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Spatial distribution of mercury in southeastern Alaskan streams influenced by glaciers, wetlands, and salmon

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ABSTRACT

Southeastern Alaska is a remote coastal-maritime ecosystem that is experiencing increased deposition of mercury (Hg) as well as rapid glacier loss. Here we present the results of the first reported survey of total and methyl Hg (MeHg) concentrations in regional streams and biota. Overall, streams draining large wetland areas had higher Hg concentrations in water, mayflies, and juvenile salmon than those from glacially-influenced or recently deglaciated watersheds. Filtered MeHg was positively correlated with wetland abundance. Aqueous Hg occurred predominantly in the particulate fraction of glacier streams but in the filtered fraction of wetland-rich streams. Colonization by anadromous salmon in both glacier and wetland-rich streams may be contributing additional marine-derived Hg. The spatial distribution of Hg in the range of streams presented here shows that watersheds are variably, yet fairly predictably, sensitive to atmospheric and marine inputs of Hg.

1. Introduction

Mercury (Hg), a widespread, naturally occurring heavy metal, is a potent neurotoxin that biomagnifies up trophic levels as methylmercury (CH_3Hg^+, abbreviated here as MeHg) (National Research Council, 2007). Although typically occurring at trace levels, the world's atmosphere, oceans, and terrestrial ecosystems contain 2–6 times more Hg than in the preindustrial era (Fitzgerald and others, 1998; Sunderland and others, 2009). While Hg emissions in the USA have decreased in recent decades, global outputs continue to rise, particularly by industrializing Asian nations that are rapidly increasing their coal consumption (Streets and others, 2009; Pirrone and others, 2010).

Much of the Hg released from Asian coal combustion is carried via long-range atmospheric pathways to the northwest coast of North America (Dastoor and Larocque, 2004; Munthe and others, 2011). Additionally, marine Hg data linked with atmospheric transport models suggest that the North Pacific Ocean adjacent to Alaska has incurred substantial increases in Hg over the past two decades (Sunderland and others, 2009). Mercury deposition in Alaska appears to be similar in magnitude to that in lower latitudes despite few local sources (Fitzgerald and others, 2005). Lake sediment studies in southeastern Alaska indicate that Hg accumulation levels are 2–3 preindustrial levels and likely rising (Engstrom and Swain, 1997; Engstrom, unpublished data). In addition, recent work on the Yukon River found that its Hg yields are up to 32 times greater than those in eight other major Northern hemisphere river basins (Schuster and others, 2011). Beginning in 2007, the state of Alaska has recommended limiting consumption of several coastal species of fish due to MeHg (ADEC, 2007).

The impacts of Hg deposition to southeastern Alaskan streams have not previously been examined, and there is a scarcity of information on Hg in glacier-fed streams. Numerous studies have shown that MeHg, which is 10–100 times more toxic than inorganic Hg (Boening, 2000) and readily biomagnifies by multiple orders of magnitude up trophic levels (van der Velden and others, 2013), is efficiently converted from atmospherically-deposited

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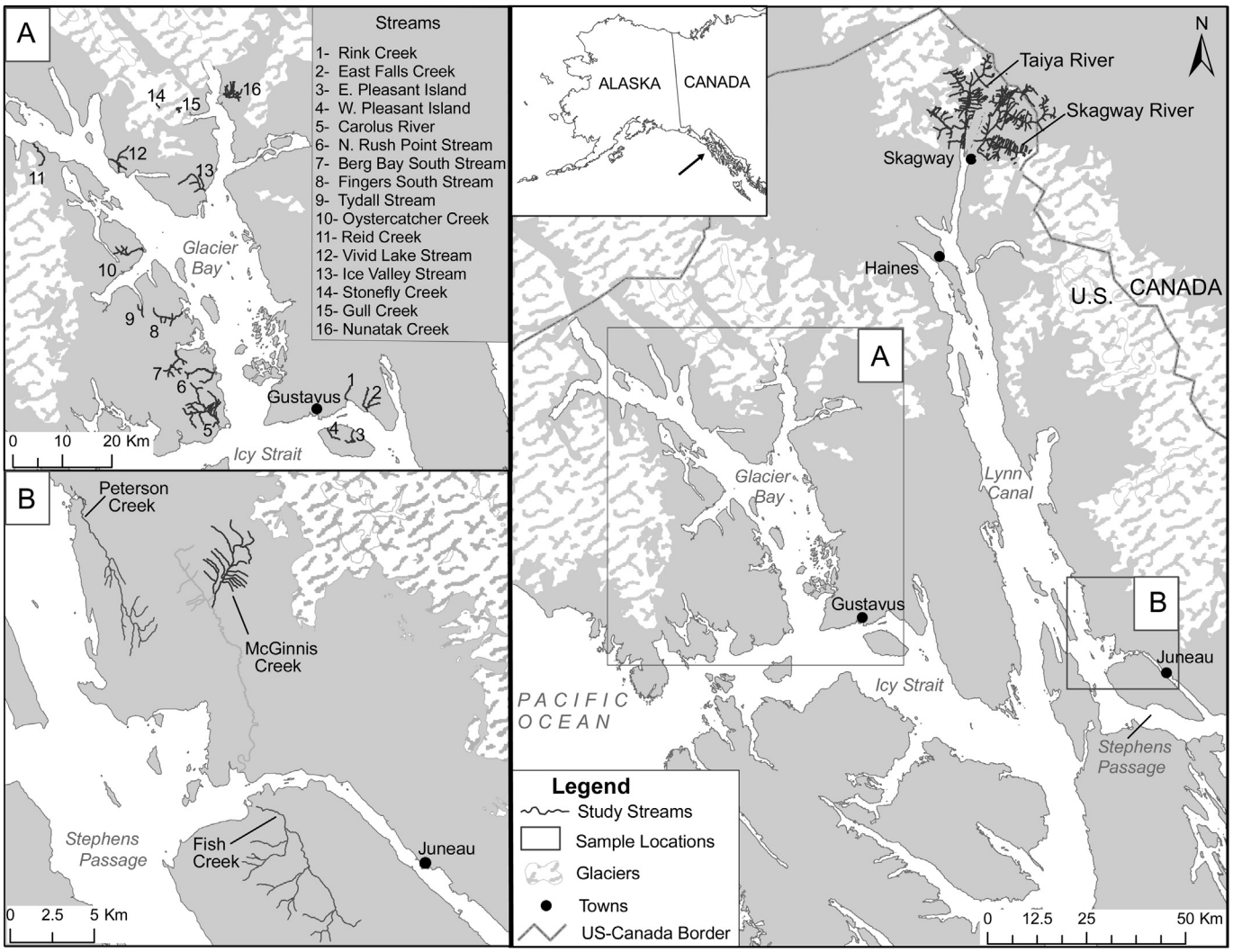

Fig. 1. Location of study watersheds in southeastern Alaska. Inset A shows the Glacier Bay watersheds, and Inset B shows the Juneau area watersheds. The Taiya and Skagway Rivers are shown on the main map.

inorganic Hg by sulfate-reducing bacteria in wetland environments (Wiener and others, 2003). MeHg concentrations in biotic and abiotic components of streams and lakes are typically positively correlated with the percentage of the watershed covered by wetlands (St.Louis and others, 1996; Wiener and others, 2006; Brigham and others, 2009). MeHg can also be imported into watersheds via migrating birds and spawning anadromous fish (Sarica and others, 2004; Blais and others, 2007; Baker and others, 2009).

