service (NPS) mandate to leave park resources “unimpaired for the enjoyment of future generations.” The NPS Inventory and Monitoring (I&M) Program was created to institutionalize a response to this basic need by supporting the 270 Parks containing significant natural resources with basic inventory and monitoring information for use in science-based stewardship activities. One key facet of this program is the Vital Signs monitoring program, whereby long-term monitoring of a select suite of ecological indicators is used to advance understanding of resource condition and ecosystem function in support of science-based stewardship.

As one of the 32 networks of the NPS I&M Program, the Southeast Alaska Network (SEAN) supports three NPS units: Glacier Bay National Park and Preserve (GLBA), Klondike Gold Rush National Historical Park (KLGO), and Sitka National Historical Park (SITK), encompassing nearly 3.3 million acres (8.2 million hectares) of parklands in Southeast Alaska (Figure 1) and approximately 4% of the total area managed by the NPS. The landscape of Southeast Alaska is generally remote and oftentimes considered pristine. However, even within this largely undeveloped landscape, long-range transport and subsequent deposition of contaminants, as well as several local emission sources, remain concerns for Park natural resource managers. In response, three contaminant-related Vital Signs (Marine Contaminants, Freshwater Contaminants, and Airborne Contaminants) were identified during development of the SEAN Vital Signs Monitoring Plan (Moynahan et al. 2008). We define “airborne contaminants” to include the suite of potential airborne pollutants, both airborne toxics such as mercury as well as criteria pollutants such as nitrogen and sulfur compounds. While it is a goal to integrate the three Vital Sign monitoring efforts to the extent practical in the future, this report contributes most directly to the development of a final design for monitoring airborne contaminants and associated environmental effects. In this chapter, we describe the setting of the SEAN, primary air quality and airborne contaminant concerns within this setting, and summarize related research and monitoring activities to date.

The Southeast Alaska Network (SEAN) Parks

GLBA is one of the largest and most pristine glacial fjord wilderness areas in the Northern Hemisphere. The protected marine area comprises a notable portion of the 24.3 million-acre Kluane/Wrangell-St. Elias/Glacier Bay/Tatshenshini-Alsek World Heritage Site. More than 2.7 million acres of GLBA are federally designated wilderness areas. GLBA was first appointed as a National Monument in 1925, which protected the extensive ice fields, alpine, and tidewater glaciers. The park is known to have over 30 species of land mammals, over 240 species of birds, as well as a wide array of marine life. It also encompasses the largest length of coastline in NPS jurisdiction at over 1,180 miles.

Established in 1976, KLGO is comprised of three separate units of land totaling 13,191 acres (5,338 hectares). It is positioned at the northern terminus of Lynn Canal and surrounded by steep, glaciated mountains. KLGO was set aside specifically to maintain cultural landscapes that also include

important ecological features, such as: a high diversity of vegetation, intense variations in land-use type, hundreds of species of migratory and resident waterfowl, as well as a considerable population of harbor seals, mountain goats, black bear, and moose. The park setting exemplifies the linkage between interior and coastal Alaskan ecosystems.

SITK was designated a federal parkland in 1890 and contains a total of 113 acres (46 hectares) of coastal lowlands and riparian forest. The park preserves a battleground between invading Russian traders, the site of the Kiks.ádi fort *Shiskinoow* (the “village”), and the Russian Memorial associated with the 1804 Battle of Sitka, as well as several Tlingit and Haida totem poles. The convergence of the Indian River and coastal rainforest provide a biologically rich environment for Sitka spruce and western hemlock trees, in addition to over 160 vascular and nonvascular plants. A central feature of the Park is the Indian River, which harbors substantial runs of Pacific salmon.

Airborne Contaminant Concerns

Although Southeast Alaska has relatively pristine air quality due to low population densities and limited sources of anthropogenic emissions (Dillman et al. 2007), small levels of pollution have the ability to affect visibility, sensitive ecosystems, and visitors’ experience in the region’s three National Parks (Lane 2013; Malm 1999). NPS managers value the unspoiled nature of the region, aiming to preserve the natural and historical scenery, while also keeping it open for science, discovery, and enjoyment (NPS 2009). Both the long-range transport of atmospheric contaminants from Asia, and the assimilation of contaminants from local sources have the potential to adversely affect the ecosystems of Southeast Alaska’s National Parks.

Since coastal Alaska is the first land that Asian air masses encounter after crossing the Pacific Ocean, orographically enhanced precipitation over the Coastal Range may deposit significant loads of latent contaminants originating from Asia and international shipping lanes. Of particular concern are persistent pollutants, such as mercury, that have the potential for biomagnification after entering the food web. Emissions of such pollutants are expected to increase with the rapid industrialization of Asia and associated combustion of fossil fuels.

The most prevalent sources of air pollution in Southeast Alaska are linked to vehicular traffic, mining operations, incinerators, winter fuel burning (including wood and/or oil), and marine traffic emissions (i.e. cruise-ship, ferry, and fishing vessel emissions). While prevailing winds off the Pacific Ocean tend to moderate air quality, air stagnation associated with temperature inversions can concentrate air pollution from local sources and result in visible haze, causing the captured polluted air to undergo photolytic chemical reactions.

Class I is the highest level of protection designated by the Clean Air Act. There are no designated Class I airsheds in the SEAN, however all SEAN parks are still protected under somewhat less stringent protection as Class II airsheds. Currently, ship emissions are only modestly regulated (Eyring et al. 2005), but are expected to decrease significantly by 2016 (EPA 2010a, Mölders et al. 2013) when new low-sulfur fuel regulations are enacted. In 2010, the International Maritime Organization (IMO) declared all waters up to 200 miles off North America’s coastlines Emission

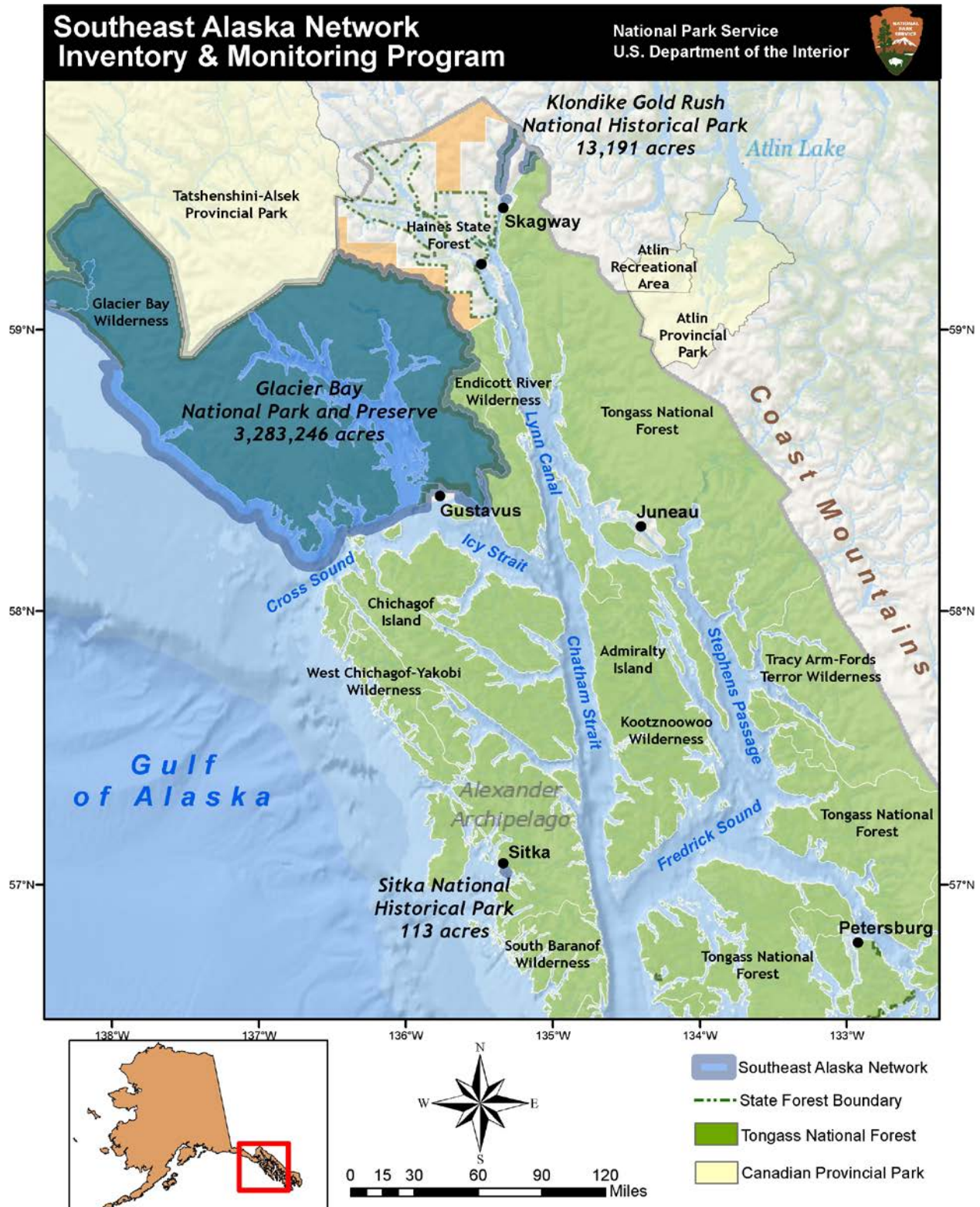


Figure 1. The Alexander Archipelago with the Southeast Alaska Network (SEAN) Parks and major landmarks. The Canadian border is delineated with the solid gray line.

Control Areas (ECAs). Large vessels will be required to reduce the sulfur content of fuel to 0.1% of 1000 ppm and lower NO_x emissions by 80%.

Sullivan et al. (2011a, b) has developed rankings of I&M Networks by degree of pollutant exposure, ecosystem protection, and overall risk for atmospheric nitrogen enrichment and acid deposition. The SEAN ranks in the lowest quintile among all nationwide I&M Networks for nitrogen enrichment and sulfur acid deposition *Pollutant Exposure* since emission sources are generally very limited (Table 1). Most of the vegetation in SEAN parkland, with lichens in particular, is expected to be moderate to highly sensitive with regards to both nitrogen enrichment and acid deposition (Dillman et al. 2007). A large percentage of the SEAN is designated as wilderness or protected land, earning it a moderate to very high rating for *Park Protection*.

Table 1. Relative rankings of the SEAN I&M Network Parks¹ regarding pollutant exposure, ecosystem sensitivity, park protection, and overall summary of risk for atmospheric nitrogen enrichment and acid deposition. Adapted from Sullivan et al. (2011a, b).

SEAN I&M Parks ^B	Pollutant Exposure Ranking ¹		Ecosystem Sensitivity Ranking ¹		Park Protection Ranking ^A		Summary Risk Ranking ^A	
	Nitrogen enrich.	Acid dep.	Nitrogen enrich.	Acid dep.	Nitrogen enrich.	Acid dep.	Nitrogen enrich.	Acid dep.
<i>Glacier Bay (GLBA)</i>	Very Low	Very Low	Low	High	Very High	Very High	Low	Moderate
Klondike Gold Rush (KLGO)	Very Low	Very Low	High	High	Moderate	Moderate	Very Low	Moderate
Sitka (SITK)	Very Low	Very Low	Moderate	Low	Moderate	Moderate	Very Low	Low

^A Relative park rankings are designated according to quintile ranking, among all I&M Parks, from the lowest quintile (very low risk) to the highest quintile (very high risk).

^B Park name is printed in italic for parks larger than 100 square miles.

Glacier Bay National Park and Preserve

The primary sources of local anthropogenic emissions include watercraft inside Glacier Bay, as well as various activities such as diesel power generation, vehicle use, and wood heating in the developed portion of the Park near Bartlett Cove and the nearby town of Gustavus (pop. 429). During the summer months, up to two cruise ships per day navigate past Bartlett Cove en route to glacier viewing opportunities at the head of Glacier Bay. The NPS has set a restriction of two daily cruise-ship entries, with a seasonal cap of 153 plus a shoulder season quota of 92, to limit environmental impacts imposed by large vessels, while also sustaining a considerable visitor volume. The quota is revisited each year, but has not been increased since 2007.

There have been growing concerns and official complaints from the public over cruise ships' effects on air quality and visibility in Glacier Bay (ADEC 2009). In response to these complaints, cameras were installed to monitor the frequency of haze from cruise ship emissions during the summer of 2004. Ships were observed in the camera view during 97 of the 154 days during the monitoring season, with 18% of the observations having visible vessel exhaust (ARS 2005).

Temperature inversions frequently develop in GLBA during high-pressure weather systems. These synoptic and mesoscale weather patterns influence the duration and severity of particulate matter and haze accumulations under temperature inversions in GLBA (Pirhalla et al. 2014). Inversions typically last an average of 9 hours, but have been shown to exist for several days under calm weather conditions. While cruise ship emissions can affect visibility and contaminant concentrations for a period of hours to days until fresh air becomes recirculated, Glacier Bay otherwise has pristine air quality.

Klondike Gold Rush National Historical Park

Cruise ship emissions commonly result in noticeable haze and odors throughout downtown Skagway and the KLGO-Skagway Historic District (Geiser et al. 2010b). During calm days with stable conditions in the atmospheric boundary layer (ABL), temperature inversions trap exhaust fumes from as many as five cruise ships simultaneously in port. Unlike GLBA, KLGO has limited jurisdiction in mitigating cruise ship emissions since the docks are outside of park boundaries. Approximately 1,100 pounds per hour of nitrogen oxides (NO_x) and 800 pounds per hour of sulfur dioxide (SO₂) are released from ship emissions in Skagway during busy periods, which is nearly 5 to 10 times greater than seen in SITK and GLBA (Graw et al. 2010). Other local emission sources include the town's garbage incinerator, residential wood burning, air traffic, and small fishing vessels. Levels of nitrogen and sulfur in lichen tissue were elevated in KLGO compared to those in remote sites in the Tongass National Forest (TNF; Geiser et al. 2010b), but no widespread or adverse ecological effects have been detected from this elevated deposition. Wet sulfate deposition has been found to exceed 10 kg/ha at some locations close to the cruise ship docks (Schirokauer et al. 2014), which is up to 40 times greater than estimated background levels of 0.25 kg/ha (FLAG 2010).

Sitka National Historical Park

In comparison to remote sites in the TNF, elevated levels of nitrogen and sulfur have been found in lichen tissues sampled from SITK (Geiser et al. 2010b); however, no adverse ecological effects have been described. SITK receives less cruise ship traffic than more popular ports-of-call in KLGO and GLBA, but may still be impacted by emissions from guided marine tours, fishing vessels, and air transportation, and residential wood burning.

Airborne Contaminants Monitoring in the SEAN

Within and nearby the SEAN parks, a suite of inventories and ongoing monitoring efforts serve as the baseline from which to design a long-term sampling strategy (Table 2). These include a variety of efforts sponsored by the NPS to establish a baseline of airborne contaminant conditions within Southeast Alaska parks, as well as several active monitoring programs implemented by partner agencies and institutions.

As the first step toward development of a long-term monitoring design for the SEAN's Airborne Contaminants Vital Sign, Schirokauer et al. (2014) completed an inventory of ambient air quality (Ogawa samplers), open and throughfall deposition (IERs or Fenn Tubes; Figure 2), lichen tissue contaminant concentrations, and lichen community compositions during the summers of 2008 and 2009. The authors included Standard Operating Procedures (SOPs) for the implementation of individual monitoring elements, as well as a suite of recommendations for further research to

facilitate development of a final monitoring design. Some of those recommendations included: a complete analysis of wet deposition data from the Juneau NADP-NTN site, investigation of the relationships between mercury deposition in Glacier Bay with contaminant concentrations from lichen tissue, development of a calibration between bulk wet deposition data and passive IER tubes, and an interpretation of the results from WRF/Chem simulations by Mölders et al. (2013) to inform future monitoring strategies. Subsequent chapters build upon this prior work by advancing several of the authors' recommendations.



Figure 2. Open (OD; left) and throughfall (TD; right) ionic exchange resin tube (IER) deposition samplers deployed in KLGO during the summer of 2008 (Schirokauer et al. 2014).

In addition to these baseline inventories, the SEAN supported operation of a National Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN) wet deposition monitoring site in Bartlett Cove, GLBA from 2010-2013 to establish baseline rates of mercury deposition. The station was discontinued due to budget constraints and the perception that deposition rates fell within the range of observations from other Alaska MDN stations. Additional analysis of station data, including comparisons with other Alaska and Pacific Northwest stations, is the subject of Chapter 3 of this report.

Several active monitoring programs are also present within and adjacent to network parks that continue to collect pertinent airborne contaminant and air pollution information. These include active monitoring efforts by the NADP National Trends Network (NTN), Environment and Climate Change Canada, and the U.S. Forest Service.

The NADP NTN monitors precipitation chemistry, including concentrations of primary pollutants of concern [i.e. sulfate, nitrate, ammonium, and various natural anions and cations], at a site in Juneau, Alaska. Weekly samples of precipitation have been collected from this site since 2004, making it the

longest-running record of pollutant deposition in Southeast Alaska. Analysis of data from this station is the subject of Chapter 2 of this report.

The Global Atmospheric Passive Sampling (GAPS) Network of Environment and Climate Change Canada monitors a suite of legacy, current, and candidate POPs at over 50 sites worldwide. Many sites are located in remote areas to establish background concentrations, with a smaller number located in closer proximity to urban and agricultural pollutant sources. Results are being used to assess regional and global transport patterns as well as responses to regulations stemming from the Stockholm Convention (Pozo et al. 2006; Kallenborn et al. 2009). Samples are also being archived to enable future retrospective analyses. A GAPS site has been maintained within KLGO at Dyea since 2006. Full results are available through the United Nations Environment Program Global Monitoring Plan database and visualization tools (<http://www.pops-gmp.org/index.php?pg=gmp-data-warehouse/>). Continued monitoring for trends in air concentrations of POPs at this site serves as a needed compliment to SEAN efforts targeting criteria pollutants.

The U.S. Forest Service (USFS) conducts long-term biomonitoring using lichens as surrogates of air quality and contaminant deposition at two scales: the national scale, run by the Forest Inventory and Analysis (FIA) Program, and the regional Forest scale, run by Tongass National Forest staff. Lichen tissue concentrations of primary contaminants of concern are used as indicators of air quality. Lichen community compositions are also monitored to connect ecological responses with regional air pollution.

The use of lichens as indicators of air quality and contaminant deposition has a long history in Southeast Alaska due to their ability to directly assimilate airborne contaminants or pollutants into their tissues (Geiser et al. 1994; Furbish et al. 2000). Sensitive lichens are also thought of as effective sentinels to help detect ecosystem change (Geiser 2004; Geiser and Neitlich 2007, Otnyukova and Sekretenko 2008, Sutton et al. 2009, Wolseley et al. 2009). KLGO is reported to have the most diverse number of lichen species per unit acre than any other U.S. National Park (Spribille et al. 2010), representing an ideal region to study their ecosystem response.

Table 2. Summary of historical and ongoing airborne contaminant or air pollution studies within and nearby SEAN parks.

Historic Study	Study Years	KLGO	GLBA	SITK	TNF	Important Findings	Citation
Wet deposition of nitrogen and sulfur at open-canopy (OD) and throughfall (TD) sites (SEAN inventory)	2008-2009	● 3 OD 5 TD	● 1 OD 2 TD	● 1 OD 1 TD	-	- Wet deposition values for total inorganic nitrogen deposition were some of the lowest in North America (3-25 times lower than Pacific Northwest) - Sulfur TD elevated in KLGO	Schirokauer et al. (2014)
Passive atmospheric sampling of air quality indicators (SEAN inventory)	2008-2009	● 5 sites	● 1 site	● 1 site	-	- Levels of NO₂ and NO_x in KLGO elevated, generally on par with rural California - Lower Dewey frequently showed elevated ambient contaminant concentrations, with peak levels as high as 8-10x greater than sites in GLBA and SITK	Schirokauer et al. (2014)
General precipitation chemistry (NADP NTN program)	2004-present	-	-	-	● 1 site, Juneau	- Overall rates of pollutant deposition have been low relative to regulatory thresholds - Summertime deposition has exceeded wintertime deposition for common nitrogenous and sulfurous pollutants associated with fossil fuel combustion - Summarized in Chapter 2, this report	-
Wet deposition of mercury (NADP MDN program)	2010-2013	-	● 1 site	-	-	- Very low rates of Hg deposition overall - Site not well represented by other Hg monitoring locations, the closest of which is 900 miles away in western Washington. - Summarized in Chapter 3, this report	-
Passive atmospheric sampling of POPs (GAPS Program, Environment Canada)	2006-present	● 1 site	-	-	-	- Several banned and current-use pesticides of global concern have been detected - Both long-range transport from Asian sources and remobilization from prior water or ice sinks have been implicated	Pozo et al. (2006); Kallenborn et al. (2009); Shunthirasingham et al. (2010)

Table 2 (continued). Summary of historical and ongoing airborne contaminant or air pollution studies within and nearby SEAN parks.

Historic Study	Study Years	KLGO	GLBA	SITK	TNF	Important Findings	Citation
Lichen Tissue Elemental Analysis and Community Composition (multiple programs)	1989-1992	-	-	-	● 80 plots 130 temp	Set the stage for lichen study in Southeast Alaska with the establishment of study plots and vegetation classifications	Pawuk and Kissinger (1989); Geiser et al. (1994)
	1998-1999	● 4 sites	-	-	-	- SEAN pilot lichen study to set baseline values - Higher levels of heavy metals and sulfur than baseline values observed in unpolluted regions of Southeast Alaska	Furbish et al. (2000)
	Early 2000s	-	-	-	● 127 plots	Developed a series of threshold concentrations that identify baselines for elemental exceedances in lichen tissue	Dillman et al. (2007)
	2002-2007	-	● 1 site	-	-	Lichen concentrations showed elevated N conc. at a sea-level, but higher elevations were within background ranges expected for Southeast Alaska	WACAP, Landers et al. (2008)
	2008-2009	● 7 sites	● 2 sites	● 1 site	● 2 sites	- KLGO sites impacted; Lower Dewey showed the most effect due to cruise ships and fugitive dust from ore-loading - Sulfur impacts possible to lichen communities in KLGO - No adverse S and N effects in SITK or GLBA	Schirokauer et al. (2014)

Chapter 2 –Seasonal Patterns of Wet Deposition

Introduction

In this chapter, we present a summary of results from the NADP-NTN AK02 site in Juneau, as recommended by Schirokauer et al. (2014), to inform the development of a long-term airborne contaminants deposition-monitoring program. We first provide background information about the NADP program and data quality at the NADP-NTN AK02 site in Juneau (Figure 4). We then present our methods and results summarizing seasonal deposition loads. Finally, we relate our findings to a specific monitoring design assumption, first presented by Schirokauer et al. (2014), that nitrogen and sulfur compounds should show larger deposition loads during the summer months because of increased tourism through ship, air, and automobile traffic.

While we had initially hoped to calibrate results from a deposition sampler (i.e., IER or Fenn tube) co-located with the NTN-AK02 site during the summers of 2008 and 2009, we encountered difficulties in relating results from the samplers with different deployment periods, as well as issues with poor and usable data quality. The calibration could have enabled an evaluation of the Juneau site's representativeness for long-term monitoring of regional wet deposition. Since it is assumed that the NADP site is the “truth”, or the realistic amount of wet deposition in Juneau, it is hypothesized a correction factor can be developed to calibrate IER resin tubes with the NADP data. A method for calibrating IER throughfall deposition with lichen tissue was developed by Root et al. (2013) in the Pacific NW, and it is understood a similar method could be used with the NADP data (H. Root, personal communication, 2014). However, linking NADP data with IER depositions have not been attempted due to the sparse NADP network and datasets, especially in Alaska.

NADP-National Trends Network (NTN)

Since 1978, the NADP-NTN (National Atmospheric Deposition Program – National Trends Network) has been providing long-term records of precipitation chemistry across the United States, Canada, and Mexico. As of April 2016, the NTN had 264 operational sites across North America, with five located in Alaska (Juneau, King Salmon, Denali National Park, Poker Creek, and Bettles).

The NADP-NTN monitoring locations are typically positioned far from point sources of pollution. Each site gathers weekly samples of rainfall, which are measured for volume, weight, and precipitation depth. To facilitate a collection standard, the samples are typically gathered on Tuesday morning and sent to the Central Analytical Laboratory (CAL) at the Illinois State Water Survey where they undergo chemistry analyses. The weekly samples are analyzed for precipitation depth and anion and cation concentrations (mg/L). Samples are composited to seasonal and annual time scales and converted to precipitation-weighted deposition (kg/ha), which takes into account sample concentration and precipitation depth. Each sample passes a stringent quality assurance/quality control (QA/QC) check. Samples that may have been contaminated by foreign matter (organic contamination, bird droppings, etc.), or skewed due to collector malfunction, are flagged as *invalid* and are not reported in the NTN's statistics. Invalid samples have the potential to skew long-term trends or potentially bias data analysis in unpredictable ways. Further information regarding the

QA/QC of NTN data is available through the website: <http://nadp.sws.uiuc.edu/documentation/notes-depo.html>.

CAL analyzes precipitation samples for H^+ (hydrogen ion acidity, pH), anions (negative ions), and cations (positive ions) including: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), and ammonium (NH_4^+). Positive metal ions such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ are determined through flame photometry. Through this method, radiation is absorbed by metal ions in a flame. NH_4^+ and the other anions (SO_4^{2-} , NO_3^- , and Cl^-) are calculated through colorimetric analysis (Boubel et al. 1994).

The Juneau NTN site (AK02) began collecting weekly precipitation deposition data on June 22, 2004, and as of April 2016, it was still in operation. The site is located at an elevation of approximately 25 m at 58.38° N, 134.63° W, and is managed by the United States Forest Service (USFS) Pacific Northwest Research Station and the University of Alaska Southeast (UAS). It was moved in 2010 from a remote location northwest of Juneau to a more accessible site with a reliable source of electricity on the UAS campus (Figure 3). The new location is near Auke Bay, which is approximately 12 miles from downtown Juneau, and because of its distant location, is generally believed to avoid major point-sources of emissions from automobiles, commercial operations, and marine vessels.

Methods

Data Compilation and Validation

Valid weekly data is freely available to download through NADP's website. The NADP provides invalid data upon request. While the NADP collects precipitation throughout the year, winter sampling posed several issues at the Juneau site due to freezing of the equipment. During five consecutive winter seasons from 2004-2010, most of the weekly data collected at the AK02 site were flagged as *invalid* according to NADP's stringent QA/QC procedures. The NADP warns that the analysis of invalid data may lead to misleading conclusions. According to the quality assurance manager at the NADP (M. Rhodes, personal communication, 2014), samples may become invalidated for reasons such as:

- 1) errors in operation ("*bulk mode*", i.e. the collector was consistently open),
- 2) equipment malfunction,
- 3) sample mishandling, and
- 4) physical contamination of the sample, leading to elevated concentrations.

Most of the invalid deposition data was flagged as "open" or "bulk" and likely points to prevalent issues with freeze and thaw conditions (D. D'Amore, personal communication, 2014). When the data is considered bulk, the collection bucket is continuously open due to malfunctions with the arm mechanism controlled by the motor box. The wet deposition collection bucket is typically covered with a lid when it is not raining to avoid evaporation and/or contamination of the sample via dry

deposition (Figure 4). When the collector is operating in bulk mode, wet deposition is being captured along with some fraction of dry deposition.

