

LIMNOLOGY AND OCEANOGRAPHY

July 2004
Volume 49
Number 4

Limnol. Oceanogr., 49(4), 2004, 891–899
© 2004, by the American Society of Limnology and Oceanography, Inc.

Salmon-derived mercury and nutrients in a Lake Ontario spawning stream

José Sarica

Institut National de la Recherche Scientifique (INRS), Eau, Terre et Environnement, Université du Québec, 2800 rue Einstein, C.P. 7500, Sainte-Foy, Québec G1V 4C7, Canada

*Marc Amyot*¹

Département des sciences biologiques, Université de Montréal, C.P. 6128, succ. Centre-Ville, Montréal, Québec H3C 3J7, Canada

Landis Hare and Marie-Renée Doyon

Institut National de la Recherche Scientifique (INRS), Eau, Terre et Environnement, Université du Québec, 2800 rue Einstein, C.P. 7500, Sainte-Foy, Québec G1V 4C7, Canada

Les William Stanfield

Ontario Ministry of Natural Resources, Picton, Ontario K0K 2T0, Canada

Abstract

We tested the hypothesis that concentrations of mercury species (Hg) and nutrients (NH_4^+ , NO_3^- , P, and dissolved organic carbon) in abiotic and biotic components would be altered by the decomposition of salmon carcasses in streams. We investigated a tributary stream of Lake Ontario receiving spawning runs of Chinook salmon (*Oncorhynchus tshawytscha*) for 2 yr with contrasting bear activity. Stations with high carcass densities had significantly higher levels of aqueous total Hg, methylmercury (MeHg), particulate Hg, and nutrients than did stations with lower carcass densities. Hg levels in aquatic and terrestrial invertebrates feeding on carcasses increased by up to 25-fold. In 2001, a bear removed most carcasses at the downstream station, and aqueous Hg and nutrient concentrations were significantly lower than during the preceding year, when no bear was active at that station. A preliminary budget for this stream shows that (1) salmon carcasses can be an important source of Hg and nutrients to aquatic and terrestrial food webs, and (2) terrestrial invertebrates and vertebrates can be important water-to-land vectors of Hg.

In North America and Scandinavia, mercury (Hg) is present in some native fish at unacceptably high concentrations ($>0.5 \text{ mg kg}^{-1}$ wet weight; Ontario Ministry of the Environment 1999). Because methylmercury (MeHg) concentra-

tions increase along aquatic food chains, most of the MeHg in the water columns of lakes tends to be present in fish (Porcella 1994). In spite of the importance of fish as an MeHg sink, processes involved in the recycling of MeHg following fish death are little known. Most Pacific salmon species, including Chinook salmon (*Oncorhynchus tshawytscha*), die after spawning, resulting in a great number of fish carcasses in receiving streams (Cederholm et al. 2000). Studies have concluded that salmon carcasses, eggs, and gametes can contribute nutrients and dissolved organic carbon (DOC) to streams (Cederholm et al. 1999), resulting in the stimulation of primary production (Cederholm et al. 2000), heterotrophic activity (Sobczak 1996), and secondary production (Cederholm et al. 2000). These increases in primary and secondary production can result in aquatic invertebrate densities 25-fold higher in streams receiving Pacific salmon runs than in other streams (Wipfli et al. 1998). Salmon carcasses

¹ Corresponding author (m.amyot@umontreal.ca).

Acknowledgments

Special thanks to B. Anderson and her pupils from Wilmot Creek School and to S. Marriott and her pupils from Trinity College. J. Laroulandie, X. de Rouvroy de Saint-Simon, provided technical assistance in the field. D. Lean and J. Holmes helped with MeHg analysis, and M. G. Bordeleau, P. Fournier, S. Saint-Pierre, and S. Duval performed nutrient analysis. I. D. Cameron and F. Smith from the Ontario MNR provided discharge data. F. Boudreau, G. Cabana, C. Gobeil, M. Lucotte, R. Schetagne, and A. Tessier reviewed an earlier version of the manuscript. We gratefully acknowledge financial support from NSERC, COMERN, and FQRNT to M.A. J.S. was supported by a scholarship from INRS.

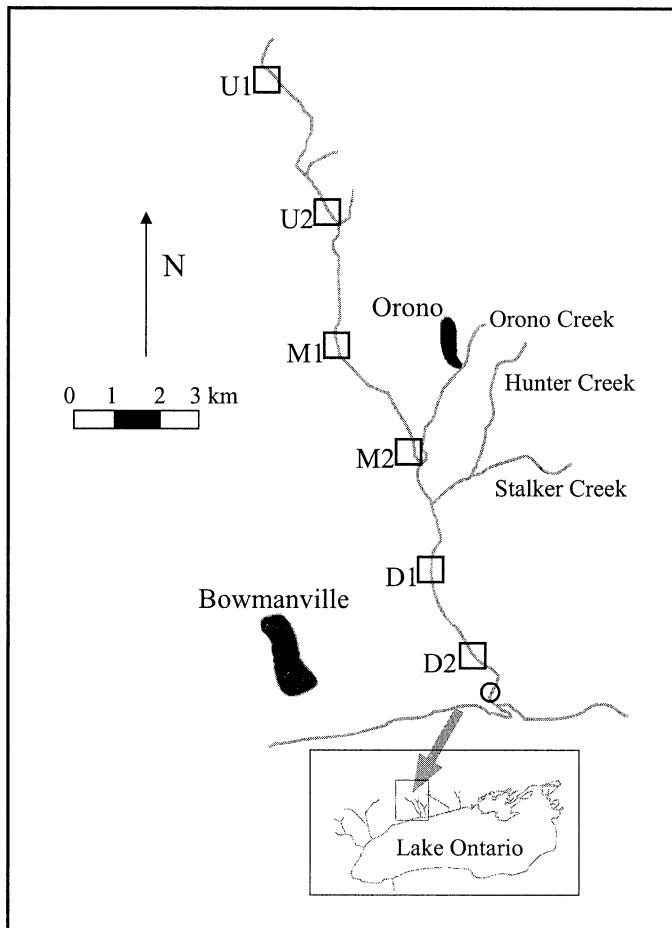


Fig. 1. Location of Wilmot Creek (43°59'N, 78°38'W) and our six sampling stations (U1, U2, M1, M2, D1, and D2). The open circle at the mouth of the stream indicates the location where the discharge was measured. Redrawn from Gibson (unpubl. data).

influence invertebrate densities through changes in the quantity or quality of biofilm for scrapers, of fine particulate organic material for collectors, of coarse particulate organic material for shredders, and of invertebrates for predators (Chaloner and Wipfli 2002). Recently, Krümmel et al. (2003) demonstrated that, after spawning, sockeye salmon (*Oncorhynchus nerka*) can assimilate polychlorinated biphenyls (PCBs) from the ocean and deliver these contaminants to their natal spawning lakes. Indeed, these authors reported that sedimentary PCB concentrations were strongly correlated with the density of salmon runs.