Southeastern Alaska contains >4000 salmon streams supporting an industry that is the core of one of the last intact coastal-marine fisheries in the world and worth about $1 billion annually (TCW Economics, 2010). Considering the high abundance of wetlands (29% of land area (Cowardin and others, 1979)), the large number of salmon streams in the region, and rising Hg emissions from Asia (Pacyna and others, 2010), southeastern Alaska is likely vulnerable to Hg contamination. Moreover, the rapid thinning and retreat of glaciers is facilitating dramatic changes in landcover and the biogeochemistry of coastal streams as glacier ice is replaced by new forests and wetlands (Hood and Scott, 2008). This study presents data from the first survey of Hg occurrence in streamwater, sediments, benthic macroinvertebrates, and rearing salmonids in southeastern Alaska. It focuses on the spatial patterns that elucidate the role that landcover plays in facilitating the attenuation, release, and conversion of atmospherically deposited Hg to MeHg within the region's coastal watersheds.

2. Material and methods

2.1. Study area

Southeastern Alaska is dominated by wetland-rich coastal temperate rainforest and contains 16,800 km^2 of glaciers (Neal and others, 2010). We sampled 21 streams (Fig. 1) that span a broad spectrum of watershed characteristics largely controlled by biological succession following deglaciation since the end of the Little Ice Age (Milner and others, 2007). Sixteen of the 21 streams are located in and around Glacier Bay National Park and Preserve (GBNPP). The watersheds located in the uppermost part of GBNPP are the youngest (<150 years old) and still receive some glacier runoff (2–31% glacier cover). Deglaciated watersheds further south are progressively older (ca. 150–200 years old) and contain developed forests (mainly spruce, hemlock, and cottonwoods) with stable stream channels. Still older watersheds (>1400 years old) escaped ice cover and have substantial (12–69%) wetland coverage. Three streams in the Juneau area were sampled as well (Fig. 1b). Fish and Peterson Creeks are shallow sloping watersheds with high

wetland coverage (30 and 53% of watershed area, respectively) and host dense salmon runs in late summer. McGinnis Creek is largely alpine, with permanent snowfields and small remnants of glacial ice (ca. 4% watershed area). Lastly, the Northern Lynn Canal streams (Skagway and Taiya Rivers) are larger transboundary rivers (~25× watershed area of the other study streams) with high glacier coverage (17% and 33% respectively) and mixtures of old growth coniferous forest, peatlands, and alpine vegetation (Table 1).

All study watersheds were grouped into three categories: Glaciated ("G"; includes watersheds that have any amount of glacier contributions); Recently Deglaciated ("RD"); and wetland-rich ("WR") (Table 1). Some stream names are unofficial and are taken from Milner and others, (2000). All study watersheds are negligibly impacted by direct human activity. Stream drainage boundaries, watershed area and watershed slope were derived from a USGS (http://www.nrcs.usda.gov/) watershed boundary feature in GIS. Wetland coverage was calculated from the National Wetland Inventory (NWI, http://alaska.fws.gov/fisheries/nwi/index.htm) and glacial extent was calculated from the 2010 Global Land Ice Measurements from Space dataset (GLIMS; http://nsidc.org/).

2.2. Selection of physical and biological stream components

Between June 18-July 3, 2007, we collected samples of filtered streamwater, filter-retained particles, bulk streambed sediment (likely including biofilms), mayfly larvae (families Baetidae and Heptageniidae), and juvenile coho salmon *(Oncorhynchus kisutch)* once from each of the GBNPP and Northern Lynn Canal streams ($n = 18$). During the same period, the three Juneau-area streams were sampled for filtered water; fish were collected in August, 2007; and mayfly larvae were subsequently collected in Peterson Creek in July 2010. During the main 2 weeks sample period, streamflow was dominated by snowmelt in most streams, and total precipitation during the sampling period was only 9.7 mm at the Glacier Bay weather station (NOAA, 2013). Additionally, we sampled water from Juneau-area streams twice more in 2007 – in August during salmon spawning and in October, post-spawning.

Streamwater and suspended particles represent water-column conditions over short time scales (minutes to hours), while bed sediments, mayfly larvae, and fish represent contaminant conditions in the stream integrated over longer time periods (weeks to months). Baetidae mayfly larvae feed by gathering fine particulate organic matter, and Heptageniidae mayfly larvae scrape living biofilms (bacteria, algae, fungi) from streambed substrates. As primary consumers, mayflies represent one of the lowest trophic levels for Hg to enter into aquatic food webs (Cremona and others, 2009). Larvae are an important link between primary producers and secondary consumers (i.e. juvenile coho salmon), providing a potential pathway for pollutant transfer into higher trophic levels (Walters and others, 2008). We targeted both the larvae and young-of-the-year coho salmon that had not yet migrated out of their natal streams in order to characterize watershed-specific Hg exposures (Baker and others, 2009). All sampling occurred above tidal influence.

2.3. Field and lab-processing methods

Water samples for Hg were collected in 2 L PETG Nalgene bottles using clean techniques and immediately stored on ice. On the same day as they were collected, samples were filtered through ~0.7 μm ashed quartz fiber filters using a portable, metal-free, vacuum filtration apparatus and subsequently acidified with ultraclean HCl (0.2% of sample volume). All pre-cleaned filtration equipment was provided by the USGS Mercury Research Laboratory (MRL). Particulate Hg was measured by analysis of glass microfiber filters through which 1 L of sample was passed. Additional water samples were filtered (through 0.45 μm high capacity disposable filter by Geotech) into amber glass bottles for dissolved organic carbon (DOC) and anion analyses. Discharge was measured using standard USGS methods (Rantz and others, 1982). Streambed sediment was collected by scraping several grams of the top ~1 cm of fine unsieved sediment into a Teflon vial. Mayfly larvae were dislodged from the streambed by foot and collected in a net. For each stream, up to 100 larvae from each family were picked into a Teflon vial. Up to 15 (mean = 6) individual juvenile coho salmon were captured at

Table 1
Category grouping, geographical, physical, and chemical characteristics of sampled streams. G = Glaciated, RD = Recently Deglaciated, and WR = Wetland-rich watersheds. NA = No data collected; NQ = detected but not quantifiable.

