



# Scale and Distribution of Global Pollutants in Southeast Alaska Network Park Watersheds

Natural Resource Technical Report NPS/SEAN/NRTR—2011/496



**ON THE COVER**

Top left: Measuring streamflow in Reid Creek (GLBA); Top Right: Approaching Nunatak Creek (GLBA); Bottom Left: Sorting insects at Vivid Lake Stream (GLBA); Bottom Right: Indian River at sampling site upstream of footbridge (SITK).  
Photographs by: S. Nagorski

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## Executive Summary

In June–July 2007, we sampled streamwater, suspended particulates, streambed sediments, benthic macroinvertebrates, and juvenile coho salmon (*Oncorhynchus kisutch*) in 19 streams in and immediately adjacent to national park units in the Southeast Alaska Inventory and Monitoring Network for the purposes of establishing a baseline of contaminant concentrations and evaluating spatial differences in their occurrence. Selected watersheds were the Indian River in Sitka National Historical Park (SITK), the Taiya and Skagway Rivers in Klondike Gold Rush National Historical Park (KLG0), and 16 watersheds in and near Glacier Bay National Park and Preserve (GLBA). The GLBA watersheds represent a range of ages (relative to recent glaciations) and landscape characteristics related to successional development following deglaciation.

The highest concentrations of filtered total mercury ( $Hg_T$ ) were found in the two old (not recently glaciated), peatland-rich watersheds from Pleasant Island (adjacent to GLBA), where values were ~10-fold higher than in GLBA, SITK, and KLG0. Filtered methylmercury (MeHg) was low in all of the newer, recently glaciated streams in GLBA, and in KLG0 and SITK compared with several of the medium- and old-aged GLBA-area streams draining landscapes with developed peatlands. Up to 21% of the filtered mercury in the old GLBA streams was in the methylated form. The microbial conversion of inorganic Hg to MeHg is known to depend greatly on the prevalence of organic-rich peatlands, which are more common in older watersheds in southeast Alaska. The concentration of  $Hg_T$  in water was strongly correlated with the mapped percent of the watershed covered by wetlands and with the concentration of dissolved organic carbon (in particular the hydrophobic fraction, which increases with runoff from wetlands). Spatial patterns of MeHg concentrations in resident mayflies and juvenile coho, combined with comparisons of Hg concentrations in precipitation, indicate that in older watersheds, the amount of Hg released via streamwaters is roughly equivalent to that in wet deposition and that a fraction of it is converted to MeHg, which is taken up in the food web. Limited data on older coho fry indicate bioaccumulation taking place within the fish.

Stratification of the GLBA study streams by age group (young, <100 years; medium, 100–200 years; and old, >1000 years) reveals that mercury concentrations systematically increase as watersheds age. Mercury increased from the young to medium to old groups for filtered water ( $Hg_T$  and MeHg), streamwater particulates ( $Hg_T$ ), both groups of mayflies ( $Hg_T$  and MeHg), and the juvenile coho salmon. Our data also show that in general, the older the watershed, the lower the stream pH and dissolved solid concentrations (sulfate, Ca, Mg, and Si), and the higher the DOC and Cl concentrations. No age-related patterns were found for the persistent organic pollutants (POPs) in fish.

Concentrations of  $Hg_T$  in streamwater were 3–4 orders of magnitude below EPA levels of concern for human health or for aquatic organisms. Mercury in age 0+ juvenile coho easily met standards (100 ng/g) set by the U.S. Environmental Protection Agency National Fish Tissue Survey for the protection of piscivorous birds and mammals that consume them. However, several samples of age 1+ coho were as high as 80 ng/g, which closely approaches the criterion and is more than double the reported values for adult coho in Alaska. Streambed sediment concentrations of mercury were all below the national median value of 60 ng/g (dry weight), and

well below probable effect levels. Mercury concentrations in mayflies and juvenile coho were generally on the low end to midrange values of samples reported for elsewhere in the nation.

Of the 77 POPs analyzed in the juvenile coho samples, most were below quantification limits, notably both current-use pesticides (endosulfan I and lindane) and all HCHs, PBDEs, aldrin, and mirex. Yet, quantifiable HCB, chlordanes, dieldrins, several congeners of PCBs, DDE, and DDT were found in at least some samples. DDTs and PCBs were detectable in fish from all streams except one. The Skagway River sample contained the highest levels of HCBs,  $\Sigma$ CHLs,  $\Sigma$ DDTs, the second highest concentrations of  $\Sigma$ PCBs, and together with the nearby Taiya River, the only quantifiable dieldrin. The Indian River (SITK) had the highest  $\Sigma$ PCBs—nearly twice that of the Skagway River and 3-8 times levels found in GLBA streams. Relatively high PCB levels in the Sitka area have also been found in murre (*Uria* spp.) eggs and in intertidal mussels. Of streams in GLBA, Gull Creek stands out in that its coho samples had the highest number of different types of POPs, perhaps due to contributions by spawning salmon carcasses in this particularly productive stream. Most of the detected POPs compounds have been banned for over 30 years, but they and some of their breakdown products continue to occur in organisms in remote areas such as in southeast Alaska, albeit at levels currently below environmental and human-health concerns.

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## List of Commonly Used Abbreviations

BMI	Benthic macroinvertebrates
CHLDS	Chlordanes
DOC	Dissolved organic carbon
DDTs	Dichlorodiphenyl polychloro-ethanes and -ethylenes
EPA	Environmental Protection Agency
FFGs	Functional feeding groups
GLBA	Glacier Bay National Park and Preserve
HCB	Hexachlorobenzene
HCHs	Hexachlorocyclohexanes
Hg <sub>T</sub>	Total mercury
HPOA	Hydrophobic organic acid fraction of the dissolved organic carbon
KLGO	Klondike Gold Rush National Historical Park
MeHg	Methylmercury
NAWQA	National Water Quality Assessment
NOAA	National Oceanic and Atmospheric Administration
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
POPs	Persistent organic pollutants
SEAN	Southeast Alaska Inventory and Monitoring Network (National Park Service)
SITK	Sitka National Historical Park
SOCs	Semi-volatile organic compounds
SUVA	Specific UV absorbance (254nm)
TSS	Total suspended solids
UVA	Ultraviolet absorbance (254nm)
WACAP	Western Airborne Contaminants Assessment Project



## Introduction

Mercury (Hg) and Persistent Organic Pollutants (POPs) are global pollutants, traveling far from their sources and reaching remote areas where they are neither used nor produced (Nriagu and Pacyna 1988, Fitzgerald et al. 1998, AMAP 2002). They are carried to Alaska via long-range atmospheric pathways (Schroeder and Munthe 1998, Wania et al. 1999, Landers et al. 2008) or via biovectors such as birds and fish (Blais et al. 2007), and upon deposition they can biomagnify as they pass up trophic levels (EPA 2002). Mercury and POPs in northern latitudes show significant concentration increases over the last few decades, and these trends are reflected in the unusually high concentrations of some of these chemicals in the bodies of otters, whales, seals, bears, eagles, and indigenous peoples who rely on subsistence harvests (Braune et al. 1999, Dietz et al. 2006). While recent attention has been placed on elevated Hg (Lindberg et al. 2002) and POPs (AMAP 2004) deposition in polar regions, including Alaska, very little attention has been placed on these contaminants in southern Alaska, even though available evidence indicates that the region is accumulating many potentially toxic chemicals imported from distant sources (Engstrom and Swain 1997, Vander Pol et al. 2004).

The purpose of this project was to gain an initial determination of the presence, concentration, and location of global contaminants in southeast Alaskan watersheds relatively unimpacted by human activity. This study provides a benchmark of contamination levels against which future monitoring efforts can be compared and evaluates the role that landscape type may play in the attenuation, release, and transformation of the contaminants. In this project, we obtained a “snapshot” survey of Hg and POPs in waters, sediments, benthic macroinvertebrates, and fish from streams within the Southeast Alaska Network (SEAN) of the National Park Service (NPS): Glacier Bay National Park and Preserve (GLBA); Klondike Gold Rush National Historical Park (KLG0); and Sitka National Historical Park (SITK).

### Mercury Background

Mercury (Hg), a widespread, naturally occurring heavy metal, is a potent neurotoxin that can cause irreversible neurological and developmental damage. Although typically present at trace levels, the world’s atmosphere, oceans, and terrestrial ecosystems currently contain 2–6 times more Hg than in the preindustrial era due to anthropogenic-related atmospheric emissions (Swain et al. 1992, Mason et al. 1994, Engstrom and Swain 1997, Fitzgerald et al. 1998, Bindler et al. 2001, Schuster et al. 2002, Lindberg et al. 2007). A recent evaluation of the global Hg cycle indicated that Hg concentrations in the oceans are increasing by several percent annually (Mason and Sheu 2002). While Hg emissions in the USA have decreased in recent decades, global emissions continue to increase, particularly in Asia, where China and India are undergoing rapid industrialization, and as a result are drastically increasing their coal consumption rates for power production (Pacyna and Pacyna 2002). China is expected to more than double its energy demand in the next 20 years, and on average, a new coal-fired power plant large enough to serve a major metropolitan area opens in China every 7–10 days (International Energy Agency 2008). China and India together account for 79% of the expected increase in world coal consumption from 2005–2030 (Energy Information Administration 2008), and global Hg emissions, driven mainly by these Asian sources, are expected to increase by up to 96% by 2050 (Streets et al. 2009).

Much of the Hg released from this coal combustion is carried atmospherically to the north coast of North America, and models show that Alaska is on the receiving end of rapidly rising releases

of the toxin (Dastoor and Larocque 2004, Landers et al. 2008). Currently, anthropogenic mercury deposition to Alaska appears to be similar in magnitude to that in temperate latitudes although local sources are minimal and scarce (Fitzgerald et al. 2005). Evidence for increasing Hg deposition in southern Alaska is derived from several lines of evidence. First, two lake sediment accumulation studies—one in GLBA itself, and the other on nearby Chichagof Island—indicate that recent Hg accumulation levels are 2-3 times preindustrial levels and rising. This is contrary to what is seen at lower latitudes, which generally show Hg accumulation levels in lakes have fallen since the mid 1970s (Engstrom and Swain 1997, Fitzgerald et al. 2006). Another study showed disproportionately high concentrations of methylmercury (MeHg) in murre (*Uria aalge* and *U. lomvia*) eggs in the Gulf of Alaska region—including one site in Sitka Sound (Day et al. 2006). In 2007, the Alaska Department of Environmental Conservation issued a report showing that, for the first time, several species of Alaskan fish contain unsafe levels of mercury for unlimited consumption (ADEC 2007). Last, a recently published study (Sunderland et al. 2009) calibrated linked oceanic and atmospheric transport models with recently collected field data, and concluded the North Pacific Ocean has incurred substantial increases in Hg over the past two decades.

Spawning salmon may deliver marine-derived Hg to southeast Alaskan watersheds as well. There is little published information on the direct contribution by anadromous fish to the Hg concentrations in streams, but a study of Bering Sea salmon returning to spawn in the Bristol Bay watersheds of southwestern Alaska showed that salmon may be major transporters of marine-derived Hg into freshwater environments (Zhang et al. 2001). Additionally, a study of several tributary streams of Lake Ontario showed that significantly higher concentrations of Hg and MeHg occurred in water and sediments along stream segments with high salmon carcass densities (Sarica et al. 2004).

To date, little is known about the extent of environmental Hg pollution in southeast Alaska. There is no known prior research on the occurrence, forms, transport dynamics, and landscape controls on regional Hg levels. Among landscapes, wetlands play a critical role in the post-deposition cycling of Hg and its subsequent bioavailability (Wiener et al. 2003), and much of the southeast Alaskan landscape is covered by wetlands. The extent to which regional coastal wetlands may be facilitating the conversion of atmospheric Hg fallout to toxic, bioavailable forms that are readily exported to downstream marine ecosystems is unknown, and estimating this is a central goal of this project. Methylmercury ( $\text{CH}_3\text{Hg}^+$ , abbreviated here as MeHg), an organic form of Hg, is a potent neurotoxin that is 100 times more toxic than elemental Hg (Wolfe et al. 1998), bioavailable, and readily biomagnified (up to  $10^6\times$ ) up the food chain. Other studies have identified wetlands as sites of major MeHg generation (i.e., methylation) and have demonstrated that the percentage of the landscape covered by wetlands is positively correlated with both the MeHg concentrations in outflowing streams and the MeHg accumulation in fish (Hurley et al. 1995, St. Louis et al. 1996, Brumbaugh et al. 2000). Results of recent USGS National Water Quality Assessment (NAWQA) studies show that some of the highest streambed sediment MeHg concentrations nationally were found in a remote, undeveloped basin in the upper Cook Inlet Basin—the watershed also had one of the greatest percentages of wetland coverage (Frenzel 2000). All three NPS units in SEAN include wetland areas, and although they are not the dominant landscape form in the watersheds, they undoubtedly play important ecological roles, supporting terrestrial, riparian, and downstream intertidal biota.

The combination of increasing Hg atmospheric imports to Alaska, the abundance of wetlands in portions of the SEAN landscape, and the use of many watersheds by salmon suggests that Hg contamination in SEAN may be a growing threat to the health of the freshwater systems as well as downstream receiving intertidal and marine environments. This project is the first known examination of the magnitude and distribution of Hg in SEAN coastal catchments by measuring total Hg and MeHg in streamwater, stream sediments, freshwater benthic macroinvertebrates (BMI), and fish in watersheds with variable landscape characteristics.

## **POPs Background**

Persistent organic pollutants (POPs) comprise a long list of highly toxic and very stable organic, human-produced compounds such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), chlordane, and their breakdown products that have been used as pesticides, industrial chemicals and industrial waste products (EPA 2002). While 12 of the most dangerous POPs have been legally phased out (according to the Stockholm Convention of the United Nations Environment Programme), numerous other forms of POPs are still being manufactured and released into the environment in large quantities with unknown consequences (Giles 2004).

POPs, also known as semi-volatile organic compounds (SOCs or SVOCs), travel far from their production areas to Alaska due to their property of slow degradation, their ability to repeatedly evaporate and recondense, and the dominant south-to-north flow of air currents (AMAP 2002, Landers et al. 2008). Upon deposition, these compounds persist for long periods of time, resist environmental degradation, bioaccumulate in organisms, and biomagnify up food chains (AMAP 2004, USEPA 2009). As with Hg, POPs can also be imported into watersheds via spawning salmon and migratory birds (Blais et al. 2007), and aquatic insects can in turn transfer the contaminants to terrestrial ecosystems (Walters et al. 2008). As salmon develop their biomass (95% in the marine environment), they incorporate marine contaminants such as the POPs (and Hg) and transport them into watersheds where they spawn (Ewald et al. 1998, Zhang et al. 2001, Krümmel et al. 2003, Senkowsky 2004). Krümmel et al. (2003) report strong correlations between the density of salmon runs and PCB concentrations in lake sediments in southwestern Alaska. Sediment records from the high density salmon lakes indicated that the input of PCBs by spawning salmon was six-fold higher than the amount contributed by atmospheric deposition. Marine-derived POPs in freshwater systems have also been shown to magnify up trophic levels. For example, a study on grizzly bears (*Ursus arctos horribilis*) in British Columbia, Canada, found that salmon delivered 70% of the organochlorine pesticides, up to 85% of the lower brominated PBDE congeners (fire retardants), and 90% of PCBs measured in salmon-eating grizzly bears. These pollutant levels in the salmon-eating bears were significantly higher than in their vegetarian or non-salmon-eating counterparts in inland areas (Christensen et al. 2005).

Geographic differences in POP concentrations are not understood, but may be products of global wind and ocean current patterns that result from variable deposition characteristics within Alaska. The same group of studies that showed enhanced MeHg accumulation in murre eggs in the Gulf of Alaska also found significantly higher POPs concentrations in the region (Kucklick et al. 2002, Vander Pol et al. 2002a, Vander Pol et al. 2002b). That is, eggs from St. Lazaria (in Sitka Sound) had higher concentrations of  $\Sigma$ PCBs (sum of 46 congeners of PCBs) than eggs from any other Alaskan colonies (Vander Pol et al. 2002a). Additionally, results of a recent major survey of contaminants in Alaskan and western US NPS units show that historic-use POPs

compounds were found in every Alaskan park unit, many at the same or higher concentration as in parks in the lower 48 states (Landers et al. 2008). Specifically relevant to southeast Alaska, the study found that conifer samples in GLBA contained relatively high concentrations of some types of historic-use POPs.

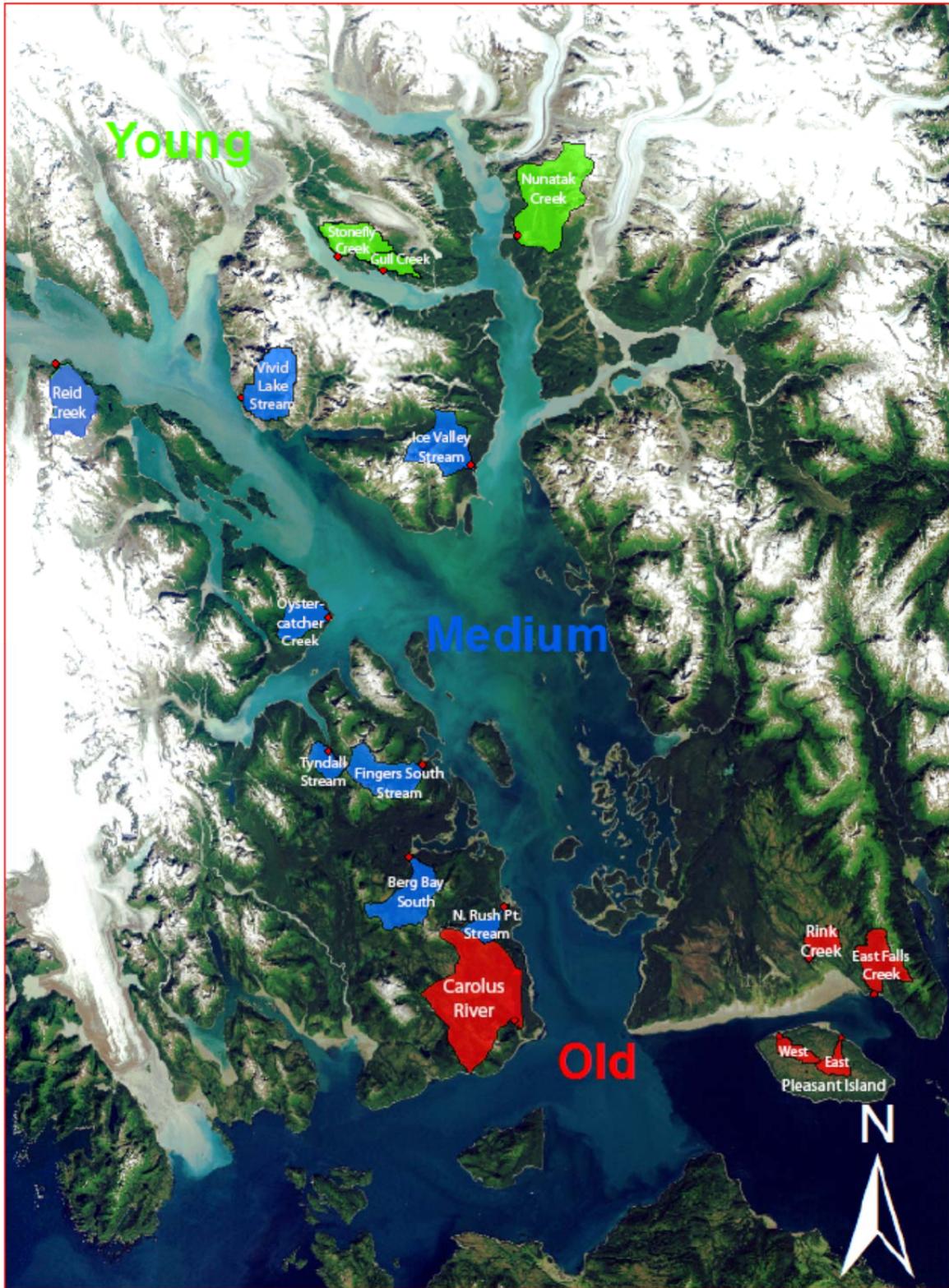
This study investigates the presence of a subset of POPs (organochlorine pesticides and industrial/urban use chemicals such as PCBs, PBDEs, DDT, and their breakdown products) in juvenile coho salmon (*Oncorhynchus kisutch*) in SEAN streams. In light of recent revelations of the ubiquitous and, in some cases, high concentrations of these global contaminants in the Alaskan environment, this project provides a baseline dataset that will be useful for future monitoring purposes and a measure of the scale of the contamination by these human-made and potentially toxic compounds.

## Study Area

The study took place in 19 streams within or adjacent to three NPS units in southeast Alaska: GLBA, SITK, and KLGO. Samples were collected from 16 streams in or immediately adjacent to GLBA (Figure 1), Indian River in SITK (Figure 2), and the Taiya and Skagway Rivers that both flow through KLGO (Figure 3), for a total of 19 streams.