We tested the hypothesis that salmon carcasses can also be an important source of Hg to streams receiving Chinook salmon runs from Lake Ontario. We considered the impact of fish decomposition on Hg levels in both abiotic (sediment and water) and biotic (invertebrates feeding on carcasses) compartments in one of those streams, Wilmot Creek. Furthermore, we were able to compare Hg transfer between the aquatic and terrestrial environment at one site in the presence and absence of bear consumption, as during the second year of our study, a black bear took up residence in the lower reaches of our study stream.

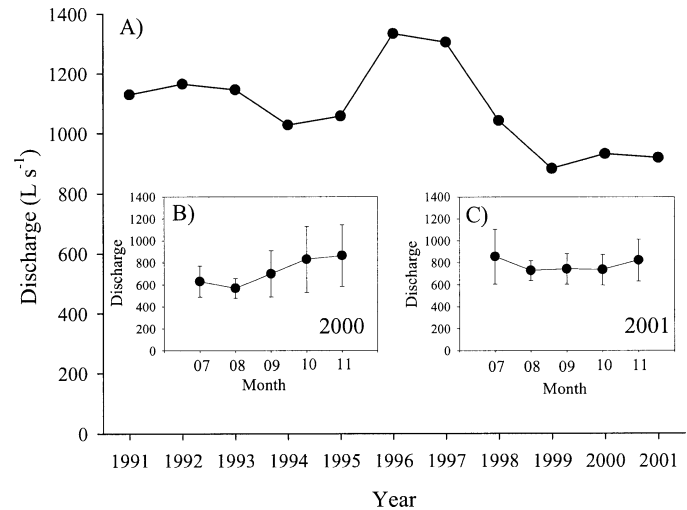


Fig. 2. (A) The yearly mean discharge ($L s^{-1}$) of Wilmot Creek from 1991 to 2001 as well as its monthly mean ($\pm SD$) discharge ($L s^{-1}$) measured in (B) 2000 and (C) 2001.

Materials and methods

Study design—In the first year of our study, we used a control-impact design, in which control sites were (1) upstream sites in Wilmot Creek where no salmon spawned or died; or (2) a site in a neighboring stream similar to Wilmot Creek but in which few salmon spawned. The second year, we added a temporal component to our sampling protocol by sampling sites in Wilmot Creek before and after the spawning of Chinook salmon.

Study site—Wilmot Creek (43°59'N, 78°38'W; Fig. 1) is a cold-water stream that drains into Lake Ontario approximately 22 km downstream of its origin. The mean width is 7 m (Gibson unpubl. data). The most abundant migratory piscivorous fish in Wilmot Creek is the Chinook salmon, of which approximately 20,000 spawn in the autumn of each year (Stanfield et al. unpubl. data).

We selected six sampling stations along this creek (Fig. 1). Each sampling station corresponded to a stretch of 250 m. Stations “upstream 1” (U1), “mid-stream 1” (M1), and “downstream 1” (D1) were sampled in 2000 after Chinook spawning (20 October). These stations were sampled again in 2001 before (20 August) and after (26 October) Chinook spawning with three additional stations, that is, “upstream 2” (U2), “mid-stream 2” (M2), and “downstream 2” (D2). Chinook can usually reach Sta. M1, whereas few salmon were observed upstream of this site (i.e., at U1).

The discharge of Wilmot Creek was measured between Sta. D2 and the creek mouth by the Ontario Ministry of Natural Resources (Fig. 1). Although it varied between 882 and 1,334 $L s^{-1}$ from 1991 to 2001 (Fig. 2A), stream discharge was similar for our two sampling periods (summer and fall 2000: $740 \pm 140 L s^{-1}$; summer and fall 2001: $765 \pm 219 L s^{-1}$; Fig. 2B,C).

In 2000, we also sampled a second watercourse, the Ganaraska River (GR), which is located 20 km east of Wilmot Creek. This stream receives few salmon. We collected sam-

ples at a station (GR) located 10 km upstream from the mouth of this river.

Sampling and analysis—The following paragraphs outline our methods of sampling and analysis.

Aqueous Hg: All sampling bottles and laboratory glassware were washed in 15% HNO₃, followed by 1% HCl, and were then rinsed seven times in ultrapure water (Milli-Q system water, >18 Mohm cm⁻¹) while the technician wore unpowdered latex gloves. To obtain samples for total aqueous Hg, we filled five 60-ml Teflon bottles with creek water at each sampling station in each year. For the analysis of dissolved Hg ([Hg]_D) and particulate Hg ([Hg]_P), we collected water in three 60-ml Teflon bottles at each station in 2001 both before and after spawning. Samples for the analysis of total [MeHg]_(aq) were collected in four Teflon bottles (1 liter each) at each station in 2001, preserved with HCl (5% [v/v]), and held in the dark.

We determined total Hg and Hg_D (quartz microfiber-A [QM-A] filters, pore size = 0.7 μm) concentrations in water following method 1631 (revision D) from the U.S. Environmental Protection Agency (2001). Briefly, BrCl oxidation is followed by hydroxylamine addition, reduction with SnCl₂, sparging of elemental Hg to gold amalgamation traps, thermal desorption of the Hg, and finally, detection using atomic fluorescence spectrometry with a Tekran 2600 (the detection limit, estimated as 3 times the standard deviation of 10 blanks, was 60 pg L⁻¹). Samples of interlaboratory reference material diluted 50-fold (rainwater, FP-HG77-5 and FP-HG77-2, Environment Canada; mean ± SD certified values = 2.22 ± 0.08 and 0.11 ± 0.04 ng L⁻¹, respectively) were submitted to the same measurement procedures; the concentrations of Hg in these standards varied little over time (mean ± SD measured values = 2.27 ± 0.06 and 0.13 ± 0.005 ng L⁻¹; C.V. = 2–4%) and were within the intercalibrated ranges. Blanks were also run, and no appreciable Hg contamination was detected.

For measurements of particulate Hg, we followed the procedure of Sarica et al. (2004). Briefly, water samples were passed through QM-A filters (pore size = 0.7 μm) in the field; then, the filters were freeze-dried (lyophilizer, FTS Systems) for storage. Total particulate Hg was measured with a direct Hg analyzer (DMA-80, Monroe) using thermal combustion (drying: 10 s at 160°C; thermal desorption: 150 s at 750°C). Samples of a certified reference material (oyster, National Bureau of Standards [NBS]-1566; mean ± SD certified values = 57 ± 15 ng g⁻¹ dry weight) were submitted to the same measurement procedures. The concentrations of Hg in these standards varied little over time (mean ± SD measured values = 67 ± 4.69 ng g⁻¹; C.V. = 7%) and were within the certified range. Blanks were also run, and no appreciable Hg contamination was detected. The detection limit of the DMA-80 was 0.01 ng of Hg.

