

Selective Trapping of Organochlorine Compounds in Mountain Lakes of Temperate Areas

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The study of fish concentrations and sediment inventories in 19 European high mountain lakes (40–67°N) shows that a fraction of organochlorine compounds (OCs), the less volatile compounds (LVC; subcooled liquid vapor pressure $\leq 10^{-2.5}$ Pa), are trapped in the higher locations. This general trend is not significantly influenced by possible local sources. Compound distribution is related to average air temperatures. The phase-change pseudoenthalpies calculated from the sediment inventories closely match the summed theoretical volatilization and dissolution enthalpies. This fractionation effect is responsible for the accumulation of high concentrations of the LVC, the more persistent and toxic according to literature data, in organisms inhabiting sites far from the locations of synthesis or use.

Introduction

Semivolatile organochlorine compounds (OCs) such as polychlorobiphenyls (PCBs), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), and DDTs are ubiquitous in the

planet. Atmospheric transport is one of the most efficient and rapid ways for the transfer of these persistent organic pollutants to remote sites. Atmospheric pollutant dispersion is currently assumed to follow a dilution pattern, e.g. higher concentrations are found closer to the emission sites than at distant locations. However, this pattern is not always followed by OCs. For instance, some compounds exhibit a latitudinal gradient from lower concentrations in temperate areas to higher levels in high latitude sites, e.g. HCB in tree bark (1) or α -(-)HCH in seawater (2, 3).

A global distillation effect has been proposed as justification for this distribution patterns (3–5). According to this model, organochlorine compounds (OCs) follow successive evaporation and condensation steps resulting into migration from the temperate areas, the production sites, and preferential accumulation of the more volatile compounds (MCV) in high latitude, cold and remote, regions (1, 5–7). Likewise, these compounds have also been observed to accumulate in the snow from the Canadian Rocky Mountains (8).

However, cold sites may also be encountered in temperate areas, namely in the high mountain regions. To this end, lakes are ideal ecosystems for the study of the atmospherically transported OC burden in these cold environments. Accordingly, high mountain lakes in Europe (40–67°N, Figure 1) have been selected for study. These lakes are distributed among the main mountain ranges, including the Alps, Pyrenees, and Tatra mountains, and those in Scandinavia, Iberian Peninsula, Ireland, and Scotland. The series comprises altitude sites between 430 and 2800 m above sea level. In previous studies, the sedimentary composition of polycyclic aromatic hydrocarbons (PAH) in these lakes has been examined (9, 10). Now, OC were analyzed in fish from 18 of these lakes and sediments in eight of them. Both average concentrations in fish muscle and sedimentary deposition inventories (1978–present) show a significant dependence of the less volatile compounds (LVC) with altitude.

Materials and Methods

Materials. Residue analysis *n*-hexane, dichloromethane, isoctane, acetone, concentrated sulfuric acid 95–97%, powder copper (size < 63 μ m), neutral aluminum oxide 90 (70–230 mesh), and anhydrous sodium sulfate pro analysi were from Merck (Darmstadt, Germany). The purity of solvents was checked by concentration of 100 mL to 50 μ L and examination by gas chromatography-electron capture detection (GC-ECD). No significant peaks should be detected for acceptance. Cellulose cartridges (20 mm \times 80 mm, Whatman Ltd), aluminum oxide, and sodium sulfate were Soxhlet extracted before use. The purity of the cleaned reagents was checked by ultrasonic extraction with *n*-hexane: dichloromethane (4:1; 3 \times 20 mL), concentration to 50 μ L and analysis by GC-ECD. No interferences were detected. Sodium sulfate and aluminum oxide were activated overnight by heating at 300 °C and 120 °C, respectively. Copper was activated by sonication with 35.5% hydrochloric acid (3 \times 3 mL), and then it was rinsed several times with Milli-Q water to neutral pH and, subsequently, with acetone for water removal. This powder was stored under *n*-hexane prior to use (not later than 2 days after activation).

γ -HCH and 1,2,4,5-tetrabromobenzene (TBB) were from Aldrich-Chemie (Steinheim, Germany), α -HCH and PCBs were from Promochem (Wesel, Germany), and 1,2,3,4-tetrachloronaphthalene (TCN), octachloronaphthalene (OCN), 4,4'-DDE, and 4,4'-DDT were from Dr. Ehrenstorfer (Augsburg, Germany). The standard mixtures of HCH isomers,

