Organochlorine Pesticide and Polychlorinated Biphenyl Concentrations in Snow, Snowmelt, and Runoff at Bow Lake, Alberta

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FIGURE 1. Map of Bow Lake catchment illustrating the locations of the weather station, snowmelt lysimeters, and snowpack sampling sites, as well as the gauging station and sampling sites for the glacial stream (GL) and Bow River (BR) catchments.

We present analyses of the concentrations of organochlorine (OC) contaminants (including organochlorine pesticides and PCBs) in snow, snowmelt, and runoff in glacier and snowmelt fed streams at Bow Lake, Alberta in two contrasting hydrological years (1997 and 1998). The study investigates the variability in OC burdens in snow across the catchment, the elution of OCs from the snowpack, and the relationship between OC concentrations in streams and the annual snowpack. Snowpacks in forested sites were thinner and had lower OC concentrations than snowpacks in open or sparsely vegetated sites. The first snowmelt samples exhibited very high contaminant concentrations relative to the snowpack, and even the more hydrophobic compounds (Dieldrin, DDTs, and PCBs) were highly concentrated in meltwater. Interannual changes in the mean OC concentrations in streams did not reflect year-to-year changes in the snowpack contaminant concentrations. The results indicate that the extent of glacial ice melt may be more important than mean snowpack burdens as a control on OC concentrations in runoff in glacial catchments.

Introduction

Organochlorine (OC) contaminants are transported long distances in the atmosphere and deposited in many cold remote locations, including the Arctic and the Canadian Rocky Mountains (*1–3*). The fate and transport of OC contaminants stored in the annual snowpack are controlled by partitioning processes (e.g., revolatilization, and particle sorption) induced by the settling and metamorphism of the snowpack and by the routing of meltwater within the catchment (*4–7*). Where snow overlies ground, the fraction of OCs that drains from the snowpack with meltwater is subject to retention by sorption to soils or organic matter upon infiltration. Where organic matter and vegetation are sparse (e.g., snow over till or glacial ice), or where the ground
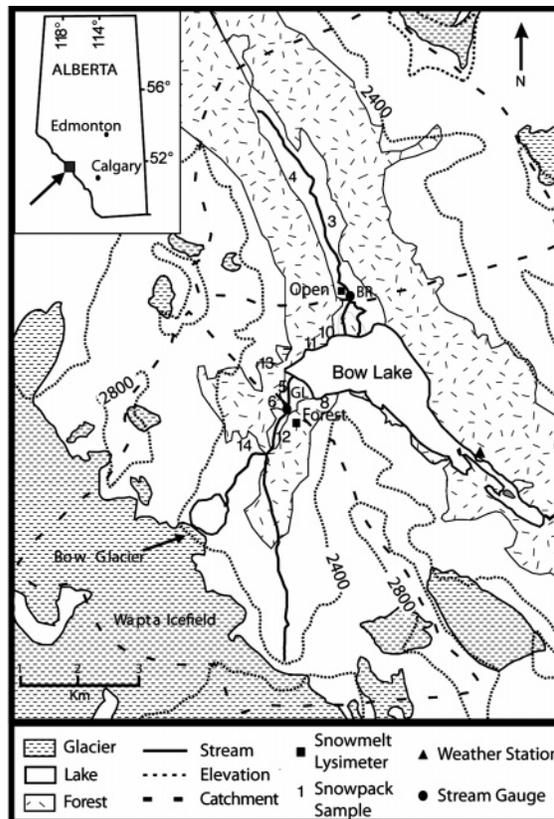
surface is frozen or otherwise impermeable, catchment retention may be limited and most of the OCs in the melt should be transferred to streams via surface flow.

This study investigates the deposition and transfer of OCs from the snowpack to the glacial and nonglacial streams draining into Bow Lake (51° 40 N, 116° 27 W), Banff National Park, Alberta. (Figure 1). Recent studies at Bow Lake indicate that, after deposition, surface runoff becomes a major route of transport of OCs to the lake, and that glacial runoff is the dominant input of most OCs to the lake (*8–9*). However, it is not clear how the amount of snow, the snowpack contaminant load, and the extent of snow and ice melt influence the delivery of contaminants to the aquatic ecosystem. The aims of this study are to (1) assess the variability in snowpack OC load across the catchment; (2) investigate the elution of OCs from the snowpack, using measurements of OC concentrations in meltwater prior to contact with the ground surface; and (3) investigate the relationship between OC concentrations in streams and the average annual snowpack OC load. We present analyses of snow, snowmelt, and stream samples collected at Bow Lake in two contrasting hydrological years (1997 and 1998). This study is the first to examine spatial and inter-annual variability in OC deposition to the snowpack, and the transfer of OCs from snow to snowmelt and runoff in an alpine catchment.

