

Article 1.

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TROPOSPHERE OF THE NORTHEASTERN ATLANTIC**

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Research

Semivolatile Organochlorine Compounds in the Free Troposphere of the Northeastern Atlantic

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Polychlorobiphenyls (PCBs), hexachlorobenzene (HCB), hexachlorocyclohexanes, and DDTs were analyzed over 1 entire year period in the air of a high altitude remote site (2367 m above sea level) located in Teide (Tenerife, Canary Islands, 28°N16°W) in the Eastern North Atlantic region. Twenty samples were collected providing information on the concentrations of these semivolatile organochlorine compounds (SOCs) in the free troposphere since the stable and persistent temperature inversion in the subtropics defines a clear separation from the marine boundary layer. More than 80% of total SOCs were in the gas phase. HCB was the individual SOC in higher concentration, 51 pg m⁻³, well above than the other SOCs identified, 1–11 pg m⁻³. Sum PCB concentrations were 78 pg m⁻³. These concentrations range among the lowest described in atmospheric samples. The collected air originated from four main sectors, high and middle latitudes in the north Atlantic, Europe, and Africa, as determined from isentropic backward air mass trajectories. No significant differences were observed for the concentrations of these compounds between air masses showing a high uniform SOC composition of the free troposphere. Only the more volatile PCB congeners, #18 and #28, exhibited significant differences between air masses from northern and southern latitudes. A seasonal temperature dependence for the less volatile PCB congeners, five or more chlorine substituents, was also observed. Free tropospheric concentrations of all SOCs except HCB were lower than those measured near sea level for reference. PCB concentrations at the two altitudes exhibited consistent differences according to degree of chlorination. The stronger decrease of the more volatile compounds with altitude might reflect higher photodegradation.

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Introduction

Several studies have documented the occurrence of semivolatile organochlorine compounds (SOCs) in the atmosphere of remote areas, where these environmentally persistent pollutants were not used neither produced (1–3). These results have shown the importance of the atmosphere for the transport of SOCs to these remote sites and for their distribution through air–soil and air–water exchange (4–6). However, full understanding of the role of the atmosphere in the global distribution of these compounds also requires the investigation of their occurrence in the free troposphere, far away from interactions with the continental and oceanic boundary layers. To our knowledge, this problem has only been addressed once from aircraft measurements (7).

In the present study, air samples were collected in the subtropical Northeastern Atlantic area. The meteorological conditions in this region are under the influence of the descendent branch of the Hadley cell, which basically consists on an energy net flux transport from the equator to the pole, and produces an area of strong subsidence circulation in the middle and lower troposphere at around 30°N (8). This circulation results in a dry and dynamically stable free troposphere, inhibiting convective processes. At sea level the circulation is dominated by the Trade-winds (NE winds) which transport relatively humid and cool air from middle latitudes. A stable temperature inversion separates the air masses below and above the boundary layer. This inversion obstructs vertical motions (Figure 1) and generates a typical stratocumulus sea–cloud between 900 and 2000 m above sea level.

In these subtropical latitudes, high altitude sites allow the continued sampling of free tropospheric air. The remote site selected for sampling has been the Izaña Atmospheric Observatory (IZO), situated at 2367 m above sea level in Teide (Tenerife Island, 28°18'N, 16°29'W; Figure 2), which is representative of background free tropospheric conditions and is not affected from local pollution sources.

Air samples were collected on a 15-m high tower during night time when the mountain–valley breeze system is well established. Twenty samples of gas and particulate phases were collected between June 1999 and July 2000, encompassing all year seasons. For reference of the SOC composition of air masses within the marine boundary layer, four samples were taken on the top of a 47-m high lighthouse ('Punta del Hidalgo', PHO) located at sea level at the northeastern part of the island (28°34'N 16°20'W). This location is open to the Trade-winds. Nineteen PCB congeners were analyzed in all samples, including tri- (#18, #28), tetra- (#52, #70), penta- (#90, #101, #105, #110, #118, #123), hexa- (#132, #138, #149, #153, #158, #160), hepta- (#180), and octachlorinated (#199, #194) congeners. Hexachlorobenzene (HCB), hexachlorocyclohexanes, α -HCH and γ -HCH, and 4,4'-DDT and 4,4'-DDE were also analyzed.