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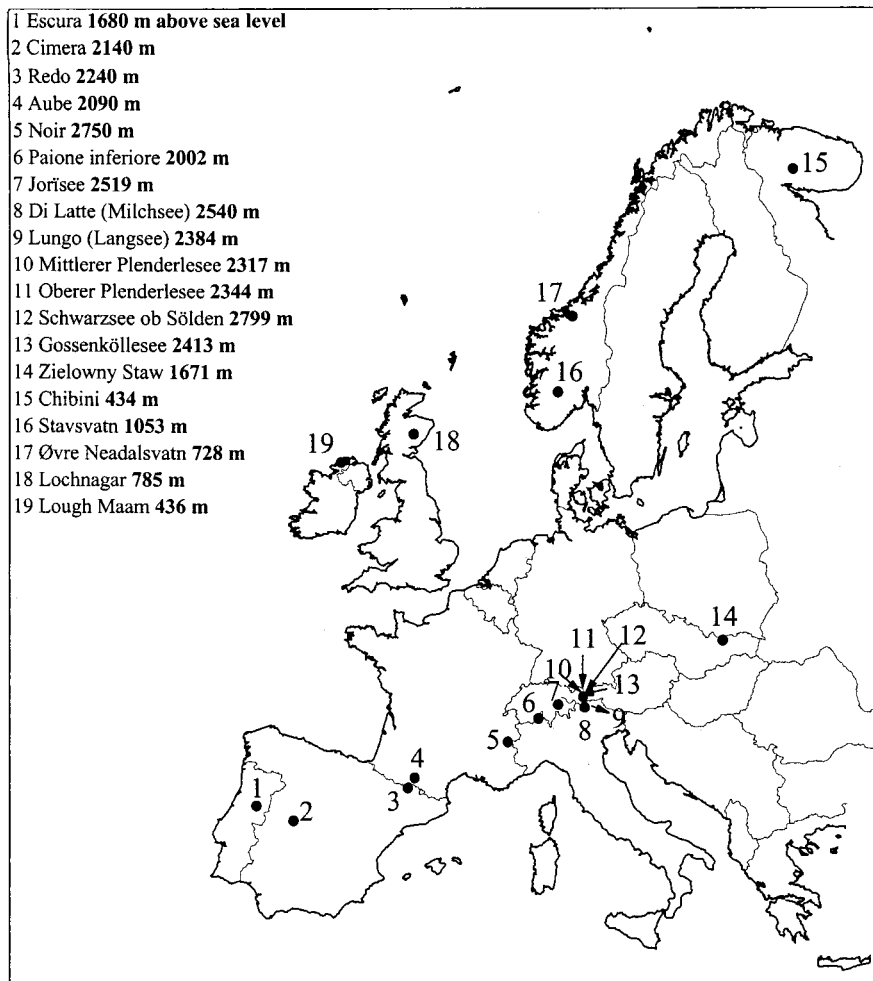


FIGURE 1. High altitude lakes selected for study.

HCB, PCBs (congeners nos. 28, 52, 101, 118, 138, 153, and 180), 4,4'-DDE, and 4,4'-DDT and surrogate solution composed of TBB and PCB 209, TCN, and OCN were prepared in isooctane. In sediments TBB was substituted by PCB-30.

Fish Collection and Handling. Fish sampling followed standard testfishing procedures with multifilament gillnets (11) which excluded individuals of lengths < 10 cm, e.g. 1–2 years. Muscle tissues were cut and stored frozen (–20 °C) until analysis.

Muscle tissue (5 g) was ground with activated sodium sulfate until a fine powder was obtained. This mixture was introduced into cellulose cartridges and Soxhlet extracted with 80 mL of *n*-hexane–dichloromethane (4:1) for 18 h. After extraction, the total volume was adjusted to 100 mL, and 20 mL was separated for lipid analysis (vacuum and nitrogen evaporation to dryness and weight). The other 80 mL of the extract were fortified with TBB and PCB 209 standards and concentrated under vacuum to 2 mL. Two milliliters of sulfuric acid was added to this solution. After vigorous stirring in a Vortex (2 min) the mixture was centrifuged to remove any foam in the interface, and the sulfuric acid layer was discarded. This cleanup step was repeated until a colorless transparent *n*-hexane layer (2 mL) was obtained (4–6 times). The final sulfuric acid mixture was re-extracted with *n*-hexane (2 × 2 mL), and all *n*-hexane solutions were combined and concentrated by vacuum rotary evaporation (20 °C, 20 Torr) to small volumes (ca. 300 μL). The solutions were then transferred to vials and evaporated just to dryness under a gentle stream of nitrogen (10–20 °C). The cleaned extract was redissolved to 50 μL with a solution of TCN and OCN in isooctane for instrumental analysis.

Sediment Collection and Handling. Samples were obtained by sediment coring (7.5 cm diameter) in the deepest point of the lake. At lake shore, the cores were then divided in sections of 0.25 cm (radiometric dating) or 0.5 cm (OC analysis), wrapped with prerinsed aluminum foil, and stored frozen at –20 °C until analysis in the laboratory.

Wet sediment sections (0.1–0.5 g) were extracted by sonication with methanol (1 × 20 mL; 20 min) and subsequently with dichloromethane–methanol (2:1; 3 × 20 mL; 20 min). The combined extracts were fortified with PCB-30 and PCB-209 standards and vacuum evaporated to 10 mL. They were then hydrolyzed overnight with 20 mL of 6% KOH in methanol. The neutral fractions were recovered with *n*-hexane (3 × 10 mL), vacuum evaporated until dryness, and diluted into 400 μL of *n*-hexane:dichloromethane (95:5). They were then transferred to a glass column (35 cm × 0.9 i.d.) packed with 2 g of activated aluminum oxide (120 °C overnight). OC were collected with 5 mL of *n*-hexane:dichloromethane (95:5). About 0.5 g of activated copper were added to each of these extracts. After manual stirring the suspensions were kept overnight at room temperature. Then, the mixtures were transferred to another flask and concentrated under vacuum to 1 mL and to nearly dryness under nitrogen. The extracts were redissolved to 50 μL with a solution of TCN and OCN in isooctane for instrumental analysis.

Total organic carbon was determined with a CHN analyzer after acidification for carbonate removal.