Experimental Section

Study Site. Bow Lake has two main inflows: the glacial stream (GL), fed primarily by meltwater from the Wapta Icefield,

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TABLE 1. OC Concentrations (pg/L) for 1997 Snow Samples[a]

sample	snow density (g/cm³)	SWE (mm)	α-HCH (pg/L)	γ-HCH (pg/L)	HCB (pg/L)	Dieldrin (pg/L)	endosulfan α (pg/L)	endosulfan β (pg/L)	ΣDDT (pg/L)	ΣPCB (pg/L)	α-HCH/ γ-HCH	HCB/ Dieldrin	β/α endosulfan	(α+γHCH)/ ΣPCB
site 3	0.23	366	370	210	15	43	230	66	23	1500	1.76	0.35	0.29	0.39
site 4	0.24	384	430	230	28	39	250	70	33	1600	1.87	0.72	0.28	0.41
site 5	0.28	373	380	210	12	45	300	130	36	1500	1.81	0.27	0.43	0.39
site 6	0.23	325	360	240	21	35	300	180	51	2000	1.50	0.60	0.60	0.30
open	0.25	373	290	280	19	74	NA	NA	0.0	1700	1.04	0.26		0.34
site 14	0.20	297	300	160	5.0	25	290	76	8.1	870	1.88	0.20	0.26	0.53
mean	0.24	353	350	220	17	43	270	110	25	1500	1.64	0.40	0.37	0.39
CV%	11	10	15	18	47	38	11	40	75	25	20	53	39	20
site 7	0.20	251	100	77	4.9	27	180	78	3.9	1300	1.29	0.18	0.43	0.14
site 8	0.21	165	48	66	8.6	35	110	32	9.2	1500	0.73	0.24	0.30	0.08
site 10	0.06	90	150	96	3.9	32	220	50	26	826	1.56	0.12	0.23	0.30
site 11	0.17	218	210	150	11	33	240	64	2.2	1300	1.40	0.32	0.27	0.28
site 12	0.16	193	240	130	6.1	34	240	68	14	900	1.85	0.18	0.28	41
site 13	0.15	201	110	100	9.1	30	190	34	4.6	1300	1.10	0.30	0.18	0.16
forest	0.20	318	82	62	7.9	28	80	26	61	1300	1.32	0.29	0.33	0.11
mean	0.16	205	140	97	7	31	180	50	17	1200	1.32	0.23	0.29	0.21
CV%	30	34	50	34	33	10	35	40	121	21	27	32	28	58
Δ (pg/L)	0.07	148	210	120	9.3	12	90	60	7.8	310	0.3	0.2	0.1	0.2
%Δ	32	53	86	76	78	32	40	75	37	23	22	52	26	61
p	0.007	0.000	0.000	0.000	0.003	0.035	0.001	0.023	0.242	0.043	0.051	0.035	0.113	0.001
Δ (ng/m²)			99	59	4.5	9.3	59	26	4.8	284				
%Δ (ng/m²)			129	121	118	85	90	112	75	71				

[a] Mean concentrations and coefficients of variation (CV%) in snow according to site type (open vs forested). Δ (pg/L) is the difference in the mean concentrations (open − forested), Δ% = (open − forest)/(open + forest)/2)100, p is the significance of the difference between the means (z-test). The difference (Δ) and percent difference (Δ%) of the mean OC burdens (ng/m²) are also shown. For sample locations see Figure 1.

TABLE 2. OC Concentrations in Snows and Streams, 1997 and 1998[a]

site		SWE (mm)	α-HCH	γ-HCH	HCB	Dieldrin	endosulfan α	endosulfan β	ΣDDT	ΣPCB
Snow 1997 (pg/L) ($n = 13$)	C_S	273	240	154	12	37	220	73	21	1400
	SD_{C_S}	94	130	72	7.2	12	70	43	20	340
	CV%	34	54	47	62	34	31	60	94	25
Snow 1998 (pg/L) ($n = 6$)	C_S	244	27	33	3.7	12	76	29	3.8	830
	SD_{C_S}	7	20	91	1.6	5.9	44	17	3.2	240
	CV%	3	74	28	44	51	59	59	85	29
Snow 1998−1997	%Δ	−8	−144*	−110*	−85*	−85*	−78*	−66*	−121	−37*
GL 1997	C_{RO} (pg/L)		220	110	5.7	22	19	25	5.3	480
	CV%		45	73	41	46	80	35	55	90
GL 1998	C_{RO} (pg/L)		150	98	5.6	16	8.4	73	24	363
	CV%		49	56	47	29	112	32	57	88
GL Δ 1998−1997			−70	−12	0	−6	−11	−18	18	−120
%Δ			−38	−12	−2	−34*	−78	−110*	127*	−29
BR 1997	C_{RO} (pg/L)		23	20	5.0	7.0	5.2	18	2.5	410
	CV%		40	102	33	26	74	41	89	37
BR 1998	C_{RO} (pg/L)		29	27	4.9	4.5	5.6	3.4	10	280
	CV%		92	54	22	37	102	70	64	100
BRΔ1998−1997			6	7	0	−2	0	−14	8	−130
%Δ			22	31	−2	−43*	8	−135*	120*	−38