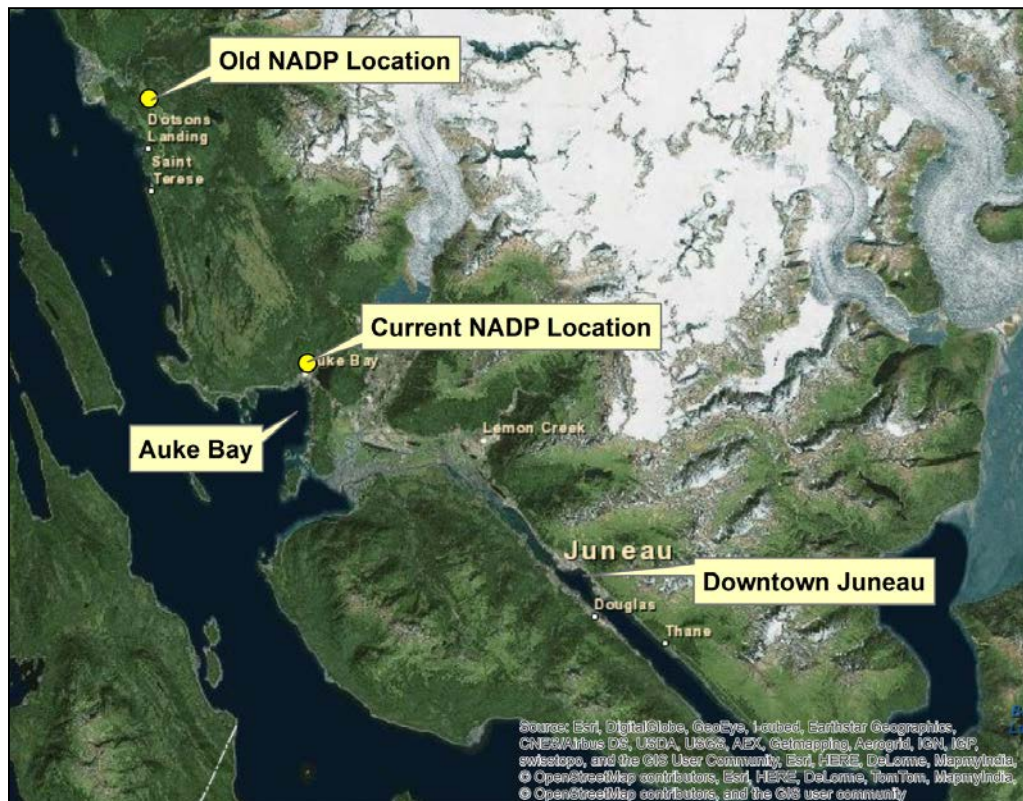


Figure 3. Satellite imagery showing the locations of the current and historical NADP-NTN collection sites in relation to Downtown Juneau. The current site is on the University of Alaska Southeast (UAS) campus adjacent to Auke Bay, and at least 10-12 miles from downtown Juneau.



Figure 4. The NADP-NTN AK02 rain gauge (top) and precipitation collector (bottom) on the UAS campus in Juneau. Image was taken in October 2014.

A sensor normally opens the lid during a rain event and automatically closes it once the rain stops. During winter, wet snow would freeze onto the device and burn out the motor box that moves the arm covering the sample. A sample exposed to both wet and dry deposition is typically not a large issue when analyzing it on a long-term scale (D. Schirokauer, personal communication, 2014) because dry deposition is a small component of total deposition at Juneau due to the abundance of precipitation and water vapor in the ambient air. While evaporation of the liquid sample could be a source of error while the bucket operated in bulk open mode, winter humidity levels in Juneau are frequently high, which slows down the evaporation process. Evaporation is also less of a concern since the NTN does not measure particularly volatile species, such as mercury (Hg) or trace organics that could be lost through this process. Despite the fact that the winter samples may be partially exposed to the elements and prone to some evaporation, we hypothesize that summer depositions will be higher than winter due to additional sources of anthropogenic activity associated with seasonal tourism.

In 2010, a heating element was installed to melt ice and snow, which largely fixed the freeze-thaw problems. Samples collected after the spring of 2010 are more complete and accurate (flagged as “valid”). The heating element remained operational after installation of a reliable power source on the UAS campus. The NTN device was also outfitted with a triangular heated roof to the collector lid, which enables it to shed snow and further avoid freeze-ups.

Despite the fact that much of the winter data were classified as bulk invalid samples by NADP, for the reasons cited above, it is thought to be largely representative of winter chemical deposition (E. Hood, personal communication, 2014). However, the samples may be slightly contaminated with small amounts of organic debris such as twigs and leaves, particularly during windy sampling periods (D. D’Amore, personal communication, 2014). Bird droppings were unlikely. Although the site operators knew the samples would not pass QA/QC publication criteria by NADP due the freeze/thaw issues, samples continued to be analyzed by the CAL until the problems could be resolved.

Since there are no other valid winter observations until winter 2011, we chose to include both invalid and valid weekly data in calculating pseudo-seasonal depositions to help understand interseasonal differences between winter and summer. Only valid NADP data were used in seasonal calculations when the majority of the season had valid observations (approximately 70%; Table 3). Ten out of twenty seasons in our period of interest from 2004-2014 incorporated fully valid data. A combination of valid and invalid data was used during 10 seasons when the precipitation collector experienced malfunctions. We rejected weeks of invalid data that contained obvious errors (i.e. chemical values were an order of magnitude higher than normal). These errors generally propagated over all anion and cation quantities.

Table 3. Seasonal deposition values of atmospheric contaminants from the Juneau NADP-NTN AK02 monitoring site. All values are in kg/ha. The periods used here are modified from the seasons reported by NADP and collapsed into twice-yearly values. Summer typically ranged from April 10 to October 10, while winter was the opposite.

Year	Season	Invalid Used?	% Invalid Used	% Complete	Ca ⁺	Mg ⁺	K ⁺	Na ⁺	NH ₄ ⁺	NO ₃ ⁻	Inorganic Nitrogen	Cl ⁻	SO ₄ ²⁻
2004	Summer *	N	0.0	81.3	0.11	0.10	0.05	0.98	0.12	0.66	0.24	1.83	1.11
	Winter 04-05	Y	73.1	92.0	0.24	0.21	0.11	1.98	0.10	0.88	0.28	3.69	1.36
2005	Summer	N	0.0	84.6	0.15	0.08	0.05	0.76	0.07	0.64	0.20	1.34	1.38
	Winter 05-06	Y	69.2	92.3	0.21	0.15	0.09	1.42	0.08	0.60	0.19	2.62	1.14
2006	Summer	N	0.0	92.3	0.17	0.06	0.08	0.60	0.10	1.31	0.37	1.11	2.13
	Winter 06-07	Y	100.0	84.6	0.26	0.26	0.14	1.72	0.07	0.84	0.24	3.20	1.55
2007	Summer	N	0.0	76.9	0.14	0.06	0.06	0.61	0.22	0.99	0.39	1.17	1.85
	Winter 07-08	Y	66.7	100.0	0.27	0.18	0.09	1.60	0.08	1.13	0.32	2.59	1.51
2008	Summer	Y	77.8	88.9	0.21	0.09	0.08	0.88	0.12	1.35	0.40	1.67	2.64
	Winter 08-09	Y	100.0	73.1	0.27	0.16	0.10	1.63	0.09	1.04	0.31	2.98	1.47
2009	Summer	Y	100.0	80.8	0.18	0.09	0.10	0.84	0.11	1.11	0.33	1.57	2.67
	Winter 09-10	Y	100.0	73.1	0.23	0.11	0.07	1.05	0.07	0.71	0.21	1.91	0.84
2010	Summer	Y	42.3	76.9	0.19	0.11	0.08	1.02	0.08	0.65	0.21	1.87	1.80
	Winter 10-11	Y	69.2	80.8	0.16	0.17	0.17	1.87	0.09	0.66	0.22	2.70	1.05
2011	Summer	N	0.0	92.3	0.15	0.10	0.07	0.78	0.12	1.00	0.32	1.38	2.62
	Winter 11-12	N	0.0	69.2	0.26	0.36	0.19	3.18	0.14	0.74	0.27	5.75	1.59
2012	Summer	N	0.0	84.6	0.13	0.11	0.11	0.95	0.17	1.40	0.44	1.77	2.37
	Winter 12-13	N	0.0	84.6	0.23	0.18	0.10	1.49	0.13	0.78	0.27	2.72	1.01
2013	Summer	N	0.0	88.5	0.31	0.14	0.09	0.88	0.24	1.43	0.51	1.65	2.41
	Winter 13-14	N	0.0	96.2	0.26	0.17	0.09	1.37	0.18	0.92	0.34	2.53	1.09
2004-2013	Mean Summer	-	-	-	0.17	0.09	0.08	0.83	0.13	1.05	0.34	1.57	2.10
	Mean Winter	-	-	-	0.24	0.20	0.11	1.73	0.10	0.83	0.27	3.07	1.26
	Mean Overall	-	-	-	0.21	0.15	0.09	1.28	0.12	0.94	0.30	2.30	1.68

*Note that Summer 2004 is not a complete 26 weeks of data. The actual term is 16 weeks since the site did not start recording precipitation until 6/22/2004

All of the valid and invalid data seasons had more than 73% completeness, with the exception of winter 2011-12 which was just under 70% complete. The percentage of invalid data measurements used in each season's deposition calculation can also be found in Table 3. Figure 5 shows a graphical representation of seasons when only valid data was used (black), both invalid and valid data were used (blue), and when no valid observations were available (red). The latter was the case during the winter 2006-07 and from the winter 2008-09 extending through the winter 2009-10, which was likely just before the collector was moved to UAS and outfitted with the heating element.

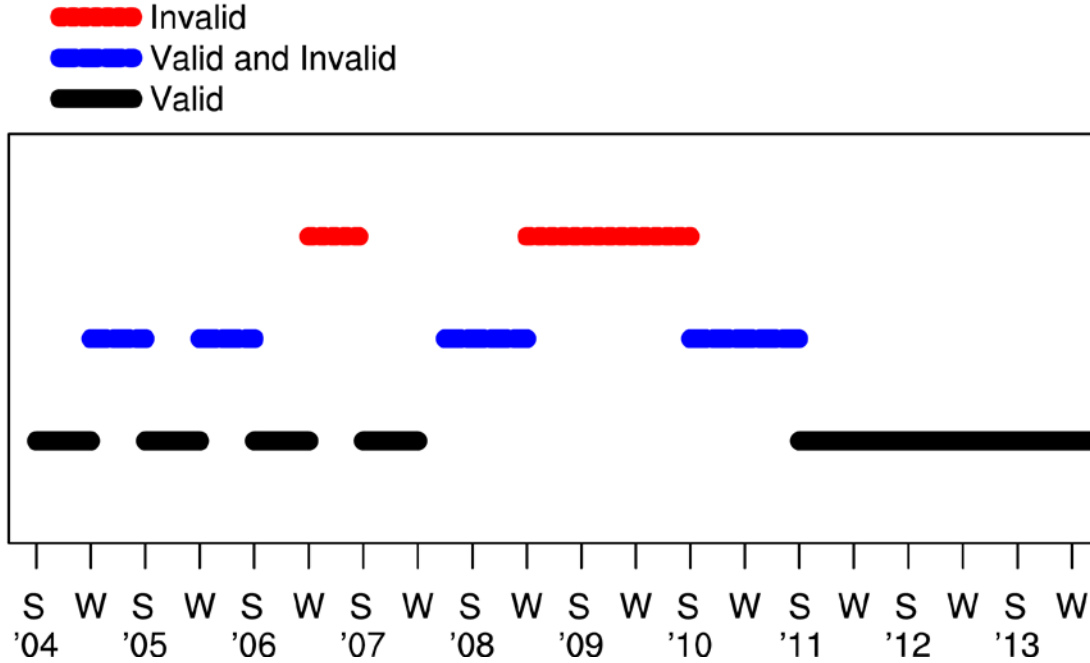


Figure 5. NADP-NTN AK02 data quality during the period of record. Each x-axis label represents the summer (April to October) and winter (October to April) seasons. Black bars indicate seasons when we only used valid weeks of deposition data since there were significant quantities of these observations (> 70%). Blue bars indicate use of both valid and invalid data. These seasons typically did not have enough valid data to substantiate a deposition value. Red bars indicate periods without valid observations.

Data Analysis

NADP calculates annual precipitation-weighted mean (PWM) concentrations by taking the product of the weekly concentrations for all weeks of valid measurements by the ratio of the precipitation received during that week against the total precipitation for the summary period, and then sums the values. Deposition is determined by multiplying the PWM concentration by the total precipitation received during the period of interest (POI), including valid and invalid samples. The value is divided by 10 to make the units agree.

The following calculations were performed to determine the deposition for NTN constituents:

$$PWM \text{ Conc.} = \sum_{i=1}^n \text{Weekly Conc.} \left(\frac{mg}{L} \right) \times \left(\frac{\text{Precip. depth in collector for that week (cm)}}{\text{Total precip for VALID samples in POI (cm)}} \right)$$

$$Deposition = \frac{PWM\ Conc. \left(\frac{mg}{L} \right) \times Total\ precip\ for\ ALL\ samples\ in\ POI\ (cm)}{10}$$

The NADP calculates and publishes seasonal and annual deposition from valid data only, meaning that statistics including any invalid data must be manually recalculated. For invalid data, we followed the NADP convention by normalizing the deposition loads based on the weekly concentrations and measured precipitation. We collapsed the data into half-yearly values to portray the differences between summer and winter deposition. This procedure also separates two contrasting seasons:

- 1) **Summer (early April to early October)**, when cruise ships and a majority of tourists are present in Southeast Alaska; and
- 2) **Winter (late October to early April)**, during non-tourist season, but seasonal emissions from heating fuel dominate.

After manually calculating the seasonal deposition loads, we plotted the ten year trends and presented mean and quartile values.

Results and Discussion

Nitrogen and Sulfur Compounds

Sulfate (SO₄²⁻)

Over the ten-year monitoring period, the mean sulfate deposition for the winter and summer months were 1.26 and 2.10 kg/ha, respectively. While there was greater variation in the first and third quartiles of summer deposition (1.81-2.53 kg/ha compared to 1.06-1.50 kg/ha for the winter), the average summer deposition was consistently higher than those for winter (Figures 6 and 8).

The winter 2009-2010 sulfate deposition at the NTN site incurred the lowest value during our 10-year sampling period at 0.84 kg/ha, a drop in 0.63 kg/ha from the previous winter. The highest seasonal sulfate deposition of 2.67 kg/ha was in summer 2009, which was around the time Mount Redoubt erupted. The volcano is located on the western edge of the Cook Inlet a few hundred kilometers southwest of Anchorage, and began its explosive eruption phase in late March 2009 (Lopez et al. 2013). It is possible that the degassing and subsequent transport of the elevated SO₂ plume slightly affected the sulfate levels in Juneau's summer rainfall.

Even though we noticed a slight increase in Juneau's sulfate levels between the summer and winter months, the deposition was still quite low compared to other locations across the United States, even when summing both summer and winter values. Analysis of yearly nationwide NADP data by the EPA has determined that yearly average sulfate deposition from 2010-12 has decreased as much as 50% or more since the early 1990's (EPA 2014). Current sulfate deposition tends to range from 6-15 kg ha⁻¹ yr⁻¹ east of the Mississippi River, with higher amounts in the Mid-Atlantic and Midwest. Most annual deposition in the Western States do not exceed 2-4 kg ha⁻¹ yr⁻¹ (Figure 9).

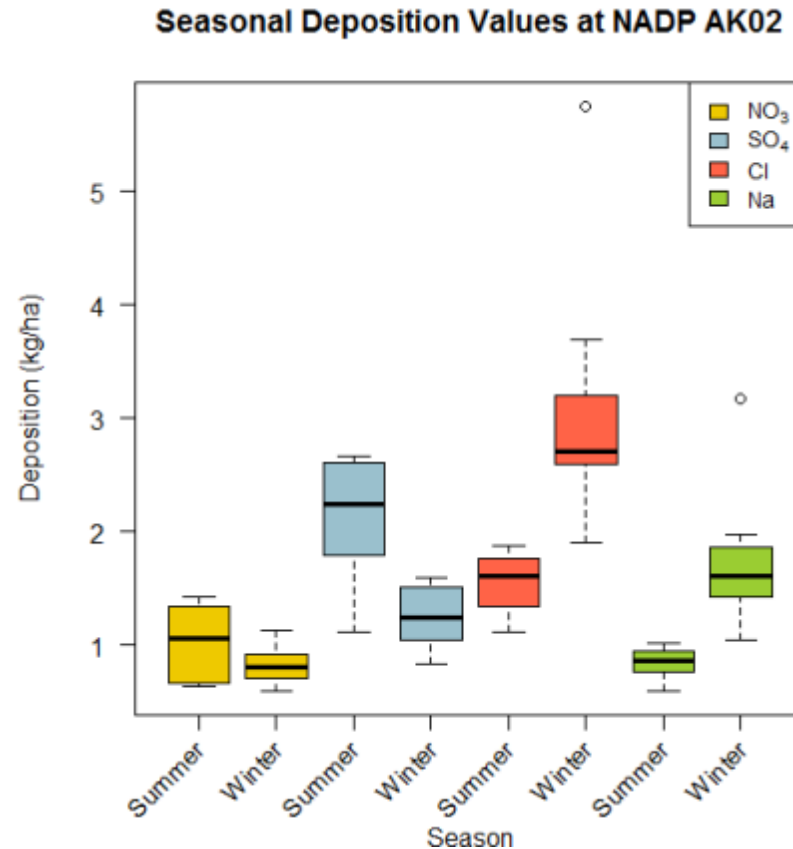
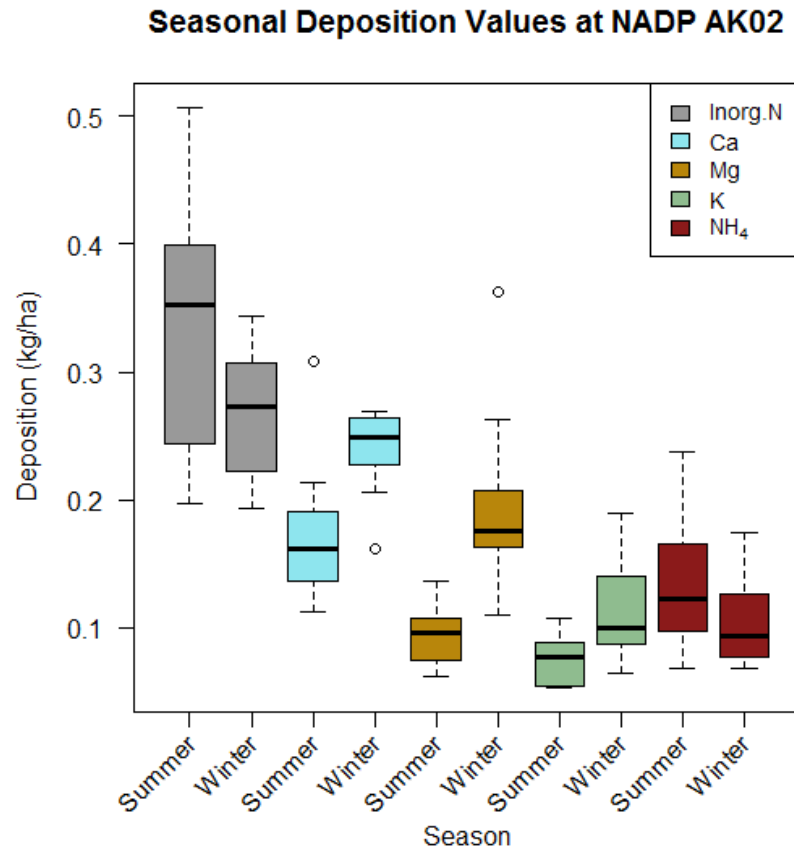


Figure 6. Boxplots of winter and summer seasonal deposition for atmospheric contaminants at the Juneau NADP-NTN AK02 site ranging from Summer 2004 to Winter 2013-2014. Contaminants with smaller deposition loads are plotted on the left hand side plot. Larger depositions are plotted on the right to avoid scaling the axes.

Seasonal Precipitation at the NADP AK02 Site

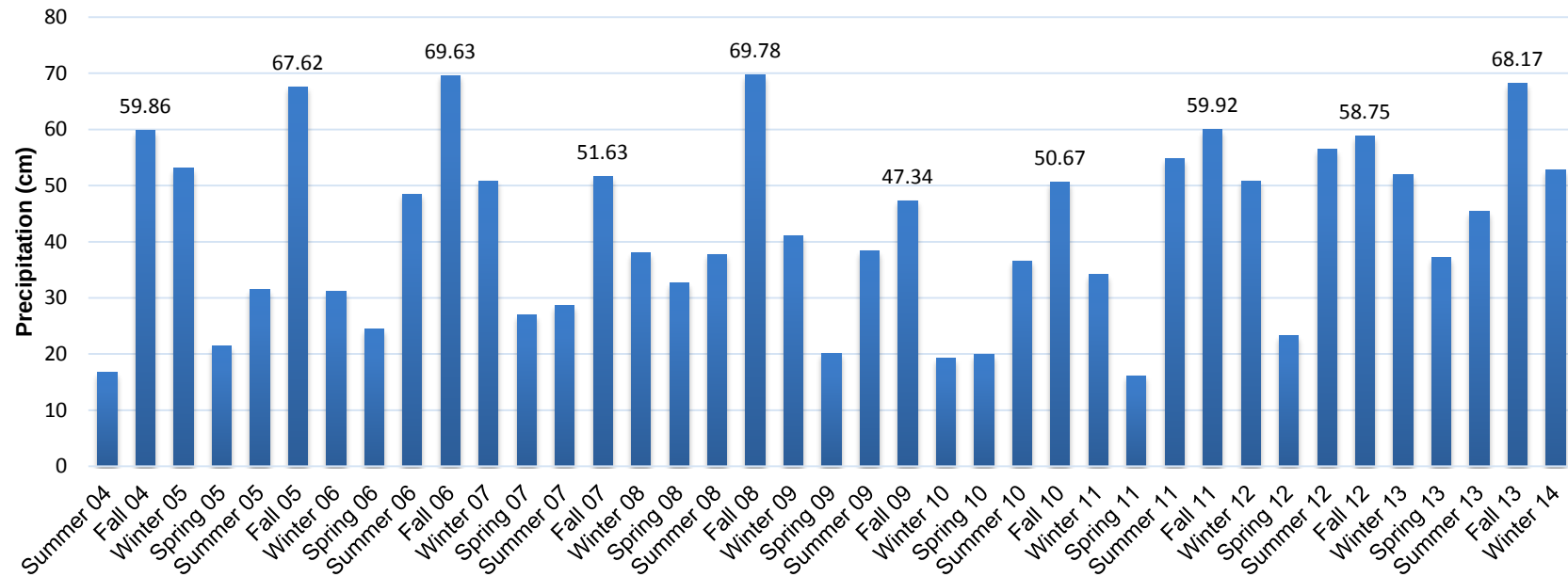


Figure 7. Seasonal precipitation recorded at the Juneau NADP AK02 wet deposition site. Fall and Winter are generally the rainiest seasons of the year.

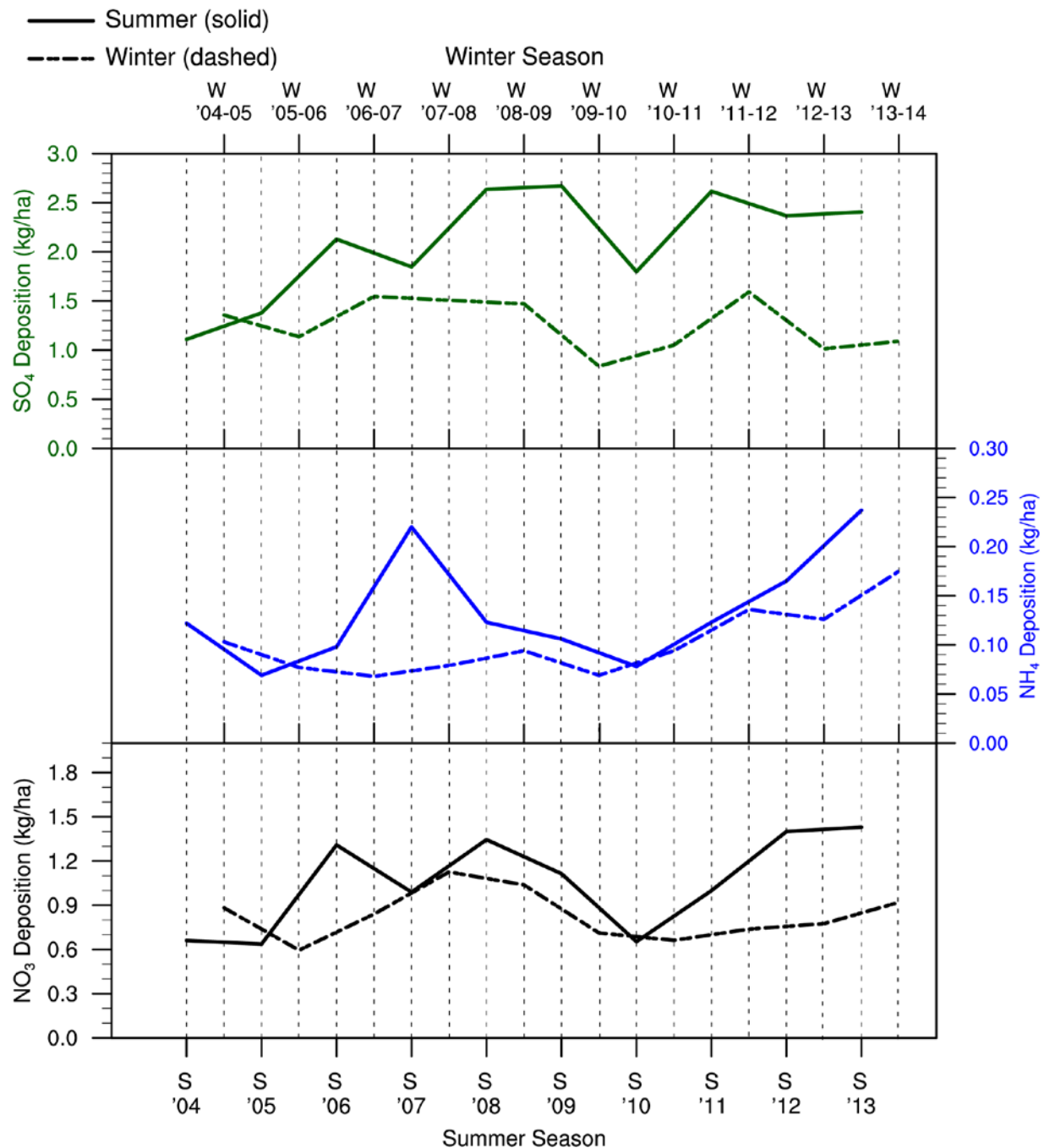


Figure 8. Time series plots of SO_4^{2-} (top), NH_4^+ (middle), and NO_3^- (bottom). The solid lines indicate summer deposition and follow the bottom x-axis. Dashed lines represent winter deposition and follow the top x-axis. The plot illustrates that summer depositions are almost consistently higher than winter depositions for these three compounds.

Regional Deposition Differences

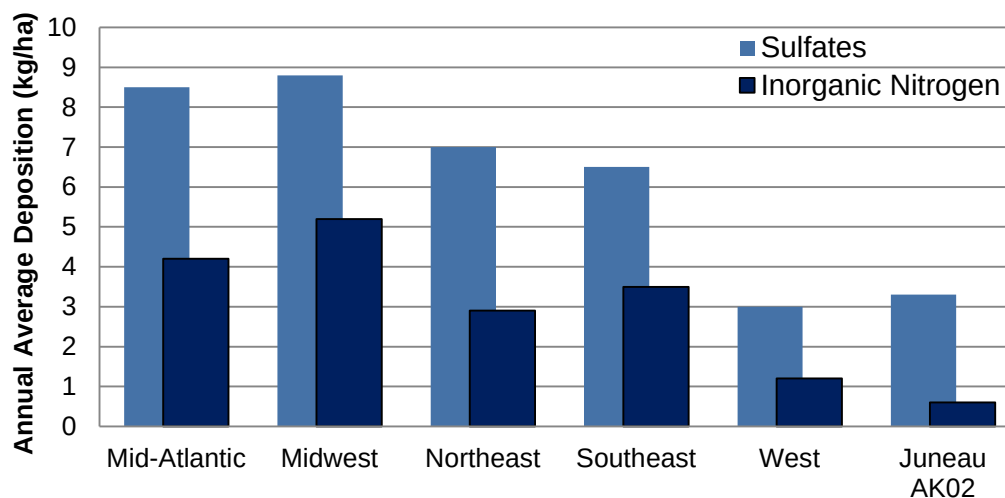


Figure 9. Average annual sulfates and total inorganic nitrogen depositions by region. Adapted from NADP data and the EPA (2014). The Juneau AK02 data is extrapolated from our summer and winter deposition loads.

NH₄⁺ (Ammonium Ion)

Ammonium levels were generally quite low and did not show much variation between the winter and summer periods. The average summer deposition was 0.13 kg/ha compared to 0.10 kg/ha for the winter months (Table 3). The first and third quartiles for the summer and winter seasons were 0.10-0.15 and 0.08-0.12 kg/ha, respectively. The summer of 2007 and 2013 saw the ammonium levels increase above 0.22 kg/ha. Values are typically lower in the winter when biological activity reaches a minimum. The ammonium ion levels are very low compared to most regions in the Continental US, and perhaps some of the lowest values in the country. Annual deposition values range from 1-5 kg ha⁻¹ yr⁻¹ in the Eastern US, and up to 6 kg/ha in the Central US where farming and animal production is prevalent. The Western US does not typically exceed 1-2 kg ha⁻¹ yr⁻¹ deposition of ammonium.