Materials and Methods

Back Trajectories. The origin of the air masses arriving to Tenerife was calculated from back-trajectories using the HIRLAM model (High-Resolution Limited Area 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 (9, 10). The calculations were performed at 00:00 UTC and 12:00 UTC for 5 days (5-D) back with 1 h step. The isentropic surfaces for each back-trajectory at IZO and PHO

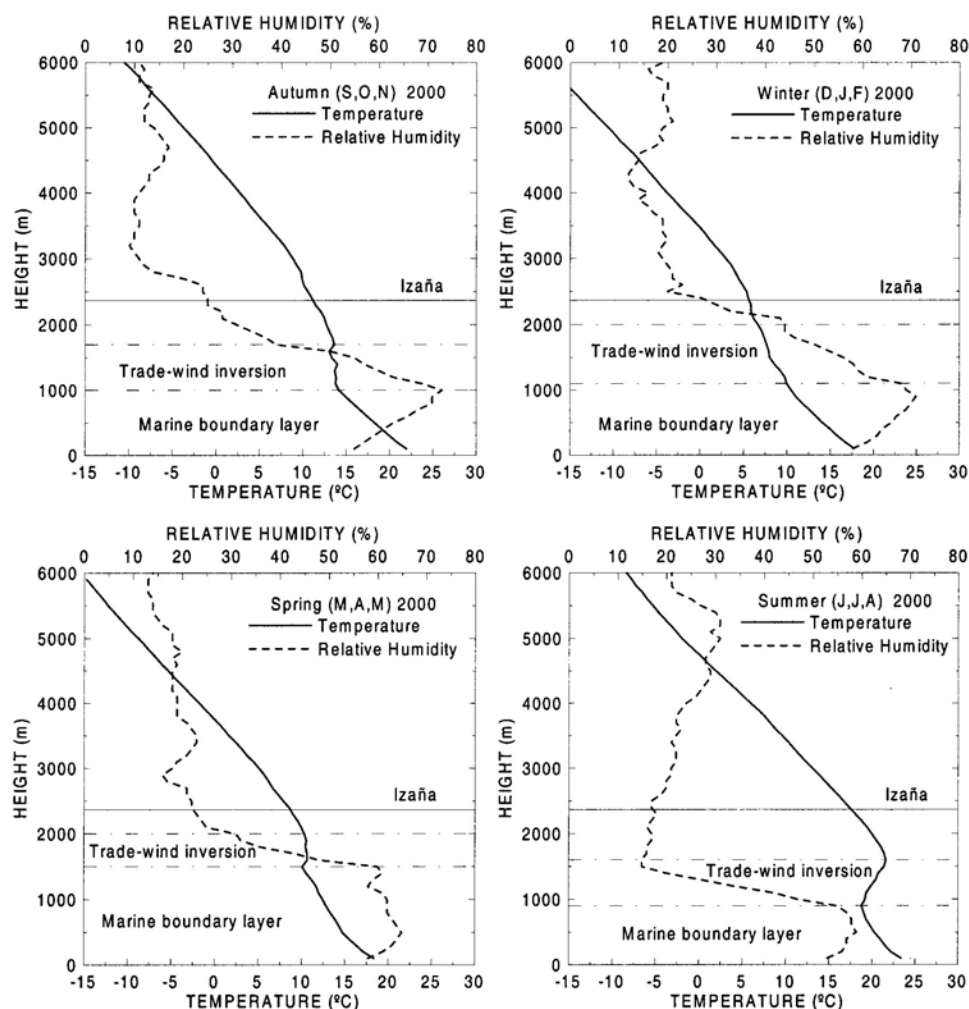


FIGURE 1. Averaged vertical profiles of temperature and relative humidity over Tenerife ($28^{\circ}18'N$ $16^{\circ}29'W$) for autumn, winter, spring, and summer. The profiles have been calculated with weekly ozone sonde data from Tenerife (#60020 Meteorological Station – INM) during year 2000. Trade-wind inversion is bounded by two dash-dot lines. The marine boundary layer is below the Trade-wind inversion.

stations were selected according to the observed potential temperature at 2367 and 47 m above sea level, respectively.

Sample Collection. Air was collected with a high volume sampler (MCV S.A., Collbato, Catalonia, Spain). SOC in the gas phase were extracted from the air matrix with two polyurethane foam (PUF) plugs (diameter 6 cm; height 10 cm; density 28.5 kg/m^3) packed inside a Teflon tube. Glass fiber filters (GFF; Whatman International Ltd., Maidstone, England) were used to collect the particulate phase ($20.3 \times 25.4 \text{ cm}$; $1.0 \mu\text{m}$ pore size). Before sampling PUFs were Soxhlet extracted with *n*-hexane for 48 h. GFFs were cleaned by ashing at 400°C for 24 h. PUFs were packed into the Teflon tubes which were subsequently wrapped in aluminum foil and introduced into heat sealed polyester bags (Kapak Corporation, Minneapolis, U.S.A.) for transport between Tenerife and Barcelona. GFFs were also wrapped in aluminum foil and introduced into polyester bags for transport. This was performed in approximately 2 days.