[a] Mean snowpack OC concentrations (C_S pg/L), standard deviations (SD_{C_S}), coefficients of variations (CV%), and SWE for 1997 and 1998. Mean concentrations in runoff samples (C_{RO}) from the glacial stream (GL) and the Bow River (BR). The percent difference between the average concentrations in 1998 and 1997 is calculated as %Δ = [(1998 − 1997)/(1997 + 1998)/2)100]. Asterisks indicate the difference between the means (z-test) was significant ($p < 0.05$).

and the nonglacial Bow River (BR, Figure 1). The GL catchment is approximately 27 km² and consists primarily of glacier ice (41%, 11 km²), till, and moraines on which soils are absent or poorly developed (47% of catchment area). The BR catchment is approximately 17 km². There is less than 1.5% ice cover in this catchment, and 67% of the area consists of subalpine meadow and spruce-fir forests.

Sample Collection and Analysis. *Snow.* In 1997, snowpack samples were taken from 13 sites between March 24th and March 30th (Figure 1): one adjacent to each snowmelt lysimeter site (Open and Forest), and 11 other sites around the lake (Table 1). The average snow water equivalence (SWE) of the snowpack was determined using snow tube measurements (3−5 measurements per site). Snowpack samples were collected, sealed in plastic bags, and slowly melted in the lab to suppress volatilization. In March 1998, 3 snowpack samples were taken in the vicinity of each lysimeter site (Table 2). Air temperature and precipitation were measured at an automatic weather station (AWS) located near the outflow from Bow Lake (Figure 1). Daily mean air temperatures at this

TABLE 3. Contaminant Properties, Concentrations, and Enrichments in 1997 Snowmelt[a]

		α-HCH	γ-HCH	HCB	Dieldrin	endosulfan		ΣDDT	ΣPCB
						α	β		
	P_L (Pa)	0.100	0.027	0.245	0.016	0.008	0.394	0.002	0.0467
	C_L (mol/m³)	0.115	0.184	0.002	0.0142	0.008	0.071	0.006	0.439
	log K_{ow}	3.81	3.70	5.50	5.20	3.62	3.83	5.92	6.03
	H (Pa·m³/mol)	0.87	0.15	131.00	1.12	1.00	5.55	4.28	38.08

	sample	α-HCH	γ-HCH	HCB	Dieldrin	endosulfan		ΣDDT	ΣPCB
						α	β		
F1	7-May-01 V_{M1}(L) 9.9 C_{M1} (pg/L)	3971	1335	10.0	58.4	129	60	1.5	2481
	E_{M1}	15.5	7.7	−0.1	0.6	−0.4	−0.2	−0.9	0.8
	$(C_{M1}-C_s)/SD_{Cs}$	28.7	16.3	−0.2	1.7	−1.3	−0.3	−1.0	3.2
F2	7-May-01 V_{M1}(L) 12.3 C_{M1} (pg/L)	2793	1065	9.4	71.4	958	442	11.9	1163
F2	18-May-01 V_{M2}(L) 19.7 C_{M2} (pg/L)	240	100	7.3	9.1	87	84	5.0	824
	E_{M1}	10.6	5.9	−0.2	0.9	3.4	5.1	−04	−0.2
	$(C_{M1}-C_s)/SD_{Cs}$	19.6	12.6	−0.3	2.8	10.6	8.6	−0.5	−0.7
	fl	0.88	0.87	0.45	0.83	0.87	0.77	0.60	0.47
OP1	4-May-01 V_{M1}(L) 17.9 C_{M1} (pg/L)	3249	1194	8.9	58.5	775	290	8.7	1229
OP1	17-May-01 V_{M2}(L) 5.7 C_{M2} (pg/L)	67	39	2.8	5.1	24	16	0.6	1303
	E_{M1}	12.5	6.7	−0.2	0.6	2.5	3.0	−0.6	−0.1
	$(C_{M1}-C_s)/SD_{Cs}$	23.1	14.4	−0.4	1.7	7.9	5.0	−0.6	−0.5
	f1	0.99	0.99	0.91	0.97	0.99	0.98	0.98	0.75
OP2	4-May-01 V_{M1}(L) 3.3 C_{M1} (pg/L)	1650	551	19.1	113.3	490	321	18.3	4017
OP2	17-May-01 V_{M2}(L) 19.7 C_{M2} (pg/L)	ND	ND	82	ND	ND	ND	0.0	845
	E_{M1}	5.9	2.6	0.6	2.1	1.2	3.4	−0.1	1.9
	$(C_{M1}-C_s)/SD_{Cs}$	10.8	5.5	1.0	6.1	3.9	5.8	−0.1	7.7
	fl	1.0	1.0	0.3	1.0	1.0	1.0	1.0	0.4