Potential sources for the higher ammonia readings could be the result of municipal or cruise-ship wastewater treatment, or dead and decaying plants (of particular interest may be the foliage and trunks of the mountain hemlock trees; Schirokauer et al. 2014). Nitric acid (HNO₃), which is produced by a sunlight-driven chemical reaction between NO_x and other hydroxyl radicals, is able to scavenge NH₃ out of the atmosphere (Finlayson-Pitt and Pitts 2000). Thus, ammonia is an important source of total nitrogen deposition, but the long-term implications of its accumulation in the soil are unclear (Jacob 1999). Unfortunately, the Clean Air Act (Stephen and Aneja 2008) or the National Ambient Air Quality Standards (NAAQS) do not regulate NH₃ emissions, which may subsequently lead to high amounts of inorganic nitrogen deposition.

NO₃⁻ (Nitrate)

Nitrate levels were generally higher in the summer months, but also showed greater variability between the first and third quartiles of data. The average summer and winter nitrate depositions were 1.05 kg/ha and 0.85 kg/ha, respectively. During the summer, nitrate levels showed a spread from

0.74-1.33 kg/ha in their first and third quartiles. Winter ranged from 0.72-0.91 kg/ha. Nitrate deposition in Juneau was again quite low compared to the rest of the United States. Annual deposition typically ranges from 4-9 kg ha⁻¹ yr⁻¹ in the Northeast and Southeast, 7-10 kg ha⁻¹ yr⁻¹ in the Central Plains, and 2-4 kg ha⁻¹ yr⁻¹ in the Western US.

The forest canopy tends to assimilate most of the nitrates present in rainwater, and as a result, studies using throughfall wet deposition collectors under tree crowns have yielded lower deposition values of nitrate than those located outside of the canopy (Schirokauer et al. 2014). Similar results have been shown at National Parks in Washington State (Fenn et al. 2013; Klopatek et al. 2006). Based on these findings, we believe that the nitrate levels collected at the Juneau NADP site should be higher than those sampled under the forest canopy.

Inorganic Nitrogen

Inorganic nitrogen deposition factors in the nitrogen proportions from NO₃⁻ and NH₄⁺ in the rainfall and was quite low, showing little difference among summer and winter seasons. Summer deposition averaged 0.34 kg/ha, while winter averaged 0.27 kg/ha. If these values are extrapolated to full year depositions, they are likely well below 0.75 kg ha⁻¹ yr⁻¹. This amount is somewhat greater than recorded deposition from other areas of Alaska, though well below results from rural sites in the Pacific NW (Figure 9, Table 5).

Table 4. Variation in emission sources and levels between summer and winter in Juneau, AK. Adapted from ADEC (2013).

Source	Summer	Winter
Fuel Combustion	Increased fuel and diesel combustion associated with vehicles, cruise ships, and other vessels	Home heating fuel and vehicle combustion
Tourism	Tourist season increases the local population, which results in more anthropogenic use of ground transportation and shipping	Little to no tourism
Temperature	Higher temperatures and more hours of sunlight speed up sunlight-driven chemical reactions, especially between NO _x and CO products from fuel combustion	Lower temperatures and less hours of sunlight, leading to the use of power and home heating fuel
Home Heating	Little, mainly for household hot water systems	Higher presence of wood and home heating fuel combustion
Vegetation	Dead and decaying plants release ammonia, especially with higher temperatures	Less plant decay, especially if covered in snow
Waste	More municipal waste/ waste water treatment from cruise ships and tourists	Less effect than in summer
Wildfires	Rare, but possibility of smoke advection from distant wildfires	Little to no winter wildfire effects
Storms	Storms are not as intense in summer than in winter. Calm weather increases air stagnation.	Stronger storms may lead to the lofting of more sea salt and other natural aerosols

Table 5. Established and reference nitrogen critical loads for portions of the Northwestern USA, along with prior studies for comparison.

Applicable Area	Measured Through	Nitrogen Critical Load (kg ha ⁻¹ yr ⁻¹)	Source
Marine Pacific Northwestern Coastal forests	Lichen communities	2.70 – 9.20	Geiser et al. (2010a)
Coastal Alaska	Fungal communities	~5.0	Whytemare et al. (1997); Lilleskov (1999)
Inland Pacific NW	Throughfall N wet deposition; lichen communities	1.54; 2.51	Root et al. (2015)
High elevation Rocky Mountain National Park	Lake, soil, wet deposition, vegetation samples	3.00-5.00	Baron et al. (2000)
Rural Pacific NW	IER Tubes	1.60	Fenn et al. (2003)
Various sites in Coastal Alaska	IER Tubes	0.06 – 0.55 (~150 day exposure)	Schirokauer et al. (2014)
Interior Alaska	NADP wet deposition	~0.20	Linder et al. (2013)
Interior Alaska	IER Tubes and Snowpack	~0.35	Brumbaugh et al. (2012)
Juneau, Coastal Alaska	NADP wet deposition	< 0.75	This report

Critical loads for inorganic nitrogen deposition in the Pacific Northwest have been developed by Geiser et al. (2010a) to estimate the amount of nitrogen that can be deposited before causing long-term ecosystem damage (Table 5). Critical loads are tools to quantify harmful levels of pollution and set goals for resource protection or restoration (Porter et al. 2005). Lichen communities in marine Pacific Northwest coastal forests typically can tolerate between 2.7 kg N ha⁻¹ yr⁻¹ and 9.2 kg N ha⁻¹ yr⁻¹ for wet forests (Geiser et al. 2010a), while other studies (Whytemare et al. 1997; Lilleskov 1999) suggest some fungal communities in coastal Alaska can tolerate around 5 kg N ha⁻¹ yr⁻¹. The extrapolated value of 0.75 kg N/ha for a full year of data from the Juneau NADP site would fall well below established critical load-levels for the Pacific NW. However, critical load estimates specific to Southeast Alaska are needed to better understand the potential for local ecological responses.

Summary of Nitrogen and Sulfur Deposition

The summer season generally saw higher deposition loads of NH₄⁺, NO₃⁻, and SO₄²⁻ (Figure 6 and Table 3) despite the fact that more precipitation typically accumulated during the fall and winter seasons (Figure 7). If similar levels of contaminants were deposited in the winter as in the summer, winter deposition loads would be more diluted due to higher amounts of rainfall. However, our results show enhanced deposition loads in addition to lower summer precipitation rates, which are taken into account using PWM concentrations in the deposition calculation.

The higher ammonium and nitrate levels in the summer also led to higher deposition of inorganic nitrogen than in winter. The opposite trend was observed for most of the base cations, which typically originate from natural sources, such as airborne dusts or sea spray. The three higher summer deposition values of NH₄⁺, NO₃⁻, and SO₄²⁻ may be of highest concern due to their potential ties with

anthropogenic-related influences. Potential explanations for the deposition variation between summer and winter seasons are presented in Table 4. For additional background information regarding the individual analytes, see Appendix A.

The increase in summer sulfate, nitrate, and ammonium deposition could be the result of fuel and diesel combustion associated with automobiles, planes, and a diverse population of marine vessels, including fishing boats, ferries, and private and commercial watercraft during peak summertime activity (Nuka Research and Planning Group 2012). Primary pollutants, such as nitrogen and sulfuric oxides, are typically emitted from anthropogenic sources and then dissolve in water vapor droplets or react in the atmosphere to form secondary particles. These aerosols, along with any suspended dust and organic carbon in the air, fit into the broad spectrum of airborne particulate matter (PM) that can be transported long distances. The main sources of PM inside the Mendenhall Valley are residential wood smoke, dust from playgrounds and baseball fields, automobile exhaust, dust from construction and land clearing, and smoke from open burning (ADEC 2013). Depending on meteorological conditions, dust from gravel pits and glacial silt from the Mendenhall Glacier (and the banks of the Mendenhall River) may become lofted in the air.

The Mendenhall Valley in Juneau was designated a nonattainment area by the Environmental Protection Agency (EPA) in 1990 after it consistently exceeded the $150 \mu\text{g}/\text{m}^3$ 24-hour average NAAQS of PM_{10} (particulate matter with diameter less than $10 \mu\text{m}$) (EPA 2012). High PM concentrations were also well correlated with low temperature periods, weekends, and holidays when people frequently used wood stoves and fireplaces (Watts et al. 1988). Downtown Juneau, including the area where cruise ships are docked, was not part of the nonattainment area. Juneau has not exceeded this violation since 1994 after implementing numerous improvements, such as extensively paving roads to reduce airborne dust, educating the residents about emissions from wood stoves, and limiting the use of wood stoves during stable, stagnant winter conditions (ADEC 2013).

Base Cations

Analyte Summary

The average summer and winter calcium (Ca^{2+}) deposition loads were 0.17 and 0.24 kg/ha, respectively (Table 3, Figure 6). The summer months showed slightly higher variations between their first and third quartiles. Summer deposition values ranged from 0.14-0.19 kg/ha while the winter deposition ranged from 0.23-0.26 kg/ha in their first and third quartiles.

Potassium (K^+) deposition values were also slightly higher in the winter months, and likely reflect similar sources and trends as calcium. The average summer and winter potassium deposition values were 0.075 and 0.113 kg/ha. First and third quartiles of data ranged from 0.058-0.087 kg/ha in the winter and 0.087-0.132 kg/ha.

Deposition values for magnesium (Mg^{+}) were generally higher and more variable in the winter season than in summer. A high value of 0.36 kg/ha occurred during the winter of 2011-2012. Average summer and winter magnesium deposition values were 0.094 and 0.196 kg/ha, respectively. The ranges in the first and third quartile of summer and winter depositions were 0.079-0.106 and 0.165-0.201 kg/ha, respectively.

The average sodium (Na^+) deposition values were almost double during the winter months compared to summer months, with values of 1.61 and 0.83 kg/ha, respectively. The range between first and third quartiles of data for the summer was 0.77-0.93 kg/ha. Winter had a much larger spread of 1.44-1.73 kg/ha compared to the summer.

A similar result was seen for average chloride (Cl^-) deposition. Amounts were much higher in the winter versus the summer months at 3.07 and 1.57 kg/ha, respectively. Summer chloride levels in the first and third quartiles ranged from 1.35-1.74 kg/ha, while winter deposition ranged from 2.60-3.15 kg/ha. A large chloride deposition outlier of 5.75 kg/ha occurred during the winter of 2011-2012. The highest deposition of sodium also occurred during this season at 3.18 kg/ha (which was also an outlier in its dataset), pointing to the fact that the sources of Na^+ and Cl^- are related. The average wind speed during the winter of 2011-2012 was a bit higher than other years, pointing to the fact that sea salts were likely lofted with the added sea chop.

Reasoning for Higher Winter Depositions

The higher values of winter Ca^{2+} , Mg^+ , K^+ , Na^+ , and Cl^- deposition may be the result of added local dust and sea salts transported by stronger winds, as well as Asian dust that may have been lofted into the atmosphere by strong winds from springtime synoptic storms over the Gobi and Taklimakan Deserts (Rahn et al. 1977). Higher wind speeds tend to loft particulates from adjacent glacier fields in British Columbia, Yukon, and the Juneau Icefield through the Lynn Canal. Wood burning is also a common method of home heating in Juneau, potentially adding to the higher deposition values.

Calcium deposition levels are generally similar or slightly higher than most regions on the East and West US coasts. Some desert regions in the Southwest, as well as agricultural and prairie regions of the Central Plains also show elevated calcium deposition, which is likely due to dust transport. Calcium deposition values may rise upwards of 4-5 kg ha⁻¹ yr⁻¹ in these locations. Higher values of magnesium in precipitation may also be sourced from dust, sea salts, or wood smoke that is particularly common during the fall and winter months.

Fall and winter are the most active seasons for storm systems in Southeast Alaska, therefore higher sodium and chloride levels during the winter are most likely due to sea spray. The larger contrasts between the atmosphere and ocean temperatures in the fall months have a tendency to increase the intensity of storms (Shulski and Wendler 2007). Water has a higher heat capacity than air so it takes longer for the sea surface temperature to cool, creating large temperature gradients and strong storms with high winds. With the NTN site being located a few kilometers from the marine waters of Auke Bay, it is likely that Na^+ is sourced from salts lofted into the air by winds and sea spray. Total annual Cl^- wet deposition maps from NADP demonstrate that chloride levels are chiefly associated with maritime effects because the highest deposition values are located within 100 miles of the ocean. Some of the highest chloride deposition values are in the Gulf Coast, Florida, and Pacific Northwest, where as much as 15 kg/ha or more may become deposited in precipitation (NADP 2007).

Summary of Findings Pertinent to Monitoring Program Design

Seasonal trends at the Juneau NTN precipitation-chemistry site illustrate that the summer season has higher average and median deposition values each year for nitrate (NO_3^-), sulfate (SO_4^{2-}), and ammonium (NH_4^+) compounds compared to their winter counterparts over the ten years of data. These conclusions match Schirokauer et al.'s (2014) assumption that most of the nitrogen and sulfur deposition occurred during the summer months when there are high amounts of tourist activity. These species are of particular interest in the design of an air pollution monitoring program since they are typically sourced from anthropogenic emissions. To a lesser extent, nitrogen and sulfur contaminants can also be sourced from a host of naturally occurring sources, such as wildfires, sea salts, or airborne dust. Base cations, which are presumed to originate from natural sources, have the opposite trend with higher winter deposition loads.

The use of invalid data may raise concerns about the credibility of the analysis, however, we are confident that our results are robust enough to make sound conclusions. We contacted individuals who were familiar with the device's operation during periods of extensive invalid data, and all agreed the data was viable for long-term analysis. While errors from invalid data are definitely possible, we want to stress that inter-seasonal variations using periods of 100% valid data show similar trends as years with invalid NTN data. This means that any elevated deposition loads from invalid data periods are not necessarily outliers.

Since ice and snow kept the collector's motor arm from closing, the site may have been subject to small amounts of dry deposition and evaporation, exposing the sample to small amounts of dust or sea salts. Any evaporation would basically cause *concentrations* of a particular substance in the sample to slightly increase, since the precipitation depth would slightly decrease. The product of these two values yields the deposition. If anything, the invalid winter data is more likely to have *higher* deposition loads than the summer data since the sample was partially exposed to the elements. However, our results still show that the summer N and S depositions are consistently higher for all ten years, and we believe this is quite robust in proving that there is higher acid and nitrogen deposition during the summer.

Lastly, as we were unable to assess the representativeness of the AK02 site for monitoring deposition in the 3 SEAN parks due to differences in sampler deployment lengths, future efforts could be pursued to better understand spatial and temporal variation in wet deposition to help inform selection of monitoring sites.

Chapter 3 – Wet Deposition of Atmospheric Mercury

Introduction

Mercury is one of the primary pollutants of concern in SEAN parks due to its toxicity, persistence, and ability to bioaccumulate in aquatic food webs. Even though small amounts of mercury exist naturally in the environment, most of the mercury deposited in Southeast Alaska is thought to originate from coal combustion in Asia, which is then transported across the Pacific Ocean in global atmospheric circulations.

In response to recommendations in the SEAN Vital Signs Monitoring Plan (Moynahan et al. 2008), a mercury precipitation collector was deployed in Bartlett Cove, GLBA (AK05, Figure 10) from March 2010 to May 2013. The station was operated by the NPS though NADP's Mercury Deposition Network (MDN). Our goal was to summarize the severity of mercury deposition at the Bartlett Cove site and document the overall spatial variation between nine surrounding MDN sites to inform an airborne contaminants monitoring program design. A preliminary summary of station data determined that annual mercury deposition was lower or similar to the three other Alaska MDN locations, and were generally much lower than other MDN sites in the Northwestern US and Western Canada. We discuss differences in mercury concentrations, deposition, and potential mercury sources during the period of AK05's deployment. Given small sample sizes, it was not feasible to directly assess the degree of correlation among stations on an ecologically relevant time scale (e.g., seasonal or annual) to quantify the importance of sustaining station operation. We do, however, offer several general observations regarding the value of the station's data within the context of the SEAN's contaminants monitoring programs.



Figure 10. The NADP-MDN precipitation collector in Bartlett Cove. NPS Photo.

NADP-Mercury Deposition Network (MDN) Background

As of April 2016, the MDN network consisted of approximately 112 active sites in 44 different states and providences, including Puerto Rico. The goal of the NADP/MDN is to provide consistent, long-term records of mercury concentrations in precipitation. Through this effort, long term patterns and changes in mercury levels can be used for future policy, climate, and modeling applications. Four mercury deposition sites are currently operational in Alaska: Dutch Harbor, Bettles, Kodiak, and Nome. The Nome AK04 MDN site is the newest in the state and was deployed on September 25, 2013. Many of the NTN precipitation collectors across the USA are co-located with MDN sites. However, the Bettles site in the Gates of the Arctic National Park is the only paired site in Alaska.

Similar to the NTN, MDN sites are strategically placed away from point sources of pollution. The wet deposition sites monitor precipitation and mercury concentration, from which a deposition load can be determined. Also keeping consistent with NTN, the samples must go through a stringent QA/QC test in order to qualify for publishing on the NADP website and use in seasonal and yearly statistics. Samples may be flagged for precipitation collector failure, mishandling, or contamination from foreign matter. Instead of a collector bucket, MDN sites are outfitted with a glass funnel and tube connecting the collection bottle to a specially designed enclosure. The sample is insulated and heated to maintain a temperature of 10-15°C. Heat rises up the collection element to melt any ice or snow. During warm weather, a fan draws filtered air from outside into the sampling enclosure. These precautions aid against the loss of the dissolved mercury sample. The samples are typically collected on Tuesday mornings and sent to the Mercury Analytical Laboratory (HAL) at Eurofins Frontier Global Sciences, Inc. in Seattle, WA, which analyzes the samples and sends the data back to the NADP.

The MDN follows many of the same protocols and standards as the NTN, and weekly data is freely available to download through the NADP's website. The NADP strongly encourages researchers not to use the invalid mercury data due to its volatility. If the device incurred a malfunction, the measurement is likely not correct due to evaporation or freezing. If the collection arm remains open during dry periods, the mercury sample becomes exposed to the ambient air and has the ability to re-cycle.

Methods

Only valid MDN data were used in our calculations of annual deposition loads because of the high volatility of mercury. Weekly mercury observations were much more complete than the Juneau NTN data, so the use of invalid data was not necessary. We gathered weekly data directly from the NADP/MDN website and calculated the annual PWM concentration and deposition loads for 2011 and 2012, since these were the only two complete years of data documented at the Bartlett Cove site. To avoid wasting the partial years of data from Bartlett Cove, we then calculated the deposition for March-December 2010 and January-May 2013 when the site was discontinued. We compared deposition at Bartlett Cove with nine other regional MDN sampling sites using the same length of data observations. Refer to the methodology section in the NTN analysis (Chapter 2) to learn how deposition and concentrations were calculated.

Mercury Monitoring Locations

We made direct comparisons with other MDN locations in Alaska and the regional vicinity. Besides Bartlett Cove, there were deposition data for three MDN locations in Alaska: Kodiak, Dutch Harbor, and Bettles. With relatively few local sources of mercury emissions in Alaska, we expected deposition to be fairly low. We then selected six more MDN sites that had data during the 2010-2013 period of study that were in the closest radial distance from Southeast Alaska. These locations were: Genesee, Alberta; Saturna Island, British Columbia; Makah National Fish Hatchery, WA; Seattle, WA; Glacier National Park, MT; and Yurok Tribal Lands, CA (Table 6 and Figure 11), some of which served to compare mercury deposition-severity in urban areas. Locations, data quality, climate specifics, and potential contaminant sources for the sites are outlined in Table 7.

Table 6. Details of the MDN sites used in this analysis.

Site	State/ Prov. & ID	Operating Agency	Latitude	Longitude	Elevation (m)
Bartlett Cove – Glacier Bay National Park	AK05	NPS Air Resources Division	58.4566	-135.8674	2
Bettles – Gates of the Arctic National Park	AK06	NPS Air Resources Division and Bureau of Land Management	66.9060	-151.6830	630
Dutch Harbor	AK00	State of AK Dept. of Environ. Conservation	53.8454	-166.5048	58
Kodiak	AK98	State of AK Dept. of Environ. Conservation	57.7189	-152.5617	7
Genesee	AB14	West Central Airshed Society and Jacques Whitford Stantec Axys Limited	53.3016	-114.2016	761
Glacier National Park – Fire Weather Station	MT05	NPS Air Resources Division	48.5102	-113.9970	964
Makah National Fish Hatchery	WA3	Makah National Fish Hatchery, NPS Air Resources Division	48.2892	-124.6519	6
Seattle / NOAA	WA18	Frontier Global Sciences and Illinois State Water Survey	47.6843	-122.2588	11
Saturna Island	BC16	Environment Canada	48.7753	-123.1281	196
Yurok Tribe – Requa	CA20	Yurok Tribe and Electric Power Research Institute	41.5588	-124.0916	110



Figure 11. Locations of the MDN sites used in this analysis.

Table 7. Start date, percentage of observations, location, and climate descriptions of each MDN site used in this analysis.

Location	Start Date	Data availability (% of valid obs)				Location / Potential Contaminant Sources	Approx Yearly Precip	Climate Description
		2010	2011	2012	2013			
AK05 Bartlett Cove	3/16/2010	93*	90*	75*	95*	Located on the edge of the 24.3 million-acre marine protected area in SE Alaska. Local emissions from small watercraft, Gustavus (pop. 429), and during the summer months, up to 2 cruise ships sailing past Bartlett Cove	200 cm	Maritime, temperate rainforest
AK06 Bettles	11/4/2008	79*	81*	71*	65*	Interior/Northern Alaska just south of Brooks Range near the small village of Bettles (pop. 12) on Koyukuk River	40 cm	Subarctic climate, with most of precip occurring during the mild summer months
AK00 Dutch Harbor	9/25/2009	24	81*	81*	20	500 miles west of the AK mainland, making it the closest to any anthropogenic transport from Asia. 4 mi. from town of Unalaska/Dutch Harbor (pop. 4,300)	110 cm	Rainy, maritime location
AK98 Kodiak	9/18/2007	38	88*	92*	80*	Located on Kodiak Island, approximately 8 mi. from the town (pop. 6,500). Centered around marine transportation and commercial fishing	250 cm	Subpolar-oceanic: precip is heavy year-round
AB14 Genesee	7/18/2006	60	69	75*	70*	Flat and agrarian region 40 mi. SW of Edmonton, AB	50 cm	Cold continental climate with cool short summers
MT05 Glacier National Park	10/28/2003	83*	90*	92*	95*	Near Lake McDonald and town of West Glacier, MT. 30 miles from Kalispell, MT. Large mountains surrounding area in the western side of the national park	110 cm	Typically a warmer and wetter climate than the rest of the park since in Pacific Watershed
WA03 Makah National Fish Hatchery	3/2/2007	86*	90*	79*	95*	Located on the grounds of a fish hatchery and Indian Reservation on Cape Flattery in extreme western WA	240 cm	Maritime climate heavily influenced by Pacific Ocean
WA18 Seattle	3/19/1996	64	100	87*	95*	Only MDN location in a densely populated, urban city	100 cm	Temperate marine/oceanic climate: rain and cloudy skies common (rain shadow)
BC16 Saturna Island	9/1/2009	83*	27	96*	100*	Gulf Islands National Park and Preserve in BC, 35 mi south of Vancouver and about 90 mi NW of Seattle	90 cm	Mild, with relatively dry Mediterranean-like influences (rain shadow)
CA20 Yurok Tribe	8/18/2006	88*	98*	92*	100*	Furthest location from AK05. Northern CA directly adjacent to the Pacific Ocean and redwood forests	200 cm	Oceanic, semi-Mediterranean climate, often being one of the wettest locations in CA

*Data period contains more than 70% of observations (also shaded in gray).

Results and Discussion

Yearly Time Scale

According to the annual PWM concentrations and deposition values for all ten MDN sites (Table 8 and Figures 12-13), the Alaska locations generally had the least amount of mercury contamination in precipitation samples. During the 2010-2012, Bartlett Cove received the second lowest annual mercury *deposition* (1.939, 2.899, 3.104 $\mu\text{g}/\text{m}^2$, respectively), only surpassing Bettles and Kodiak by small amounts. It is likely that Kodiak received the lowest deposition in 2010 (1.261 $\mu\text{g}/\text{m}^2$) because there were not enough valid observations. The highest mercury deposition generally occurred in Seattle and Makah National Fish Hatchery, WA (Table 8). These measurements are likely accurate since all years had a notable number of observations; however Seattle fell slightly short to 64% completeness in 2010. Wet deposition in Table 8 denoted with an asterisk should be inferred with caution, as there were less than 70% of possible valid observations in the dataset. Bartlett Cove, however, was more than 90% complete, with the exception of 78% in 2012.

With the exception of the partial year of 2013, yearly PWM mercury *concentrations* (Figure 12) were the lowest in Bartlett Cove compared to the nine other sites. The concentrations for 2010-2013 were 1.546, 1.495, 2.251, and 1.733 ng/L, respectively. Dutch Harbor did not have enough valid observations in 2013, which likely reflects the low reading. The low rainfall concentrations mean that with any given rainfall observation at Bartlett Cove, its concentration of mercury was typically the lowest in the sample set. The second and third lowest rainfall concentrations generally occurred in Dutch Harbor and Kodiak. One reason for the lower mercury concentrations at these sites compared to Bettles can be explained by the amount of precipitation received. Since Bartlett Cove, Dutch Harbor and Kodiak are rainy locations, atmospheric mercury may tend to get rained-out during the beginning of a storm, resulting in lower, more diluted PWM concentrations. Drier locations will accumulate atmospheric mercury in clouds and water vapor until it is removed by rainfall. The highest PWM concentrations occurred in Genesee, AB, which was one of our driest MDN locations. Seattle, WA also had high PWM concentrations, likely because of its urban location (Table 8).

From this analysis, deposition at many of the Pacific NW sites was 2-3 times higher than most Alaska locations, including Bartlett Cove. This is the same case for the PWM concentrations, where some Northwestern US sites can be 2-8 times higher. To put these values in perspective, a study by Guo et al. (2008) determined that the annual PWM concentration and deposition values of total mercury at an industrial region in China to be 36 ng/L and 34.7 $\mu\text{g}/\text{m}^2$, respectively. These values were averages measured from five sites in the Wujian River Basin in Guizhou, China, one of the most mercury-contaminated region in Asia. Mercury concentrations and deposition in this part of China are upwards of 18 (and 12) times as much as seen in Bartlett Cove, respectively.

Table 8. Mercury statistics at each MDN site in Alaska, and in the broad geographical region.

Year	Parameter	Poss	Bartlett Cove (AK05)	Bettles (AK06)	Dutch Harbor (AK00)	Kodiak (AK98)	Saturna Island (BC16)	Seattle (WA18)	Makah Nat'l Fish Hatchery (WA03)	Genesee (AB14)	Glacier Nat'l Park (MT05)	Yurok Tribe (CA20)
2010	<i>N</i> ^A	42	39 ^D	33	10	16	35	27	36	25	35	37
	Weekly Mean Deposition (ng/m ²) ^B	-	44.83	84.32	96.42	87.20	64.46	111.86	211.75	92.03	121.42	167.43
	Total Precipitation (cm)	-	125.38	27.61	88.18	57.26	65.17	78.19	150.69	44.06	83.79	155.02
	Yearly PW Mean Concentration (ng/L)	-	1.546	5.855	4.404	2.203	5.548	5.081	5.058	13.996	5.730	4.392
	Yearly PWT Deposition (µg/m ²) ^C	-	1.939	2.857	3.884*	1.261*	3.615	3.973*	7.622	6.167*	4.801	6.809
2011	<i>N</i> ^A	52	47	42	42	46	14	52	47	36	47	51
	Weekly Mean Deposition (ng/m ²) ^B	-	54.44	53.73	115.00	106.42	95.49	113.24	136.61	116.82	123.54	144.97
	Total Precipitation (cm)	-	190.38	43.51	225.51	223.66	81.24	85.59	242.86	45.72	105.97	167.08
	Yearly PW Mean Concentration (ng/L)	-	1.495	5.509	2.464	2.569	3.920	6.605	3.241	11.075	6.132	4.401
	Yearly PWT Deposition (µg/m ²) ^C	-	2.899	2.397	5.554	5.743	3.126*	5.652	7.871	5.046*	6.498	7.353
2012	<i>N</i> ^A	52	39	37	42	48	50	45	41	39	48	48
	Weekly Mean Deposition (ng/m ²) ^B	-	68.63	45.96	81.42	77.81	146.85	193.46	173.81	135.00	166.97	156.73
	Total Precipitation (cm)	-	137.96	32.741	105.97	177.33	90.19	114.50	235.17	49.73	117.27	236.00
	Yearly PW Mean Concentration (ng/L)	-	2.251	5.909	3.286	2.221	8.56	8.919	3.405	12.843	7.435	3.673
	Yearly PWT Deposition (µg/m ²) ^C	-	3.104	1.935	3.481	3.937	7.720	10.211	8.007	6.387	8.718	8.668

^A *N* = number of weeks with valid samples.