The 16 streams studied in or immediately adjacent to GLBA span a broad spectrum of stream characteristics, largely controlled by biological succession following deglaciation (Milner et al. 2007). The watersheds located in the uppermost part of the Glacier Bay proper (hereafter “the bay”) are the most recently deglaciated, and those further south are progressively older, dating to ca. 1750, when glaciers in the bay began retreating. Several watersheds were refugia from the glaciation, including watersheds such as the Carolus River on the west side, and the streams draining Excursion Ridge near Gustavus, including the upper portions of Rink Creek and East Falls Creek in this study (Connor et al. 2009). The two streams on Pleasant Island also escaped glaciation and are characterized by watersheds with thick peatland soils, extensive muskegs, ponds and small lakes and channels that are narrow, bedrock dominated, and with relatively low biological productivity.

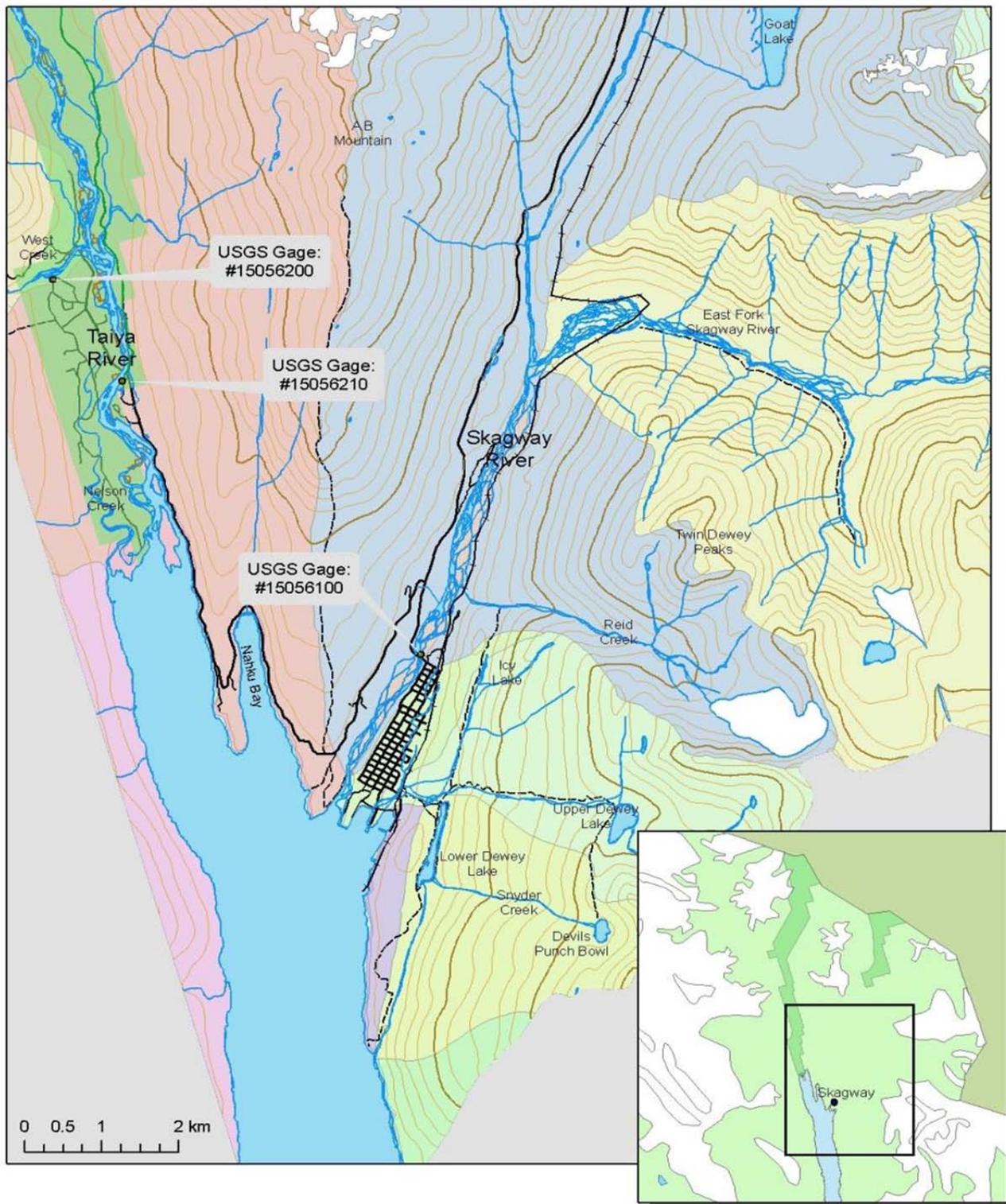
The watershed of the Indian River in SITK is typical of southeast Alaskan coastal temperate rainforest catchments, consisting predominantly of western hemlock (*Tsuga heterophylla*) and Sitka spruce (*Picea sitchensis*), shallow, well-drained soils, and steep topography. The section of the Indian River that flows through SITK (the lowermost mile of the stream) is a low gradient, gravel-cobble bed, alluvial channel (Eckert et al. 2006). The Taiya and Skagway Rivers are by far the largest watersheds included in this study and both contain substantial glacier coverage (Table 1). These transboundary rivers drain the Coast Mountains, and their watersheds contain a mixture of old growth coniferous forest, peatlands, alpine vegetation, and successional communities (Paustian et al. 1994, Hood et al. 2006). Unlike most of the GLBA study streams, the Indian (SITK), Taiya (KLGO), and Skagway (KLGO) Rivers and Rink Creek (GLBA) have some development (e.g., roads, houses) that is confined to their lower reaches.



**Figure 1.** Map of sampled watersheds in GLBA. Streams color-coded by age grouping: Young= <100 years old; Medium = 100–200 years old; Old= >1000 years old.



**Figure 2.** Indian River watershed in SITK. Historical USGS gaging stations are shown. Sampling for this project occurred in the vicinity of USGS 15097700, the lower gage. *Source:* Eckert et al. 2006.



**Figure 3.** Location of the Taiya and Skagway Rivers near Skagway. USGS streamflow gages on West Creek, the Taiya River, and the Skagway River are shown. The three watersheds and their sub-basins are shown in different colors. Samples for this project were taken at the USGS Gage site #15056210 (Taiya River) and USGS gage site #15056100 (Skagway River). *Source:* Hood et al. 2006.

**Table 1.** Geographic location, watershed area, elevation, age, and landscape characteristics of the study watersheds. Many streams in GLBA are unofficially named but consistent with Milner et al. (2000). Portions of Rink Creek and East Falls Creek and all of the Pleasant Island streams lie outside NPS boundaries.

<b>Stream</b>	<b>NPS unit</b>	<b>Latitude (N)</b>	<b>Longitude (W)</b>	<b>Area (km<sup>2</sup>)</b>	<b>Max. Elevation (m)</b>	<b>Glacier Cover (%)</b>	<b>Wetland Cover (%)</b>	<b>Freshwater Emergent Wetland (%)</b>	<b>Freshwater Forest/Shrub Wetland (%)</b>	<b>Lake influence</b>	<b>Stream age</b>
Stonefly Creek	GLBA	58.957679	136.355922	13.2	693	31.4	2.1	0.6	1.5	Yes	47
Gull Creek	GLBA	58.948616	136.289684	5.7	213	0.0	11.9	1.6	10.2	Yes	54
Nunatak Creek	GLBA	58.976447	136.094709	38.0	1414	1.8	1.1	0.6	0.6	No	73
Reid Creek	GLBA	58.872278	136.762057	17.4	1271	0	1.9	0.5	1.4	No	128
Tyndall Stream	GLBA	58.585418	136.355724	5.7	689	0	0.0	0.0	0.0	No	133
Ice Valley Stream	GLBA	58.802536	136.157216	18.5	910	0	1.3	0.9	0.4	No	138
Vivid Lake Stream	GLBA	58.850257	136.492503	21.6	1265	0	0.5	0.2	0.3	Yes	139
Oystercatcher Stream	GLBA	58.686193	136.359759	9.7	697	0	2.2	1.4	0.7	No	148
Fingers South	GLBA	58.506682	136.23625	17.0	939	0	0.3	0.3	0.0	No	153
Berg Bay South	GLBA	58.575632	136.218886	18.7	755	0	15.6	8.5	7.2	No	168
Rush Point Stream	GLBA	58.471031	136.098364	5.2	639	0	1.6	1.2	0.4	No	203
Carolus River	GLBA	58.385181	136.08101	58.2	769	0	25.8	13.4	12.4	No	1388
East Falls Creek	GLBA	58.408761	135.564703	13.6	1023	0	17.7	0.6	17.1	No	9000
Rink Creek	GLBA	58.434411	135.658232	5.9	284	0	69.5	28.2	41.3	No	9000
E. Pleasant Island	GLBA	58.375468	135.61006	4.6	188	0	67.0	0.5	66.5	Yes	13000
W. Pleasant Island	GLBA	58.376191	135.699523	4.3	168	0	47.1	0.2	46.9	No	13000
Indian River	SITK	57.053333	135.314444	19.8	1158	0	18.6	N/A	N/A	No	N/A
Taiya River	KLGO	59.511944	135.346031	466.2	1829	33%	1.9	N/A	N/A	No	N/A
Skagway River	KLGO	59.467222	135.283333	375.6	2134	17%	1.1	N/A	N/A	No	N/A



# Methods

## Study Design

### ***Selection of Watersheds***

The Indian, Skagway, and Taiya Rivers were selected in SITK and KLGO as the only major streams in those park units. The GLBA streams were selected based on balancing the target of similarly-sized, similarly-elevated, variably-aged, wetland-mapped streams with the logistical constraints presented by accessibility and wadability at the time of sampling. The practical limitations involved with challenging stream access under a limited budget and time-frame trumped efforts at selecting streams based on statistically randomized designs. Still, GLBA watersheds included in this study represent a range of ages and landscape characteristics related to vegetative succession following deglaciation and generally fall into the following three categories:

- 1) Young: recently deglaciated (or minimally glaciated) watersheds (<100 years old) with relatively little vegetative, stream channel, and soil development, but enough to support diverse benthic macroinvertebrate communities and salmonid populations;
- 2) Medium: older watersheds (100–200 years old) with developed forests (consisting largely of spruce, hemlock, and cottonwood); stable stream channels; and increasing aquatic biodiversity;
- 3) Old: much older watersheds (>1000 years old) with high channel complexity, mature forests, and significant wetland coverage.

Streams visited in GLBA and on adjacent Pleasant Island are shown in figure 1 and listed in table 1, which also provides geographic coordinates, watershed area, and watershed landscape features for them and the streams in KLGO and SITK. Stream sites in SITK and KLGO are shown in figure 2 and figure 3. It is notable that the Taiya and Skagway River watershed areas are an order of magnitude larger than the watersheds sampled in GLBA and SITK.

Data for GLBA were evaluated largely from a chronosequence perspective, while the SITK and KLGO rivers were not included in the age framework analyses due largely to their distance from the GLBA streams (and therefore potentially different atmospheric contaminant loading), their much larger watershed sizes, and their more heterogeneous underlying geology, glacial history, and surface geomorphology.

### ***Selection of Physical and Biological Stream Components***

Within streams, MeHg occurs dissolved in the water column and bound to mineral and organic particles, where it is available for uptake into aquatic food webs. A generalized pathway for MeHg transfer to higher trophic levels of SEAN streams include algae and various microorganisms, including fungi, bacteria, and protozoa (collectively biofilms), benthic macroinvertebrates, and fishes. Therefore, at each site we collected streamwater, filter-retained particulates in the streamwater, streambed sediment, BMI (mayfly larvae), and juvenile coho salmon. Although we did not specifically sample biofilms, sediment samples likely included various biofilm constituents. Streamwater and suspended particulates represent water column

conditions over very short time scales (likely changing on the scale of minutes to hours), while bed sediments, mayflies, and fish represent contaminant conditions in the stream integrated over much longer time periods (weeks to years). Because streambed sediments, BMI, and fish inhabit small areas for extended periods of time, they biologically integrate pollutants which may not be detected during standard water sampling, either because the pollutant is present at undetectable levels or only intermittently through time (Krabbenhoft et al. 1999). For this study, Hg<sub>T</sub> and MeHg were measured in surface water, particulates, bed sediments, and mayflies (Table 2). Fish samples were analyzed for Hg<sub>T</sub>, assuming that >90% of the total was present as MeHg (Bloom 1992), and for a suite of POPs (Table 3). Water, sediment, and mayflies were not analyzed for POPs due to their likely undetectable concentrations and the high expense of the analyses.

As primary consumers, benthic macroinvertebrates such as mayflies represent one of the lowest trophic levels for pollutants to enter into and biomagnify within aquatic food webs. The BMI communities in SEAN streams are comprised of insects, crustaceans, mollusks, mites, and annelids. These invertebrates feed on plants, bacteria, fungi, detritus and other invertebrates, and in turn are prey for a variety of aquatic and terrestrial secondary consumers, including fishes, birds, mammals, and predatory invertebrates (Allan and Castillo 2007). Thus, BMI, including the terrestrial winged form of aquatic insects, are an important link between primary producers and secondary consumers providing a potential pathway for pollutant transfer into higher trophic levels (Hall et al. 1998, Pennuto et al. 2005, Walters et al. 2008). Juvenile coho salmon rely on BMI as a source of food (Groot and Margolis 1991), and they in turn are an important food source for a great variety of freshwater and marine fishes, birds, and small mammals (Larkin 1977, Zarnowitz and Raedeke 1984, Willson and Halupka 1995).

Because BMI obtain Hg through their food, the food resources utilized by mayfly larvae may influence exposure levels. BMI are characterized into Functional Feeding Groups (FFGs) based on their morpho-behavioral adaptations for obtaining food (Cummins 1973). Baetidae and Heptageniidae mayflies—the two mayfly families targeted in this study—are in the collector-gatherer and scraper FFGs, respectively. Although larva from these two families obtain their food differently, the diets of both can consist of periphyton (primarily diatoms), biofilms, bacteria and fungi, and detritus, the latter in the form of fine particulate organic matter and associated microorganisms (Merritt et al. 2008, Allan and Castillo 2007). The relative contribution of these food resources to the diet likely varies among streams and taxa, as well as with body size.

The two mayfly families and the coho salmon were selected because they were present in most (in the case of the mayflies) and all (in the case of the coho) study streams. Another important criterion that these biota met is that they had not migrated out of their native streams. In order to evaluate the spatial variations of the contaminants in the study area, we collected samples that reflected the conditions in each specific watershed alone. We assume that the body burdens of contaminants in BMI and juvenile coho salmon were derived from within the watershed where they were collected, and moreover, that each group occupied the same trophic position across the various streams sampled.

## **Field Methods**

All samples from the three NPS units were collected between June 18 and July 3, 2007. With the exception of Rink Creek, which was accessed by road in Gustavus, travel to the sites in GLBA

was accomplished using the NPS research vessel Capelin, followed by walking upstream until clearly above tidal influence. Tidal influence was determined based on examination of both physical characteristics of the stream and the composition of stream plants and macroinvertebrates. All sites in GLBA were visited within a one-week period to help minimize seasonal and climatic variations between watersheds. The Indian River was sampled five days after the GLBA sampling (on June 27, 2007), and the Skagway and Taiya Rivers were visited six days after that (on July 3, 2007).

At each site we took in situ water quality measurements (pH, dissolved oxygen, specific conductance, temperature, and turbidity) and measured streamflow (except for at Skagway River (unwadable) and Taiya River (streamflow value taken from operating USGS gage). A handheld YSI 556 multiparameter sonde, calibrated daily, was used to measure pH, dissolved oxygen, specific conductance, and temperature. Turbidity was measured in the field using a Hach turbidometer, checked daily for calibration. For all these field-measured parameters, three individual readings were taken. Data presented in this report are the averages of the triplicate measurements. Streamflow was measured using standard USGS protocols (Rantz et al. 1982).

We collected 4 liters of water (3 liters for dissolved organic carbon quantification and characterization—GLBA samples only due to logistical and budgetary constraints; and 1 liter for total suspended solid (TSS) quantification), which were filtered directly into amber glass bottles that were chilled and overnight-mailed to the lab in Boulder, Colorado within three days of collection. TSS concentrations were quantified (in the lab at University of Alaska Southeast, within one week of collection) by weighing the mass of particulates retained on a glass microfiber filter following a vacuum driven filtration of at least 500 mL of sample.

We collected several grams of streambed sediments by submersing the collection vial into the stream and scraping the top ~1 cm of fine sediment (unsieved) directly into the Teflon vial. Up to 100 mayfly larvae were collected using a kicknet to dislodge them from the streambed, followed by manual picking (using forceps) through the collected material and storing in small Teflon vials. Up to 20 juvenile coho salmon were captured either by manual netting (using small aquarium nets) or by collection in baited minnow traps. Fish samples collected for Hg determination were stored in small Teflon vials, while those destined for POPs analyses were wrapped in aluminum foil and zip-close bags. Teflon vials holding sediment, mayfly larvae, and fish were all double-bagged in zip-close bags. All sampling material was handled by personnel wearing clean nitrile gloves. All biological samples were stored on ice.

Water, BMI, half of the fish, and all of the particulate and streambed sediment samples were sent to the USGS Mercury Research Laboratory in Middleton, WI for HgT and MeHg determinations. Filtration of water samples (through ~0.7  $\mu$ m filters) for Hg analyses of dissolved and particulate fractions was conducted within one day of sample collection using a portable, metal-free filtration station and equipment extensively precleaned at the USGS laboratory prior to sampling (Lewis and Brigham 2004). The other half of the fish samples was sent to the NOAA Northwest Fisheries Science Center in Seattle, WA for analyses of POPs. Water samples were split between USGS water quality labs (for chemical analyses), the University of Colorado in Boulder (for dissolved organic carbon quantification and characterization) and the University of Alaska Southeast (for sediment quantification).

## **Analytical Methods**

### ***Dissolved Organic Carbon Quantity and Quality***

Dissolved organic carbon is a heterogeneous mixture of soluble organic material that can vary widely in size and chemistry. Because the chemical quality of DOC affects its ability to complex with and transport contaminants like Hg, it is helpful to evaluate the character of DOC in addition to measuring its bulk concentration. The hydrophobic fraction of DOC in streamwaters is composed primarily of fulvic acids (Thurman 1985), which are more effective at complexing with Hg compared to the low molecular weight compounds that comprise the bulk of the hydrophilic fraction of DOC. Thus, concentrations of HPOA DOC can be used as an indicator of Hg transport potential in surface waters. We also measured UV absorbance (UVA) which is the total UV absorbance of DOC at 254 nm. Specific UV absorbance (SUVA) is the carbon normalized UV absorbance of DOC and is highly correlated with the aromatic carbon content of DOC. Similar to HPOA DOC, aromatic carbon content is a useful indicator of the potential of DOC to complex and mobilize Hg.

The samples were analyzed for DOC concentration and quality at the USGS National Research Program laboratory in Boulder, CO within two working days of receipt, and DOC fractionation was completed within two weeks. DOC concentrations were measured using the platinum catalyzed persulfate wet oxidation method on an O.I. Analytical Model 700 TOC Analyzer (Aiken 1992). UV-Visible absorbance measurements were made on a Hewlett-Packard Model 8453™ photo-diode array spectrophotometer every 1 nm between 200 and 800 nm. SUVA (Weishaar et al. 2003), defined as the UV absorbance of the sample measured at a given wavelength divided by the DOC concentration, values were calculated at 254 nm and are reported in units of [L / (mg C \*m)] by normalizing to a 1 m pathlength. Excitation-Emission Matrices (EEMs) were collected to further characterize the optically active portion of the dissolved organic matter on a Jobin-Yvon Horiba Fluoromax-3 fluorometer using a 5 nm bandwidth for both excitation and emission over an excitation range of 240–450 nm every 5 nm, with an emission range of 300–600 nm every 2 nm. EEMs were blank subtracted using a nanopure water EEM obtained the same day, corrected for instrument optics, Raman-normalized using the area under the Raman emission scatter peak (350 nm excitation wavelength) and inner filter corrected using the UV-Visible absorbance scan (McKnight et al. 2001). The fluorescence index (FI) was calculated as a ratio of emission intensity at 470 nm over 520 nm obtained at an excitation wavelength of 370 nm (McKnight et al. 2001). The DOC in each sample was chromatographically fractionated into five fractions (hydrophobic organic acids, hydrophobic organic neutrals [calculated by difference], low molecular weight hydrophilic acids, transphilic organic acids and transphilic organic neutrals [not reported]) utilizing Amberlite XAD-8 and XAD-4 resins (Aiken et al. 1992).

### ***Mercury Analytical Methods (Water, Particulates, Sediment, Benthic Macroinvertebrates, and Fish)***

All Hg<sub>T</sub> and MeHg analyses were performed at the USGS Mercury Research Laboratory in Middleton, WI (<http://wi.water.usgs.gov/mercury-lab/>). A brief description of the analytical methods is provided here, but it should be noted that all Hg-related analyses are conducted using strict ultraclean methods for sample handling, which are intended to ensure contamination-free samples (water, particulate, biological tissue). Detection limits and specific methods used for each type of analysis are listed in table 2.