[a] Mean snowpack concentrations: C_{Cs}; standard deviations: SD_{Cs}; concentrations in the 1st and 2nd snowmelt samples: C_{M1} and C_{M2}; enrichment in 1st melt sample: E_{M1}. Forest lysimeters: F1 and F2; and open site lysimeters: OP1 and OP2. Physical properties: aqueous solubility (C_L), octonal-water partition coefficient (K_{ow}), supercooled liquid vapor pressure (P_L), and air−water partitioning coefficient or Henry's law constant (H) (21, 22).

station indicate minimal snowmelt prior to sampling. The hourly temperature rose above 0 °C on only 5 occasions between January 1st and March 31st of each year (1997 and 1998) (Lafrenière, unpublished data). Snowfall was much higher during the winter of 1996/1997 than 1997/1998 (462 mm SWE in 1997 and 257 mm SWE in 1998), and the mean spring/summer temperatures were much lower in 1997 than in 1998 (10). These differences in hydroclimatological conditions resulted in lower runoff in the BR and higher runoff from GL in 1998 (10).

Snowmelt and Streamwaters: Four snowmelt lysimeters were installed at two different sites (2 lysimeters per site) in February 1997. One of the lysimeter sites was in an open subalpine meadow (Open, Figure 1), and the other was in a spruce-fir forest (Forest, Figure 1). In 1997, snowmelt was collected from three lysimeters (F2, Op1, Op2) on two occasions, once between May 3rd and 6th, and again between May 16 and 17th, after the entire snowpack had melted (Table 3). The F1 lysimeter was damaged after the first sample was collected, so only one sample was retrieved from this site. The lysimeters (Figure 1 in the Supporting Information) were cleaned prior to installation by scrubbing first with soap and water, and then with distilled water, covered in plastic until installation, and then scrubbed with snow onsite. BR and the GL were each sampled on seven occasions in both 1997 and 1998 (Figure 1, Table 1 in the Supporting Information).

All samples (snow, melt, and stream waters) were extracted into dichloromethane using a high volume Goulden Extractor (11) as described in Blais et al. (9). The extracts were concentrated by rotoevaporation and analyzed using a gas chromatograph equipped with a ^{63}Ni μ-electron capture detector (8, 9). Stream and lysimeter samples were collected in airtight aluminum cans that were pre-rinsed with acetone and hexane, and transported to the lab for extraction and analysis. They were then filtered through precombusted

Gelman GF/A filters before extraction, so the contaminant concentrations reported represent only the dissolved fraction. The melted snow samples (15−20 L) were not filtered, however, so they potentially included contaminants from both the dissolved and particle-sorbed phases. Because contaminants in the snow can repartition to the particle-sorbed phase during melting (12), analysis of an unfiltered sample was required to quantify the total snowpack OC load.

Laboratory blanks (ultrapure water that was extracted and analyzed as a sample) were consistently clean (pesticides all nondetectable, PCBs between 0 and 0.2 pg/L (mean 0.06)), so no blank corrections were applied to the data. Laboratory surrogate recoveries were 75±4% for 1,3-dibromobenzene, 67±5% for endrine ketone, 61±6% for PCB 30, and 78±5% for PCB 204. Nine samples with poor surrogate recoveries were excluded from the analysis. The concentrations of endosulfans in the snow sample from the Open site in 1997 were also omitted, as the concentrations of these chemicals were approximately an order of magnitude higher than in the other snow samples, and the chromatograms suggest that there was interference in the elution of the endosulfans in this sample. OC concentrations were not adjusted for extraction efficiencies. We considered 7 OC pesticides (hexachlorocyclohexanes (α- and γ-HCH), hexachlorobenze (HCB), Dieldrin, endosulfans (α and β), the sum of 4 dichloro-diphenyl-trichloroethane (DDT) isomers and metabolites (ΣDDT = p,p′-dichloro-diphenyl-dichloroethylene (DDE) + p,p′-dichloro-diphenyl-dichloroethane (DDD), + o,p-DDT + p,p′-DDT)), and the total PCBs (ΣPCB, representing 121 congeners).

Data Analysis. *Elution from Snowpack.* The enrichment (or depletion) of contaminant concentrations in the first melt samples (E_{M1}) was calculated as the difference between the contaminant concentration in the first snowmelt sample (C_{M1}) and the mean concentration of the contaminant in the 1997

snowpack (C_S, Table 2), divided by the mean snowpack concentration:

$$E_{M1} = (C_{M1} - C_S)/C_S \qquad (1)$$

This enrichment results from the combined effects of OC losses due to volatilization and adsorption to organic particles in the snowpack during melt, and enrichment due to preferential flushing and concentration of solutes in the early phases of snowmelt (*5*, *6*, *13*). A low enrichment, or a depletion (negative value), indicates that losses (due to volatilization or particle adsorption) during metamorphism and melt were high relative to the preferential flush and concentration of the contaminant during elution and drainage from the snowpack. Enrichment was considered significant if the difference between the contaminant concentration in the meltwater and snowpack exceeded the standard deviation (SD) of the concentration in the snowpack (i.e., $(C_{M1} - C_S)/SD_{Cs} > 1$).