^B The weekly mean deposition (ng/m²) is calculated by taking the precipitation value and multiplying it by the Hg concentration (ng/L) of the sample.

^C Yearly Hg depositions are reported in µg/m² (1000 ng/m² = 1 µg/m²), and reflect only valid samples during the period of interest.

^D Recall that 2010 and 2013 contain partial years of data when the Bartlett Cove site was operational.

Table 8 (continued). Mercury statistics at each MDN site in Alaska, and in the broad geographical region.

Year	Parameter	Poss	Bartlett Cove (AK05)	Bettles (AK06)	Dutch Harbor (AK00)	Kodiak (AK98)	Saturna Island (BC16)	Seattle (WA18)	Makah Nat'l Fish Hatchery (WA03)	Genesee (AB14)	Glacier Nat'l Park (MT05)	Yurok Tribe (CA20)
2013	<i>N</i> ^A	20	19 ^D	13	4	16	20	19	19	14	19	20
	Weekly Mean Deposition (ng/m ²) ^B	-	72.34	28.15	62.95	89.86	109.62	202.89	226.35	49.44	84.62	116.60
	Total Precipitation (cm)	-	79.32	9.30	19.13	85.83	33.61	38.10	91.90	11.25	27.46	48.21
	Yearly PW Mean Concentration (ng/L)	-	1.733	3.908	1.316	1.885	6.524	10.118	4.680	7.408	5.905	4.837
	Yearly PWT Deposition (µg/m ²) ^C	-	1.374	0.363*	0.252*	1.618	2.193	3.855	4.301	0.834*	1.622	2.332
2010- 2013	AVERAGE Weekly Deposition (ng/m ²)	-	58.04	56.62	96.59	89.84	110.32	150.14	178.14	109.33	132.07	150.28

^A *N* = number of weeks with valid samples.

^B The weekly mean deposition (ng/m²) is calculated by taking the precipitation value and multiplying it by the Hg concentration (ng/L) of the sample.

^C Yearly Hg depositions are reported in µg/m² (1000 ng/m² = 1 µg/m²), and reflect only valid samples during the period of interest.

^D Recall that 2010 and 2013 contain partial years of data when the Bartlett Cove site was operational.

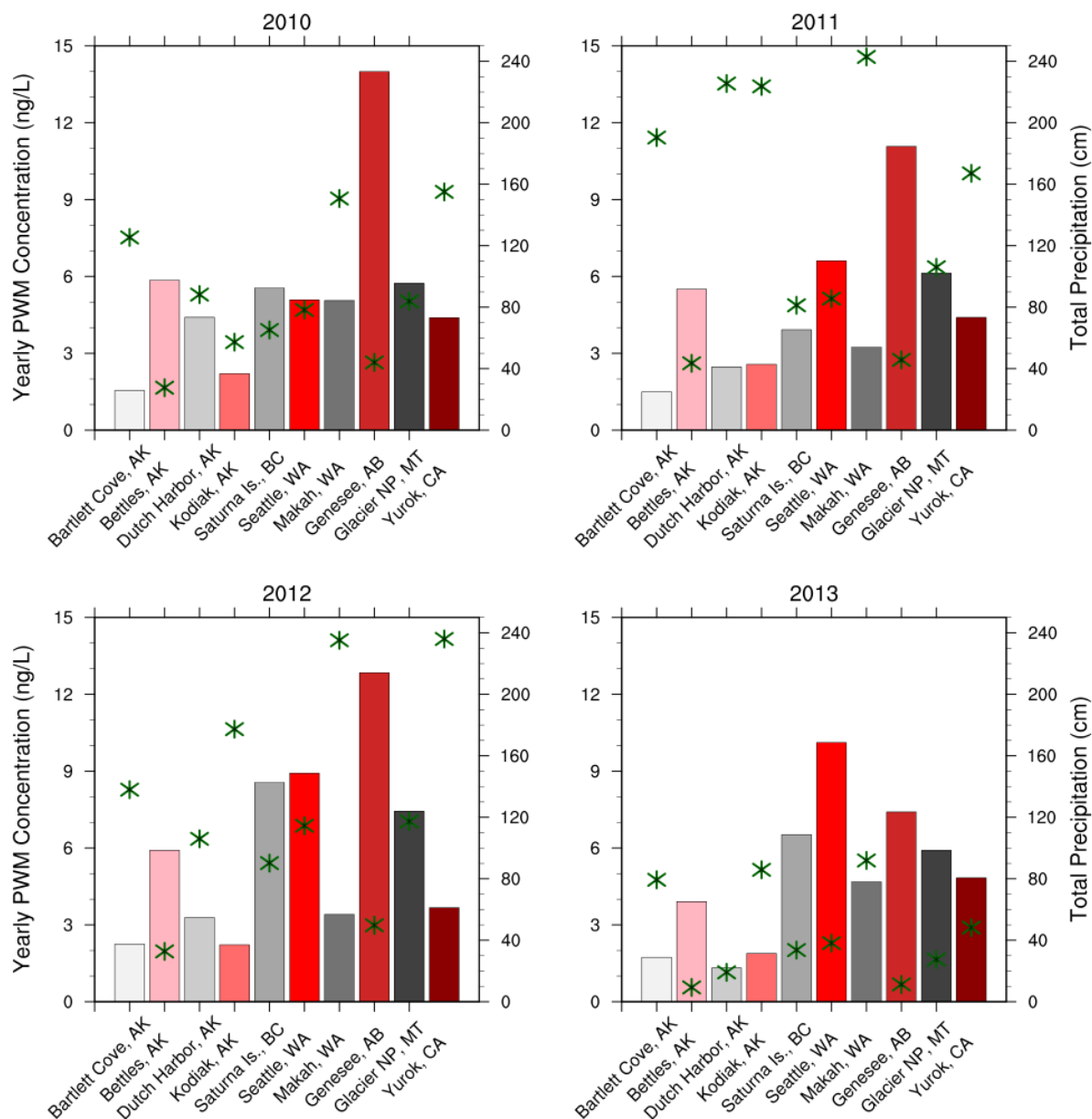


Figure 12. Annual precipitation-weighted mean (PWM) concentrations for each year of the study period. Recall that 2010 and 2013 are partial years. Green asterisks represent the total precipitation received at each site during the period of interest. The precipitation scale is on the right y-axis.

Weekly Time Scale

On the weekly time scale, Bettles and Bartlett Cove represent the two locations with lowest average weekly mercury deposition, at 56.62 and 58.62 ng/m², respectively. These are direct laboratory measurements from the precipitation sample (weekly concentration multiplied by precipitation depth) and are not precipitation-weighted. It is important to remember that there is only measurable mercury wet deposition if it actually rains. Therefore, weekly measurements were considered “valid” even if the precipitation collector did not receive any accumulation. The reading for that week would be 0

ng/m². Dry deposition of mercury is not measured at these locations, but may be an important contributor to total mercury deposition, particularly in dry climates like Bettles or Genesee, AB.

In contrast to the lowest averages, the locations with the highest average weekly depositions were the Yurok Tribal Lands, CA and Seattle, WA at around 150.2 ng/m², as well as Makah National Fish Hatchery, WA at 178.14 ng/m². Rainfall at some of these locations can have upwards of 2.5-3 times the mercury concentration than seen in Bartlett Cove.

A negative correlation in weekly rainfall depth and weekly mercury concentration in Figures 14-16 generally indicates that mercury concentrations in precipitation decrease with increasing amounts of rainfall. This is likely due to the fact that much of the gaseous and particulate mercury is removed from the atmosphere upon start of the rain event (Hall et al. 2005; Seo et al. 2012). Some variability in this data shows that other processes could contribute to this effect (Guo et al. 2008). Locations with higher overall mercury content in precipitation generally showed a larger spread in weekly concentrations along the y-axis, and experienced higher frequency events with high concentrations. Hall et al. (2005) showed that samples with a volume of less than 100 mL were significantly higher than those with larger volumes, indicating the potential for mercury “wash out.”

Figures 14-16 also provide a glimpse on the amount of precipitation that fell during each week of sample collection. Samples that show more spread on the x-axis are generally rainy locations (e.g. Bartlett Cove, Kodiak, Dutch Harbor, Makah Fish Hatchery, WA, and Yurok, CA), while drier locations are more concentrated towards the lower end of the x-axis scale (Bettles, Genesee, AB, and Glacier National Park, MT). Figure 17 illustrates how precipitation depth and mercury deposition are related at Bartlett Cove during the period of interest. Since the weekly deposition (ng/L) is a function of the rainfall depth (mm), we expect a good relationship to occur. Almost 75% of the change in mercury deposition is predicted by the change in rainfall at Bartlett Cove ($r=0.738$; Figure 17). Other locations showed a similar trend. The total deposition generally increases with increasing amounts of rainfall, but is not always the case. Seo et al. (2012) found a similar trend.

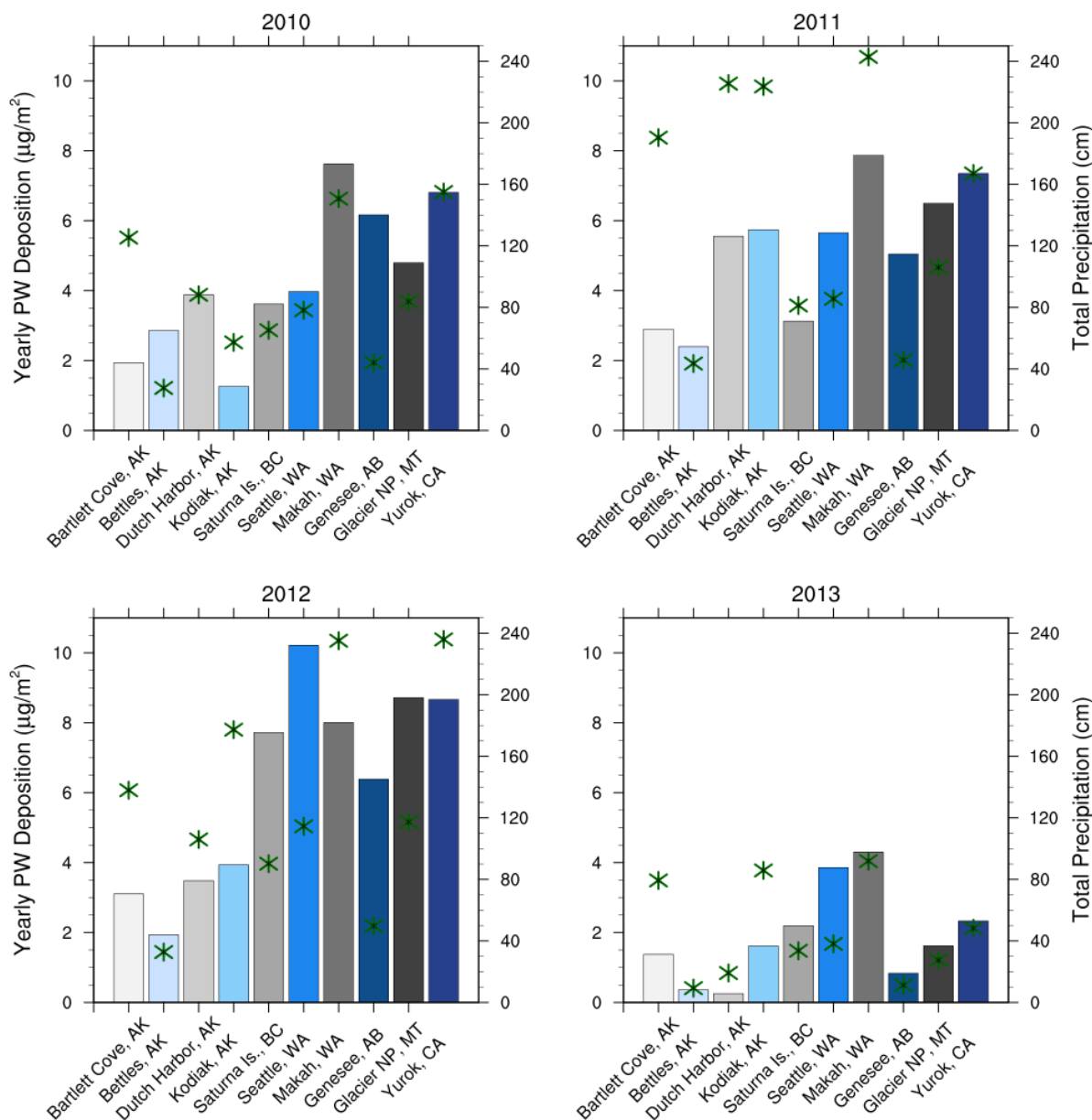


Figure 13. Annual total deposition for each year of the study period. Recall that 2010 and 2013 are partial years. Green asterisks represent the total precipitation received at each site during the period of interest. The precipitation scale is on the right y-axis. Deposition is calculated by multiplying the precipitation-weighted mean concentration by the total precipitation during that period of interest.

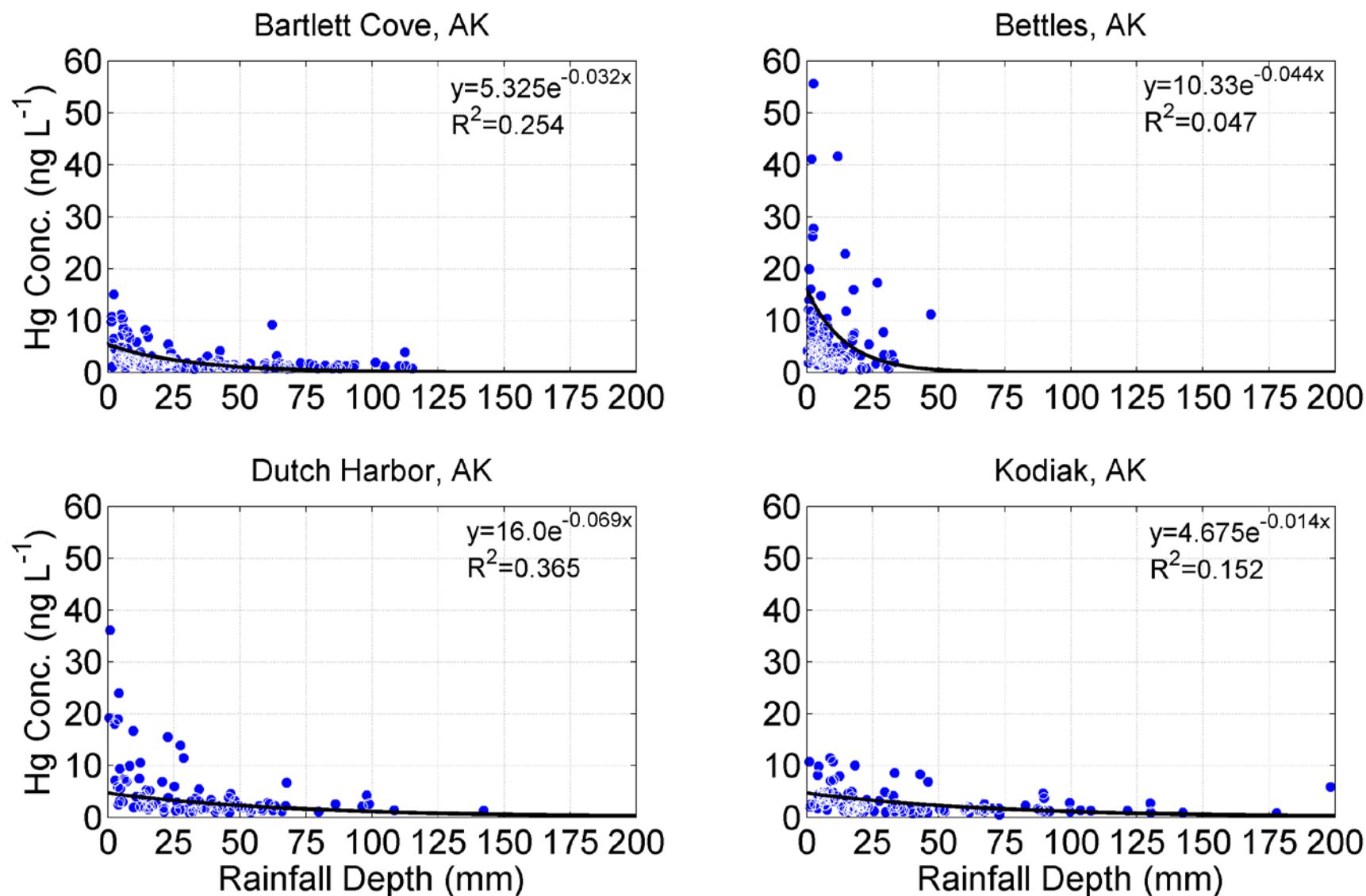


Figure 14. Rainfall depth (mm) versus mercury concentration (ng/L) for the four Alaska NADP-MDN locations with exponential trend-lines to illustrate mercury “washout”. The plots represent only valid MDN observations from spring 2010 to spring 2013.

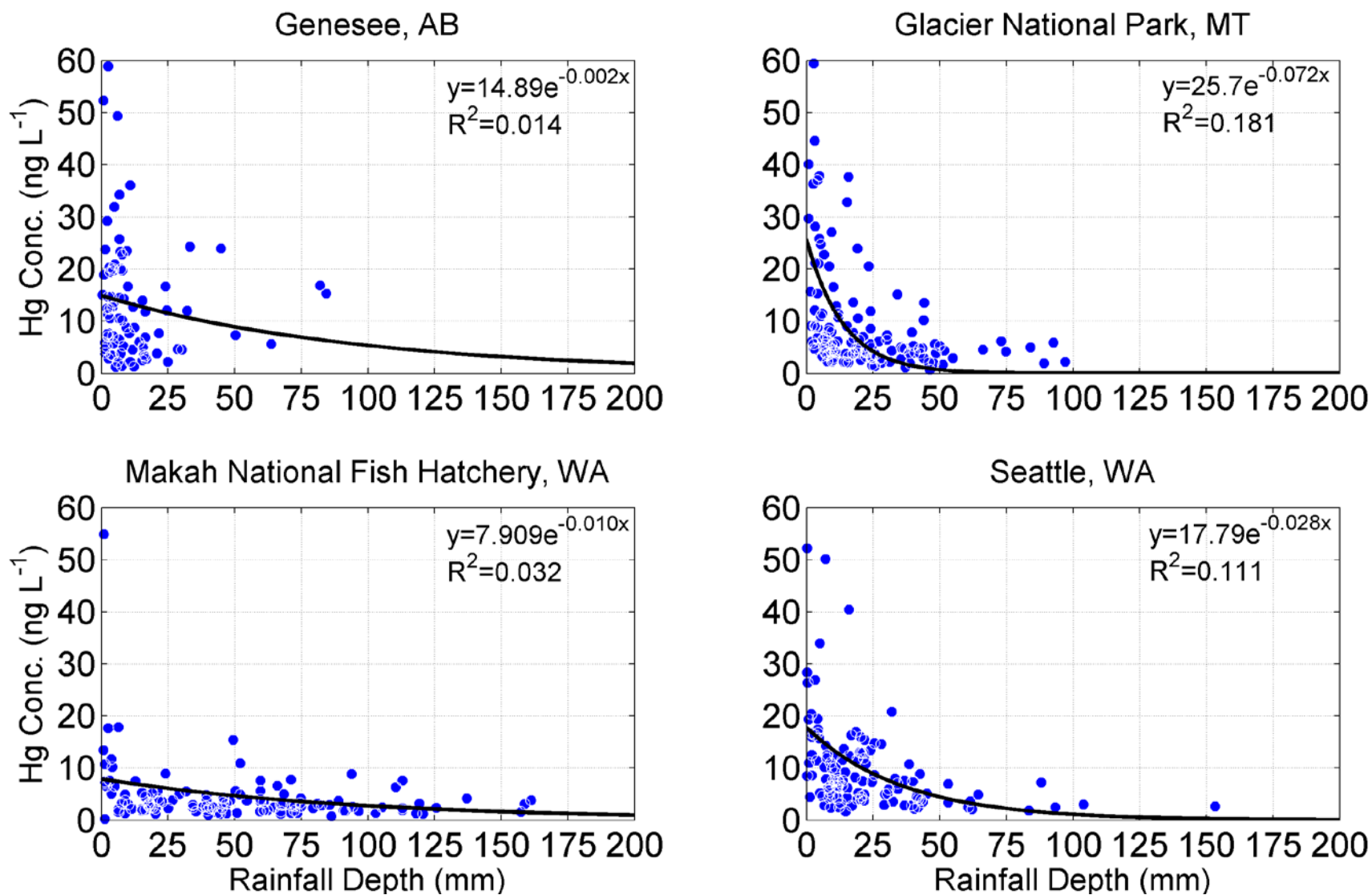


Figure 15. Rainfall depth (mm) versus mercury concentration (ng/L) plots for a regional comparison between the Alaska NADP-MDN locations. The plots include exponential trend lines to illustrate mercury “washout”. Only valid MDN observations from spring 2010 to spring 2013 are represented.

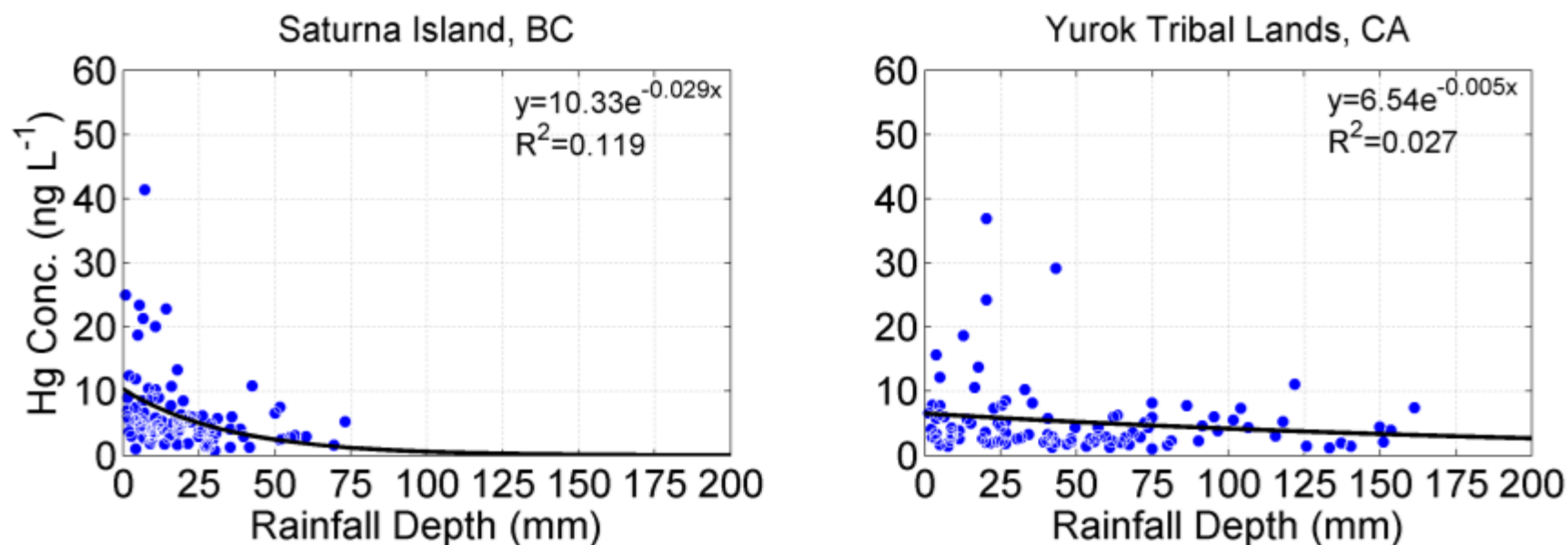


Figure 16. Rainfall depth (mm) versus mercury concentration (ng/L) plots for a regional comparison between the Alaska NADP-MDN locations. The plots include exponential trend lines to illustrate mercury “washout”. Only valid MDN observations from spring 2010 to spring 2013 are represented.

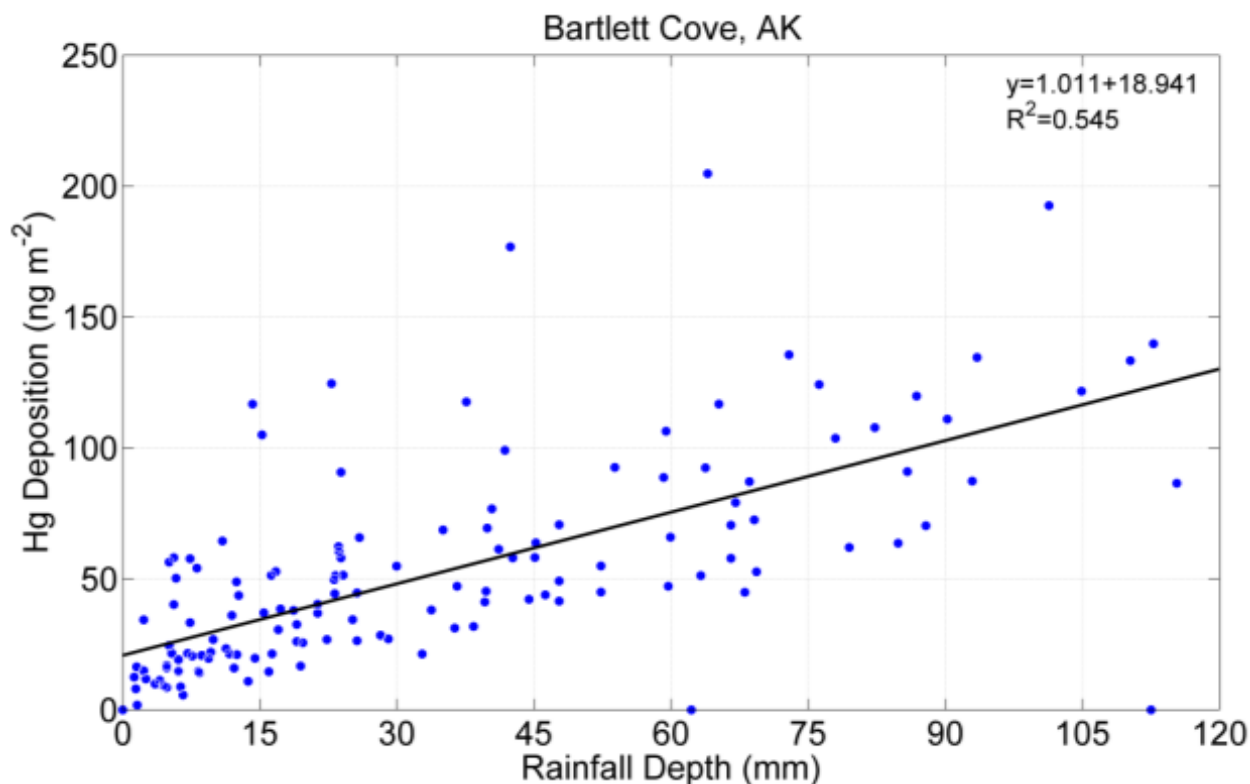


Figure 17. Relationship between precipitation depth and weekly mercury deposition (ng/m^2) at the Bartlett Cove NADP-MDN site. Only valid MDN observations from spring 2010 to spring 2013 are presented (Table 8). Mercury deposition is calculated by multiplying the depth (in mm) by the mercury concentration (ng/L). Since the deposition is a function of the depth, we expect a good relationship to occur ($r=0.738$). This means that almost 75% of the change in mercury deposition is predicted by the change in rainfall for this location. Wet deposition generally increases with increasing depth, even though the sample becomes diluted (Seo et al. 2012).

Potential Sources and Variability

There are very few local sources of atmospheric mercury in Alaska, meaning that most of the detectable mercury in Southeast Alaska's precipitation is sourced from thousands of miles away. China is regarded by some studies as the world's largest contributor of atmospheric mercury (Zhang and Wong 2006; Jiang et al., 2006). The burning of high-mercury coal is the predominant source of mercury emissions, which is generally used in manufacturing, winter heating, and cooking (Feng et al. 2004). Higher mercury concentrations in winter and spring precipitation may be the direct result of increased winter coal burning (Guo et al. 2009). Yellow-sand dust storms over Asia have also resulted in elevated spring mercury precipitation concentrations, particularly over Korea (Seo et al. 2012), and have been known to become transported over long distances (Sassen 2005). Studies by Prestbo and Gay (2009) and Hall et al. (2005) however, show that rainfall mercury concentrations in the US are the highest in the summer, indicating that seasonal trends in precipitation patterns, meteorological transport, and seasonal emissions play important roles. Due to increased convection and mixing, warmer summer temperatures may result in increased mercury deposition (Keeler et al. 2005).

