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# Atmospheric Semivolatile Organochlorine Compounds in European High-Mountain Areas (Central Pyrenees and High Tatras)

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Atmospheric samples from two European high-mountain areas showed similar composition of semivolatile organochlorine compounds (SOC), such as polychlorobiphenyls (PCBs), DDTs, endosulfans, hexachlorobenzene (HCB), and hexachlorocyclohexanes (HCHs). Nearly all compounds were predominantly found in the gas phase and only the less volatile such as some PCBs (e.g., 149, 118, 153, 138, and 180) were found in higher abundance in the particulate phase. HCB, 49–85  $\text{pg m}^{-3}$ , is the dominant SOC. This compound is only found in the gas phase exhibiting uniform concentrations irrespective of season and air mass origin. SOC of present use, like HCHs and endosulfans, were found in higher concentrations in the warm periods, 32–46 and 4–10  $\text{pg m}^{-3}$  in the gas + particulate phases, respectively, reflecting their seasonal pattern of use in many European countries. PCB and 4,4'-DDE, 39–42 and 4–6  $\text{pg m}^{-3}$  in the gas + particulate phases, respectively, also showed a seasonal trend despite neither the former nor the precursor of the latter (4,4'-DDT) being manufactured with their use drastically restricted since the 1980s. The seasonal differences are mainly due to a higher occurrence of air masses with strong continental inputs in the warm than in the cold periods. In this respect, samples whose air masses traveled at the high troposphere (backward air mass trajectories > 6000 m) have been observed to carry considerably smaller PCB and 4,4'-DDE loads ( $9.3 \pm 2.8$  and  $0.4 \pm 0.05 \text{ pg m}^{-3}$ , respectively) than overall average.

## Introduction

Studies in the past decade have shown the presence of organochlorine compounds in considerable amounts in atmospheric deposition, soils, lake waters, sediments, and

fish from European (1–3), African (4, 5) and North American (6, 7) high-mountain sites. These areas are situated above the local tree line, far away from pollution sources or direct impact of human activity, and receive the pollutants resistant to chemical and photochemical degradation during long-range atmospheric transport (LRAT) (8).

Several semivolatile organochlorine compounds (SOC) are included in this group of compounds resistant to degradation during LRAT. Between the 1930s and the 1980s, these compounds were produced and used in large quantities for agricultural and industrial purposes in the mid- and low latitudes of the Northern Hemisphere (9). Due to their toxic effects in wildlife and humans, the production and use of most SOC compounds [like DDTs, hexachlorobenzene (HCB), polychlorobiphenyls (PCB), and technical hexachlorocyclohexane (HCH; including the  $\alpha$ -,  $\beta$ -, and  $\delta$ -isomers besides the active  $\gamma$ -isomer)] were severely restricted or prohibited, which resulted in strong emission decreases (e.g., on the order of 90% for PCB) (9). However, nowadays some amounts are still incorporated into the environment as a consequence of accidental release and/or their presence in products or equipment of current use (9), and they may cause deleterious effects (10, 11). Other SOC, such as pure  $\gamma$ -HCH, are restricted to uses in non-aerial applications such as soil and seed treatment, veterinarian and human insecticide, indoor, etc. (12); others (e.g., endosulfan) are still used in agriculture.

The differences in physicochemical properties of the individual SOCs, like vapor-pressure and water solubility, in combination with meteorological conditions give rise to their fractionation and selective trapping during transport and deposition in remote areas (13, 14). Studies on sediments and fish from European high-mountain lakes showed that a selective trapping effect is also occurring in these ecosystems (3) where a significant positive correlation was found between the concentration of the less volatile organochlorine compounds (vapor pressure <  $10^{-5}$  Pa) in these samples and altitude. Higher concentrations were found at higher altitude. However, no correlation was observed for the more volatile compounds (vapor pressure >  $10^{-5}$  Pa).

The occurrence of these pollutants in high-mountain areas requires a better understanding of the mechanisms involved in their atmospheric transport. For this purpose, atmospheric gas and particulate phase samples were collected in the Central Pyrenees (Catalonia, Spain) and the High Tatras (Republic of Slovakia) (Figure 1). The first mountain range is situated in the periphery of the European continent, and the second is located in Central Europe. Air in the Central Pyrenees was sampled near the lake Estany Redon ( $42^{\circ}38'33.5''$  N;  $0^{\circ}46'12.7''$  E; 2240 m) and in the High Tatras near the lake Skalnaté Pleso ( $49^{\circ}06'36''$  N;  $20^{\circ}08'24''$  E; 1778 m). PCBs, HCB, HCHs, endosulfans, and DDTs were analyzed in the samples. Meteorological data and atmospheric back-trajectories were obtained corresponding to each sampling date. To the best of our knowledge, this is the first report on the SOC composition in the atmosphere of European high-mountain areas.

## Methods and Materials

**Sample Collection, Extraction, and Analysis.** Sampling and analytical procedures were described elsewhere (4). Briefly, samples were collected with a high-volume device (HVS) (MCV, S.A., Collbato, Catalonia, Spain) consisting of a pump equipped with two polyurethane foams (PUFs) and a glass fiber filter (GFFs). Collected sample volumes were between 120 and 280  $\text{m}^3$ . Field blanks were obtained by installing PUF and GFF in the HVS and leaving them there for 6 h without running the pump. After the sampling, PUFs and

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FIGURE 1. Atmospheric sample site in the Central Pyrenees (Estany Redon) and the High Tatras (Skalnáté Pleso).

GFFs and their blank equivalents were stored below 0 °C and transported to the laboratory.

PUFs and GFFs were Soxhlet extracted for 24 h in hexane and hexane:dichloromethane (DCM) (4:1 v/v), respectively. The extracts were concentrated to 1 mL by vacuum rotary evaporation and then cleaned up by adsorption chromatography on a column packed with 2 g of aluminum oxide (Fluka Type 507C, Fluka AG, Switzerland) and elution with 8 mL of hexane:DCM (1:2 v/v). They were then concentrated in isoctane (Merck, Darmstadt, Germany) until 50  $\mu$ L. Before instrumental analysis, tetrachloronaphthalene was added to the vials for correction of possible small differences in injection volume or dilution.