Instrumental Analysis. Samples were analyzed in a Hewlett-Packard gas chromatograph Model HP-5890 equipped with an electron capture detector and an HP-7673-A

TABLE 1. Altitude, Annual Average Air Temperature, Dissolved Organic Carbon, Dissolved Phosphorous, Fish Lipid Content (Muscle), Organochlorine Concentrations, Sedimentary Organic Matter, and Organochlorine Inventories for the Lakes Studied (Figure 1)

lakes	alt, m ^a	temp, °C	DOC, total P,		fish						sediments				
			mg·L ⁻¹	μg·L ⁻¹	ng·g ⁻¹ wet weight				OM, ^d mg·g ⁻¹	pg·cm ⁻² (%)					
					lipid, %	HCB	PCB-52	PCB-153		PCB-180	HCB	PCB-52	PCB-153	PCB-180	
1. Escura	1680	8.05	1.2	9	3	1.6 ^c	0.053 ^c		0.10 ^c	0.066 ^c	110	170(3.4)	7.2(66)	28(31)	24(39)
2. Cimera	2140	4.95	1.6	7	5	1.0	0.3	0.49 ^c	0.70	0.43	28	410(2.6)	110(17)	100(15)	90(19)
3. Redo	2240	3.5	0.76	6	23	2.4	0.83	0.24	2.6	1.6	40	140(2.8)	36(19)	62(10)	52(12)
4. Aube	2091	3.5		3	15	3.7	1.0	0.34	1.4	1.0					
5. Noir	2750	0									35	160(3.3)	21(42)	65(12)	58(14)
6. Jorisee	2519	0.32		9	1.9	0.4	0.66	3.0	1.8						
7. P. inferiore	2002	3.3	0.59	2	5	0.90	0.24	0.17	1.3	1.1					
8. Di Latte	2540	0.09	0.9	4	6	4.0	1.5	0.68	11	7.4					
9. Lungo	2384	1.0	0.9	5	6	1.2	0.056	2.7	4.2	2.8					
10. M. Plenderlesee	2317	1.4	0.77		4	2.3	0.20	0.32	7.2	3.8					
11. O. Plenderlesee	2344	1.3	0.7		6	0.88	0.48	0.22	2.7	1.9					
12. S. Solden	2799	-1.45	0.4	4	3	4.4	1.6	0.25	17	9.3	45	47(11)	83(11)	230(3.4)	180(4.6)
13. Gossenköllesee	2413	0.85	0.45	3	23	1.9	0.37	0.18	2.2	1.8	90	12(4.5)	24(10)	170(2.2)	91(2.4)
14. Zieloni Staw	1671	2.4	1.6	3	5	1.6	0.11	0.97	1.5	1.4					
15. Chibini	434	-	0.3		4	1.8	0.41	0.14	0.16	0.15					
16. Stavsvatn	1053	0.6	0.73	2	10	1.9	0.51	0.28	1.6	1.6					
17. Ø. Neadalsvatn	728	2.25	0.73	2	26	2.9	0.58	0.18	0.36	0.18	64	73(8.2)	26(9.2)	62(5.5)	24(5.1)
18. Lochnagar	785	4.85	0.8	3	5	1.8	0.20	0.23	0.64	0.49					
19. Lough Maam	436	8.7		4	5	1.7	0.13	0.79	0.30	0.14	230	57(7.7)	66(11)	17(38)	15(47)

^a Altitude, meters above sea level. ^b Individuals analyzed per lake. ^c Mean of all the individuals analyzed in the lake. ^d Organic carbon/dry sediment. ^e Summed analytical and dating errors. Fish from lake no. 5 and sediment cores from lakes nos. 4, 6–11, 14–16, and 18 were not available.

autosampler. The separation was achieved with a 30 m × 0.25 mm i.d. DB-5 column (J&W Scientific, Folsom, CA) coated with 5% diphenylpoly(dimethylsiloxane) (film thickness 0.25 μm). The oven temperature was programmed from 80 °C (holding time 2 min) to 150 °C at 15 °C/min and finally to 280 °C at 4 °C/min, keeping the final temperature for 10 min. Injector and detector temperatures were 270 °C and 310 °C, respectively. Injection was performed in the splitless mode, keeping the split valve closed for 35 s. Helium was the carrier gas (50 cm/s).

Some samples were examined by negative ion chemical ionization mass spectrometry coupled to gas chromatography (GC-MS-NICI) for structural identification. These analyses were performed using a Fisons MD 800 instrument (quadrupole detector, THERMO Instruments, Manchester, United Kingdom). The gas chromatograph was equipped with a nonpolar fused silica capillary column HP-5-MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness). Helium was used as carrier gas (1.1 mL/min). The oven temperature was programmed from 90 °C (1 min) to 120 °C at 15 °C/min and then to 300 °C at 4 °C/min with a final holding time of 10 min. The samples were injected in split/splitless mode (48 s) at 280 °C (hot needle technique), and data acquisition started after a solvent delay of 4 min. Ion source and transfer line temperatures were 150 and 280 °C, respectively. Ammonia was used as reagent gas. Ion source pressure (currently 1.6 Torr) was adjusted to maximize the perfluorotributylamine ions (*m/z* 312, 452, 633, and 671). Ion repeller was 1.5 V. Data were scanned from *m/z* 50 to 450 at 1 s per decade. Data were also acquired in selected ion monitoring mode with dwell time and span of 0.06 s and 0.10 amu, respectively. The selected ion programs are reported elsewhere (12).

Identification and Quantification. OC were identified by retention index comparison by reference to TCN and OCN. In some cases, structural identification was confirmed by GC-MS-NICI. External standards of all identified compounds were injected at several concentrations in order to make calibration straight lines in the adequate concentration range in the samples. Quantification was performed by reference

to TCN and OCN in order to correct for instrumental instabilities. The values were also corrected by recoveries of PCB-30 and PCB-209.

