



Environmental Contaminants Monitoring Protocol for the National Park Service, Southeast Alaska Inventory and Monitoring Network

Version EC-2018.1

Natural Resource Report NPS/SEAN/NRR—2018/1768



ON THE COVER

Clockwise from top left: Bay mussels for contaminants analysis; colorful lichen; brown bear feeding on mussels in the intertidal; measuring the mass of Dolly Varden

Photographs courtesy of National Park Service (mussels and lichen), Craig Murdoch/NPS (Dolly Varden) and Tania Lewis/NPS (brown bear)

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Contents

	Page
Figures.....	vi
Tables.....	vii
Executive Summary	viii
Acknowledgments.....	ix
List of Acronyms	x
1. Background and Objectives	1
1.1 Protocol Synopsis	1
1.2 Goals and Measurable Objectives	2
1.3 Environmental Setting.....	3
1.3.1 Atmospheric Environment.....	3
1.3.2 Freshwater Environment	4
1.3.3 Marine Environment.....	4
1.4 Purpose of Sampling.....	4
1.5 The Value of Monitoring Each Category of Contaminants.....	5
1.5.1 Mercury (Hg).....	6
1.5.2 Other Inorganic Elements.....	6
1.5.3 Persistent Organic Pollutants (POPs)	6
1.5.4 Polycyclic Aromatic Hydrocarbons (PAHs)	7
1.6 Selecting Long-term Sampling Media for Each Priority Contaminants Concern	7
1.6.1 Monitoring Airborne Contaminants Using Lichens (mainly from Pirhalla and Bower 2016)	7
1.6.2 Monitoring Freshwater Contaminants Using Riverine Dolly Varden	8
1.6.3 Monitoring Marine Contaminants Using Mussels (mainly from Tallmon 2012).....	10
2. Sampling Design	11
2.1 Rationale for Site Selection	11

Contents (continued)

	Page
2.2 Sampling Sites	11
2.2.1 Airborne Contaminants Monitoring Sites	11
2.2.2 Freshwater Contaminants Monitoring Sites	12
2.2.3 Marine Contaminants Monitoring Sites	12
2.3 Definition of the Sampling Boundaries	13
2.4 Sampling Frequency and Replication	13
2.5 Trend and Variability Detection	14
3. Overview of Field and Laboratory Methods	16
3.1 Field Season Preparations	16
3.2 Field Procedures	16
3.2.1 Airborne Contaminants	16
3.2.2 Freshwater Contaminants	17
3.2.3 Marine Contaminants	17
3.3 Laboratory Methods	18
4. Data Handling, Analysis, and Reporting	21
4.1 Overview of Data Products	21
4.2 Dissemination: Accessing the Data Deliverables	21
4.3 Repository: Data Archiving	23
4.4 Deliverable Validation and Certification	24
4.5 Data Acquisition: Scheduling Deliverable Production	24
4.6 Managing the Production Environment	Error! Bookmark not defined.
5. Personnel Requirements and Training	25
5.1 Roles and Responsibilities	25
5.1.1 Project Leader (SEAN Ecologist, currently Chris Sergeant)	25
5.1.2 SEAN Data Manager (currently Bill Johnson)	26
5.1.3 SEAN Program Manager (currently Mike Bower)	26

Contents (continued)

	Page
6. Operational Requirements	27
6.1 Annual Workload and Field Schedule.....	27
6.2 Facility and Equipment Needs.....	28
6.3 Start-up Costs and Budget Considerations	28
6.4 Protocol Revision Process	29
Literature Cited	31
Appendix A: Power to detect contaminant concentration differences in freshwater fish between sites and long-term trends within sites.....	38
Introduction	38
Methods	38
Results	40

Figures

	Page
Figure 2.1. Map of SEAN permanent airborne contaminants monitoring stations in GLBA, KLGO, and SITK.	11
Figure 2.2. Map of SEAN permanent freshwater contaminants monitoring stations in GLBA, KLGO, and SITK.	12
Figure 2.3. Map of SEAN permanent marine contaminants monitoring stations in GLBA, KLGO, and SITK.	13
Figure 3.1. Photos of lichen species used for elemental tissue analysis.	17
Figure 4.1. Deliverables referenced on the environmental contaminants Data Store project page.	23
Figure A1. Power to detect a statistical difference in two site means based on sample sizes ranging from 2 to 30.	40
Figure A2. The power to detect a linear long-term trend in contaminant loads at a single site.	41

Tables

	Page
Table 1.1. Standard operating procedures followed in this protocol.....	1
Table 1.2. Primary studies supporting development of the environmental contaminants protocol.	2
Table 1.3. Key distant and local drivers of contaminant concentrations within southeastern Alaska.	5
Table 1.4. Classes of contaminants monitored by each component of the SEAN environmental contaminants protocol.	5
Table 2.1. Summary of core SEAN environmental contaminants monitoring program and sampling locations.	15
Table 3.1. Summary of analytical methods used for the SEAN environmental contaminants monitoring protocol.	19
Table 4.1. The SEAN data deliverables provided by this monitoring program.	22
Table 6.1. Budget estimates for analytical fees associated with one five-year iteration of the SEAN environmental contaminants monitoring protocol.	29
Table A1. Summary of data sources used to perform long-term trend and sample size power analysis.	38
Table A2. Parameter input for <i>pwr.t.test</i> function in the R statistical package <i>pwr</i>	39
Table A3. Parameter input for <i>powertrend</i> function in the R statistical package <i>fishmethods</i>	39
Table A4. Statistical power to detect a 5% or 10% linear annual change at a single site after 10 or 50 years of monitoring.	41

Executive Summary

Airborne, freshwater, and marine contaminants were designated as priority long-term monitoring programs (vital signs) for the Southeast Alaska Inventory and Monitoring Network (SEAN). Here, we integrate these three vital signs into one environmental contaminants monitoring program in order to increase data collection and reporting efficiency for tightly connected ecosystem components that are exposed to a common suite of pollutants. This document describes the context and justification for contaminants sampling, describes monitoring program methodology, and prescribes staff roles and data management procedures. The standard operating procedures (SOPs) referenced throughout this protocol narrative contain detailed instructions for all aspects of field sampling, lab routines, data collection, storage, analysis, and reporting. In many cases, these SOPs were already developed by existing and widely accepted contaminants monitoring programs.

The goal of the environmental contaminants monitoring program is to monitor a suite of priority pollutant or contaminant threats to the parks of Southeast Alaska. This will be accomplished by implementing two primary priorities. First, this protocol will produce a long-term surveillance record of priority airborne, freshwater, and marine pollutants or contaminants in sentinel species at select sites in SEAN parks to enable comparisons with future conditions. Second, the protocol establishes a means to compare pollutant and contaminant concentrations against state, federal, or other relevant criteria for human and ecological health, as a means of evaluating the potential for impairment of NPS resources.

Three specific program objectives are:

- 1) Monitor lichen tissue concentrations for nitrogen, sulfur, and 25 additional elements in conformance with protocols developed for the Tongass National Forest
- 2) Monitor total mercury in riverine Dolly Varden tissue using existing Environmental Protection Agency (EPA) protocols
- 3) Monitor a broad suite of metals, polycyclic aromatic hydrocarbons (PAHs), and persistent organic pollutants (POPs) in bay mussels, in conformance with national protocols developed by the National Oceanic and Atmospheric Administration (NOAA) Mussel Watch Program.

Starting in 2018, sampling for each objective will occur every five years at 19 sites defined within the protocol (6 airborne, 6 freshwater, and 7 marine). At a minimum, data and report products generated by this program will be publicly available on the SEAN website. These products will inform park staff, managers, and outside parties of the status of contaminants in biological samples collected in Southeast Alaska national parks. If we observe contaminant levels of concern during the course of monitoring, SEAN staff will consult with network parks to determine what extended reporting is necessary (e.g., immediate visitor advisory, report to external agencies, peer-reviewed scientific article, or other communication medium).

Acknowledgments

This narrative is derived from work conducted by the NPS, SEAN, and other collaborators since 2000. The text and concepts presented here were initially presented in many of the documents cited within, especially those in Table 1.2. The authors extend their sincere appreciation to the many people who helped create the environmental contaminants monitoring protocol or collected supporting data. In alphabetical order, we thank: Dennis Apeti, Jami Belt, Steve Bryan, Brinnen Carter, Maggie Castellini, Karen Dillman, Lisa Etherington, Scott Gende, Lisa Hoferkamp, J. Andres Lopez, Craig Murdoch, Sonia Nagorski, Emily Noyd, Todd O'Hara, Keith Oster, Mike Pirhalla, Rebecca Pugh, Dave Schirokauer, Lewis Sharman, Chad Soiseth, David Tallmon, and Jessica Wilbarger. Krista Bartz provided especially helpful reviews and conversations along the way. Current and past members of the SEAN technical committee helped shape the environmental contaminants monitoring vision. We thank Nina Chambers and Margaret Beer for technical editing and formatting support. The protocol benefited from thoughtful peer reviews by Angela Matz and Carol Woody.

List of Acronyms

As – Arsenic

Ca – Calcium

Cd – Cadmium

Cu – Copper

DDT – Dichlorodiphenyl polychloro-ethanes and –ethylenes

DOI – Department of the Interior

EPA – Environmental Protection Agency

FIA – United States Forest Service Forest Inventory and Analysis Program

GLBA – Glacial Bay National Park and Preserve

HCB – Hexachlorobenzene

Hg – Mercury

IER – Ion exchange resin

IMD – Inventory and Monitoring Division of the National Park Service

IRMA – Integrated Resource Management Applications

KLGO – Klondike Gold Rush Historical National Park

LRAT – Long Range Atmospheric Transport

MDN – Mercury Deposition Network

MeHg – Methylmercury

MWP – Mussel Watch Program

N – Nitrogen

NADP – National Atmospheric Deposition Program

NRDS – Natural Resource Data Series

Ni – Nickel

NPS – National Park Service

NOAA – National Oceanic and Atmospheric Administration

NRSS – National Resource Stewardship and Science Directorate

OCs – Organochlorines

PAC – Polycyclic aromatic compounds

PAH – Polycyclic aromatic hydrocarbons

Pb – Lead

PBDEs – Poly-Brominated Diphenyl Ethers

PCBs – Poly Chlorinated Biphenyls

POP – Persistent Organic Pollutant

QA – Quality assurance

QC – Quality control

S – Sulfur

Se – Selenium

SEAN – Southeast Alaska Network

SITK – Sitka National Historical Park

SOP – Standard Operating Procedure

SPMD – Semi-permeable membrane devices

THg – Total mercury

USFS – United States Forest Service

ww – Wet Weight

Zn – Zinc

1. Background and Objectives

1.1 Protocol Synopsis

The Southeast Alaska Network (SEAN) is one of 32 National Park Service (NPS) Inventory and Monitoring networks and comprises three park units: Glacier Bay National Park and Preserve (GLBA), Klondike Gold Rush National Historical Park (KLGO), and Sitka National Historical Park (SITK). The SEAN has designated airborne, freshwater, and marine contaminants as priority long-term monitoring programs, also referred to as vital signs, for all three parks based on their potential to impair sensitive park ecosystems (Moynahan et al. 2008). This protocol integrates these three vital signs into one environmental contaminants monitoring program in order to increase data collection and reporting efficiency for tightly connected ecosystem components that are exposed to a common suite of pollutants.

SEAN parks contain a diverse assemblage of flora and fauna available for biomonitoring of contaminants (Lenz et al. 2002; Hahr and Trapp 2004; Bernatz et al. 2010; Stark et al. 2012). Due to their abundance, ease of capture, and demonstrated value as effective sentinels for contaminants surveillance, we have chosen lichen, fish, and saltwater mussels as the primary groups of organisms for our program.