Stream	Group	Area (km^2)	Max elev (m)	Slope (avg %)	Lake	Glacier (% area)	Wetland (% area)	[a]Q ($m^3\ s^{-1}$)	Temp (°C)	pH (units)	SO_4^{2-} (mg L^{-1})	NO_3^- (mg L^{-1})	DOC (mg C L^{-1})	[b]HPOA DOC (mg C L^{-1})	[c]UVA (cm^{-1})	[d]SUVA (L/mg/cm)
Stonefly	G	13.2	693	17.3	Yes	31	2.1	1.3	10.6	8.04	10.63	0.24	1.00	0.31	0.037	3.7
Gull	G	5.7	213	8.8	Yes	1.5	11.9	0.33	13.5	8.29	13.47	0.08	1.20	0.52	0.034	2.7
Nunatak	G	38.0	1414	17.7	No	1.8	1.1	4.3	7.1	7.88	7.05	0.14	0.40	0.14	NQ	NQ
Reid	G	17.4	1271	18.7	No	5.0	1.9	6.1	5.3	7.89	5.32	0.16	0.40	0.13	0.011	2.5
Ice Valley	G	18.5	910	17.9	No	0.0	0.5	2.3	5.8	8.04	5.80	0.31	0.50	0.08	0.005	1.0
Vivid Lake	G	21.6	1265	24.2	No	0.0	0.0	3.9	5.8	7.93	5.82	NA	0.40	0.07	0.010	2.8
Taiya	G	466	1829	10.3	No	33	1.9	99	4.5	6.81	4.48	NA	0.8	NA	NA	NA
Skagway	G	376	2134	6.3	No	17	1.1	NA	6.9	6.76	6.91	0.17	1.2	NA	NA	NA
McGinnis	G	23	1449	13.8	No	4.0	2.0	NA	6.9	6.81	6.91	0.00	0.3	NA	0.004	1.3
Oystercatcher	RD	9.7	697	15.1	No	0	2.2	1.2	4.3	7.90	4.33	0.71	1.20	0.52	0.043	3.5
Fingers South	RD	17.0	939	20.6	No	0	0.3	3.5	7.5	7.54	7.54	0.67	1.20	0.42	0.027	2.3
Tyndall	RD	5.7	689	21.4	No	0	1.3	0.74	4.5	7.02	4.48	0.47	1.00	0.48	0.035	3.5
Berg Bay South	RD	18.7	755	15.4	No	0	16	NA	3.2	7.54	3.22	0.23	1.30	0.47	0.040	3.1
N. Rush Point	RD	5.2	639	15.4	No	0	1.6	3.1	4.9	7.77	4.86	0.07	1.10	0.38	0.023	2.1
Carolus River	WR	58.2	769	13.1	No	0	26	2.5	6.1	7.50	6.11	0.14	1.50	0.69	0.053	3.5
East Falls	WR	13.6	1023	15.3	No	0	18	0.91	6.5	7.85	6.54	0.02	1.10	0.47	0.039	3.5
Rink Creek	WR	5.9	284	8.4	No	0	69	0.16	10.2	7.66	10.18	0.11	5.10	2.70	0.203	4.0
E. Pleasant Is.	WR	4.6	188	2.6	Yes	0	67	0.02	12.7	6.46	12.68	0.09	12.00	8.16	0.597	5.0
W. Pleasant Is.	WR	4.3	168	4.1	No	0	47	0.01	12.4	7.11	12.37	0.13	10.80	7.24	0.532	4.9
Peterson	WR	24.1	308	6.3	Yes	0	53	NA	12.8	6.34	12.79	0.01	3.86	1.95	0.160	4.1
Fish	WR	35.6	487	7.1	No	0	30	NA	6.6	6.90	6.55	0.00	1.9	0.64	0.051	2.7

[a] Measured flow at time of sampling.
[b] Hydrophobic portion of DOC 0.035.
[c] UV-visible absorbance.
[d] UV absorbance at 254 nm normalized to DOC concentration.

Table 2
Total and methyl mercury in filtered water, particles, bed sediments, mayfly larvae (Baetidae and Heptageniidae, as dry weight concentrations), and juvenile coho salmon (wet weight) from the sample streams. BDL = below detection limit; NA = no sample collected; ND = no data (sample lost); NF = none found; IM = insufficient mass.

Stream	Filtered water		Particulates		Particulates		Bed sediment		Baetid mayflies		Hepta mayflies		Juv. Coho
	FHg_T (ng L^{-1})	FMeHg (ng L^{-1})	PHg_T (ng L^{-1})	PMeHg (ng L^{-1})	PHg_T (ng g^{-1}, dw)	PMeHg	SHg_T (ng g^{-1}, dw)	SMeHg	Hg_T (ng g^{-1}, dw)	MeHg	Hg_T (ng g^{-1}, dw)	MeHg	Hg_T (ng g^{-1}, ww)
Stonefly	0.47	0.02	0.97	0.01	33	0.4	6.8	0.05	IM	IM	NF	NF	5.2
Gull	0.39	0.04	0.20	0.02	130	10	11.1	0.44	22.2	14.5	NF	NF	4.2
Nunatak	0.08	0.01	0.19	<0.01	NQ	NQ	4.7	0.01	12.6	4.7	21.0	13.0	3.3
Reid	0.89	0.04	3.73	0.01	90	0.2	36.6	0.02	59.3	20.5	IM	IM	14.1
Ice Valley	0.22	0.10	0.11	<0.01	NQ	NQ	19.3	0.01	12.4	5.3	17.2	8.43	2.8
Vivid Lake	0.35	0.01	1.39	<0.01	145	BDL	40.8	0.02	31.7	10.1	NF	NF	3.4
Taiya	0.35	0.02	0.53	<0.01	*15*	0.2	3.0	0.02	41.6	24.5	48.2	28.7	1.7
Skagway	0.37	0.01	ND	0.01	BDL	BDL	1.7	0.02	21.5	10.7	36.2	21.2	3.1
McGinnis	0.29	0.02	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	9.0
Oystercatcher	0.84	0.06	0.13	<0.01	NQ	NQ	12.9	0.03	52.5	29.2	50.6	15.1	5.1
Fingers South	0.39	0.02	0.99	<0.01	45	BDL	NA	NA	19.5	7.1	51.1	9.5	2.5
Tyndall	1.28	0.03	0.07	<0.01	NQ	NQ	12.7	0.03	38.4	13.1	67.5	27.2	3.1
Berg Bay South	0.56	0.02	0.77	0.01	94	0.7	23.2	0.04	24.9	10.5	28.2	12.6	8.9
N. Rush Point	0.33	0.04	0.18	<0.01	NQ	NQ	22.3	0.1	36.3	27.6	57.6	38.4	3.4
Carolus River	0.42	0.02	0.26	0.01	108	2	22.2	0.01	29.3	19.1	44.8	21.5	13.4
East Falls	0.53	0.01	*0.09*	<0.01	NQ	NQ	112	0.05	36.5	19.0	64.8	20.5	3.5
Rink Creek	0.98	0.21	0.16	0.01	NQ	NQ	7.0	0.04	51.3	58.0	NF	NF	9.2
E. Pleasant Is.	3.37	0.09	0.17	0.01	NQ	NQ	16.4	0.04	IM	IM	55.2	26.6	13.9
W. Pleasant Is.	3.08	0.06	0.17	<0.01	NQ	NQ	13.7	0.06	IM	IM	52.8	39.2	5.6
Peterson	1.84	0.11	NA	NA	NA	NA	NA	NA	57.8	NA	98.5	NA	73.1
Fish	0.76	0.03	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	33.7