Collected sample volumes were between 80 m^3 and 240 m^3 . After sampling, PCB#30 and PCB#209 were added as

internal standards. The recoveries of these compounds were used to correct for losses during transport and analysis.

Sample Extraction and Analysis. PUFs and GFFs were Soxhlet extracted for 24 h in 250 mL of *n*-hexane (Merck, Darmstadt, Germany) and in 250 mL of hexane:dichloromethane (DCM; Merck, Darmstadt, Germany) (4:1 v/v), respectively. The extracts were vacuum evaporated until 1 mL. Samples and blanks were cleaned-up by adsorption on 2 g of aluminum oxide (Fluka Type 507C, Fluka AG, Switzerland) and elution with 8 mL of hexane:DCM (9:1 v/v) and 7 mL of hexane:DCM (1:2 v/v). The collected fractions were vacuum evaporated to 1 mL and to near dryness under a gentle stream of nitrogen. Finally, they were redissolved in isooctane (Merck, Darmstadt, Germany) to $50 \mu\text{L}$.

Tetrachloronaphthalene and octachloronaphthalene (Ehrenstorfer, Augsburg, Germany) were added to the vials before instrumental analysis for correction of possible instabilities. The extracts were injected into a gas chromatograph equipped with an electron capture detector (GC-ECD, Hewlett-Packard 5890 Series II). A 50 m fused silica capillary column (0.25 mm

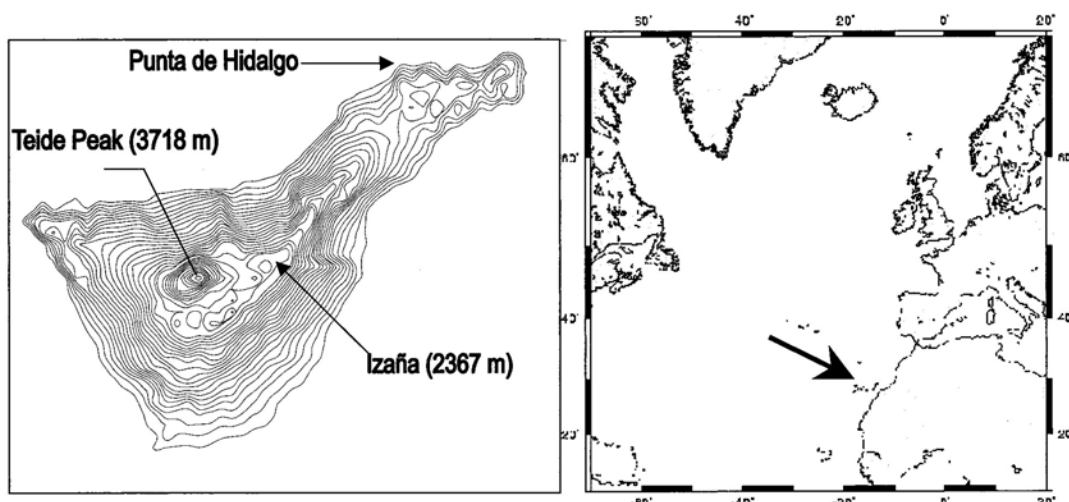


FIGURE 2. Location of the sampling sites in Tenerife Island.

i.d. 0.25 μm film thickness) coated with 5% phenyl 95% methylpolysiloxane (DB-5, J&W Scientific, Folsom, CA) was used for the analyses. The oven temperature program was started at 100 $^{\circ}\text{C}$ (holding time 1 min), increased to 150 $^{\circ}\text{C}$ at 15 $^{\circ}\text{C}/\text{min}$, followed by heating at 4 $^{\circ}\text{C}/\text{min}$ to 240 $^{\circ}\text{C}$ (holding time 12 min), and finally increased to 300 $^{\circ}\text{C}$ at 4 $^{\circ}\text{C}/\text{min}$ (holding time 10 min). Injector and detector temperatures were 250 $^{\circ}\text{C}$ and 310 $^{\circ}\text{C}$, respectively. Helium and nitrogen were used as carrier (0.33 mL/min) and makeup (60 mL/min) gases, respectively.