MeHg_(aq) was preconcentrated and extracted following the procedure of Cai et al. (1997) using a gas chromatography–atomic fluorescence spectrometric system (model 5860, Hewlett Packard; detection limit = 0.02 ng L⁻¹). A standard MeHgCl stock solution was prepared by dissolving approximately 20 mg of MeHgCl (ACS reagent 99%, Aldrich) in

20 ml of methanol (ACS reagent 99.91%, EM Science) to yield a concentration of approximately 1,000 ppm MeHgCl as Hg. Further dilutions with water were made as needed. Recoveries from internal standard additions were within acceptable limits (i.e., >90%).

Hg in sediments: At each sampling station, four cores (4.4-cm diameter) were used to collect sediments at about 1 m from the shore. The uppermost centimeter was removed from each sediment core and frozen in a plastic container until total Hg analysis. Quality assurance/quality control (QA/QC) was assessed by using certified material (BEST-1, National Research Council of Canada [NRCC]; mean ± SD certified values = 92 ± 9 ng g⁻¹ dry weight; mean ± SD measured values = 86 ± 3 ng g⁻¹; C.V. = 3%).

Hg in fish, invertebrates, and biofilm: To assess the level of contamination of fresh carcasses, 10 salmon were captured by electrofishing, and samples of their dorsal muscle and livers were retrieved, placed in a plastic bag, and frozen until analysis.

Aquatic macroinvertebrates in the vicinity of the carcasses were collected with a Surber sampler until a sufficient biomass of invertebrates was obtained. Principal species of aquatic invertebrates were sorted to the lowest taxonomic level possible (Merritt and Cummins 1996; Wiggins 1996) and allowed to depurate for 48 h to eliminate Hg bound to gut contents. They were then placed on Teflon sheets in 1.5-ml high-density polyethylene microcentrifuge tubes (small invertebrates; Croteau et al. 2001) and frozen until Hg analyses. The four most abundant taxa collected were two caddisflies (*Hydropsyche* sp. and *Limnephilus* sp.), a tipulid (*Hexatoma* sp.), and a stonefly (*Claassenia* sp.). *Hydropsyche* feeds on algae, detritus, and animals; *Limnephilus* is a shredder that feeds on leaf litter; *Hexatoma* consumes oligochaetes and dipterans; and *Claassenia* feeds on trichopterans, ephemeropterans, and chironomids (Merritt and Cummins 1996). Terrestrial fly (Diptera: Calliphoridae) adults and larvae found on beached salmon carcasses were also collected, placed on Teflon sheets in 1.5-ml microcentrifuge tubes, and frozen. We also collected the biofilm growing on three submerged salmon carcasses. Samples were filtered with QM-A filters (pore size = 0.7 μm), and the filters were frozen until analysis.

For all biological samples, Hg concentrations were measured by direct combustion, using the same analytical protocol as for particulate Hg. QA/QC was assessed by using reference material for appropriate matrices: Hg concentrations in reference material varied little over time and were within the certified ranges (DORM-2, Environmental Chemistry Institute; mean ± SD certified values = 230 ± 50 ng g⁻¹ dry weight; mean ± SD measured values = 205 ± 21 ng g⁻¹; C.V. = 10%; TORT-1, NRCC, mean ± SD certified values = 330 ± 30 ng g⁻¹ dry weight; mean ± SD measured values = 325 ± 10 ng g⁻¹; C.V. = 3%; oyster, NBS-1566, mean ± SD certified values = 57 ± 15 ng g⁻¹ dry weight; mean ± SD measured values = 56 ± 2 ng g⁻¹; C.V. = 4%).

Carcass densities: To estimate carcass densities at each station in 2000 and 2001, flags were first attached on trees

along the shore every 50 m, over a distance of 250 m. Then, the numbers of submerged, half-submerged, and beached carcasses were counted. At the time the census was conducted, spawning had just ended; therefore, the total number of carcasses did not change during sampling.

Rate of carcass decay: A stretch of 250 m of the creek was intensively monitored (1) to determine the partitioning of carcasses based on their state of immersion (beached, half-submerged, and submerged), and (2) to estimate the decomposition time of carcasses. Twenty-eight carcasses present on this stretch of creek were monitored for 24 d, at which point all carcasses had completely decayed.

Water chemistry: Five high-density polyethylene bottles (250 ml) were filled with water at each station for $[\text{NH}_4^+]_{(\text{aq})}$, $[\text{NO}_3^-]_{(\text{aq})}$, and $[\text{P}]_{(\text{aq})}$ analyses. Nitrates were determined with method 300.0 from the U.S. Environmental Protection Agency (1993a) using ionic chromatography (DX300, DIONEX; detection limit = $0.02 \mu\text{g ml}^{-1}$) and an anionic column (AS14, DIONEX). Ammonium and total P were measured following U.S. Environmental Protection Agency methods 351.2 (1983) and 365.1 (1993b), respectively, by spectrophotometry (QuickChem FIA+ 8000, LACHAT instruments; detection limit for ammonium = $0.003 \mu\text{g ml}^{-1}$; detection limit for total P = $1 \mu\text{g ml}^{-1}$).

Four amber bottles filled with water were collected at each site to measure DOC. These bottles were pretreated by heating at 400°C in a combustion oven for 6 h and were rinsed with ultrapure ELGA water (Milli-Q system organofree, $>18 \text{ Mohm cm}^{-1}$). Total and dissolved organic carbon values (filtered with glass fiber filters [GF/F], pore size = $0.45 \mu\text{m}$) were determined with an organic carbon analyzer (TOC-5000A, Shimadzu; detection limit = 0.05 mg L^{-1}). In our study, $>90\%$ of the total organic carbon was dissolved. For this reason, only DOC concentrations are mentioned in this paper.

For all of these analyses, samples of a certified reference material were submitted to the same procedures; measured concentrations in the reference material varied little over time (ammonium: nutrients 2185, Belpre, mean \pm SD certified values = $5.53 \pm 0.05 \text{ mg-N L}^{-1}$, mean \pm SD measured values = $5.55 \pm 0.11 \text{ mg-N L}^{-1}$; C.V. = 2%; nitrates: rain-water, FP-73SW-7, mean \pm SD certified values = $2.1 \pm 0.1 \text{ mg L}^{-1}$, mean \pm SD measured values = $2.00 \pm 0.06 \text{ mg L}^{-1}$; C.V. = 3%; P: nutrients 2185 mean \pm SD certified values = $6.55 \pm 0.02 \text{ mg-P L}^{-1}$, mean \pm SD measured values = $6.54 \pm 0.19 \text{ mg-P L}^{-1}$; C.V. = 3%; organic carbon: DEMAND 42.02, Belpre, mean \pm SD certified values = $42.02 \pm 0.17 \text{ mg L}^{-1}$, mean \pm SD measured values = $41.94 \pm 1.26 \text{ mg L}^{-1}$; C.V. = 3%) and were within the certified range. Blanks were also run, and no appreciable contamination was detected.