each site with a hand net or in baited minnow traps and also stored in small Teflon vials. All samples were double bagged, stored on ice, and handled by personnel wearing clean nitrile gloves. Sediment and biological specimens were frozen within 2 days.

2.4. Analytical methods for Hg

All Hg analyses were performed at the USGS MRL. Aqueous total Hg (Hg_T) analysis followed U.S. EPA Method 1631 (USEPA, 2002). Aqueous MeHg analyses were performed following standard distillation and ethylation procedures described elsewhere (Horvat and Bloom, 1993; DeWild and others, 2001) followed by analysis by cold-vapor atomic fluorescence spectrometry. Particulate, sediment, and biological tissue samples were analyzed for Hg_T and MeHg using the procedures described above, however, for each of these solid-phase samples a solubilization step was added. For Hg_T in sediments and particles, about 100 mg of homogenized, dried sample was digested in Aqua Regia (Olund and others, 2004). MeHg in sediment and particles was solubilized with methylene chloride and heat (DeWild et al., 2004). Fish and invertebrates were digested in Teflon bombs using a concentrated mixture of nitric and sulfuric acids (5/2 vol. to vol. ratio) and placed in an oven at 75 °C for 2 h. For MeHg solubilization of invertebrates, a weak nitric acid method was used and included the heating to 60 °C in an oven and subsequent neutralization with KOH (Hammerschmidt and Fitzgerald, 2006).

Reference materials for Hg_T were within 97–101% of the reported values for fish analyses, 85–93% for macroinvertebrates, 85–105% for particulates, and 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 relative standard deviation of triplicate sample analyses of Hg_T and MeHg in biological tissues averaged 2.3% and 9.4%, respectively. Each sample of aqueous Hg_T was run in duplicate, with an average difference of 1.8%. 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 range of 0.01–0.04 ng L^{-1}, and one measured slightly above, at 0.05 ng L^{-1} for Hg_T, and representing a negligible contribution to sample concentrations.

2.5. Analysis of other parameters

DOC was measured using the platinum catalyzed persulphate wet oxidation method on an O.I. Analytical Model 700 TOC Analyzer at the USGS National Research Program laboratory in Boulder, CO within two days of receipt (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. Specific ultraviolet absorbance (SUVA (Weishaar and others, 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. The DOC in each sample was also chromatographically fractionated using Amberlite XAD-8 and XAD-4 resins (Aiken and others, 1992) to measure the hydrophobic organic acid fraction (HPOA), which contains aquatic humic substances. Major ion concentrations were analyzed in Boulder using standard techniques (Fishman and Friedman, 1989).

2.6. Statistics

Evaluation of the differences among the three landscape categories was conducted using SPSS 17.0 software. The non-parametric Kruskal–Wallis test was selected due to the non-normal distribution of the data in each category, and the small sample size ($n = 9$, 5, and 7) of streams per category (G, RD, and WR). Pairwise multiple comparisons (using Dunn's method on ranked data) were conducted in SigmaPlot 12.0.

3. Results

3.1. Aqueous Hg

All streams sampled during the 2 week survey contained detectable filtered total Hg (FHg_T) ranging from 0.1 to 3.4 ng L^{-1} (median = 0.5 ng L^{-1}) (Table 2). Streams that receive runoff from glaciers (Category "G" streams) had among the lowest concentrations of FHg_T (0.1–0.9 ng L^{-1}). Median concentrations increased