Quality Assurance. Procedural blanks were performed with each set of eight samples. A detailed evaluation of the method for fish analysis is reported elsewhere (13). Briefly, detection and quantification limits were in the order of 10 pg/g wet weight. The dispersion of the method is smaller than the dispersion between fish of similar length and age from the same lake (13). The method for sediments was validated by replicate (*n* = 4) analysis of reference sample BCR 536 (Community Bureau of Reference, Brussels, Belgium). The results obtained were in agreement with the certified values. Reproducibility was lower than 10% for all compounds and 13% for 4,4'-DDE. Quantification and detection limits were calculated from real samples as 10 times the signal/noise ratio and were in the order of 10–40 pg.

Radionuclide Analysis. Subsamples of dried sediments from each section were analyzed for ²¹⁰Pb, ²²⁶Ra, ¹³⁷Cs, and ²⁴¹Am using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (14). The down-core decline in ²¹⁰Pb activity in excess of that supported by in situ ²²⁶Ra decay was used to determine a chronology. The results were validated where possible from stratigraphic records of the artificial radionuclides ¹³⁷Cs and ²⁴¹Am. These can be used to identify the depth of the 1963 level, the year of peak fallout from the atmospheric testing of nuclear weapons, and 1986, the year of the Chernobyl reactor fire.

Results and Discussion

All selected lakes are of natural origin, far from any pollution site. They are situated in siliceous catchments (granite-gneiss bedrock geology) and above the local tree line. Their hydrology only depends on atmospheric deposition. Water properties are rather uniform: low concentrations of dissolved organic matter (DOC, 0.4–1.6 mg·L⁻¹ in most cases), low alkalinity, and slightly acidic to neutral pH.

The dominant or only fish species are salmonids, e.g. arctic charr (*Salvelinus alpinus*; lakes 4, 8–12, and 15 in Figure 1),

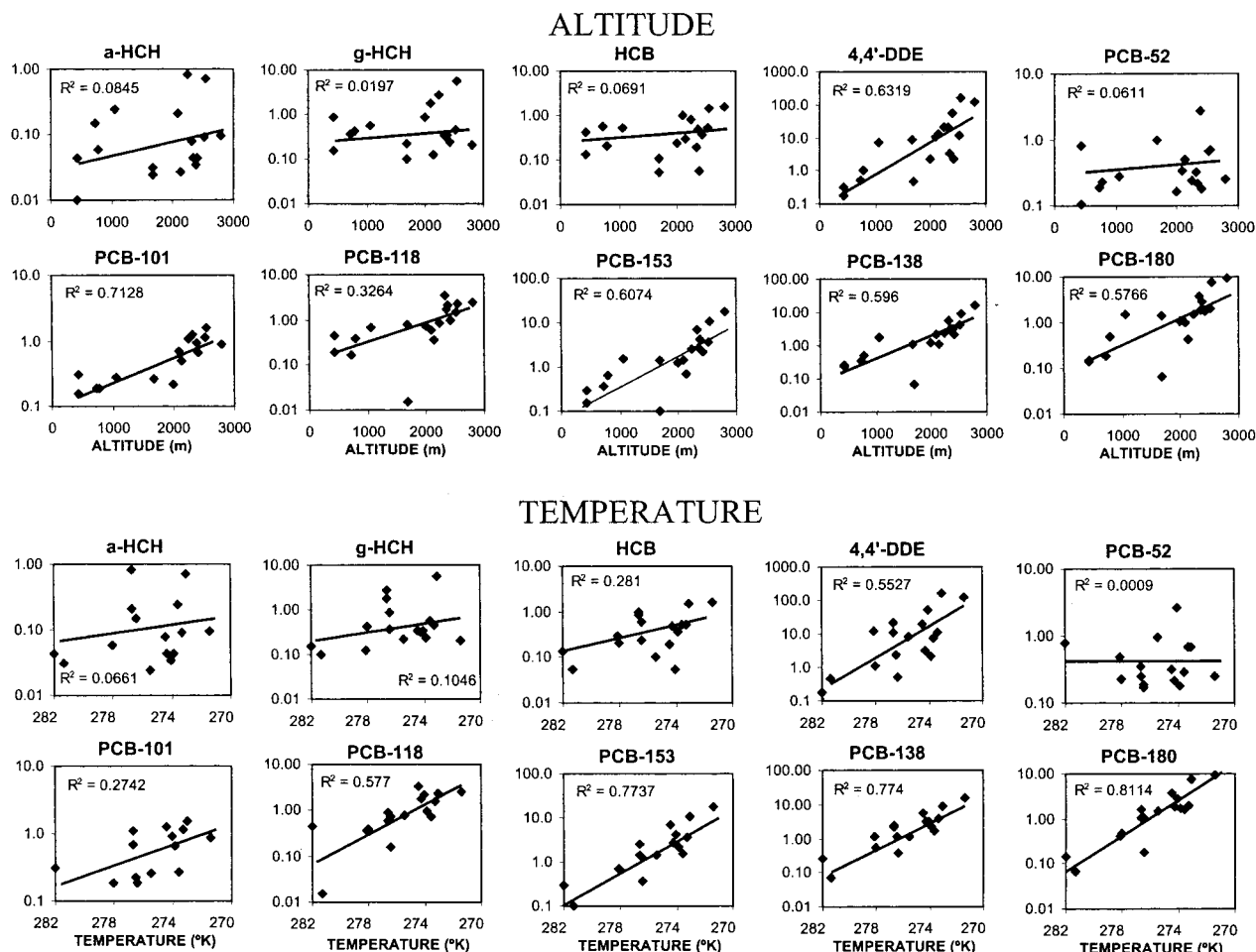


FIGURE 2. Fish concentrations ($\text{ng}\cdot\text{g}^{-1}$ wet weight) of selected OC vs lake altitude and temperature. The points represent the average values of the specimens analyzed individually in each lake (Table 1).