The extracts were injected into a gas chromatograph equipped with an electron capture detector (GC-ECD) for the analysis of HCB; PCB congeners 18, 28, 52, 101, 110, 149, 118, 153, 138, and 180; and DDTs (4,4'-DDE and 4,4'-DDT). HCHs ( $\alpha$ - and  $\gamma$ -HCH) and endosulfans ( $\alpha$ - and  $\beta$ -endosulfan) were analyzed on a gas chromatograph coupled to a mass spectrometer with negative ion chemical ionization (GC-MS-NICI). A Fisons MD 800 instrument (quadrupole detector, THERMO Instruments, Manchester, U.K.) was used. Both instruments were equipped with a capillary column HP5-MS (30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness). Helium was used as carrier gas (1.1 mL min<sup>-1</sup>). The oven temperatures were programmed from 90 °C (1 min) to 120 °C at 15 °C min<sup>-1</sup> and then to 300 °C at 4 °C min<sup>-1</sup> with a final holding time of 10 min. Samples were injected in split/splitless mode at 280 °C in both instruments. In the GC-MS-NICI, 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 acquired in selected ion monitoring mode with dwell time of 0.06 s and span of 0.10 amu. The ions selected for  $\alpha$ - and  $\gamma$ -HCH were  $m/z$  71 and 255, respectively.  $\alpha$ - and  $\beta$ -endosulfan were quantified with  $m/z$  406 and 272, respectively (15).

**Quality Control and Assurance.** PUF breakthrough was determined by injection of PCB congeners 40, 155, and 185 into the first PUF; transport to the field; and adsorption of 300 m<sup>3</sup> with the HVS. All congeners were present in the first PUF, and no traces of these standards were observed in the second PUF plug after this test. LODs (determined as three times the standard deviation of the chromatographic noise near the peaks of the analyzed compounds) were 0.04–0.23, 0.03, 0.20, 0.08, 0.12–0.15, and 0.05–0.11 pg m<sup>-3</sup> for PCBs, HCB, 4,4'-DDE, 4,4'-DDT, HCHs, and endosulfans, respectively. Field blanks for PUF and GFF were collected in all sampling periods as described above for control of possible

contamination during transport and processing. These blanks were treated and analyzed as regular samples and subtracted from the sample concentrations. PUFs field blank values were below limit of detection (LOD) for HCB, HCHs, endosulfans, 4,4'-DDT, and PCB 180; in the range of 1–10% sample concentrations for 4,4'-DDE, PCB 18, and PCB 28 (ca. 0.25 pg m<sup>-3</sup>); between 10 and 20% for PCB 52, PCB 101, PCB 110, and PCB 149 (ca. 0.7 pg m<sup>-3</sup>); and 20–30% for PCB 118, PCB 153, and PCB 138 (ca. 0.5 pg m<sup>-3</sup>). Field blank values of GFFs were below LOD for HCB, HCHs, endosulfans, 4,4'-DDT, PCB 18, PCB 28, and PCB 180 and in the range of 20–40% of sample concentrations for 4,4'-DDE, PCB 52, PCB 101, PCB 110, PCB 149, PCB 118, and PCB 153 (ca. 0.2 pg m<sup>-3</sup>). Injection of PCB 30 and PCB 209 standards into the samples and blanks did not show significant losses during transport (recoveries >81%). Average recoveries for PCB 30 and PCB 209 were 70  $\pm$  8% and 92  $\pm$  17% in the PUFs, respectively, and 63  $\pm$  10% and 83  $\pm$  16%, respectively, in the GFFs.

**Temperature Measurements.** An automatic weather station (AWS) situated at the border of the lake Estany Redon allowed the measurement of average air temperatures every 30 min during sampling. Compilation of these data provided mean temperature values for each sampling period. In Skalnáté Pleso, the mean atmospheric temperatures for each sampling period were obtained from online measurements of the Slovakian Meteorological Institute (SAV), which has a meteorological station at this site.

**Back-trajectories.** The origin and altitude of the air masses arriving at the two sample sites were calculated from back-trajectories using the HIRLAM model of the Spanish National Institute of Meteorology (INM). This model is based on isentropic surfaces that provide a more realistic representation than those elaborated from isobaric surfaces (16, 17). The calculations were performed at 0:00 UTC and 12:00 UTC for 5 days backwards for each sampling period with 1-h step. The isentropic surfaces for each back-trajectory at Estany Redon and Skalnáté Pleso stations were selected according to the observed potential temperature at 2240 and 1778 m, respectively.

## Results and Discussion

The data of the samples collected at each site are summarized in Table 1. In both cases, samples cover cold and warm seasonal periods distributed over 2 years (Redon) and 12 months (Skalnáté). Snow cover was present in all cases except in the samples taken in June 2001 and June 2002 at both sites.

**Atmospheric Concentrations.** A summary of the atmospheric SOC data is given in Table 1. Most of these compounds were predominantly found in the gas phase, which is in agreement with the atmospheric partitioning of these compounds reported in other studies (4, 18–20). HCB is the most predominant gas-phase SOC at both sample sites, followed by  $\gamma$ -HCH,  $\alpha$ -HCH, 4,4'-DDE, the individual PCB congeners (namely, 18, 28, 52, 101, 110, and 149), and endosulfans. 4,4'-DDT was not found in any of the samples.  $\gamma$ -HCH is the most predominant SOC in the particulate phase, followed by 4,4'-DDE,  $\alpha$ -HCH, endosulfans, and the less volatile PCBs. HCB and 4,4'-DDT were below detection limits in this phase.