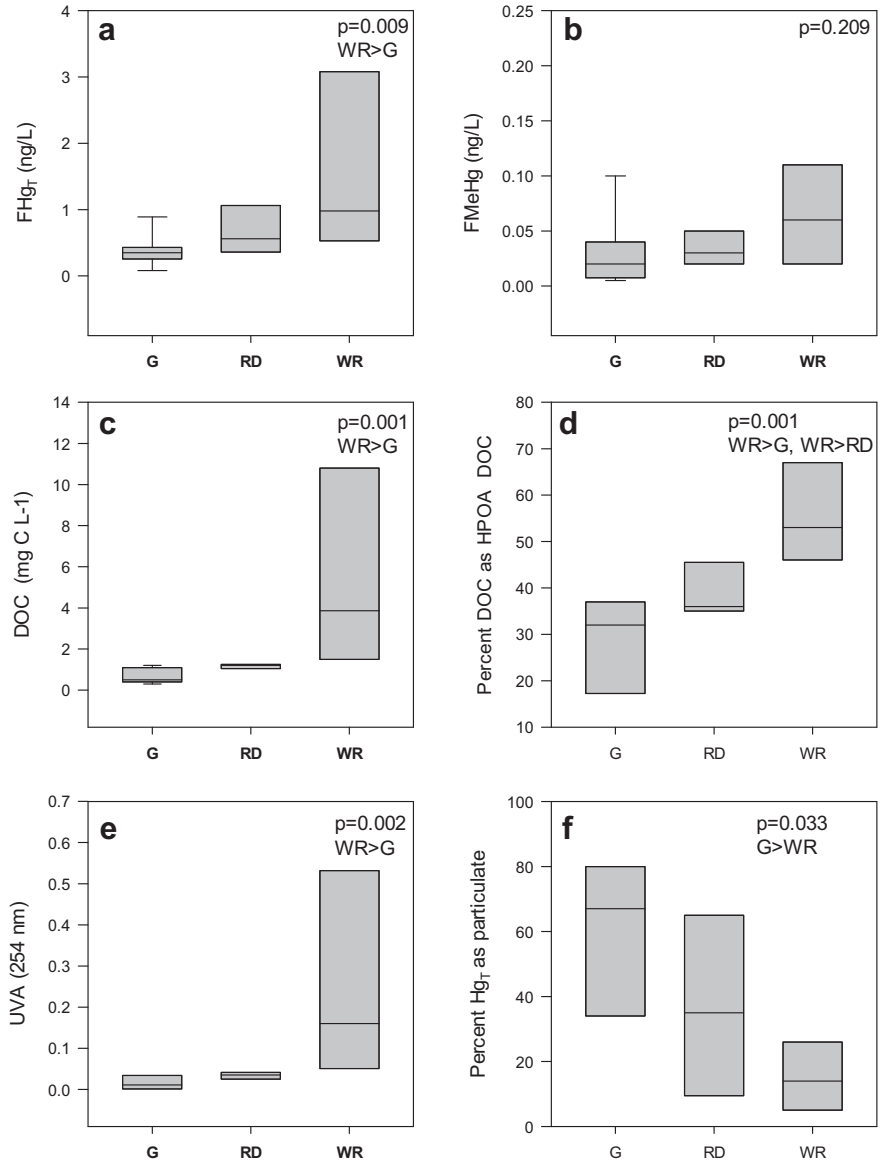

Fig. 2. Boxplots of (a) Filtered total mercury (FHg_T), (b) Filtered methylmercury (FMeHg), (c) Dissolved organic carbon (DOC), (d) Percent DOC occurring as hydrophobic organic acids (HPOA DOC), (e) UV absorption, (f) Percent of total mercury associated with filter-retained particles in the three watershed categories: Glaciated (G), Recently Deglaciated (RD), and Wetland-rich (WR). *p*-values are results of non-parametric (Kruskal–Wallis) analyses of distributions among sites, followed by specification of significant differences between categories according to Dunn's test of multiple comparisons.

from 0.4 to 0.6–1.0 ng L^{-1} in the G, RD, and WR categories, respectively (Fig. 2a). Non-parametric pairwise multiple comparisons of FHg_T concentrations among the three landscape categories showed that concentration distributions in WR streams were significantly higher than in G streams ($p = 0.009$). FHg_T concentrations in the mature, peatland-dominated watersheds such as the two on Pleasant Island (3.1 and 3.4 ng L^{-1}) and in Peterson Creek (1.8 ng L^{-1}) were as much as 30 times higher than those in most of the G and RD streams. Across the sequence of watersheds, FHg_T showed strong and similar, positive linear correlations ($r^2 = 0.876$–0.884, $p < 0.001$) with DOC concentrations (Fig. 3a), HPOA concentrations, and UVA.

Although filtered methylmercury (FMeHg) concentration distributions were not statistically different by landscape group ($p = 0.209$; Fig. 2b), the highest concentrations occurred in the WR streams, and most FMeHg values in the G and RD streams were close to or below the limit of quantification (<0.01–0.04 ng L^{-1}). In the WR streams, FMeHg accounted for an average of 6%, and up to 21% (Rink Cr) of the filtered Hg_T. Across the sequence of watersheds, the percent wetland cover explained about half the variance of FMeHg concentrations ($r^2 = 0.512$, $p < 0.001$). This relationship shows no correlation in watersheds with <20% wetland cover but a much stronger linear regression considering only the WR watersheds ($r^2 = 0.754$, $p < 0.001$) (Fig. 3b).

3.2. Dissolved organic carbon

Similar to aqueous Hg, DOC concentrations in G and RD streams were relatively low (0.3–1.3 mg C L^{-1}) (Table 1). Streams with the highest DOC concentrations were those with the greatest wetland coverage: Rink (5.1 mg C L^{-1}), East and West Pleasant Island (12.0 and 10.8 mg C L^{-1}), and Peterson (3.9 mg C L^{-1}). The median concentration (1.95 mg C L^{-1}) of HPOA DOC in all WR streams was 14 times higher than in the G group (0.14 C L^{-1}) and 4 times higher

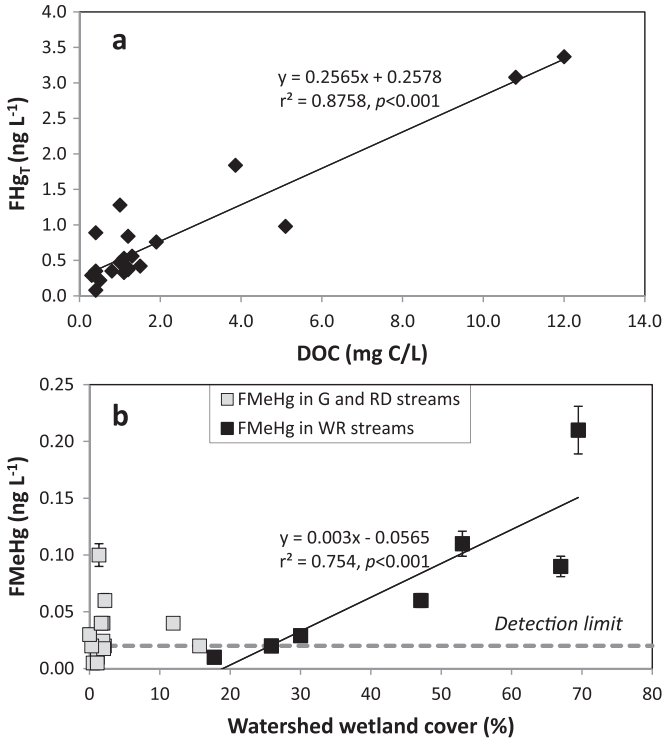

Fig. 3. Linear regression of (a) dissolved organic carbon vs filtered total mercury (FHg_T) and (b) Watershed wetland cover vs. filtered methylmercury (FMeHg) in the sampled streams. The regression line in (b) is fitted only to the wetland-rich (WR) streams.

than in the RD streams (0.47 C L^{-1}). The percentage of the DOC occurring as HPOA DOC was also highest in the WR streams (median 26% in G, 36% in RD, and 50% in WR streams). Predictably, UVA in the streams increased with watershed age, with median values of 0.011, 0.035, and 0.160 in the G, RD, and WR groups, respectively. Moreover, the DOC was generally more aromatic in the WR streams, with SUVA values in 4 of the 7 streams exceeding 4.0. Differences in distributions among the 3 landscape categories for DOC and HPOA concentrations, UVA, and the percent of DOC occurring as HPOA were statistically significant ($p < 0.002$; Fig. 2c, d and e).

3.3. Mercury in particles and streambed sediments

Total Hg in the particulate fraction (PHg_T) was detected (with a maximum of 3.7 ng L^{-1}, Reid Creek) in all streams with available samples. Conversely, particulate MeHg (PMeHg) was at or below the quantification limit (0.01 ng L^{-1}) in all streams except Gull Creek in upper Glacier Bay (Table 2). The PMeHg concentration in Gull Creek (0.02 ng L^{-1}) accounted for 10% of the total particulate Hg at the site. All other G and RD streams had no more than 1% of the total particulate Hg occurring as MeHg. Of the three WR streams with detectable PMeHg, the methyl fraction comprised 4–6% of the total.