Suspended particulate matter: Three 1-liter Teflon bottles were filled with creek water at each sampling station (before and after spawning in 2001) and then filtered on a preheated clean filter (GF/F, Whatman, pore size = $0.45 \mu\text{m}$). These filters were placed in a Teflon in-line filtration unit (series 47 filter holder, Saville), and water from each 1-liter bottle

was field pumped (Cansun) through the unit. Filters were then frozen for transport, freeze-dried, and reweighed to determine the weight of suspended particulate matter (SPM).

Fecal coliforms: To assess if our water chemistry data were biased by leaks from neighboring septic tanks, we measured fecal coliforms in the water. Four water samples were collected at each site in 2001 (before and after spawning), filtered on a sterile membrane (pore size = $0.45 \mu\text{m}$), and incubated for $24 \pm 2 \text{ h}$ at $44.5 \pm 2^\circ\text{C}$ on an m-Fc (membrane-fecal coliform) environment. The identification of fecal coliforms was confirmed by a negative reaction with cytochrome-oxidase, a positive reaction with ONPG (ortho-nitrophenyl- β -D-galactopyranoside) and with MUG (4-methyl-umbelliferyl- β -D-glucuronide). The detection limit of this method is 1 unit representing one colony. In our study, 80–100% of all fecal coliform colonies were made up of *Escherichia coli*. For this reason, we use the term *E. coli* to refer to fecal coliforms in water.

Results and discussion

Effect of carcass densities on Hg and nutrient concentrations in water and sediments—The smallest densities of salmon carcasses (Fig. 3, lowermost panels) were observed at the GR station in 2000 as well as at the Wilmot Creek upstream stations in both 2000 (U1) and 2001 (U1 and U2). After spawning in 2000, the highest density of salmon carcasses was observed at Sta. D1. In 2001, most carcasses disappeared from Sta. D1 (mostly as a result of bear activity), and the site with the highest density of salmon carcasses remaining was Sta. M1 (Fig. 3). Note that bears have been absent from this watershed for many decades and that the presence of bears in our study was exceptional.

Concentrations of total Hg, Hg_p , MeHg, DOC, P, NH_4^+ , NO_3^- , and SPM were significantly higher at stations of maximum carcass density than at other stations in both years (ANOVA, $p < 0.02$, $n = 15\text{--}30$; Fig. 3). Furthermore, in 2001, the concentrations of these substances were higher at Sta. M1 after spawning than before spawning (*t*-test, $p = 0.001\text{--}0.007$, $n = 6\text{--}10$; Fig. 2). When pooling all data (after spawning, both years), concentrations of these substances were positively correlated with carcass density ($r_s = 0.70\text{--}0.85$; $p = 0.003\text{--}0.035$; Fig. 4A–F). These results strongly indicate that salmon carcasses altered the water chemistry of the stream. Although similar nutrient increases at spawning stations have been reported previously (Cederholm et al. 1999, 2000), this is the first evidence of carcass-induced contamination of a stream by Hg. Note that interannual or monthly variations in stream hydrology are unlikely to explain these differences in water chemistry, since discharges varied little during the summer and fall of 2000 and 2001 (Fig. 2B,C).

The influence of carcasses on water chemistry is further evidenced by the fact that, after spawning, DOC and SPM were correlated to total and particulate Hg as well as MeHg, whereas no such correlation was observed before spawning (Fig. 5A–C). The presence of carcasses, a source of DOC and SPM, likely caused these positive correlations. Indeed, many studies have shown that salmon carcasses can provide

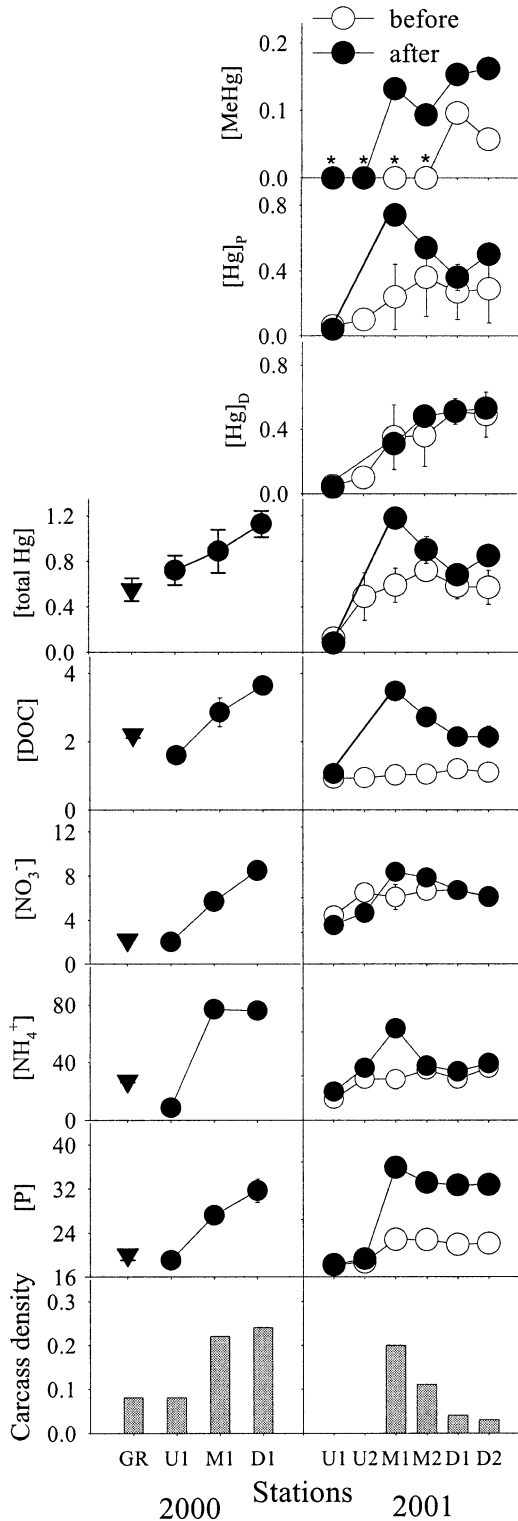


Fig. 3. Mean concentrations (\pm SD) of Hg (ng L^{-1}), DOC (mg L^{-1}), nitrate (mg L^{-1}), ammonium ($\mu\text{g L}^{-1}$), and P (mg L^{-1}) and the density of salmon carcasses ($\text{individuals m}^{-2}$) measured in the Ganaraska River (GR; inverted triangle) and at each station in Wilnot Creek in 2000 (left panel) and 2001 (right panel). Data were collected before and after spawning. * indicates data under the detection limit.