The geometric mean HCB concentration at Skalnáté Pleso, 85 pg m<sup>-3</sup> (standard deviation, SD, 28 pg m<sup>-3</sup>), is significantly higher than at Estany Redon, 49 pg m<sup>-3</sup> (SD, 19 pg m<sup>-3</sup>) (ANOVA,  $p < 0.001$ ). These levels were relatively constant throughout the entire sampling period (Figure 2), indicating that the amounts of this compound arriving at both sites are relatively constant. The observed concentrations are in the same range as those found in the free-troposphere at Tenerife and Bermuda, 98 and 51 pg m<sup>-3</sup>, respectively (4, 21). They are lower than those at Spitsbergen or Lake Baikal, 205 and 190 pg m<sup>-3</sup>, respectively (22, 23).

TABLE 1. Atmospheric Concentrations of Main SOC at Two Mountain Areas<sup>a</sup>

location and sampling dates	HCB (pg/m <sup>3</sup> )	α-HCH (pg/m <sup>3</sup> )	γ-HCH (pg/m <sup>3</sup> )	4,4'-DDE (pg/m <sup>3</sup> )	4,4'-DDT (pg/m <sup>3</sup> )	α-endosulfan (pg/m <sup>3</sup> )	β-endosulfan (pg/m <sup>3</sup> )	ΣPCB (pg/m <sup>3</sup> )	ref
Estany Redon (Central Pyrenees) (Nov 27–29, 2000; May 11–12, 2001; Feb 4–5, 2002; Mar 25, 2002; Jun 17–18, 2002; Jan 14, 2003; <i>n</i> = 20)	49 (36–98) <sup>b</sup> <LOD <sup>c</sup>	8 (2–25) <sup>b</sup> 0.3 (LOD–1.9) <sup>c</sup>	22 (5–91) <sup>b</sup> 1.9 (0.4–10.1) <sup>c</sup>	3.3 (0.9–12) <sup>b</sup> 0.3 (0.2–0.6) <sup>c</sup>	<LOD	2.3 (0.8–6) <sup>b</sup> 0.4 (0.2–0.6) <sup>c</sup>	0.7 (0.4–1.3) <sup>b</sup> 0.2 (0.1–0.3) <sup>c</sup>	34 (16–70) <sup>b,d</sup> 5.5 (3.5–8.8) <sup>c,d</sup>	this study
Skalnáté Pleso (High Tatras) (Jun 29–30, 2001; Sep 20–22, 2001; Dec 19–20, 2001; Mar 27, 2002; Jun 16–17, 2002; <i>n</i> = 10)	85 (62–119) <sup>b</sup> <LOD <sup>c</sup>	15 (34–7) <sup>b</sup> 0.2 (0.1–0.5) <sup>c</sup>	30 (11–86) <sup>b</sup> 0.8 (0.3–2.2) <sup>c</sup>	5 (2–12) <sup>b</sup> 0.8 (0.5–1.2) <sup>c</sup>	<LOD	7 (1.3–42) <sup>b</sup> 0.3 (0.1–0.8) <sup>c</sup>	2.3 (0.5–7) <sup>b</sup> 0.3 (0.2–0.5) <sup>c</sup>	38 (23–64) <sup>b,d</sup> 4.0 (2.9–5) <sup>c,d</sup>	this study
<b>Other Locations (Gas + Particulate Phases)</b>									
Tenerife, 2367 m <sup>f</sup> (sampling period 1999–2000)	51	6	11	4	1			78 <sup>d</sup>	4
Tenerife, 47 m <sup>f</sup> (1999–2000)	72	22	26	22	10			190 <sup>d</sup>	4
North Atlantic (1989–1990)		200	66	3	4			290 <sup>e</sup>	27
Bermuda, 3000 m <sup>f</sup> (1986)	98	300	16					160 <sup>e</sup>	21
Bermuda, 500 m <sup>f</sup> (1986)	89	120	43					330 <sup>e</sup>	21
Spitsbergen (1992)	205	140	32					13 <sup>d</sup>	22
Spitsbergen (1993)	92	77	14	0.29	0.26				39
Alert (1993–1994)	56	60	11	0.45	0.14		4.2 <sup>g</sup>		28
Tagish (1993–1994)	48	79	12	0.53	0.19		7.0 <sup>g</sup>		28
Dunai (1993)	55	40	9.8	0.36	0.14		3.0 <sup>g</sup>		28
Eastern Arctic Ocean (1996)		37	17						29
Lake Baikal (1991)	190	490	105	8	8			89 <sup>d</sup>	23
Swedish west coast (1996)								40 <sup>d</sup>	26
rural U.K. (1992–1999)								38 <sup>d</sup>	25
Senga Bay (1997–1998)	11	9.4	25	<LOD	12	24			30

<sup>a</sup> Geometric means and lower and upper levels. Mean values of other locations are given for reference. <sup>b</sup> Gas phase. <sup>c</sup> Particulate phase. <sup>d</sup> Sum of PCB 18, 28, 52, 101, 110, 149, 118, 153, 138, and 180. <sup>e</sup> No data on individual congeners. <sup>f</sup> Meters above sea level. <sup>g</sup> Total endosulfans.