This document describes the context and justification for contaminants sampling, describes monitoring program methodology, prescribes staff roles, data management procedures, and reporting requirements. The standard operating procedures (SOPs) referenced throughout this protocol narrative contain detailed instructions for all aspects of field sampling, lab routines, and data collection, storage, analysis, and reporting (Table 1.1). In many cases, these SOPs were already developed by existing and widely accepted contaminants monitoring programs. Together, the protocol narrative and SOPs contain the information necessary to implement and sustain a long-term monitoring program. Protocol development was supported by data from numerous pilot and interim studies conducted since network establishment (Table 1.2).

Table 1.1. Standard operating procedures followed in this protocol.

SOP Number	Subject
SOP 1	Operational safety for all field-based duties
SOP 2	Field and lab guidelines for lichen tissue analysis
SOP 3	Field and lab guidelines for mercury analysis of Dolly Varden tissue
SOP 4	Field and lab guidelines for bay mussel tissue analysis
SOP 5	Periodic reporting
SOP 6	Protocol revision
SOP 7	Data availability

Table 1.2. Primary studies supporting development of the environmental contaminants protocol. Much of the text originally drafted in these documents was integrated into this protocol.

Vital sign	Primary studies supporting protocol development
Airborne contaminants	Pirhalla and Bower 2016, Schirokauer et al. 2014, Furbish et al. 2000
Freshwater contaminants	Cyr et al. 2017, Cyr et al. 2014, Nagorski et al. 2014, Nagorski et al. 2011
Marine contaminants	Tallmon 2012, Tallmon 2011

In addition to the studies above, components of this protocol were developed with significant contributions from proven methodologies developed by other NPS networks, other federal agencies (e.g., NOAA and EPA), and instrument manufacturers (see Table 3.1). Some structural elements of the protocol and step-by-step instructions are derived from the SEAN water quality (Sergeant et al. 2013) and oceanography (Johnson and Sharman 2014) monitoring protocols. In some places, the document structure varies slightly from the original monitoring protocol guidelines presented by Oakley et al. (2003) to fit the most intuitive organizational structure for this group of vital signs.

Relative to other SEAN vital signs such as oceanography (Johnson and Sharman 2014) and Kittlitz’s Murrelets (Hoekman et al. 2013), field work for contaminants monitoring involves much less time and effort, but lab analyses are very expensive (see Section 6 for sample budgets). For example, at the time of publishing this protocol, analysis and reporting for a single Mussel Watch site cost over \$2,500 (field personnel, travel, and shipping costs not included). Therefore, limited program funds need to be allocated carefully to maintain sustainability. Since SEAN parks are relatively pristine and no contaminant concentrations from previous studies (Table 1.2) have approached any known ecological or human health concern thresholds, we have chosen to rely on surveillance monitoring of primary pollutant threats at a limited number of index sites using biological tissues having the highest probability of demonstrating elevated contaminant concentrations in response to changes in contaminant source levels or acute threats (Harris et al. 2007).

The marine shorelines of SEAN parks, in comparison to terrestrial and freshwater landscapes, are most susceptible to acute pollution events and receive cumulative contamination from the atmosphere and freshwater drainages. Additionally, polluted marine shorelines could have the most immediate relevance to park management since catastrophic events and long-term trends may be caused, in part, from permitted visitor activities. Therefore, the SEAN is prioritizing funding for monitoring marine contaminants by maintaining seven Mussel Watch sites (five in GLBA, one in KLGO, one in SITK), five of which have been monitored every two years since 2007 (see SOP 4). Airborne and freshwater contaminants also play an important role in understanding the condition of park natural resources, though the lack of NPS jurisdiction over adjacent or distant contaminant sources can limit the number of feasible management actions as problems are detected.

1.2 Goals and Measurable Objectives

The goal of the environmental contaminants monitoring program is to monitor a suite of priority pollutant or contaminant threats to the parks of Southeast Alaska. Two primary priorities advance this goal:

1. To create a long-term surveillance record of priority airborne, freshwater, and marine pollutants or contaminants in sentinel species at select sites in Glacier Bay National Park and Preserve, Klondike Gold Rush National Historical Park, and Sitka National Historical Park to enable comparisons with future conditions.
2. To compare pollutant and contaminant concentrations against state, federal, or other relevant criteria for human and ecological health, when available, as a means of evaluating the potential for impairment of NPS resources (see Section 1.6 for citations related to these criteria).

Within the context of these broad program priorities, specific objectives for airborne, freshwater, and marine monitoring include the following:

- Monitor lichen tissue concentrations for nitrogen, sulfur, and 25 additional elements in conformance with protocols developed for the Tongass National Forest
- Monitor total mercury in riverine Dolly Varden tissue using existing EPA protocols
- Monitor a broad suite of metals, polycyclic aromatic hydrocarbons (PAHs), and persistent organic pollutants (POPs) in bay mussels, in conformance with national protocols developed by NOAA Mussel Watch.

The sections below provide further context and justifications for the objectives listed here.

1.3 Environmental Setting

SEAN parks encompass nearly 3.3 million acres and represent the full range of landscapes within Southeast Alaska. Maritime influence and steep topography create abundant precipitation in this region. Weather patterns are dominated by a strong Aleutian Low in the northern Gulf of Alaska in the fall, winter, and spring, and by weak high pressure systems in the summer. Low elevations are dominated by temperate rainforest while higher elevations in GLBA and KLGO have significant and rapidly changing glacial coverage. Some coastal and high-elevation locations in GLBA and SITK exceed 330 cm of rainfall annually (Shulski and Wendler 2007), while KLGO is influenced by a rain shadow effect and receives as little as 76 cm each year. These atmospheric patterns affect the transport of contaminants to terrestrial, freshwater, and marine systems.

1.3.1 Atmospheric Environment

Since coastal Alaska is typically the first land that Asian air masses encounter after crossing the Pacific Ocean (Jaegle 2010), orographically enhanced precipitation over the Coastal Range may deposit significant loads of latent contaminants. For example, the highest rates of atmospheric Hg deposition in Alaska are found along the southern coastal mountain ranges, where precipitation is abundant (Obrist et al. 2016; Pirhalla and Bower 2016). Although prevailing winds from the Pacific Ocean tend to moderate air quality, air stagnation associated with temperature inversions can also occasionally concentrate air pollution from local sources.

Southeast Alaska has relatively pristine air quality due to low population densities and limited sources of anthropogenic emissions (Dillman et al. 2007), but environmental pollutants within SEAN

parks still have the potential to disrupt sensitive ecosystems. The growing tourism industry and long-range transport of atmospheric contaminants increase the potential to pollute and impair park resources (Moynahan et al. 2008).

All parks within the SEAN are designated as Class II airsheds under the Clean Air Act of 1977, which receive less-stringent air pollution protection than Class I airsheds. Since air quality in the SEAN is regulated by the EPA under less-strict standards, surveillance for air pollution and tracking the potential for resource impairment are of high importance to NPS managers (Moynahan et al. 2008).

1.3.2 Freshwater Environment

Freshwater bodies within the SEAN are diverse and numerous, including upland and subalpine lakes, wetlands and ponds, groundwaters, and glacial and non-glacial streams. GLBA, the largest unit in the SEAN, has more than 310 streams flowing for over 3,380 km (Soiseth and Milner 1995), but this is likely an underestimate of total stream length. Two large, glacial, trans-boundary rivers, the Taiya River and the Skagway River, flow through KLGO. The lowest portion of only one river, the Indian River, is within the boundaries of SITK. Both the SEAN freshwater water quality monitoring protocol (Sergeant et al. 2013) and NPS coastal watershed assessments (Eckert et al. 2006a, 2006b; Hood et al. 2006) provide more detailed descriptions of the physical environment and condition of freshwater resources in the SEAN.

A large volume of freshwater in GLBA and KLGO remains as ice. Approximately 39% of GLBA is covered in ice (Loso et al. 2014), but significant glaciated portions of the watersheds extend beyond the park and U.S. border. KLGO is estimated to have less than 3% glacial coverage; however, the watersheds of the two major rivers in the park contain a significantly higher percentage of glacial coverage: 36% in the Taiya River watershed (Sergeant and Nagorski 2014) and 17% in the Skagway River watershed (Bernatz et al. 2010). Most of the glaciers in GLBA and KLGO are receding with climate change, resulting in the establishment of new water bodies and land (Loso et al. 2014) and an increase in glacial discharge to marine environments (Hill et al. 2015).

1.3.3 Marine Environment

Marine waters cover over 2,000 km² within GLBA boundaries. The park's approximately 1,900 km of coastline is the longest in NPS jurisdiction. Although coastal-estuarine portions of KLGO and SITK are very small in comparison to GLBA, both parks are directly influenced by marine processes (Moynahan et al. 2008). All three parks are exposed to vessel traffic ranging in size from small private boats to large cruise ships; thus, there remains a persistent potential for catastrophic events such as oil spills. In GLBA, more than 95% of visitors enter the park via cruise ship during the peak tourism period of June through August (Mölders and Gende 2015). In addition to the potential for oil spills, cruise ships emit gas and particulates that can deposit contaminants within park boundaries.

1.4 Purpose of Sampling

By many standards, Southeast Alaska is considered pristine, but it is still exposed to a variety of anthropogenic contaminants transported from distant and local sources. While a large body of research has documented higher-than-expected contaminant concentrations in air, water, sediments,

flora, and fauna at high latitudes, little long-term information on these dynamics exists within the region. We have identified eight important drivers that guided the design of our monitoring program (Table 1.3).

Table 1.3. Key distant and local drivers of contaminant concentrations within southeastern Alaska. The list is not exhaustive, but represents the drivers well represented in scientific literature and most likely to influence SEAN parklands. See accompanying text in this protocol narrative section for more details and citations. LRAT = Long-range atmospheric transport.

Driver	Specific example	Associated monitoring program(s)
LRAT	Coal-burning emissions deposit mercury on terrestrial and aquatic habitats	Freshwater/marine
Heavy precipitation	Large annual rainfall enhanced by steep regional topography may encourage deposition of latent contaminants	Freshwater/marine
Local emissions	Cruise ship smokestacks release nitrogen and sulfur compounds	Airborne
Biovectors	Adult salmon transport marine-derived contaminants to rivers during spawning migration	Freshwater
Glacier volume loss	Contaminants deposited on then locked in ice are released to downstream freshwater and marine environments during glacial run-off events	Freshwater/marine
Watershed age	In GLBA, older watersheds have greater wetland coverage, which increases the rate of mercury methylation	Freshwater
Aqueous hydrocarbons	Marine vessels travelling in or near parks emit from internal combustion engines	Marine
Catastrophic events	Marine vessel oil spill	Marine

1.5 The Value of Monitoring Each Category of Contaminants

To accurately reflect the monitoring considerations and priorities of the SEAN, this protocol describes four distinct categories of contaminants: mercury (Hg), other inorganic elements, POPs, and PAHs (Table 1.4).

Table 1.4. Classes of contaminants monitored by each component of the SEAN environmental contaminants protocol. The marine contaminants vital sign is the most comprehensive monitoring program, but specific analytes measured within each contaminant class differ for each monitoring program (see SOPs 2-4 for the analytical details of each component).