The fraction of the total contaminant load found in the first meltwater fraction (*f1*) was also calculated:

$$f1 = C_{M1} V_{M1}/(C_{M1} V_{M1} + C_{M2} V_{M2}) \qquad (2)$$

where C_{M1} and C_{M2} are concentrations in the 1st and 2nd snowmelt samples, and V_{M1} and V_{M2} are the volumes of the 1st and 2nd samples. This indicates the degree to which contaminants that drain from the snowpack were preferentially eluted (concentrated) in the first fraction of the melt (Table 3).

Transfer from Snow to Streams. To investigate the efficiency of transfer of OCs from the snowpack to the streams, the concentrations in each stream sample were compared to the concentrations in the snowpack at the end of winter of the same year. The enrichment of the OCs in each sample from the two streams was calculated as the difference between the concentration of the contaminant in stream runoff (C_{RO}, Table 2) and the mean end of winter snowpack concentration (C_S), divided by the mean snowpack concentration:

$$E_{RO} = (C_{RO} - C_S)/C_S \qquad (3)$$

The enrichment was considered significant if the difference between the runoff and snowpack concentrations exceeded the standard deviation of the snowpack concentrations (i.e., $(C_{RO} - C_S)/SD_{Cs} > \pm 1$). The enrichment or depletion of a compound in runoff relative to snow results from the combined effects of OC losses (volatilization and adsorption to organic matter) from the snowpack during melt and from meltwater during runoff, and OC enrichment due to the preferential flush of solutes in the early part of the snowmelt. Thus, the enrichment of a contaminant in the stream indicates that there was minimal loss of contaminants during the transfer of snowmelt to the channel, and likely also preferential elution. Since glaciers in the Rockies are known to store OCs (*3*) and because OC concentrations tend to increase with altitude (*1*), meltwater inputs from glacier ice, or snowmelt from high elevations, represent sources of OCs that could elevate the streamwater OC concentration relative to the mean snowpack concentrations at lake level.

Results and Discussion

Spatial Variability in OCs in the Snowpack 1997. The snowpack contaminant concentrations varied considerably across the catchment. The coefficients of variation (CV% = SD/mean × 100) for all samples ranged from 25 to 94% (Table 2). The only notable spatial trend was that forested sites (7, 8, 10, 11, 12, 13, and Forest) had lower snow accumulation and, with the exception of ΣDDT, lower contaminant concentrations than open or sparsely vegetated sites (3, 4,

5, 6, 14, Open) (Table 1). The concentrations of several contaminants (α-HCH, γ-HCH, HCB, and ΣPCBs) were strongly correlated with SWE (*r* values 0.56−0.71, and $p < 0.05$). As a result, the differences in snowpack contaminant loads (ng/m²) between open and forested sites were greater than the differences in contaminant concentrations (Figure 2 in the Supporting Information). The snowpack concentrations for open sites were 23−86% higher than those for the forested sites, while the snowpack contaminant loads (ng/m²) for open sites were 71−129% higher than those for the forested sites (Table 1).

It is known that forests intercept snow and increase sublimation due to the high surface area-to-volume ratio of intercepted snow (*14*), and also that forests in alpine areas accumulate OC pesticides by gaseous uptake and wet deposition (*15*, *16*). These factors could enhance volatilization and reduce atmospheric deposition of contaminants to the snowpack in a forest. Lower snow depth and lower density at the forest sites (Table 1) might also enhance the volatilization of gaseous OCs from snow accumulating on the ground relative to the open sites, because the diffusion of a chemical through the snowpack is a function of the volume fraction of air in the snowpack (density) and the mean diffusion path length (snow depth) (*7*). Lower wind velocities in forested sites might also reduce rates of dry particle and gaseous deposition of contaminants to the snowpack relative to those of open sites (*7*). Hence, differences in OC concentrations observed between the forested and open sites are probably due to the combination of enhanced volatilization from the relatively shallow snowpack on the forest floor, reduced atmospheric deposition as a result of lower wind velocities, and the interception and volatilization of snow and contaminants in the canopy. A decrease in forest cover with altitude might therefore contribute to the increases in contaminant deposition to the snowpack with increasing elevation observed in Western Canada (*1*).

