

Supplementary Materials

Ambient Air Levels of Organochlorine Pesticides at Three High Alpine Monitoring Stations: Trends and Dependencies on Geographical Origin

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Chemical Analysis

Exposed XAD-2 cartridges (were Soxhlet-extracted by using a mixture of n-hexane/acetone (3:1) after spiking with ¹³C-chloropesticide standards (pentachlorobenzene ¹³C₆, α-HCH ¹³C₆, γ-HCH ¹³C₆, β-HCH ¹³C₆, δ-HCH ¹³C₆, PCA ¹³C₆, HCB ¹³C₆, heptachlor ¹³C₁₀, aldrin ¹³C₁₂, OCS ¹³C₆, oxy-chlordane ¹³C₁₀, cis-heptachloroepoxide ¹³C₁₀, 2,4'-DDE ¹³C₁₂, 4,4'-DDE ¹³C₁₂, trans-chlordane ¹³C₁₂, endosulfan-I ¹³C₉, endosulfan-II ¹³C₉, endosulfan sulphate ¹³C₉, 4,4'-DDD D₈, dieldrin ¹³C₁₂, 2,4'-DDT ¹³C₁₂, 4,4'-DDT ¹³C₁₂, methoxychlor ¹³C₁₂, and mirex ¹³C₁₀). The volume of the extracts was reduced and split into halves; one half was stored as backup at -20 °C, and the other half underwent cleanup. All organic solvents were of picograde quality and were obtained from LGC standards (Wesel, Germany).

A glass column was filled (from bottom to top) with 10 g of silica gel (LGC Standards, Wesel, Germany) and 5 g of alumina B (LGC Standards, Wesel, Germany; deactivated with 3% distilled water). To eliminate impurities, the filled column was rinsed with 60 mL of n-hexane:dichloromethane (1:1, v/v). The extract, reduced to a volume of approximately 0.5 mL, was transferred onto the column and eluted with 100 mL of n-hexane:dichloromethane (1:1, v/v). Subsequently, 0.5 mL of acetonitrile was added to the concentrated sample (1–2 mL) and evaporated using a gentle stream of nitrogen to 0.5 mL. All bulk solvent volumes were reduced by employing a rotary evaporator. The reduction to smaller volumes was executed by nitrogen blow down.

A solid phase extraction glass column was filled with 1 g of C₁₈-modified silica gel (CHROMABOND C₁₈ ec, Macherey-Nagel, Düren, Germany) and conditioned with 5 mL of acetonitrile. The sample was transferred onto the column and eluted with 5 mL of acetonitrile. Finally, the eluate was concentrated to 0.5 mL and transferred to a 2-mL autosampler vial featuring a microinsert, spiked with a recovery standard (pentachlorotoluene, 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin ¹³C₁₂). The eluate was further evaporated using a gentle stream of nitrogen to a final volume of 20 µL and stored at –20 °C until analysis. The OCPs were measured using a gas chromatograph (Agilent, 5890 Series II) coupled to a high resolution mass spectrometer (GC–HRMS). The HRMS (Thermo, MAT 95S) was operated in a single-ion-monitoring mode, and the two most intense ions of the molecular ion cluster or of an abundant fragment ion cluster were monitored. Table S1 shows the details of the GC-HRMS conditions.

Quality Assurance and Quality Control

The executing lab operates a quality management system according to DIN EN ISO/IEC 17025 and is accredited for the type of analyses performed. Procedures were validated using

internal reference materials and by means of international interlaboratory comparison studies. The quantification criteria included confirmation of retention times and isotope ratios of the ^{13}C -labeled internal standards and respective analytes. The mass fragment with the highest intensity of the molecular or fragment ion cluster was used for routine quantification. Calculating concentrations involved comparing the analyte signal height with the analyte signal labeled analogue. Compounds for which no labeled analogue was present in the internal standard mixture (i.e., four OCPs) were quantified by employing a structural isomer. Quality control samples (laboratory blanks and field blank samples) were included in the analytical batch, and the data were corrected accordingly. The calculation of Nm^3 was executed by using the law of Avogadro (Ackerman and Knox, 2006). For that temperature T was set to 273K and air pressure p to 1013,3 hPa. After each measurement of actual T and p the instrument software immediately calculated this for each measurement interval. The measurement interval for averaged T and p was 1 s.