**Table 2.** Types of Hg analyses performed at the USGS Mercury Research Lab, with method detection limits and method references.

Lab Code	Description	Detection Limit	Method Reference
FTHG	Filtered total mercury	0.04 ng/L	<a href="#">EPA Method 1631, Rev. E</a>
FMHG	Filtered methylmercury	0.04 ng/L	<a href="#">USGS Open-File Report 01-445</a>
UTHG	Unfiltered total mercury	0.04 ng/L	<a href="#">EPA Method 1631, Rev. E</a>
UMHG	Unfiltered methylmercury	0.04 ng/L	<a href="#">USGS Open-File Report 01-445</a>
PTHG	Particulate total mercury	0.059 ng/filter	<a href="#">USGS Techniques and Methods 5A-8</a>
PMHG	Particulate methylmercury	0.01 ng/filter	<a href="#">USGS Techniques and Methods 5A-7</a>
<b>Bed Sediment and Soil</b>			
		0.3 ng/ analytical aliquot	<a href="#">USGS Techniques and Methods 5A-8 - acid digestion</a>
STHG	Sediment total mercury	1.38 ng/g	<a href="#">EPA Method 7473 (SW-846) Rev. 0 - direct combustion</a>
SMHG	Sediment methylmercury	0.08 ng/g	<a href="#">USGS Techniques and Methods 5A-7</a>
DRY_WT	Dry weight percent (percent solids)	not applicable	<a href="#">USGS Techniques of Water-Resources Investigations 5-A1, 3rd ed., p. 48</a>
LOI	Percent loss on ignition	not applicable	<a href="#">USGS Techniques of Water-Resources Investigations 5-A1, 3rd ed., p. 451</a>
<b>Plant and Animal Tissue</b>			
BMHG	Biological methylmercury	determined per analytical batch	<p><a href="#">1. dilute nitric acid digestion per "Bioaccumulation and Trophic Transfer of Methylmercury in Long Island Sound," 2006, Chad R. Hammerschmidt and William F. Fitzgerald, Arch. Environ. Contam. Toxicol. 51(3):416-424 doi:10.1007/s00244-005-0265-7</a></p> <p><a href="#">2. USGS Open-File Report 01-445 with modifications</a> 1. sulphuric:nitric acid digestion</p>
BTHG	Biological total mercury	determined per analytical batch	<p><a href="#">2. dilute nitric acid digestion per "Bioaccumulation and Trophic Transfer of Methylmercury in Long Island Sound," 2006, Chad R. Hammerschmidt and William F. Fitzgerald, Arch. Environ. Contam. Toxicol. 51(3):416-424 doi:10.1007/s00244-005-0265-7</a></p> <p><a href="#">3. EPA Method 7473 (SW-846) Rev. 0 - direct combustion</a></p>

Total mercury analysis followed U.S. EPA Method 1631. Aqueous samples were pretreated by the addition of 1–2 percent (v/v) 0.2 N Bromine monochloride (BrCl) to solubilize and oxidize all forms of Hg to reactive mercuric ion (Hg<sup>2+</sup>). Samples were placed in an oven at 50°C for a minimum of 12 hours to accelerate the oxidation reaction. Oxidation was considered complete when excess BrCl was present, detectable by a faint yellow color. Immediately prior to analysis, a small amount of hydroxylamine hydrochloride (NH<sub>2</sub>OH–HCl) was added to each sample until the residual color from added BrCl disappeared. Approximately 10 minutes after BrCl reduction,

0.5 ml of stannous chloride ( $\text{SnCl}_2$ ) was added to the sample within the bubbling flask to reduce the  $\text{Hg}^{2+}$  to  $\text{Hg}(0)$ . The  $\text{Hg}(0)$  was purged from samples with Hg-free  $\text{N}_2$  gas and concentrated onto a gold-coated, glass-bead trap. Finally, gold traps were heated and the  $\text{Hg}(0)$  thermally desorbed into an Argon gas stream and quantified by cold vapor atomic fluorescence spectroscopy (CVAFS).

MeHg analyses were performed following standard distillation and ethylation procedures described in detail elsewhere (De Wild et al. 2002, Horvat et al. 1993). Briefly, this method calls for isolation of all ambient MeHg from the sample matrix by atmospheric pressure water vapor distillation. The MeHg in the distillates were derivatized using sodium tetraethylborate and preconcentrated onto Carbo traps. Detection and quantification was achieved after thermodesorption, isothermic GC separation, and detection by CVAFS.

Particulate, sediment, and biological tissue samples are analyzed for  $\text{Hg}_T$  and MeHg using the procedures described above, however, for each of these solid-phase samples a solubilization step is first conducted to transform the sample into an aqueous state. For  $\text{Hg}_T$  in sediments and particulates, about 100 mg of homogenized, dried sample is digested in Aqua Regia (Olund et al. 2004); whereas MeHg in sediment and particulates is solubilized with methylenechloride and heat (DeWild et al. 2004). Fish tissues and benthic invertebrates were digested in Teflon bombs using a concentrated mixture of nitric and sulfuric acids (5/2 volume to volume ratio) and placed in an oven at  $75^\circ\text{C}$  for 2 hours. For MeHg solubilization of benthic invertebrates, the weak nitric acid method of Hammerschmidt and Fitzgerald (2006) was used, and included the heating to  $60^\circ\text{C}$  in an oven and subsequent neutralization with KOH.

### ***POPs Analytical Methods***

The POPs targeted in this study fall into three general groups: industrial/urban use compounds, current use pesticides, and North American historic-use pesticides (Table 3). Coho salmon were analyzed for 77 types of POP. All POPs analyses were conducted at the NOAA Northwest Fisheries Science Center in Seattle, WA.

POPs in the whole bodies of juvenile coho were extracted using an accelerated solvent extractor (ASE) and measured by gas chromatography/mass spectrometry (GC/MS) as described in (Sloan et al. 2005). Briefly, whole body samples (0.6–2.0 g) were weighed and mixed with sodium sulfate and magnesium sulfate. Each sample mixture was transferred to a 33-mL extraction cell of the ASE and the POPs were extracted by adding 25 mL methylene chloride to each extraction cell at  $100^\circ\text{C}$  and 2,000 psi for five minutes. This extraction step was repeated and the sample extracts (50 mL) were combined. Prior to the cleanup step, a 1-mL aliquot of each sample extract was removed for lipid quantification by thin layer chromatography with flame ionization detection (TLC/FID; Ylitalo et al. 2005). The sample extract was filtered through a column of silica gel and alumina and concentrated for further cleanup to remove interfering lipid compounds. Size exclusion chromatography with high-performance liquid chromatography (HPLC) was used to collect the fraction containing the POPs. The HPLC fraction was analyzed for POPs (e.g., chlordanes, DDTs, PCBs, PBDEs) on a low resolution quadrupole GC/MS system equipped with a 60-meter, DB-5 GC capillary column. The instrument was calibrated using sets of up to ten multilevel calibration standards of known concentrations.

**Table 3.** List and description of POPs measured in juvenile coho salmon.

Category	Name	Description	Use in USA and Canada
Current use pesticides	Endosulfan I	Organochlorine sulfide insecticide	1954–present
	Lindane	Organochlorine insecticide	1948–present
Historic use pesticides	HCH-a,b	Organochlorine insecticides	1948–1978
	HCB	Chlorobenzene fungicide	1945–1984
	Aldrin	Organochlorine insecticide	1949–1990
	Dieldrin	Organochlorine insecticide	1949–1990
	Heptachlor	Organochlorine insecticide	1952–1988
	Heptachlor epoxide	Organochlorine degradation product	N/A
	Oxy-chlordane	Organochlorine degradation product	N/A
	Mirex	Organochlorine insecticide	1959–1978
	p,p'DDT and o,p'DDT	Organochlorine insecticides	1942–1989
	p,p'DDD and o,p'DDD	Organochlorine degradation products	N/A
	p,p'DDE and o,p'DDE	Organochlorine degradation products	N/A
	Chlordanes: g-, a-, trans-nonachlor, cis-nonachlor, and nonachlor III	Organochlorine pesticides	1948–1988
Urban/industrial use chemicals	45 congeners of polychlorinated biphenyls (PCBs): 17,18,28,31,33,44,49,52,66,70,74,82,87,95, 99,101/90,105,110,118,128,138/163/164,149, 151,153/132,156,158,170,171,177,180,183, 187/159/182,191,194,195,199,205,206,208,209		1929–1977
	10 congeners of polybrominated diphenyl ethers (PBDEs) 28,47,49,66,85,99,100,153,154,183		1970s–present

Total PCBs ( $\sum$ PCBs) were calculated by adding the concentrations of 45 PCB congeners (PCBs 17, 18, 28, 31, 33, 44, 49, 52, 66, 70, 74, 82, 87, 95, 99, 101/90, 105, 110, 118, 128, 138/163/164, 149, 151, 153/132, 156, 158, 170/190, 171, 177, 180, 183, 187, 191, 194, 195, 199, 205, 206, 208, 209) and total PBDEs ( $\sum$ PBDEs) were calculated by adding the concentrations of 10 PBDE congeners (28, 47, 49, 66, 85, 99, 100, 153, 154 and 183). Total DDTs were calculated by adding the levels of o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE, o,p'-DDT and p,p'-DDT; total chlordanes were calculated by adding heptachlor, heptachlor epoxide, oxychlordane, *gamma*-chlordane, nonachlor III, *alpha*-chlordane, *trans*-nonachlor, and *cis*-nonachlor and total hexachlorocyclohexanes (HCHs) includes the sum of *alpha*-, *beta*-, and *gamma*-HCH isomers.

Concentrations of lipid (reported as percent lipid) of coho whole bodies were measured by TLC/FID using an Iatroscan Mark 6. Each lipid sample extract was spotted on a Chromarod SIII and developed in a solvent system containing 60:10:0.02 hexane:diethyl ether:formic acid (v/v/v). Various classes of lipids (i.e., wax esters/sterol esters, triglycerides, free fatty acids, cholesterol and phospholipids/other polar lipids) were separated based on polarity, with the non-polar compounds (i.e., wax esters/sterol esters) eluting first, followed by the more polar lipids. Data were acquired and analyzed using Waters Millennium software. A four-point linear external calibration was used for quantifying each lipid class. Total lipid concentrations were calculated by adding the concentrations of the five lipid classes for each sample and were reported as

percent total lipid. Duplicate TLC/FID analyses were performed for each sample extract and the mean value reported.

### ***Laboratory Quality Assurance***

#### Quality Assurance for Mercury Analyses

Accuracy (measured against certified reference materials and spike recoveries) and precision (measured by replicate runs of samples) all showed excellent results for the Hg analyses. All reference materials analyzed with the biological (fish and invertebrates), particulate, and sediment samples were well within the reported 95% confidence intervals of their certified concentrations. Specifically, for Hg<sub>T</sub>, reference materials were within 97–101% of the reported values for fish analyses, 85–93% for macroinvertebrate analyses, 85–105% for particulates, 93–98% for sediments. For MeHg, reference materials were recovered at 84–101% for fish, 97–106% for particulates, and 79–82% for sediments. The percent relative standard deviation of triplicate sample analyses of Hg<sub>T</sub> and MeHg in biological tissues averaged 2.3% and 9.4%, respectively. Each sample of Hg<sub>T</sub> in water samples was run in duplicate, and the average difference between runs was 1.8%. (If the difference between duplicate runs ever exceeded 10%, as it did once, the sample was rerun until the %RSD of the values did not exceed 10%.) Spike recoveries (run in duplicates) on MeHg in water samples averaged 104% (range 93–117%). Of the 8 field filtration blanks, 7 were below the detection limit of 0.04 ng/L, and one measured slightly above, at 0.05 ng/L for Hg<sub>T</sub>, and this represents a negligible contribution to sample Hg<sub>T</sub> concentrations.

#### Quality Assurance for POPs Analyses

A method blank and a National Institute of Standards and Technology (NIST) fish homogenate Standard Reference Material (SRM 1947) were analyzed with each sample set containing 10–12 field samples as described in (Sloan et al. 2006). For each sample set, concentrations of  $\geq 70\%$  of individual analytes that were measured in SRM 1947 were within 30% of either end of the 95% confidence interval range of the certified concentrations. Duplicate analyses were done for 10% of the whole body samples, with relative standard deviations  $\leq 15\%$  for more than 90% of analytes that had concentrations  $\geq 1$  ng/g. Method blanks contained no more than five analytes that exceeded four times the lower limit of quantitation (LOQ), unless the analyte was not detected in the associated field samples in the set.

# Results

## Mercury in Streamwater, Particulates, Bed Sediment, and Biota

### *Filtered Total Mercury (Hg<sub>T</sub>) and Dissolved Organic Carbon*

All streams contained detectable Hg<sub>T</sub>, which ranged from 0.2 to 3.4 ng/L (mean= 0.8, std. dev.= 0.9 ng/L), in filtered water samples (Table 4, Appendix A). This Hg<sub>T</sub> concentration range is somewhat low compared to other stream studies (Krabbenhoft et al. 1999, Wiener et al. 2006, Brigham et al. 2009). The highest concentrations (3.4 and 3.1 ng/L) were found in the two old, peatland-rich watersheds from Pleasant Island, adjacent to GLBA. In GLBA proper, concentrations were as much as an order of magnitude lower, ranging from 0.2 to 1.3 ng/L. The Indian River (SITK) and the two KLG0 rivers (Taiya and Skagway) contained some of the lowest values for Hg<sub>T</sub> (0.3–0.4 ng/L; Table 4).

Consideration by age category shows that mean filtered Hg<sub>T</sub> concentrations in GLBA streams increased from 0.3 to 0.6 to 1.7 ng/L, going from the young, medium, to old categories, respectively (Table 4). Sample sizes were too small for formal statistical significance testing by ANOVA or similar.

Evaluation of the fraction of Hg<sub>T</sub> in the water column present as filterable or particulate reveals an increasing tendency for Hg<sub>T</sub> to be in the filterable phase in older watersheds (Table 4). In the young and medium-aged streams, the percent of bulkwater Hg<sub>T</sub> occurring in the filterable phase was highly variable (from 19–95%; mean=43% in young streams, mean=53% in medium-aged streams), but in the old watersheds, between 62–95% (mean=85%, SD=13%) of the Hg<sub>T</sub> was filterable.

Filter-passing Hg<sub>T</sub> shows a strong positive linear correlation with parameters that are indicative of the influence of wetlands: the mapped %wetland cover in the watershed (specifically the %forest shrub wetland), average watershed slope, DOC, HPOA DOC, SUVA, UVA, and stream age (Table 5 and Figure 4). Many of these wetland indicators were correlated with one another as well. For example, the DOC (and HPOA DOC) concentrations in the streams were well correlated not only with Hg<sub>T</sub> but with the percent of the watershed mapped as forest shrub wetland, UVA, SUVA, watershed slope, and age. (GLBA only; Tables 5 and 6). All KLG0 and SITK rivers, as well as the majority of GLBA streams, had low DOC concentrations, between 0.4–1.6 mg/L. The only streams with higher concentrations were Rink Creek (5.1 mg/L) and the two streams on Pleasant Island (12.0 and 10.8 mg/L).

**Table 4.** Dissolved organic carbon (DOC), UV absorbance (UVA), specific UV absorbance (SUVA), % and quantity of hydrophobic DOC (HPOA DOC), filtered and particulate Hg<sub>T</sub> and MeHg in sampled streams. "SW total" is the sum of filtered and particulate concentrations. Text color for GLBA streams follows the scheme presented in figure 1.

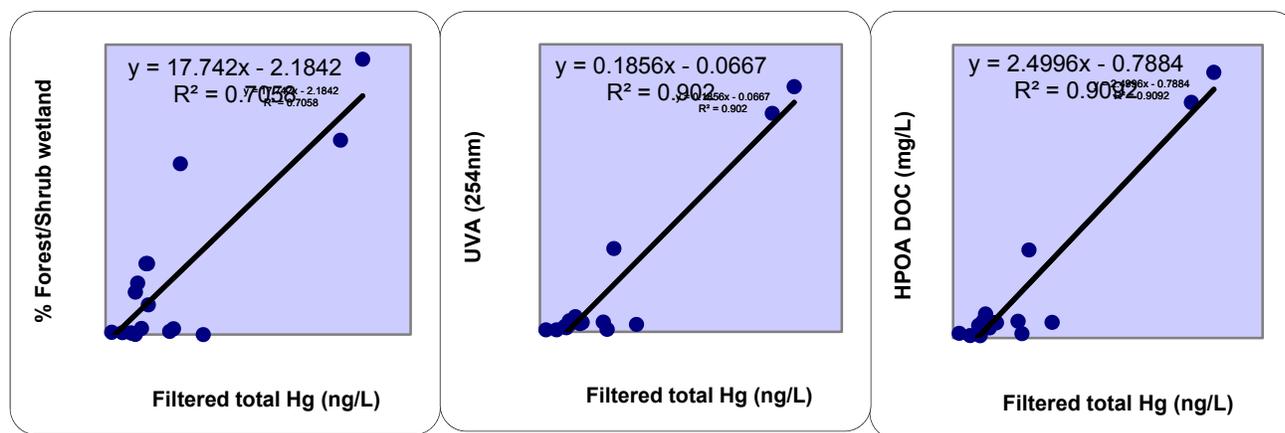
Age group	Stream	DOC mg/L	UVA 254nm	SUVA 254nm	HPOA (%)	Total Hg			Methyl Hg				
						HPOA DOC mg/L	Filtered (ng/L)	Particulate (ng/L)	SW total (ng/L)	% Hg <sub>T</sub> in filtered	Filtered (ng/L)	Particulate (ng/L)	SW total (ng/L)
Young (GLBA)	Stonefly Cr.	1.00	0.037	3.7	31	0.31	0.47	0.97	1.44	33%	0.02	0.01	0.03
	Gull Creek	1.30	0.018	1.4	40	0.52	0.39	0.20	0.59	67%	0.04	0.02	0.05
	Nunatak Creek	0.40	0.005	1.2	36	0.14	0.08	0.19	0.27	30%	0.01	<0.01	0.01
	<i>mean</i>	<i>0.90</i>	<i>0.020</i>	<i>2.1</i>	<i>36</i>	<i>0.32</i>	<i>0.31</i>	<i>0.45</i>	<i>0.76</i>	<i>43%</i>	<i>0.02</i>	<i>0.01</i>	<i>0.03</i>
	<i>std. dev.</i>	<i>0.46</i>	<i>0.02</i>	<i>1.4</i>	<i>5</i>	<i>0.19</i>	<i>0.21</i>	<i>0.45</i>	<i>0.60</i>	<i>20%</i>	<i>0.01</i>	<i>0.01</i>	<i>0.02</i>
Medium (GLBA)	Reid Creek	0.40	0.006	1.4	33	0.13	0.89	3.73	4.62	19%	0.04	0.01	0.04
	Tyndall	1.00	0.018	1.8	48	0.48	1.28	0.07	1.35	95%	0.03	<0.01	0.03
	Ice Valley	0.50	0.005	1.2	15	0.08	0.22	0.11	0.33	66%	0.10	<0.01	0.11
	Vivid Lake Cr.	0.40	0.010	2.8	18	0.07	0.35	1.39	1.74	20%	<0.01	<0.01	<0.01
	Oystercatcher	1.20	0.024	1.9	43	0.52	0.84	0.13	0.97	86%	0.06	<0.01	0.06
	Fingers South	1.20	0.027	2.3	35	0.42	0.39	0.99	1.38	28%	0.02	<0.01	0.03
	Berg Bay So.	1.30	0.023	1.7	36	0.47	0.56	0.77	1.33	42%	0.02	0.01	0.02
	Rush Point	1.10	0.013	1.2	35	0.39	0.33	0.18	0.51	65%	0.04	<0.01	0.04
	<i>mean</i>	<i>0.89</i>	<i>0.016</i>	<i>1.8</i>	<i>33</i>	<i>0.32</i>	<i>0.61</i>	<i>0.92</i>	<i>1.53</i>	<i>53%</i>	<i>0.04</i>	<i>&lt;0.01</i>	<i>0.04</i>
<i>std. dev.</i>	<i>0.39</i>	<i>0.01</i>	<i>0.6</i>	<i>11</i>	<i>0.19</i>	<i>0.36</i>	<i>1.24</i>	<i>1.34</i>	<i>30%</i>	<i>0.03</i>	<i>&lt;0.01</i>	<i>0.03</i>	
Old (GLBA)	Carolus River	1.60	0.027	1.8	46	0.74	0.42	0.26	0.68	62%	0.02	0.01	0.02
	East Falls Cr.	1.10	0.020	1.9	43	0.47	0.53	0.09	0.62	86%	0.01	<0.01	0.02
	Rink Creek	5.10	0.203	4.0	53	2.70	0.98	0.16	1.14	86%	0.21	0.01	0.21
	E. Pleasant Is.	12.00	0.597	5.0	68	8.16	3.37	0.17	3.54	95%	0.09	0.01	0.10
	W. Pleasant Is.	10.80	0.532	4.9	67	7.24	3.08	0.17	3.25	95%	0.06	<0.01	0.07
	<i>mean</i>	<i>6.12</i>	<i>0.28</i>	<i>3.5</i>	<i>55</i>	<i>3.86</i>	<i>1.68</i>	<i>0.17</i>	<i>1.85</i>	<i>85%</i>	<i>0.08</i>	<i>&lt;0.01</i>	<i>0.08</i>
<i>std. dev.</i>	<i>5.08</i>	<i>0.27</i>	<i>1.6</i>	<i>12</i>	<i>3.62</i>	<i>1.43</i>	<i>0.06</i>	<i>1.43</i>	<i>13%</i>	<i>0.08</i>	<i>&lt;0.01</i>	<i>0.08</i>	
(S/TK)	Indian R.	1.5	N/A	N/A	N/A	N/A	0.27	0.05	0.32	84%	0.03	<0.01	0.03
(KLGO)	Taiya R.	0.8	N/A	N/A	N/A	N/A	0.35	0.53	0.88	40%	0.02	0.01	0.03
(KLGO)	Skagway R.	1.2	N/A	N/A	N/A	N/A	0.37	-	-	-	<0.01	<0.01	<0.01

**Table 5.** Pearson's r correlation values for filtered total Hg (GLBA only) regressed against parameters which showed significant two-tailed correlations. All were significant at the 0.01 level.