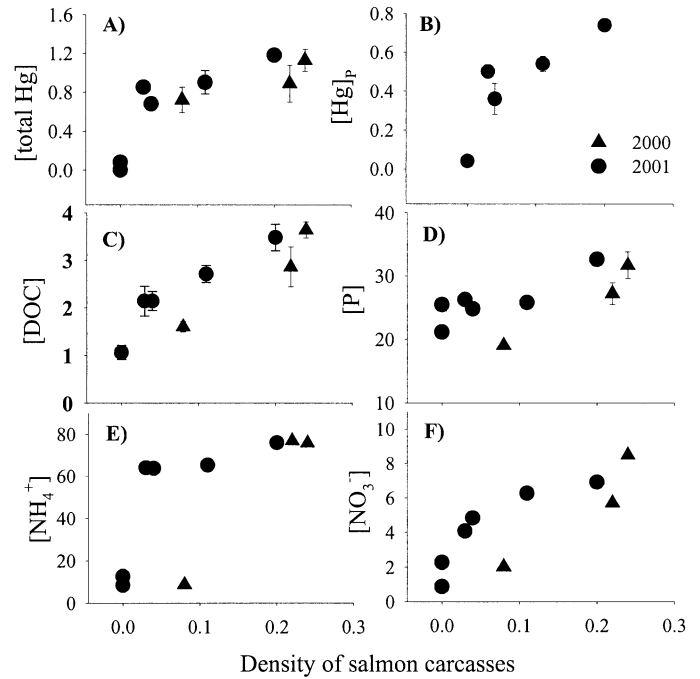


Fig. 4. Mean concentrations (\pm SD) of (A) total Hg (ng L^{-1}), (B) total particulate Hg (ng L^{-1}), (C) DOC (mg L^{-1}), (D) P (mg L^{-1}), (E) ammonium ($\mu\text{g L}^{-1}$), and (F) nitrates (mg L^{-1}) as a function of the density of salmon carcasses ($\text{individuals m}^{-2}$) in the stream after spawnings in 2000 and 2001.

an important source of allochthonous organic matter (Cederholm et al. 2000). For instance, Bilby et al. (1996) estimated that small salmon runs (approximately 1,000 individuals) can contribute 25–40% of allochthonous organic matter inputs to a given stream. Since measured densities of *E. coli* were not significantly different (paired *t*-test, $p > 0.05$) before and after spawning at all stations, these patterns in water chemistry were more likely due to the presence of fish carcasses than to inputs from septic tanks. At the station with maximum carcass density (Sta. M1 in 2001), we measured two- and threefold increases in the concentrations of particulate Hg and total Hg, respectively (Fig. 3). [MeHg] also increased dramatically at this station (Fig. 3). Prior to spawning, MeHg and Hg_p represented, respectively, 2% and 40% of the total Hg, whereas after spawning, these proportions increased to 10% and 60%. We measured no increase in the concentration of dissolved Hg, $[\text{Hg}]_d$, after spawning in 2001, and the station with maximum carcass density was not the site with the highest $[\text{Hg}]_d$. These results can be explained if carcass decomposition resulted in the release of fish tissue as small particles, therefore increasing the levels of particulate and total Hg but not of dissolved Hg. Hg in particles of fish tissue must first be metabolized by bacteria to yield dissolved Hg, which could take some time. Furthermore, laboratory experiments by Bloom and Kuhn (unpubl. data) suggest that bacteria release Hg assimilated from fish carcasses as elemental Hg, a gaseous form that would be lost to the atmosphere. The low concentrations measured in biofilm on salmon carcasses (Table 1) are also consistent

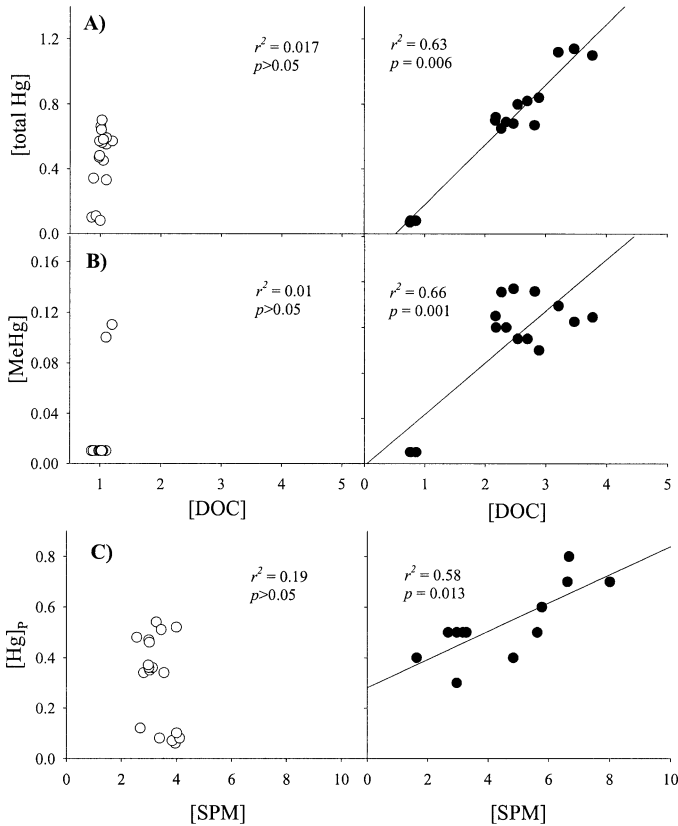


Fig. 5. Relationships between (A) total Hg (ng L^{-1}) and DOC (mg L^{-1}) concentrations, between (B) MeHg (ng L^{-1}) and DOC (mg L^{-1}) concentrations, and between (C) total particulate Hg (ng L^{-1}) and SPM (mg L^{-1}) concentrations before (open circles) and after (closed circles) spawning in 2001. Each symbol represents one sample, and data from all stations are combined. Regression coefficients (r^2) and associated p values are given for significant relationships.

with low $[\text{Hg}]_D$ and the release of Hg assimilated by the biofilm as volatile gaseous Hg.

An alternative explanation for the link between Hg_p concentrations and carcass density is that salmon resuspended sediments during spawning. However, at the time of sampling, salmon had been dead for ~ 3 d; it is therefore unlikely that sediment resuspension was a contributing factor.