Quality Control and Assurance. Field blanks were inserted between the samples for monitoring for possible contaminations during transport and processing. These blanks were treated and analyzed as regular samples constituting about 30% of total samples analyzed. Field blank values were in the range of 1–10% of sample concentrations in the case of α -HCH, HCB, γ -HCH, PCB#28, PCB#90+101 and PCB#199, these levels were in the range of 10–20% for 4,4'-DDE, 4,4'-DDT, PCB#52, PCB#70, PCB#110, PCB#149+123, PCB#153, PCB#138, PCB#180, and PCB#194 and in the range of 20–30% for PCB#18, PCB#105+132, PCB#118, and PCB#160+158. For each batch of samples and blanks, sample concentrations were handled after subtraction of blank levels. Recoveries in PUF for PCB#30 and PCB#209 were $68 \pm 20\%$ and $77 \pm 19\%$, respectively, and in GFF they were $66 \pm 25\%$ and $84 \pm 17\%$, respectively. Injection of standards of the investigated SOC into clean PUFs in Tenerife and subsequent transport and analysis in Barcelona gave recoveries between 81% and 118%. Detection limits (determined as three times the standard deviation of the chromatographic noise near the SOC peaks) were 0.04–0.23 pg m^{-3} for PCBs, 0.03 pg m^{-3} for HCB, 0.12 pg m^{-3} and 0.15 pg m^{-3} for α -HCH and γ -HCH, respectively, and 0.20 pg m^{-3} and 0.08 pg m^{-3} for 4,4'-DDE and 4,4'-DDT, respectively. PUF breakthrough was determined by injection of a mixture of PCB congeners #40, #155, and #185 into the first PUF plug before air adsorption of the regular sampling volumes. Replication of this test in four occasions did not show any traces of these compounds in the second PUF plug. Previous examination of possible adsorption effects into the filter by analysis of a second filter installed between the first filter and PUF showed that these could be in the level of 10% at the most which is consistent with other reports in the literature (11–13). The present results have therefore not been corrected by adsorptions in the second filter.

Results and Discussion

Free Troposphere Concentrations. More than 80% of all SOC analyzed are in the gas phase (Table 1) which is in agreement with previous studies (13–15). HCB is the individual gas-phase SOC found in highest concentration at IZO (51 pg m^{-3} ; Table 1). However, the summed PCB congeners are in higher abundance (78 pg m^{-3} ; Table 1). The other SOC identified, α -HCH, γ -HCH, 4,4'-DDE, and 4,4'-DDT, are in much lower concentrations (1–11 pg m^{-3} ; Table 1).

In the free troposphere, the average concentrations of α -HCH, γ -HCH, HCB, 4,4'-DDE, and 4,4'-DDT are lower than those reported at sea level in previous studies on remote sites such as the Arctic (5, 16, 17) and North Atlantic (2, 3) oceans (Table 2). Transformation of the measurements reported in Table 1 to normal air volume (multiplication by a density factor of 1.4) still show that the samples collected at IZO exhibit lower values than in these previously studied remote sites. PCB are also in very low amounts in comparison to results previously reported in other remote sites. The normal volume average value of ΣPCBs at IZO is 109 pg m^{-3} . Only the sea level atmospheric concentrations reported at Spitsbergen (13 pg m^{-3} (17)) or ground level near Baikal Lake (89 pg m^{-3} (16)) are lower than this concentration (Table 2).

HCB, γ -HCH, and total PCB concentrations at IZO are also lower than those found in aircraft measurements between 2438 and 3048 m above sea level (7). However, the differences are within a factor of 2 at the most (Table 2). In contrast, this is not the case of α -HCH which in aircraft measurements was found to be about 50 times higher than at IZO (Table 2). These high aircraft α -HCH values range among the highest reported for remote sites (Table 2).

Temperature Dependence. Air temperatures at IZO range from 5.5 $^{\circ}\text{C}$ (average winter) to 17 $^{\circ}\text{C}$ (average summer). No temperature dependence has been observed for the changes in concentration of the pesticides and the PCB congeners with three or tetra chlorine substituents, but those with higher degree of chlorination exhibit temperature dependence. These dependences can be evidenced by representation of the natural logarithm of the concentrations vs the inverse of the absolute temperatures (18–20). The slopes and the correlation coefficients increase for the congeners with higher degree of chlorination, showing a strong negative correlation for PCB#180 (Figure 3). Higher temperatures involve higher

TABLE 1. Arithmetic Mean and Range of SOC Concentrations (pg m^{-3}) at the Two Sampling Sites, IZO (Izaña (2367 m asl)) and PHO (Punta de Hidalgo (47 m asl))