The partitioning of Hg_T between the suspended particulate and filtered water column fractions was significantly different among landscape groups ($p = 0.033$). In the G streams, the majority (median 70%) of the Hg_T occurred in the particulate fraction, while in the RD streams only 35% did, and in the WR streams the percent associated with particles was only 14% (Fig. 2f).

Sediment MeHg (SMeHg) comprised <1% of the total sediment Hg at all sites except for Gull Creek, where the MeHg fraction was 4% of the total and its concentration (0.44 ng g^{-1}) was 4–40 times higher than any of the other samples (0.01–0.1 ng g^{-1}). The lowest SHg_T concentrations were found in the Taiya and Skagway Rivers (1.7–3.0 ng g^{-1}) and the highest (112 ng g^{-1}) came from East Falls Creek. Significant differences were not detected in the concentration distributions of particulate Hg and bed sediments by landscape category ($p > 0.018$).

3.4. Mercury in benthic macroinvertebrates

Baetidae and Heptageniidae mayfly larvae were present and in sufficient abundance to meet minimum sample mass requirements in most but not all of the targeted study streams. Baetid mayfly taxa included *Baetis bicaudatus* and *Baetis tricaudatus*; Heptageniid mayfly taxa included *Rhithrogena* sp., *Cinygmula* sp., and *Epeorus grandis*, *Epeorus deceptivus*, and *Epeorus longimanus.* Not all taxa were found in every stream. The Heptageniidaes (scrapers) consistently had higher mean concentrations of both MeHg and Hg_T than the Baetidae (gatherers), with 21 vs 14 ng g^{-1} dry weight (dw) for MeHg, and 51 vs. 34 ng g^{-1}(dw) for Hg_T, respectively (paired *t*-tests, $p < 0.001$). The MeHg fraction in the larvae varied widely across the sites, ranging from 19 to 100% of Hg_T, and averaging 49% and 53% for the Heptageniidae and Baetidae, respectively.

Despite upward trends of MeHg and Hg_T in both mayfly taxa from the G to WR groups, a significant difference was found only for the Heptageniidae Hg_T by landscape category ($p = 0.046$; Fig. 4a–d). Additionally Hg_T in the Baetidae correlated significantly with FTHg ($r^2 = 0.564$, $p < 0.001$, $n = 16$), and MeHg in the Baetidae with FMHg ($r^2 = 0.562$, $p = 0.001$, $n = 15$).

3.5. Mercury in fish

We collected young-of-the-year coho salmon in all study streams. Mean fork length was 33 mm ($\sigma^2 = 2$ mm). These salmon contained between 1.7 and 73 ng g^{-1} wet weight (ww) Hg_T, with a median of 5.1 ng g^{-1} (Table 2). The Taiya River coho had the lowest Hg_T (1.7 ng g^{-1}), while Peterson and Fish Creek had the highest (73 and 34 ng g^{-1}, respectively). In Glacier Bay area watersheds with the highest wetland cover (Pleasant Island streams and Rink Creek), median Hg_T in coho (5.6–13.9 ng g^{-1}) was approximately double the concentrations found in most G and RD streams. However, one G stream sample (Reid Creek) had the highest Hg value (14.1 ng g^{-1}) of all Glacier Bay streams. Comparisons of Hg_T in fish samples by landscape category indicate a significant difference among the three groups, with coho from WR streams having higher Hg than those from both the G and RD watersheds ($p = 0.021$) (Fig. 4e).

3.6. Aqueous Hg during and after salmon spawning

Following the main sampling survey, the Juneau-area streams were resampled for water both during and after salmon spawning. Spawner density at Peterson and Fish Creeks have been reported to be 0.53 and 0.14 spawners m^{-2}, respectively (Chaloner and others, 2004), and our visual estimate of the spawner density at McGinnis was at least an order of magnitude lower, with very few visible fish.

Filtered Hg_T and MeHg in both Peterson and Fish Creeks doubled between the pre-spawn and spawning period, with MeHg at Peterson reaching 0.24 ng L^{-1}, the highest value in our study (Table 3). After spawning, MeHg in Peterson dropped to 0.08 ng L^{-1}, although Hg_T remained at the during-spawn level of 5 ng L^{-1}, which was the highest Hg_T detected in all our stream samples. In Fish Creek, MeHg concentrations dropped in the post-spawn sample (0.08–0.01 ng L^{-1}). In salmon-poor McGinnis Creek, there was essentially no change in MeHg concentrations (Table 3).