In sediments, Hg concentrations varied greatly among stations and at the same station during two consecutive years (Fig. 6). Because sediments can move downstream during spates (Sarica et al. 2004), it would be difficult to use sediments to monitor Hg inputs from salmon carcasses. This high variability may be caused by salmon, which can disturb sediments during spawning.

Effect of carcasses on Hg in biota—The main taxa of aquatic insects (collectors, shredders, and predators) collected at the site of maximum carcass density were 1.4–3.1 times more contaminated with Hg than were individuals of the same genera at the U1 and GR stations (Table 1; t -test, $p = 0.000$ – 0.041 , $n = 6$ – 10 individuals per taxa). Also, insects collected after spawning at Sta. M1 in 2001 were 1.4–2.0 times more contaminated than were those collected

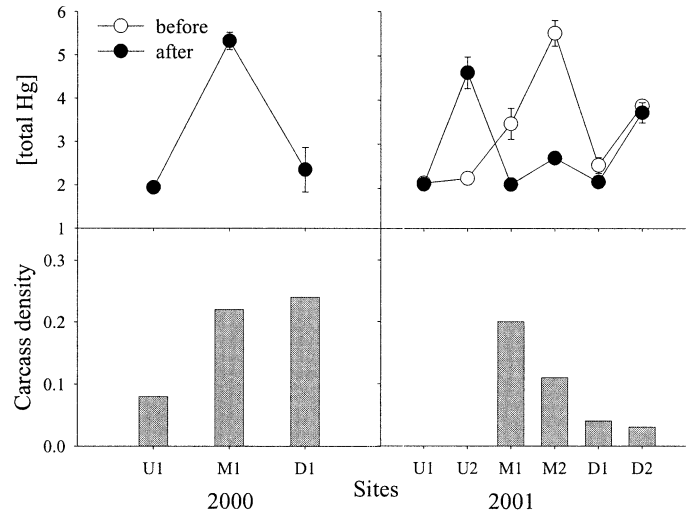


Fig. 6. Mean concentrations (\pm SD) of total Hg (ng g^{-1} dry weight) in sediments and the density of salmon carcasses (individuals m^{-2}) measured at each station in the stream during spawnings in 2000 and 2001. Hg data were collected before and after spawning.

before spawning. The only exception to these patterns was the lack of a statistical difference between Hg concentrations in *Hexatoma* before and after spawning in 2001. This difference among taxa suggests that their biology and trophic relationships influence the degree to which they accumulate Hg from spawning salmon.

Hg concentrations in two taxa (*Hydropsyche* and *Claasenia*) differed between 2000 and 2001 at a site with similar carcass densities (Sta. M1). These differences may be due to yearly changes in invertebrate growth and total biomass. Alternatively, our estimate of carcass density may not fully reflect the mean carcass density to which invertebrates were exposed prior to our arrival. Indeed, we expect carcass densities to be more directly related to short-term indicators such as water chemistry variables.

From a survey conducted on a 240-m stretch of the stream, approximately 68% of carcasses were fully or partly available for colonization by terrestrial insects (beached or half submerged; Fig. 7). Calliphorid fly maggots used carcasses as a source of food and accelerated the time for complete decomposition by a factor of 2 for beached carcasses (Fig. 7). The 12-d decomposition time in the presence of maggots is similar to those reported elsewhere for salmon (Cederholm et al. 2000). Calliphorid larvae feeding on carcasses had Hg concentrations 25 times greater than those of their parents collected at the same station and levels twofold higher than those of salmon (Table 1). Consequently, terrestrial larvae feeding on carcasses biomagnified Hg and transferred it from the aquatic to the terrestrial ecosystem.

Influence of carcass removal by bears—Bears can be important vectors of salmon-derived nitrogen to the terrestrial environment, transporting between 70% and 80% of salmon to the forest during spawning (Reimchen 2000). In 2001, a bear removed approximately 80% of the carcasses at Sta. D1, the site of maximum carcass density in 2000. As a con-

Table 1. Density of salmon carcasses (individuals m⁻²) as well as mean concentrations of Hg (ng g⁻¹ dry weight) in the dorsal muscle and liver of salmon carcasses, in aquatic and terrestrial invertebrates, and in biofilm as measured during spawnings in 2000 (after) and 2001 (before and after) at various stations in Wilmot Creek and at one station in the Ganaraska River (GR) in 2000. Values in parentheses represent SD; — indicates no data; * represents a significant difference at a given station between upstream (U1) and spawning station (M1) in 2000, between upstream and GR stations in 2000, or before and after spawning in 2001 (*t*-test, *p*<0.05).

	2000				2001			
	GR	U1	M1	D1	U1		M1	
					Before	After	Before	After
Carcass density	0.08	0.08	0.22	0.24	0	0	0	0.20
[Total Hg]								
Chinook salmon:								
Dorsal muscle	—	740 (90)	—	990 (380)	—	—	—	—
Liver	—	580 (100)	—	540 (250)	—	—	—	—
Aquatic invertebrates:								
<i>Hydropsyche</i> sp.	163 (54)	114 (34)	352* (35)	—	75 (10)	117 (30)	111 (9)	224* (22)
<i>Claassenia</i> sp.	210 (60)	153 (15)	338* (43)	—	173 (18)	162 (26)	163 (26)	225* (14)
<i>Hexatoma</i> sp.	183 (40)	192 (36)	285* (15)	—	206 (29)	135 (54)	345 (68)	289 (103)
<i>Limnephilus</i> sp.	—	—	—	—	126 (4)	155 (35)	136 (8)	240* (24)
Biofilm on carcasses	—	—	54 (2)	—	—	—	—	—
Terrestrial invertebrates:								
Calliphoridae adults	—	—	56 (30)	—	—	—	—	—
Calliphoridae larvae	—	—	1,650 (200)	—	—	—	—	—

sequence, concentrations of total Hg, Hg_p, Hg_D, and NO₃⁻ were not statistically different at Sta. D1 before and after spawning in 2001, whereas these elements peaked after spawning at this station in 2000 (Fig. 3). Furthermore, concentrations of DOC and NH₄⁺ at Sta. D1 were lower after

spawning than were those at upstream M1 and M2 stations. Removal of carcasses by bears likely led to a decrease in local levels of Hg and nutrients in the water column at Sta. D1. These results indicate that bears transported substantial amounts of salmon-derived Hg to the terrestrial ecosystem.