	PUF			GFF		
	mean	max	min	mean	max	min
IZO ($n = 20$)						
α -HCH	5.9	19	1.3	0.4	2.1	<0.12
HCB	51	110	23	0.4	3.7	<0.03
γ -HCH	11	37	1.6	1.0	9.1	<0.15
4,4'-DDE	4.2	6.9	1.1	0.4	1.6	<0.20
4,4'-DDT	1.0	3.0	<0.08	0.3	3.1	<0.08
PCB18	8.0	18	2.8	0.5	1.2	<0.07
PCB28	9.3	20	2.4	0.7	1.2	<0.2
PCB52	9.6	16	3.5	0.8	1.5	<0.19
PCB70	7.0	13	3.4	0.8	1.8	<0.05
PCB90+101	10	19	1.8	0.7	1.9	<0.12
PCB110	9.4	20	2.6	0.9	1.6	<0.08
PCB149+123	4.7	11	1.9	0.4	0.7	<0.1
PCB118	4.4	9.8	1.0	0.6	1.8	<0.02
PCB153	4.5	9.9	1.2	0.5	0.9	<0.12
PCB105+132	3.1	5.9	0.3	0.6	1.1	<0.15
PCB138	4.5	8.6	0.5	0.5	0.9	<0.15
PCB158+160	0.9	4.0	0.0	0.5	0.8	<0.15
PCB180	2.3	5.1	0.3	0.5	1.0	<0.15
PCB199	0.7	1.0	<0.15	<0.09		
PCB194	0.4	0.9	<0.15	<0.1		
Σ PCB	78	130	44	4.2	9.4	<1.7
PHO ($n = 4$)						
α -HCH	22	25	19	0.6	0.9	0.4
HCB	72	79	69	<0.12		
γ -HCH	26	31	18	1.5	2.8	0.9
4,4'-DDE	22	29	11	2.2	2.5	2.1
4,4'-DDT	9.8	14	6.6	1.1	1.9	<0.08
PCB18	25	31	19	1.4	1.4	<0.07
PCB28	24	29	20	0.7	0.8	<0.2
PCB52	28	34	15	1.9	2.4	1.0
PCB70	23	28	16	1.4	1.8	1.0
PCB90+101	19	20	17	1.6	1.8	1.2
PCB110	18	19	16	3.1	3.5	2.6
PCB149+123	14	16	11	1.9	2.3	1.4
PCB118	7.7	11	5.1	1.7	2.0	1.6
PCB153	8.8	12	6.6	1.4	1.4	1.3
PCB105+132	8.0	9.6	6.3	1.4	1.7	1.2
PCB138	8.3	11	5.3	2.0	2.1	1.9
PCB158+160	3.7	6.9	1.9	0.5	0.6	0.4
PCB180	2.7	3.4	2.1	0.5	0.9	0.2
PCB199	0.3	0.4	0.3	<0.09		
PCB194	0.6	0.9	<0.15	<0.09		
Σ PCB	190	220	160	18	20	17

concentrations which is consistent from SOC degassing at warmer climate. This relationship is currently stronger near potential sources (19, 20). In this case, the restricted temperature dependence to the congeners with higher degree of chlorination is consistent with a PCB origin from diffuse sources reflecting long-range transport.

Back-Trajectories. Air masses sampled during the study had their origins over the northwestern Atlantic (North Atlantic High Latitude = NAHL), the western Atlantic (North Atlantic Mid Latitude = NAML), the western African continent (A), and western Europe (E; Figure 4). To evaluate whether geographical effects could be related to the occurrence of SOC, the samples have been grouped according to origin (Figure 4).

No significant differences (ANOVA, $p < 0.05$) are observed for the concentrations of the pesticides when comparing these four groups. HCB, HCH, and DDTs seem to be well mixed in the free troposphere (Figure 5). However, the relative content of 4,4'-DDT evidences some minor differences. Thus,

air masses from the Atlantic (NAHL and NAML) exhibit very low 4,4'-DDT/(4,4'-DDT + 4,4'-DDE) fractions, 0.1 or <0.1, whereas in those originating from Europe and Africa this fraction is higher, 0.3–0.4, probably reflecting some influence of 4,4'-DDT residues from the continents (Figure 5).

The levels of α -HCH and γ -HCH are considerably lower than those found at other remote locations, namely in the case of α -HCH (Table 2). This difference is consistent with the banning of technical mixtures, α -HCH rich, in the past (21). Despite total isomers range between 13 and 23 pg m^{-3} between sectors significant differences are observed in the relative content of the α -isomer. The NAHL, NAML, Europe, and Africa air masses have α -HCH/(α -HCH + γ -HCH) fractions of 0.45, 0.39, 0.29, and 0.17, respectively. These differences are consistent with previous reports since α -HCH is found in higher relative amounts than γ -HCH in remote locations such as the eastern Arctic or the North Pacific Oceans (1, 22). Accordingly the higher relative content of α -HCH is found in NAHL and NAML, namely NAHL. In turn, the lower relative content of α -HCH of the samples originating from Europe and Africa, namely this last one, may reflect the recent use of γ -HCH in these continental areas.