Behavior of OCs during Snowmelt 1997. Contaminant concentrations in the first melt samples were high, and usually enriched relative to the snowpack (Table 3). The observed variations in enrichments between lysimeter sites are to be expected given that the snowpack concentrations at each site will differ from the mean snowpack value (C_S) (hence the enrichments are only considered significant if $(C_{M1} - C_S)/SD_{Cs} > 1$). Furthermore, differences in particulate organic matter (POM) content, melt rate, and structure (e.g., flow fingers and ice lenses) within the melting snowpack would also produce variations in the elution of contaminants at different sites. Despite the variations, however, several patterns are apparent. The HCHs were consistently enriched in the early meltwater samples (E_{M1} between 5.9 and 15.5 for α-HCH, and between 2.6 and 7.7 for γ-HCH, Table 3). The endosulfans were also significantly enriched (except for lysimeter F1), with E_{M1} between 1.2 and 5.1 (Table 3). The HCHs and endosulfans also exhibited nearly complete elution from the snowpack in the first melt samples (*f1*'s from 0.83 to 1.0). The more hydrophobic Dieldrin displayed relatively small enrichments (E_{M1} usually < 2), but these were significant (Table 3). ΣDDT was always slightly depleted in the early snowmelt, while the ΣPCBs were enriched in the first melt samples from F1 and OP2, but slightly depleted for F2 and OP1. Relatively high fractions of the Dieldrin (*f1* = 0.83 to 0.97) and ΣDDT (*f1* = 0.60 to 0.98) that drained from the snowpack were found in the first melt samples (Table 3). HCB and the ΣPCBs displayed the lowest *f1* values, suggesting slower, and probably less complete, elution of these compounds from the snow.

The higher fractions of the less hydrophobic compounds (HCHs and endosulfans, physicochemical properties listed in Table 3) in the first meltwater samples, relative to the more hydrophobic compounds (HCB, Dieldrin, PCBs, and

DDTs), are consistent with results from other studies (5–7, 13, 17). As liquid water appears in the snowpack, the less hydrophobic compounds partition strongly into the aqueous phase. This results in the concentration of these compounds in the first melt fractions (70–80% of snowpack HCH (α- and γ-HCH) load in the first 40% of the melt (17), 50–60% of γ-HCH in first 40% (13)). Modeling and other field investigations have demonstrated that DDT and PCBs do not show a first flush behavior due to their high hydrophobicities (K_{ow}). These compounds are normally concentrated in the final phases of the melt because of their tendency to sorb to particulate organic matter (5–7). For example, Wania (5) determined that after melting, ∼85% of DDT in a snowpack (with 10 ppm organic carbon) was partitioned on organic carbon, 14% was volatilized, and only 2% drained with the meltwater. More recent models also showed that chemicals that are not sufficiently water soluble, and not volatile enough to evaporate (e.g., PCBs and benzo-a-pyrene), tend to sorb to particles in the snowpack (7). Although the $f1$'s for DDT and PCBs are low relative to those of the HCHs and endosulfans, the proportions of these contaminants that drain from the snowpack are much greater than has been found in other field studies, and greater than is predicted by model simulations.

Therefore, these results suggest that there was little POM in the lysimeter snow, or snowmelt water. Because the lysimeter samples were filtered, these included only dissolved phase contaminants, while the unfiltered snowpack samples included both particle-sorbed and dissolved contaminants; the presence of POM in the lysimeter snow should yield significant depletions for hydrophobic contaminants such as Dieldrin, PCBs, and DDT, due to their strong tendency to associate with particles during the melt (5, 7). Instead we find the dissolved concentrations of the more hydrophobic compounds are only slightly lower, or in some cases significantly higher, in the filtered meltwater samples than in the snow samples. Snows collected around Bow Lake in 2000 also indicate that the dissolved organic carbon (DOC) concentration in the snow is typically very low (0.35 ppm on average), and there was too little particulate matter on the filter papers from these samples to determine the mass or organic content (18). Results from studies elsewhere indicate that particulate organic carbon (POC) concentrations in alpine snows are typically less than 0.10 ppm (19). Using the formulas from Blais et al. (9) to calculate the fraction of contaminants sorbed to the particulate phase, and assuming 0.35 ppm POC, we calculate that the sorbed fraction of OCs would be less than 1% for all pesticides, except for p,p-DDT, for which up to 5% could be sorbed. Between 3 and 8% of the tri-, tetra-, and penta-chloro PCBs would be sorbed to particles, and up to 26% of the heavier PCBs (e.g., the hexa PCB 153) might be found on particles. However, the hexa-chloro PCBs only account for 20% of the sum of PCBs in our samples, and the heavier homologue groups account for only a few percent of the total.

Therefore, the lysimeter results indicate that organic matter in the snowpack at these sites likely has little effect on the elution of these compounds during snowmelt and that, in the absence of significant quantities of organic matter, most OCs (including the more hydrophobic compounds such as Dieldrin, DDTs, and PCBs) are effectively eluted from the snowpack.