Component	Hg	Other inorganic elements	POPs	PAHs
Airborne	–	Y	–	–
Freshwater	Y	–	–	–
Marine	Y	Y	Y	Y

1.5.1 Mercury (Hg)

Monitoring Hg across multiple ecosystem components has been identified as a high scientific priority by environmental toxicologists (Harris et al. 2007). It is recognized as a human health concern because of its ability to cause oxidative stress (Farina et al. 2011), lead to endocrine disruption (Barregard et al. 1994), and cross the blood-brain barrier (Weil et al. 2005). Hg is a potent neurotoxin at many concentration levels and can harm developing human fetuses at low levels (Jewett and Duffy 2007).

Hg is widespread in distribution and found in trace amounts across many parts of the earth. Although Hg occurs naturally and can be mobilized by geologic erosion (particularly cinnabar ore), forest fires (Kelly et al. 2006), and volcanic eruptions (AMAP 2013), it is also released from human activities such as fossil fuel combustion (Pirrone et al. 2010) and mining. Hg from historic or legacy anthropogenic sources can also be mobilized by melting glaciers and permafrost.

Elemental Hg exists in three different forms (Hg vapor, Hg^0 ; mercurous, Hg^{1+} , or mercuric, Hg^{2+}). Hg^0 can be atmospherically transported to areas far from original emission sources. Hg^0 can be converted to Hg^{2+} and deposit on the earth's surface via rain or snow. Under anaerobic conditions, typically in the sediments of wetlands, bacteria can convert Hg^{2+} to monomethylmercury (CH_3Hg^+ , hereafter, MeHg^+), which is 5-10 times more toxic than elemental Hg (Wolfe et al. 1998). Because of the tendency of Hg to methylate in wet environments and assimilate in aquatic organisms, MeHg tends to accumulate at greater concentrations in aquatic biota than terrestrial.

Due to anthropogenic releases, the world's atmospheric, oceanic, and terrestrial ecosystem components contain approximately 2-6% more Hg today than in pre-industrial times (Swain et al. 1992). The prevailing wind and ocean currents in the Western Hemisphere proceed from west to east across the Pacific Ocean, but very little is known about the effects of atmospheric transport on Hg contamination in Southeast Alaska.

1.5.2 Other Inorganic Elements

Inorganic contaminants refer to elements such as nitrogen (N), sulfur (S), lead (Pb), arsenic (As), cadmium (Cd), calcium (Ca), copper (Cu), nickel (Ni), selenium (Se), and zinc (Zn). The ecological effects of excess N and S deposition include eutrophication and acidification, respectively (Erisman and Draaijers 1995; Gold and Sims 2005). Some elements are required in small concentrations for stabilizing the body's internal environment (Ca, Cu, Se, Zn, among others), whereas others can be toxic even in small concentrations (Cd, Pb, As). Some elements, such as Cu, Cd, Zn, As, and Se can undergo LRAT (Lantzy and Mackenzie 1979) and potentially accumulate in environments and biota where they were never produced or used. In southeastern Alaska, inorganic elements are important when assessing the composition of fugitive dusts, excess sea spray, and/or smoke (Schirokauer et al. 2014; Pirhalla and Bower 2016). Other important anthropogenic sources include wood, coal, and oil burning, as well as cement production, logging, and steel-making processes.

1.5.3 Persistent Organic Pollutants (POPs)

POPs are a broad class of carbon-based chemicals defined by: 1) remaining intact for many years; 2) distributing widely through the environment; 3) efficiently storing in fatty tissues; 4)

bioaccumulating and biomagnifying at higher concentrations in higher trophic-level organisms; and 5) toxicity to humans and wildlife (AMAP 2002). At higher latitudes, POPs are oftentimes found in lower concentrations than in more temperate regions where these chemicals were more commonly used. However, some Arctic species may still contain high concentrations of POPs as a consequence of inhabiting relatively short and lipid-rich food chains (AMAP 2002).

POPs can be grouped into three general categories (Nagorski et al. 2011): current-use pesticides, industrial/urban use compounds, and North American historic-use pesticides:

- *Current-use pesticides*: Environmentally persistent pesticides currently used in modern agriculture. Examples include Dacthal and Trifluralin.
- *Industrial/urban compounds*: Compounds for industrial or urban purposes, including hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), and poly brominated diphenyl ethers (PBDEs).
- *North American historical-use pesticides*: Pesticides phased out voluntarily, heavily restricted, or banned from use by the 2001 Stockholm Convention. Examples include DDT (and its breakdown products), aldrin, chlordane, mirex, dieldrin, or toxaphene.

1.5.4 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a large group of organic pollutants that are of concern for human and wildlife health. Many individual PAH compounds have been classified as probable or possible carcinogens. They can be released directly from petroleum product spills or as combustion by-products (Abdel-Shafy and Mansour 2016). Air emissions of PAHs can originate from natural sources such as volcanoes and forest fires or anthropogenic sources such as fossil fuel combustion. In addition to local sources such as oil spills and transportation sector emissions, PAHs from far-field sources such as Asian coal-fired power plants have the potential to be deposited in the SEAN parks following long-range atmospheric transport.

1.6 Selecting Long-term Sampling Media for Each Priority Contaminants Concern

The following three sub-sections describe the core sampling targets for each ecosystem component and represent the minimum SEAN commitment into the future. Since this protocol relies on a large body of preceding research across three ecosystem components, prior findings are briefly handled in this section and citations point the reader to primary references.

1.6.1 Monitoring Airborne Contaminants Using Lichens (mainly from Pirhalla and Bower 2016)

Based on the results of previous work described below, we will pursue lichen tissue chemistry at six index sites across SEAN parks as an affordable and informative long-term option (Chapter 5, Pirhalla and Bower 2016).

The airborne component of this environmental contaminants protocol represents an effort to quantify the exposure of terrestrial, freshwater, and marine environments to airborne pollutants over time. Among the three ecosystem components in this protocol, airborne contaminants are the most extensively studied within the SEAN. Based on previous research, we expect heavy precipitation and local emissions to be the major drivers of observed patterns in inorganic elemental concentrations

(Table 1.3). Several air quality studies, conducted within the SEAN from 1989 to the present, have led to the creation of monitoring objectives and sampling design (Table 2, Pirhalla and Bower 2016). These studies measured ambient air quality, contaminant deposition, lichen tissue concentrations, and lichen community composition. By establishing a series of reference sites for long-term monitoring, the SEAN can build upon this initial research to determine whether indicators of air pollution are crossing critical thresholds, indicating the potential for impairment of sensitive park resources (Pirhalla and Bower 2016).

Lichens assimilate contaminants from ambient air and are becoming increasingly popular as bioindicators of air quality (e.g., Root et al. 2014). Several common epiphytic macrolichen species are widespread throughout SEAN parklands, making them easy to locate and collect. For these reasons, inorganic elemental analysis of lichen tissues has a long history of use in Southeast Alaska including KLGO and the Tongass National Forest (Geiser et al. 1994; Furbish et al. 2000; Geiser 2004; Derr et al. 2007; Dillman et al. 2007; Schirokauer et al. 2014). The USFS Forest Inventory and Analysis Program (FIA) conducts long-term air quality biomonitoring using lichens at the national scale, while Tongass National Forest staff also collect additional samples regionally to increase spatial resolution. In comparison to individuals sampled in the Tongass National Forest, some lichen tissues from KLGO and SITK contained elevated levels of nitrogen and sulfur (Geiser et al. 2010).

1.6.2 Monitoring Freshwater Contaminants Using Riverine Dolly Varden

Based on the results of previous work described below, we will monitor freshwater contaminants in the SEAN by measuring total Hg (THg) in whole body Dolly Varden in at least one river per park.

Freshwater contaminants are an important indicator of the health of aquatic ecosystems across Southeast Alaska (Moynahan et al. 2008). The methods chosen here represent an effort to assess the threats presented to freshwater ecosystems by biovectors (primarily, migrating adult salmon), glacier volume loss, and watershed age (Table 1.3). The SEAN parks contain a large diversity of rivers and streams representing varying degrees of salmonid abundance, glacier coverage, and watershed age. Two studies conducted within the SEAN, from 2007 to the present, have led to the creation of monitoring objectives and sampling design (Table 1.2).

Migrating adult salmon are one of several anadromous fish species in the northern Pacific Ocean that transport marine-derived contaminants to freshwater during their upstream spawning migration (Davidson et al. 2012; Nehlsen 1997). Organisms that carry pollutants across ecosystem boundaries are sometimes referred to as biovectors. With millions of salmon entering southeastern Alaska rivers each year, biovectors may be a major force driving patterns in freshwater contaminants. For some watersheds with year-round ice coverage, contaminants locked in glaciers release as ice volume decreases and eventually become assimilated into downstream ecosystem components such as sediments and fish (Blais et al. 2001; Villa et al. 2006; Bogdal et al. 2010; Arellano et al. 2011). Within GLBA, watershed ages range from tens to thousands of years. As watersheds become older, wetland coverage increases and sulfate-reducing bacteria present in the rich soils convert Hg to MeHg which, due to its high assimilation efficiency, is more quickly accumulated in food webs (King et al. 2002; Nagorski et al. 2011).

In general, fishes are ideal sentinels for detecting freshwater contaminants. Species with high lipid contents can incorporate lipophilic contaminants (such as POPs and PCBs) on a time scale ranging from months to years (Ewald et al. 1998; Zhang et al. 2001; Letcher et al. 2010). Bioaccumulation and biomagnification increase the concentrations of many contaminants in fish tissues, enabling consistent detection across many classes of chemicals (Zhang et al. 2001; Jewett and Duffy 2007). Additionally, contaminant concentrations in fish can be directly compared to consumption advisory levels for humans and wildlife (for example, Hg; Eagle-Smith et al. 2014).

Based on pilot sampling (Cyr et al. 2014), six riverine fish species are readily available to sample with minnow traps in SEAN park units during the summer: coho salmon (*Oncorhynchus kisutch*); Chinook salmon (*O. tshawytscha*); chum salmon (*O. keta*); coastrange sculpin (*Cottus aleuticus*); and Dolly Varden (*Salvelinus malma*). Of these six species, only Dolly Varden was sufficiently abundant to obtain adequate sample sizes for contaminants analysis (Cyr et al. 2014). Additionally, the diverse life history traits, habitat preferences, and relatively high trophic status make Dolly Varden a desirable species for monitoring Hg concentrations across broad watershed types (Cyr et al. 2017). In upper trophic level fishes, MeHg, which is much more toxic to organisms than inorganic Hg (Boening 2000), often composes > 90% of THg accumulation (Bloom 1992; Harris et al. 2007; Wang 2012). Thus, our monitoring program can reduce the cost of lab analyses by focusing on THg concentrations and assuming a large portion is MeHg.

Despite their important roles in freshwater ecosystem dynamics, water, sediment, and invertebrates are less ideal for freshwater contaminants monitoring (Harris et al. 2007). Water is a highly transient medium in which contaminant concentrations can change rapidly, creating high variability across sample locations and times. Sediments in many riverine systems, especially those in southeastern Alaska, transport downstream constantly and do not incorporate contaminants efficiently. Invertebrates typically have short life spans and low lipid contents, reducing their potential for bioaccumulation.