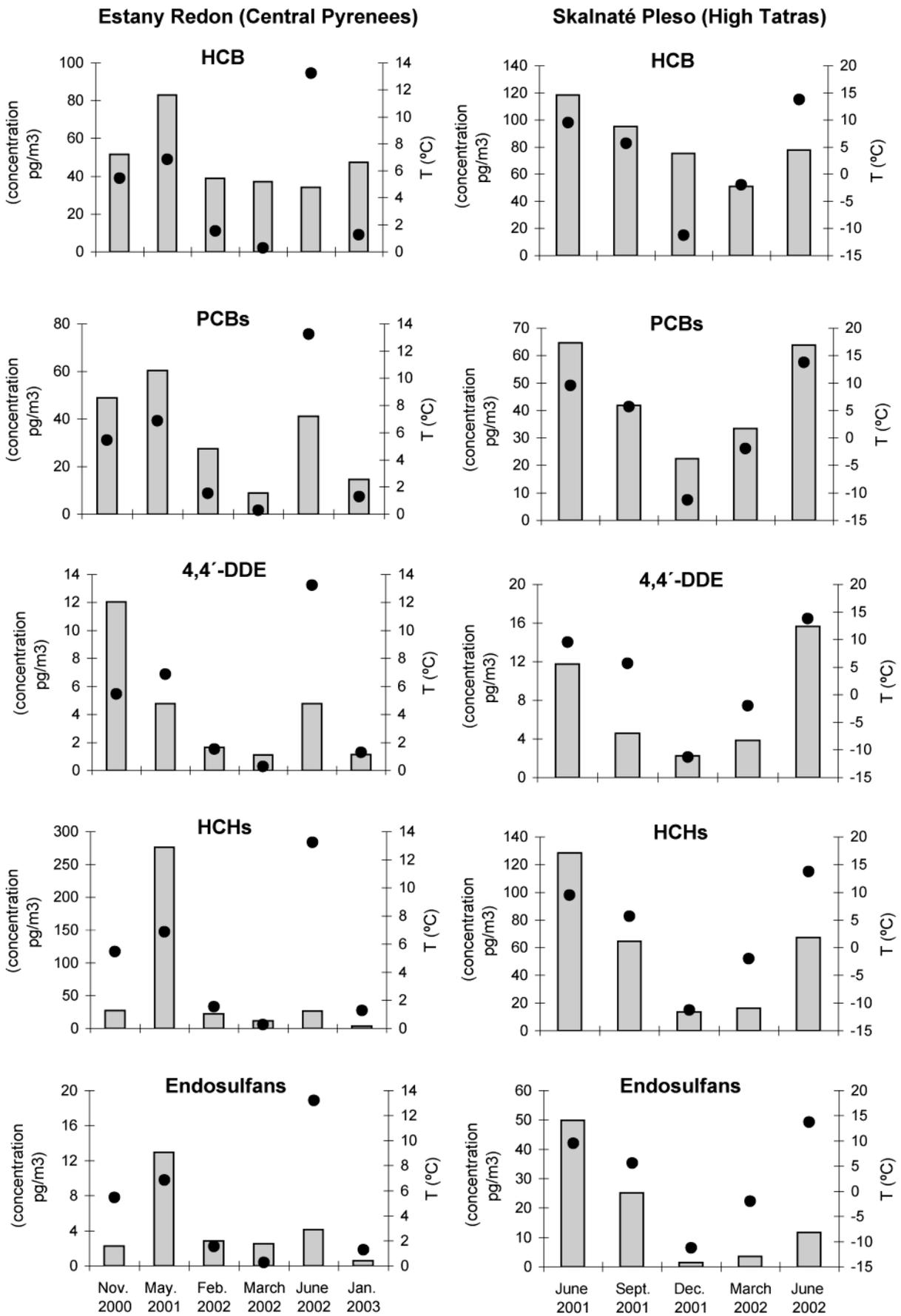


FIGURE 2. Geometric means of gas-phase SOC in different sampling periods (bars) and the average ambient temperature (dots).

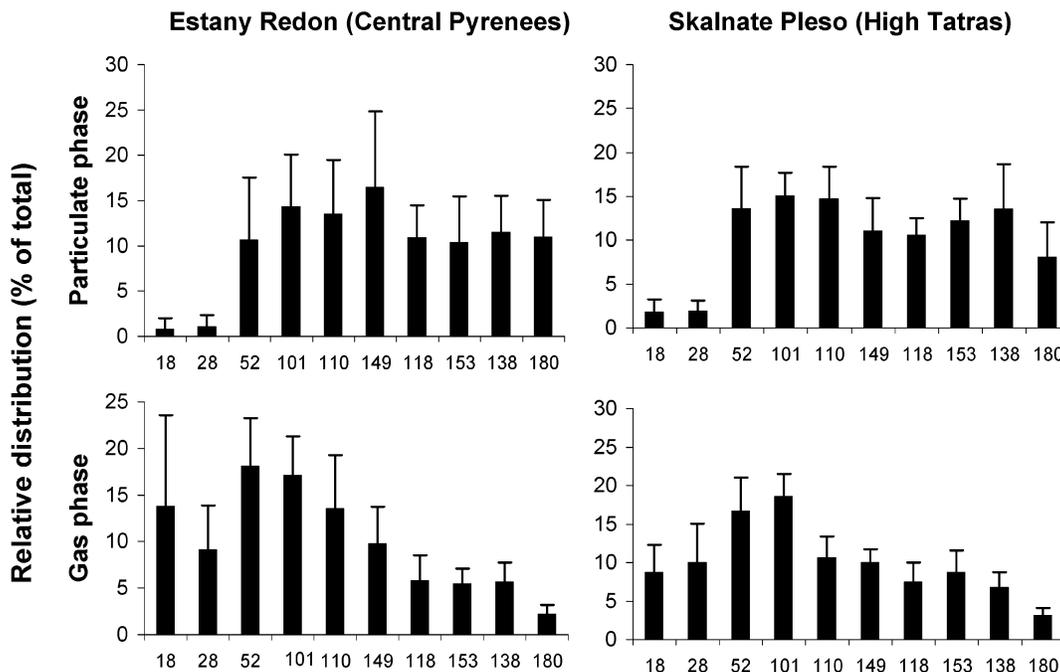


FIGURE 3. Geometric mean values of the relative distribution of PCB congeners in the particulate and gas phases. Error bars indicate standard deviations.

The measured PCB congener profiles in the air particulate fraction from the two sample sites are very similar showing a rather homogeneous congener distribution except for PCB 18 and 28 that are present in much lower abundance (Figure 3). The gas phase PCB congener distributions are less uniform being predominated by PCB 52 and 101. PCB 18 and 28 are in higher abundances in the gas phase than in the particulate phase. The less volatile compounds (such as PCB 149, 118, 153, 138, and 180) are less abundant in the gas phase than in the particulate phase. These results are consistent with previously reported gas-particulate phase distributions (24).