Table S1. Type and working conditions of the GC-HRMS analyzing system (sampling media used: XAD).

<i>Gas chromatograph, Agilent 5890 Series II</i>	
Column (Restek)	Rtx-CLPesticides2, 30 m, 0.25 mm ID, 0.20 μm film thickness
Temperature program	60°C, 1.5 min, 12°C min ⁻¹ , 140 °C, 6 °C min ⁻¹ , 300 °C, 10 min
Carrier gas	helium, head pressure 16 psi
Injector	Cold injection system CIS 3 (Gerstel)
Temperature program injector	120 °C, 12 °C s ⁻¹ , 300 °C, 5 min
Temperature transfer line	300 °C
Injection volume	0.7 μL splitless
<i>Mass spectrometer, MAT 95S (Thermo)</i>	
Ionization mode	EI, 50 eV
Temperature ion source	260 °C
Resolution	>9000
Detection	SIM mode

Table S2. Data availability (Av) and frequency of the air flow regimes NW, NE, S, and UD as % of the total sampling period at the three summit stations UFS, SON and WEI. Data availability is reduced in the case of extreme weather, blackout or building operations. Flow regimes were defined on the basis of daily forecasts.

Period	UFS Av %	SON Av %	WEI Av %	UFS NW %	UFS NE %	UFS S %	UFS UD %	SON NW %	SON NE %	SON S %	SON UD %	WEI NW %	WEI NE %	WEI S %	WEI UD %
W="Winter"															
S="Summer"															
12/05 – 3/06 (W)	46	84	38	42	21	17	20	38	20	15	27	42	19	18	21
3/06 – 7/06 (W)	83	80	81	24	23	36	17	26	19	32	23	21	12	41	26
7/06 – 11/06 (S)	95	94	62	37	12	32	19	40	6	32	22	77	0	23	0
11/06 – 2/07 (W)	76	78	87	2	31	25	42	38	8	27	27	28	8	29	35
2/07 – 6/07 (W)	73	100	84	13	0	50	37	44	24	26	6	34	22	36	8
6/07 – 10/07 (S)	47	54	100	16	8	40	36	33	17	39	11	30	4	32	34
10/07 – 1/08 (W)	0	58	83	-	-	-	-	28	10	32	30	32	21	28	19
1/08 – 4/08 (W)	7	67	98	-	-	-	-	35	5	29	32	34	9	25	32
4/08 – 7/08 (S)	31	96	43	19	17	53	11	27	17	40	16	20	18	39	23
7/08 – 11/08 (S)	19	90	6	-	-	-	-	38	15	25	22	41	0	46	13
11/08 – 3/09 (W)	73	89	34	32	13	39	16	30	21	25	24	26	0	56	18
3/09 – 5/09 (W)	83	100	73	14	16	61	10	26	16	43	15	21	15	49	15
5/09 – 10/09 (S)	83	100	98	33	10	37	19	32	13	38	17	31	12	38	19
10/09 – 1/10 (W)	71	90	54	20	8	34	38	24	7	38	31	20	2	40	39
1/10 – 4/10 (W)	95	95	100	23	14	27	36	26	15	25	35	37	3	42	17
4/10 – 7/10 (S)	76	56	71	31	19	38	12	23	11	52	14	37	4	50	9
7/10 – 11/10 (S)	88	80	99	37	7	30	25	39	7	31	23	38	6	38	18
11/10 – 4/11 (W)	88	49	100	44	11	30	15	31	32	11	26	43	15	28	15
4/11 – 7/11 (S)	100	100	95	36	14	31	19	32	15	34	18	32	8	36	23
7/11 – 10/11 (S)	91	100	100	28	5	26	40	30	11	26	34	26	11	28	34
10/11 – 2/12 (W)	82	59	97	27	11	32	30	20	15	46	18	24	15	34	28
2/12 – 5/12 (W)	100	79	100	39	16	20	25	32	22	32	14	27	10	44	19
5/12 – 7/12 (S)	57	94	100	15	0	56	29	13	11	57	19	15	8	48	29
7/12 – 10/12 (S)	100	74	91	28	4	49	19	24	8	47	21	35	4	23	38
10/12 – 1/13 (W)	97	64	68	27	7	38	28	33	11	31	24	42	12	0	47
1/13 – 4/13 (W)	80	50	67	31	12	31	27	36	8	28	28	54	13	0	31