Long-range transport in Southeast Alaska is shown in Figure 18 by the National Oceanic and Atmospheric Administration (NOAA) HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectories; Draxler and Rolph 2014) model backward trajectory. The plot depicts the origin of air parcels at 500 m, 1000 m, and 5000 m starting heights, with the starting-point set at Bartlett Cove. This seven-day backward trajectory from June 7, 2011 shows that the air parcels impacting Southeast Alaska had East Asian origins. Wet mercury deposition during this week of observations were low due to low amounts of precipitation, but concentrations were relatively high (11 ng/L).

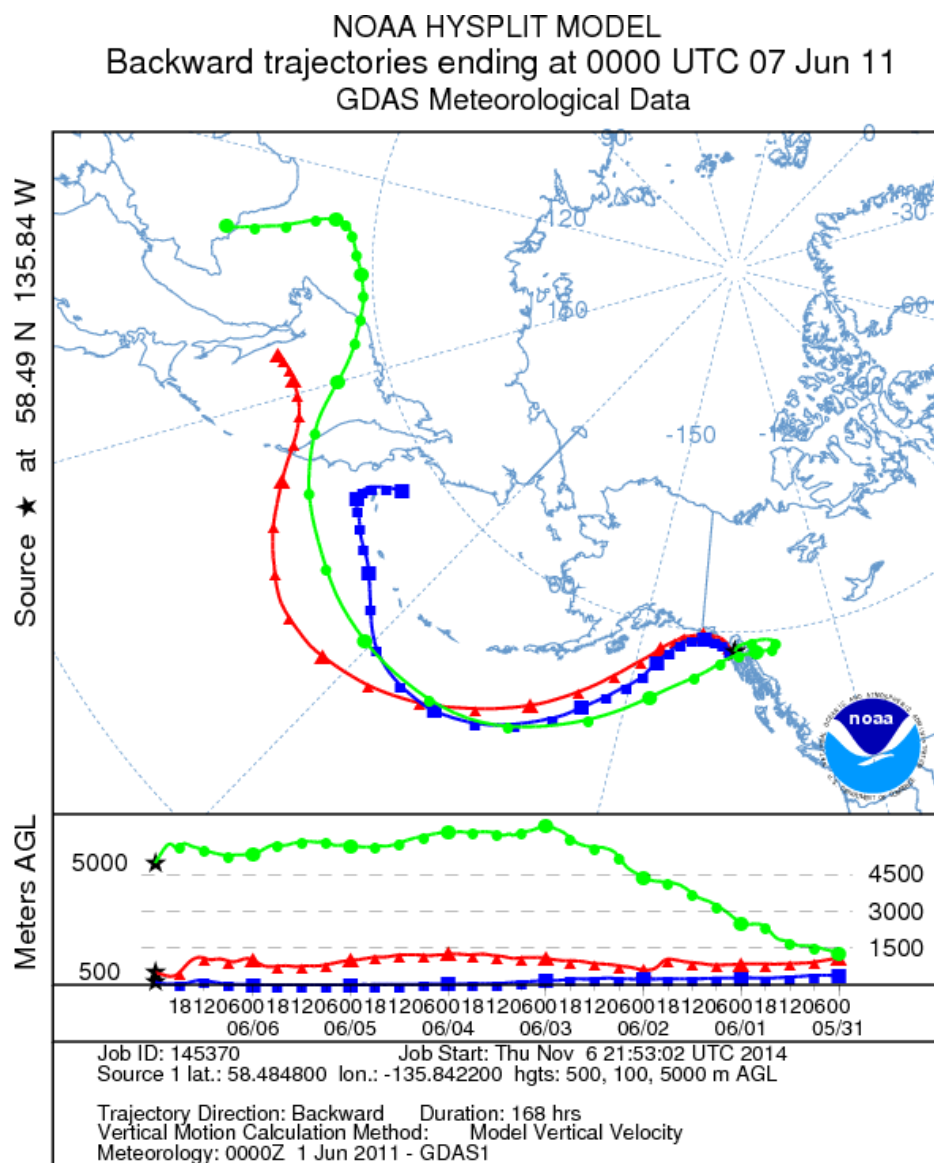


Figure 18. Example of a NOAA HYSPLIT model backward trajectory for 500 m, 1000 m, and 5000 m heights starting May 31, 2011 and ending at Bartlett Cove on June 6, 2011. Trajectories can be retrieved from <http://www.arl.noaa.gov/HYSPLIT.php>.

Long periods of data are necessary in order to evaluate atmospheric models and the rate of wet deposition. A study by Jaegle (2010) used the GEOS-Chem chemical transport model (Bey et al.

2001) to simulate atmospheric mercury. Figure 19 shows the shaded contours of modeled annual mean mercury wet deposition plotted with the observed annual deposition of 103 MDN sites in 2008. Jaegle (2010) found that the model slightly overestimated annual mercury deposition ($9.7 \pm 4.2 \mu\text{g}/\text{m}^2/\text{yr}$ vs. $10.6 \pm 3.7 \mu\text{g}/\text{m}^2/\text{yr}$). The model showed good agreement with the Kodiak MDN measurements. The author found that anthropogenic emissions from Asia were the single largest source of mercury deposition over Alaska, the Bering Sea, and the North Gulf of Alaska, amounting to approximately 22-24% of the total deposition load. When this report was published, there was no long-term MDN site in Southeast Alaska, and it was suggested for a MDN site be deployed in Southeast Alaska since the model results simulated some of the highest state-wide deposition loads here (roughly $7\text{-}10 \mu\text{g}/\text{m}^2/\text{yr}$ compared to $2\text{-}5 \mu\text{g}/\text{m}^2/\text{yr}$ in the rest of Alaska; Jaegle 2010). However, we have shown that the annual deposition loads from 2011 and 2012 in Bartlett Cove were as much as 2-3 times lower than predicted, averaging around $3 \mu\text{g}/\text{m}^2/\text{yr}$. These values indicate that the model overestimated the amount of mercury transport, rainfall amounts, and/or local maritime or continental mercury sources. While the resolution of the model was only $4^\circ \times 5^\circ$, it still offers a glimpse at mercury distribution and transport, even though predictions were inaccurate for Southeast Alaska.

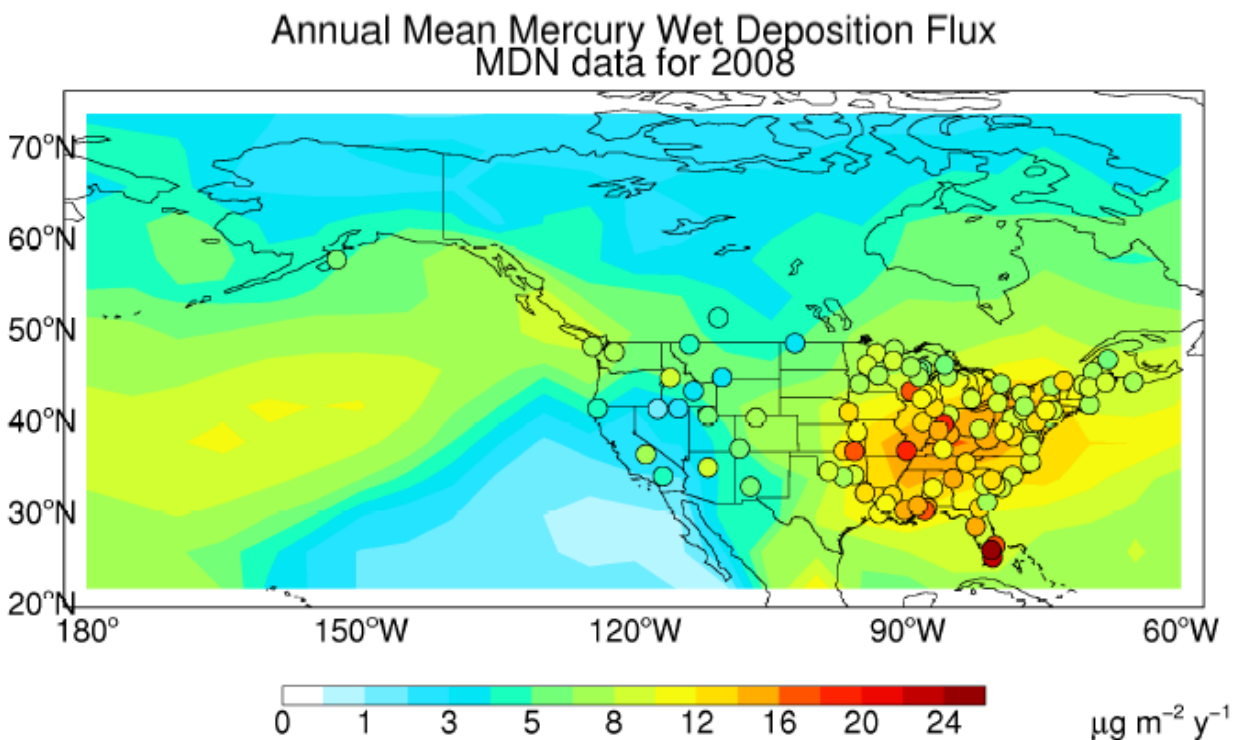


Figure 19. GEOS-Chem atmospheric model simulation of mercury wet deposition for 2008. The shaded dots represent the annual observed mercury deposition at 108 MDN sites with over 75% complete observations (adopted from Jaegle 2010).

It is also possible that yearly variations in mercury deposition could be the result of certain large-scale weather patterns that influence the amount of precipitation. One that may affect Southeast Alaska is the Pacific Decadal Oscillation (PDO), a detectable sea surface temperature (SST) anomaly in the Pacific Ocean. During the positive phase, SSTs are warmer than normal in the eastern Pacific, resulting in above average temperatures and precipitation for Southeast Alaska. The negative phase results in the opposite. The PDO has been fluctuating since the mid-2000s, but more negative PDO years appear to outweigh the positive phases. The strong variability in the PDO makes it difficult to use as the sole predictor for Southeast Alaska's weather. The total precipitation in Bartlett Cove for the 2011 and 2012 was 190.38 and 137.96 cm, respectively, with the average being approximately 175 cm. Negative PDO years should experience lower than average rainfall, potentially resulting in lower total depositions and higher mercury concentrations.

Summary of Findings Pertinent to Monitoring Program Design

Our results show that Bartlett Cove currently remains relatively pristine with regards to precipitation-mercury content. Since local sources of mercury are limited, model studies have shown that a great fraction of the mercury deposited over Alaska and the Western US are likely to be of Asian origin. There are large spatial differences between mercury concentrations and depositions in the 900 miles between Bartlett Cove and several of the MDN sites in Western Washington. The discontinuation of the AK05 site in GLBA has opened a 1,400 mile gap between Kodiak and the Makah, WA MDN sites, and there is now little data versus evidence to determine the current trends in wet mercury deposition in the SEAN. The varying latitudes and longitudes of the other MDN sites in Alaska mean that they are not exactly representative of the deposition occurring in the SEAN since precipitation patterns, intensities, and sources of local pollution vary. Furthermore, the climate characteristics of the regions are quite different. While there are other efficient, cost-effective methods of monitoring mercury accumulation in ecosystems, including periodic sampling of tissue concentrations from natural bioaccumulators such as lichens or fish, the consequences of missing detection of important short-term mercury deposition events, as well as long-term increasing or decreasing deposition trends, should be considered during development of a long-term airborne contaminants monitoring program for the SEAN.

Chapter 4 – Comparisons of Ambient Air Quality between Model Simulations and Observed Measurements

Introduction

Cruise ships have the potential to impact the ambient air quality and visibility in each SEAN Park by releasing large quantities of nitrogen and sulfur emissions through the combustion of marine diesel fuel. The goal in this chapter was to compare results from WRF/Chem model simulations from Mölders et al. (2013) with ambient atmospheric pollutant samplers (Ogawa samplers) deployed in the SEAN parks in 2008 and 2009 (Schirokauer et al. 2014). This comparison tested how well the model predicted ambient air quality and assessed the spatial variation in airborne concentrations of nitrogen and sulfur derivatives from cruise ship emissions. It also estimated the contribution of cruise ship emissions towards ambient NO_2 , NO_x , HNO_3 , and SO_2 concentrations. Therefore, the purpose of this chapter is twofold: 1) the model results may help inform a future long-monitoring program design and the potential placement of future Ogawa samplers in the SEAN parks; and 2) all numerical computer models must be evaluated through actual in-situ observations in order to test the model's credibility for other applications.

WRF/Chem stands for the Weather Research and Forecasting Model (Skamarock et al. 2008) inline coupled with a Chemistry module (Grell et al. 2005; Peckham et al. 2011). WRF/Chem is a non-hydrostatic mesoscale weather forecasting model, meaning that complex mathematical equations are solved over a regional domain, rather than globally. The model has been shown to produce relatively good results for meteorological applications in Alaska (Hines and Bromwich 2008, Mölders and Kramm 2010, Mölders et al. 2011, among others). This version of the model simulated meteorological conditions well for the 2008 summer season (Pirhalla 2014).

Background information regarding the model's advantages and limitations is presented first, followed by the methodology of our analysis. We then provide detailed explanations and correlations between simulated and observed NO_2 , NO_x , HNO_3 , and SO_2 data. The chapter concludes with a summary of pertinent information that could influence the design of a long term monitoring program.

Methods

The model was run for a period of 124 days from May 15 to September 15 of each year to account for the typical summer cruise ship season. Idealized vertical profiles of background chemistry species typical for Southeast Alaska were used to initialize the chemical boundary conditions (Mölders et al. 2013). Anthropogenic emissions were fed into the model through an activity-based cruise ship emission inventory. Automated Information Systems (AIS) aboard cruise ships store exact speed and GPS locations of the vessel. Based on the speed documented in the AIS, a ship's operating mode could be determined (e.g. berthing, maneuvering, and cruising). Each operation mode assumed a certain percentage of the full engine load, which allowed for an emission rate to be calculated. These WRF/Chem simulations only consider cruise ship emissions, since the original modeling goal was to understand cruise ships' effect on visibility and particulate matter concentrations in Southeast Alaska, with special emphasis on GLBA. The model simulations do not take into account long-range

transport or other emissions sources such as automobiles, factories, wood burning, or forest fires. However, it does include natural emissions such as sea salts, dust, and gas-phase chemistry reactions.

We retrieved the archived Ogawa data and compared it against NO_2 , NO_x , SO_2 , and HNO_3 variables in the WRF/Chem simulations. Eight passive ambient sites [KLGO (6), GLBA (1), and SITK (1)] were deployed from April to October in 2008 and 2009, and their filters were analyzed on a weekly basis. The eight ambient Ogawa sites fell within four different locations, or grid cells, over the WRF/Chem domain. This occurred because the model's resolution was $7 \text{ km} \times 7 \text{ km}$ and some sites were located in close proximity of each other, but within the same grid cell. Four sites were included in the same grid cell in Skagway: Lower Dewey, Dewey 1700, Sturgills, and Icy Junction. These sites were located relatively close to each other, but at varying elevations. WRF/Chem assumed this grid cell to have a terrain height of over 800 m, so changing the vertical levels to match these sites would not apply. We later discarded the Icy Junction site since there were problems with the Ogawa data. Dyea and Chilkoot Saintry Hill were also in the same grid cell.

We first extracted hourly WRF/Chem data from the same latitude and longitude as each of the 8 Ogawa sites, which corresponded to a particular model grid cell. The hourly information was converted to average weekly airborne concentrations that matched the same time scale as the Ogawa exposure periods. To aid us in visually demonstrating the spatial distribution of atmospheric contaminants in Southeast Alaska, we then plotted the average weekly atmospheric contaminant concentrations, which provide a helpful way of visualizing the severity and spread of the pollutants (Figure 20). We then made comparisons with the WRF/Chem-simulated parameters against the average weekly Ogawa concentrations through non-parametric Spearman's rank correlation coefficients (r_s) in to test the statistical dependence between the two datasets using the *cor.test* function in *R* (R Core Team 2013). Since the measured Ogawa data had high variability due to large dips and spikes in weekly airborne concentrations (Appendix B), we decided to use the non-parametric Spearman correlation instead of the Pearson pair-wise product-moment correlation. The Pearson approach assumes a normal distribution, which this data did not have. After running both correlation methods, the results were not drastically different, but we present Spearman's correlation since it is most appropriate.

Results and Discussion

In general, WRF/Chem underestimated most of the NO_2 , NO_x , SO_2 , and HNO_3 concentrations, which was to be expected because cruise ships were the only anthropogenic emission source considered in the model. However, the model did overestimate NO_2 and SO_2 concentrations at some locations during the 2008 and 2009 tourist seasons (Table 9 and Appendix B). It also had difficulties picking up large changes or sudden spikes in the data and typically did not capture them.

NO_2 and NO_x

NO_2 is a gaseous air pollutant that typically forms through fossil fuel combustion. It is an orange-brown gas that strongly absorbs visible light, dramatically contributing to visibility reduction, especially in regions with high relative humidity (Finlayson-Pitts and Pitts 2000). WRF/Chem most accurately simulated ambient concentrations of NO_2 . The model captured the general temporal pattern of NO_2 concentrations, but accurately simulated large spikes or dips only occasionally.

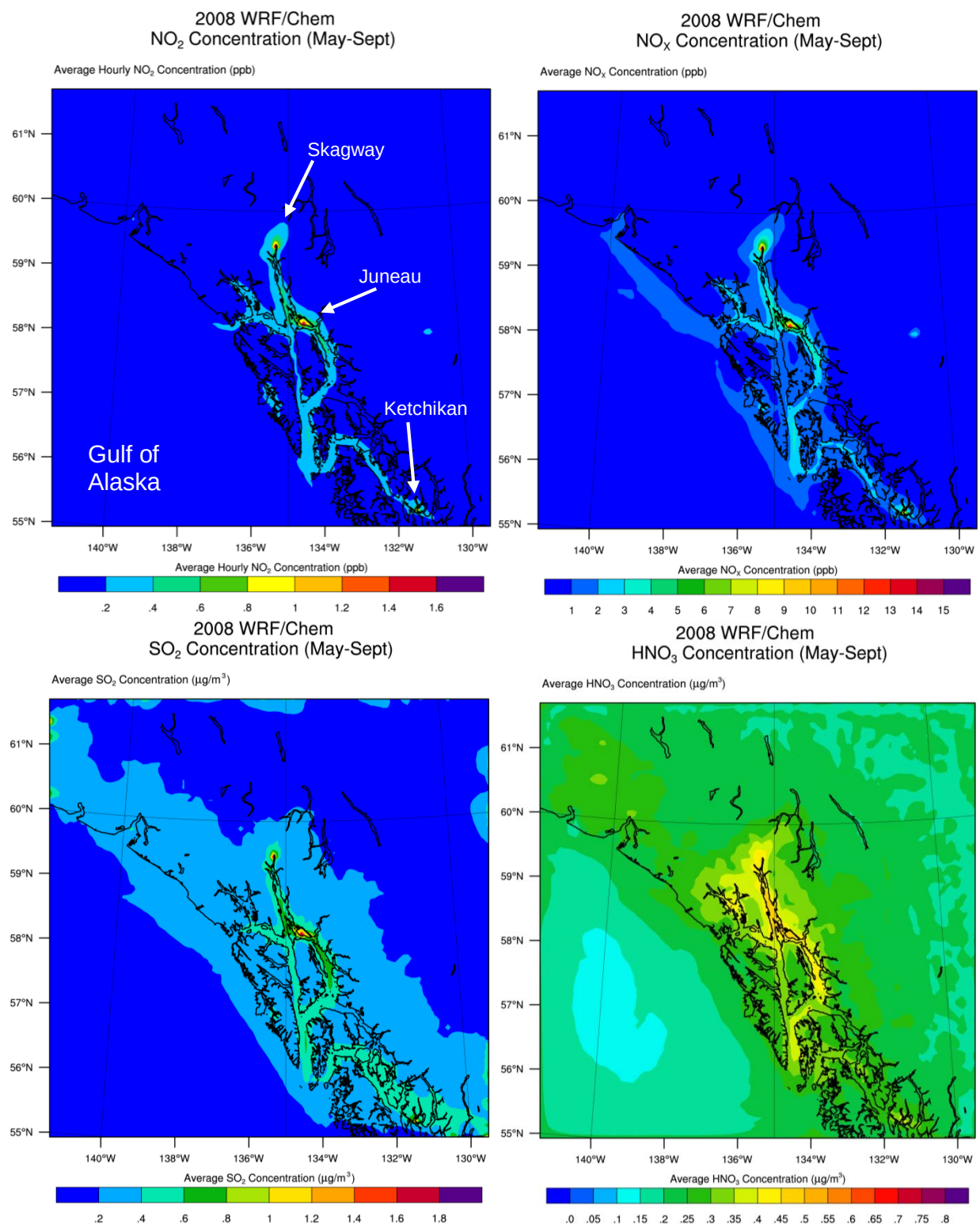


Figure 20. WRF/Chem simulated average weekly concentrations of NO₂, NO_x (NO+NO₂), SO₂, and HNO₃ for the 2008 summer tourist season. The plots show the distribution of cruise ship emissions at the surface model level.

Table 9. Mean seasonal ambient atmospheric concentrations of primary and secondary combustion products during the WRF/Chem simulation period.

Analyte	Year	Obs/ Sim	GLBA	SITK	KLGO		Skagway		
			Bartlett Cove	Sitka	Chilkoot Saintly Hill	Dyea	Dewey 1700	Lower Dewey	Sturgills
NO ₂ (ppb)	2008	Obs	1.67	2.94	2.64	3.69	15.05	3.65	4.62
		Sim	1.76*	1.99	6.86*	6.86*	4.92	4.92	4.92*
	2009	Obs	1.63	2.28	2.76	2.99	4.30	15.89	5.27
		Sim	1.86*	2.10	7.21*	7.21*	3.26	3.26	3.26
NO _x (ppb)	2008	Obs	10.49	11.23	11.19	14.14	18.85	69.91	19.04
		Sim	1.90	2.25	7.96	7.96	5.79	5.79	5.79
	2009	Obs	6.45	8.39	9.80	11.50	12.01	63.35	15.15
		Sim	2.05	2.39	8.44	8.44	3.81	3.81	3.81
HNO ₃ (µg/m ³)	2008	Obs	1.66	1.23	1.44	2.48	0.26	2.62	1.97
		Sim	0.35	0.30	0.44	0.44	0.38	0.38	0.38
	2009	Obs	2.59	1.95	3.99	5.30	2.39	7.19	3.31
		Sim	0.38	0.36	0.43	0.43	0.39	0.39	0.39
SO ₂ (µg/m ³)	2008	Obs	0.37	0.43	0.88	1.64	1.80	9.87	3.04
		Sim	0.40*	0.47*	0.94*	0.94	4.95*	4.95	4.95*
	2009	Obs	0.41	0.54	1.09	1.63	2.63	8.28	3.51
		Sim	0.36	0.48	0.96	0.96	3.56*	3.56	3.56*

* Values in red have been overestimated by the model (also shown in red font).

Weekly model concentrations were occasionally higher at Sturgill's Landing, Dewey 1700, Chilkoot Saintly Hill, and Dyea, but across all sites the average bias between simulated and observed values was still negative (-0.64 ppb), meaning that the Ogawa sites generally recorded higher weekly concentrations. NO₂ emissions were best simulated at Dewey 1700 ($r_s=0.76$, $p<0.0003$) and Dyea ($r_s=0.73$, $p<0.0008$, Table 10) in 2009. The highest positive correlations between the simulated and observed values occurred in 2009 for most locations, where the temporal pattern was moderately correlated ($r_s > 0.40$).

In comparison to Ogawa observations, the WRF/Chem model underestimated NO_x emissions on average of -15.09 ppb across all sites. NO_x is primarily composed of NO₂+NO, meaning that WRF/Chem had issues simulating NO concentrations. The majority of nitrogen ship emissions are released as NO (Cooper and Gustafsson 2004) but are quickly oxidized to NO₂. Therefore, this reaction probably occurred at a quicker time scale in WRF/Chem. The ambient sites in Skagway: Dewey 1700 ($r_s=0.52$, $p=0.026$ in 2009) and Lower Dewey ($r_s=0.47$, $p=0.07$ in 2008) showed the best correlation with the modeled NO_x concentrations. Some of the peaks in Ogawa measurements may be the result of other local emissions sources, such vehicles or other ships. The simulations here only considered cruise ship emissions as the anthropogenic emissions source, oftentimes resulting in underestimations.

Table 10. Non-parametric Spearman correlations between WRF/Chem-simulated weekly contaminant concentrations and weekly average Ogawa observations.

Analyte	Year	GLBA	SITK	KLGO		Skagway		
		Bartlett Cove	Sitka	Chilkoot Sainly Hill	Dyea	Dewey 1700	Lower Dewey	Sturgills
NO ₂ (ppb)	2008	0.56*	0.11	0.29	-0.27	0.20	-0.05	-0.31
	2009	0.44*	0.26	0.51*	0.73*	0.76*	-0.02	0.47*
NO _x (ppb)	2008	0.15	0.07	0.21	0.10	0.371	0.47*	-0.21
	2009	0.01	0.27	-0.08	0.37	0.52	0.18	0.18
HNO ₃ (µg/m ³)	2008	0.64*	0.19	0.37	0.11	0.22	0.06	0.21
	2009	0.12	-0.45	0.04	0.20	-0.24	0.35	0.01
SO ₂ (µg/m ³)	2008	0.47*	0.29	0.53*	0.56*	0.32	0.40*	-0.12
	2009	-0.14	-0.12	0.54*	0.44*	0.64*	0.18	0.27

* Moderately correlated observations ($r_s > 0.40$) (also in bold font).

Nitric Acid (HNO₃)

Nitric acid levels were generally very low at all Ogawa sites, except when large spikes occurred. WRF/Chem accurately captured the low concentrations of HNO₃, which typically remained around 0.5 µg/m³. However, all sites were subjected to large spikes in nitric acid concentrations, where some weekly values rose upwards of 30 to 40 µg/m³. This exposure period above background levels of <0.5 µg/m³ (Legge and Krupa 1989) confirms that atmospheric reactions occurred with local emissions, which WRF/Chem could not capture. Background concentrations are accepted reference values for pollutants that arise from natural processes, and are generally measured in pristine areas free from anthropogenic effects (Table 11). It is possible that the nitric acid spikes in the Ogawa measurements may be due to its accumulation in the atmosphere during dry weather days. The primary source of daytime HNO₃ is due to the sunlight-driven chemical reactions between OH radicals and NO₂. While nitric acid is not a primary product of fuel combustion, the spikes in HNO₃ may be the result of NO_x emissions from local or regional pollution sources (Lin et al. 2012). Since it is highly soluble in water vapor, HNO₃ will quickly deposit out of the atmosphere once scavenged by rain. Otherwise, HNO₃ concentrations are frequently low in Southeast Alaska because of prevalent rainfall. The otherwise long lifetime of HNO₃ permits long-range transport, especially higher up in the troposphere. Thus, the observed HNO₃ may be from emission sources located outside the model domain that the model could not capture.

The ambient monitoring site at Dewey showed the most dramatic spikes in HNO₃. The concentrations at the Lower Dewey site reduced from approximately 45 µg/m³ to background levels within a two-week time span. The Lower Dewey site also showed some of the highest concentrations of NO_x, NO₂, and SO₂. The site is likely located just at or below the inversion level where ship emissions commonly get trapped. Due to these large spikes, the only moderate correlation existed at

Bartlett Cove in 2008 ($r_s=0.64$, $p<0.004$). The average mean bias between the model and the ambient sites was -2.35 µg/m³ over all locations.

Table 11. Approximate background concentrations and National Ambient Air Quality Standards (NAAQS) for compounds measured by the Ogawa sampler.

Parameter	Analyte			
	NO ₂	HNO ₃	SO ₂	NH ₃
Approximate Concentration	0.1-0.3 ppb	< 0.5 µg/m ³	< 0.13 µg/m ³	~0.26 µg/m ³
Applicability	Level for North America, but unknown for AK (EPA 2010b)	Rural regions of Alberta (Legge and Krupa 1989)	Remote regions (Bandy et al. 1993)	Rural Western Canada (Krupa 2003)
Primary NAAQS ^A	100 ppb (1 hour average)	-	75 ppb (1 hour average) ~196 µg/m ³	-
Secondary NAAQS ^B	53 ppb (yearly average)	-	0.5 ppm (3 hour average) ~1300 µg/m ³	-

^A Primary NAAQS are designed to protect human health, including sensitive populations suffering from respiratory diseases.

