POPs and other persistent organic compounds in fish from remote alpine lakes in the Grisons, Switzerland

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Introduction

Global transfer of persistent semivolatile organic compounds, such as persistent organic pollutants (POPs), is effected by long-range atmospheric transport in combination with condensation and volatilization processes. Within the global atmosphere, evaporation in warm latitudes and deposition in cold latitudes leads to a transfer of contaminants towards the poles. The phenomenon of atmospheric migration of semivolatile chemicals, such as PCB and DDT, has been predicted and associated with the term "global distillation" by Goldberg[1], and the model has been extensively reviewed by Mackay and Wania[2]. For comparatively less volatile components such as PCDD/F and PBDE, particle-bound deposition is the dominating transfer mechanism. Therefore, the input of these compounds in remote alpine regions without point sources is controlled by atmospheric deposition (dry and wet) and condensation. For organochlorine compounds, such as pesticides and polychlorinated biphenyls (PCB), it has been shown that accumulation is enhanced by temperature-controlled condensation also in alpine regions with low average temperatures[3]. The hydrology of remote alpine lakes is determined by direct atmospheric deposition feeding and feeding with water from the surrounding catchment area, without significant inputs from tributaries or from nearby anthropogenic activities. Fish dwelling in these ecosystems represents an excellent indicator for the long-term input of bioaccumulating contaminants, such as POPs and other persistent organic compounds. In the present study, fish from 7 alpine lakes from the Grisons (Switzerland) situated between 2062 and 2637 m above sea level were investigated (see Table 1). With the exception of Laghetto Moesola which is situated adjacent to a mountain pass road, input from local anthropogenic emissions can be excluded for these lakes. Concentrations of pesticides (4,4'-DDE, 2,4'-DDT, 4,4'-DDT, dieldrin, heptachlor *exo*-epoxide (HEPX), hexachlorobenzene (HCB), γ-hexachlorocyclohexane (γ-HCH)), polychlorinated biphenyls (PCB), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F), brominated flame retardants (polybrominated diphenyl ethers (PBDE) and hexabromocyclododecane (HBCD)), and synthetic musk compounds (musk ketone (MK), musk xylene (MX), Fixolide (AHTN) and Galaxolide (HHCB)) were determined in pooled muscle tissue of 2 to 19 individuals per lake.

Methods and Materials

Sample material: Fish (brown trout (*Salmo trutta fario*), brook trout (*Salvelinus fontinalis*), alpine char (*Salvelinus alpinus*), and lake trout (*Salvelinus namaycush*)) were caught in August and September 2003 in the lakes given in Table 1. Whole fish were wrapped in aluminium foil and stored at – 20 °C until analysis.

Table 1: Parameters of lakes and fish species included in the present study.

Lake	Longitude (E)	Latitude (N)	Altitude (m)	Fish species	Average fat content (%)
Lai da Tuma	8.6735	46.6339	2345	alpine char, brown trout	2.0
Lägh dal Lunghin	9.6756	46.4188	2484	lake trout	2.9
Lej da Diavolezza	9.9740	46.4218	2573	lake trout	3.8
Lagh dal Teo	10.1132	46.3655	2353	brown trout	1.3
Surettasee (Untersee)	9.3486	46.5385	2193	alpine char, brook trout	1.9
Lai Grond (Macun)	10.1266	46.7305	2637	brown trout	1.3
Laghetto Moesola[1)]	9.1718	46.4955	2062	brown trout	2.8

[1)] local input by nearby road traffic and increased tourism to be taken into consideration

Sample preparation: Muscle tissue was cut in pieces and sample pools of approx. 300 g were prepared and homogenized in a mixer. Fat extraction followed a method described by Fürst et al.[4]. The fat content was determined gravimetrically. Sample clean-up for the analysis of PCDD/F and dioxin-like PCB followed a method described in the literature[5]. For the remaining components, separation of fat was effected by gel permeation chromatography[4].
Quantitative analysis: Quantitative determination of the contaminants was based on gas chromatography / high resolution mass spectrometry with single ion monitoring using isotope-labelled internal standards.