For reference, the most conservative threshold of human health concern for Hg concentration is 300 ng/g (EPA 2001). All fish tissues collected by previous studies within the SEAN have fallen well below this threshold. Age-0 juvenile coho salmon tended to have very low concentrations of THg (≤ 14.1 ng/g ww), but concentrations generally increased for older individual fish (age-1 and age-2 coho) and within older watersheds encompassing greater wetland surface area (Nagorski et al. 2011). Dolly Varden sampled from West Creek (KLGO), lower Taiya River (KLGO), and Indian River (SITK) contained similarly low concentrations of THg (≤ 53 ng/g ww; Cyr et al. 2017). Dolly Varden populations above apparent anadromous barriers had higher mean THg concentrations (26.1 ng/g ww) than those below barriers (17.3 ng/g ww); this pattern appears to be controlled by both age and targeted consumption of salmon eggs by Dolly Varden during the salmon spawning season (Cyr et al. 2017). Salmon eggs are naturally low in Hg (Zhang et al. 2001); therefore, shifting salmon abundance in SEAN park rivers may significantly affect long-term trends in Dolly Varden THg concentrations. Dolly Varden from GLBA lakes had considerably higher THg concentrations (78 to 203.1 ng/g ww; Eagles-Smith et al. 2014), although this comparison is confounded by site-specific differences in fish size and trophic position.

1.6.3 Monitoring Marine Contaminants Using Mussels (mainly from Tallmon 2012)

Based on the results of previous work described below, we will monitor marine contaminants in the SEAN by partnering with the NOAA Mussel Watch Program (MWP) to measure a comprehensive suite of contaminants in bay mussels (*Mytilus trossulus*) across seven sites in SEAN parks (five in GLBA, one in KLGO, and one in SITK). The MWP is responsible for monitoring over 200 contaminants in mussel tissue collected at approximately 300 sites since 1986 and maintains the longest-running contaminants sampling program in the United States (D. Apeti, personal communication)

Partnering with the MWP represents an effort by the SEAN to assess the threats to marine nearshore ecosystems presented by aqueous hydrocarbons and catastrophic marine events such as oil spills (Table 1.3). Bay mussels are useful contaminants study organisms because they are sessile filter feeders and live up to 20 years, providing insight into contamination that has occurred over the previous several years as well as indicating any recent catastrophic events in nearby areas. In contrast with highly migratory species such as marine mammals, mussels are not likely to provide misinformation about park contamination status as a result of contamination occurring elsewhere.

Contaminant concentrations from mussels can be compared to data in the MWP database. Existing MWP sites along the Gulf of Alaska coastline add context to SEAN data and allow for future inferences on whether contaminant sources are driven by local, regional, or global trends. Mussels collected and analyzed in a manner consistent with MWP protocols will meet a universal goal in contaminant assessment studies of providing data that can be compared to similar data collected outside the sampling area. In general, marine contaminant concentrations in SEAN parks measured since 2007 are low or below detection limits (Tallmon 2012).

2. Sampling Design

2.1 Rationale for Site Selection

Due to the relatively pristine conditions found by previous studies and baseline contaminants inventories in the SEAN parks, an index-site based design was chosen as an efficient means of long-term surveillance of a limited number of resource impairment threats (see Table 1.3). For each monitoring objective (i.e., airborne, marine, and freshwater contaminants), sites were chosen for their exposure to primary pollution threats, representativeness along important ecological gradients (e.g., watershed age), and for accessibility. At a minimum, one sampling site was established for each monitoring objective in each park unit for long-term surveillance. Where possible, sites are collocated with other SEAN vital signs monitoring sites for efficiency.

2.2 Sampling Sites

2.2.1 Airborne Contaminants Monitoring Sites

Six lichen tissue chemistry monitoring sites are located in SEAN parks (Figure 2.1). In GLBA, Bartlett Cove and Blue Mouse Cove locations represent lower and mid-bay reference sites along cruise ship paths. In KLGO, a low-elevation site at Dyce, mid-elevation site at Chilkoot Pass, and mid-elevation site at Glacier Gorge establish reference conditions at sites exposed to very little human activity. In SITK, a single site has been chosen next to the Indian River and is co-located with existing SEAN water quality and streamflow monitoring programs.

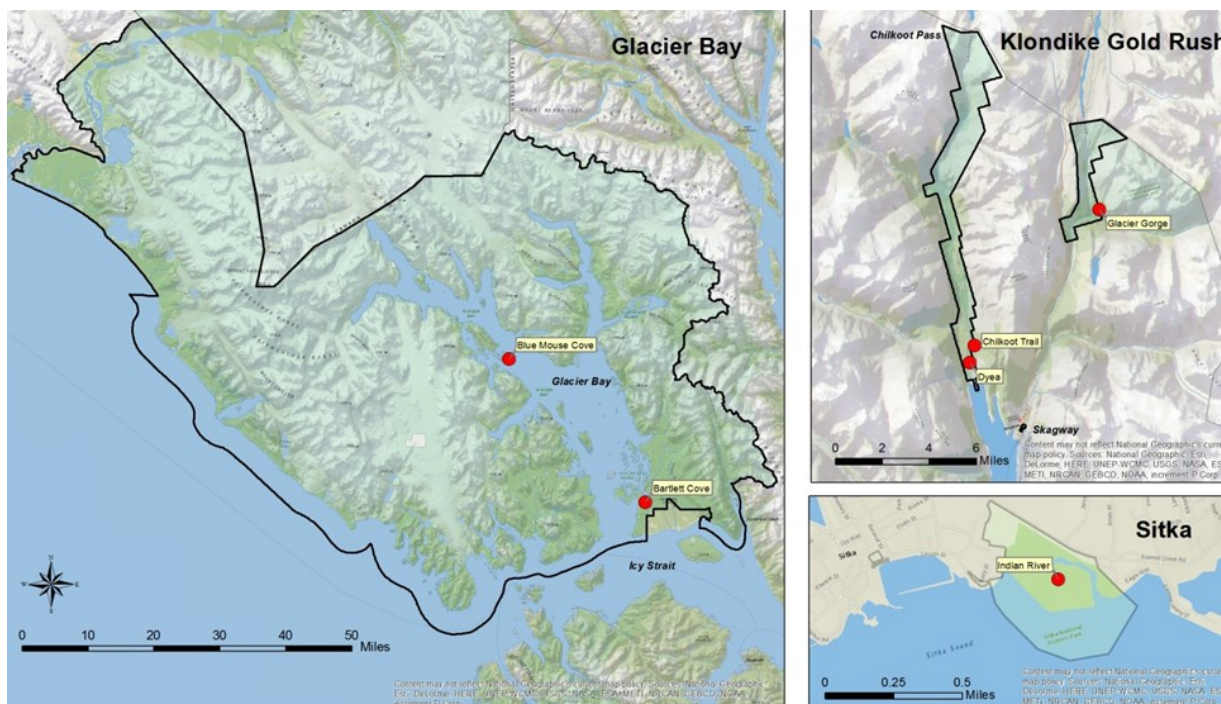


Figure 2.1. Map of SEAN permanent airborne contaminants monitoring stations in GLBA, KLGO, and SITK. Red dots represent lichen tissue analysis collection sites.

2.2.2 Freshwater Contaminants Monitoring Sites

Six Dolly Varden tissue monitoring sites are located in SEAN parks (Figure 2.2). Except for Nunatak Creek and Bartlett River in GLBA, the remaining three sites are co-located with freshwater water quality and streamflow vital signs. Within GLBA, one stream will represent younger up-bay watersheds (Nunatak Creek) and two will represent older down-bay watersheds (Bartlett and Salmon Rivers). In KLGO, we will sample the Taiya River because it is glacially influenced and encompasses an area with relatively concentrated visitor use (Chilkoot Trail and Dyea). The Indian River is the only significant freshwater resource in SITK and is influenced by urbanization and exceptionally dense salmon populations (Cyr et al. 2017; Sergeant et al. 2017). Due to budget constraints, sampling Dolly Varden above anadromous barriers will happen only within the Indian River watershed. GLBA lakes will not be covered despite the elevated—but thus far not of human-health concern—Hg concentrations present in lake resident fish (Eagles-Smith et al. 2014).

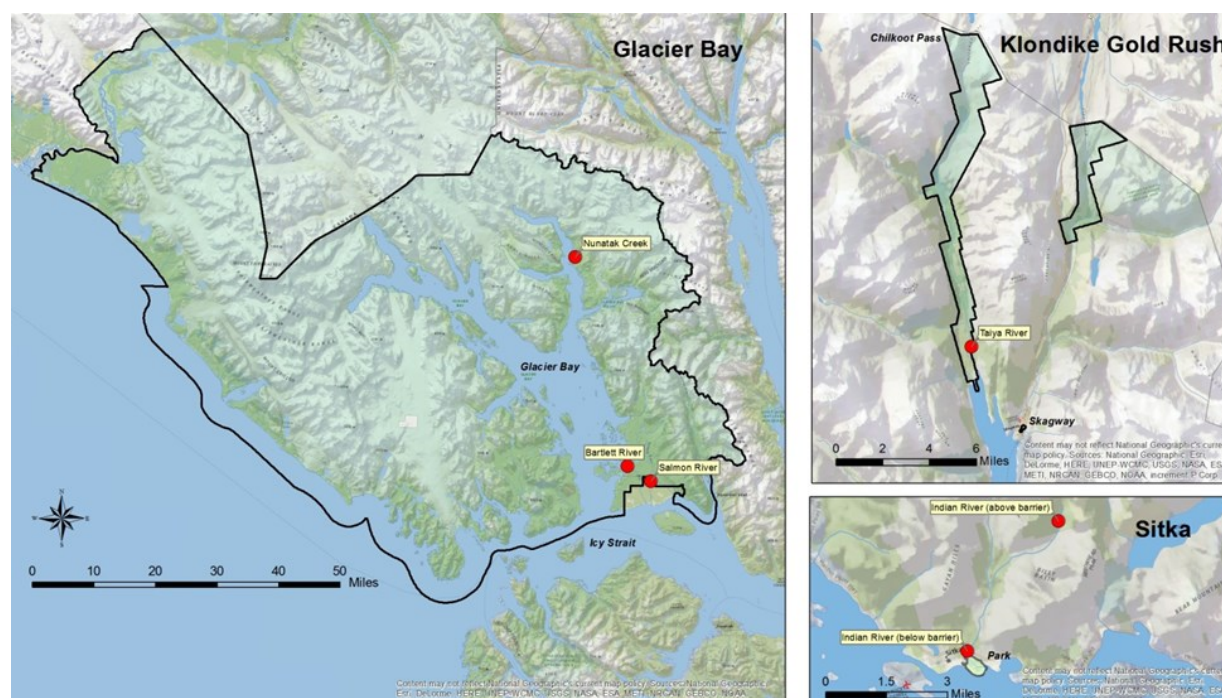


Figure 2.2. Map of SEAN permanent freshwater contaminants monitoring stations in GLBA, KLGO, and SITK. Red dots represent Dolly Varden tissue analysis collection sites.

2.2.3 Marine Contaminants Monitoring Sites

In 2007, the SEAN conducted an extensive baseline inventory of contaminants in mussel tissues at 53 sites in and adjacent to parklands (48 in GLBA, two in KLGO, and three in SITK; Tallmon 2011). These sites represented a range of relatively pristine to heavily human-modified sites. Since that initial 2007 survey, a subset of five sites has been monitored every two years (four in GLBA, one in SITK). For the long-term marine contaminants program, the SEAN has committed to monitoring seven sites (Figure 2.3). Four of the five long-term sites in GLBA follow the cruise ship path from lower to upper bay, while one site is near a fish processing plant in Excursion Inlet that may potentially contribute pollution to intertidal areas within park boundaries. SITK encompasses a small

marine shoreline; therefore, one monitoring site is sufficient for characterizing marine contaminants within the park. A site adjacent to KLGO, Nahku Bay, is currently monitored as part of the NOAA Mussel Watch Program, but it is unknown when the next national assessment will be conducted. Therefore, additional sampling at this site will be conducted by SEAN or KLGO staff.