The gas-phase PCB concentrations are very similar in the two sites (geometric means of the sum of all analyzed congeners 34 and 38  $\text{pg}\cdot\text{m}^{-3}$  at Estany Redo and Skalnate Pleso, respectively). PCB 52 and 101 are the most abundant congeners in both sites. PCB 18 shows slightly higher concentrations at Estany Redon. The distributions found in this study are also similar to those found in the free-troposphere at other sites (e.g., at Tenerife) (4) and in the same range as those found in temperate areas such as Stoke Ferry, High Muffles, or Hazelrigg (U.K.) (35–46  $\text{pg}\cdot\text{m}^{-3}$ ; 25) or in the Swedish West Coast (40  $\text{pg}\cdot\text{m}^{-3}$ ; 26). However, they are higher than those found in at high latitudes, for example, Pallas (Finland), 11  $\text{pg}\cdot\text{m}^{-3}$  (not published), and Svalbard, 10  $\text{pg}\cdot\text{m}^{-3}$  (23).

Similar gas-phase concentrations of 4,4'-DDE at Estany Redon and Skalnate Pleso are found, with geometric means of 3.3 and 5  $\text{pg}\cdot\text{m}^{-3}$ , respectively. They are in the same range as those in remote areas of the Northern Atlantic or in the free troposphere (Tenerife), 3 and 4  $\text{pg}\cdot\text{m}^{-3}$ , respectively (4, 27). Again, they are higher than those reported in Arctic sites such as Alert (Canada), 0.1–0.21  $\text{pg}\cdot\text{m}^{-3}$ , or Alesund (Europe), 0.29–1.9  $\text{pg}\cdot\text{m}^{-3}$  (28). In all atmospheric samples, 4,4'-DDE is detected while 4,4'-DDT is below LOD. As shown in Table 1, 4,4'-DDT may be found in air samples collected in remote sites that correspond to air mass trajectories indicative of LRAT. Thus, the absence of this insecticide cannot simply indicate a higher degree of decomposition than 4,4'-DDE but the predominance of aged SOC mixtures instead of the influence of recent emissions in the samples collected.

HCHs are predominantly found in the gas phase (Table 1).  $\gamma$ -HCH is the isomer with highest individual concentration

at both sites. The concentrations are highest in May 2001 at Estany Redon with geometric mean values of 204  $\text{pg}\cdot\text{m}^{-3}$ . At Skalnate Pleso, the highest geometric mean values, 93  $\text{pg}\cdot\text{m}^{-3}$ , were observed in June 2001. The geometric mean values for the entire sampling periods at Estany Redon and Skalnate Pleso were 22 and 30  $\text{pg}\cdot\text{m}^{-3}$ , respectively. These values are similar to those found in the atmosphere of the Northern Atlantic and Spitsbergen, 11–66  $\text{pg}\cdot\text{m}^{-3}$  (4, 21, 22, 27), or in the Arctic Ocean (29).  $\alpha$ -HCH was found at concentrations of 8 and 15  $\text{pg}\cdot\text{m}^{-3}$  at Estany Redon and Skalnate Pleso, respectively, being similar to those found at Tenerife (6–22  $\text{pg}\cdot\text{m}^{-3}$ ; 4) but lower than those found in the Arctic Ocean (37  $\text{pg}\cdot\text{m}^{-3}$ ; 29), in Spitsbergen (140  $\text{pg}\cdot\text{m}^{-3}$ ; 22), or in Bermuda (120–300  $\text{pg}\cdot\text{m}^{-3}$ ; 21). The observed  $\alpha/(\alpha + \gamma)$  gas-phase average ratios at Estany Redon and Skalnate Pleso,  $0.27 \pm 0.13$  and  $0.34 \pm 0.08$ , respectively, reflect direct inputs of the  $\gamma$ -isomer that is still used for agriculture purposes. HCH mixtures from remote marine sites are dominated by the  $\alpha$ -isomer resulting in  $\alpha/(\alpha + \gamma)$  ratios higher than 0.5.

The  $\alpha$ -endosulfan/ $(\alpha$ -endosulfan +  $\beta$ -endosulfan) ratio observed in the samples from Estany Redon and Skalnate Pleso,  $0.73 \pm 0.12$  and  $0.76 \pm 0.11$ , respectively, are very similar to the ratios of technical endosulfan used in agriculture. Skalnate Pleso shows significantly higher gas-phase concentrations of endosulfans than Estany Redon, with geometric means of 7 and 2.3  $\text{pg}\cdot\text{m}^{-3}$  respectively (ANOVA,  $p < 0.05$ ). They are mainly present in the gas phase (Table 1) as observed in previous studies (30).  $\alpha$ -Endosulfan levels are in the same range as the concentrations found in remote sites such as the Arctic (0.04–3.4  $\text{pg}\cdot\text{m}^{-3}$ ; 28) or Senga Bay (0–61  $\text{pg}\cdot\text{m}^{-3}$ ; 31).

**Seasonal Patterns and Temperature Dependence.** The temperature intervals represented by the sampling periods of Estany Redon and Skalnate Pleso are 14 °C (–1 to 13 °C) and 25 °C (–11 to 14 °C), respectively. A rough examination of the average concentrations in these two sites evidences a parallelism between the atmospheric concentrations of most SOCs and ambient temperature differences (Figure 2). At both Estany Redon and Skalnate Pleso, linear regression of the natural logarithm of the gas-phase SOC concentrations versus the reciprocal of absolute temperature (22, 31–33) shows a significant correlation for all SOCs with vapor

**TABLE 2. Linear Regression Model of the Natural Logarithmic Gas-Phase SOC Concentrations versus the Reciprocal of the Absolute Temperature**