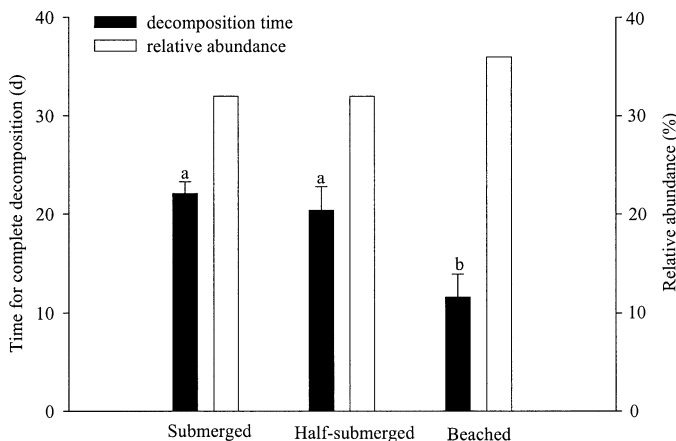


Fig. 7. Time of complete decomposition and relative abundance for submerged, half-submerged, and beached salmon carcasses in Wilmot Creek. Different letters represent a significant difference (ANOVA, *p* < 0.05). SD is presented.

A budget for salmon-derived Hg in Wilmot Creek—In Fig. 8, we integrate our data from Sta. D1 to describe the fate of salmon-derived Hg in the presence and absence of bears and other potential scavengers. We assumed that whole salmon have a mean concentration of total Hg of 0.20 ± 0.05 mg kg⁻¹ wet weight and a mean wet weight of 6.6 kg (adult salmon from Lake Ontario; Scott and Crossman 1984). We also assumed that Sta. D1 (length = 250 m) is representative of a 3-km stretch of stream having a mean width of 5 m and thus an area of 15,000 m². Since a carcass density of 0.24 salmon m⁻² was measured at Sta. D1 in the absence of bears, the total flux of salmon-bound Hg from Lake Ontario to this reach of stream is 4.75 g (Fig. 8) for the 21-d period covered by this study. Without bears, we presume that all of the Hg in beached salmon, which represent 36% of the total number of carcasses (Fig. 7) and thus contain 1.71 g of Hg, is transferred to the riparian zone by maggots (Fig. 8, left panel). The assumption that beached carcasses were totally eaten by maggots was supported by regular visual inspections of de-

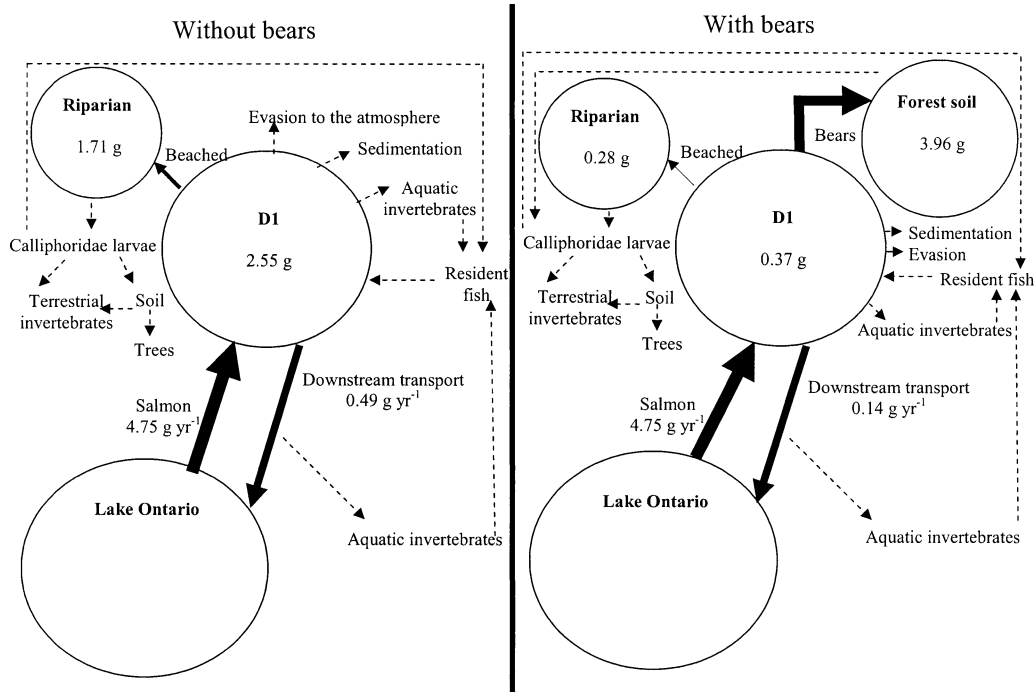


Fig. 8. Assessments of Hg pools (g) and Hg fluxes (g yr⁻¹) at Sta. D1 (riparian area, water, downstream transport, and forest soil) with or without bears. The dashed lines represent processes for which fluxes are unknown.

caying carcasses and has also been established by others (Cederholm et al. 2000). Downstream transport is calculated from the difference between total water-column Hg concentrations when carcasses are present and those when they are absent (Fig. 3). This difference (0.35 ng L⁻¹) multiplied by the median stream discharge during the salmon run in 2001 (765 L s⁻¹; Fig. 2C) gives a downstream Hg flux of 0.49 g over 21 d. By difference, we obtain the amount of Hg remaining in the aquatic system at Sta. D1 (2.55 g). As shown in Fig. 8 (left panel), 54% of the carcass-bound Hg stays at

the site where salmon died, and 36% is transferred to the riparian zone.

The number of salmon carcasses removed by bears corresponds to the difference between the density of carcasses measured at Sta. D1 in 2000 and 2001 after spawning, i.e., 0.20 salmon m⁻² (Fig. 8, right panel). Therefore, 83% of the salmon-bound Hg was consumed by bears and other scavengers. When considering the added impact of maggots on the beached carcasses, approximately 90% of the Hg (4.24 g) will end up in the terrestrial system in the presence of bears, compared to 36% in their absence.

During our 21-d study, the amount of Hg transported by salmon to the whole stream (Fig. 9) was 10.3 g, which corresponds to an annual flux of 29.4 g if we assume that the salmon run lasted 60 d. This annual Hg flux is close to the 26.4 g of Hg that we calculated from unpublished estimates of salmon runs in Wilmot Creek, assuming the same mean salmon weight and Hg concentration as above (Stanfield et al. unpubl. data). For the whole stream (Fig. 9), we observe that (1) when bears are active at site D1, they are the main force dictating the fate of salmon-bound Hg, leading to a water-to-land transfer of 40% of the salmon-bound Hg; and (2) without bears, the majority of the Hg pool (54%) stays at the site of salmon death, with one third being transferred to the terrestrial systems by maggots. As shown by the dashed lines in Fig. 8, many of the processes involved need to be further investigated to refine this assessment.