TABLE 2. R^2 Coefficients of Fish Concentrations and Sediment Inventories vs Height above Sea Level and Mean Annual Atmospheric Temperature in the Lakes Described in Figures 1–3^f

compounds	fish concentrations			sediment inventories (1978–present)			fish–sediment correlations R^2	vapor pressure ^e subcooled liquid (Pa)
	R^2		slopes ^b ($10^3\cdot\text{K}$)	R^2		slopes ^d ($10^3\cdot\text{K}$)		
	height	temp ^a		height	temp			
α -HCH	0.0845	0.0661		n.d. ^c	n.d. ^c		$10^{-0.92}$	
γ -HCH	0.0197	0.1046		n.d. ^c	n.d. ^c		$10^{-0.70}$	
HCB	0.0691	0.281		0.0006	0.1192	0.0576	$10^{-1.2}$	
PCB 28 (2,4,4')	0.0123	0.0391		0.0001	0.0001	0.0091	$10^{-1.5}$	
PCB 52 (2,2',5,5')	0.0611	0.0009		0.0009	0.0266	0.5691	$10^{-1.8}$	
4,4'-DDE	0.6319	0.5527	17.3	0.1958	0.0035	0.5498	$10^{-2.5}$	
4,4'-DDT	0.5390	0.5877	14.6	n.d. ^c	n.d. ^c	n.d. ^c	$10^{-3.3}$	
PCB 101 (2,2',4,5,5')	0.7128	0.2742		0.2297	0.2458	0.1848	$10^{-2.5}$	
PCB 118 (2,3',4,4',5)	0.3264	0.5770	11.8	0.5825	0.32	0.0938	$10^{-3.0}$	
PCB 153 (2,2',4,4',5,5')	0.6074	0.7737	14.1	0.5295	0.7248	6.7	$10^{-3.3}$	
PCB 138 (2,2',3,4,4',5)	0.596	0.774	14.3	0.4582	0.6725	6.3	$10^{-3.2}$	
PCB 180 (2,2',3,4,4',5,5')	0.5766	0.8114	14.6	0.7611	0.6342	6.1	$10^{-3.9}$	

^a Correlated vs $1/\text{temp}$ (K). ^b Slopes of the straight lines correlated vs $1/\text{temp}$, only those corresponding to R^2 higher than 0.5 are considered (degrees of freedom 15). ^c n.d. alkaline hydrolysis did not allow for the determination of α -HCH, γ -HCH, and 4,4'-DDT in the sediments. ^d Degrees of freedom 6. ^e Data from ref 37. ^f The differences in correlation coefficients define two groups which are coincident with the differences in volatility: α -HCH, γ -HCH, HCB, PCB-28, and PCB-52 (the more volatile compounds) and 4,4'-DDE, 4,4'-DDT, PCB-101, PCB-118, PCB-153, PCB-138, and PCB-180 (the less volatile compounds).

brown trout (*Salmo trutta*; 3, 6, 13, 16–19), rainbow trout (*Oncorhynchus mykiss*; 1, 7), or brook trout (*Salvelinus fontinalis*; 2, 14). Food available to fish is similar in all lakes: benthic invertebrates, mostly chironomids, with additional insects in summer. Zooplankton is represented by few

species, mostly *Cyclops abyssorum*. Piscivorous fish are absent. Muscle tissues of 163 fish were analyzed (Table 1).

Fish Concentrations. Most of the observed fish concentrations are in the range of low altitude freshwater systems (15–18), but the levels of DDTs and PCBs in the lakes situated