The average concentrations of sum PCB in the four backward trajectory sectors are 67.5, 99, 75, 64 pg m^{-3} for NAHL, NAML, Europe, and Africa, respectively (Figure 5). Overall analysis of variance of these four sectors shows the absence of significant differences for the concentrations of nearly all PCB congeners. Only the lighter PCB congeners #18 and #28 show significant differences between these sectors ($p < 0.005$ and $p < 0.05$ in the ANOVA tests, respectively; Table 3). The differences involve a higher concentration in the air masses originating from southern middle latitudes. Thus, comparison of means between the southern middle (NAML + Africa) and the northern (NAHL + Europe) sectors, 11 and 6 pg m^{-3} for #18 and 13 and 7 pg m^{-3} for #28, respectively, shows significant differences ($p < 0.005$). This difference is essentially due to the influence of the air masses from Africa, which are those showing most distinct composition with respect to the other sampled air masses (Table 3). However, the concentrations of #18 and #28 in NAML air masses, 10–12 pg m^{-3} , also show a distinct composition from the air masses originating from NAHL, with concentrations of #18 and #28 5–6 pg m^{-3} ($p < 0.05$, Table 3). In contrast, there were no significant differences between the two northern sectors (NAHL and Europe), showing that the air masses from Europe do not necessarily reflect higher background PCB concentrations, as measured in former studies (23). However, it is possible that the European air masses arriving to IZO could have never been in direct contact with potential pollution sources, since they were travelling at high altitudes as calculated with the HIRLAM-model. Differences in composition between the African and the other air masses also involve compounds #105+132 (Africa-NAHL and Africa-Europe), #70 (Africa-NAML), and #153 (Africa-NAML), representing lower concentrations of these congeners in Africa (Table 3).

Evaluation of the PCB distributions of these air masses provides further insight into the differences in composition. NAHL, NAML, and Europe exhibit a close composition (Figure 5). This homogeneity contrasts with the results on PCB concentrations measured in other studies near sea level, or at lower altitudes, where a geographical effect could be recognized (23, 24). In the samples collected at IZO, the significant differences only concern the African sector (Table 3). The higher abundance of PCB#18 and PCB#28 in this sector involves a statistically significant lower relative content of congeners such as #110, #70, #153, and #105/#132 (Table 3). This higher abundance of PCB#18 and #28 could reflect a higher temperature enhancement of the more volatile PCB congeners over the African continent. In addition, sampled

TABLE 2. Comparison of the Atmospheric SOC Concentrations at Tenerife with Those from Other Remote Sites Reported in the Literature^a

ref	sampling year	location	height (masl)	ΣPCB	α-HCH	γ-HCH	HCB	44'-DDE	44'-DDT
(7)	1986	Bermuda	3000	160 ^a	300	16	98		
			500	330 ^a	120	43	89		
(17)	1991	Lake Baikal		89 ^b	490	105	190	8	8
(18)	1992	Spitsbergen		13 ^c	140	32	205		
(3)	1992–1993	Bermuda	23	150 ^d					
(23)	1996	E. Arctic Ocean			37	17			
(2)	1989–1990	N. Atlantic		290 ^a	200	66		3	4
	1999–2000	Tenerife	2367	78	6	11	51	4	1
			47	190	22	26	72	22	10

^a Different PCB congeners are considered in each case complicating comparison between different studies. The values indicated in this table correspond to the sum of the congeners considered in this study as indicated in the Introduction section: (a) no data on individual congeners reported by the authors; (b) #28, 52, 70, 101, 110, 118+149, 153+105+132, 138, 180; (c) #28, 31, 52, 101, 105, 118, 153, 156, 180; #18, 28, 52, 70, 101, 110, 149, 118, 153, 138, 180; (d) #18, 28, 52, 70, 101, 110, 149, 118, 153, 138, 180.