^B Secondary NAAQS protect public welfare from adverse pollutant effects, including decreased visibility

Sulfur Dioxide (SO₂)

While WRF/Chem slightly overestimated SO₂ concentrations at some sites, both Dyea and Chilkoot Sainly Hill were at least moderately correlated ($r_s \approx 0.50$, $p < 0.05$) for both 2008 and 2009 tourist seasons. Bartlett Cove ($r_s = 0.47$, $p = 0.05$ in 2008) and Dewey 1700 ($r_s = 0.64$, $p = 0.005$ in 2009) also showed some degree of moderate correlation. The slight overestimation in SO₂ concentrations in the model means that a bulk of the SO₂ emissions in Southeast Alaska is locally emitted from cruise ship emissions and other marine vessels. SO₂ sourced from highly polluted areas in Asia is also largely oxidized and deposited before it reaches Alaska. The average mean bias between the simulated and observed values was -0.36 µg/m³.

Ammonia (NH₃)

The model predicts little, if any, ammonia concentrations. They have been omitted from our analysis since the values are so small. The land-use types in the model consider no livestock usage or large meadows in SE Alaska, which are typically major sources of ammonia. These natural emissions are calculated based on land-use categories inputted into the model, so many sources that produce ammonia are sub-grid-scale and not calculated with respect to the biogenic emission module.

Spatial Distribution

Figure 20 shows the average weekly WRF/Chem-simulated spatial concentrations of NO₂, NO_x, SO₂, and HNO₃ for the 2008 summer tourist season (2009 showed a similar distribution). Note that the model showed the highest concentrations of contaminants occurred where cruise ships traveled: in port and throughout the Inside Passage waterways. It is clear through these simulations that cruise ships caused elevated concentrations of pollutants in port at Ketchikan, Juneau, and Skagway, as we see greater increases of airborne concentrations close to these ports (the warmer colors indicate higher concentrations in Figure 20). The ships travel from Ketchikan to Juneau through Clarence Strait, Sumner Strait, Chatham Strait, and Fredrick Sound. There are also elevated concentrations in

the Lynn Canal between Juneau and Skagway. Higher emissions also exist in Icy Strait, portions of Glacier Bay and exiting out into the Gulf of Alaska, while Sitka remains much less affected.

Summary of Findings Pertinent to Monitoring Program Design

While models incur errors from boundary, initialization, and parameterization effects, they are good tools to aid in the understanding of physical processes that are hard to physically document, especially over large spatial regions where placing an array of sites is impossible. The simulations show spatial variations in ambient air quality based on the typical routes of cruise ships, which are mainly restricted to major ports and waterways. Hotspots with elevated ambient atmospheric contaminant concentrations exist in the port cities frequented by cruise ships: Juneau, Skagway, and Ketchikan.

Although Spearman correlations between WRF/Chem and Ogawa samples were not strong in all cases, likely because cruise ships were the only anthropogenic sources inputted into the model, it is apparent that cruise ships do impact the local air quality in Southeast Alaska by contributing to a notable portion of the overall airborne contaminants burden. If the model considered all known anthropogenic emissions sources (which is extremely hard to accurately portray; one method would be to run the model using the EPA's National Emissions Inventory), we would be able to identify the percentage of emissions that cruise ships contribute to the overall air quality. Sites in KLGO (particularly Dyea and Chilkoot Slightly Hill) demonstrated the best correspondence between the model and passive samplers, suggesting that cruise ships contribute more strongly to the ambient air quality in the KLGO-Skagway area.

Chapter 5 – Recommendations for Long Term Monitoring Program Design

The purpose of this chapter is to integrate findings from our current analyses (Chapters 2-4) with prior work, such as the inventory of Schirokauer et al. (2014), to recommend a design for long-term monitoring of airborne contaminants and associated ecological effects as one of three contaminant-related vital signs of the SEAN. We anticipate that the airborne contaminants monitoring recommended in this chapter will be integrated with the freshwater and marine contaminant monitoring recommendations to produce a comprehensive program to track current and emerging pollutants that may pose a threat to the generally pristine condition of NPS resources in Southeast Alaska.

General Program Design

The Vital Signs Monitoring Plan for the SEAN (Moynahan et al. 2008) describes a comprehensive index site-based approach for monitoring airborne contaminants or pollutants in the three NPS units of Southeast Alaska. The vision, implemented in large part during the summers of 2008 and 2009 with the inventory of Schirokauer et al. (2014), incorporated lichen biomonitoring with direct measures of airborne contaminant deposition and ambient air quality. Schirokauer et al. (2014) found conditions to be generally pristine, with a couple of notable exceptions in and adjacent to KLGO where signals of cruise-ship emissions and historic lead-ore transportation were evident.

Given this pattern, we envision a scalable monitoring design that can be focused towards priority air pollution concerns, similar to the conceptual framework proposed by Blett et al. (2003; Figure 21). As its foundation, we recommend the establishment of a series of index sites, based on prior sampling locations, to serve as long-term locations for monitoring of air pollution in the three Southeast Alaska parks and adjacent airsheds (Figures 22-23).

We propose that lichens be employed as sentinels of air pollution by using lichen tissue chemistry to identify and monitor potential concerns. Where lichen tissue concentrations are elevated, particularly for nitrogen and sulfur, we suggest additional quantification of wet deposition rates to help evaluate the potential for park resource impairment in relation to published critical loads and other ecological thresholds (See Table 5 for known critical loads. Additional USFS threshold values and lichen tissue inventory can be found at: <http://gis.nacse.org/lichenair/index.php>). In cases where potential concerns relate more to ambient air quality than contaminant deposition, per se, we suggest that additional direct assessments of atmospheric pollutant concentrations be considered.

We also recommend re-initiation of the NADP-MDN station formerly operated in GLBA, as a reliable means to monitor long-term trends in mercury deposition, given the propensity of this contaminant to accumulate in aquatic and terrestrial food webs in otherwise pristine regions. While lichens have been successfully employed as sentinels for common air pollutants including nitrogen and sulfur compounds, their use for monitoring mercury deposition or bioaccumulation has been less thoroughly tested.

This overall design is recommended as a single, comprehensive air pollution and airborne contaminants monitoring program but could also be scaled to fit future budget scenarios or the availability of partner contributions (Table 12). Such an adaptive approach would help ensure the sustainability of a core monitoring commitment by the SEAN while also facilitating key partnerships needed to extend the scope of inference for understanding local and regional air pollution threats to NPS resources. Finally, we recommend periodic synthesis of results, including those from companion freshwater and marine contaminants sampling programs of the SEAN to identify emerging threats that might warrant program adaptation.

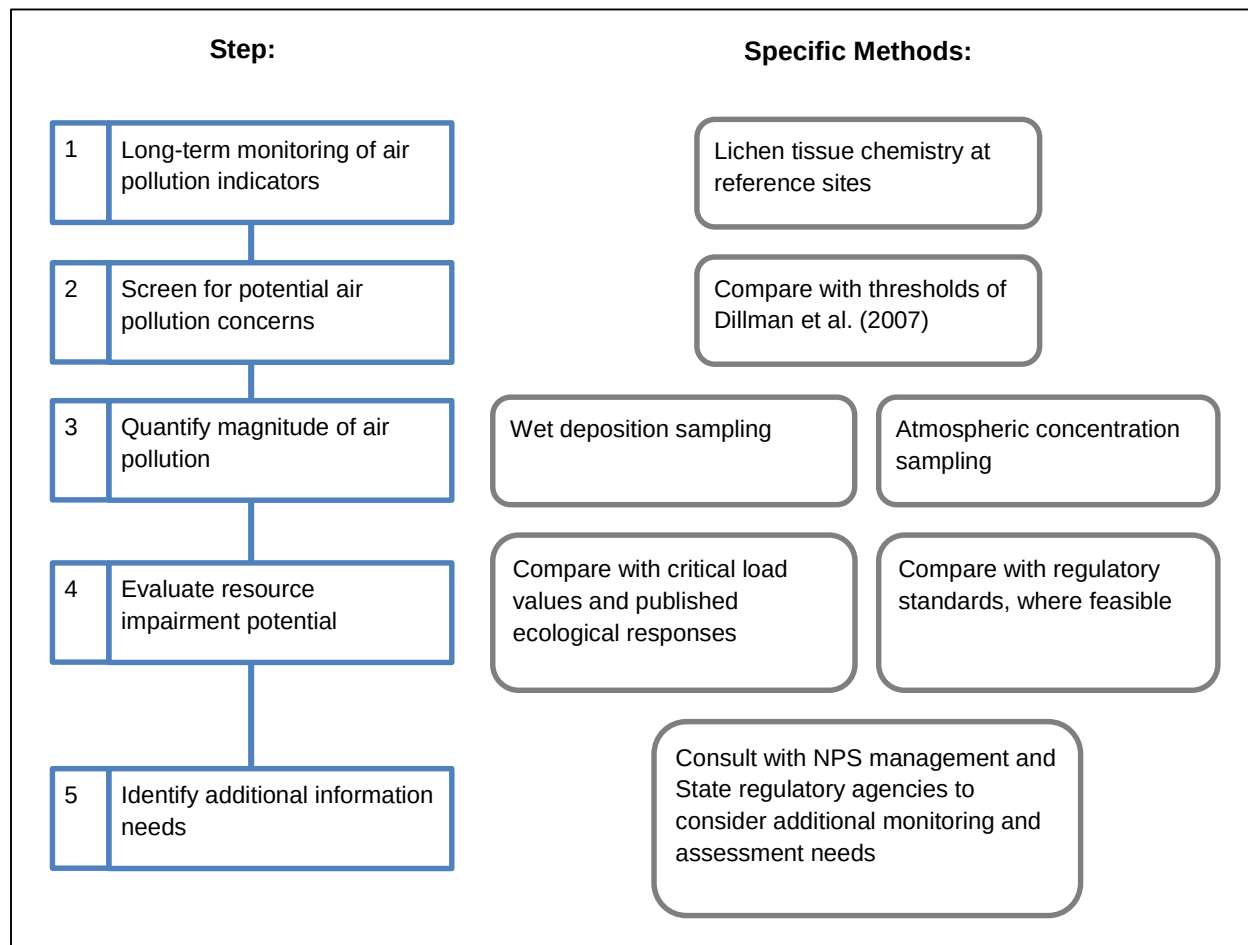


Figure 21. Conceptual framework for monitoring air pollution in Southeast Alaska's National Parks and neighboring airsheds. Adapted from Blett et al. (2003)

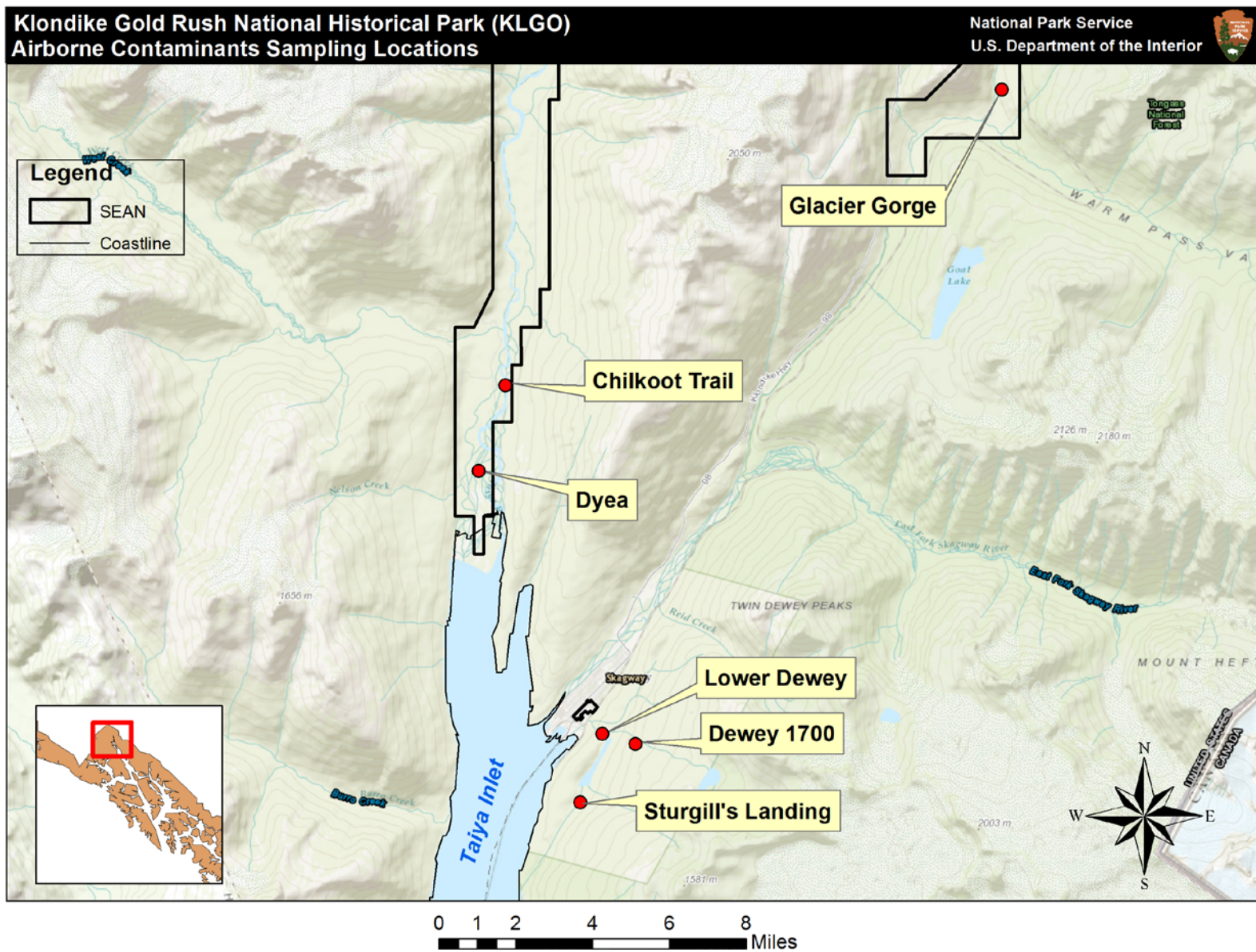
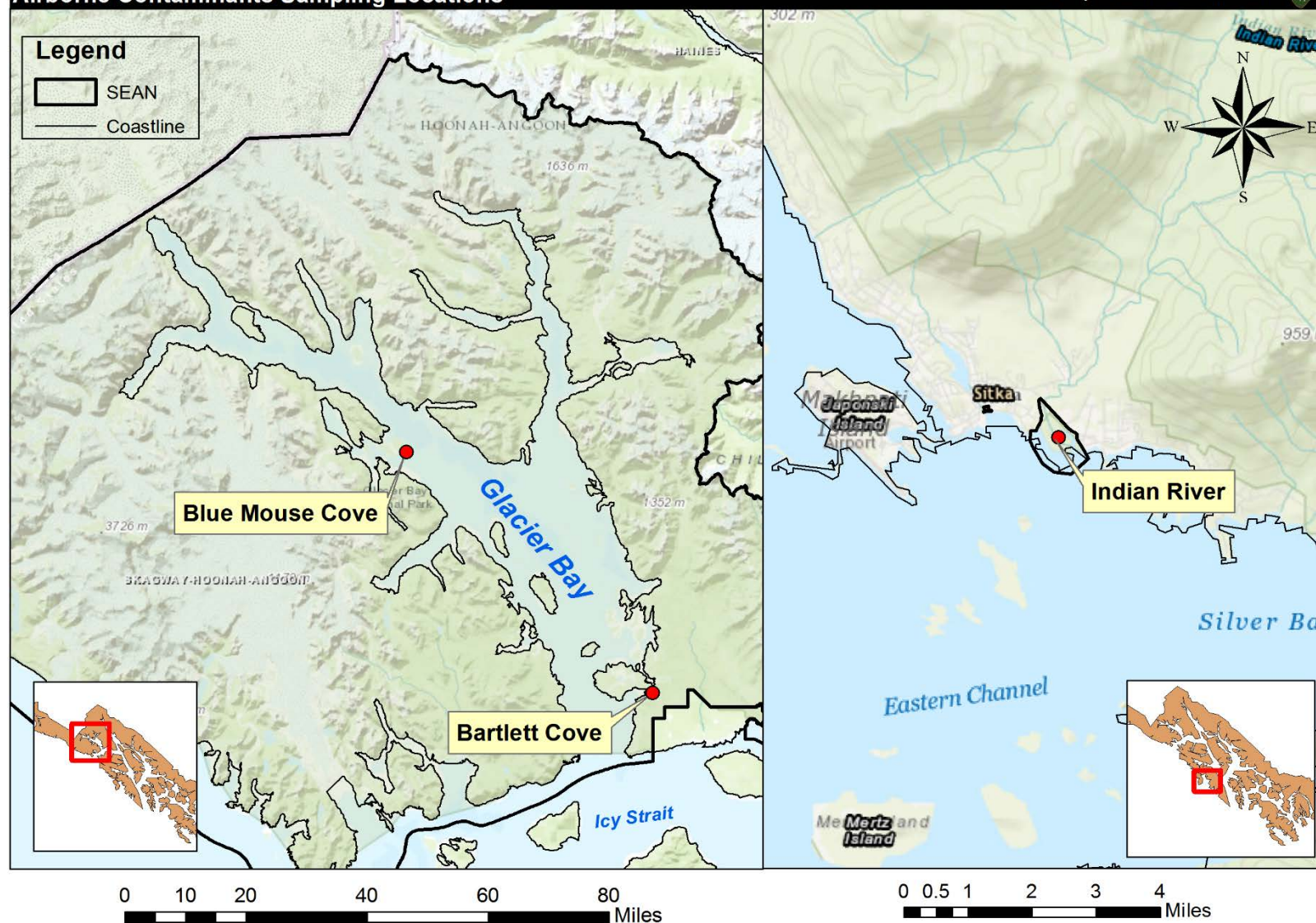


Figure 22. Map of proposed index sites for monitoring airborne contaminants in KLGO and adjacent airsheds.

Glacier Bay National Park & Preserve (GLBA) and Sitka NHP (SITK) Airborne Contaminants Sampling Locations

National Park Service
U.S. Department of the Interior



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Figure 23. Map of proposed index sites for monitoring airborne contaminants in GLBA, SITK, and adjacent airsheds.

Table 12. Summary of scalable monitoring design components recommended for incorporation into the SEAN's airborne contaminants vital sign monitoring program. Additional sampling location details, by site name, can be found in Schirokauer et al. (2014). Components are presented in priority order to facilitate future scaling of the monitoring design. Detailed cost estimates can be found in Appendix C.

Monitoring Component	Purpose	Proposed sampling frequency	Proposed sampling locations	KLGO	GLBA	SITK	MOS	Juneau	Total SEAN Cost	Total Partner Cost
Lichen tissue chemistry	- Reference sites for long-term monitoring of elemental concentrations as indicators of resource impairment potential - Monitoring previously impacted sites adjacent to the Port of Skagway and lead ore transport route	2-5 years	<u>KLGO</u> - Dyea: low elevation reference site and control site away from the Port of Skagway - Chilkoot: low-mid elevation reference site and control site away from both the Port of Skagway and lead ore transport route - Glacier Gorge: mid elevation reference site and secondary control site away from Port of Skagway <u>MOS</u> - Lower Dewey: previously impacted mid-elevation site - Sturgill's: previously impacted mid-elevation - Dewey 1700: previously impacted mid-upper-elevation site <u>GLBA</u> - Bartlett Cove: lower bay reference site - Blue Mouse Cove: mid-bay reference site along cruise ship path <u>SITK</u> - Indian River: reference site	3	2	1	3	-	\$3,868	\$1,877
Hg wet deposition	Detection of trends in mercury deposition	Continuous	UAS Auke Lake campus in Juneau	-	-	-	-	1	\$10,916	-
N and S wet deposition	- Linkage to published critical loads - Calibration of IER tube results with NADP-NTN	Decadal	<u>Juneau</u> - UAS campus <u>KLGO</u> - Chilkoot: control site away from Port of Skagway <u>MOS</u> - Lower Dewey: previously impacted site	1	-	-	1	1	\$5,600	\$2,800

Table 12 (continued). Summary of scalable monitoring design components recommended for incorporation into the SEAN's airborne contaminants vital sign monitoring program. Additional sampling location details, by site name, can be found in Schirokauer et al. (2014). Components are presented in priority order to facilitate future scaling of the monitoring design. Detailed cost estimates can be found in Appendix C.

Monitoring Component	Purpose	Proposed sampling frequency	Proposed sampling locations	KLGO	GLBA	SITK	MOS	Juneau	Total SEAN Cost	Total Partner Cost
Atmospheric pollutant concentrations	Assessment of ambient air quality concerns	Decadal	<u>KLGO</u> - Chilkoot: control site away from Port of Skagway <u>MOS</u> - Lower Dewey: previously impacted site	1	-	-	1	-	\$12,643	\$10,618

Lichen Tissue Chemistry

Lichens have a long history of use as biological sentinels for monitoring the exposure of ecosystems to air pollution, including in Southeast Alaska (Schirokauer et al. 2014). Lichens are useful passive monitors of pollutant exposure, as they assimilate compounds in proportion to ambient concentrations. Importantly, Schirokauer et al. (2014) found lichen tissue elemental concentrations of nitrogen and sulfur (as % dry weight) from Southeast Alaska parks to be correlated with atmospheric pollutant concentrations and several measures of contaminant deposition. For example, *Hypogymnia* tissue concentrations of sulfur (% dry weight) were highly correlated with all measures of summertime sulfur deposition ($r > 0.98$), offering strong support for the use of lichen tissue chemistry for monitoring deposition of this primary air pollutant of concern in Southeast Alaska.

A framework within which to employ results from lichen tissue chemistry analyses has been developed by the U.S. Forest Service for use in monitoring air pollution in Pacific Northwest and Alaska National Forests (Geiser et al. 1994, 2004; Dillman et al. 2007). Extensive sampling has been employed to produce thresholds that indicate the likelihood of exposure to air pollution in relation to “clean sites” located in wilderness settings distant from common anthropogenic emission sources.

We propose building upon this existing foundation by conducting routine sampling of lichen tissues at a set of index sites on NPS lands as the core commitment of the SEAN airborne contaminants monitoring program, with the potential to expand the scope of monitoring in partnership with adjacent land owners such as the Municipality of Skagway and U.S. Forest Service. Such a simple, efficient program would take maximum advantage of the existing monitoring programs and analytical framework of the neighboring Tongass National Forest to increase the spatial context for interpretation of results. Furthermore, tissue collection is straightforward and analysis costs are modest, helping to improve long-term program sustainability.

Specific recommendations:

- Establish six long-term reference sites in the SEAN parks.
- Partner with the Municipality of Skagway to monitor three previously impacted sites on municipal lands near the Port of Skagway.
- Sample every 2-5 years to establish an initial level of inter-annual variability, then perform power analysis after 10 years to consider alternative frequencies.
- Analyze samples for the following elements: S, N, P, K, Ca, Mg, Na, Al, Fe, Mn, Zn, Cu, B, Pb, Ni, Cr, Cd, Co, Mo, Si, Ti, Be, Sr, Rb, Li, V, and Ba.
- Use the standard operating procedures (SOPs) found in Appendix C of Schirokauer et al. (2014) to guide sample collection and processing.
- We recommend postponing mercury analysis for lichen tissue until methods and related threshold values for interpretation of results have been refined.
- Compare lichen elemental analysis results with threshold values of Dillman et al. (2007).
- Conduct additional direct wet deposition monitoring where provisional thresholds of N and S have been exceeded in consecutive sampling events.

- Share findings with the USFS lichen monitoring program (<http://gis.nacse.org/lichenair/index.php>) to ensure results are incorporated into regional and national-scale databases to facilitate future uses, and to view that data in a great spatial picture. The latter is of importance to assess whether changes are most likely due to local changes in air composition or due to regional or large-scale changes, i.e. from long-range transport of pollutants. In the latter case, similar changes should be seen over a large area at various sites. In the cases of local causes, only site in the major downwind should show similar signals, if at all.

Nitrogen and Sulfur Deposition

Lichen-based air quality monitoring results can be difficult to relate to existing regulatory standards or ecological thresholds (Blett et al. 2003). To partially address this limitation, regression models have been developed to link lichen tissue concentrations of nitrogen with deposition measures commonly used in establishment of ecological critical loads (Root et al. 2013). However, such tools are not currently available to estimate sulfur deposition a potentially more notable pollution concern in Southeast Alaska (Schirokauer et al. 2014), though they are in the process of being developed. At present, we suggest that lichen tissue chemistry results be supplemented where Tongass National Forest “clean site” thresholds are exceeded. We suggest using passive wet deposition samplers (ion-exchange resin or Fenn tubes), to enable direct comparisons to critical load values or other published ecological responses to contaminant deposition to assess resource impairment potential.

Specific recommendations:

- Monitor wet deposition of nitrogen and sulfur compounds using IER tube samplers at the Lower Dewey and Chilkoot sites of Schirokauer et al. (2014) to enable comparisons among previously impacted and control sites.
- Concurrently deploy IER tube samplers at the NADP-NTN site in Juneau to facilitate calibration and extrapolation of results. Partner with the Municipality of Skagway to incorporate monitoring of site on municipal lands near the Port of Skagway (Lower Dewey).
- Decadal sampling frequency for synoptic assessment.
- Deploy both open and throughfall IER tube samplers at each site to maximize potential for comparison to published results for different pollutants (for example, N can be taken up by the canopy).
- Maintain a year-long deployment period to facilitate comparisons with annual critical load values ($\text{kg ha}^{-1} \text{ yr}^{-1}$).
 - IER tubes are generally deployed in six-month periods, and the ionic resin will need to be changed on a winter/summer seasonal basis (Fenn et al. 2013). The winter season deployment will require the IER to be outfitted with a snow tube, allowing snow meltwater to drain into the resin. Additional details can be found at: http://www.fs.fed.us/psw/topics/air_quality/resin_collectors/fenn_iermethods.pdf.
- Use the standard operating procedures (SOPs) found in Appendix B of Schirokauer et al. (2014) to guide sample collection and processing, and to exclude systematic differences in

the data. Using the same measurement protocol ensures comparability of past and future measurements, and hence assessment of change, if any.

- The snow tube will result in a different collection diameter, and will change the calculation of seasonal deposition loads. Refer to the documentation at: http://www.fs.fed.us/psw/topics/air_quality/resin_collectors/ for additional details.

Ambient Air Quality

It is important to recognize that some commonly cited concerns among KLGO visitors and members of the Skagway community relate primarily to ambient air quality rather than the deposition of airborne contaminants and subsequent ecological effects. For example, community members have expressed concerns about noticeable haze and the smell of diesel fumes on days where temperature inversions trap cruise ship emissions near the Port of Skagway. While such conditions have been related to elevated rates of contaminant deposition and ecological responses (Schirokauer et al. 2014), we suggest that a monitoring program specifically aligned with State regulatory processes is needed to sufficiently address air quality concerns. As such, we recommend interagency consultations to consider the need for additional monitoring and assessment in the future, as air quality concerns are identified.

In addition to the lichen tissue chemistry and wet deposition monitoring described above, one relatively simple step that we recommend in assessing the need for a more comprehensive ambient air quality monitoring program for KLGO and the Municipality of Skagway is to re-deploy passive membrane samplers near the Port of Skagway. This action would enable assessment of changes in ambient air quality that may have occurred since the inventory of Schirokauer et al. (2014) during the summers of 2008 and 2009. Repeating this sampling would help establish air quality responses to new emission regulations for ocean vessels and large ships, future installation of “cold-ironing” capacity in downtown Skagway to offset electrical demand for on-board electricity, or other changes that affect emissions from the marine transportation and cruise ship industries. It is important to recognize that the weekly average concentrations resulting from such sampling will not align directly with National Ambient Air Quality Standards (NAAQS) for NO₂ (average annual and 1-hour maximum) or SO₂ (1-hour and 3-hour maximums). Consultation with the State will be critical for considering results within the larger regulatory context and evaluating the need for additional monitoring or evaluation.

Specific recommendations:

- Assess ambient air quality using passive Ogawa atmospheric samplers at the Lower Dewey and Chilkoot sites of Schirokauer et al. (2014) to enable comparisons among previously impacted and control sites. These samplers will measure ambient NO_x, NO₂, HNO₃, and NH₃.
- Initially target a decadal sampling frequency for reassessment.
- Partner with the Municipality of Skagway to incorporate monitoring of a site on municipal lands near the Port of Skagway (Lower Dewey).
- Deploy samplers during the summer tourist season to align with the period of maximum air quality impairment potential (Chapter 2).

- Switch filters weekly to help establish seasonal patterns of air quality, which could be important for linking observed conditions with potential emission sources and designing more targeted monitoring programs, and assess possibilities for mitigation.
- Use the SOPs found in Appendix A of Schirokauer et al. (2014) to guide sample collection and processing.
- Consult with Alaska Department of Environmental Conservation (DEC) regarding results of decadal wet deposition and ambient atmospheric contaminant monitoring to consider the need for additional assessment of ambient air quality in relation to the NAAQS or Alaska Marine Visible Emissions Standards.