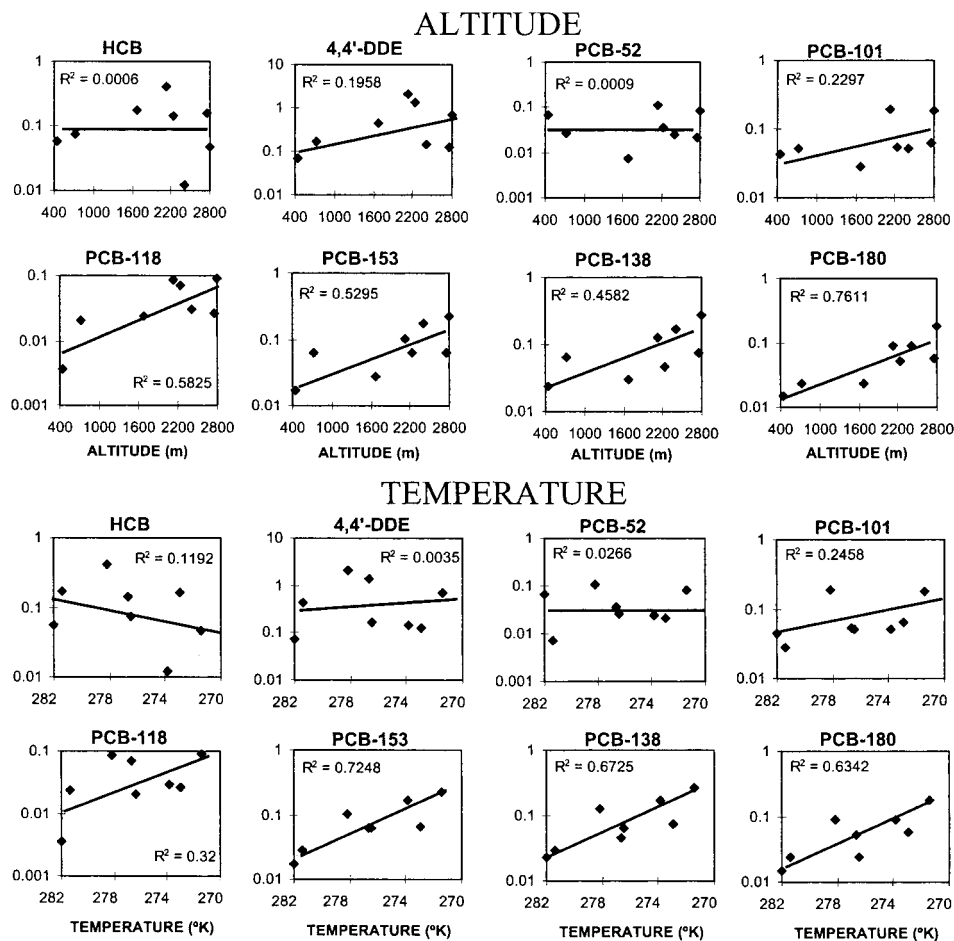


FIGURE 3. Sediment inventories ($\text{ng}\cdot\text{cm}^{-2}$; 1978–present) of selected OC vs lake altitude and temperature.

at higher elevation are higher, 4,4'-DDE, 4,4'-DDT, and the penta- to heptachlorobiphenyls increase between 2 and 3 orders of magnitude from 400 to 2800 m (Table 1; Figure 2). This concentration gradient reflects a strong correlation of the LVC with elevation (coefficients > 0.5 ; $p < 0.01$; Figure 2, Table 2) which cannot be statistically explained by differences of fish species, age, length, weight, or lipid content. For instance, LVC and lipids are not correlated. However, similar correlation coefficients are observed when LVC concentrations are referred to lipid content instead of fresh weight. Nonparametric Kendall and Spearman coefficients also show similar significant ($p < 0.01$) values, 0.54–0.70 and 0.72–0.87, respectively. In contrast, the MVC are not correlated with elevation (Table 2, Figure 2).

Correlation of toxaphene content in fish with altitude and water productivity was observed in lakes from western Canada (19). Conversely, in these European high mountain lakes, LVC in fish are not related to productivity (no correlation with DOC or total phosphorous, $2\text{--}9\ \mu\text{g}\cdot\text{L}^{-1}$). Moreover, these LVC concentrations are not correlated with catchment/lake differences, mean annual rainfall ($800\text{--}2800\ \text{mm}\cdot\text{y}^{-1}$), deposition of ^{210}Pb ($90\text{--}400\ \text{Bq}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$) or sulfur ($0.2\text{--}2.7\ \text{gS}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$). Differences in atmospheric precipitation load, e.g. total particulate matter, cannot explain the observed OC gradients nor the specific differences related with volatility.

Temperature Dependence. The obvious parameter related to altitude is temperature. Lake site air temperatures have been estimated from the 1983–1994 annual averages of meteorological stations situated at closest distance from each lake. Stations from the UK Meteorological Institute have been used in most cases: Penhas Dauradas for lake no. 1;

Avila, lake no. 2; Pian Rosa, lakes nos. 5–13; Lomnický S., lake no. 14; Carmoney, lake no. 18; and Fealar L., lake no. 19. The air temperatures in the Norwegian lakes, nos. 16 and 17, were estimated from close stations of the Norwegian Meteorological Institute: Moesstrand and Anrsjøen, respectively. For the Pyrenean lakes, nos. 3–4, these temperatures were estimated from data of the Catalan Cartographic Institute. Reliable data for lake no. 15 were not available. Altitude differences between stations and lakes were offset with a ratio of $6\ ^\circ\text{C}/1000\ \text{m}$. Independent on site measurements were consistent with these estimates when available (20).

The correlation coefficients between fish concentrations and these air temperatures also show high and low values for the LVC and MVC, respectively (Table 2 and Figure 2). Volatility (hence temperature) is therefore the key parameter determining the specific OC distribution in these environments. Thus, in Escura lake the LVC deviate from the general trend when represented vs elevation (1680 m; Figure 2) but fit well when represented vs temperature ($8.05\ ^\circ\text{C}$; Figure 2), consistently with the “warmer” air temperatures due to its location. This volatility-dependent mechanism involves redistribution and grouping of OC introduced in the environment from different sources. Accordingly, low volatility PCB of industrial origin and DDTs of agricultural use are found following the same distribution pattern. Conversely, low and high volatility PCBs, which were released into the environment in the same industrial mixtures, are separated, and their occurrence reflects different distribution processes.

Sediment Inventories. Fluxes were calculated by multiplication of the concentrations in the top cores ($0.25\text{--}0.5\ \text{cm}$) with the sedimentation rates of the same upper core