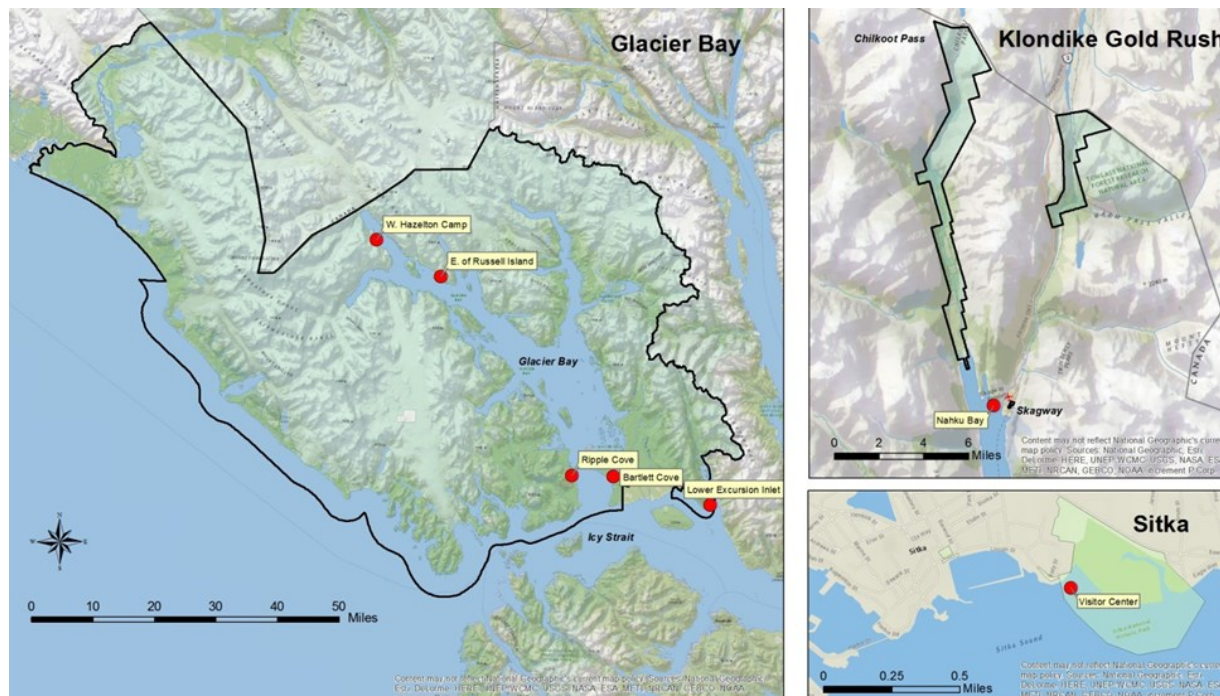


Figure 2.3. Map of SEAN permanent marine contaminants monitoring stations in GLBA, KLGO, and SITK. Red dots represent bay mussel tissue analysis collection sites.

2.3 Definition of the Sampling Boundaries

Since drivers of contaminant concentrations originate from local to long-range sources (Table 1.3), the scales of inference across this environmental contaminants protocol can range from hundreds of meters (e.g. bay mussels exposed to an oil spill) to thousands of kilometers (e.g. wet deposition Hg transported across the Pacific Ocean). The program's scope of inference can be altered by major changes in adjacent land use, modifications to the physical-chemical composition of the atmosphere or watersheds, or changes to monitoring locations.

2.4 Sampling Frequency and Replication

Due to the high laboratory costs associated with contaminants analysis, sampling frequency is in part controlled by budget limitations. All sampling sites across SEAN parks should be visited in the same year, and preferably within the same month to decrease temporal variability. Starting in 2018, each collection of sites for each medium will be sampled every five years. One exception to this will be mussel collection in 2017. At the time this protocol was drafted, staff from the SEAN and the MWP were unable to complete a synthesis for data collected from 2007 through 2017. After a synthesis of existing data is completed (likely in early 2019), a new sampling frequency will be chosen based on the findings and variability over time. Reports summarizing all environmental contaminants

monitoring results will be drafted every five years and will consider whether the sampling frequencies for each medium require adjustment (SOP 5).

2.5 Trend and Variability Detection

Contaminant concentrations in biological media tend to vary greatly based on individual age, body size, and trophic level. The SEAN environmental contaminants protocol describes, by necessity, a surveillance program designed primarily to record conditions for comparison with future site conditions and to detect contaminant concentrations approaching or crossing thresholds of ecological or human health concern. Therefore, we do not expect the sampling designs presented here to have a strong ability to detect trends in contaminant concentrations. To illustrate this point, we conducted a power analysis using Hg data from Dolly Varden reported in Cyr et al. (2017; see Appendix A). This effort collected replicate samples within single sites and is the SEAN's best available dataset for illustrating potential power to detect change in Hg concentration over time. For samples collected every five years, the power to detect a linear annual change of 5% in THg concentrations at a single site after 50 years of monitoring ranges from 3-11%. The sampling design proposed in this protocol recognizes that surveillance monitoring for contaminant concentrations of concern is the most realistic goal, and that trend detection is unlikely unless large and acute changes in contaminant concentrations occur in the environment over short time periods.

Table 2.1. Summary of core SEAN environmental contaminants monitoring program and sampling locations. Detailed location descriptions are found in pertinent SOPs. The site codes listed here match with external database site names for the NOAA Mussel Watch and USFS Lichen Plot databases.

Program component	Location	Site code	Media	Program	Frequency
Airborne	GLBA – Bartlett Cove	GLBA_BC	Lichen	Tongass National Forest/University of Minnesota	Quinquennial
	GLBA – Blue Mouse Cove	GLBA_BM	Lichen	Tongass National Forest/University of Minnesota	Quinquennial
	KLGO – Dyea	KLGO_DY	Lichen	Tongass National Forest/University of Minnesota	Quinquennial
	KLGO – Chilkoot Trail	KLGO_CH	Lichen	Tongass National Forest/University of Minnesota	Quinquennial
	KLGO – Glacier Gorge	KLGO_GG	Lichen	Tongass National Forest/University of Minnesota	Quinquennial
	SITK – Indian River	SITK_IR	Lichen	Tongass National Forest/University of Minnesota	Quinquennial
Freshwater	GLBA – Salmon River	GLBA_SA	Dolly Varden	Certified contract lab or IAA with USGS laboratory	Quinquennial
	GLBA – Bartlett River	GLBA_BA	Dolly Varden	Certified contract lab or IAA with USGS laboratory	Quinquennial
	GLBA – Nunatak Creek	GLBA_NU	Dolly Varden	Certified contract lab or IAA with USGS laboratory	Quinquennial
	KLGO – Taiya River	KLGO_TA	Dolly Varden	Certified contract lab or IAA with USGS laboratory	Quinquennial
	SITK – Indian River (above)	SITK_IN_A	Dolly Varden	Certified contract lab or IAA with USGS laboratory	Quinquennial
	SITK – Indian River (below)	SITK_IN_B	Dolly Varden	Certified contract lab or IAA with USGS laboratory	Quinquennial
Marine	GLBA – Excursion Inlet	GBEI	Bay mussel	NOAA Mussel Watch	Quinquennial
	GLBA – Bartlett Cove	GBBC	Bay mussel	NOAA Mussel Watch	Quinquennial
	GLBA – Ripple Cove	GBRC	Bay mussel	NOAA Mussel Watch	Quinquennial
	GLBA – E. of Russell Island	GBRI	Bay mussel	NOAA Mussel Watch	Quinquennial
	GLBA – W. Hazelton Camp	GBHC	Bay mussel	NOAA Mussel Watch	Quinquennial
	KLGO – Nahku Bay	NBES	Bay mussel	NOAA Mussel Watch	Quinquennial
	SITK – Visitor Center	SITK	Bay mussel	NOAA Mussel Watch	Quinquennial

3. Overview of Field and Laboratory Methods

Due to the breadth of these monitoring programs, this section provides a brief overview of field and laboratory methods. Complete details for airborne contaminants are presented in SOP 2, freshwater contaminants in SOP 3, and marine contaminants in SOP 4. SEAN staff will not perform analytical laboratory work, but instead will rely on qualified contractors or government laboratories that meet nationally accepted standards such as EPA protocols.

The project leader for this protocol, currently the SEAN ecologist, is responsible for project logistics, sample collection, and reporting. The SEAN program manager leads administration of any necessary agreements or contracts for lab analyses, reporting, or other unforeseen needs. Park staff will likely support some aspects of sample collection. The SEAN data manager assists with archiving deliverables (such as spreadsheets of lab results) specified in SOPs to the appropriate repositories. Specific roles and responsibilities are detailed in Section 4 and the relevant SOPs.

3.1 Field Season Preparations

Prior to the start of each field season, the project leader must ensure that:

- Park and state (if necessary) research permits have been acquired
- Sampling equipment (such as minnow traps) is purchased, available, and in working order
- Park staff time and resources (such as boats) necessary to conduct the work have been confirmed
- Necessary data forms and data submission procedures are in place
- All project personnel have the necessary personal protective equipment required to perform their job safely in all forms of weather (SOP 1)

Each ecosystem component has some specialized pre-season preparations to consider. The project leader must review each relevant SOP at least six months in advance of the approximate sampling dates to create a timeline and action list in consultation with the program manager and appropriate park staff. Field collections are relatively simple for all the efforts, but samples must be treated especially well during transit in the field and shipping to laboratories for analysis. In general, necessary equipment should be purchased and/or compiled two to three months prior to sampling. At the time of writing this protocol, all proposed sampling sites are within NPS park boundaries, but if any future sampling takes place outside of parks, the project leader must review land ownership and access rights to ensure there are no restricted areas.

In general, all environmental contaminants sampling should be completed between mid-July through September. Specific time frames for each ecosystem component are detailed below.

3.2 Field Procedures

3.2.1 Airborne Contaminants

Not including travel, lichen tissue sampling will take three people 2-3 d for KLGO, 1-2 d for GLBA, and one day for SITK. Three lichen species are collected at each site: *Hypogymnia enteromorpha*,

Hypogymnia inactiva, and *Platismatia glauca*. Samples are collected with clean, non-powdered vinyl or nitrile gloves and stored in clean, sealable plastic bags. Since lichens must be dried as soon as possible after collection to prevent decay, additional time is needed to dry samples and will vary based on lichen dampness (SOP 2). Each sample consists of at least 14 grams of clean, dry lichen. Sampling is conducted from mid-August to the end of September. Detailed field and lab methods are available in SOP 2.



Figure 3.1. Photos of lichen species used for elemental tissue analysis. From left to right: *Hypogymnia enteromorpha*, *Hypogymnia inactiva*, and *Platismatia glauca*.

3.2.2 Freshwater Contaminants

Not including travel, trapping fish and preserving Dolly Varden samples takes two people approximately 3-4 d for GLBA and 1-2 d each for KLGO and SITK. To remain consistent with previous efforts, sampling should occur from late July to early August. Detailed field and lab methods are available in SOP 3. Researchers access sampling sites using the GPS coordinates and site descriptions provided in SOP 3, and select approximately five individual locations in the vicinity to bait and deploy minnow traps. At KLGO and SITK, where site access is simple, crews should soak traps up to eight hours before retrieval and consider overnight soaking if catch rates are low and river levels are forecasted to be stable. The number of fish to be euthanized and retained for Hg analysis will vary depending on the permit specifications and available funds, but the goal should be a minimum of ten fish per site (SOP 3; Appendix A). Proper procedures, including wearing nitrile gloves and storing samples in sterilized, certified contaminant-free aluminum foil, must be followed to minimize the chances of any outside contamination contaminating the samples (SOP 3). These foil-wrapped samples must be kept cool after capture and be placed in a -20°C freezer within a maximum of eight hours.