OC Concentrations in Runoff. In 1997, the only runoff sample that displayed significant enrichment (E_{RO}, eq 3) in OCs (α-HCH and γ-HCH) with respect to the average snowpack concentrations was the June 7th sample from the glacial stream (GL, Figure 2a). For all the other 1997 stream runoff samples, the OC concentrations were either depleted or not significantly different from the average snowpack concentrations (Figure 2a and b). In 1998 the OCs in
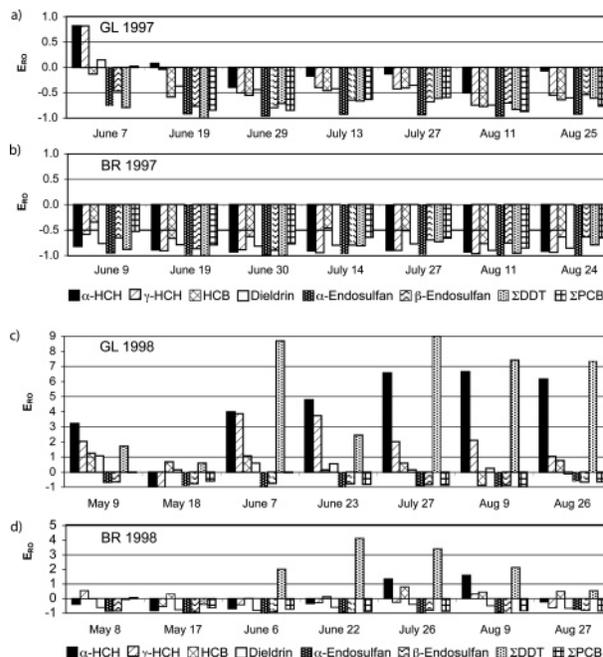
FIGURE 2. Enrichment ($E_{RO} = (C_{RO} - C_S)/C_S$) of OC pesticides and ΣPCB concentrations in runoff: (a) Glacial (GL) stream 1997; (b) Bow River (BR) 1997; (c) Glacial stream 1998; and (d) Bow River 1998.

streamwaters displayed higher and more frequent enrichments than in 1997 (Figure 2c and d). In the GL stream, all the 1998 samples, except the May 18th sample, were strongly and significantly enriched in α-HCH, γ-HCH, and ΣDDT (Figure 2c). Dieldrin and HCB also displayed frequent, but smaller, enrichments in the 1998 GL samples (Figure 2c).

The inter-annual variations in the OC enrichments (Figure 2a and b vs c and d) in runoff indicate that the amounts of contaminants exported from the catchments are not solely a function of the OC concentration in the previous winter's snowpack. The mean snowpack concentrations for all OCs were all significantly higher (z-test, $p < 0.05$, except for ΣDDT) in 1997 than in 1998 (Table 2). In contrast, the mean OC concentrations in the streams were usually only marginally higher in 1997 than in 1998 (Table 2). Snowfall, air temperatures, and discharge were very different between 1997 and 1998. Snowpack accumulation was much higher over the winter of 1996–1997 than for 1997–1998, and snowmelt occurred approximately one month later in 1997 than in 1998 (10). Positive degree day (PDD) totals (sum of the mean air temperature, for days when temperatures were above 0 °C) at the AWS at Bow Lake (Figure 1) illustrate that there was more energy available for melt in 1998 than in 1997. PDD totals for April and May 1997 were 4 and 82, respectively, and 24 and 174 for April and May 1998, respectively (Lafrenière, unpublished data). The higher air temperatures in April and May 1998, combined with the thin snowpack, resulted in a very fast melt. Modeling results from simulations conducted by Daly and Wania (7) illustrate that a longer melt period increases the loss of contaminants to the atmosphere, because there is more time for volatilization from the snowpack. Therefore, the higher enrichments of OCs in 1998 runoff (Figure 2c and d) relative to the enrichments in the streams in 1997 (Figure 2a and b) may be due in part to reduced volatilization from the thin, fast-melting 1998 snowpack, relative to the deep, slow-melting snowpack in 1997.

OC enrichments were always higher and more frequent in the glacial stream than in the Bow River. This is evident in the early season samples in 1997 and 1998 (e.g., June 7,

1997, Figure 2a and b, and May 8, 1998, Figure 2c and d). The higher enrichments in GL samples relative to the BR samples suggest that the routing of early snowmelt to the stream in the BR catchment resulted in greater OC losses than in the GL catchment. Other research at Bow Lake (1998, 1999, and 2000) found that only a small fraction of snowmelt had contact with soil-covered or vegetated areas in the GL catchment, whereas a significant amount of snowmelt was routed through subsurface soils in the BR catchment (*18*). Therefore, the lower OC enrichments in the BR samples are likely due to runoff having greater contact with, and thus higher sorption of OCs to, soils or to other organic matter during the routing of early season snowmelt in the catchment. The virtual absence of enrichments in the early spring BR samples in both years suggests that, in this catchment, retention and volatilization losses remove such a large proportion of the available OCs that the annual snowpack burden has little effect on the flux of OCs to the stream.

Significant enrichments were observed in both streams well into late summer 1998: α-HCH, γ-HCH, and ΣDDT in GL, and ΣDDT and αHCH in BR (Figure 2c and d). The high summertime enrichments in both streams suggests some or all of the following were factors: (i) snowmelt was just beginning at higher elevations in the catchments at the time, and more contaminated snow from higher altitudes (*1*), was making significant contributions to runoff; (ii) late summer flow routing of snow and/or ice melt resulted in minimal losses of contaminants by volatilization and/or sorbtion to particles (because of flow routing through englacial or subglacial channels); and/or (iii) glacier ice and firn had higher OC concentrations than the winter snowpack and these meltwaters were making significant contributions to runoff volumes.