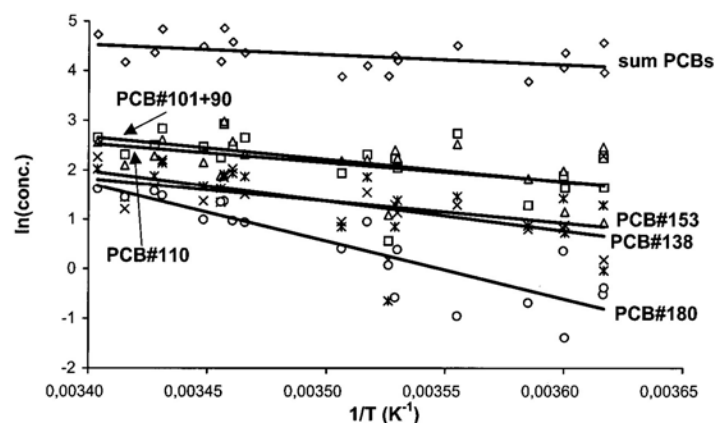


FIGURE 3. Dependences between air PCB congener concentrations and temperature. Sum PCB ($y = -1983/T + 11.3$; $r^2 = 0.20$), PCB101+90 ($y = -4540/T + 18.1$; $r^2 = 0.31$), PCB153 ($y = -4478/T + 17$; $r^2 = 0.27$), PCB110 ($y = -3833/T + 16$; $r^2 = 0.26$), PCB138 ($y = -6059/T + 23$; $r^2 = 0.36$), and PCB180 ($y = -11681/T + 41$; $r^2 = 0.77$). Concentrations in pg m^{-3} .

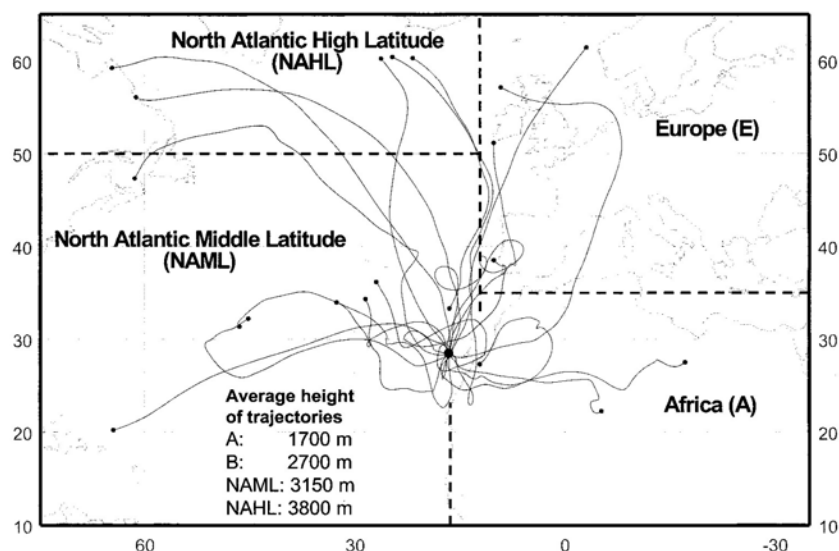


FIGURE 4. Isentropic back-trajectories of the samples collected at IZO between June 1999 and July 2000.

air masses from Africa originated near the ground in the Saharan desert which could facilitate the incorporation of these trichlorinated PCB congeners.

Vertical Distributions. Although the sampling strategy of this study was devoted to determine the concentrations in the free troposphere, as indicated above, some samples

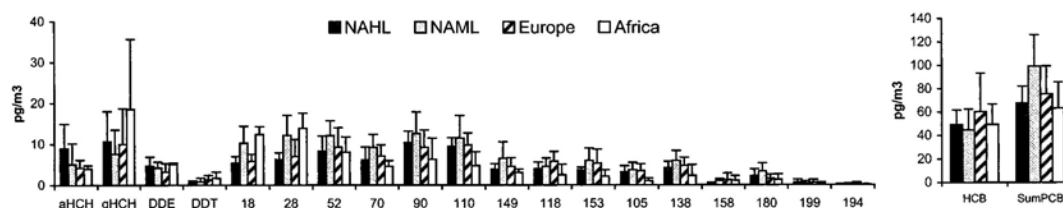


FIGURE 5. Mean SOC concentrations in the four sectors of IZO.

TABLE 3. Bilateral *t*-Test Comparison of the Means of the PCB Congener Concentration and Relative Distributions of the Air Masses Corresponding to the Samples Collected in the Free Troposphere at IZO^a