Results and Discussion

An overview of the contaminant concentrations is given in Table 2. Literature data on the occurrence of persistent organic contaminants in fish from mountain lakes is sparse. In an study on the cold trapping of semivolatile organic compounds in mountain lakes, Grimalt et al. have gathered fish data from another alpine lake located in the same region (Jörisee) [3]: Levels of PCB and HCB in brown trout were within the range of concentrations of the present study. Vives et al. have determined organochlorine compounds[6], as well as polybrominated diphenyl ethers (PBDE)[7], in fish from high mountain lakes in Europe and from a lake in Greenland: Again, corresponding concentrations and similar congener patterns (PCB, PBDE) have been observed. In contrast to organochlorine pesticides and PCB, a relatively minor temperature effect is expected for PBDE. Due to their low vapour pressure, deposition of these compounds is expected to be mainly particle-mediated. In an investigation on the occurrence of PBDE, Zennegg et al. have determined PBDE levels in whitefish (*Coregonus sp.*) from 8 lakes situated in the plateau of Switzerland[8]. Based on a comparison of the concentrations with lake parameters, the authors concluded that input of PBDE to these lakes is likely to be mainly due to atmospheric deposition. This hypothesis is supported by the data of the present study: The PBDE concentrations of the present work are slightly below to similar to the levels reported by Zennegg et al., indicating that additional cold-trapping is insignificant. Furthermore, concurrent congener patterns were observed.

Table 2: Concentrations of persistent organic pollutants in fish from alpine lakes in the Grisons, Switzerland (ng/g, lipid weight based).

	Lai da Tuma	**Lägh dal Lunghin**	**Lej da Diavolezza**	**Lagh dal Teo**	**Surettasee (Untersee)**	**Lai Grond (Macun)**	**Laghetto Moesola**
Pesticides:							
4,4'-DDE	735	306	81	510	273	556	548
Sum 2,4'-DDT / 4,4'-DDT	89	24	32	23	23	30	23
Dieldrin	57	43	103	12	22	19	16
HCB	22	22	14	11	12	12	15
γ-HCH	1.8	1.6	1.8	1.1	2.6	1.4	4.9
HPEX	8.5	6.2	14	3.0	4.3	4.2	4.0
PCB and PCDD/F:							
Sum 6 PCB[1)]	1308	481	176	517	467	939	1297
Dioxin-like PCB[2)]	0.12	0.10	0.030	0.057	0.059	0.088	0.12
PCDD/F[2)]	0.017	0.0066	0.0022	0.0035	0.0046	0.0056	0.019
Brominated flame retardants:							
Sum 7 PBDE[3)]	52	30	13	28	24	25	107
Sum HBCD	33	32	14	<10	14	<20	36
Synthetic musks:							
Sum MK / MX	4.1	4.1	3.2	5.4	4.3	4.3	15
Sum AHTN / HHCB	81	63	73	80	288	64	115

[1)]PCB 28, 52, 101, 138, 153, and 180
[2)]calculated as WHO-TEQ
[3)]PBDE 28, 47, 99, 100, 153, 154, and 183

Synthetic musks are used as fragrances in laundry detergents and in cosmetic products. Due to their usage pattern, they enter aquatic systems mainly via waste water or via release from waster water treatment plants. In contrast, the mountain lakes in investigation are exclusively fed by direct or indirect atmospheric input. As the range of vapour pressures of synthetic musks is similar to the range covered by the PCB, it can be supposed that they are transferred by evaporation from water systems fed by direct input followed by wet and gaseous deposition in mountain lakes. According to the global distillation model, accumulation is expected to be less pronounced for the more volatile polycyclic musks than for nitro musks[3]. Vapour pressures of AHTN and HHCB (0.073 and 0.068 Pa) are similar to the vapour pressure of HCB (0.063 Pa), whereas the volatility of MK and MX (0.00004 and 0.00003 Pa[9]) is below that of PCB 180 (0.00013 Pa). Until now, no reference data have been available for levels of these compounds in fish from remote aquatic ecosystems, where immission is exclusively based on atmospheric deposition.

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References

1 Goldberg E. D. (1975) Proc. R. Soc. London, B 189, 277-289.
2 Mackay D. and Wania F. (1995) Sci. Total Environ. 160-161, 25-38.
3 Grimalt J. O., Fernandez P., Berdie L., Vilanova R. M., Catalan J., Psenner R., Hofer R., Appleby P. G., Rosseland B. O., Lien L., Massabuau J. C. and Battarbee R. W. (2001) Environ. Sci. Technol. 35, 2690-2697.
4 Fürst P., Fürst C., Meemken H.-A. and Groebel W. (1989) Z. Lebensm. Unters. Forsch. 189, 338-345.
5 Schmid P., Gujer E., Degen S., Zennegg M., Kuchen A. and Wüthrich C. (2002) J. Agric. Food Chem. 50, 7482-7487.
6 Vives I., Grimalt J. O., Catalan J., Rosseland B. O. and Battarbee R. W. (2004) Environ. Sci. Technol. 38, 690-698.
7 Vives I., Grimalt J. O., Lacorte S., Guillamón M., Barceló D. and Rosseland B. O. (2004) Environ. Sci. Technol. 38, 2338-2344.
8 Zennegg M., Kohler M., Gerecke A. C. and Schmid P. (2003) Chemosphere 51, 545-553.
9 Peck A. M. and Hornbuckle K. C. (2004) Environ. Sci. Technol. 38, 367-372.