Parameters	Filtered Hg <sub>T</sub>
UVA	0.950**
SUVA	0.784**
HPOA DOC	0.954**
DOC (mg/L)	0.940**
% Wetland	0.705**
% Forest shrub wetland	0.849**
Avg. watershed slope	-0.709 **
Stream age	0.803**

**Table 6.** Pearson's r correlation values for DOC and HPOA DOC against parameters which showed significant two-tailed correlations at the 0.01 level (GLBA samples only). The parameters listed are not independent of one another but are listed to show the strength of correlation with DOC/ HPOA DOC.

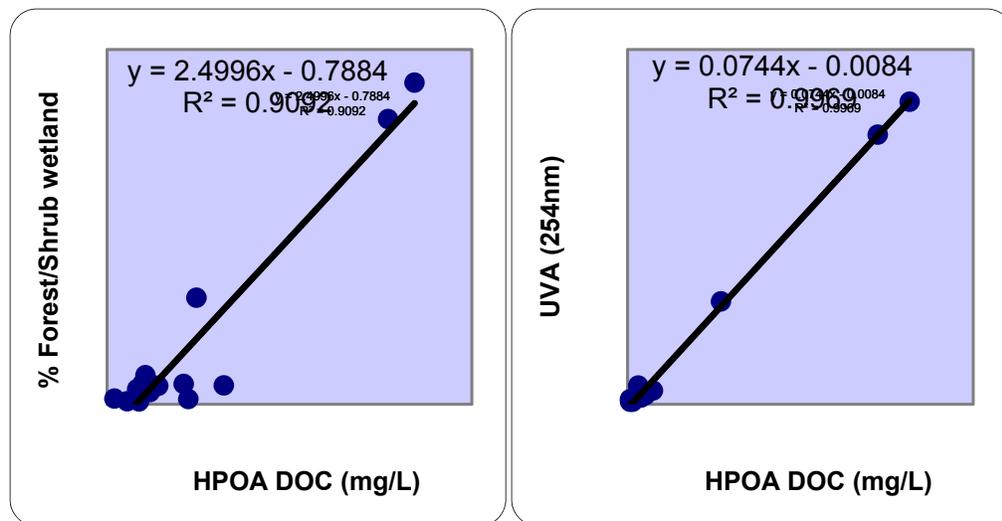
Parameters	DOC (mg/L)	HPOA DOC (mg/L)
% Wetland	0.847(**)	0.819(**)
% Forest shrub wetland	0.949(**)	0.937(**)
Avg. watershed slope	-0.838(**)	-0.821(**)
Stream age (GLBA only)	0.882(**)	0.873(**)
UVA	0.997(**)	0.998(**)
SUVA	0.851(**)	0.998(**)



**Figure 4.** Filtered Hg<sub>T</sub> vs. percent forest/shrub wetland cover, UV absorbance, and hydrophobic dissolved organic carbon (HPOA\_DOC) in the GLBA streams (p<0.001).

Across the GLBA sites, the HPOA DOC concentrations were very low in the young and medium age streams (average=0.32 mg C/L), but increased by an order of magnitude to 3.86 mg C/L in the old group (Table 4). The UVA and SUVA similarly increased strongly in the old watersheds. In southeast Alaska, dissolved organic carbon derived from wetlands is rich in fulvic acids and aromatic carbon (Fellman et al. 2008) and is readily mobilized to streams via overland flowpaths during frequent storm events (Fellman et al. 2009). Thus, the changes in the quality of streamwater DOC we observed across GLBA are consistent with increased runoff from wetlands

in older watersheds in the lower reaches of the bay (Figure 5). Moreover, the high correlations between streamwater Hg and HPOA DOC and SUVA are consistent with the idea that humic substances are effective at mobilizing Hg from soils and wetlands to streams (Ravichandran et al. 1998).



**Figure 5.** HPOA DOC concentration (mg/L) regressed against (a) the percent of watershed area mapped as forest-shrub wetland and (b) the UV absorbance ( $p < 0.001$ ) in GLBA streams.

### **Filtered Methylmercury**

Filtered MeHg concentrations in the newer, recently glaciated streams in GLBA, as well as the rivers in KLGO and SITK, were close to or below the limit of quantification (0.01 ng/L) but were higher (comprising up to 21% of the total Hg (Rink Creek)) in several of the medium- and old-aged GLBA-area streams draining landscapes with developed wetlands (Table 4). Stratified by age group, mean concentrations of filtered MeHg doubled from young (0.02 ng/L) to medium (0.04 ng/L), and again from medium to old (0.08 ng/L) watersheds. Streams with the highest filtered MeHg included Ice Valley Stream (0.10 ng/L), Oystercatcher (0.06 ng/L), Rink (0.21 ng/L), and both streams on Pleasant Island (0.09 and 0.06 ng/L). At the two Pleasant Island streams, MeHg accounted for 2–3% of the total Hg; and in Rink Creek, 21% of the filtered  $Hg_T$  was in the methyl form. At other streams, concentrations for both  $Hg_T$  and MeHg were close enough to the quantification limits that the %MeHg is not reliably calculated.

### **Particulate Mercury**

All samples were at or below the quantification limit for MeHg (0.01 ng/L) in the particulate fraction (the suspended material retained by the  $\sim 0.7\mu m$  filter), except for Gull Creek (with 0.02 ng/L). However, particulate  $Hg_T$  was detected in all streams except the Indian and Skagway Rivers (Table 7). Particulate concentrations (in terms of ng/g, adjusted for total suspended solid (TSS) concentrations) ranged from below detection in the Indian and Skagway Rivers to 940 ng/g (dry weight) on East Pleasant Island. Two of the three highest particulate  $Hg_T$  concentrations were from the Pleasant Island stream samples (with 350 and 935 ng/g for the East and West Pleasant Island streams, respectively). Overall, particulate  $Hg_T$  was weakly but significantly correlated with filtered  $Hg_T$  (Pearson's  $r = 0.676$ ,  $p < 0.05$ ). Multiple linear regression models did not yield any better predictors for particulate  $Hg_T$  than filtered  $Hg_T$  alone. Broken up

by age class, the mean particulate Hg<sub>T</sub> rose from 116 (SD=77) to 256 (SD=237) to 297 (SD=325) ng/g dry weight (young, medium, and old categories, respectively; Table 7).

Particulate Hg, measured in terms of concentration per liter of streamwater (uncorrected for TSS), did not follow a pattern by age group. Instead, it was significantly correlated with discharge ( $r=0.719$ ,  $p=0.003$ ) and TSS ( $r=0.688$ ,  $p=0.002$ ). Multiple linear regression analysis shows that TSS and turbidity together predicted particulate Hg (adjusted  $r^2=0.908$ ).

**Table 7.** Total and MeHg concentrations in filter-retained particulates (in the water column) and in bed sediments. Particulate Hg concentrations (in ng/g) were calculated from the particulate concentration (ng/liter of streamwater) adjusted for the measured TSS concentration.

Stream	Particulates		Bed Sediment	
	Hg <sub>T</sub> (ng/g)	MeHg (ng/g)	Hg <sub>T</sub> (ng/g)	MeHg (ng/g)
Stonefly Cr.	33	0.4	7	0.05
Gull Creek	131	10.0	11	0.44
Nunatak Creek	184	BDL	5	0.01
<i>mean</i>	116	BDL	8	0.17
<i>std. dev.</i>	77		3	0.24
Reid Creek	92	0.2	N/A	0.02
Tyndall	742	BDL	13	0.03
Ice Valley	231	0.0	19	0.01
Vivid Lake Cr.	145	BDL	41	0.02
Oystercatcher	235	BDL	13	0.03
Fingers South	45	BDL	N/A	N/A
Berg Bay So.	94	0.7	23	0.04
Rush Point	467	BDL	22	0.10
<i>mean</i>	256	BDL	22	0.04
<i>std. dev.</i>	237		10	0.03
Carolus River	108	2.1	22	0.01
East Falls Cr.	122	BDL	N/A	0.05
Rink Creek	125	4.5	7	0.04
E. Pleasant Is.	935	40	16	0.04
W. Pleasant Is.	347	BDL	14	0.06
<i>mean</i>	327	BDL	15	0.04
<i>std. dev.</i>	354		6	0.02
Indian R.	BDL	BDL	9	0.10
Taiya R.	15	0.2	3	0.02
Skagway R.	BDL	BDL	2	0.02

### Mercury in Streambed Sediments

Total Hg in streambed sediments (unsieved grab samples) ranged from 2 to 41 ng/g dry weight (mean=15, SD=11; Table 7, Appendix A). The lowest concentrations were in Skagway and Taiya Rivers in KLG0 and in the young GLBA streams (1.7–11.1 ng/g dry wt.). MeHg in streambed sediments was very low, with the highest value in Gull Creek (0.4 ng/g), Rush Point Stream (0.1 ng/g) and the Indian River (0.1 ng/g). MeHg in streambed sediment comprised <1% of the Hg<sub>T</sub>, except for in Gull Creek, where the MeHg fraction was 4% of the total. Bed sediment Hg<sub>T</sub> and MeHg concentrations did not correlate well with any of the other measured parameters and had consistently lower concentrations of Hg than did the finer-grained particulates in the water column.

### **Mercury in Benthic Macroinvertebrates**

Mayflies were the most abundant macroinvertebrate found in all streams and were therefore targeted for sampling (Figure 6). Most streams contained mayflies in the Baetidae and Heptageniidae families. Baetid mayfly taxa included *Baetis bicaudatus* and *B. tricaudatus*; heptageniid mayfly taxa included *Rhithrogena* sp., *Cinygmula* sp., and *Epeorus grandis*, *E. deceptivus*, and *E. longimanus*. Not all taxa were found in every stream, either because the stream lacked suitable habitat or because the taxa had transformed into the adult form prior to our sampling. Stonefly Creek and the two streams on Pleasant Island contained insufficient numbers of baetid mayflies for analysis, and Stonefly, Gull, Reid, Vivid, and Rink Creeks did not contain any or sufficient numbers of heptageniid mayflies.



**Figure 6.** Benthic sampling photographs. Clockwise from top left: a typical benthic sample from which mayflies were obtained; D. Engstrom using the kicknet to collect mayflies in Vivid Stream; the heptageniid mayfly *Rhithrogena*; the baetid mayfly *Baetis*.

Of the two groups of mayflies sampled, the heptageniid mayflies consistently had higher concentrations of  $Hg_T$  (mean 46 ng/g, SD=15) than the baetid mayflies (mean 34 ng/g, SD=15; paired t-test,  $p < 0.001$ ; Table 8). However, the two families had similar mean concentrations of MeHg (23 and 18 ng/g, respectively). The percent of Hg in mayflies that was in the methyl form (%MeHg) varied greatly across the sites (19 to ~100% of  $Hg_T$ ), although %MeHg averaged 50% and 51% for the heptageniid and baetid mayflies, respectively.

**Table 8.** MeHg, Hg<sub>T</sub>, and the percent Hg as MeHg in the two mayfly families, Baetidae and Heptageniidae. GLBA samples are partitioned into Young (<100 years), Medium (100–200 years), and Old (>1000 years) watersheds, and mean and standard deviations are shown for these subgroups as well as for composited samples. NP= Not present; NS= present but not sufficient mass for analysis.

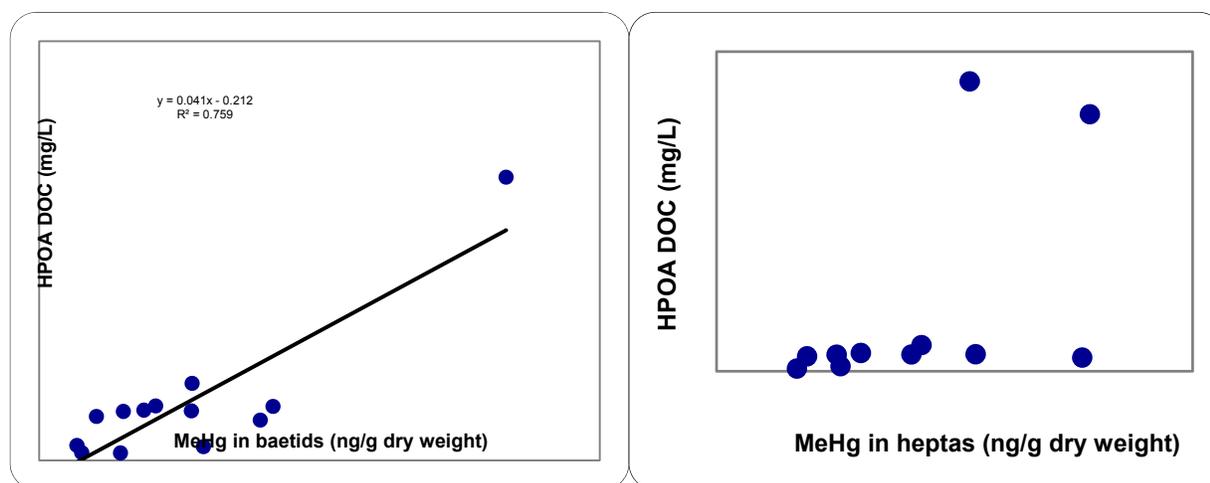
Park/Age Classes	Stream	Baetidae			Heptageniidae		
		MeHg (ng/g)	Hg <sub>T</sub> (ng/g)	% methyl	MeHg (ng/g)	Hg <sub>T</sub> (ng/g)	% methyl
"Young" (GLBA)	Stonefly Creek	NS	NS	NS	NP	NP	NP
	Gull Creek	14.5	22.2	66%	NP	NP	NP
	Nunatak Creek	4.7	12.6	37%	13.0	21.0	62%
	Mean	9.6	17.4	0.5	13.0	21.0	0.6
	Std. Dev.	7.0	6.8	0.2	N/A	N/A	N/A
"Medium" (GLBA)	Reid Creek	20.5	59.3	35%	NS	NS	NS
	Tyndall Stream	13.1	38.4	34%	27.2	67.5	40%
	Ice Valley Stream	5.30	12.37	43%	8.43	17.24	49%
	Vivid	10.1	31.7	32%	NP	NP	NP
	Oystercatcher Stream	29.2	52.5	56%	15.1	50.6	30%
	Fingers South	7.1	19.5	37%	9.5	51.1	19%
	Berg Bay South	10.5	24.9	42%	12.6	28.2	45%
	Rush Point Stream	27.6	36.3	76%	38.4	57.6	67%
	Mean	15.43	34.38	0.44	18.55	45.37	0.42
Std. Dev.	9.20	15.92	0.15	11.83	18.89	0.17	
"Old" (GLBA)	Carolus River	19.1	29.3	65%	21.5	44.8	48%
	East Falls Creek	19.0	36.5	52%	20.5	64.8	32%
	Rink Creek	58.3	51.3	114%	NP	NP	NP
	E. Pleasant Island	NS	NS	NS	26.6	55.2	48%
	W. Pleasant Island	NS	NS	NS	39.2	52.8	74%
	Mean	32.1	39.0	0.8	26.9	54.4	0.5
Std Dev	22.7	11.2	0.3	8.6	8.2	0.2	
SITK and KLGO	Indian River- SITK	16.0	60.4	26%	32.6	44.1	74%
	Taiya River- KLGO	24.5	41.56	59%	28.7	48.2	60%
	Skagway River-KLGO	10.7	21.5	50%	21.2	36.2	58%
All samples	Mean	18.1	34.4	51%	22.5	45.7	50%
	Std. Dev.	13.1	15.5	0.2	10.1	15.2	0.2
	Min	4.7	12.4	26%	8.4	17.2	19%
	Max	58.3	60.4	114%	39.2	67.5	74%

In GLBA, the MeHg concentrations in the baetid mayflies correlated well with numerous parameters that are indicative of the influence of wetlands within the watershed: UVA, SUVA, DOC, HPOA DOC, and mapped % wetland (Table 9). However, this correlation is disproportionately influenced by one outlier from Rink Creek (Figure 7a). MeHg in baetid mayflies also correlates well ( $r=0.742$ ) with MeHg in water (Figure 8). Baetid mayflies from Rink Creek showed the highest MeHg concentrations in the study (58 ng/g dry weight), as well as the largest proportion of Hg in the methyl form, 114% (>100% indicates some error of measurement or heterogeneity in the samples from which the MeHg and Hg<sub>T</sub> analytical subsamples were drawn). However, it is notable that there were insufficient baetid mayflies in the Pleasant Island streams for Hg analyses, although Hg concentrations in water, particulates, and fish tissues were among the highest found. Therefore, any comparisons between the Heptageniidae and Baetidae mayflies do not include these high Hg and DOC end-member streams.

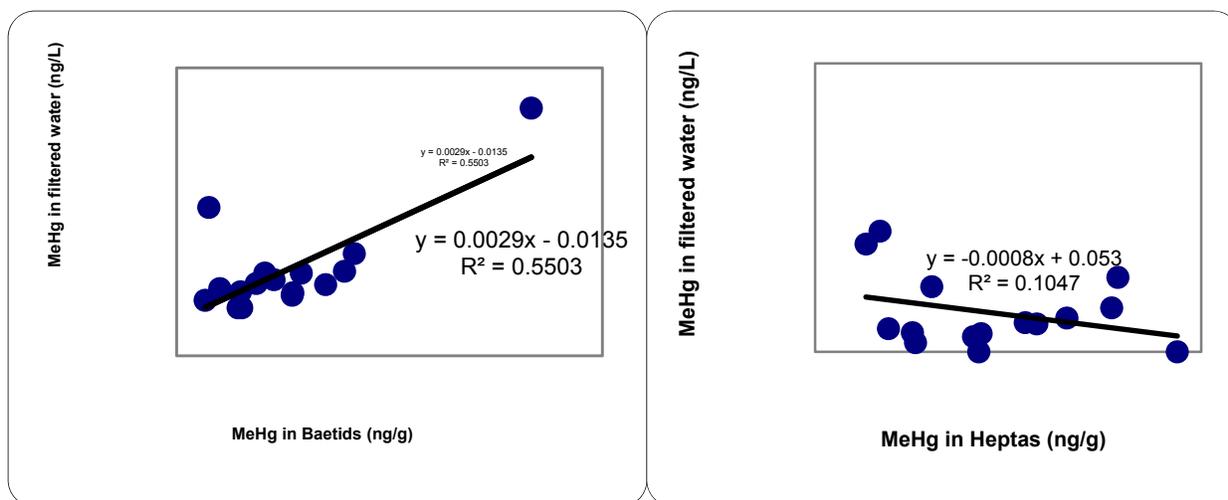
**Table 9.** Pearson's r correlation values for Hg<sub>T</sub> and MeHg in the two mayfly families (Baetidae and Heptageniidae) regressed against parameters which showed significant two-tailed correlations at the 0.01 level(\*\*) or 0.05 level (\*). Only GLBA stream water samples used for UVA, SUVA, and HPOA DOC.

	MeHg - Baetids	Hg <sub>T</sub> - Baetids	MeHg - Heptas	Hg <sub>T</sub> - Heptas
UVA	0.851(**)	0.377	0.522	0.238
SUVA	0.645(*)	0.368	0.474	0.344
HPOA DOC	0.871(**)	0.388	0.537	0.256
DOC (mg/L)	0.821(**)	0.318	0.442	0.277
% Wetland	0.793(**)	0.302	0.445	0.222
% Forest shrub wetland	0.777(**)	0.306	0.472	0.269
Watershed elevation	-0.554(*)	-0.151	-0.666(*)	-0.451
D.O. (% saturation)	-0.716(**)	-0.406	-0.691(**)	-0.210
Sulfate (mg/L)	-0.130	-0.208	-0.615(*)	-0.441
MeHg- streamwater	0.742(**)	0.224	0.052	-0.064
MeHg - Baetids	1.000	0.612(*)	0.614(*)	0.607(*)
Hg <sub>T</sub> - Baetids		1.000	0.655(*)	0.571
MeHg - Heptas			1.000	0.564(*)
Hg <sub>T</sub> - Heptas				1.000

MeHg in the heptageniid mayflies, which unlike the baetid mayflies were found in the Pleasant Island streams but not in Rink Creek, failed to show a strong relationship with wetland factors in the watersheds. Total Hg in both the taxa was also uncorrelated with other measured parameters. However, the two samples from Pleasant Island (which had the highest DOC), did have among the highest MeHg concentrations in heptageniids as well (Figure 7b).