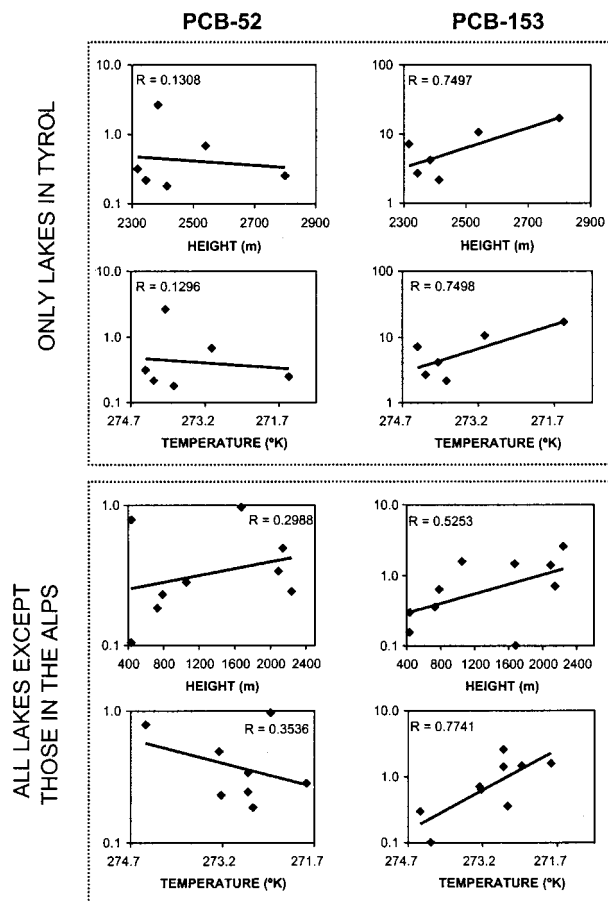


FIGURE 4. Fish concentrations ($\text{ng}\cdot\text{g}^{-1}$ wet weight) of PCB congeners nos. 52 and 153 vs lake altitude and temperature for the lakes studied in Tyrol and those in Europe after exclusion of those in the Alps.

sections. OC inventories can be calculated by numerical integration of the OC concentrations vs depth for the interval between 1978–present, measured in terms of cumulative dry mass of sediment (21). In general, the LVC exhibit a good agreement between the distribution of OC in fish muscle and sediment inventories. Higher concentrations in fish correspond to high deposition inventories (Table 1). These deposition inventories also show a remarkable correlation with elevation and temperature (Figure 3; Table 2). However, in one case, 4,4'-DDE, the dependence with altitude or temperature is weak or not observed.

Geographic Influence. One aspect to be elucidated is the possible dependence of the observed trends from lake position. To this end, it is important to check for the expected compound distribution in the worst possible case. That is, whether the observed data could be explained by a hypothetical high polluted zone in central Europe, close to the Alps.

A straightforward approach for the evaluation of this influence is representation of the fish concentration data available for Tyrol, since six of the lakes considered within this study are located in this area (nos. 8–13). The largest linear distance between any of these lakes is smaller than 51 km. As shown in Figure 4, representation of the concentrations of PCB congeners nos. 52 and 153 exhibits the same trend as described for all high altitude lakes considered in the study (Figures 2 and 3). The lakes at higher elevation are those most polluted. This trend is obviously against the possibility of a local source accounting for the pollution levels; such potential sources would be preferentially located at low elevation.

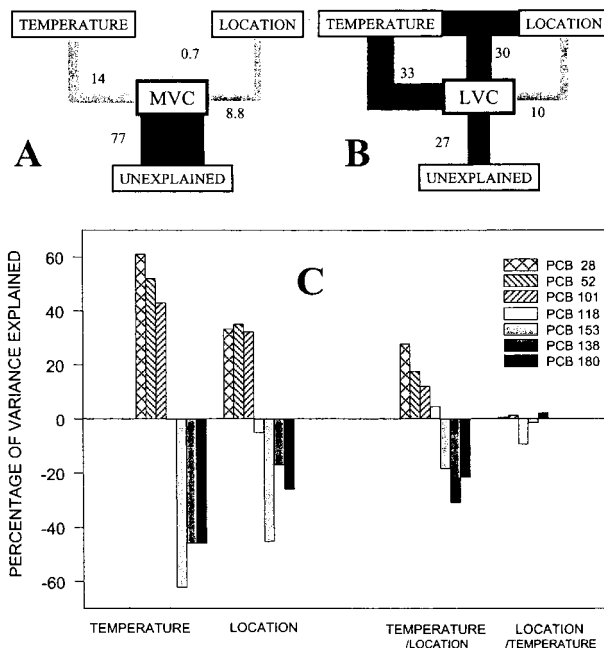


FIGURE 5. Redundancy analyses (RDA) of the variance of OC concentrations in fish grouped as more (MVC) and less (LVC) volatile compounds as defined in Table 2. (A) and (B) indicate the percentage of variance uniquely explained by temperature, location, jointly by temperature and location or unexplained. The block connections are scaled proportionally to the variance explained and those in black are significant ($p < 0.05$). (C) Calculation over the variance obtained from the relative PCB composition (% of each congener). Location refers to distance (in km) to lake Schwarzsee ob Sölden calculated by transformation of the coordinate differences.

Alternatively, all lakes except those in the Alps may be considered. As shown in Figure 4, a positive dependence between fish concentration and elevation is observed also in this case. The dependence is again related to temperature. Thus, the correlation for PCB-153 (a representative compound of LVC) exhibits even higher correlation coefficients with temperature. Accordingly, the concentration of this compound in Escura lake fits well with the curve fitting straight line when represented vs temperature and not vs elevation. As indicated above, this difference reflects the “warmer” temperature of this lake vs altitude due to its location. In any case, the temperature dependence after exclusion of all lakes from the Alps indicates that the observed trend is not biased by the lakes in this area which also reinforces the independence of the observed global data from a possible pollution site in central Europe.