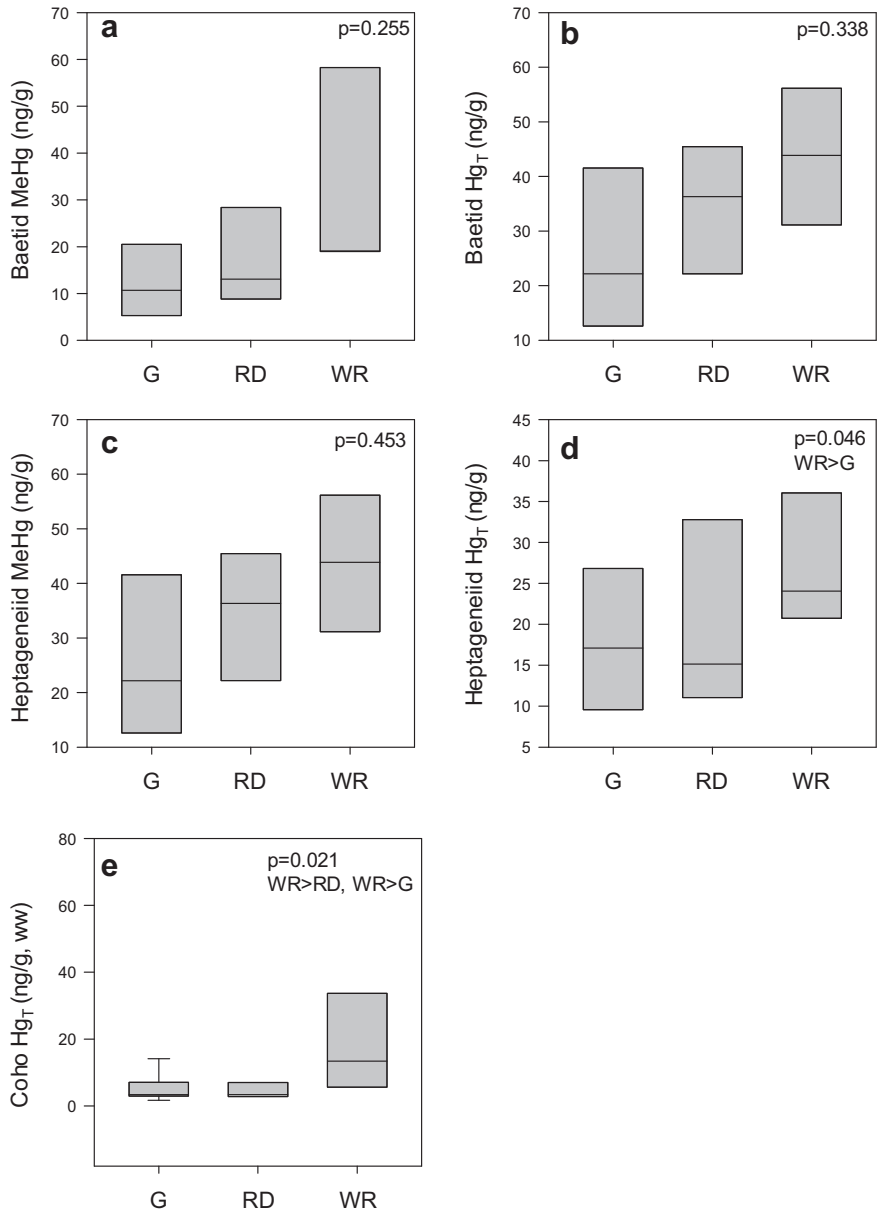

Fig. 4. Boxplots of (a) Methylmercury (MeHg) in Baetidae larvae, (b) Total mercury (Hg_T) in Baetidae larvae, (c) MeHg in heptageniidae larvae, (d) Hg_T in heptageniidae larvae, (e) Hg_T in young-of-the-year coho salmon in the three watershed categories: Glaciated (G), Recently Deglaciated (RD), and Wetland-rich (WR). *p*-values are results of non-parametric (Kruskal–Wallis) analyses of distributions among sites, followed by specification of significant differences between categories according to Dunn's test of multiple comparisons.

4. Discussion

4.1. Landscape controls on stream Hg

Our results show that in southeastern Alaska, landscapes across a chronosequence of deglaciation vary in their sensitivity to Hg contamination in a largely predictable manner. In general, glacier-fed watersheds, with thin, unweathered soils; exposed bedrock; shifting, dynamic stream channels; and low DOC appear to have little ability to methylate Hg. As found in glacier runoff elsewhere (St. Louis and others, 2005), Hg largely occurs in association with particles in these streams carrying high suspended loads. MeHg concentrations were very low (near or below detection) in water samples from the G and most RD watersheds. In most cases, Hg was low in particles, mayfly larvae, and juvenile fish in these streams as well. In contrast, watersheds with substantial wetland coverage contained higher streamwater Hg concentrations, a much greater proportion of Hg in the filtered phase compared with the particulate fraction, and higher Hg levels in biota. These results are similar to the findings by many other studies that report strong relationships between MeHg concentrations in stream biota and watershed wetland coverage (Brigham and others, 2009; Chasar and others, 2009; Shanley and others, 2012). The significant association between MeHg in Baetidae mayflies with MeHg in water indicates that the biotic uptake of MeHg may be tied to streamwater concentrations, as shown by Chasar and others (2009).

Numerous studies, including those in northern latitudes, have shown that the conversion of inorganic Hg to MeHg depends greatly on the presence of organic-rich wetlands, which support sulfate-reducing bacteria that methylate Hg (Ullrich and others, 2001; Tjerngren and others, 2012). Wetlands also provide an abundance of dissolved organic matter, which stimulates microbial

Table 3
Total and methyl Hg concentrations in water samples from Juneau-area streams before, during, and after salmon spawning. N.D. = none detected. Discharge at Montana Creek (non-glacial watershed that McGinnis Creek feeds into) measured by USGS and provided for context of local flow conditions.

	Stream	Spawnerdensity (relative)	Date	Q at Montana Cr $m^3 s^{-1}$	FHg_T ($ng L^{-1}$)	FMeHg ($ng L^{-1}$)
Pre-spawn	Peterson	N.D.	6/26/2007	2.32	1.8	0.11
	Fish	N.D.	6/28/2007	2.49	0.8	0.03
	McGinnis	N.D.	6/28/2007	2.49	0.3	0.02
Spawning	Peterson	High	8/27/2007	1.78	5.0	0.24
	Fish	Moderate	8/28/2007	1.50	1.5	0.08
	McGinnis	Very low	8/29/2007	1.53	0.3	<0.01
Post-spawn	Peterson	N.D.	10/10/2007	4.08	5.1	0.08
	Fish	N.D.	10/11/2007	4.08	N/A	0.01
	McGinnis	N.D.	10/9/2007	3.23	0.5	<0.01

activity and Hg methylation, complexes and mobilizes MeHg, and transports it downstream (Driscoll and others, 1998; Graham and others, 2012). Streams with elevated HPOA concentrations and $SUVA_{254}$ are especially effective at binding Hg and facilitating its transport (Thurman, 1985; Hall and others, 2008; Dittman and others, 2010). Therefore, wetland-rich watersheds typically act as net sources of MeHg to downstream aquatic systems (Porvari and Verta, 2003; Wiener and others, 2006). This appears to hold true in our study region, where streams draining peatlands have higher levels of total and methyl Hg in their waters than do neighboring watersheds where much of the streamflow is sourced from snow and glacial melt.

However, exceptions to this pattern were present; for example, the highest Hg_T concentration in Baetidae larvae and in juvenile coho in the Glacier Bay samples came from a turbid stream receiving glacial runoff (Reid Cr; Tables 1 and 2). Furthermore, another young, glacially influenced stream (Gull Cr) had anomalously high bed sediment and suspended particulate MeHg. In these streams, elevated MeHg may be derived from various unidentified instream methylating agents such as algal autotrophs (Tsui and others, 2009), and/or as discussed below, inputs by colonizing salmonids.

4.2. Potential role of salmon as additional Hg contributors

Although most sampling for this project occurred prior to the arrival of adult spawners, a set of likely salmon signatures emerged in the dataset. First, the highest PMeHg and relatively high SMeHg concentrations were in Gull Creek, which had by far the highest abundance of multiple species of juvenile salmon and benthic macroinvertebrates encountered in our study and a thick coating of filamentous algae on the streambed. Previous work has demonstrated the strong influence of marine-derived nutrients from decaying salmon carcasses on the nutrient budget in this (Milner and others, 2000) and other streams' food webs (Wipfli and others, 1998). These conditions may be supporting the dense growth of streambed algae, which may in turn be efficient sites of in-stream Hg methylation (Tsz Ki Tsui and others, 2009). Carcasses from previous seasons in the riparian zone or in the upstream lake may be an important local source of MeHg (Sarica and others, 2004; Sarica and others, 2005; Baker and others, 2009).