3.2.3 Marine Contaminants

Not including travel, collecting mussels takes two people approximately 2-3 d for GLBA and one person one day each for KLGO and SITK. To remain consistent with previous efforts, sampling should occur from late July through early September. Detailed field and lab methods are specified in SOP 4. All of the sites in GLBA can be accessed by boat, but only Bartlett Cove can be accessed by foot from the park frontcountry. KLGO and SITK sites can be accessed by foot. At each site, 100-180 individual mussels are collected depending on shell size. Samples must stay cold after collection,

so mussels must be kept in sealable plastic bags on ice until shipped to labs for analysis. If shipping is delayed, samples for contaminants analysis may be frozen until shipped. Samples for histopathological analysis cannot be frozen. At the time of writing this protocol, it was undecided whether histopathological analysis will be continued in the SEAN program. This determination will be made when 2007-2017 results are synthesized by SEAN and Mussel Watch staff during fiscal year 2018.

3.3 Laboratory Methods

References supporting laboratory methods used for various aspects of the SEAN environmental contaminants monitoring protocol include EPA methods documents, peer-reviewed literature, and proprietary methods from contract labs. SOPs 2, 3, and 4 have more details regarding each of the methods identified here. Depending on labs used for future analyses, it is imperative for the project leader to confer with analysts and ensure that future measurements are directly comparable to previous measurements. Minor modifications to analytical methods should be clearly described in supporting documentation and periodic summary reports.

Table 3.1. Summary of analytical methods used for the SEAN environmental contaminants monitoring protocol. Bay mussel tissue analytical methods can be downloaded at <https://www.coastalscience.noaa.gov/publications/>.

Analysis	Method Names	Citations or Description	Reporting Units
Lichen tissue chemistry (Nitrogen)	Total Nitrogen (Dumas method)	1. Simone, H.A., J.B. Jones, Jr., D.A. Smitties, and C.G. Hussey. 1994. A comparison of analytical methods for nitrogen analysis in plant tissues. <i>Communications in soil science and plant analysis</i> 25(7&8):943-954. 2. Matejovic, I. 1995. Total nitrogen in plant material determined by means of dry combustion: A possible alternative to determination by Kjeldahl digestion. <i>Communications in soil science and plant analysis</i> 26(13&14): 2217-2229.	% within a given lichen species (dry weight)
Lichen tissue chemistry (Sulfur)	Total sulfur	1. Description from University of Minnesota Research Analytical Lab: A 0.100-0.150 g sample is weighed into a ceramic boat and covered with Com-Cat Accelerator (LECO trade name for tungsten oxide compound). The boat is placed in a furnace at a temperature of 1350°C in an oxygen rich atmosphere. Total Sulfur is determined by infrared absorption of evolved sulfur dioxide upon the dry combustion on a LECO Sulfur Determinator, Model No. S144-DR.	% within a given lichen species (dry weight)
Lichen tissue chemistry (25 additional elements)	ICP-dry ash method	1. Fassel, V.A., and R.N. Kniseley. Nov. 1974. Inductively coupled plasma optical emission spectroscopy. <i>Analytical Chemistry</i> 46 (13):1110A-1120A. 2. Dahlquist, R.L. and J.W. Knoll. 1978. Inductively coupled plasma-atomic emission spectrometry: Analysis of biological materials and soils for major trace, and ultra-trace elements. <i>Applied Spectroscopy</i> 32:1-30. ICP: ARL (Fisons) Model 3560 ICP-AES Ref. Source N. 2. Munter, R. C. and R. A. Grande. 1981. Plant tissue and soil extract analysis by ICP-AES. in R. M. Barnes (ed.) <i>Developments in atomic plasma spectrochemical analysis</i>. p.653-673. Heydon and Son, Philadelphia, PA. Also: Munter, R.C., T.L. Halverson, and R.D. Anderson. 1984. Quality assurance for plant tissue analysis by ICP-AES. <i>Communications in soil science and plant analysis</i> 15(15):1285-1322.	µg/g or ng/g dry weight

Table 3.1 (continued). Summary of analytical methods used for the SEAN environmental contaminants monitoring protocol. Bay mussel tissue analytical methods can be downloaded at <https://www.coastalscience.noaa.gov/publications/>.

Analysis	Method Names	Citations or Description	Reporting Units
Dolly Varden fish tissue preparation	Must be consistent and comparable with Section 2.2 of Cyr et al. 2017	Cyr, A., C. J. Sergeant, J. A. Lopez, and T. O'Hara. 2017. Assessing the influence of migration barriers and feeding ecology on total mercury concentrations in Dolly Varden (<i>Salvelinus malma</i>) from a glaciated and non-glaciated stream. Science of the Total Environment 580: 710-718.	n/a
Dolly Varden tissue total mercury	EPA method 7473 (SW-846)	1. EPA. 1998. Method 7473 (SW-846): Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry. 2. Cyr, A., C. J. Sergeant, J. A. Lopez, and T. O'Hara. 2017. Assessing the influence of migration barriers and feeding ecology on total mercury concentrations in Dolly Varden (<i>Salvelinus malma</i>) from a glaciated and non-glaciated stream. Science of the Total Environment 580: 710-718.	Total mercury concentration in ng/g wet weight
Bay mussel tissue preparation	B&B 1012	Kimbrough, K.L., Lauenstein, G.G., and Johnson, W.E. "Organic contaminant analytical methods of the National Status and Trends Program: Update 2000-2006." NOAA Technical Memorandum NOS NCCOS 30, June 2007	n/a
Bay mussel (organics extraction)	B&B 1010	McDonald, S. J., Frank D. S., Ramirez J. A., Wang B., Brooks J.M., "Ancillary methods of the National Status and Trends Program: 2000-2006 Update." NCCOS Technical Memorandum 28, 2006 Silver Spring, MD.	n/a
Bay mussel tissue (trace metals)	TERL	The Geochemical and Environmental Research Group, Texas A&M Research Foundation "NOAA National Status and Trends Program: Mussel Watch Program Year IV analytical methods." 1990.	µg/g dry weight
Bay mussel tissue (PAHs)	B&B 1006	Lauenstein, G.G., Cantillo, A.Y., Koster, B.J., Schantz, M.M., Stone, S.F., Zeisler, R. and Wise S.A., "National Status and Trends Program specimen bank: Sampling protocols, analytical methods, results, and archive samples." NOS ORCA 98, 1996.	ng/g dry weight
Bay mussel tissue (OCs and PCBs)	B&B 1007	Lauenstein, G.G., Cantillo, A.Y. and Dolvin S.S., "NOAA National Status and Trends Program Development and Methods," 1993.	ng/g dry weight

4. Data Handling, Analysis, and Reporting

This section describes the general approaches to generating, maintaining, and disseminating the ultimate products of this monitoring protocol. Detailed procedures are provided in product-specific SOPs. Data generated by the environmental contaminants program are managed according to the standard methods used by all SEAN programs, as described in the SEAN Data Management Plan (Johnson and Moynahan 2008). Dissemination of all data is done electronically from the SEAN and partner websites, including the NPS Data Store. A periodic report will be published following completion of each protocol cycle under the Natural Resource Data Series (NRDS), which provides a standardized template designed for efficient reporting of data. The specific content of the periodic report is established in SOP 5. If we observe contaminant levels of concern during the course of monitoring, SEAN staff will consult with network parks to determine what extended reporting is necessary (e.g., immediate visitor advisory, report to external agencies, peer-reviewed scientific article, or other communication medium).

4.1 Overview of Data Products

The environmental contaminants program creates and maintains ten specific data products (deliverables) for customers. Each deliverable is disseminated by SEAN and partner websites. The NPS Data Store repository is the single authoritative source for these deliverables. In the event that any data product distributed by a partner ever diverges from the values disseminated by Data Store, the Data Store version should be used.

4.2 Dissemination: Accessing the Data Deliverables

Deliverables for the environmental contaminants protocol are linked to partner sites or made directly available from the NPS Data Store at <https://irma.nps.gov/DataStore/>. The SEAN public facing web site (<https://www.nps.gov/im/sean/contaminants.htm>) also provides access to selected deliverables. Figure 4.1 illustrates the Data Store project reference, which has links to the deliverables from this program. Note the correspondence between the deliverable identifiers in Table 4.1 and the web site's project page. Figure 4.1 is intended to illustrate content only. The actual layout, graphics, and enterprise links used will follow the latest guidance of the national Inventory and Monitoring Division. While the dissemination services are publicly available worldwide, the target audiences are NPS resource managers and specialists as well as the broader scientific community.

Table 4.1. The SEAN data deliverables provided by this monitoring program.

Deliverable	Description	Provided as	Frequency	Responsibility	SOP
EC_A: Lichen field collection sheets	Two-sided color scans of the original field collection sheets	One PDF file	Once per sampling event (approximately every 5 years)	Project leader	2
EC_B: Lichen tissue elemental analysis results	A single spreadsheet of all results as they come from the contracted lab	One CSV file	Once per sampling event (approximately every 5 years)	Project leader	2
EC_C: Dolly Varden field collection sheets	Two-sided color scans of the original field collection sheets	One PDF file	Once per sampling event (approximately every 5 years)	Project leader	3
EC_D: Dolly Varden tissue mercury analysis laboratory technical report	Report detailing procedures from contracted lab, raw sample data, and accompanying data descriptions	One PDF file	Once per sampling event (approximately every 5 years)	Project leader	3
EC_E: Dolly Varden tissue mercury analysis results	A single spreadsheet of all results as they come from the contracted lab	One CSV file	Once per sampling event (approximately every 5 years)	Project leader	3
EC_F: Bay mussel field collection sheets	Two-sided color scans of the original field collection sheets	One PDF file	Once per sampling event (approximately every 5 years)	Project leader	4
EC_G: Bay mussel tissue contaminants analysis technical report	Report detailing QA/QC procedures from Mussel Watch contracted lab, raw sample data, and accompanying data descriptions	One PDF file (there could be multiple files for different groups of analytes depending on lab)	Once per sampling event (approximately every 5 years)	Project leader	4
EC_H: Periodic NRDS report	Summary report of most recent contaminants analysis for all media	One PDF file	Approximately every 5 years depending on timeliness of lab results	Project leader	5
EC_I: Protocol	The protocol package, explaining the complete details of the monitoring program as currently implemented, contains a narrative, data quality standards or quality assurance plan, and an SOP set	One PDF file for each component	As required	Program manager	6

and Restore Routines; SOP 1101: Network Archiving Process). That same document presents, in Chapter 11, the philosophy of records management at the SEAN.

4.4 Deliverable Validation and Certification

Since samples collected under the environmental contaminants protocol are ultimately analyzed by a certified laboratory contracted by the SEAN or partners, no deliverables require data management tools (e.g., database query) to aggregate data or apply quality ratings. Still, each deliverable goes through a validation processes to ensure file names, file types, and other details are correct before archiving. After a submitted product meets all mandatory criteria, the originator reviews the final version and, if completely satisfied, accepts it. Once accepted, the data manager installs it in the repository and ensures it is properly accessible from the dissemination website. The SEAN Data Management Plan describes the approach to validation and acceptance (Johnson and Moynahan 2008, Section 6.4 and SOP 601: Procedures for Certifying Project Data).