A more global appraisal of the potential influence of geography can be evaluated by redundancy analysis (22, 23) (RDA). This is a principal component analysis method that allows the partialing out of the overall variance of a dataset between components which are constrained to be linear combinations of a supplied set of explanatory variables. The significance of the results is determined by Monte Carlo permutation tests (24). Application of this technique to fish OC concentrations using all distances between lakes as explanatory variables showed that only distance to the lakes in the Alps were significant, the most significant being those to the highest lake, Schwarzsee ob Sölden (SOS). Whether this fact merely reflects the location of the highest lakes in these mountains (hence highest low-temperature effects) or possible local pollution sources has been elucidated by further RDA in which either “distance to SOS” or temperature were partialled out (Figure 5).

For this purpose, the compounds were grouped as MVC and LVC as defined in Table 2 from the observed correlation

coefficients and their volatility properties. The variance of these two groups was partitioned out between (a) unexplained factors, variance uniquely explained by (b) temperature and (c) location (distance to SOS) and (d) variance jointly explained by the two factors. As shown in Figure 5B, 33% of the variance of LVC is uniquely explained by temperature and 31% jointly explained by temperature and location. Only 10% of the variance of LVC is uniquely explained by location. Conversely, most of the variance of MVC, 77%, is due to unexplained factors (Figure 5A).

The qualitative congener distribution of PCB (% of each congener) also provides useful information. These compounds were released to the environment as complex industrial mixtures, never as individual congeners. Their distributions are therefore independent from quantitative inputs. Partitioning out with respect to temperature and location confirms the explanatory capacity of temperature even when location is partitioned out (Figure 5C). In contrast, location has no significance if temperature is partitioned out. Note that in these qualitative calculations significant correlation of the LVC involves significant inverse correlation of the MVC. A relationship between the two component groups is involved by the representation of the data as relative composition of each congener.

Implications for the Global Distillation Model. The observed correlations are consistent with previous studies describing the latitudinal OC distribution (1, 25). Thus, areas of high accumulation of the MVC such as HCB ($P_a = 10^{-1.2}$) are located at 60 and 70°N, with mean temperatures between -7 and -12 °C (26). The average air temperatures of the highest lakes in Figure 1 range between -2 and 1 °C (Table 1) which is insufficient for trapping volatile compounds such as HCB but allow the retention of the LVC. These, in turn, are mobilized at sea level mean temperatures such as 5–10 °C (4). Likewise, the selective accumulation of the MVC in Western Canada mountains corresponds to January temperatures between -8° and -18 °C (8), whereas the January temperatures range between -3 and -8 °C in the highest lakes of this study.

These OC exhibit distinct long-range transport mechanisms than other compounds currently emitted to the atmosphere such as PAH. PAH of higher molecular weight than pyrene are long-range transported in association to atmospheric particles (27, 28). Their distribution depends on particle dynamics, and their accumulation in high altitude lakes is not related to temperature effects (9). PAH with molecular weights lower than pyrene have higher volatility being mostly encountered in the gas phase. Their volatilities range between $10^{-0.39}$ and $10^{-2.35}$ Pa (29) and therefore belong to the MVC group (Table 2). Accordingly, they should not accumulate in the higher altitude lakes following a temperature dependence pattern. Correlation of previously reported sedimentary data (9) vs temperature shows R^2 values lower than 0.1 in agreement with the trends reported in the present study.

The phase change pseudoenthalpies resulting from these temperature correlations provide further assessment on these OC temperature dependences ($\Delta H = S \cdot R \cdot \ln(10)$, S = slope of the regression straight line, $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $\ln(10) = 2.303$). The slopes of the low volatility PCB sediment inventories, $6100\text{--}6700 \pm 1900 \text{ K}$ (Table 2), result in enthalpies of $117\text{--}128 \pm 36 \text{ kJ} \cdot \text{mol}^{-1}$ (taking precision as the standard deviation of the regression slope). These experimental values are close to $131\text{--}145 \text{ kJ} \cdot \text{mol}^{-1}$, the summed theoretical volatilization (30) ($86\text{--}97 \text{ kJ} \cdot \text{mol}^{-1}$) and solubilization (31) ($45\text{--}48 \text{ kJ} \cdot \text{mol}^{-1}$) enthalpies.

In contrast, the slopes of the fish concentrations are higher, $11\ 800\text{--}17\ 300 \pm 1800 \text{ K}$ (Table 2), providing pseudoenthalpy values of $225\text{--}279 \pm 34 \text{ kJ} \cdot \text{mol}^{-1}$. The difference from the sediment inventories must reflect some additional temper-

ature dependent mechanism enhancing OC accumulation in fish. Higher preservation of OC at lower temperatures is unlikely since the relative content of the more labile species, e.g. 4,4'-DDT vs 4,4'-DDE, is not altitude correlated. Furthermore, as indicated above, variations in water properties or fish length, weight, or age are not in correspondence with elevation gradients. Changes in trapping efficiencies by fog, mist, clouds, or snow cannot explain this difference since they should also have an effect on the sediment data. The origin of these higher pseudoenthalpies in fish remains open. Ice cover length may be relevant since longer periods may result in higher ingestion of OC-rich benthic organisms vs allochthonous insects. Temperature-related bioaccumulation changes, namely variations in the depuration rate constant (32), may also be relevant since they could also amplify temperature effects.

In any case, the accumulation of LVC in high mountain lakes may involve significant environmental implications. Thus, the concentrations of DDTs and low volatility PCBs in salmonids are higher in the studied lakes above 2000 m than in the Arctic regions (33), showing a selective enrichment vs HCB of 15 and 4–5 times, respectively. These compounds are more toxic (34–36) than the MVC preferentially trapped in the Arctic ecosystems (1, 25), suggesting that the damage associated to the global OC distribution may be more serious and immediate in the mountain ecosystems of temperate regions than in the polar zones.

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