Previous work indicates that snowmelt was likely the dominant source of meltwater in both streams in June 1998, but that glacier ice (or firn/snow on the glacier surface) was a significant source of meltwater through July and August 1998 (*10*). Thus, the source of the high HCH and DDT enrichments in the June stream samples is likely the 1998 snowpack. By the first week of July 1998, however, there was significant exposure of glacier ice (and little snow remaining even at the highest altitudes) in the glacial catchment, and by early August 1998 major channels had probably developed within the glacial drainage system (*10*). At Snow Dome on the Columbia Icefield (<100 km from Bow Lake), concentrations of many OC contaminants in ice formed between 1970 and 1990 are equal to or higher than those in the snowpack concentrations at Bow Lake (*1*, *3*). If these concentrated ice layers make a significant contribution to runoff, OC concentrations in glacial runoff could exceed the annual snowpack concentrations. Another possible added source of OCs to glacial meltwaters could be OCs that are retained in the snow/firn aquifer on the glacier in low-melt years (like 1997), stored (frozen) over winter, and then flushed during high-melt years (like 1998). Residual contaminants from meltwater that was trapped subglacially over winter (*20*) might also be released in the subsequent summer with the renewed development of the subglacial drainage system. Furthermore, the routing of meltwater through englacial or subglacial channels would virtually eliminate the loss or removal of contaminants by volatilization and sorption to particulate matter, as meltwater would have limited contact with the atmosphere, and OCs have little affinity for glacial sediments (*9*, *21*). Thus, the enrichments of DDT and HCH in GL in the summer of 1998 are likely due to contributions from the melting of ice, snow, or firn on the glacier with higher OC concentrations.

The enrichments of α-HCH and γ-HCH in the July 25 and August 9, 1998 BR samples are consistent with the discharge hydrograph, which indicates a continuing input of melt-induced runoff from the small area of ice cover in the catchment in July and August (*10*) (Figure 1). Lower enrichments in the BR samples relative to the July and August samples from GL (Figure 2c and d) indicate that there was either greater loss/retention of OCs en route to the stream relative to the GL catchment, or that glacier melt comprised a smaller proportion of the total runoff in BR. Analyses of the hydrographs and runoff chemistry indicate that neither flow routing through organic-rich environments, nor differences in organic matter concentrations between the two streams, can explain the large discrepancies in OC concentrations in runoff from the two catchments at the end of 1998 (*10*, *18*). Therefore, the OC enrichments are probably lower in BR than in GL in late summer 1998 because glacial meltwaters account for only a small fraction of late summer water flux in this stream. These late summer enrichments in BR in 1998 indicate that even a seemingly insignificant glacier-covered area in a catchment may have a noticeable effect on stream OC concentrations when this becomes a significant source of runoff (in high ablation years).

The very high enrichments in GL in 1998 also indicate that the extent of glacial ablation is an important control on the release of OCs in runoff from ice covered catchments. The enrichments suggest that (a) melt of contaminated ice (formed after ~1950) contributed significant amounts of OCs to runoff in 1998, and/or (b) the OCs from snow deposited on the glaciers in 1997 may not have been completely flushed from the glacier that year, and that some 1997 OC residues (i.e. in firn /ice) were flushed by the extensive melt in 1998. Therefore, the concentration (and seasonal flux) of contaminants in glacial runoff will depend on the OC burden of the current winter's snowpack, the extent of glacial ablation, and perhaps also on the snowpack OC burden and melt conditions in the previous year. Thus, lower snowfalls (and snowpack OC burdens) and higher glacial ablation (as observed under El Niño conditions at Bow Lake in 1998) may yield higher annual OC fluxes than years when snow accumulation and snowpack OC burden are higher (like 1997).

This research highlights that high-altitude lake catchments are likely subject to higher pulses of OC contaminants in runoff as a result of the decreasing presence of vegetation, higher snowfall, and increased accumulation of OCs in the snow, and less particulate matter available for binding in the snow and on the ground. In addition, aquatic ecosystems in these lakes may be subject to peak exposures of a wide range of organic contaminants in spring, and in summer where melt from glacier ice deposited in the mid-20th century is contributing to flow. The potential impact of peak OCs fluxes on aquatic ecosystems suggests a need for better understanding of the magnitude and temporal variability of OC concentrations in these environments, especially during a period when climate warming is rapidly decreasing glacial ice mass.

Supporting Information Available

Figure 1 illustrates the snowmelt lysimeter apparatus; Figure 2 is a graph of the 1997 snowpack OC burdens; Table 1 lists

the OC concentrations for the stream samples for 1997 and 1998. This material is available free of charge via the Internet at http://pubs.acs.org.

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