4.5 Data Acquisition: Scheduling Deliverable Production

In contrast to other SEAN monitoring protocols, no deliverable defined for the environmental contaminants protocol depends on the prerequisite completion of other deliverables. In other words, each deliverable can be submitted for validation and certification as it is available. Generally, field collection sheets (EC_A, EC_C, and EC_F) will be submitted before laboratory results. Laboratory results (EC_B, EC_D, EC_E, and EC_G) will be available at widely variable times depending on contracted or government lab workloads. The NRDS report (EC_H) should be completed within one year of SEAN receiving all laboratory results for a single round of sampling.

5. Personnel Requirements and Training

5.1 Roles and Responsibilities

The project leader is responsible for overseeing field collection of samples, ensuring appropriate research permits are in place before field activities, and assembling data deliverables such as technical reports (Table 4.1; SOPs 1-5). The project leader, in collaboration with the SEAN program manager, will secure appropriate laboratory contracts or agreements to perform sample analyses according to protocol specifications. Park staff are occasionally needed for one to several days to assist with field activities and logistics. The project leader and data manager work together to create, validate, and accept data products (Table 4.1). The resulting accepted deliverables are installed in the NPS repository archive, linked on the appropriate SEAN webpage, and transmitted to external facilities by the data manager as specified in each product's SOP.

5.1.1 Project Leader (*SEAN Ecologist, currently Chris Sergeant*)

- Ensure completion of pre-season preparations before field work is conducted
- Ensure expertise is available in field for properly identifying fish and lichen samples
- Train park and volunteer field assistants to perform field activities in a safe and efficient manner
- Coordinate visits to each park and ensure the superintendent, chief of resources, and other staff are aware of field work
- Schedule and execute safe and successful field operations, including canceling scheduled efforts due to poor weather or other dangerous conditions
- Coordinate sample shipments to contracted laboratories
- In cooperation with the data manager, track product delivery from data collection to lab analysis to reporting
- Assemble and submit the data deliverables specified in Table 4.1 to the data manager
- Correct deliverables as needed to meet specifications in each SOP
- Formally accept deliverables that pass mandatory validation
- Recommend to program manager when to initiate the protocol revision process (SOP 6; EC_I)
- Coordinate contracting and agreement paperwork with program manager in a timely manner

5.1.2 SEAN Data Manager (currently Bill Johnson)

- Validate quality of deliverables against formal criteria and specifications in SOPs
- Develop tools to disseminate products over the web
- Assemble, maintain, and disseminate metadata
- Track program progress and adherence to schedules
- Archive data and metadata as appropriate to the:
 - SEAN internal repository
 - NPS IRMA Data Store repository
 - USFS National Lichen & Air Quality Database and Clearinghouse
- Coordinate corrections so that deliverables posted to external archives continue to represent the best data
- Recommend improvements to the protocol to program manager

5.1.3 SEAN Program Manager (currently Mike Bower)

- Oversee program
- Review, manage peer review, and approve periodic NRDS report for publication
- Act as lead representative for contracts and agreements
- Supervise project leader and data manager
- Oversee, coordinate, and approve protocol revisions

6. Operational Requirements

6.1 Annual Workload and Field Schedule

Since the frequency of sampling for all aspects of this monitoring protocol occurs at five-year intervals, there will be many years where no major effort is required of the SEAN staff or collaborators. At the beginning of each fiscal year, as a regular part of work planning, the project leader and program manager should confer on what supplies, field assistance, contracts, and/or agreements may be needed to complete monitoring work over the next 12 months. Then, a timeline based on current needs and staff availability should be drawn up to ensure that field efforts can proceed on schedule as proposed below. Sampling efforts are sequenced to not overlap with SEAN murrelet surveys in Glacier Bay, which take place every year in early to mid-July (on average, July 5-15) and, in order to maintain continuity in annual murrelet abundance estimates, cannot be re-scheduled. Sampling of all ecosystem components is scheduled to overlap across the same years (see early exception regarding bay mussels in bullet below). While this does create more work for SEAN staff, the work is generally not very intensive, and overlapping in time maximizes the potential future value of our contaminants data.

It should be noted that while this proposed schedule represents the SEAN's minimum commitment to contaminants monitoring, implementation of this schedule is always dependent on fund availability.

- 1) *Lichen tissue sampling.* Lichen tissues at the SEAN index sites were last collected in 2008 (Schirokauer et al. 2014) and collection will continue in summer 2018 between mid-August and the end of September (SOP 2). Sampling is proposed to continue at five-year intervals after that (2023, 2028, onward). Dried lichen samples are shipped to the contracted lab (currently, University of Minnesota Research Analytical Lab) as soon as possible after collection.
- 2) *Dolly Varden tissue sampling.* Dolly Varden tissues at SEAN index sites were last collected in 2013 (Cyr et al. 2017) and collection will continue in summer 2018 between late July and early August (SOP 3). Sampling is proposed to continue at five-year intervals after that (2023, 2028, onward). Dolly Varden samples are shipped to the contracted lab as soon as possible after collection.
- 3) *Bay mussel sampling.* Mussels were last collected at SEAN index sites (SOP 4) in 2015 and collection will continue in 2017 (SOP 4). This proposed sampling does not overlap with Dolly Varden and lichen tissue collection in 2018. At the time of drafting this protocol, SEAN staff and Mussel Watch partners have not completed a synthesis of existing Mussel Watch data in order to finalize recommendations for sampling frequency. Until that effort is complete, the current precedent of bi-annual sampling will continue in 2017 and will not overlap with other ecosystem components being sampled in 2018 (see individual bullets below). The expectation is that all sampling will overlap in future events after this marine contaminants synthesis report is completed.

6.2 Facility and Equipment Needs

Since the SEAN will not be responsible for laboratory analysis of collected samples, facility needs are minimal for the environmental contaminants protocol. Maintaining a government-rate shipping account with FedEx will reduce shipping costs greatly.

- 1) *Lichen tissue* sampling: heated storage space for field collection gear and drying lichen samples
- 2) *Dolly Varden tissue* sampling: heated storage space for field collection gear; freezer space for maintaining samples until shipping
- 3) *Bay mussel sampling*: heated storage space for field collection gear; freezer space for maintaining samples until shipping

6.3 Start-up Costs and Budget Considerations

While the costs of pilot research conducted from 2007-2016 (Table 1.2) were quite high, start-up costs for equipment to collect field specimens for the environmental contaminants monitoring program will be quite low. Each five-year sampling cycle, field collection supplies will include waterproof field sheets (lichen, Dolly Varden, mussels), sealable plastic bags (lichen, Dolly Varden, mussels), nitrile gloves (lichen, Dolly Varden), ultra-clean aluminum foil (Dolly Varden), metal mesh minnow traps (Dolly Varden), small plastic coolers (Dolly Varden, mussels), and sieves (mussels). Minnow traps are very common and will likely be available for loan, and the remaining supplies will cost, at the most, several hundred dollars.

Lab costs for the five-year recurring samples of lichen, Dolly Varden, and mussels add up to approximately \$20,000 for years when all samples are collected (Table 6.1). Due to the low sampling frequency for this program, cost should be re-evaluated before each five-year sampling cycle to determine if the protocol's sampling effort is still reasonable relative to SEAN budget and staff capacity. Additionally, some samples may be preserved for analysis in subsequent fiscal years.

This program presumes that travel to remote sampling sites within parks is provided in-kind by those parks with no additional costs charged to the SEAN.

Table 6.1. Budget estimates for analytical fees associated with one five-year iteration of the SEAN environmental contaminants monitoring protocol. Costs were estimated March 2017 and are likely to change in future years as a function of inflation.

Monitoring Component	Sub-component	Number of Sites	Total Cost
1. Lichen tissue chemistry (Nitrogen, Sulfur, and 25 additional elements) ¹	–	6	\$3,868
2. Dolly Varden fish tissue preparation and total mercury analysis	–	6	\$3,600
3. Bay mussel tissue preparation (shell length, volume, wet/dry weights, lipid content)	–	7	\$372
	Bay mussel tissue (standard organics, including PAHs and OCs)	–	\$5,544
	Bay mussel tissue (butyltins)	–	\$1,750
	Bay mussel tissue (metals)	–	\$2,821
	Bay mussel tissue (PCBs)	–	\$291
	Bay mussel tissue (gonadal index/histopathology) ²	–	\$1,372
Total			\$19,618

¹ Additional cost details found in Pirhalla and Bower 2016

² Pending Mussel Watch data synthesis in fiscal year 2018, the gonadal index/histopathology component of marine contaminants monitoring may be permanently removed.

6.4 Protocol Revision Process

This protocol will be updated or revised as new knowledge, technologies, equipment, and methods become available. Revisions will balance the advantages of new techniques with possible disadvantages associated with disrupting data continuity. The protocol comprises the narrative, data quality standard document or quality assurance plan, and SOP set.

All revisions require review for clarity and technical soundness. Minor changes to the current protocol document (for example, formatting; clarification of existing content; alterations to the task schedule, work flow, or project budget) may be reviewed internally by project cooperators and SEAN staff. Major changes such as altering sampling design, parameters measured, or analytical techniques, typically trigger an external peer review. Revising the SOP set generally does not require external peer review. Protocol component review requirements are occasionally revised. The designated peer review manager should seek the latest guidance before launching any review.

The SEAN program manager will periodically poll the project leader and data manager on the need to initiate a protocol revision cycle. Every effort will be made to ensure that complete, approved protocol revisions are completed before the beginning of a new five-year interval sampling effort.

The protocol package is defined as data deliverable EC_I. Technical details of the method for protocol revision are specified in SOP 6.

The protocol revision process will be cooperatively managed by the project leader, SEAN data manager, and SEAN program manager. In the course of a revision cycle, proposed revisions may originate from any of these three individuals. One shall agree to be revision coordinator and be responsible for overseeing document content additions and deletions. The revision coordinator will manage proposed contributions and internal tracked-changes until consensus is reached on a final draft document. If an external peer review is performed, the coordinator will address received review comments in consultation with the other two participants.

A revised Protocol Narrative or SOP set must be given a new formal version identifier in order to link data with the methods and rules used to collect it, as detailed in the SEAN Data Management Plan (Johnson and Moynahan 2008, SOP 602: Version Control). The new protocol publication will be disseminated and archived after receiving any needed approval from the Natural Resources Publication Management group.

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Appendix A: Power to detect contaminant concentration differences in freshwater fish between sites and long-term trends within sites

Andrew Cyr and Chris Sergeant

Introduction

We present two power analyses to illustrate the potential implications of sample size and sampling frequency choices for the Southeast Alaska Network (SEAN) freshwater contaminants monitoring program. Previous data on total mercury (THg), DDT, and PCB concentrations in Dolly Varden (*Salvelinus malma*) and juvenile coho salmon (*Oncorhynchus kisutch*) from Southeast Alaska national parks were used to create baseline conditions for power scenarios. Our two questions were:

- 1) For sample sizes ranging from 2 to 30, what is the power to detect a statistical difference in contaminant concentrations between two sites sampled at a single point in time?
- 2) For monitoring programs running from 10 to 50 years, what is the power to detect a linear long-term trend in contaminant concentrations within a single site?

Methods

Mean and standard deviation values for contaminant concentrations of three analytes (THg, $\sum$ DDT, and $\sum$ PCB) were derived from two studies conducted in SEAN park units during 2007 (Nagorski et al. 2011) and 2013 (Cyr et al. 2016; Table 1).

Table A1. Summary of data sources used to perform long-term trend and sample size power analysis. “Barrier” refers to apparent anadromous barriers blocking the upstream movement of fish. Sixteen streams from Glacier Bay National Park and Preserve were pooled under the label, “GLBA.”