Mercury Wet Deposition

There is concern that mercury deposition may be increasing in Southeast Alaska, as a function of its long atmospheric residence time and increases in emissions from Asian coal combustion (Schirokauer et al. 2014). Elevated concentrations in freshwater fish from Southeast Alaska (e.g., Nagorski et al. 2011, Eagles-Smith et al. 2014) are also evidence of the potential for mercury to accumulate in aquatic food webs, even in the remote and sparsely developed landscapes of Southeast Alaska, potentially affecting ecological integrity. Within this context, long-term monitoring of mercury deposition is a priority for understanding ecosystem exposure within the SEAN's integrated airborne, freshwater, and marine contaminants monitoring program.

While lichen tissue analysis has been used to assess rates of mercury deposition (see Schirokauer et al. 2014), methods continue to be refined and thresholds for the interpretation of results are currently lacking. While a NADP-MDN site was formerly operated in GLBA (Bartlett Cove), there is currently no active monitoring of mercury deposition in Southeast Alaska and no suitable surrogate has been identified (Chapter 3). Given these constraints, we suggest re-initiation of the former NADP-MDN station operated in GLBA (Bartlett Cove) as a reliable means to monitor trends in mercury deposition into the future. This approach maximizes the comparability of the program's results by participation in a standardized national program, allowing direct comparisons of mercury deposition rates among sites throughout Alaska, Canada, and the lower-48 States. Participation in this standardized national program also ensures high data quality and accessibility of information through institutional repositories.

While the station could simply be re-installed at its former location in GLBA (near the park administrative buildings at Bartlett Cove) to extend the period of record, we believe it would be advantageous to co-locate the station with the existing NADP-NTN station on the University of Alaska Southeast Auke Lake campus in Juneau. The majority of mercury deposited in Southeast Alaska is thought to originate from far-field sources and relatively modest variation in rates of mercury deposition was observed among sites sampled by Schirokauer et al. (2014) in the summers of 2008 and 2009. For these reasons, it seems likely that the magnitude of deposition would be similar among the two sites. Any differences could be outweighed by the value of the comparative data provided by the NADP-NTN site as well as logistical benefits that could increase data continuity.

Specific recommendations:

- Support continuous station operation if feasible; otherwise consider supporting station operation for one out of every 5-10 years as a means to assess coarse differences in the magnitude of mercury deposition.
- Move the station from its former location in GLBA to the UAS campus where it would be co-located with the NADP-NTN AK02 station.
- Calculate precipitation-weighted deposition totals to allow comparison among NADP-MDN stations, using results from this report (Chapter 3) as a basis for future comparisons.

Additional Research Needs

Critical loads are a primary means by which air pollution can be linked to ecological responses (Porter et al. 2005). This field has received much attention, leading to published critical loads for atmospheric nitrogen deposition applicable to several regions (Chapter 2, Table 5), but site-specific critical loads for Southeast Alaska have not been developed. Furthermore, there has been minimal progress toward development critical loads at the local, regional or national level for atmospheric sulfur deposition. According to Dillman (2016, personal communication), sulfur models are currently being developed by Linda Geiser's group at the USFS, and the status of this should be periodically reviewed. Schirokauer et al. (2014) suggested that sulfur-containing pollutants are currently a primary concern in Southeast Alaska due to the ecological consequences of acidification and potential for visibility impairment.

While lichen-air quality models developed for other regions provide a reference to help interpret monitoring results from SEAN parks (see Schirokauer et al. 2014), efforts to develop critical loads of nitrogen and sulfur specific to Southeast Alaska would enhance our ability to assess the potential for impairment of NPS resources including sensitive lichen communities. However, a general lack of a gradient of air quality conditions in Southeast Alaska owing to a lack of industrial development has impeded the development of such models. Opportunities to refine or expand the scope of existing lichen-air quality models should be pursued at the regional and national scale to provide improved tools for relating lichen tissue chemistry to the potential for resource impairment. Such projects offer great potential for productive inter-network, inter-region, and interagency partnerships. For example, the U.S. Forest Service Forest Inventory and Analysis program and Tongass National Forest sustain long-term lichen community survey plots suitable for development of lichen-air quality models.

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Appendix A – Description of Primary Airborne Contaminants in Southeast Alaska

The following sections in this appendix outline the specific analytes monitored in Southeast Alaska (Table A1), including a general description of their background, sources, and the potential risks from high concentration or deposition. Most of these contaminants have been identified as primary pollutants that are likely to influence Air Quality Related Values (AQRVs) in the SEAN parks, or those resources sensitive to air quality, including a wide array of vegetation, soils, water, fish, wildlife, and visibility. The Federal Land Managers' Air Quality Related Values Work Group (FLAG 2010) reports that the typical range of natural background nitrogen and sulfur depositions are approximately between 0.25-0.50 kg ha⁻¹ yr⁻¹, with the higher end of the range more likely to occur in the Eastern US. These values are conservative, but also err on the low end of the regional range of estimates. Background depositions may be sourced from sea salts and other naturally present materials, such as airborne dusts. Depositions above this threshold are likely assumed to be anthropogenic in nature.

Table A1. Sources of contaminant depositions at-a-glance. The primary pollutants likely to affect Air Quality Related Values (AQRVs) in the SEAN include nitrogen and sulfur compounds. Adopted from Seinfeld and Pandis (1998), UNEP (2003), and Sullivan et al. (2011 a,b).

Pollutant	Source
Particulate Sulfate SO ₄ ²⁻	• Fossil fuel combustion and industrial processes • Biomass burning • Oceans (sea spray) • Plants and soil • Volcanoes
Sulfur Dioxide SO ₂	• Fossil fuel combustion and industrial processes • Biomass burning • Volcanoes
Particulate Nitrate NO ₃ ⁻	• Oxidation of nitrogen oxides, which include: • Fossil fuel combustion • Biomass burning • Lightning • Ammonia oxidation • Aircraft and transport from the stratosphere
Nitric Acid HNO ₃	• Oxidation of nitrogen oxides
Ammonium NH ₄ ⁺	• Ammonia from agricultural and other biological sources: • Dairy and beef cattle, buffalo, pigs, horses, sheep, goats, poultry • Wild animals • Fertilizer • Biomass burning • Vegetation • Oceans

Table A1 (continued). Sources of contaminant depositions at-a-glance. The primary pollutants likely to affect Air Quality Related Values (AQRVs) in the SEAN include nitrogen and sulfur compounds. Adopted from Seinfeld and Pandis (1998), UNEP (2003), and Sullivan et al. (2011 a,b).

Pollutant	Source
Mercury Mg	• Coal and oil fired power plants • Trash incineration • Fossil fuel burning • Rock weathering, geothermal vents, volcanoes

Table A2. Indicators for monitoring and evaluating the effects of sulfur and nitrogen deposition. Adapted from the Federal Land Managers' Air Quality Related Values Work Group (FLAG 2010).

Ecosystem	Indicators for Sulfur Deposition
Freshwater	Chemical changes (acid neutralizing capacity depression); changes in phytoplankton community composition, species diversity, and biomass
Terrestrial	Leaching on soil cations, soil acidification, mobilization of aluminum ions; changes in lichen species and diversity
Estuarine	Saltwater is not sensitive, but leaching of nutrients from sandy near-shore soils may occur
Freshwater	Same as Sulfur
Terrestrial	Changes in: litter and soil carbon and nitrogen dynamics, biomass, soil nitrogen process, litter decomposition rates, soil microbe functional groups, soil organic matter quality/quantity, lichen species and vitality
Estuarine	Changes in: phytoplankton species composition and biomass, aquatic invertebrates, seagrass health and distribution, nutrient ratios, dissolved oxygen, and trophic status

Sulfates (SO₄²⁻)

Sulfur compounds originate from both natural and anthropogenic sources, and are considered priority airborne contaminants due to their ability to cause groundwater and soil acidification. Sulfates can also reduce visibility since high relative humidity values enhance their scattering efficiencies. Sulfates affect the health of SEAN's AQRVs because once the contaminant reaches the surface through wet deposition (either in rainfall or through suspended aerosol particles), damage to sensitive plant species, leaching of base cations, soil acidification, and surface-water acidification may result (FLAG 2010). Analyses of sulfur deposition through IERs and lichen tissue yielded very low sulfate deposition rates (around 1-2 kg ha⁻¹ yr⁻¹) for most locations in Southeast Alaska. However, some sites in Skagway and KLGO had sulfate deposition rates exceeding 10 kg/ha (Schirokauer et al. 2014), which reflects potentially damaging environmental effects.

Sulfur dioxide (SO₂) is naturally released from volcanic eruptions as a primary emission product. However, anthropogenic sulfur is also a chief component of sulfur-containing fossil fuel emissions (such as coal, oil, and diesel). SO₂ may originate from local point sources and long-range transport. Sulfates (SO₄²⁻), the secondary oxidation product of sulfur, combine with water vapor in the atmosphere and are removed in precipitation. Both sulfate and nitrate particles are hygroscopic, and scatter and absorb incoming solar radiation, leading to reduced visibility through visible light

extinction and the formation of regional haze (Burns et al. 2011). Their contribution to visibility impairment is magnified in the presence of water vapor, especially wet and humid portions of Southeast Alaska.

Significant quantities of sulfate deposition may also be sourced from sea salt aerosols. Model studies have shown that sulfate aerosols attributable to sea spray may penetrate as far as 10-180 km inland (Dennis et al. 2013). Other model studies have also shown that certain atmospheric circulations are conducive for long range transport of sulfates from anthropogenic sources, particularly originating from international shipping lanes and/or industrial activity in Canada and Asia. While a bulk amount of atmospheric sulfur dioxide is oxidized and deposited prior to arrival in coastal Alaska, these sources may still lead to elevated risks of SO_4^{2-} (Tran et al. 2011).

The following chemical reaction from Jacob (1999) illustrate how sulfur dioxide emissions combine with water vapor in the atmosphere:

Chemical Reaction	Description
$\text{SO}_2(\text{g}) \leftrightarrow \text{SO}_2 \cdot \text{H}_2\text{O}$	Most of the atmospheric oxidation of SO_2 occurs in clouds and rain droplets.
$\text{SO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{HSO}_3^- + \text{H}^+$	Sulfur dioxide combines with water vapor in the air where it dissociates to HSO_3^- (bisulfite).
$\text{H}_2\text{O}_2(\text{g}) \leftrightarrow \text{H}_2\text{O}_2(\text{aq})$	It rapidly oxidizes in the liquid phase by H_2O_2 (hydrogen peroxide) produced by a self-reaction with HO_2 .
$\text{HSO}_3^- + \text{H}_2\text{O}_2(\text{aq}) + \text{H}^+ \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O}$	The final reaction is acid-catalyzed, with the presence of an H^+ ion, and the net reaction yields sulfate, SO_4^{2-} , water, and two acidic hydrogen ions.

Ammonium (NH_4^+)

Ammonia is present in aerosols and precipitation in the form of an ammonium cation, NH_4^+ . The release of ammonia and deposition of the ammonium ion is typically associated with fertilizers and livestock in agricultural regions. Naturally occurring ammonia may also be sourced from plant and animal decay, seawater spray, as well as the suspension of soil dust from arid climates. Ammonium depositions are generally very low in Southeast Alaska due to the lack of livestock and agriculture. However, any ammonium deposition still contributes to nitrogen enrichment, which can lead to changes in species diversity and soil nutrient cycling. The transport of Asian dust across high latitudes points to the possibility that some of the ammonium depositions in Southeast Alaska could be sourced through this manner. Although lichen analyses show no widespread adverse ecological effects from nitrogen or sulfur depositions in SEAN parks, sensitive lichen species are still monitored (Geiser et al. 2010a).

While the lifetime of ammonia in the atmosphere is short (only a few days), it readily reacts with acidic gases to form particulates, or can become transported through cloud droplets and precipitation

(ADAM 2010). Particulates of ammonia lead to the production of a solid called ammonium salt, which combines with water vapor in the air and can result in fine particulate matter (PM_{2.5}). Since the diameter of these particulates is less than 2.5 µm, they have the potential to reduce visibility.

The following are important reactions associated with the ammonia ion and its neutralizing effects on the environment (Jacob 1999).

Chemical Reaction	Description
$\text{NH}_3(\text{aq}) + \text{H}^+ \leftrightarrow \text{NH}_4^+$	Any ammonia dissolved in rainwater scavenges H ⁺ ions and acts as a strong base and neutralizing component.
$\text{HNO}_3(\text{aq}) \rightarrow \text{NO}_3^- + \text{H}^+$	In addition, gaseous ammonia can combine with nitric (HNO ₃) and sulfuric acids (H ₂ SO ₄) in the atmosphere (typically components of NO _x and SO _x) from anthropogenic sources. Nitric and sulfuric acids are the dominant contributors to rainwater acidity, and can cause substantial effects on soil acidification and terrestrial and aquatic ecosystems. The byproducts of these reactions are the formation of nitrates and sulfates.
$\text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{SO}_4^{2-} + 2\text{H}^+$	
$\text{NH}_4^+ + 2\text{O}_2 + \text{microbes} \rightarrow \text{NO}_3^- + \text{H}^+ + \text{H}_2\text{O}$	Since ammonia is a strong base, acid rain can be neutralized through the formation of the ammonium ion. However, the acidity may once again get recovered when rain containing high concentrations of ammonium ions goes through the natural microbial nitrification process.

This means that an abundance of NH₄⁺ and NO₃⁻ may lead to excess fertilization (eutrophication) and an accumulation of organic nitrogen in the soil (Gold and Sims 2005). It is also important to note that the microbial nitrification process does not exactly cancel out the basic nature of ammonium by producing nitrates.

Nitrates (NO₃⁻)

Nitrates in rainwater are produced by the oxidation of the ammonium ion through microbial nitrification. Aqueous nitric acid (HNO₃), which is water soluble, can also become scavenged by rain and get deposited into the environment. When the nitrogen input exceeds the amount that an ecosystem can assimilate, nitrates are leached from the soil and can be detectable in nearby streams and lakes (FLAG 2010). Excessive nitrogen acidification can occur when deposition is as low as 3-5 kg N ha⁻¹ yr⁻¹ (Williams et al. 1996). Nitrates are also important to consider in Southeast Alaska, as they are hygroscopic and can scatter and absorb incoming solar radiation, leading to visibility reduction. Even though most of the area is not largely affected by nitrogen deposition, hotspots in KLGO-Skagway were first identified in 1989 in sensitive lichen species (Furbish et al. 2000; Dillman et al. 2007). Additional sampling in 2008-2009 revealed values higher than clean-site reference ranges in KLGO-Dyea and Sawyer Island in the Tracy Arm-Fords Terror Wilderness of the Tongass

National Forest (Schirokauer et al. 2014). Besides work with lichens, nitrogen deposition has not been well studied in Southeast Alaska (Perakis et al. 2011).

Nitrates are sourced from both natural and anthropogenic sources, however the increase of worldwide industrialization provides additional transfers of nitrogen into the cycle. Nitrogen (N_2) is the most abundant gas in our atmosphere, composing about 78%. Atmospheric nitrogen first becomes converted to NO in either of two ways: naturally through high temperature oxidation by lightning, or through anthropogenic sources of fossil fuel combustion. The atmosphere oxidizes NO to HNO_3 , which is then scavenged by rain and deposited as NO_3^- (Jacob 1999; Figure A1). As a result, nitrogen oxides ($NO_x = NO + NO_2$) are primary products of fossil fuel combustion. Nitrogen oxides may also be sourced from wildfire smoke, although carbon monoxide, carbon dioxide, particulate matter, and other organics are the major pollutants from forest fires. Wildfire smoke carried from long distance transport from Western Canada has been known to occasionally impact Juneau and the Mendenhall Valley (ADEC 2013). Since nitrates are also sourced from the combustion of many anthropogenic processes, NO_x levels associated from ships and automobiles could contribute to the slightly higher summer values. Winter fuel and wood burning may add to the winter depositions.

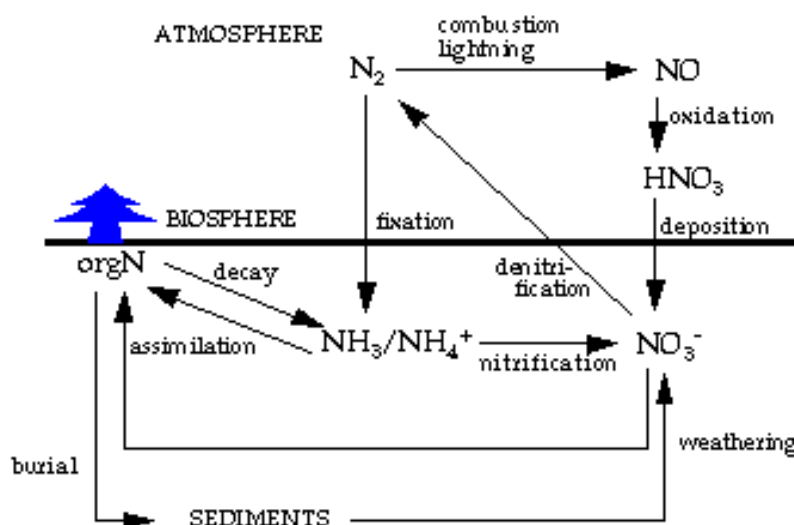


Figure A1. Major processes of the nitrogen cycle (adopted from Jacob 1999).

Airborne nitrogen compounds are generated through the combustion of automobile engines, marine transportation, and industrial activity. They can also be produced through fertilizers, animal manure, plant decay, or sewage treatment (Nolan et al. 2002). Thus, nitrate levels in precipitation tend to be the highest where the air is polluted with nitrogen oxides, such as nearby power plants, industrial centers, and areas with higher populations (Porter et al. 2000; Stensland et al. 2001). The concentration of nitrates in the ground water and soil provide a good indication of lake and stream water acidification, which could be toxic to aquatic life when concentrations are high enough (Burns et al. 2011). Microorganisms break down plant proteins and aid in their decay process, which releases ammonia. The ammonia is then taken up by plants' roots and converted into nitrates through nitrifying bacteria (Kimball 1994).

Inorganic Nitrogen

Ammonium and nitrates are both rich in nitrogen, and contribute to nearly all of the inorganic nitrogen deposition from rainfall (Porter et al. 2000; Stensland et al. 2001). The total inorganic nitrogen value represents the sum of the nitrogen fraction from both the ammonium and nitrate depositions. The molecular weight of ammonium and nitrate is 18.04 g/mol and 62.00 g/mol, respectively, resulting in nitrogen representing nearly 77.6% and 22.6% of each compound's deposition. Inorganic nitrogen depositions are important to consider, as high latitude and taiga habitats of Alaska are some of the most sensitive regions to nitrogen loadings, especially with the presence of abundant lichen communities (Pardo et al. 2011). Preindustrial depositions of total nitrogen in temperate coniferous forests in the northern hemisphere are estimated to be approximately 0.16-2.13 kg N/ha/year (Holland et al. 1999), depending on the quantity of precipitation received.

Critical Loads

A critical load is a quantitative estimate of exposure that a particular substance may reach that does not cause long-term damage to an ecosystem (Nilsson and Grennfelt 1988; Grennfelt et al. 2001). Critical loads are typically expressed in terms of N and S loading in kilograms per hectare per year ($\text{kg ha}^{-1} \text{ yr}^{-1}$), and are used to quantify the risks associated with pollution on federal lands (Porter et al. 2005). If deposition values exceed critical loads, park managers would know to appropriately respond to mitigate further impairment. While several European countries have adopted the concept of critical loads, widespread research of critical loads has not been carried through in the United States, with the exception of some regional studies. The EPA was concerned that national standards would not account for regional differences in ecosystem response (EPA 1995) since precipitation patterns, vegetation, and acid-neutralizing capacities (ANCs) differ by location (Porter et al. 2005). Regional critical loads are typically calculated based on model results, spatial studies, long-term ecological research (Williams and Tonnessen 2000), and experimental analyses that identify specific deposition-loading effects (Wright et al. 1994; Baron et al. 2000).

Critical loads for nitrogen depositions in the Pacific Northwest have been developed by Geiser et al. (2010a), and are also highly dependent on precipitation. Lichen communities in Marine Pacific Northwestern Coastal forests typically can tolerate between $2.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $9.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for wet forests (Geiser et al. 2010a). Pardo et al. (2011) reported through studies by Whytemare et al. (1997) and Lilleskov (1999) that marine coastal forests in Southeast Alaska can typically bear nitrogen deposition fluxes of around $5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. This value occurred approximately when fungal communities began to change and/or decline in diversity. Recent studies by Root et al. (2013, 2015) estimated critical loads to be $1.54 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for through-fall N deposition in lichen communities and $2.51 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for lichen N concentrations. These values are slightly lower than critical loads developed by Geiser et al. (2010a), as most lichen samples originated from inland plots in the Pacific Northwest. While there have been several empirical studies and inventories of sensitive resources in Southeast Alaska, critical loads for N and S are still difficult to model in an area with limited observations and very complex terrain.

Base Cations and Anions

Ca^{2+} , Mg^{2+} , Na^+ , and K^+ are base cations and are common elements contained in the Earth's crust. They are mainly sourced from soil dust, unpaved roads, agricultural tillage, industrial emissions, and sea salt spray (NADP 1999). While most of these elements are typically not considered pollutants, understanding their levels in rainfall deposition are important when assessing quantities of fugitive dusts, excess sea spray, and/or smoke. Some anthropogenic base cation sources may originate from wood, coal, and oil burning, as well as the cement, forestry, and steel industries (Lövblad et al. 2000). Their depositions in rainwater are important for quantifying the critical loads and exceedances of pollutants, as well as gauging the effects of ecosystem acidification.

Areas with high winds (>5 m/s) have the potential to speed up the mineral weathering process by eroding or lofting dusts into the atmosphere. Dusts transported from Asia are common during the spring (Watts 1969), often becoming transported for thousands of miles by upper level winds across Alaska, and have shown to impact aerosols (Sassen 2005) and the radiative balance (Stone et al. 2007). Asian dust is frequently a mixture of both natural and anthropogenic pollutants (Alfaro et al. 2003), as aerosols released from factories and manufacturing may also become lofted with the dust. Spring is the most common season for Asian dust events due to low rainfall, high winds associated with frequent cold fronts, and freshly plowed fields for spring crops (Ing 1972). Dust is also commonly kicked up over the Gobi and Mongolian deserts, lofted into the upper atmosphere, and transported across the North Pacific in the Westerlies. Much of the spring season for Asia is contained during our period of winter depositions (Chapter 2).

Base cations elements react with and neutralize acids in precipitation. The neutralizing effect is important for soil productivity and plant health so that some of the acidic effects from anthropogenically produced compounds can be reduced. However, acids present in rain may leach base cations from the soil and groundwater, thereby affecting sensitive species, altering the soil chemistry, and making acid neutralization less effective (Likens et al. 1996). Depending on the extent of acid deposition into the environment, there is an exchange between hydrogen ions (H^+) that enter the ecosystem with sulfates and nitrates in precipitation. As the sulfates and nitrates leave soil or water bodies, base cations are also removed, leaving the acidic H^+ ion behind (Pardo 2010).

Thus, the overall pH of any given droplet is a combination of the effects from certain acids like carbonic, sulfuric, and nitric acids, and any neutralizers, such as ammonia (Boubel et al. 1994). The effects of base cations are also highly dependent on geographic locations that influence the composition of rain droplets, such as continental or maritime source regions. Base cations originating from naturally sourced elements in the Earth may be hard to control. At many times, these depositions are influenced by weather systems and processes naturally occurring on Earth, all without the aid of humans.

Calcium (Ca^{2+})

The base cation Ca^+ is frequently contained in alkaline materials, such limestone, and has the ability to react and neutralize acids in precipitation. Limestone and many other rocks and soils contain calcium carbonate (CaCO_3), which is effective at neutralizing acids, like sulfuric acid and hydrochloric acid (Stewart 2007).

Chemical Reaction	Description
$\text{CaCO}_3(\text{s}) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$	This reaction shows how the H^+ ion can become neutralized by dissolving soil dust in water (Jacob 1999):
$\text{CO}_3^{2-} + 2\text{H}^+ \leftrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}$	

Magnesium (Mg^+) and Potassium (K^+)

The sources of magnesium and potassium base cations are likely to be the same as calcium in that they are sourced from common elements in the Earth's crust.

Sodium (Na^+)

Sodium elements are characteristically associated with seawater. It is likely that any sources of Na^+ come from salts lofted into the air by winds and sea spray, especially in coastal areas like Juneau. In addition, salts could also be linked to airborne dusts from the Earth's crustal materials.

Chloride (Cl^-)

According to Erisman and Draaijers (1995), the Cl^- compound in precipitation is mainly associated with Na^+ levels from sea salts. Chloride levels do not appear to be connected to Ca^{2+} (Slanina et al. 1990). Sodium and chloride levels have been highly correlated in other analyses of wet deposition, especially from regions close to the ocean. Chloride, however, may be sourced from more than just marine origins (Caffrey et al. 2010). It has also been shown that rainwater collected from inland cities may be susceptible to chloride deposition through continental sources, such as airborne dusts or biomass burning (dos Santos et al. 2007). While sea spray is likely the largest source of chloride in Juneau, we should also consider other sources, such as airborne dusts. Chloride may slightly increase the acidity of rainfall depending on where it is sourced from. Chloride stemming from fossil fuel combustion products comes from acidic sources, and thus yields higher acidic forms for chloride (Lear 1999). Despite the fact that sodium and chloride do not typically contribute to acidification, high levels of Na^+ and Cl^- depositions are important to note, as they can lead to corrosive fog and precipitation (Lear 1999).

Atmospheric Mercury

The SEAN has identified airborne toxics, including mercury and other heavy metals, as priority airborne contaminants that may have significant impacts to AQRVs. Mercury is extremely toxic and can accumulate in food webs, eventually reaching toxic levels in top predator species.

While lichens can be used as passive monitors for mercury deposition, there are currently no background or threshold levels. Lichens were sampled in SEAN parks in 2008 and 2009, and some locations were found to have mercury levels above detectable limits. These values were at least an order of magnitude higher than levels in Arctic-region national parks, and similar to those found in Oregon and Washington (Schirokauer et al. 2014).

The Western Airborne Contaminants Assessment Project (WACAP) analyzed fish and lake sediment samples from Interior and Arctic Alaska lakes in Noatak National Preserve (NOAT), Gates of the Arctic National Park and Preserve (GAAT), and Denali National Park (DENA). Mercury levels in

some fish exceeded human or wildlife health thresholds, but elemental mercury content in lichens did not (Landers et al. 2008). Although GLBA was a secondary park in the WACAP study, mercury was not analyzed there. Mercury was only sampled from lichens in 7 core parks, none of which exceeded the 90% distribution quintiles of background mercury concentration. The WACAP project also determined that while lake cores in the Lower 48 states had approximately four times more mercury in their sediments, fish from Alaska lakes had some of the highest concentrations of mercury of all WACAP locations. This finding may point to the fact that there is a poor relationship between mercury deposition and the complexity of fish bioaccumulation in aquatic food webs (Landers et al. 2008). Analysis of sediment cores from two remote lakes in Interior Alaska also showed an increase of mercury levels beginning in the early 1900's that continued to the surface with no leveling off or decline (Landers et al. 2008), likely pointing to the fact that mercury transport consistently reaches remote regions as a result of worldwide industrialization.

The SEAN also partnered with the USGS in 2012 and sampled Dolly Varden tissue from three remote locations (two lakes and one stream) in GLBA. The study determined that the mean mercury concentration across the sites was 90.2 ng/g ww (wet weight), which was slightly above the concentration across all 21 western national parks in the study (Eagles-Smith et al. 2014). However, concentrations varied widely among the three sampling areas, pointing to the fact that some local processes are likely driving the mercury bioaccumulation in GLBA, especially since the water bodies are land-locked.

Mercury, as well as several other contaminants and heavy metals, have been studied through concentrations in mussel tissue. The SEAN has partnered with the National Oceanic and Atmospheric Administration's (NOAA) Mussel Watch Program. The project was implemented in 1986, and has since expanded to over 300 sites measuring over 100 organic and inorganic analytes. Five sampling areas exist in Alaska, with one site in Nahku Bay, just outside of KLGO. According to twenty-year trends, all sites in Alaska have shown low mercury concentrations in mussel tissue, with little to no trends in their concentrations (Kimbrough et al. 2008). Mercury concentrations were 0.10 ppm at the Nahku Bay. In contrast, mercury concentrations from mussels and oysters in most US coastal regions of the Atlantic and Pacific Ocean show moderate to high mercury concentrations (0.18-1.28 ppm; Kimbrough et al. 2008).