**Figure 7.** Methylmercury concentrations (ng/g dry weight) in (a) Baetidae and (b) Heptageniidae mayflies regressed against HPOA DOC, which is a tracer for wetland influence, in the GLBA streams. Not all streams contained both groups of mayflies. In particular, the two Pleasant Island streams with high HPOA DOC contained sufficient numbers of heptageniid mayflies only.



**Figure 8.** Methylmercury concentrations in (a) Baetidae (ng/g) regressed against MeHg in filtered water samples from all streams (Pearson's  $r=0.742$ ;  $r^2=0.551$ ,  $p<0.001$ ) and (b) Heptageniidae, for which there was no strong correlation.

Grouped into age classes, the concentrations of both  $Hg_T$  and MeHg increase systematically from young to medium to old streams for both baetid and heptageniid mayflies (Table 8). In the baetids, mean MeHg concentrations approximately doubled between each age group: 9.6 ng/g (SD=7.0) in the young streams, 15.4 (SD=9.2) in the medium-aged streams, and 32.1 (SD=22.7) ng/g in the old streams. Mean  $Hg_T$  in the baetids also approximately doubled between age groups (Table 8). In the heptageniids, mean concentration between age groups increased by ~1.5 to 2-fold for both MeHg and  $Hg_T$  (Table 8).

In KLGO and SITK, MeHg and  $Hg_T$  concentrations in both types of mayflies were within the ranges seen at GLBA, generally occurring at concentrations similar to those in the medium-aged and older streams (Table 8).

### **Mercury in Fish**

We found and collected age 0+ coho salmon in all study streams (Figure 9). At three streams (Reid Creek, Berg Bay South, and Rush Point Stream), we also captured age 1+ coho, and at Rush Point Stream we collected a single age 2+ coho salmon. Age estimates were based on body lengths. Mean and standard deviation fork lengths were: 33mm (SD=2mm) for age 0+ coho; 48mm (SD=2mm) for age 1+; and the single age 2+ coho was 73mm long.



**Figure 9.** Age 0+ juvenile coho salmon being prepared for storage in aluminum foil and ice for later POPs analyses. Photo by S. Nagorski.

Age 0+ coho, found in all the streams, contained between 1.7 and 14 ng/g (wet weight)  $Hg_T$  (Table 10). The mean concentration across all sites was 5.9 ng/g (SD=4.0 ng/g). Based on previously published work, we assume that essentially all of the Hg found in fish tissues is in the form of MeHg (Bloom 1992).

Regression analysis yielded no good fits for fish  $Hg_T$  concentrations against other measured variables. However, average concentrations of  $Hg_T$  in fish tissues from the three watershed age strata (young, medium and old) do indicate an increase in fish Hg concentration with increasing watershed age group (Table 10). Mean values for the young, medium, and old groups were 4.2 ng/g (SD=0.9), 5.4 ng/g (SD=4.1), and 9.1 ng/g (SD=4.6), respectively.

The  $Hg_T$  concentrations in the three young GLBA streams were very similar (5.2, 4.2, and 3.3 ng/g). All but two of the medium-aged streams had  $Hg_T$  concentrations between 2.8 and 5.1 ng/g; the two outliers were Berg Bay South (8.9 ng/g) and Reid Creek (14.1 ng/g). The old watersheds exhibited a similarly large range in concentrations, from 3.5 to 13.9 ng/g. The Taiya River coho had the lowest measured  $Hg_T$  (1.7 ng/g), and the adjacent Skagway River also had a relatively low value (3.1 ng/g). The Indian River coho  $Hg_T$  level measured at 6.0 ng/g  $Hg_T$ , which is close to the average value for all the samples in the study.

The limited data on older coho fry indicate bioaccumulation taking place within the fish. Average Hg concentration in the age 1+ coho was one order of magnitude higher than in age 0+ coho (61 ng/g versus 5.9 ng/g). In Rush Point stream,  $Hg_T$  concentrations increased 24-fold from age 0 to 1, but only 15-fold from age 0 to 2 (based on the one age 2+ individual fish sample; Table 10).

**Table 10.** Total Hg (ng/g wet weight) in coho salmon tissue samples from GLBA, SITK, and KLGO. Most coho collected were young-of-the year (“age 0+”). Age 1+ coho were collected at three streams, and one age 2+ coho was collected in Rush Point Stream. The number of individuals collected and composited into a single sample at each stream is listed for each age group. Also shown are results from other studies.

Park/Age Classes	Stream	Age 0 Coho		Age 1 Coho		Age 2 Coho	
		<i>n</i>	Hg <sub>T</sub> (ng/g)	<i>n</i>	Hg <sub>T</sub> (ng/g)	<i>n</i>	Hg <sub>T</sub> (ng/g)
"Young" (GLBA)	Stonefly Creek	5	5.2				
	Gull Creek	15	4.2				
	Nunatak Creek	3	3.3				
	Mean		4.2				
	Std. Dev		0.9				
"Medium" (GLBA)	Reid Creek	5	14.1	3	70		
	Tyndall Stream	6	3.1				
	Ice Valley Stream	5	2.8				
	Vivid	8	3.4				
	Oystercatcher Stream	6	5.1				
	Fingers South	2	2.5				
	Berg Bay South	4	8.9	2	30.8		
	Rush Point Stream	11	3.4	1	80.6	1	49.2
	Mean		5.4				
	Std. Dev		4.1				
"Old" (GLBA)	Carolus River	3	13.4				
	East Falls Creek	4	3.5				
	Rink Creek	5	9.2				
	E. Pleasant Island	1	13.9				
	W. Pleasant Island	5	5.6				
	Mean		9.1				
	Std. Dev		4.6				
SITK and KLGO	Indian River- SITK	10	6.0				
	Taiya River- KLGO	8	1.7				
	Skagway River-KLGO	5	3.1				
All samples	MEAN		5.9		60.5		49.2
	STDEV		4.0		26		
	MIN		1.7		30.8		
	MAX		14.1		80.6		
<u>Other studies</u>							
Location	Reference		Hg (ng/g)	Fish species		Age	
Juneau-McGinnis Cr.	Nagorski, unpublished data		8.9	Coho		Juvenile- Age 0+	
Juneau- Fish Cr.	Nagorski, unpublished data		73	Coho		Juvenile- Age 0+	
Juneau- Peterson Cr.	Nagorski, unpublished data		34	Coho		Juvenile- Age 0+	
Innoko NWR, AK	Mueller and Matz 2002		40	Coho		Juvenile	
Kuskokwim area, AK	Gray et al. 1996		70	Coho		Juvenile	
Illinois Cr., AK	Winters 1996		12-28*	Coho		Juvenile- Age 0+ and 1+	
Voyageurs NP, MN	Wiener et al. 2006		36-190*	Yellow perch		Juvenile- Age 1	
Columbia River, OR	Webb et al. 2006		34 ± 3	Sturgeon		Juvenile	
Cook Inlet region, AK	Frenzel 2000		16-42*	Slimy sculpin		Adults	
Throughout Alaska	ADEC 2007		37	Coho		Adults	

\* Originally reported as dry weight and converted to wet weight assuming 20% solids

### **Persistent Organic Pollutants in Fish**

Of the 77 compounds analyzed in the juvenile coho samples, most were below quantification limits, notably both current-use pesticides (endosulfan I and lindane) and all HCHs, PBDEs, aldrin, and mirex (Table 11 and Appendix B). Yet, quantifiable HCB, chlordanes, dieldrins, several congeners of PCBs, DDE, and DDT were found in at least some samples. HCBs and  $\Sigma$ CHLs were above detection in about half of the streams.  $\Sigma$ DDTs (largely in the form of p,p'DDE) were detectable in all streams except for Pleasant Island East. PCBs were also detectable in fish from all streams but one (Reid Creek). Notably, the Skagway River sample (composed of five composited individuals) contained the highest levels of HCBs,  $\Sigma$ CHLs,  $\Sigma$ DDTs, the second highest concentrations of  $\Sigma$ PCBs, and together with the nearby Taiya River, the only quantifiable dieldrin. The Indian River (SITK) (composed of 12 composited individuals) had the highest  $\Sigma$ PCBs—nearly double that of the Skagway River and 3–8 times levels found in GLBA streams. Of streams in GLBA, Gull Creek and Tyndall Stream had the highest  $\Sigma$ CHLs and  $\Sigma$ DDTs. Gull Creek was also the only stream in GLBA with detectable  $\alpha$ -chlordane (at 0.26 ng/g, which is barely above the limit of quantification), as well as o,p'DDT and p,p'DDD (breakdown products of DDT).

**Table 11.** Summed concentrations (ng/g, wet weight) of various groups of POPs in the juvenile coho salmon samples (based on whole fish) from this and other Pacific Northwest studies that included POPs analyses of juvenile coho. Also shown are results of the SEAN intertidal mussel survey. LOQ= Limit of quantification. DL= Detection limit. The full dataset of all POPs analyzed is given in Appendix B.

	Stream	Location	Sample Size	% lipid	HCb	∑HCHs	∑CHLDs	∑DDTs	PCBs ∑ 40 CBs	∑BDEs	dieldrin	aldrin	mirex
This study (young of the year coho captured in native streams)	Stonefly Creek	GLBA	n=5	1.20%	<LOQ	<LOQ	<LOQ	1.2	1.7	<LOQ	<LOQ	<LOQ	<LOQ
	Gull Creek	GLBA	n=10	1.40%	0.62	<LOQ	0.6	2.1	3.2	<LOQ	<LOQ	<LOQ	<LOQ
	Nunatak Creek	GLBA	n=4	1.30%	0.29	<LOQ	<LOQ	0.7	1.1	<LOQ	<LOQ	<LOQ	<LOQ
	Reid Creek	GLBA	n=5	0.90%	<LOQ	<LOQ	<LOQ	0.92	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Tyndall Stream	GLBA	n=6	1.30%	0.58	<LOQ	0.45	2.4	3.1	<LOQ	<LOQ	<LOQ	<LOQ
	IceValley Stream	GLBA	n=5	1.10%	<LOQ	<LOQ	<LOQ	0.94	2.7	<LOQ	<LOQ	<LOQ	<LOQ
	Vivid Stream	GLBA	n=7	1.60%	0.43	<LOQ	<LOQ	0.87	1.1	<LOQ	<LOQ	<LOQ	<LOQ
	Oystercatcher	GLBA	n=4	1.20%	<LOQ	<LOQ	0.25	1.1	2.1	<LOQ	<LOQ	<LOQ	<LOQ
	Fingers South	GLBA	n=3	1.40%	<LOQ	<LOQ	<LOQ	0.9	3.8	<LOQ	<LOQ	<LOQ	<LOQ
	Berg Bay South	GLBA	n=4	1.10%	<LOQ	<LOQ	<LOQ	1.1	1.6	<LOQ	<LOQ	<LOQ	<LOQ
	Rush Point Stream	GLBA	n=1	1.60%	0.35	<LOQ	0.21	0.91	1.9	<LOQ	<LOQ	<LOQ	<LOQ
	Carolus River	GLBA	n=3	1.40%	<LOQ	<LOQ	<LOQ	0.51	0.37	<LOQ	<LOQ	<LOQ	<LOQ
	East Falls Creek	GLBA	n=4	1.40%	0.53	<LOQ	<LOQ	1.4	0.99	<LOQ	<LOQ	<LOQ	<LOQ
	Rink Creek	GLBA	n=5	1.20%	0.29	<LOQ	0.22	0.86	2.3	<LOQ	<LOQ	<LOQ	<LOQ
	Pleasant Island East	adj. to GLBA	n=1	0.50%	<LOQ	<LOQ	<LOQ	<LOQ	0.92	<LOQ	<LOQ	<LOQ	<LOQ
	Pleasant Island West	adj. to GLBA	n=7	0.90%	0.26	<LOQ	0.2	1.4	2.1	<LOQ	<LOQ	<LOQ	<LOQ
	Indian River	SITK	n=12	0.70%	<LOQ	<LOQ	<LOQ	1.3	8.2	<LOQ	<LOQ	<LOQ	<LOQ
	Indian River dup	SITK	n=12	0.90%	<LOQ	<LOQ	<LOQ	1.4	8.9	<LOQ	<LOQ	<LOQ	<LOQ
	Taiya River	KLGO	n=8	1.50%	0.71	<LOQ	0.54	1.4	2.9	<LOQ	0.23	<LOQ	<LOQ
Skagway River	DS of KLGO	n=5	1.40%	0.89	<LOQ	1.9	3.8	4.1	<LOQ	0.21	<LOQ	<LOQ	
Johnson et al. 2005 (Estuarine coho, yearlings)	Alesea Bay, OR		n=3	1.2 ±0.1%	0.20	N/A	0.17	1.4	5.9	N/A	2.5	<DL	<DL
	Coos Bay, OR		n=1	1.2 ±0.1%	0.16	N/A	0.2	1.8	14	N/A	3.3	<DL	0.64
	Grays Harbor, WA		n=1	1.2 ±0.1%	0.13	N/A	0.35	3.4	27	N/A	<DL	<DL	<DL
	Willapa Bay, WA		n=1	1.2 ±0.1%	0.13	N/A	0.44	0.9	6.4	N/A	<DL	<DL	<DL
	Yaquina Bay, OR		n=3	1.2 ±0.1%	0.09	N/A	0.1	1.7	11	N/A	<DL	<DL	<DL
Olson et al. 2008 (Estuarine coho, yearlings)	Commencement Bay, WA		n=6	4.40%	0.63	N/A	N/A	4.2	6.7	N/A	N/A	N/A	N/A
Tallmon, unpubl. data (Intertidal mussels)	GLBA avg.	GLBA	47 sites	N/A	<LOQ	<LOQ	<LOQ	<LOQ	1.0	<LOQ	<LOQ	<LOQ	<LOQ
	SITK avg. (exclude harbor)	SITK	2 sites	N/A	<LOQ	<LOQ	<LOQ	0.82	9.1	<LOQ	<LOQ	<LOQ	<LOQ
	KLGO avg.	KLGO	1 site	N/A	<LOQ	<LOQ	<LOQ	0.17	1.9	<LOQ	<LOQ	<LOQ	<LOQ

## Physical Parameters and Stream Water Chemistry

### ***Streamflow***

At the time of sampling (late June/early July), most streams were still experiencing some amount of snowmelt runoff. The previous winter brought an extraordinary amount of snowfall to the region, with a record-breaking 197 inches of snow at sea level in Juneau (NOAA 2008). This led to a late and sustained snowmelt period in regional streams, especially in high elevation watersheds. None of the GLBA streams targeted in this study are continuously gaged, and so it is unknown exactly where this study's sampling events fell on each stream's annual hydrograph. Considering the varying elevations, watershed sizes, glacier/snowfield coverage, and climatic influences among the watersheds, we assume that the streams were sampled during disparate stages of their annual hydrograph patterns, although generally within the peak snowmelt season. Discharge in the GLBA-area streams ranged from 0.5 cfs (14 L/s) in West Pleasant Island Stream to 217 cfs (6145 L/s) in Reid Creek. Discharge in the Indian River in SITK was 70 cfs, while the Taiya River was by far the largest, at 3490 cfs (98,825 L/s), which was approximately an average value for the river's summer runoff (Taiya River gage data is available from <http://waterdata.usgs.gov/ak/nwis/>, gage #15056210). The Skagway River was ungaged but visually estimated to be roughly the same size as the Taiya River at the time of sampling. See appendix A for specific values of stream physical characteristics.

### ***pH, Dissolved Oxygen, Specific Conductance, and Temperature***

Stream pH averaged 7.5 units and ranged from 6.5 at East Pleasant Island Stream to 8.3 at Gull Creek (Appendix A). The younger streams had a higher mean pH (8.07, SD=0.21) than the medium-aged streams (mean=7.70, SD=0.33), which in turn were higher than the old streams (mean=7.40, SD=0.54; Table ). All streams were well-oxygenated--dissolved oxygen concentrations varied between 11.1 and 15.3 mg/L, or 99 to 118% saturation (Table 12, Appendix A). Specific conductance averaged 0.11  $\mu\text{S}/\text{cm}$  (SD=0.07), with the highest measurement (0.30  $\mu\text{S}/\text{cm}$ ) occurring in Rink Creek. The lowest values (0.03–0.04  $\mu\text{S}/\text{cm}$ ) were from the two large glacial rivers (Taiya and Skagway Rivers) and the two small streams on Pleasant Island. The Pleasant Island streams were also particularly low in acid neutralizing capacity. Streams with the highest temperatures (between 10 and 13°C) were Stonefly and Gull Creeks (both fed by major lakes), Rink Creek (apparently devoid of snowmelt contributions) and the two streams on Pleasant Island (low elevation and lake and/or bog-fed with no apparent snowmelt contributions).

### ***Turbidity and Total Suspended Solids***

Turbidity values ranged from 0.5 to 58 NTUs, and half the samples had values of <2 NTUs (Appendix A). The highest turbidity measurement (58 NTU) came from Stonefly Creek, a young, heavily glacier-fed stream in Wachusett Inlet in GLBA. Other relatively high values were from Reid Creek (34 NTU), which is no longer glaciated but is in the upper Bay and at the time of sampling was heavily snowmelt-dominated, and the two glaciated KLGO rivers. Turbidity and total suspended solids (TSS) were well correlated (Pearson's  $r=0.878$ ). TSS values (ranging from below detection to 40 mg/L) were highest in the same streams with relatively high turbidity values. The Indian River in SITK had the lowest TSS and turbidity of all the streams sampled.

### **Nutrients**

Ammonium ( $\text{NH}_4^+$ ) concentrations were all very low, between 6–13  $\mu\text{g/L}$  for the Indian River (SITK), Skagway and Taiya Rivers (KLG0), and four of the GLBA streams (Gull, Fingers South, Berg Bay South, and Carolus River). Rink Creek (GLBA) had a higher value, 35  $\mu\text{g}$ . All other streams had either trace (unquantified) or undetectable concentrations of this ion, which can occur in streams due to direct anthropogenic pollution inputs and/or due to the presence of decaying fish carcasses. Nitrate ( $\text{NO}_3^-$ ), present in all streams, averaged 0.15 mg/L ( $\sigma=0.08$ ) in the young GLBA streams (<100 years old), increased to 0.38 (SD=0.25) in the medium-aged streams (100–200 years old), and dropped to an average of 0.09 ( $\sigma=0.04$ ) mg/L in the old streams (>1000 years old). Nitrate levels in the SITK and KLG0 rivers were between 0.17–0.24 mg/L. See appendix A for specific values for stream nutrient concentrations.

### **Major Ions**

Sulfate ( $\text{SO}_4^{2-}$ ) showed a declining trend with watershed age, from 12.2 mg/L (young) to 5.8 mg/L (medium) and 2.9 mg/L (old) average concentrations. Dissolved Ca, Mg, and Si show a pattern of declining concentration with watershed age, whereas Cl concentrations increase with watershed age. Potassium and Na showed no specific age-related trend due to high scatter of data values within each age group.

**Table 12.** Mean and standard deviation of physical and chemical parameters measured in GLBA streams, as grouped into the three age categories (green= young; blue=medium; red=old), and the SITK and KLGO streams. Parameters with many or all nondetectable values and/or with strong outliers not included. BDL= below detection limit.