At the scale of the drainage basin (94 km²), total Hg inputs by salmon runs represent approximately 1–3% of the atmospheric deposition (wet and dry: 10–30 μg of Hg m⁻² yr⁻¹; International Joint Commission and Commission for

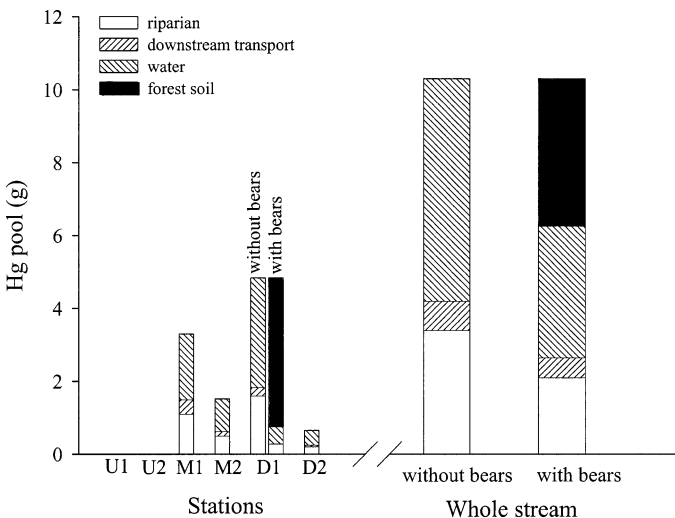


Fig. 9. Assessments of Hg pools (g) at each station and for the whole stream, with or without the presence of bears.

Environmental Cooperation 2003). Assuming that MeHg represents >95% of total Hg in piscivorous fish (Watras and Bloom 1992) and <5% of atmospheric deposition (Lindqvist 1991), salmon runs likely represent a large MeHg flux (i.e., 27.9 g MeHg yr⁻¹) at the drainage basin scale (wet and dry deposition: 47–141 g MeHg yr⁻¹). However, remember that most methylation (and demethylation) affecting aquatic bioaccumulation likely occurs in situ, near or in the stream.

This study, along with the study by Krümmel et al. (2003), provides evidence that toxic substances can be efficiently transported by Pacific salmon and delivered to their native streams. Further studies are needed to clearly assess the toxicological risk related to this pathway for the stream and terrestrial communities.

References

- BILBY, R. E., B. R. FRANSEN, AND P. A. BISSON. 1996. Incorporation of nitrogen and carbon from spawning coho salmon into the trophic system of small streams—evidence from stable isotopes. *Can. J. Fish. Aquat. Sci.* **53**: 164–173.
- CAI, Y., G. TANG, R. JAFFE, AND R. JONES. 1997. Evaluation of some isolation methods for organomercury determination in soil and fish samples by capillary gas chromatography—atomic fluorescence spectrometry. *Internat. J. Environ. Anal. Chem.* **68**: 331–345.
- CEDERHOLM, C. J., AND OTHERS. 2000. Pacific salmon and wildlife—ecological contexts, relationships, and implications for management. Special edition technical report, prepared for D. H. Johnson, and T. A. O'Neil (Managing Directors), wildlife-habitat relationships in Oregon and Washington. Washington Department of Fish and Wildlife.
- , M. D. KUNZE, T. MUROTA, AND A. SIBATANI. 1999. Essential contributions of nutrients and energy for aquatic and terrestrial ecosystems. *Fisheries* **24**: 6–15.
- CHALONER, D. T., AND M. S. WIPFLI. 2002. Influence of decomposing Pacific salmon carcasses on macroinvertebrate growth and standing stock in southeastern Alaska streams. *J. North Am. Benthol. Soc.* **21**: 430–442.
- CROTEAU, M. N., L. HARE, AND A. TESSIER. 2001. Differences in Cd accumulation among species of the lake-dwelling bio-monitor *Chaoborus*. *Can. J. Fish. Aquat. Sci.* **58**: 1737–1746.
- INTERNATIONAL JOINT COMMISSION AND COMMISSION FOR ENVIRONMENTAL COOPERATION. 2003. Addressing atmospheric mercury: Science and policy. A workshop sponsored by the International Air Quality Advisory Board of the IJC and the CEC, Research Triangle Park, NC, December 2001.
- KRÜMMEL, E. M., AND OTHERS. 2003. Delivery of pollutants by spawning salmon. *Nature* **425**: 255–256.
- LINDQVIST, O. 1991. Mercury in the Swedish environment: Physical/chemical forms of mercury. *Water Air Soil Pollut.* **80**: 715–724.
- MERRITT, R. W., AND K. W. CUMMINS [EDS.]. 1996. An introduction to the aquatic insects of North America, 3rd ed. Kendall/Hunt.
- ONTARIO MINISTRY OF THE ENVIRONMENT. 1999. Guide to eating Ontario sport fish, 21st ed. rev. Queen's Printer for Ontario.
- PORCELLA, D. B. 1994. Mercury in the environment: Biogeochemistry, p. 3–19. In C. J. Watras and J. W. Huckabee [eds.], Mercury pollution—integration and synthesis. CRC Press.
- REIMCHEN, T. E. 2000. Some ecological and evolutionary aspects of bear–salmon interactions in coastal British Columbia. *Can. J. Zool.* **78**: 448–457.
- SARICA, J., M. AMYOT, AND L. HARE. 2004. An easy method to measure total particulate Hg in water without chemical digestion. *Water Air Soil Pollut.* **151**: 3–10.
- SCOTT, W. B., AND E. J. CROSSMAN. 1984. Poissons d'eau douce du Canada. Bulletin 184. Office des recherches sur les pêcheries du Canada.
- SOBCZAK, W. V. 1996. Epilithic bacterial responses to variations in algal biomass and labile dissolved organic carbon during biofilm colonization. *J. North Am. Benthol. Soc.* **15**: 143–154.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. 1983. Method 351.2. Methods for chemical analysis of water and waste-waters. EPA-660/4-79-020.
- . 1993a. Method 300.0. Determination of inorganic anions by ion chromatography, Rev. 2.1. EPA-600/R-93-100.
- . 1993b. Method 365.1. Methods for chemical analysis of water and wastes. EPA-600/R-93-100.
- . 2001. Method 1631, rev. D. Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. EPA-821/R-02-019.
- WATRAS, C. J., AND N. S. BLOOM. 1992. Mercury and methylmercury in individual zooplankton—implication for bioaccumulation. *Limnol. Oceanogr.* **37**: 1313–1318.
- WIGGINS, G. B. [ED.] 1996. Larvae of the North America caddisfly genera (Trichoptera), 2nd ed. Univ. of Toronto.
- WIPFLI, M. S., J. HUDSON, AND J. CAQUETTE. 1998. Influence of salmon carcasses on stream productivity: Response of biofilm and benthic macroinvertebrates in southeastern Alaska, U.S.A. *Can. J. Fish. Aquat. Sci.* **55**: 1503–1511.

Received: 19 September 2003

Accepted: 15 March 2004

Amended: 3 April 2004