Background

Some studies show that more than 98% of the mercury in the atmosphere is long-lived elemental mercury (Hg^0) that can be transported large distances before removal (NADP 2011). By 2002, over half of the mercury emissions from anthropogenic sources could be traced back to somewhere in Asia (Pacyna and Pacyna 2002). While mercury has been used for many beneficial purposes over the past centuries, humans have only recently discovered the potential dangers it poses to environment. Mercury deposition is particularly problematic, as the potent neurotoxin can cause adverse health effects, and cannot be easily removed from atmosphere and land ecosystems (Driscoll et al. 2007a). Once it has been deposited on a land or water surface, it does not break down or degrade. Mercury can also become widely dispersed over great distances, cycle through the biological food chain, and persist in water and soil for many years. Mercury is never actually removed from the environment,

but instead changes location and chemical composition, where it eventually becomes sequestered in soil and sediments (NADP 2011).

Mercury is part of a class of chemicals called *persistent bioaccumulative toxins*, because it cycles back and forth through air, soil, and water while changing chemical form (NADP 2011). Thus, mercury is a particularly volatile element as it undergoes a series of complex physical transformations, some of which are still in question by the scientific community (EPA 1997). Prior to the industrial revolution, mercury only existed in trace amounts throughout the Earth. As humans became steadily reliant on fossil fuels such as coal and oil, large quantities of mercury have been released into the environment, sometimes exceeding safe limits determined by the EPA.

Pure elemental mercury, which is the most volatile and prevalent form, is released through the combustion process of coal and oil-fired power plants, as well as through trash incineration (UNEP 2003). Consequently, these rank as the two largest sources of elemental mercury emission. Once released into the air, elemental mercury may adhere to local sources of dust and deposit onto the Earth's surface, or even stay circulated in the atmosphere for up to one year (EPA 1997). Mercury's atmospheric lifetime is approximately one year, but has the potential to stay in the soil much longer (NADP 2011). Elemental mercury may also react with ozone or other oxidants to form ionic mercury (Hg^{2+} , Clean Air Network 1999). This form of mercury may also be released through fuel combustion. Ionic mercury is highly soluble, and readily combines with water vapor in the atmosphere. This characteristics allows it to be carried for great distances before it falls out of the atmosphere as rain or snow.

Once ionic mercury is deposited on the Earth's surface, some of the precipitation enters rivers and streams, where it eventually reaches large waterbodies. Complex interactions occur between specialized bacteria in the water body, converting the ionic form of mercury into organic methylmercury (MeHg; Driscoll et al. 2007b). This form is the most toxic for humans, as it bioaccumulates in food webs, eventually reaching high concentration in some of the common fish we eat (Clean Air Network 1999). Small foraging fish consume tiny microorganisms in mercury-contaminated waterbodies, such as algae and zooplankton. Predator fish then eat the small foragers. Humans become exposed to methylmercury by eating fish at the top of the food chain, especially at higher rates than our bodies can process. The potent neurotoxin is most threatening for sensitive groups, as mercury exposure is harmful during early stages of development and could result in delays in learning and motor functions (Clean Air Network 1999; Driscoll et al. 2007b). Some studies suggest between 200,000 and 400,000 children in the USA are born each year with enough pre-natal exposure of methylmercury to cause some order of neurological impairment (Mahaffey 2005). Fish are deemed unsafe to eat once the overall mercury content exceeds 0.3 ppm set by the EPA (Driscoll et al. 2007a).

Mercury is not sourced exclusively from anthropogenic combustion of fossil fuels. Natural sources of mercury occur in the Earth's crust, primarily from rock weathering, volcanic eruptions, geothermal vents (UNEP 2003), enriched soils, or evaporation from wetlands and oceans (NADP 2011). Improper disposal of mercury-rich items, such a thermometers, batteries, electronics, and fluorescent light bulbs add to the mercury burden (Driscoll et al. 2007a), especially if those items are incinerated

and not simply thrown into a landfill. Fungicides for crop use once contained mercury, and now also add to the environmental issues (EPA 1997).

While some estimates show that United States mercury emissions had peaked in the 1970s (Pirrone et al. 1998) when less restrictions were placed on heavy pollution emitters, concentrations are still at least three to five times higher than they were in the preindustrial era (Varekamp et al. 2003; Mason et al. 1994). In 1995, the EPA estimated that the global emission of mercury from natural and anthropogenic sources was 5,500 metric tons, with about 3% sources exclusively from the USA (EPA 1997). Another estimate in 2002, projected the value to be approximately 6,600 metric tons, with 33-36% attributed from anthropogenic emissions, and the remainder from natural sources or rereleased from past emissions (Mason and Sheu 2002).

The EPA (1997) and NADP (2011) have shown that humid locations have higher mercury *deposition* than arid ones, but mercury *concentrations* in rainfall may be higher in drier locations. Some rainy locations, such as Florida, have high deposition loads due to abundant precipitation, but this location is also within close proximity to anthropogenic emission sources. Since wet deposition is the primary mechanism for transporting mercury from the atmosphere to the land or water bodies (EPA 1997), estimated at nearly 50-90% of the mercury load (NADP 2011), understanding concentrations and trends is very important.

POPs and SOCs

Mercury and a suite of persistent organic pollutants (POPs) are not usually produced in Southeast Alaska, but the long-range transport of these contaminants are likely entering SEAN ecosystems. POPs comprise of a lengthy list toxic and organic compounds derived from pesticides, industrial compounds, pharmaceuticals, and combustion byproducts. They are particularly problematic as they are resistant to environmental degradation and may pose serious impacts on human and environmental health. POPs are of high concern in Alaska and high latitudes, as many were produced elsewhere and transported through wind, precipitation, or through oceanic water currents. The EPA has released a list of twelve key POPs called the “Dirty Dozen” that are of global concern. Most developed nations have agreed to reduce or eliminate the production and release of the following twelve POPs, which were either produced intentionally, or as a result of industrial combustion. They include: aldrin, chlordane, dichlorodiphenyl trichloroethane (DDT), dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (dioxins), and polychlorinated dibenzofurans (furans; EPA 2009).

Levels of POPs and SOCs were analyzed in the TNF and portions of GLBA as part of the WACAP study (Landers et al. 2008). Overall concentrations of SOCs and POPs in lichen tissue and conifer needles in Beartrack Cove ranked low compared to other WACAP parks (Landers et al. 2008). Passive air samplers in GLBA also determined that the overall concentrations of SOCs, including polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and PCBs ranked very low compared other WACAP parks (Landers et al. 2008).

In 2007, water, suspended particles, sediments, benthic macroinvertebrates, and juvenile coho salmon were sampled in 19 SEAN streams to establish baseline levels of contaminant concentrations

and their spatial differences among the parks (Nagorski et al. 2011). Concentrations of total mercury in stream water were 3-4 orders of magnitude below EPA levels of concern for humans and aquatic organisms. Mercury levels in juvenile coho salmon were well below EPA fish tissue standards; however, adult cohos were as high as 80 ng/g, which is close to the 100 ng/g exceedance criteria. DDTs and PCBs were detectable from fish samples in almost all SEAN streams, but all 77 POPs analyzed in this study were below levels of environmental and human health concerns (Nagorski et al. 2011).

Appendix B – Comparisons Among Model Predictions and Ambient Air Quality Measurements

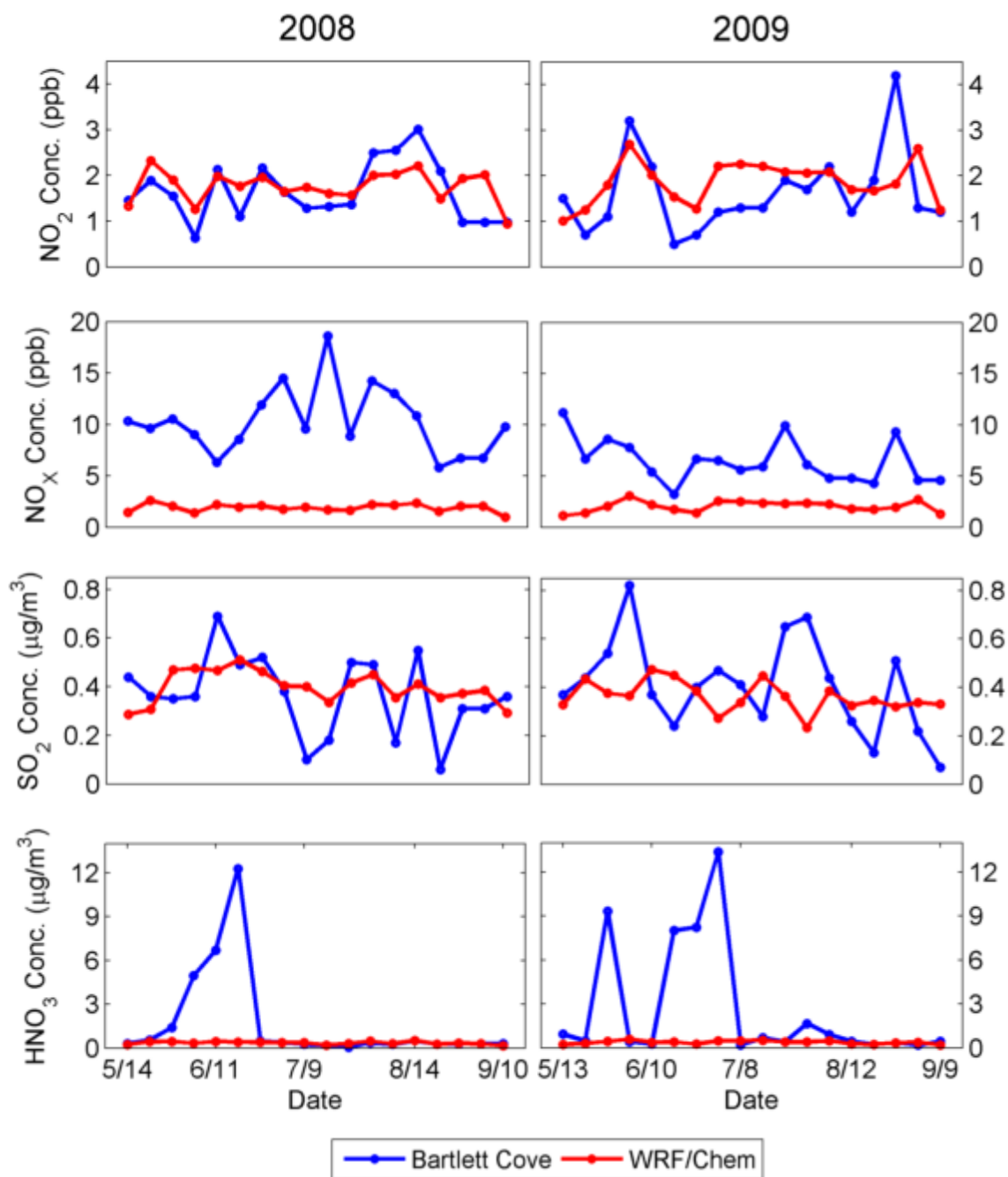


Figure B1. Time series plots of average weekly contaminant concentrations from 2008 and 2009 comparing Ogawa ambient air quality sites in Bartlett Cove, GLBA with WRF/Chem model data.

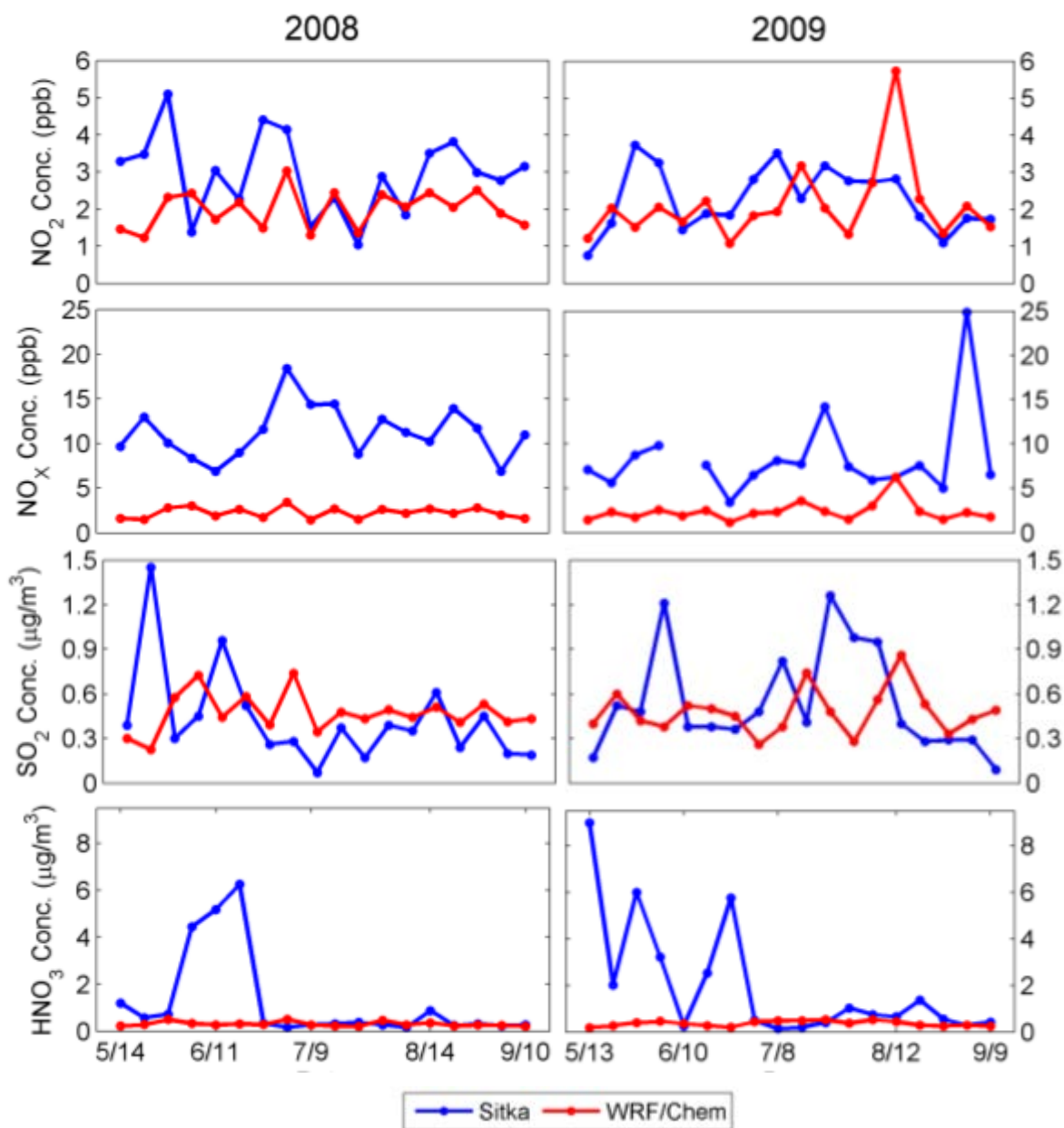


Figure B2. Time series plots of average weekly contaminant concentrations from 2008 and 2009 comparing Ogawa ambient air quality sites in SITK with WRF/Chem model data.

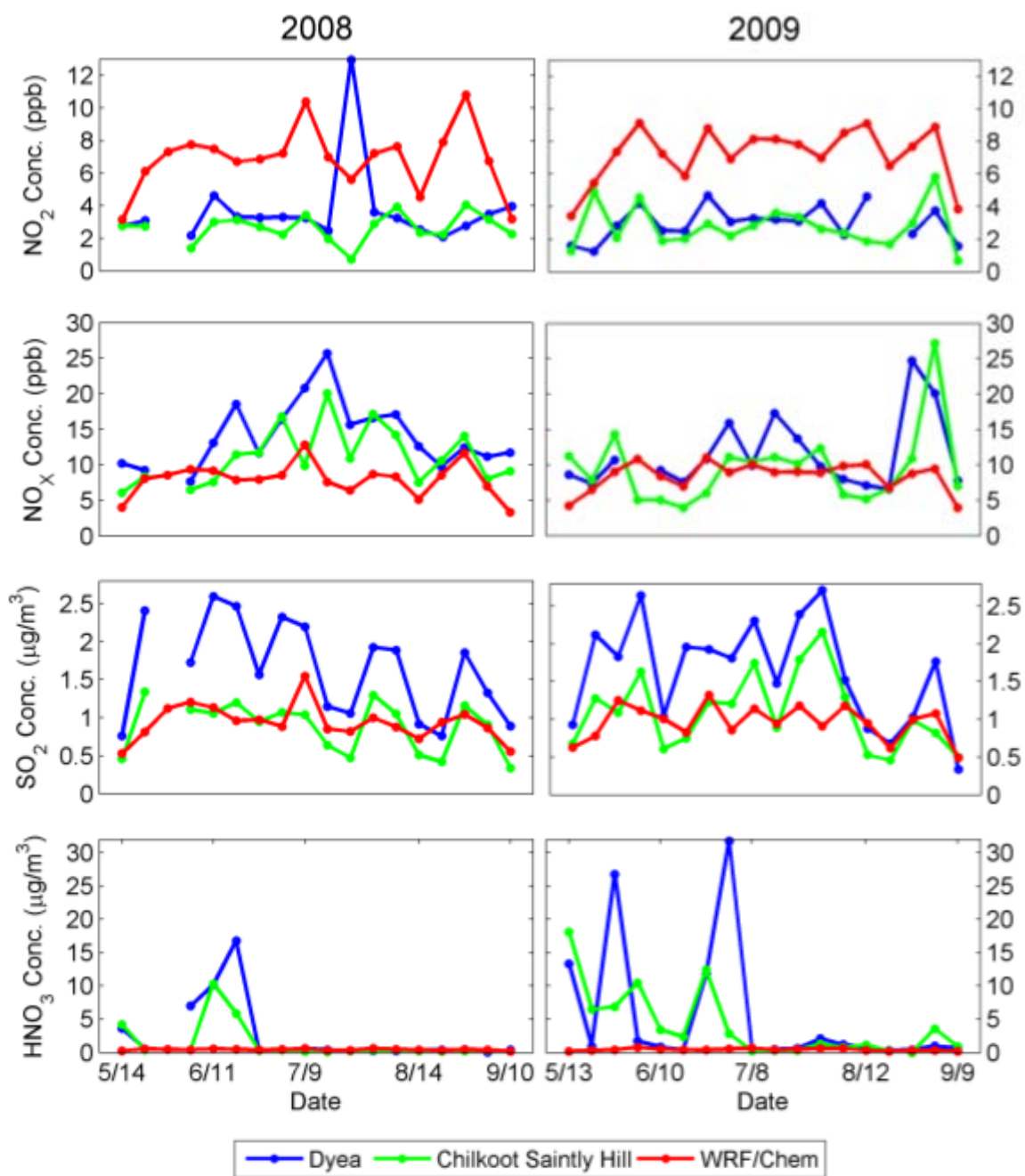


Figure B3. Time series plots of average weekly contaminant concentrations from 2008 and 2009 comparing Ogawa ambient air quality sites near KLGO-Dyea with WRF/Chem model data.

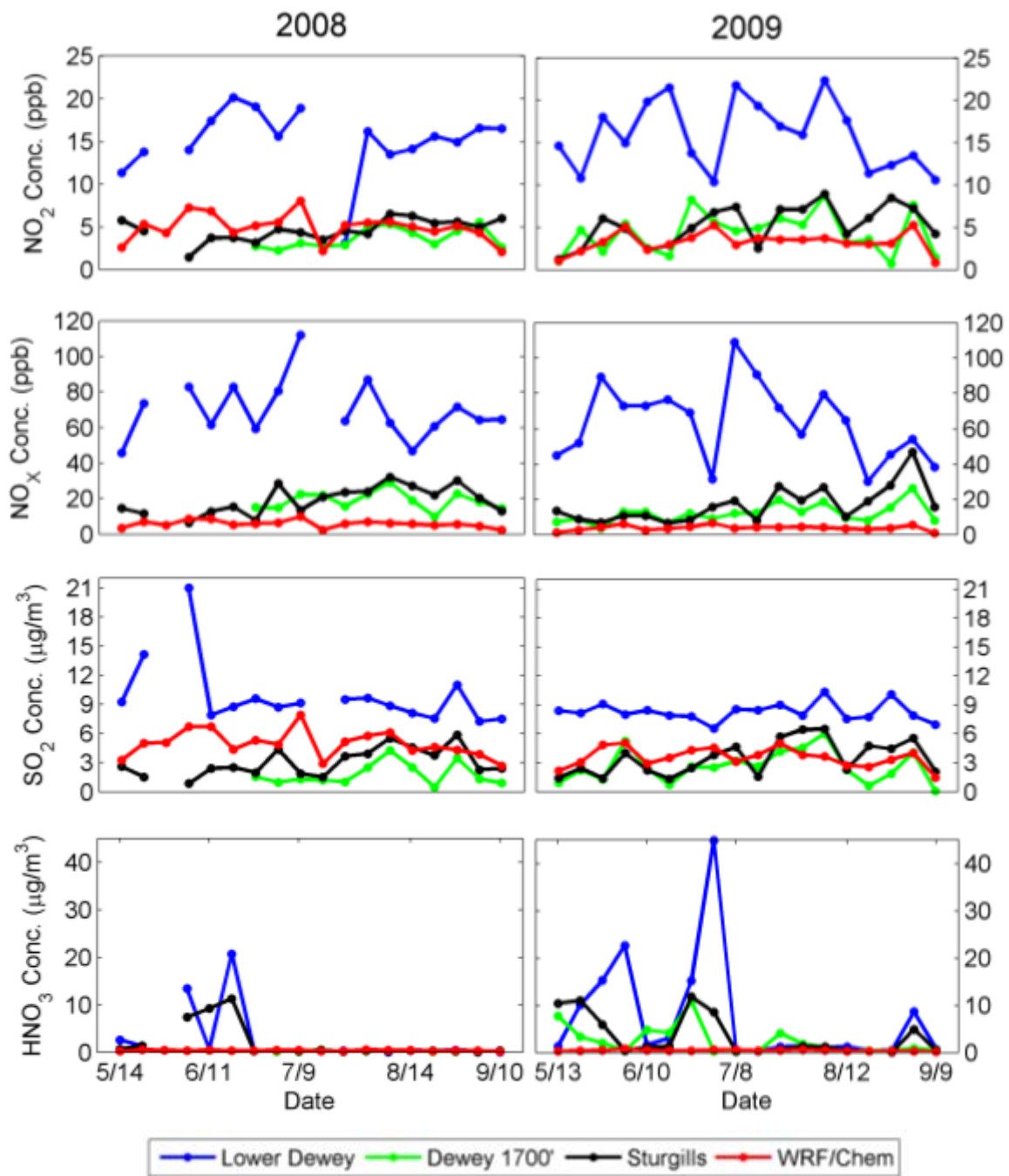


Figure B4. Time series plots of average weekly contaminant concentrations from 2008 and 2009 comparing Ogawa ambient air quality sites near KLGO-Skagway with WRF/Chem model data.

Appendix C – Detailed Cost Estimates

Table C1. Estimated costs for analysis of lichen tissue chemistry. ^{A, B}

Analysis Type	Rate per Sample	Set-up Charge ^C	Number of samples per site ^D	Total
Grinding Fee	\$5.25	\$25	9	\$72.25
Total Nitrogen Fee	\$12.75	\$30	9	\$144.75
Total Sulfur Fee	\$17	\$30	9	\$183
P, K, Ca, Mg, Na, Al, Fe, Mn, Zn, Cu, B, Pb, Ni, Cr, Cd, Co, Mo, Si, Ti, Be, Sr, Rb, Li, V, and Ba Elemental Analysis Fee	\$34.50	\$30	9	\$340.50
Grand Total Per Site	\$69.50	\$115	9	\$740.50 ^E

^A Optional mercury analysis is offered for \$150 per sample plus \$225 set-up charge.

^B Prices valid as of February 2015. Retrieved from University of Minnesota Research Analytical Laboratory, Dept. of Soil Science: <http://ral.cfans.umn.edu/prices/>

^C The set-up charge is a one-time fee no matter how many samples are being submitted. Therefore, it is best to send all samples in one shipment to avoid multiple set-up fees.

^D Number is based on 3 samples of each species: *Hypogymnia enteromorpha*, *H. inactiva*, and *Platismatia glauca*. The actual number of species will vary by site.

^E Additional costs for postage, salary, and travel may be necessary.

Table C2. Estimated seasonal costs for throughfall and open deposition IER sites. ^A

Site Type	Component	Cost per Sampler	Cost per Site
Throughfall (forested) Site: (10 throughfall collectors)	IER Collectors: parts and assembly (IER column, hardware, funnel, bird ring, hose clamps, and filter ring)	\$45	\$450
	IER KI Extraction	\$15	\$150
	Analysis costs (2 analytical instruments): NO ₃ , NH ₄ , SO ₄ , PO ₄	\$45	\$450
	Shipping	\$5	\$50
	Throughfall Site Total ^B	\$110	\$1,100
Open Site: (6 open collectors)	IER collectors: parts and assembly (IER column, hardware, funnel, bird ring, hose clamps, & filter ring)	\$45	\$270
	IER KI Extraction	\$15	\$90
	Analysis costs (2 analytical instruments): NO ₃ , NH ₄ , SO ₄ , PO ₄	\$45	\$270
	Shipping	\$5	\$30
	Open Site Total ^C	\$110	\$660
Paired Throughfall and Open Site	Total Seasonal Cost Per Site (paired TF and OD sites)	-	\$1,760 x 2
	Less Cost of IER Parts and Assembly	-	-\$720
	Total Yearly Cost Per Site ^{D, E}	-	\$2,800

^A Budget courtesy of Mark Fenn (mfenn@fs.fed.us) as of November 5, 2014.

^B Each throughfall site has 10 IER collectors

^C Each open site has 6 IER collectors

^D Additional costs for the site operator's salary and travel may be necessary, training on how to properly collect the sample, as well as costs to install the device.

^E There are generally two yearly deployments of IERs. The winter season (October to April) will require the IERs to be outfitted with snow tubes, which may add additional costs.

Table C3. Estimated costs for sponsorship of NADP-MDN station. ^{A, B}

Component	Price
MDN device	\$0
Coordination (administrative fees, data management, QA/QC, etc.)	\$2,700
Total Mercury (TM) chemistry analysis	\$6,994 ^C
NED fee (equipment)	\$182
Total yearly costs	\$9,876
Estimated shipping to lab	\$1,040
Grand Total Per Year	\$10,916 ^D

^A Operating costs courtesy of the NADP for FY2014.

^B Optional monthly methyl mercury sampling is offered at \$1,950/yr (samples shipped with weekly TM).

^C \$134.50/week for 52 weeks = \$6,994

^D Additional costs for the site operator's salary may be necessary, training on how to properly collect the sample, as well as costs to re-install and/or relocate the device.

Table C4. Estimated costs for operation and analysis of an ambient air quality monitoring (Ogawa) site. ^A

Item	Number Required per Site per Exposure	Blanks Required per Exposure	Total Number of Filters & Samples Required	Purchase Cost Per Filter	Analyses & Handling Costs Per Sample	Weekly Filter Cost	Weekly Analysis Cost	Seasonal Filter Cost (25 weeks)	Seasonal Analysis Cost (25 weeks)	Total Seasonal Cost
Ogawa NH ₃ Filter	2	2	4	\$1.75	\$18.00	\$7.00	\$72.00	\$175.00	\$1,800.00	
Ogawa NO ₂ Filter	2	2	4	\$1.75	\$18.00	\$7.00	\$72.00	\$175.00	\$1,800.00	
Ogawa NO _x Filter	2	2	4	\$1.75	\$18.00	\$7.00	\$72.00	\$175.00	\$1,800.00	
Pel Gelman (66509) HNO ₃ Filter	3	2	5	\$3.25	\$25.00	\$16.25	\$125.00	\$406.25	\$3,125.00	
Pel Gelmam (P5PJ047) HNO ₃ Filter	3	0	3	\$5.00	NO CHARGE	\$15.00	\$0.00	\$375.00	\$0	
Total	12	8	20	-	\$79.00	\$52.25	\$341.00	\$1,306.25	\$8,525.00	\$9,831.25
Shipping	-	-	-	-	-	-	\$75.00	-	\$1,875 ^B	\$11,706.25
8% Fee	-	-	-	-	-	-	\$37.46	-	\$936.50	\$12,642.75 ^C
Grand Total (cost)	-	-	-	-	-	-	\$505.71 ^C	\$1,306.25	\$11,333.50	

^A Budget courtesy of Andrzej Bytnerowicz (abytnerowicz@fs.fed.us) and Diane Alexander (dalexander01@fs.fed.us) as of November 14, 2014.

^B One shipping cost for all sites. Omit from additional site estimates. For example, a three site weekly estimate is \$1,355.13.

^C Additional costs for the site operator's salary and travel may be necessary, training on how to properly collect the sample, as well as costs to install the device.

The Department of the Interior protects and manages the nation's natural resources and cultural heritage; provides scientific and other information about those resources; and honors its special responsibilities to American Indians, Alaska Natives, and affiliated Island Communities.

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