Parameter	Units	Glacier Bay NPP streams by age groups						Sitka NHP	Klondike NHP	
		Young		Medium		Old		Indian R.	Taiya R	Skagway R
		Mean	Std.Dev.	Mean	Std.Dev.	Mean	Std.Dev.			
Q	(cfs)	70	72	106	64	26	38	70	3490	N/A
pH		8.07	0.21	7.70	0.33	7.40	0.54	7.45	6.81	6.76
DO (%)	% saturation	115.5	2.8	114.4	1.6	107.9	6.2	109	108	110
DO (mg/L)	mg/L	12.93	0.67	14.56	0.51	12.37	1.46	13.0	14.0	13.4
Turbidity	NTU	20.64	32.08	9.14	11.23	2.46	2.18	0.5	29	22
TSS	mg/L	10.65	16.27	10.25	14.45	0.96	0.78	0	34.7	24.3
Sp Cond	uS/cm	0.139	0.007	0.116	0.044	0.126	0.109	0.05	0.03	0.03
Temperature	°C	10.38	3.22	5.17	1.28	9.57	3.12	7.9	4.48	6.91
ANC	uEQ/L	859	60	847	298	858	542	263	248	260
DOC	mg/L	0.9	0.5	0.9	0.4	6.1	5.1	1.5	0.8	1.2
UVA	254nm	0.020	0.016	0.016	0.008	0.276	0.275	N/A	N/A	N/A
SUVA	254nm	2.10	1.39	1.79	0.55	3.52	1.57	N/A	N/A	N/A
%HPOC	%	35.67	4.51	32.88	11.28	55.40	11.63	N/A	N/A	N/A
HPOC DOC	mg/L	0.32	0.19	0.32	0.19	3.86	3.62	N/A	N/A	N/A
NH4+	mg/L	0.002	0.004	0.002	0.003	0.007	0.014	0.009	0.013	0.010
Ca++	mg/L	24.36	2.26	20.15	7.32	18.03	11.38	5.16	4.45	4.77
Mg++	mg/L	1.00	0.23	1.34	0.84	1.92	1.18	0.52	0.60	0.64
Na+	mg/L	1.52	0.99	0.90	0.26	2.41	1.24	1.75	0.48	0.48
K+	mg/L	0.36	0.13	0.51	0.24	0.42	0.49	N/A	N/A	N/A
Cl-	mg/L	0.41	0.04	0.95	0.43	1.80	2.16	2.68	0.43	0.32
NO3-	mg/L	0.15	0.08	0.38	0.25	0.09	0.04	0.24	0.21	0.17
SO4=	mg/L	12.23	7.80	5.82	3.21	2.87	1.75	1.79	1.54	2.20
Si	mg/L	2.06	0.21	1.55	0.66	1.64	0.78	N/A	N/A	N/A
Filtered MeHg	ng/L	BDL	0.00	0.04	0.03	0.07	0.07	0.02	0.02	0.02
Filtered Hg <sub>T</sub>	ng/L	0.31	0.21	0.61	0.36	1.49	1.36	0.27	0.35	0.37
% Hg as Methyl	%	0%	0%	1%	3%	4%	8%	7%	6%	5%
Particulate Hg <sub>T</sub>	ng/L water	0.45	0.45	0.92	1.24	0.16	0.06	0.05	0.53	N/A
Particulate Hg <sub>T</sub>	ng/g dry wgt	116	77	256	237	297	325	BDL	15	N/A
Bed sediment Hg <sub>T</sub>	ng/g dry wgt	7.5	3.2	21.9	10.3	34.2	43.7	9.3	3.0	1.7

## Discussion

### Relationship of Mercury to Landscape Characteristics

Stratification of the study streams by age group (young, <100 years; medium, 100–200 years; and old, >1000 years) reveals that Hg concentrations in GLBA streams systematically increase with watershed age. Hg increased from the young to medium to old groups for filtered water ( $Hg_T$  and MeHg), streamwater particulates ( $Hg_T$ ), both groups of mayflies ( $Hg_T$  and MeHg), and the juvenile coho salmon. Although these evaluations by age group do not allow for formal statistical comparisons (e.g., ANOVA tests) among age groups due to the low number of watersheds per group (3–8), the patterns are consistent and compelling. This is especially so, given that each stream was sampled only once and that such spot sampling likely subsumes a great deal of hydrological and biological variability.

Our results show that in GLBA, landscapes across a chronosequence of deglaciation vary in their sensitivity to Hg contamination in a largely predictable manner. Young watersheds, with thin, well-drained soils, exposed bedrock, and shifting, dynamic stream channels have little ability to convert inorganic Hg to its more toxic methyl form that easily bioaccumulates in organisms. MeHg was extremely low in water samples from the youngest watersheds, and its concentration was relatively low in the particulates, mayflies, and juvenile fish. Conversion of inorganic Hg to MeHg depends greatly on the prevalence of organic-rich peatlands, which support sulfate-reducing bacteria that methylate Hg (Benoit et al. 1999, Ullrich et al. 2001, King et al. 2002). Peatlands also provide an abundance of dissolved organic carbon, which stimulates microbial Hg methylation and provides binding sites for MeHg and transports it downstream through riparian systems (Driscoll et al. 1998, Kolka et al. 1999). Therefore, peatland-rich watersheds typically act as net sources of MeHg to streams (St. Louis et al. 1994, Wiener et al. 2006). In contrast to peatland-dominated areas, forested uplands have been repeatedly shown to behave as net sinks of atmospherically-derived Hg, binding the metal in soils, rocks, and plant material (St. Louis et al. 1996).

In our study, the concentration of  $Hg_T$  in water was positively correlated with the mapped percent of the watershed covered by wetlands ( $r=0.85$ ), which in turn are more common in older watersheds. A better correlation ( $r=0.95$ ) is found between total Hg and the concentration of dissolved organic carbon (specifically, the hydrophobic fraction, which increases with runoff from wetlands). MeHg concentrations in resident mayflies and juvenile coho, which integrate the contaminant over much longer time periods, was higher in the older watersheds with substantial peatland coverage. This result is similar to the findings of Chasar et al. (2009), who showed strong relationships between MeHg concentrations in stream biota (invertebrates and fish) and watershed wetland cover for a variety of streams in the US. Additionally, the good correlation between MeHg in streamwater and in baetid mayflies in our study indicates that the biotic uptake of MeHg is tied to streamwater concentrations. The landscape fingerprint on the MeHg concentrations in fish occurs even though some baseline level of the MeHg in the fish was likely contributed by marine-derived Hg in the yolk sacs from which the fish emerged.

Comparison of the Hg in the streamwater samples to the average concentration of Hg arriving via wet deposition (based on a two year study in Bartlett Cove, from 2003-2005 (Fitzgerald et al. 2007) shows that Hg concentrations in the young and medium age watersheds is roughly 20-25% of the average value of incoming atmospheric deposition (2.6 ng/L), indicating net uptake of Hg

in the watershed. The older streams, however, approached or exceeded this concentration, at least during our single-event sampling effort, and contained up to 21% of the Hg as MeHg. This implies that in the older watersheds with developed peatlands, a much larger proportion of the deposited Hg is eventually released via streamwaters and that a fraction of it is converted to MeHg. It is important to note that the Hg exported in streams is almost certainly not derived from contemporary deposition, but rather from the large pool of previously deposited Hg in catchment soils. Additionally, without measurements of Hg inputs via dry deposition, Hg volatilization, and evaporative losses of water, we cannot quantify how much of the deposited Hg is exported in streamflow. Yet, because it is known that atmospherically-derived Hg contains only a trace amount of MeHg (St. Louis et al. 1995), the MeHg found in the streams has to have been produced while routed through the watershed. It is also possible that a portion of the MeHg was imported into the watershed via biovectors such as fish and birds, although many of our streams do not support large salmon runs and none was known to immediately precede our sampling event.

### **Mercury Concentrations in Comparisons with Health Standards**

Concentrations of Hg in streamwater were by 3–4 orders of magnitude below EPA levels of concern for human health or for aquatic organisms. The USEPA freshwater acute and chronic limits for total Hg in freshwater are set at 1400 and 770 ng/L, respectively (USEPA 2001). Numerous criteria are available for recommended exposure limits of Hg to aquatic organisms, birds, and mammals and are discussed in length in Eisler (2006). According to the USEPA's National Fish Tissue Survey, the Lowest Adverse Effect Concentration in prey fish should not exceed 100 ng/g (wet weight) for the protection of piscivorous birds and mammals that consume them (Eisler 2000). The age 0+ juvenile coho samples in this study easily met these standards, not exceeding 14 ng/g. However, samples of age 1+ coho (collected in three GLBA streams) were as high as 80 ng/g, closely approaching the 100 ng/g criterion.

Streambed sediment concentrations of Hg were all below the national median value of 60 ng/g (dry weight), which is based on all NAWQA study units (Gilliom et al. 1998). Concentrations in the SEAN study streams were also lower than all but 1 of 14 streams sampled throughout NAWQA's Cook Inlet region of study (Frenzel 2000). Streambed sediment concentrations of Hg were also well below the "interim freshwater sediment quality guideline" (the concentration below which adverse effects to aquatic organisms are expected to occur rarely; 0.17 mg/kg) and the "probable effect level" (the concentration above which adverse effects are expected to occur frequently; 0.486 mg/kg) established by the Canadian government for all streams sampled in this study (Canadian Council of Ministers for the Environment 1999). The USEPA does not provide streambed sediment criteria for heavy metals.

### **Mercury in SEAN Biota as Compared to Other Regions**

#### ***Mayflies***

Mercury concentrations in mayflies in this study were generally low or comparable to levels found in BMI from other studies, and much lower than levels in BMI from streams near sources of industrial Hg pollution. Concentrations in mayflies from our study fell on the low end of the spectrum of Hg in invertebrates from the contiguous US, as based on a recently published data set where Hg concentrations in freshwater invertebrates from streams in Oregon, Wisconsin, and Florida were between 5–183 ng/g dry weight (Chasar et al. 2009). Total Hg concentrations in

BMI from Sherman Creek, near the Kensington Mine north of Juneau, ranged from 40 to 60 ng/g in composite samples of mayflies, stoneflies, and caddisflies (i.e., EPT taxa; Aquatic Science 2001). Function Feeding Groups in these samples included scrapers, shredders, and predators. A study of Hg in EPT taxa from headwater streams draining historical mining areas in the upper Willamette River, Oregon found mean Hg<sub>T</sub> and MeHg concentrations in two subcatchments ranging from 48 to 198 ng/g and 21 to 112 ng/g, respectively (Henny et al. 2005). In contrast, Hg<sub>T</sub> and MeHg from a reference site averaged 19 and 13 ng/g, respectively, which is about one-half of the average values from our study sites. A study in Slovenia measured Hg concentrations in mayflies from a pristine and Hg-polluted river (Zizek et al. 2007). Total Hg and MeHg concentrations were 86 and 60 ng/g in the pristine river and 29,800 and 687 ng/g in the polluted river, respectively. Hg concentrations in a heptageniid mayfly from 9 lakes near metal smelters in Ontario ranged from 50 to 419 ng/g Hg<sub>T</sub> and from 15 to 48 ng/g MeHg (Belzile et al. 2005).

In this study, Hg levels were greater in heptageniid mayflies than in baetid mayflies, a trend also observed in four streams in western Maryland (Castro et al. 2007). Of 11 BMI taxa from the Maryland streams analyzed for Hg, the highest concentrations were found in heptageniid mayflies (50–200 ng/g Hg<sub>T</sub>). Total Hg concentrations in the other taxa, represented by shredder, filtering-collector, predator, and omnivore FFGs, were less than 75 ng/g. In New Brunswick (Canada), MeHg concentrations were greater in heptageniid mayflies (105 ng/g) than in baetid mayflies (77 ng/g; T. Jardine, Aquatic Ecologist, pers. comm., 2009).

### **Juvenile Coho**

Juvenile coho tissue samples from this study may be directly compared with contemporaneous collections of the same species and age class of fish collected from 3 streams near Juneau (UAS, S. Nagorski, unpublished data). Juvenile coho (n=10 individuals, composited into single samples) were collected from McGinnis, Fish, and Peterson Creeks, and Hg<sub>T</sub> concentrations were 9, 34, and 73 ng/g (wet weight), respectively (Table 10). Hg concentrations in the fish increased with increasing peatland coverage in the three watersheds—McGinnis, Fish, and Peterson Creeks contain approximately 8, 30, and 60% wetlands, respectively. The forested, snowfield-dominated McGinnis Creek sample was similar to values of fish in most of the older GLBA streams, although the Fish and Peterson Creek samples were many-fold higher than the average value of 6 ng/g in SEAN streams. Fish and Peterson Creeks are unlike streams in SEAN in that they drain mature watersheds with extensive areas of thick, organic, low-lying peatlands and also support runs of wild and hatchery salmon that were spawning during the time of collection—factors that likely explain their higher MeHg signature in resident juvenile fish.

Juvenile coho salmon Hg concentrations are also reported for the Innoko National Wildlife Refuge (Mueller and Matz 2002) and from Hg-mining areas in the Kuskokwim River region in western Alaska (Gray et al. 1996), where values were 3–20 times higher than the Hg concentrations in our samples; however, it is not clear if the juveniles in those studies were also young-of-the-year (Table 10). Another report on young-of-the-year (age 0+) and age 1+ coho salmon for Illinois Creek (mine site near Fairbanks) shows levels very similar to those in our study. We are unaware of other studies with reports of Hg concentrations in young-of-the-year coho salmon, although numerous studies are available for other species or for adult salmonids and other fishes. For example, in a study in Voyageurs National Park in Minnesota, 1-year old yellow perch (*Perca flavescens*) had concentrations of 182–942 ng/g (dry weight, which is approximately 36–190 ng/g wet weight assuming 20% dry mass). The lower end of this range is

similar to the concentrations in the age 1+ juvenile coho in our study (Wiener et al. 2006). Concentrations of Hg in juvenile sturgeon in the Columbia River (Webb et al. 2006) were in-between mean values for the age 0+ and age 1+ coho in our study. Although not juveniles, adult whole slimy sculpin, which are relatively small fish (~10cm in length), from the Cook Inlet region of Alaska had similar concentrations of Hg (80–210 ng/g dry weight, 16–42 ng/g wet weight; Frenzel 2000) as the juvenile coho in our study (Table 10).

Comparing the Hg in the juvenile coho to adults, whose mean concentration is 37 ng/g Hg (ADEC 2007) shows that Hg concentrations in adults, which undergo most of their growth in the open ocean, are six-fold higher than the mean concentrations in young-of-the-year juveniles from our study streams. However, the three age 1+ samples and the single age 2+ sample had Hg concentrations that are approximately twice as high as those in adults. This suggests that bioaccumulation is rapid and perhaps greatest during the freshwater rearing stage, and that a shift in diet and availability of Hg for uptake in the ocean accounts for the difference in body burdens between fry and adults.

### **Persistent Organic Pollutants in Fish**

Although no current-use pesticides were detected in SEAN juvenile coho, the presence of numerous forms of historic-use POPs points to the high stability of these compounds in the environment. Most of the detected compounds have been banned for over 30 years, but they and some of their breakdown products continue to pollute organisms in remote areas such as in southeast Alaska. A portion of the POPs load in the fish may have been acquired in the ocean by the maternal adults and passed on to her eggs and fry, but spatial differences among watersheds indicates at least partial acquisition of the pollutants in the salmonids' native streams. For example, only the Skagway and Taiya Rivers contained detectable dieldrin, and the Indian River had much higher  $\Sigma$ PCBs than all other rivers studied. A study on murre eggs throughout Alaska also found the Sitka area (on St. Lazaria Island) had the highest  $\Sigma$ PCBs of all sites in that study (Kucklick et al. 2002, Vander Pol et al. 2004). Additionally, a concurrent survey of POPs in intertidal mussels in and near SEAN parks showed that the Sitka area had the highest  $\Sigma$ PCBs of all sites measured (UAS, D. Tallmon, personal communication, 2009), providing two other lines evidence that the area may be at a disproportionately high receiving end of atmospheric deposition of this pollutant.

Even in GLBA itself, POPs occurrence was heterogeneous among watersheds. Most notably, coho from Gull Creek had three POPs compounds (a-chlordane, o,p' DDT, and p,p' DDD) not detected in any other streams, and together with Tyndall Stream, had the highest  $\Sigma$ CHLDs and  $\Sigma$ DDTs. Gull Creek was noted to be particularly biologically productive, with abundant juvenile coho and a strikingly high density of baetid mayfly larvae (heptageniids were not found, but they may have already emerged into their adult winged forms). An earlier study in GLBA by Milner et al. (2000) likewise found Gull Creek to have the highest relative mean density of meiofaunal and macroinvertebrate taxonomic groups in their study of 16 streams. During our visit to the stream, the riparian area was thickly vegetated with alder, the water was clear (turbidity = 1.3 NTU), and the course-grained streambed near the outlet hosted abundant filamentous green algae. Gull Creek also contained the highest MeHg concentrations in streambed sediments in our study streams, at 0.4 ng/g, comprising 4% of the  $Hg_T$ .



**Figure 10.** Gull Creek with the thick, overhanging alder and willow, high water clarity, and the rich green algal growth on the cobble-bed stream bottom. Photo by S. Nagorski.

Additionally, Milner et al. (2000) found that juvenile coho samples collected from Gull Creek (in 1997) were exceptionally enriched in  $\delta^{15}\text{N}$ , pointing to a relatively high amount of marine-derived nitrogen in the streams' food web. Taken together these results may indicate that the POPs found in the juvenile coho as part of this study (and the relatively high MeHg in streambed sediments) were originally derived from carcasses of spawning salmonids in this biologically productive watershed.

Although some forms of POPs were found in each of the juvenile coho samples, most concentrations were relatively low compared with many other regions and all fall well below (1–3 orders of magnitude) criteria recommended for the protection of piscivorous wildlife (Newell et al. 2000). Below we discuss comparisons of values found in this study with those in others.

#### **Comparison with SEAN Mussel Survey**

Intertidal mussels (*Mytilus* sp.) from GLBA, SITK, and KLGO were sampled during the same summer as the freshwater samples collected for this study (UAS, D. Tallmon, pers. comm., 2009). Preliminary analysis shows that mussel tissues were below

detection for most POPs analyzed (UAS, D. Tallmon, unpublished data; Table 11). However, several similarities were found in the occurrence of contaminants in the freshwater juvenile coho and intertidal mussels. First, both current-use pesticides (lindane and endosulfan) were below detection in all fish and mussel samples from all sites. PBDEs flame retardants were also undetectable in both studies (with the exception of the Skagway and Sitka Harbors and one hit on the outer coast of GLBA for the mussels). Second, samples from SITK had the highest  $\sum\text{PCBs}$  compared to the other parks for both fish and mussels. In addition, the mussels and fish tissues had the same specific congeners of PCBs detectable (about  $\frac{1}{4}$  of the 45 analyzed), although the fish samples had several additional congeners above detection compared to the mussels. This implies that either those congeners are generally more common or that they are preferentially transported to southeast Alaska compared with other forms of PCBs. Another similarity was that the majority of DDT found in both surveys was in the form of p,p'DDE. However, while DDTs were detected in all but one of the freshwater sample sites, no form of DDT was found in any of the GLBA mussels. This suggests different sources or transport mechanisms for the contaminant that regulate its occurrence within watersheds but not in the intertidal zone. Similarly, dieldrin was detected in the KLGO fish samples but not in KLGO-area mussels, again suggesting different sources and/or transport vectors of the pollutant. Another difference was that HCB and

chlordanes were found in approximately half of the fish samples, but in none of the mussels. One final comparative note is that not only were many of the same POPs found in both fish and mussels but their concentration values were typically fairly similar (of the same order of magnitude or better).

### **Comparison with Juvenile Coho in Washington and Oregon Estuaries**

Two studies, one in Puget Sound, WA, and another in estuaries along the Washington and Oregon coasts, included juvenile coho salmon in their analyses of POPs (Johnson et al. 2005, Olson et al. 2008). These coho, which were estuarine yearlings, contained concentrations of HCBs, chlordanes, and DDTs (Table 11) that were within the same ranges as those found in the freshwater coho from our study sites that had detectable hits of these compounds (about one-half of our samples). Sum of PCBs at the Washington and Oregon sites were all higher than in fish from our study, with the exception of the Indian River in SITK, which exceeded  $\Sigma$ PCB values at 3 of the 6 estuarine sites. Dieldrin, which was detected only in the Taiya and Skagway Rivers at 0.2 ng/g, was found at levels 10 times higher in Alsea Bay and Coos Bay (Oregon) coho but otherwise not detectable (Johnson et al. 2005).

### **Comparison with Results of NAWQA Study**

In a study of contamination in slimy sculpin (*Cottus cognatus*) in Cook Inlet (Alaska) streams, organochlorine compounds were detected in only 3 of 12 sites measured (Frenzel 2000). However, the concentrations of the POPs that were detected were many-fold higher than in SEAN juvenile coho salmon: 9.0 ng/g p,p'DDE and 6.1 ng/g DDT in South Fork Campbell Creek; 79 ng/g PCBs in Chester Creek, and 5.7 ng/g HCB in the Talkeetna River.

### **Comparison with Results of USEPA Study of the Columbia River**

Juvenile salmon (outmigrating Chinooks [*O. tshawytscha*]) and resident fish (sucker spp., bass spp., and mountain whitefish [*Prosopium williamsoni*]) from the Columbia River were sampled for DDT, PCBs, PBDEs, and Hg by the EPA in a study of contaminants in the basin (USEPA 2009). Fish consumption advisories for Hg, DDT, and PCBs continue to be issued throughout the river system. DDTs and PCBs in Columbia River fish (mostly adults) were 1–3 orders of magnitude more concentrated than in the juvenile coho in our study.

### **Comparison with Results of WACAP Study**

Results of a recent, major survey of contaminants in 20 remote NPS units in the western US and Alaska (Western Airborne Contaminants Assessment Project or WACAP) revealed that Alaska parks had very low concentrations of most current-use chemicals; however, the occurrence of historic-use compounds in Alaska matched levels found in the lower 48 (Landers et al. 2008). This general conclusion fits well with our study, which also reveals no detectable concentrations of the two current-use pesticides (lindane and endosulfan) but detections of many historic use pesticides and chemicals in the coho salmon samples.