Study Name	Site	Analyte(s)	Fish Species	Sample Size
Cyr et al. ¹	Indian R. below barrier	THg	Dolly Varden	19
Cyr et al.	Indian R. above barrier	THg	Dolly Varden	22
Cyr et al.	West Cr. below barrier	THg	Dolly Varden	12
Cyr et al.	West Cr. above barrier	THg	Dolly Varden	24
Nagorski et al, 2011 ²	Taiya R. below barrier	DDT & PCB	Juvenile coho salmon	1
Nagorski et al, 2011	Indian R. below barrier	DDT & PCB	Juvenile coho salmon	1
Nagorski et al, 2011	GLBA	DDT & PCB	Juvenile coho salmon	16

¹ Cyr, A., C. J. Sergeant, J. A. Lopez, T. O'Hara. 2016. Assessing the influence of migration barriers and feeding ecology on total mercury concentrations in Dolly Varden (*Salvelinus malma*) from a glaciated and non-glaciated stream. Science of the Total Environment. DOI: <http://dx.doi.org/10.1016/j.scitotenv.2016.12.017>

² Nagorski, S., D. Engstrom, J. Hudson, D. Krabbenhoft, J. DeWild, E. Hood, and G. Aiken. Scale and distribution of global pollutants in Southeast Alaska Network park watershed. Natural Resource Technical Report NPS/SEAN/NRTR - 2011/496. Natural Park Service, Fort Collins, Colorado.

To calculate the power to detect a difference in contaminant loads sampled at a single point in time using a t-test of means, we implemented the *pwr.t.test* function in R for eight different scenarios (Table 2).

Table A2. Parameter input for *pwr.t.test* function in the R statistical package *pwr*. All tests were two-tailed with $\alpha = 0.05$.

Analyte	Site pair (Site 1, Site 2)	Mean Site 1	Mean Site 2	SD Site 1	SD Site 2	d ¹
THg	Indian R. above vs. below barrier	0.0300	0.0155	0.012	0.005	1.560
	West Cr. Above vs. below barrier	0.0264	0.0174	0.004	0.002	2.837
	West Cr. above barrier vs. Indian R.	0.0264	0.0300	0.004	0.012	0.403
	West Cr. below barrier vs. Indian R.	0.0174	0.0155	0.002	0.005	0.484
Σ DDT	GLBA vs. Taiya R. ²	3.8000	1.1540	0.506	0.506	5.226
	GLBA vs. Indian R. ²	1.3000	1.1540	0.506	0.506	0.288
Σ PCB	GLBA vs. Taiya R. ²	2.9000	1.9320	0.969	0.969	0.999
	GLBA vs. Indian R. ²	8.2000	1.9320	0.969	0.969	6.469

¹ Where d is the effective size = $(\text{mean}_{\text{Site 1}} - \text{mean}_{\text{Site 2}}) / \sqrt{[(\text{SD}^2_{\text{Site 1}} + \text{SD}^2_{\text{Site 2}}) / 2]}$

² Indian and Taiya rivers each had a sample size of 1 for DDT and PCB, thus the mean is the value of the only sample, and the standard deviation is estimated to be the same as the pooled GLBA samples

To calculate the power to detect a linear long-term trend in contaminant loads at a single site, we implemented the *powertrend* function in R for six different scenarios (Table 3).

Table A3. Parameter input for *powertrend* function in the R statistical package *fishmethods*. All tests were two-tailed with $\alpha = 0.05$. For each site, sampling occurs every five years for up to 10 or 50 years. Annual linear change in contaminant loads ranged from -10% to 10%.

Analyte	Site	A1 ¹	PSE ²
Total Mercury	Indian River Above Barrier	0.0300	0.406
	Indian River Below Barrier	0.0155	0.330
	West Creek Above Barrier	0.0264	0.144
	West Creek Below Barrier	0.0174	0.138
SUM DDT	GLBA	1.1540	0.439
SUM PCB	GLBA	1.9320	0.502

¹ Starting sample mean

² CV=SD/Mean

Results

Since the power analyses presented below are based on a limited amount of data and carry multiple assumptions (such as normally distributed data and linear trends), results should be interpreted cautiously.

Based on t-test power analyses and potential cost considerations, a sample size of approximately 10 appears to produce moderate to high power to detect between-site differences in contaminant concentrations. Three exceptions to this are the West Creek above/below barrier (THg) and GLBA (DDT) concentrations compared to the Indian River (Figure 1). For above and below barrier comparison within a single watershed, 10 samples appear to have very high power to detect differences for total mercury. Potentially, below barrier influences on contaminant concentrations, such as migrating and spawning adult salmon, may be detectable during single sampling events.

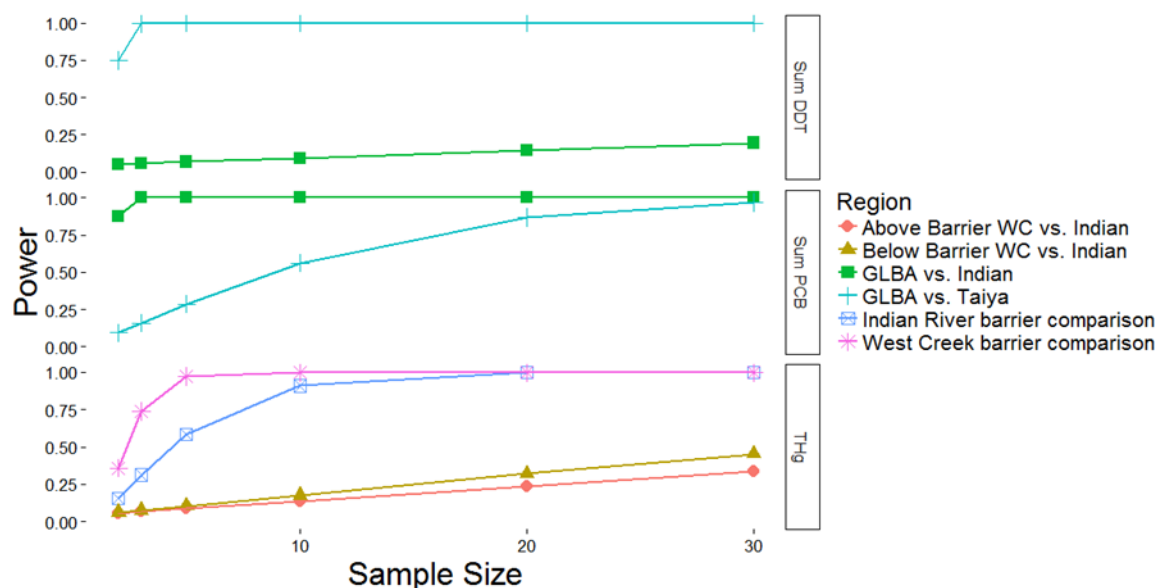


Figure A1. Power to detect a statistical difference in two site means based on sample sizes ranging from 2 to 30.

Even after monitoring contaminant loads every five years for 50 years, it appears that power to detect linear long-term trends at a single site will remain quite low (Figure 2). These results suggest that surveillance monitoring for dangerous contaminants thresholds, instead of long-term trend monitoring, is the most realistic program goal.

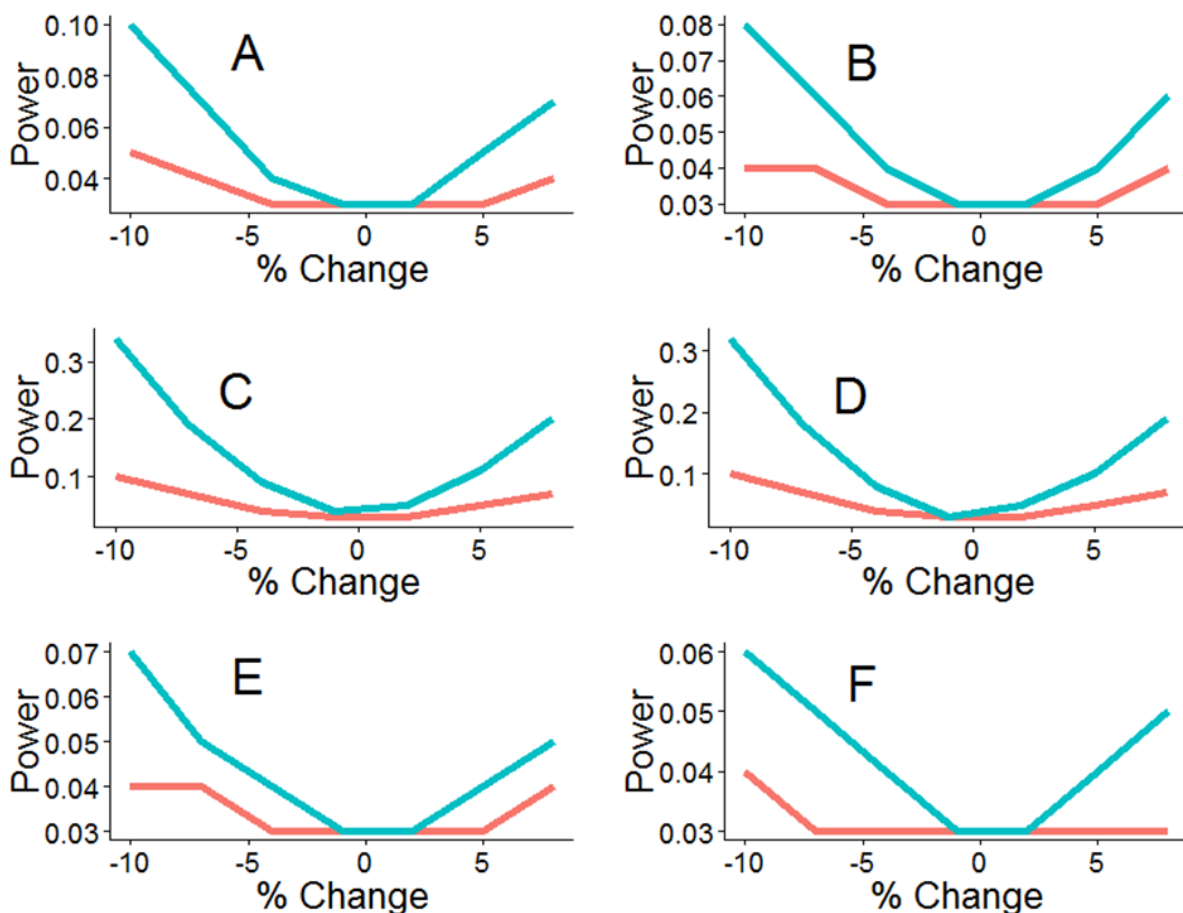


Figure A2. The power to detect a linear long-term trend in contaminant loads at a single site. A) Indian River below barrier (THg); B) Indian River above barrier (THg); C) West Creek below barrier (THg); D) West Creek above barrier (THg); E) Glacier Bay National Park and Preserve (16 streams; Σ DDT; $n = 1$ sample per river); F) Glacier Bay National Park and Preserve (16 streams; Σ PCB; $n = 1$ sample per river). Blue lines indicate 50 years of monitoring, red lines indicate 10 years of monitoring.

Table A4. Statistical power to detect a 5% or 10% linear annual change at a single site after 10 or 50 years of monitoring.

Site	Analyte	10 years		50 years	
		5 % change	10 % change	5 % change	10 % change
Indian R. above barrier	THg	0.03	0.04	0.04	0.07
Indian R. below barrier	THg	0.03	0.04	0.05	0.09
West Cr. above barrier	THg	0.05	0.09	0.10	0.27
West Cr. below barrier	THg	0.05	0.09	0.11	0.29
GLBA	Σ DDT	0.03	0.04	0.04	0.06
GLBA	Σ PCB	0.03	0.04	0.04	0.06

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