NAHL	NAHL				NAML				Europe			
	congener	mn _{NAHL}	mn _{NAHL}	sig.								
	#18	10	5	$p < 0.05$								
	#28	12	6	$p < 0.05$								
Concentrations												
Europe	congener	mn _{Europe}	mn _{NAHL}	sig.								
	#18	6	10	$p < 0.05$								
Africa	congener	mn _{Africa}	mn _{NAHL}	sig.	congener	mn _{Africa}	mn _{NAHL}	sig.	congener	mn _{Africa}	mn _{Europe}	sig.
	#18	12	5	$p < 0.01$	#70	4.5	9.1	$p < 0.05$	#18	12	6	$p < 0.01$
	#105/132	1.0	3.2	$p < 0.05$	#153	2.1	6	$p < 0.05$	#105/132	1	3.5	$p < 0.05$
					#105/132	1.0	3.7	$p < 0.05$				
Relative Distributions ^b												
Africa	congener	mn _{Africa}	mn _{Europe}	sig.	congener	mn _{Africa}	mn _{NAHL}	sig.	congener	mn _{Africa}	mn _{Europe}	sig.
	#18	0.87	0.50	$p < 0.05$	#28	0.97	0.77	$p < 0.05$	#110	0.33	0.86	$p < 0.05$
	#28	0.97	0.57	$p < 0.005$	#70	0.33	0.65	$p < 0.05$	#153	0.17	0.44	$p < 0.05$
	#110	0.33	0.85	$p < 0.05$	#105/132	0.07	0.23	$p < 0.05$	#105/132	0.07	0.32	$p < 0.01$
	#105/132	0.07	0.30	$p < 0.001$								

^a The origins of these air masses were calculated from backward air mass trajectories: Europe, Africa, and North Atlantic high and medium latitudes, NAHL and NAML, respectively. Mean PCB relative distributions are summarized in Figure 5. Nonreported cases, e.g. most PCB congeners, did not show significant differences between any of the air masses of different origins, pointing to a rather uniform PCB composition. ^b Percent with respect to maximum PCB congener concentration.

have been measured close to sea level at Tenerife for reference. PCB concentrations at PHO, 191 pg m^{-3} , are similar to those reported at sea level near Bermuda (150 pg m^{-3} (3)), higher than those found near Lake Baikal (89 pg m^{-3} (16)) or at Spitzbergen (13 pg m^{-3} (17)) and lower than those reported in the North Atlantic (290 pg m^{-3} (2)). HCB at PHO, 72 pg m^{-3} , is lower than in other sea level remote sites, $120\text{--}200 \text{ pg m}^{-3}$ (Table 2). HCH, 22 and 26 pg m^{-3} for the α - and γ - isomers, are also found in lower concentrations than in other remote sites, but the differences are more significant for the α - than for the γ - isomer (Table 2).

The air concentrations at IZO are significantly lower than those measured at PHO (Table 1). The ratios between average measurements are 2.5 for sum PCB and 1.4 for HCB, 3.2 and 2.5 for α - and γ -HCH, respectively, and 5.5 and 9.8 for 4,4'-DDE and 4,4'-DDT, respectively. *t*-Tests of significance between means show that the differences are significant in all cases ($p < 0.05$ or lower) except for some highly chlorine substituted PCB congeners, e.g. #158/160 and #180. Transformation of the measurements at IZO to normal air volumes using the above-mentioned factor of 1.4 reflects a vertical concentration difference for all compounds except HCB. The concentrations of this compound show a uniform distribution below and above the boundary layer.

The fraction 4,4'-DDT/(4,4'-DDT + 4,4'-DDE) at PHO is 0.3 being higher than the fraction at IZO for NAHL and NAML

air masses, 0.1 or <0.1 , but similar to the European and African air masses. This higher fraction suggests some contribution of 4,4'-DDT from the ground in the air masses within the boundary layer. On the other hand, the mean fraction of α -HCH/(α -HCH + γ -HCH) at PHO is 0.40, an intermediate value between the fractions observed at IZO for NAHL and NAML and higher than that in air masses from Europe and Africa.

PCBs at PHO within the boundary layer are dominated by the lighter congeners (tri- and tetrachloro substituted), whereas above the inversion, at IZO, the mixtures are dominated by pentachlorinated congeners. Comparison of the average normal volume concentrations between the two altitudes shows a progressive depletion from the more to the less chlorinated compounds with factors of 0.36, 0.43, 0.5, 0.56, and 0.77 for the tri-, tetra-, penta-, hexa-, and heptachlorinated congeners, respectively. These differences in PCB distributions cannot be explained by diffusion processes. Would this be the case, tri- and tetrachlorinated congeners would also dominate the PCB composition at IZO. The differences in composition might be an effect of photodegradation by hydroxyl radicals since, as shown under laboratory conditions (25), these compounds with lower degree of chlorination exhibit higher reaction rates with these oxidants.

In this respect, concentrations of hydroxyl radicals in summer at 30°N latitude are higher at 2000 m than at sea

surface (26). However, these differences, 25×10^5 and 15×10^5 molecules cm^{-3} , respectively, are smaller in the other seasons. Latitudinal concentration gradients are also observed for these reagents which involve higher levels at the warmer regions (26). These latitudinal differences may also be relevant during SOC atmospheric transport.

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