Secondly, concentrations of Hg in the juvenile coho from Peterson and Fish Creeks (at 73 and 34 ng g^{-1}) were vastly higher than in coho from all other watersheds (mean 6.2 ng g^{-1}), including other wetland-rich streams (mean 10.0 ng g^{-1}) that had higher DOC concentrations. The other WR streams sampled host relatively few salmon and then only in the lowest reaches, whereas both Peterson and Fish Creeks support hatchery-augmented, dense salmon runs. Studies on Peterson and Fish have shown that epilithon and some epilithic macroinvertebrates are stimulated by the presence of salmon spawners, and that nutrients from decaying salmon carcasses directly benefit multiple species of consumers (Chaloner and others, 2004; Heintz and others, 2010). Thus, the contribution of salmon-derived MeHg to the aquatic food webs in these streams may account for the relatively high Hg values in their juvenile coho. It may also explain why Peterson had the highest concentration of Hg_T in Heptageniidae larvae and the second highest in Baetidae larvae of all the study streams.

Finally, the increase in FHg_T and FMeHg concentrations in Peterson and Fish Creeks during active salmon spawning indicates that carcasses may also be contributing Hg to the water column. Although our few samples cannot conclusively make this connection, the coincidence of the concentrations with the salmon timing is worthy of further exploration. Moreover, the elevated post-

Table 4
Mercury concentrations in benthic macroinvertebrates (including or limited to mayfly larvae) and in juvenile coho and similarly sized or aged taxa as reported in other studies.

Location	Reference	Taxa, age	Hg_T ($ng g^{-1}$, dw)
Benthic macroinvertebrates			
Southeast Alaska	Current study	Heptageneiid mayflies	17–99
Southeast Alaska	Current study	Baetidae mayflies	12–59
OR, WI, FL	Chasar et al., 2009	Various macroinvertebrates	5–183
Sherman Cr., AK	Aquatic Science, 2001	EPT taxa	40–60
Willamette R., OR-Mined	Henny et al., 2005	EPT taxa	48–198
Willamette R., OR-Reference	Henny et al., 2005	EPT taxa	19
Slovenia-Mined	Zizek et al., 2007	Mayflies	29,800
Slovenia-Reference	Zizek et al., 2007	Mayflies	86
Northern California	Tsui et al., 2009	Heptageneiid mayflies	63–265 (MeHg)
Western Maryland	Castro et al., 2007	Heptageneiid mayflies	50–200
Ontario lakes-Near smelters	Belzile et al., 2006	Heptageneiid mayflies	50–419
Fish			
Southeast Alaska	Current study	Juvenile coho, age 0+	2–73
Innoko NWR, AK	Mueller and Matz, 2002	Juvenile coho	40
Kuskokwim area, AK	Gray et al., 1996	Juvenile coho	70
Illinois Cr., AK	Winters, 1996	Juvenile coho, age 0+, 1+	12–28[a]
Voyageurs NP, MN	Wiener et al., 2006	Yellow perch, age 1	36–190[a]
Columbia River, OR	Webb et al., 2006	Juvenile sturgeon	34 ± 3
Cook Inlet region, AK	Frenzel, 2000	Adult slimy sculpin	16–42[a]
Throughout Alaska	ADEC, 2007	Adult coho	37

[a] Reported as dry weight and converted to wet weight assuming 20% solids.

spawning concentrations of Hg_T in Peterson may be explained by the release of Hg with nutrients from salmon carcasses in the riparian zone after spawning ended (Fellman and others, 2008).

4.3. Comparisons with standards and other studies

The range of FHg_T concentrations in our study streams overlaps closely with that in a nation-wide survey of a variety of streams (Brigham and others, 2009). DOC values in the WR streams were generally high, with $SUVA_{254}$ values comparable to those from blackwater streams in the southeastern U.S. (Spencer et al., 2012). However, average values of both SHg_T and SMeHg were about an order of magnitude lower than those from a national survey of 345 non-randomly selected streams across the USA (excluding Alaska) (Scudder and others, 2009). Hg concentrations in mayfly larvae and juvenile coho salmon from our study fell largely in the low to mid-range for similar taxa in other locations (Table 4). Juvenile coho salmon from Fish and Peterson Creeks had Hg concentrations equal to or double concentrations in adult coho from throughout coastal Alaska (ADEC, 2007), although growth dilution in expected (Baker and others, 2009).

Concentrations of FHg_T in streamwater were well below USEPA levels of concern for human health and aquatic organisms (USEPA, 2013), and streambed sediment Hg was below the consensus-based threshold and probable effect concentrations for all samples (MacDonald et al., 2000). All of the juvenile coho met a USEPA standard of 100 ng g^{-1} (ww) for the protection of piscivorous birds and mammals (Eisler, 2000), although the sample from Peterson approached the limit with 73 ng g^{-1}.

5. Conclusions

Although the 21 watersheds included in this study were sampled only once, the landscape patterns we found are consistent and compelling, especially considering such spot sampling likely subsumes a great deal of hydrological and biological variability. Our data suggest that variations in Hg concentrations in water, sediment, and biota are products of some combination of landscape characteristics in the basin, the magnitude of inputs by anadromous fish, and in-stream biogeochemical processes that may facilitate the conversion of Hg to MeHg. Levels of MeHg in biota were generally higher in wetland-rich watersheds, but streams with high density salmon returns, including those still influenced by glaciers, are also likely sites of elevated Hg. In spite of the complexities, however, it appears that UVA may be used as an inexpensive surrogate for FHg_T concentrations in these watersheds, and mapped wetland coverage is a good predictor of FMeHg. Information on salmon spawner density should be evaluated as another potential tool for predicting watershed MeHg concentrations.

Further study of Hg in southeastern Alaskan aquatic food webs is warranted, particularly in light of rising Asian Hg sources, the prevalence of streams used by salmon, and the abundance of peatlands. Additionally, the ongoing rapid loss of glacier ice (Larsen and others, 2007) is expected to increase forest and wetland landcover and the export of DOC in streams (Hood and Scott, 2008). Alongside DOC, MeHg export from wetlands to streams and from streams to estuaries is likely on the rise as well. The potential flux of MeHg out of this region is particularly high given that: (1) storm-driven riverine specific yields of DOC from forested watersheds in southeastern Alaska are among the highest ever measured (Fellman and others, 2009) and (2) the annual land-to-ocean flux of water is similar in volume to the annual discharge of the Mississippi River (Neal and others, 2010). Storms were not sampled in this study, but other researchers have found that Hg export from watersheds is disproportionately high during episodic events (Babiarz and others, 1998; Shanley and others, 2008). Detailed chronicles of Hg on storm, seasonal, and annual scales would help explain landscape and biotic processes controlling the release and form of Hg. As atmospheric mercury deposition rises and landscapes evolve in a warming climate, the interplay of lower within-watershed methylation potential in glacierized watersheds with rapid recolonization by salmonids and expansion of forests and wetland environments creates a changing mosaic of regional mercury sensitivity.

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