	Estany Redon					Skalnaté Pleso				
	$R^2$	$p^a$	$S$	$\Delta H$ (kJ/mol)	95% int error	$R^2$	$p^a$	$S$	$\Delta H$ (kJ/mol)	95% int error
HCB	0.06	0.314	-1427			0.15	0.265	-1028		
$\alpha$ -HCH	0.07	0.265	-5812			0.66	<b>0.004</b>	-5173	-43	$\pm 25$
$\gamma$ -HCH	0.20	<b>0.048</b>	-11711	-97	$\pm 96$	0.73	<b>0.002</b>	-7227	-60	$\pm 30$
$\alpha$ -endosulfan	0.13	0.117	-6861			0.68	<b>0.003</b>	-11528	-96	$\pm 54$
$\beta$ -endosulfan	0.25	<b>0.025</b>	-5821	-48	$\pm 41$	0.66	<b>0.004</b>	-8626	-72	$\pm 42$
4,4'-DDE	0.32	<b>0.009</b>	-13294	-111	$\pm 79$	0.84	<b>0.000</b>	-6565	-55	$\pm 19$
PCB 18	0.14	0.105	-7111			0.38	0.057	-2605		
PCB 28	0.30	<b>0.012</b>	-9043	-75	$\pm 59$	0.29	0.107	-3432		
PCB 52	0.32	<b>0.010</b>	-8470	-70	$\pm 51$	0.52	<b>0.019</b>	-3265	-27	$\pm 21$
PCB 101	0.36	<b>0.005</b>	-6980	-58	$\pm 38$	0.83	<b>0.000</b>	-4381	-36	$\pm 13$
PCB 110	0.28	<b>0.015</b>	-9300	-77	$\pm 61$	0.53	<b>0.017</b>	-3187	-26	$\pm 20$
PCB 149	0.43	<b>0.002</b>	-12740	-106	$\pm 60$	0.77	<b>0.001</b>	-3981	-33	$\pm 15$
PCB 118	0.35	<b>0.006</b>	-10580	-88	$\pm 60$	0.55	<b>0.014</b>	-3726	-31	$\pm 23$
PCB 153	0.52	<b>0.0001</b>	-10421	-87	$\pm 41$	0.78	<b>0.001</b>	-5291	-44	$\pm 19$
PCB 138	0.23	<b>0.032</b>	-5914	-49	$\pm 44$	0.79	<b>0.001</b>	-4285	-36	$\pm 15$
PCB 180	0.30	<b>0.012</b>	-6356	-53	$\pm 40$	0.76	<b>0.001</b>	-4159	-35	$\pm 16$

<sup>a</sup> Statistical significance level. Bold values refer to correlations significant at  $p < 0.05$ .

pressure lower than  $10^{-1.8}$  Pa (Table 2); that is, 4,4'-DDE, PCB 52, and the more chlorinated congeners. In contrast, HCB and PCB 18 do not show any temperature dependence. The differences are due to more uniform concentrations of the compounds with higher vapor pressure all year (Figure 2). The correlation coefficients ( $R^2$ ) are higher in Skalnaté Pleso than in Estany Redon, 0.55–0.84 and 0.20–0.52, respectively (Table 2), which is in agreement with the larger temperature span represented in the former.

HCH and endosulfans also exhibit temperature dependence despite their relative high volatility (e.g.,  $10^{-0.7}$ – $10^{-0.92}$  Pa for HCH and  $10^{-2.1}$ – $10^{-2.7}$  Pa for endosulfans). All isomers are significantly correlated to reciprocal of temperature in Skalnaté Pleso.  $\gamma$ -HCH and  $\beta$ -endosulfan are correlated in Estany Redon, which is in agreement with the measurements of atmospheric deposition at this site where higher levels of these SOCs were also found in the warm periods (1, 2). Since these compounds are still in use, the linear dependence mainly reflects their seasonal pattern of application for crop protection purposes, involving the release of higher amounts of these pesticides during the warm periods. The absence of correlation between the atmospheric concentrations of  $\alpha$ -HCH and temperature in Estany Redon may reflect the lack of present-day application of the technical HCH mixture in the southern Europe. This mixture contains  $\alpha$ -HCH in significant proportion (60–70%) and was replaced by pure  $\gamma$ -HCH. Despite the discontinued use of the technical HCH,  $\alpha$ -HCH (together with  $\gamma$ -HCH) is still present in the soils of these southern areas (34). Thus, simple degassing due to temperature increases should be equally reflected in seasonal variations of both  $\alpha$ - and  $\gamma$ -isomers, and in Lake Redon this is not the case. Thus, the correlation between these compounds and reciprocal of temperature does not reflect an environmental redistribution process due to the SOC physicochemical constants but seasonal application patterns related to human activities.

In a first approach, the observed temperature dependence of the less volatile compounds points to evaporation/condensation effects or solid–gas-phase transfer as main factors for SOC occurrence in the gas phase. The slopes of the straight lines can be used for the calculation of the phase-change pseudo-enthalpies ( $\Delta H = S \cdot R$ , with  $S$  = slope of the linear regression,  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ). In Skalnaté Pleso, the site where highest linear correlation coefficients between gas-phase concentrations and temperatures have been found, the enthalpies obtained range between 27 and 36 kJ mol<sup>-1</sup> for the PCB and have values of 55 kJ mol<sup>-1</sup> for 4,4'-DDE (Table 2). The 95% confidence errors for these enthalpies are about  $\pm 40\%$  of the absolute values for the enthalpies obtained

from linear correlations with significance  $p < 0.001$  (4,4'-DDE and PCB 101, 149, 153, 138, and 180) or up to  $\pm 75\%$  for those derived from correlations with  $p < 0.05$  (PCB 52, 110, and 118).

The volatilization enthalpies for the PCB measured in laboratory conditions range between 70 and 97 kJ mol<sup>-1</sup> (35, 36). Coincidence between laboratory and field volatilization enthalpies could indicate that the pollution sources are situated nearby since the compounds could reach the area of study rapidly after evaporation from local sources. On the contrary, when small enthalpy values are obtained from field data (e.g. field-volatilization enthalpies are smaller than laboratory-measured enthalpies), LRAT has been proposed to be the main mechanism controlling the distribution of atmospheric SOC (32). Thus, the enthalpies measured at Skalnaté Pleso represent about one-third of the laboratory-measured values pointing to LRAT as control mechanism.