Although GLBA, SITK, and KLGO were not core study parks in the WACAP project, GLBA was subject to air and vegetation (lichen and conifers) sampling. Results of the WACAP study showed that POPs concentrations in air at GLBA ranked very low compared to those at other WACAP sites, although HCBs and a-HCH in lichens and g-HCH in conifers ranked very high in comparison (Landers et al. 2008). Indeed, HCBs were detected in half of the GLBA juvenile

coho samples, yet HCH-a was not detectable in any samples, indicating some variability in the uptake of HCBs in the ecosystem. In our study, g-HCH was not measured.

WACAP study sites in Alaska that included fish analyses were in Denali National Park and Preserve, Noatak National Preserve, and Gates of the Arctic National Park and Preserve, all in central and northern Alaska. In those parks, several historic-use POPs were in the mid to high range in the WACAP survey. Specifically, exceedences for dieldrin were found in all three parks, which was not an issue in our samples from southeast Alaskan. Dieldrin was detected only in the Skagway and Taiya River coho samples. The 0.2 ng/g concentrations in Skagway and Taiya River coho samples is comparable to concentrations in adult brook trout (*Salvelinus fontinalis*) in Olympic National Park, and about 2–10 times lower than fish from the other WACAP study units (Landers et al. 2008). It is important to note, however, that adult trout, burbot (*L. lota*), and whitefish spp. were collected in the WACAP units, whereas juvenile coho salmon were the only species targeted in our study, and species and age differences likely account for a large part of the variation in the uptake of contaminants and prohibit meaningful direct comparison of concentrations between fish samples.

On a WACAP-wide basis (8 park units), the dominant POPs in fish were p,p'DDE, dieldrin, PBDE 47, PBDE 99, PCB 153, PCB138, dacthal, trans-nonachlor, HCB, and endosulfan sulfate (Landers et al. 2008). In our study, the dominant POPs in fish were also HCB, p,p'DDE, and trans-nonachlor, but dieldrin was detected in only two samples; endosulfan and PBDEs were not detectable at all, dacthal was not measured, and a slightly different suite of PCB congeners dominated SEAN fish samples: PCB 17, 31, 95, 101, 105, 110, 118, 138, 153. Although many of the same contaminants were found in the coho salmon in our study as in the trout, burbot, and whitefish from the WACAP studies, the concentrations of the contaminants were decidedly lower in the young-of-the-year coho salmon from our study and all were below the thresholds of human subsistence and human recreational threshold levels.

### **Physical Parameters and Stream Water Chemistry Reveal Deglaciation Chronosequence**

Our survey of GLBA streams reveals the strong influence of watershed age on determining stream chemistry. Our data show that in general, the older the watershed, the lower the stream pH and dissolved solid concentrations (sulfate, Ca, Mg, and Si), and the higher the DOC concentration. This pattern conforms to the results of a deglaciation chronosequence study of GLBA lakes (Engstrom et al. 2000), which found that young lakes (<100 years old) are characterized by high pH, high dissolved solids, and low DOC, because overland flow across mineral soils and high inputs from groundwater are the dominant sources of water to the lakes. As terrestrial vegetation and mature soils develop, precipitation is increasingly routed through acidic, organic-rich soils, and as a result, the pH decreases and the DOC increases (Engstrom et al. 2000). In contrast, the trend exhibited by Cl of increasing concentrations with watershed age is explained by a sea-spray influence regulated by the location of older sites closer to the open ocean.

Also consistent with the lake findings (Engstrom et al. 2000), nitrate levels in our study streams were highest in the medium-aged watersheds (100–200 years old), and this is likely due to the strong influence of nitrogen-fixing plants (e.g., *Dryas drummondii* and *Alnus sinuate*) that dominate the landscape in recolonizing watersheds following deglaciation (Chapin et al. 1994).

These N-fixing species enhance nitrogen mineralization and soil N pools in terrestrial ecosystems (Hobbie et al. 1998), and N inputs from alder have been shown to produce very high rates of nitrate-N export in streamwater (Compton et al. 2003), which is consistent with the relatively high yields of nitrate from the 100–200 year old watersheds in this study. Nitrogen levels in streams later decline with the replacement of N-fixing species by mature forests.

Measured physical parameters, such as discharge, TSS, and turbidity generally exhibited predictable spatial patterns; that is, glacially influenced streams (Stonefly Creek, Nunatak Creek, Taiya and Skagway River) had higher values of these parameters than similarly-sized nonglacial streams. Temperature measurements show that lake presence or absence exerted the strongest control on values in receiving streams, making for warm stream temperatures even in the young, upper-bay watersheds that are lake-fed. Specific conductance and some of the major ions did not exhibit trends based on watershed age or type of landscape cover. However, it is important to note that our single-event sampling of the streams provides only a snapshot of stream hydrochemical conditions, many of which can vary strongly on short time-scales and are influenced by complex local controls (by groundwater, lithologic differences, etc) that are not considered in this study.

Finally, it is notable that sulfate's decline with watershed age occurs in spite of the increasing Hg methylation potential with age. Studies from elsewhere in North America show that sulfate availability typically increases Hg methylation and that it is often a key predictor (together with DOC and pH) of MeHg concentrations in watersheds (Heyes et al. 2000, Wiener et al. 2006). In GLBA, however, sulfate is not a good predictor of Hg<sub>T</sub> or MeHg across variably-aged watersheds due to the overwhelming influence played by watershed successional development and the evolution of soils post-glaciation.

## Conclusions

Mercury concentrations in GLBA streamwaters, particulates, two groups of mayflies, and juvenile coho salmon generally increased with watershed age following deglaciation. The oldest watersheds, with extensive developed peatlands, contained up to 10 times higher concentrations of  $Hg_T$  in water as the young streams in the upper Bay, and most had detectable MeHg. Specifically, Rink Creek, which drains relatively old peatlands along Excursion Ridge, contained 21% of its Hg in the methyl form, a remarkably high percentage. The pattern of Hg concentrations in the streams increasing with watershed age indicates that watersheds are variably sensitive to atmospheric Hg inputs and that the landscape characteristics (e.g., forested upland vs. peatland dominated) play a critical role in determining whether Hg is stored, released, and/or converted to MeHg and carried out via streams. Comparison with wet deposition data (Fitzgerald et al. 2007) indicates that in general, Hg in GLBA streams is taken up into storage in the younger watersheds but is released and partially converted to MeHg in the older watersheds. The importance of wetlands in controlling the form and flux of Hg through watersheds is well established in the literature, and here we show that this paradigm holds true for our study areas in southeast Alaska.

Water quality changes along the deglaciation chronosequence of our GLBA study streams were also evident for stream pH, Ca, Mg, Si, sulfate, which declined with stream age, and for dissolved organic carbon, which increased. Both the quantity and quality of DOC strongly influenced the transport of filtered  $Hg_T$ . Dissolved organic carbon concentrations (specifically the hydrophobic fraction) as well as UVA/SUVA values were good predictors of  $Hg_T$  in stream water and one of the two taxa of aquatic invertebrates. The strong correlation between filtered  $Hg_T$  and UVA suggests that the much simpler and less expensive method of UVA measurements could serve as an excellent proxy for filtered  $Hg_T$  in future studies.

The Indian, Skagway, and Taiya Rivers had among the lowest  $Hg_T$  and MeHg concentrations in water and juvenile coho. They had the lowest values for Hg in suspended particulates and streambed sediments as well. However, although juvenile coho from the Skagway, Taiya, and Indian River samples had low Hg concentrations, they had the highest concentrations of many of the detectable POPs.

Mercury and persistent organic pollutants were found in all SEAN streamwaters, sediments, and juvenile coho, but none exceeded criteria for the protection of human health or wildlife. Nonetheless, the concentrations of Hg in the age 1+ juvenile coho were higher than in spawning adults and approached levels of concern for piscivorous birds and wildlife, warranting further study of Hg in aquatic food webs in SEAN, especially in light of the predicted continuation of rises in Hg output from downwind industrializing nations. In particular, it would be informative to examine pollutant levels in higher trophic levels than those examined here. Also of interest would be a specific examination of the contributions of marine-derived pollutants by spawning salmon, as our results from Gull Creek indicate a measurable impact for both Hg and POPs. Future studies would benefit from repeated sampling as well as inclusion of watersheds along GLBA's outer coast.

No current-use pesticides were found in the coho samples, although numerous forms of historic use pesticides such as DDT and PCBs were detected in many samples, indicating that these 30+-

year old banned chemicals continue to work their way into remote ecosystems such as those of southeast Alaskan parks. Our study provides a baseline dataset for Hg and POPs in SEAN watersheds to which future evaluations of these contaminants can be compared.

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## Appendix A. Physical characteristics and chemical concentrations of streams sampled in GLBA, SITK, and KLGO.

Table APP A.1. Location information of streams sampled at GLBA, SITK, and KLGO.

Age class	Stream	Sample Date	Latitude (N)	Longitude (W)	Area (km <sup>2</sup> )	Elev. (m)	Glacier Cov (%)	Wetland Cov (%)	Freshwater Emergent Wetland (%)	Freshwater Forest/Shrub Wetland (%)	Average Slope Degrees	Lake Influence	Stream Age
"Young"	Stonefly Cr.	6/21/2007	58.95768	136.3559	13.2	693	31.4	2.1	0.6	1.5	17.3	Yes	47
	Gull Creek	6/21/2007	58.94862	136.2897	5.7	213	0	11.9	1.6	10.2	8.8	Yes	54
	Nunatak Cr.	6/21/2007	58.97645	136.0947	38.0	1414	1.8	1.1	0.6	0.6	17.7	No	73
"Medium"	Reid Creek	6/20/2007	58.87228	136.7621	17.4	1271	0	1.9	0.5	1.4	18.7	No	128
	Tyndall	6/22/2007	58.58542	136.3557	5.7	689	0	0.0	0.0	0.0	21.4	No	133
	Ice Valley	6/21/2007	58.80254	136.1572	18.5	910	0	1.3	0.9	0.4	17.9	No	138
	Vivid	6/20/2007	58.85026	136.4925	21.6	1265	0	0.5	0.2	0.3	24.2	No	139
	Oystercatcher	6/20/2007	58.68619	136.3598	9.7	697	0	2.2	1.4	0.7	15.1	No	148
	Fingers So.	6/19/2007	58.50668	136.2363	17.0	939	0	0.3	0.3	0.0	20.6	No	153
	Berg Bay So.	6/18/2007	58.57563	136.2189	18.7	755	0	15.6	8.5	7.2	15.4	No	168
	Rush Point	6/18/2007	58.47103	136.0984	5.2	639	0	1.6	1.2	0.4	15.4	No	203
"Old"	Carolus River	6/19/2007	58.38518	136.081	58.2	769	0	25.8	13.4	12.4	13.1	No	1388
	East Falls Cr.	6/23/2007	58.40876	135.5647	13.6	1023	0	17.7	0.6	17.1	15.3	No	9000
	Rink Cr.	6/19/2007	58.43441	135.6582	5.9	284	0	69.5	28.2	41.3	8.4	No	9000
	E. Pleasant Is.	6/22/2007	58.37547	135.6101	4.6	188	0	67.0	0.5	66.5	2.6	Yes	13000
	W. Pleasant Is.	6/22/2007	58.37619	135.6995	4.3	168	0	47.1	0.2	46.9	4.1	No	13000
	Indian River-SITKA	6/27/2007	57.05333	135.3144								No	
	Taiya River-SKAGWAY	7/3/2007	59.51194	59.46722								No	
	Skagway River-SKAGWAY	7/3/2007	59.46722	135.2833								No	

Scale and Distribution of Global Pollutants in Southeast Alaska Network Park Watersheds

**Table APP A.2.** Physical characteristics of streams sampled at GLBA, SITK, and KLGO.

Stream	Q (cfs)	TSS (mg/L)	pH	DO (%)	DO (mg/L)	Sp Cond	Temp	Turbidity	ANC uEQ/L	H+ uEQ/L	DOC mg/L	UVA 254nm	SUVA 254nm	%HPOA	HPOA DOC
Stonefly Cr.	47	29.4	8.04	115	12.8	0.15	10.63	58	914	0.02	1.00	0.037	3.7	31	0.31
Gull Creek	11.7	1.5	8.29	118	12.3	0.13	13.47	1.3	795	0.02	1.30	0.018	1.4	40	0.52
Nunatak Creek	151	1.0	7.88	113	13.7	0.14	7.05	2.9	868	0.01	0.40	0.005	1.2	36	0.14
Reid Creek	217	40.7	7.89	115	14.5	0.12	5.32	34	853	0.01	0.40	0.006	1.4	33	0.13
Tyndall	26	0.1	7.02	113	14.6	0.04	4.48	1.2	338	0.04	1.00	0.018	1.8	48	0.48
Ice Valley	82	0.5	8.04	116	14.5	0.19	5.80	1.8	1382	0.01	0.50	0.005	1.2	15	0.08
Vivid Cr.	138	9.6	7.93	115	14.4	0.12	5.82	9.7	846	0.02	0.40	0.010	2.8	18	0.07
Oystercatcher	44	0.6	7.90	116	15.1	0.13	4.33	1.5	936	0.01	1.20	0.024	1.9	43	0.52
Fingers South	125	21.9	7.54	114	13.7	0.10	7.54	14.7	714	0.02	1.20	0.027	2.3	35	0.42
Berg Bay So.		8.2	7.54	115	15.3	0.09	3.22	9.4	693	0.01	1.30	0.023	1.7	36	0.47
Rush Point	110	0.4	7.77	111	14.2	0.15	4.86	1.0	1013	0.03	1.10	0.013	1.2	35	0.39
Carolus River	89	2.4	7.50	111	13.8	0.12	6.11	4.0	894	0.01	1.60	0.027	1.8	46	0.74
East Falls Cr.	32	0.7	7.85	115	14.1	0.14	6.54	0.7	1076	0.02	1.10	0.020	1.9	43	0.47
Rink Creek	5.7	1.3	7.66	99	11.1	0.30	10.18	5.5	1670	0.01	5.10	0.203	4.0	53	2.70
E. Pleasant Is.	0.75	0.2	6.46	106	11.2	0.03	12.68	0.8	187	0.09	12.00	0.597	5.0	68	8.16
W. Pleasant Is.	0.49	0.5	7.11	109	11.6	0.04	12.37	1.3	321	0.04	10.80	0.532	4.9	67	7.24
Indian R.	70	BDL	7.45	109	13.0	0.0547	7.9	0.48	263	0.03	1.5	N/A	N/A	N/A	N/A
Taiya R.	3490	34.7	6.81	108	14.0	0.0290	4.48	29	248	0.03	0.8	N/A	N/A	N/A	N/A
Skagway R.		24.3	6.76	110	13.4	0.0325	6.91	22	260	0.02	1.2	N/A	N/A	N/A	N/A

Scale and Distribution of Global Pollutants in Southeast Alaska Network Park Watersheds

**Table APP A.3.** Physical characteristics and chemical concentrations of streams sampled at GLBA, SITK, and KLGO.

Stream	NH4+ uEQ/L	Ca++ uEQ/L	Mg++ uEQ/L	Na+ uEQ/L	K+ uEQ/L	Cl- uEQ/L	NO3- uEQ/L	SO4= uEQ/L	PO4 3- uEQ/L	Si uMOLES/L	Mn uMOLES/L	IP uMOLES/L
Stonefly Cr.	trace	1323.85	98.06	118.75	17.19	12.50	3.94	414.59	0.32	79.81	0.07	0.11
Gull Creek	0.39	1224.05	61.94	50.46	8.62	11.99	1.35	259.44	u	75.62	<0.07	u
Nunatak Creek	trace	1098.30	89.83	35.41	11.53	10.24	2.21	89.98	u	65.38	<0.07	u
Reid Creek	u	1080.34	98.31	36.54	17.70	16.98	2.61	192.46	u	29.33	<0.07	u
Tyndall	trace	344.76	39.24	37.80	6.44	20.34	7.63	32.31	u	63.85	<0.07	u
Ice Valley	u	1542.42	241.86	42.32	27.52	33.65	4.94	216.59	u	33.82	<0.07	u
Vivid Cr.	u	1022.95	184.27	25.62	12.10	14.70	u	150.47	u	105.70	<0.07	u
Oystercatcher	trace	1095.81	77.74	37.63	28.31	21.47	11.50	156.80	u	62.10	<0.07	u
Fingers South	0.38	866.27	58.41	36.23	15.86	27.25	10.81	78.93	u	50.56	<0.07	u
Berg Bay So.	0.33	753.49	61.94	39.19	8.72	27.50	3.69	58.25	u	46.70	0.07	u
Rush Point	trace	1339.82	125.04	66.55	23.30	52.69	1.18	83.95	u	48.90	<0.07	u
Carolus River	0.42	889.72	132.03	188.34	23.60	171.92	2.34	66.58	1.04	67.74	0.24	0.35
East Falls Cr.	u	1244.01	220.47	56.11	3.12	27.47	0.34	95.36	u	51.04	<0.07	u
East Falls Cr. Dup	u	1233.03	206.48	53.94	3.04	27.50	1.02	94.15	u	50.25	<0.07	u
Rink Creek	1.99	1581.34	293.68		44.96		1.71	72.58	0.37	109.32	1.44	0.12
E. Pleasant Is.	trace	163.22	44.18	123.53	5.14	40.42	1.40	12.08	0.36	32.95	0.07	0.12
W. Pleasant Is.	trace	287.82	61.37	119.62	5.70	37.94	2.03	18.34	0.32	38.45	<0.07	0.11
Indian R.	0.51	257.49	43.02	78.30		75.59	3.92	37.18	u			u
Taiya R.	0.71	222.06	50.02	21.66		12.27	3.34	32.08	0.36			0.12
Skagway R.	0.58	238.02	52.98	21.66		9.11	2.68	45.89	0.38			0.13

Scale and Distribution of Global Pollutants in Southeast Alaska Network Park Watersheds

**Table APP A.4.** Total Hg and MeHg concentrations of streams, aquatic insects, and fish sampled at GLBA, SITK, and KLGO.

Stream	Filtered water		Particulates		Bed sediment		BMI: Baetids		BMI: Heptas		Fish
	Tot. Hg (ng/L)	MeHg (ng/L)	Tot. Hg (ng/L)	MeHg (ng/L)	Tot. Hg (ng/L)	MeHg (ng/L)	Baetids MeHg (ng/L)	Baetids THg (ng/L)	Heptas MeHg (ng/L)	Heptas THg (ng/L)	Age 0 Coho (ng/g Dry weight)
Stonefly Cr.	0.47	0.02	0.965	0.01	6.78	0.05	Insufficient mass	Insufficient mass	None found	None found	28.2
Gull Creek	0.39	0.04	0.196	0.02	11.1	0.44	14.5	22.2	None found	None found	22.9
Nunatak Creek	0.08	0.01	0.189	<0.01	4.7	0.01	4.7	12.6	13.0	21.0	19.9
Reid Creek	0.89	0.04	3.731	0.01		0.02	20.5	59.3	Insuff. mass	Insuff. mass	85
Tyndall	1.28	0.03	0.072	<0.01	12.7	0.03	13.1	38.4	27.2	67.5	18.4
Ice Valley	0.22	0.10	0.111		19.34	0.01	5.30	12.37	8.43	17.24	16
Vivid Cr.	0.35	<0.01	1.392	<0.01	40.8	0.02	10.1	31.7	None found	None found	18.8
Oystercatcher	0.84	0.06	0.133	<0.01	12.9	0.03	29.2	52.5	15.1	50.6	25.3
Fingers South	0.39	0.02	0.986	<0.01	Sample lost		7.1	19.5	9.5	51.1	15.6
Berg Bay So.	0.56	0.02	0.768	0.01	23.2	0.04	10.5	24.9	12.6	28.2	45.6
Rush Point	0.33	0.04	0.178	<0.01	22.3	0.10	27.6	36.3	38.4	57.6	17.6
Carolus River	0.42	0.02	0.255	0.01	22.2	0.01	19.1	29.3	21.5	44.8	65.9
East Falls Cr.	0.53	0.01	0.086	<0.01	111.9	0.05	19.0	36.5	20.5	64.8	25.2
East Falls Cr. Dup	0.55		0.104								19.6
Rink Creek	0.98	0.21	0.162	0.01	7.0	0.04	58.3	51.3	None found	None found	46.9
E. Pleasant Is.	3.37	0.09	0.170	0.01	16.4	0.04	Insuff. mass	Insuff. mass	26.6	55.2	79.2
W. Pleasant Is.	3.08	0.06	0.172	<0.01	13.7	0.06	Insuff. mass	Insuff. mass	39.2	52.8	34.6
Indian R.	0.27	0.03	0.051	0.01	9.3	0.10	16.0	60.4	32.6	44.1	35.8
Taiya R.	0.35	0.02	0.534	<0.01	3.0	0.02	24.5	41.56	28.7	48.2	9.46
Skagway R.	0.37	<0.01		0.01	1.7	0.02	10.7	21.5	21.2	36.2	18.2

## Appendix B. POPs concentrations in fish tissues from the sample sites in GLBA, SITK, and KLGO.

**Table APP B.1.** POPs concentrations in fish tissues from the sample sites in GLBA, SITK, and KLGO. Green shaded areas are concentrations above detection.