In Estany Redon, the observed field enthalpies for PCB and 4,4'-DDE are higher than those in Skalnaté Pleso being nearly coincident with the above-mentioned laboratory values. However, the 95% confidence errors of these values are about  $\pm 70$ – $80\%$  of the slope-derived enthalpies ( $\pm 47\%$  only for PCB 153), which is consistent with the larger scatter of the curve fitted straight lines than in Skalnaté Pleso (as reflected in lower  $R^2$  values). As mentioned above, coincidence between laboratory and experimental enthalpies could be indicative of nearby pollution inputs arriving to the site of study by volatilization (32). However, this may not be always the case since there are no pollution sources nearby Estany Redon. In addition, analysis of PCB in the soils situated nearby this lake and Skalnaté Pleso show about the same values or even higher concentrations in the latter (e.g., 0.41 and 0.87 ng g<sup>-1</sup> in Estany Redon and Skalnaté Pleso, respectively; 34). Thus, assuming that the same processes are responsible for the SOC occurrence in the atmosphere of Estany Redon and Skalnaté Pleso, the data from the latter explain better than the former the importance of LRAT as primary mechanism for SOC transfer to these remote mountain areas.

**Back-trajectories.** The air masses that arrive at Skalnaté Pleso are mainly oceanic (December 19–20, 2001; September 20–22, 2001; June 17, 2002; Figure 4) or continental (June 29–30, 2001; March 27, 2002; June 16, 2002; Figure 4). These two groups are characterized by well-defined differences in terms of SOC composition. Thus, all PCB, 4,4'-DDE, endosulfans, and HCHs (sum of isomers  $\alpha$  and  $\gamma$ ) are found in higher concentrations in the samples whose air package has passed longer time over the continent (52, 8.3, 16, and 58 pg m<sup>-3</sup>, respectively) than those of more oceanic origin (31, 3.6,

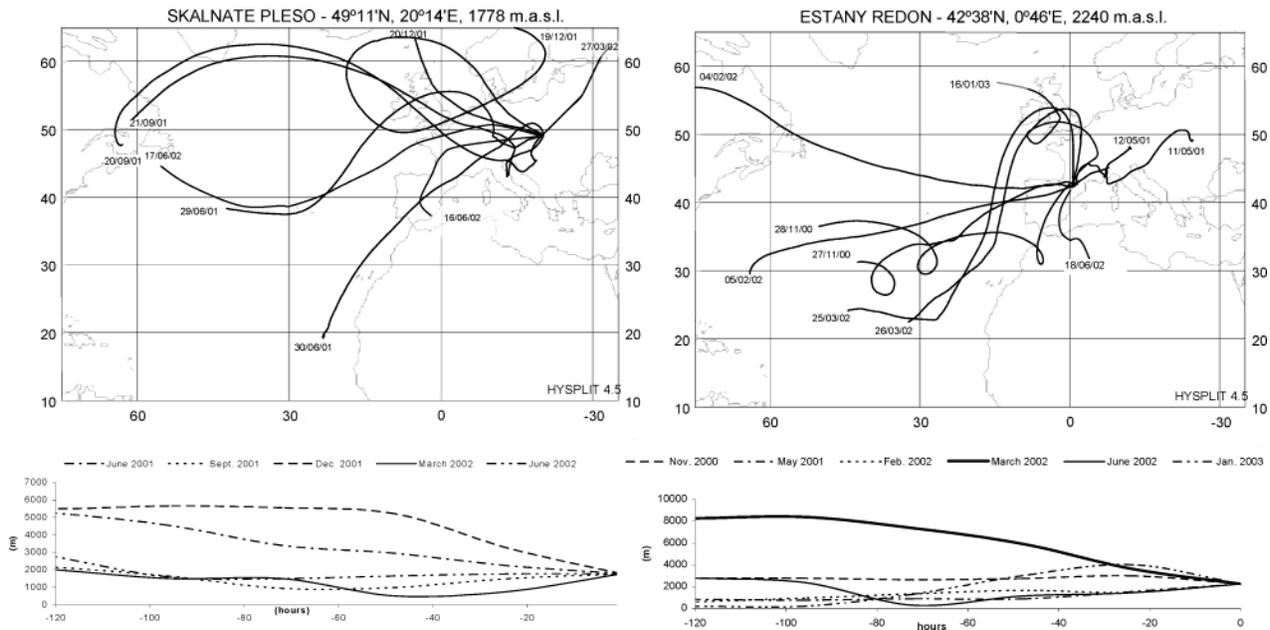


FIGURE 4. Back-trajectories of the Skalnate Pleso (left) and Estany Redon (right).

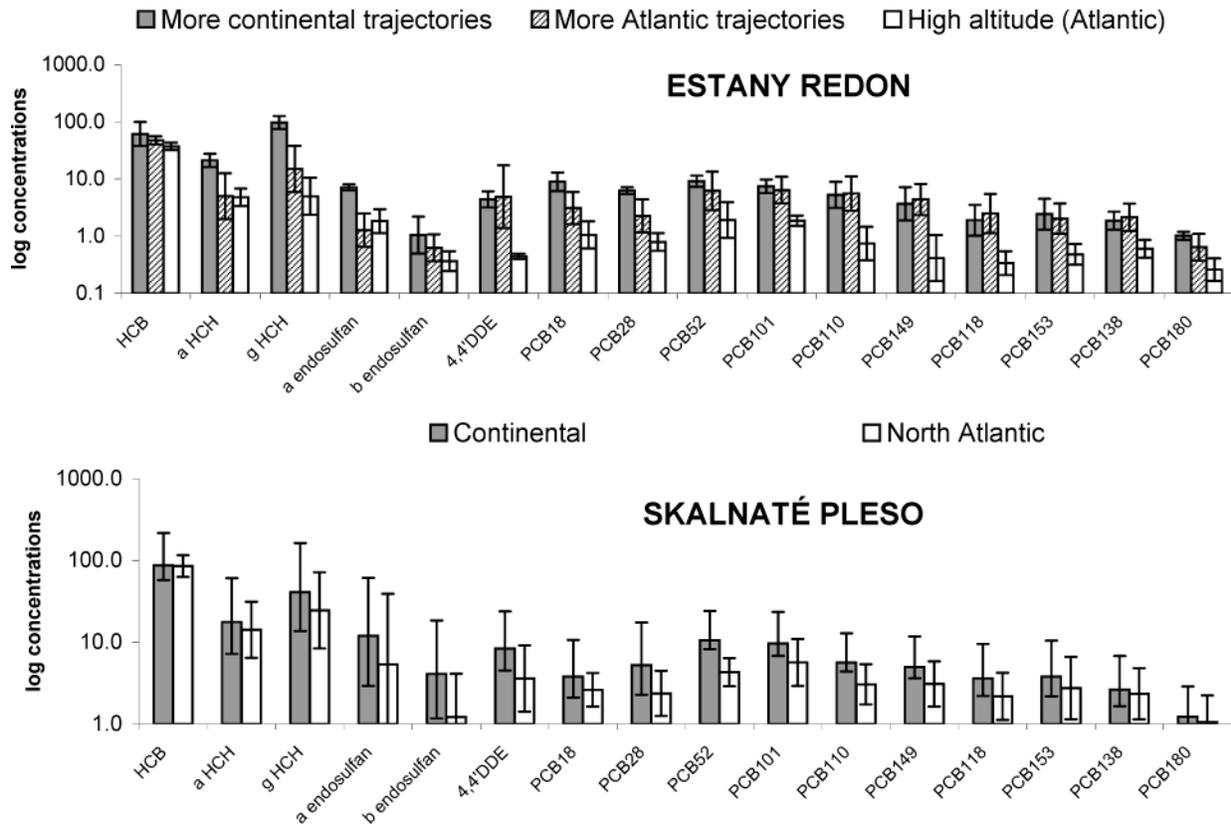


FIGURE 5. Geometric means of the composition of major (gas-phase) organochlorine compounds in the air masses collected at Estany Redon corresponding to predominant continental, oceanic, and high altitude origin. Similarly for Skalnate Pleso for continental and oceanic origin. Error bars indicate standard deviation.

6.6, and 39  $\text{pg m}^{-3}$ , respectively) (Figure 5). Only HCB shows similar concentrations in both cases, 85–87  $\text{pg m}^{-3}$ . The higher concentrations in the continental group of air samples is consistent with emissions of pollutants from the continent since, as mentioned above, these were manufactured and used in Europe some decades ago (PCB and 4,4'-DDE) or they are still in use (HCH and endosulfans). In turn, the group of air samples from continental origin were collected at warmer average in situ temperatures than those of oceanic origin, 7.8 and 1.2  $^{\circ}\text{C}$ , respectively. Thus, as suggested from

the low enthalpy values found in the previous section, the presence of SOC in the atmosphere of these high altitude sites may originate from LRAT. However, the source of these pollutants is mainly located in the European continent.

The air samples collected at Estany Redon do not have such well-defined differences such as continental or oceanic (Figure 4). This is obviously due to the situation of the sampling site, which is located on the periphery of the European continent (Figure 1). Nevertheless a group characterized by air masses of more continental origin (May 11–

12, 2001; June 17–18, 2002; Figure 4) can be differentiated from another of more oceanic trajectories (November 27–29, 2000; February 4, 2002; January 16, 2003; Figure 4). In addition, another group of very high altitude trajectories (March 25, 2002; Figure 4) has been identified. This last group is characterized by air masses travelling over 6000 m most of the time. The sample group of more continental trajectories exhibit slightly higher geometric means for the summed PCB congeners ( $60 \text{ pg m}^{-3}$ ) than the group of more oceanic origin,  $38 \text{ pg m}^{-3}$ , due to the higher abundance of the lighter PCB congeners 18, 28, and 52 in the samples with continental trajectories (Figure 5). However, these differences are not significant. Neither are significant the geometric mean differences of 4,4'-DDE showing similar levels in the samples with continental and oceanic trajectories, 4.4 and  $3.1 \text{ pg m}^{-3}$ , respectively. Thus, the concentration changes of PCBs and 4,4'-DDE are not so clearly defined as in the case of Sklanante Pleso.

In contrast, strong differences are found among the compounds of present use, HCHs and endosulfans. Thus, their gas-phase geometric means are 250 and  $17 \text{ pg m}^{-3}$  in the continental air masses and 13 and  $1.9 \text{ pg m}^{-3}$  in the more oceanic air masses. The ratios of  $\alpha/(\alpha + \gamma)$ -HCH in Estany Redon are  $0.19 \pm 0.06$  and  $0.27 \pm 0.07$  for the air masses of continental and Atlantic origin, respectively, whereas those of Skalnate Pleso are  $0.30 \pm 0.06$  and  $0.37 \pm 0.09$ , respectively. In both cases, the trajectories of more marine origin are enriched in the  $\alpha$ -isomer, which is consistent with the high proportion of  $\alpha$ -HCH with respect to the other isomers in oceanic waters (29, 37).

A strong difference in SOC concentration is found for the high altitude group, which exhibits significantly lower geometric mean concentrations for HCH, endosulfans, 4,4'-DDE, and PCB ( $9.8, 2.2, 0.4,$  and  $9.0 \text{ pg m}^{-3}$ , respectively). Air masses that travel at low altitudes can incorporate SOCs easier than air masses that travel at high altitude since the first are closer to potential pollution sources and the later are more exposed to weathering processes. The proportion of  $\alpha$ -HCH isomer in the samples corresponding to air masses at very high altitude is even higher than the previous values,  $0.49 \pm 0.11$ , which is again in agreement with the high  $\alpha$ -HCH content found in aircraft measurements at high altitude (21).

These three groups defined from air mass origin (more continental, more oceanic, and high altitude) correspond to different in situ air sampling temperatures ( $9, 4.3,$  and  $0.3^\circ\text{C}$ , respectively). The coincidence between higher air mass trajectories and lower in situ temperatures reflects that the winter atmosphere is in general more stable than the summer atmosphere (38). Again, the correspondence observed between air sampling temperatures at this site and SOC concentrations can be related to LRAT. Evaluation of the origin of the air masses illustrate that the origin of these SOC is mainly related to surface sources located in Europe.

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