Site	Current use pesticides		Historic use pesticides								
	Lindane	Endsulfan I	HCH-a	HCH-b	HCB	aldrin	dieldrin	heptachlor	heptachlor epoxide	oxy-chlordane	mirex
Stonefly Creek	< 0.20	< 0.20	< 0.21	< 0.21	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20
Gull Creek	< 0.14	< 0.14	< 0.15	< 0.15	0.62	< 0.14	< 0.14	< 0.14	< 0.14	< 0.14	< 0.14
Nunatak Creek	< 0.20	< 0.20	< 0.21	< 0.20	0.29	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20
Reid Creek	< 0.43	< 0.43	< 0.45	< 0.45	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43
Tyndall	< 0.35	< 0.36	< 0.37	< 0.37	0.58	< 0.36	< 0.35	< 0.35	< 0.35	< 0.35	< 0.36
Ice Valley Stream	< 0.27	< 0.27	< 0.29	< 0.28	< 0.27	< 0.27	< 0.27	< 0.27	< 0.27	< 0.27	< 0.27
Vivid Stream	< 0.20	< 0.20	< 0.21	< 0.20	0.43	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20
Oystercatcher Creek	< 0.23	< 0.23	< 0.24	< 0.24	< 0.23	< 0.23	< 0.23	< 0.23	< 0.23	< 0.23	< 0.23
Finger South	< 0.36	< 0.36	< 0.38	< 0.38	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36
Berg Bay South	< 0.28	< 0.28	< 0.29	< 0.29	< 0.28	< 0.28	< 0.28	< 0.28	< 0.28	< 0.28	< 0.28
Rush Point Stream	< 0.17	< 0.17	< 0.17	< 0.17	0.35	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17
Carolus River	< 0.19	< 0.19	< 0.20	< 0.20	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19
East Falls Creek	< 0.35	< 0.35	< 0.37	< 0.36	0.53	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35
Rink Creek	< 0.17	< 0.17	< 0.18	< 0.18	0.29	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17
Pleasant Island East	< 0.11	< 0.11	< 0.12	< 0.12	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11
Pleasant Island Creek	< 0.15	< 0.16	< 0.16	< 0.16	0.26	< 0.16	< 0.15	< 0.15	< 0.15	< 0.15	< 0.16
Indian River	< 0.19	< 0.19	< 0.20	< 0.20	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19
Indian River	< 0.17	< 0.17	< 0.18	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17
Taiya River	< 0.13	< 0.14	< 0.14	< 0.14	0.71	< 0.13	0.23	< 0.13	< 0.13	< 0.13	< 0.14
Skagway River	< 0.15	< 0.16	< 0.16	< 0.16	0.89	< 0.15	0.21	< 0.15	< 0.15	0.22	< 0.16

Scale and Distribution of Global Pollutants in Southeast Alaska Network Park Watersheds

**Table APP B.1.** POPs concentrations in fish tissues from the sample sites in GLBA, SITK, and KLGO. Green shaded areas are concentrations above detection (continued).

Site	Historic use pesticides, continued							Chlordanes					
	DDD, DDEs, and DDTs												
	o,p'DDD	o,p'DDE	o,p'DDT	p,p'DDD	p,p'DDE	p,p'DDT	ΣDDTs	a-chlor	g-chlor	trans-nonachlor	cis-nonachlor	non-achlor III	ΣCHLDs
Stonefly Creek	< 0.20	< 0.20	< 0.20	< 0.20	1.2	< 0.20	1.2	< 0.20	< 0.21	< 0.20	< 0.21	< 0.20	< LOQ
Gull Creek	< 0.14	< 0.14	0.17	0.25	1.6	< 0.14	2.1	0.26	< 0.15	0.35	< 0.15	< 0.14	0.6
Nunatak Creek	< 0.20	< 0.20	< 0.20	< 0.20	0.7	< 0.20	0.7	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< LOQ
Reid Creek	< 0.43	< 0.43	< 0.43	< 0.43	0.92	< 0.43	0.92	< 0.43	< 0.44	< 0.43	< 0.44	< 0.43	< LOQ
Tyndall	< 0.35	< 0.35	< 0.35	< 0.36	2.4	< 0.35	2.4	< 0.35	< 0.37	0.45	< 0.36	< 0.36	0.45
Ice Valley Stream	< 0.27	< 0.27	< 0.27	< 0.27	0.94	< 0.27	0.94	< 0.27	< 0.28	< 0.27	< 0.28	< 0.27	< LOQ
Vivid Stream	< 0.20	< 0.20	< 0.20	< 0.20	0.87	< 0.20	0.87	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< LOQ
Oystercatcher Creek	< 0.23	< 0.23	< 0.23	< 0.23	1.1	< 0.23	1.1	< 0.23	< 0.24	0.25	< 0.23	< 0.23	0.25
Finger South	< 0.36	< 0.36	< 0.36	< 0.36	0.9	< 0.36	0.9	< 0.36	< 0.37	< 0.36	< 0.37	< 0.36	< LOQ
Berg Bay South	< 0.28	< 0.28	< 0.28	< 0.28	1.1	< 0.28	1.1	< 0.28	< 0.29	< 0.28	< 0.29	< 0.28	< LOQ
Rush Point Stream	< 0.17	< 0.17	< 0.16	< 0.17	0.91	< 0.16	0.91	< 0.17	< 0.17	0.21	< 0.17	< 0.17	0.21
Carolus River	< 0.19	< 0.19	< 0.19	< 0.19	0.51	< 0.19	0.51	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< LOQ
East Falls Creek	< 0.35	< 0.35	< 0.35	< 0.35	1.4	< 0.35	1.4	< 0.35	< 0.36	< 0.35	< 0.36	< 0.35	< LOQ
Rink Creek	< 0.17	< 0.17	< 0.17	< 0.17	0.86	< 0.17	0.86	< 0.17	< 0.18	0.22	< 0.17	< 0.17	0.22
Pleasant Island East	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< LOQ	< 0.11	< 0.12	< 0.11	< 0.12	< 0.11	< LOQ
Pleasant Island Creek	< 0.15	< 0.15	< 0.15	< 0.16	1.4	< 0.15	1.4	< 0.15	< 0.16	0.2	< 0.16	< 0.16	0.2
Indian River	< 0.19	< 0.19	< 0.19	< 0.19	1.3	< 0.19	1.3	< 0.19	< 0.20	< 0.19	< 0.19	< 0.19	< LOQ
Indian River	< 0.17	< 0.17	< 0.17	< 0.17	1.4	< 0.17	1.4	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< LOQ
Taiya River	< 0.13	< 0.13	< 0.13	0.18	1.2	< 0.13	1.4	0.23	< 0.14	0.31	< 0.14	< 0.14	0.54
Skagway River	< 0.15	< 0.15	0.16	0.59	2.9	0.22	3.8	0.5	< 0.16	0.89	0.3	< 0.16	1.9

Scale and Distribution of Global Pollutants in Southeast Alaska Network Park Watersheds

**Table APP B.1.** POPs concentrations in fish tissues from the sample sites in GLBA, SITK, and KLGO. Green shaded areas are concentrations above detection (continued).

Site	Historic use pesticides, cont.												
	PCBs												
	cb17	cb18	cb28	cb31	cb33	cb44	cb49	cb52	cb66	cb70	cb74	cb82	cb87
Stonefly Creek	0.072	< 0.20	< 0.20	0.26	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.050	< 0.20
Gull Creek	0.064	0.16	0.2	0.24	< 0.14	< 0.14	< 0.14	0.22	< 0.14	0.17	< 0.15	< 0.036	< 0.14
Nunatak Creek	0.53	< 0.20	< 0.20	0.18	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.049	< 0.20
Reid Creek	< 1.1	< 0.43	< 0.43	< 0.33	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.11	< 0.43
Tyndall	0.11	< 0.36	< 0.36	0.44	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.089	< 0.36
Ice Valley Stream	0.76	< 0.27	< 0.27	0.31	< 0.27	< 0.27	< 0.27	< 0.27	< 0.27	< 0.27	< 0.27	< 0.068	< 0.27
Vivid Stream	0.52	< 0.20	< 0.20	0.16	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.049	< 0.20
Oystercatcher Creek	0.62	< 0.23	< 0.23	0.21	< 0.23	< 0.23	< 0.23	< 0.23	< 0.23	< 0.23	< 0.23	< 0.058	< 0.23
Finger South	1	< 0.36	0.4	0.44	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.091	< 0.36
Berg Bay South	0.71	< 0.28	< 0.28	0.23	< 0.28	< 0.28	< 0.28	< 0.28	< 0.28	< 0.28	< 0.28	< 0.070	< 0.28
Rush Point Stream	0.063	< 0.17	0.18	0.21	< 0.17	< 0.17	< 0.17	0.17	< 0.17	< 0.17	< 0.17	< 0.042	< 0.17
Carolus River	0.06	< 0.19	< 0.19	0.24	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.047	< 0.19
East Falls Creek	< 0.88	< 0.35	< 0.35	0.28	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.088	< 0.35
Rink Creek	< 0.43	< 0.17	< 0.17	0.17	< 0.17	< 0.17	< 0.17	0.17	< 0.17	< 0.17	< 0.17	< 0.043	< 0.17
Pleasant Island East	0.044	< 0.11	0.14	0.17	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.028	< 0.11
Pleasant Island Creek	0.059	0.16	0.18	0.23	< 0.15	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.16	< 0.039	< 0.16
Indian River	0.051	< 0.19	< 0.19	0.21	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.048	< 0.19
Indian River	0.063	< 0.17	0.19	0.25	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.042	< 0.17
Taiya River	0.065	0.16	0.21	0.26	0.14	< 0.14	< 0.13	0.2	< 0.13	0.14	< 0.14	< 0.034	< 0.14
Skagway River	0.43	< 0.16	0.21	0.24	< 0.15	< 0.16	< 0.15	0.32	< 0.15	0.21	< 0.16	< 0.039	< 0.16

Scale and Distribution of Global Pollutants in Southeast Alaska Network Park Watersheds

**Table APP B.1.** POPs concentrations in fish tissues from the sample sites in GLBA, SITK, and KLGO. Green shaded areas are concentrations above detection (continued).

Site	Historic use pesticides, cont.												
	PCBs												
	cb95	cb99	cb101	cb105	cb110	cb118	cb128	cb138	cb149	cb151	cb153	cb156	cb158
Stonefly Creek	0.13	< 0.20	< 0.20	0.099	0.22	0.26	< 0.20	0.33	< 0.20	< 0.20	0.35	< 0.051	< 0.20
Gull Creek	0.22	0.16	0.28	0.084	0.23	0.27	< 0.15	0.32	0.19	< 0.15	0.37	< 0.036	< 0.14
Nunatak Creek	0.14	< 0.20	< 0.20	0.069	< 0.20	< 0.20	< 0.20	0.23	< 0.20	< 0.20	< 0.30	< 0.050	< 0.20
Reid Creek	< 0.22	< 0.43	< 0.43	< 0.11	< 0.43	< 0.43	< 0.44	< 0.44	< 0.43	< 0.44	< 0.65	< 0.11	< 0.43
Tyndall	0.27	< 0.36	0.39	0.13	0.37	0.36	< 0.36	0.47	< 0.36	< 0.36	0.55	< 0.090	< 0.36
Ice Valley Stream	0.17	< 0.27	< 0.28	0.11	0.28	0.28	< 0.28	0.37	< 0.27	< 0.28	0.41	< 0.069	< 0.27
Vivid Stream	0.12	< 0.20	< 0.20	0.071	< 0.20	< 0.20	< 0.20	0.25	< 0.20	< 0.20	< 0.30	< 0.050	< 0.20
Oystercatcher Creek	0.16	< 0.23	0.25	0.082	0.23	0.24	< 0.23	0.31	< 0.23	< 0.23	< 0.35	< 0.058	< 0.23
Finger South	0.3	< 0.36	< 0.37	0.2	0.41	0.46	< 0.37	0.54	< 0.36	< 0.37	< 0.55	< 0.092	< 0.36
Berg Bay South	0.17	< 0.28	< 0.28	0.11	< 0.28	< 0.28	< 0.28	0.35	< 0.28	< 0.28	< 0.42	< 0.071	< 0.28
Rush Point Stream	0.14	< 0.17	0.2	0.074	0.18	0.19	< 0.17	0.24	< 0.17	< 0.17	0.28	< 0.042	< 0.17
Carolus River	< 0.095	< 0.19	< 0.19	0.066	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.28	< 0.048	< 0.19
East Falls Creek	0.19	< 0.35	< 0.35	0.12	< 0.35	< 0.35	< 0.35	0.4	< 0.35	< 0.35	< 0.53	< 0.089	< 0.35
Rink Creek	0.15	< 0.17	0.22	0.091	0.2	0.22	< 0.17	0.29	< 0.17	< 0.17	0.33	< 0.043	< 0.17
Pleasant Island East	0.067	< 0.11	< 0.11	0.05	< 0.11	0.12	< 0.11	0.15	< 0.11	< 0.11	0.18	< 0.029	< 0.11
Pleasant Island Creek	0.13	< 0.15	0.21	0.088	0.19	0.23	< 0.16	0.3	< 0.16	< 0.16	0.36	< 0.039	< 0.16
Indian River	0.2	< 0.19	0.41	0.094	0.27	0.3	< 0.19	1.6	0.76	0.2	1.9	< 0.048	< 0.19
Indian River	0.24	< 0.17	0.44	0.11	0.31	0.32	< 0.17	1.7	0.82	0.21	2	< 0.043	< 0.17
Taiya River	0.18	< 0.13	0.23	0.08	0.2	0.23	< 0.14	0.28	0.16	< 0.14	0.32	< 0.034	< 0.13
Skagway River	0.28	0.24	0.33	0.11	0.25	0.32	< 0.16	0.44	0.21	< 0.16	0.54	< 0.039	< 0.15

Scale and Distribution of Global Pollutants in Southeast Alaska Network Park Watersheds

**Table APP B.1.** POPs concentrations in fish tissues from the sample sites in GLBA, SITK, and KLGO. Green shaded areas are concentrations above detection (continued).

Site	Historic use pesticides, cont.														
	PCBs														
	cb170	cb171	cb177	cb180	cb183	cb187	cb191	cb194	cb195	cb199	cb205	cb206	cb208	cb209	Sum40CBs
Stonefly Creek	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.15	< 0.20	< 0.20	< 0.20	< 0.20	1.7
Gull Creek	< 0.14	< 0.14	< 0.15	< 0.14	< 0.14	< 0.14	< 0.15	< 0.15	< 0.15	< 0.11	< 0.14	< 0.15	< 0.15	< 0.14	3.2
Nunatak Creek	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.15	< 0.20	< 0.20	< 0.20	< 0.20	1.1
Reid Creek	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.44	< 0.33	< 0.43	< 0.44	< 0.43	< 0.43	< LOQ
Tyndall	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.36	< 0.27	< 0.36	< 0.36	< 0.36	< 0.36	3.1
Ice Valley Stream	< 0.27	< 0.27	< 0.28	< 0.27	< 0.27	< 0.27	< 0.28	< 0.28	< 0.28	< 0.21	< 0.27	< 0.28	< 0.28	< 0.28	2.7
Vivid Stream	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	< 0.15	< 0.20	< 0.20	< 0.20	< 0.20	1.1
Oystercatcher Creek	< 0.23	< 0.23	< 0.23	< 0.23	< 0.23	< 0.23	< 0.23	< 0.23	< 0.23	< 0.17	< 0.23	< 0.23	< 0.23	< 0.23	2.1
Finger South	< 0.36	< 0.36	< 0.37	< 0.36	< 0.36	< 0.36	< 0.37	< 0.37	< 0.37	< 0.27	< 0.36	< 0.37	< 0.37	< 0.37	3.8
Berg Bay South	< 0.28	< 0.28	< 0.28	< 0.28	< 0.28	< 0.28	< 0.28	< 0.28	< 0.28	< 0.21	< 0.28	< 0.28	< 0.28	< 0.28	1.6
Rush Point Stream	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.13	< 0.17	< 0.17	< 0.17	< 0.17	1.9
Carolus River	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.19	< 0.14	< 0.19	< 0.19	< 0.19	< 0.19	0.37
East Falls Creek	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.26	< 0.35	< 0.35	< 0.35	< 0.35	0.99
Rink Creek	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.17	< 0.13	< 0.17	< 0.17	< 0.17	< 0.17	2.3
Pleasant Island East	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	< 0.086	< 0.11	< 0.11	< 0.11	< 0.11	0.92
Pleasant Island Creek	< 0.15	< 0.16	< 0.16	< 0.16	< 0.15	< 0.16	< 0.16	< 0.16	< 0.16	< 0.12	< 0.16	< 0.16	< 0.16	< 0.16	2.1
Indian River	0.36	< 0.19	0.21	0.83	0.19	0.45	< 0.19	< 0.19	< 0.19	< 0.14	< 0.19	< 0.19	< 0.19	< 0.19	8.2
Indian River	0.37	< 0.17	0.21	0.86	0.2	0.45	< 0.17	< 0.17	< 0.17	< 0.13	< 0.17	< 0.17	< 0.17	< 0.17	8.9
Taiya River	< 0.13	< 0.14	< 0.14	< 0.14	< 0.13	< 0.13	< 0.14	< 0.14	< 0.14	< 0.10	< 0.14	< 0.14	< 0.14	< 0.14	2.9
Skagway River	< 0.15	< 0.16	< 0.16	< 0.16	< 0.15	< 0.15	< 0.16	< 0.16	< 0.16	< 0.12	< 0.16	< 0.16	< 0.16	< 0.16	4.1

Scale and Distribution of Global Pollutants in Southeast Alaska Network Park Watersheds

**Table APP B.1.** POPs concentrations in fish tissues from the sample sites in GLBA, SITK, and KLGO. Green shaded areas are concentrations above detection (continued).

Site	Historic use pesticides, cont.										SUM BDEs
	PBDEs										
	BDE 28	BDE 47	BDE 49	BDE 66	BDE 85	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	
Stonefly Creek	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46	< LOQ
Gull Creek	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< LOQ
Nunatak Creek	< 0.47	< 0.47	< 0.47	< 0.47	< 0.47	< 0.47	< 0.47	< 0.47	< 0.47	< 0.48	< LOQ
Reid Creek	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< LOQ
Tyndall	< 0.81	< 0.81	< 0.81	< 0.81	< 0.81	< 0.81	< 0.81	< 0.81	< 0.82	< 0.82	< LOQ
Ice Valley Stream	< 0.65	< 0.65	< 0.65	< 0.65	< 0.65	< 0.65	< 0.65	< 0.65	< 0.66	< 0.66	< LOQ
Vivid Stream	< 0.47	< 0.47	< 0.47	< 0.47	< 0.47	< 0.47	< 0.47	< 0.47	< 0.47	< 0.48	< LOQ
Oystercatcher Creek	< 0.55	< 0.55	< 0.55	< 0.55	< 0.55	< 0.55	< 0.55	< 0.55	< 0.55	< 0.55	< LOQ
Finger South	< 0.87	< 0.87	< 0.87	< 0.87	< 0.86	< 0.86	< 0.86	< 0.86	< 0.87	< 0.87	< LOQ
Berg Bay South	< 0.67	< 0.67	< 0.67	< 0.67	< 0.67	< 0.67	< 0.67	< 0.67	< 0.67	< 0.68	< LOQ
Rush Point Stream	< 0.38	< 0.38	< 0.38	< 0.38	< 0.38	< 0.38	< 0.38	< 0.38	< 0.38	< 0.38	< LOQ
Carolus River	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.44	< LOQ
East Falls Creek	< 0.84	< 0.84	< 0.84	< 0.84	< 0.83	< 0.83	< 0.83	< 0.83	< 0.84	< 0.84	< LOQ
Rink Creek	< 0.41	< 0.41	< 0.41	< 0.41	< 0.41	< 0.41	< 0.41	< 0.41	< 0.41	< 0.41	< LOQ
Pleasant Island East	< 0.26	< 0.26	< 0.26	< 0.26	< 0.26	< 0.26	< 0.26	< 0.26	< 0.26	< 0.26	< LOQ
Pleasant Island Creek	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.36	< 0.36	< LOQ
Indian River	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.43	< 0.44	< 0.44	< LOQ
Indian River	< 0.39	< 0.39	< 0.39	< 0.39	< 0.38	< 0.38	< 0.38	< 0.38	< 0.39	< 0.39	< LOQ
Taiya River	< 0.31	< 0.31	< 0.31	< 0.31	< 0.31	< 0.31	< 0.31	< 0.31	< 0.31	< 0.31	< LOQ
Skagway River	< 0.37	< 0.37	< 0.37	< 0.37	< 0.37	< 0.37	< 0.37	< 0.37	< 0.37	< 0.37	< LOQ

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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**National Park Service**  
**U.S. Department of the Interior**



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