

Temperature and Organic Matter Dependence of the Distribution of Organochlorine Compounds in Mountain Soils from the Subtropical Atlantic (Teide, Tenerife Island)

ALEJANDRA RIBES AND
JOAN O. GRIMALT*

*Department of Environmental Chemistry, Institute of Chemical and Environmental Research (ICER-CSIC),
Jordi Girona 18-26, 08034 Barcelona, Catalonia, Spain*

CARLOS J. TORRES GARCÍA AND
EMILIO CUEVAS

*Izaña Atmospheric Observatory, National Institute of Meteorology, La Marina 20, 38071 Santa Cruz de Tenerife,
Canary Islands, Spain*

Surface soil samples from Teide mountain (Canary Islands) have been analyzed for polychlorobiphenyls (PCBs), DDTs, hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), and pentachlorobenzene. The samples were situated between 10 and 3400 m above sea level being distributed below, at, and above the permanent inversion layer system characteristic of the subtropical Atlantic. All OC concentrations were, in general, low when compared with the data from urban, agricultural, or woodland soils reported elsewhere. Typical ranges were 0.04–9.2, 0.01–40, 0.001–1, or 0.01–3.2 ng·g⁻¹ dry weight for total PCBs, DDTs, HCHs, or HCB, respectively. These compounds exhibited a high dependence from the soil total organic carbon (TOC), showing high coefficients in the log(OC) versus log(TOC) correlations. The slopes of the curve fitted straight lines were, in turn, highly correlated to the log-transformed octanol–air coefficients of the compounds. This overall OC distribution points to steady-state conditions for the concentrations of these compounds in these mountain soils, in equilibrium with TOC. The equilibrium conditions are reached, despite the restrictions to convective air movement associated to the permanent atmospheric inversion layer at these latitudes. In addition, the log-transformed TOC-normalized concentrations of most PCBs, HCB, and pentachlorobenzene exhibit a good correlation with the reciprocal of average annual atmospheric temperatures also showing a temperature dependence for their distribution in the high mountain system. The calculated pseudo-enthalpies for this dependence, 120–160 kJ·mol⁻¹, exhibit higher values than those of octanol–air phase change calculated from laboratory experiments in previous studies, 66–93 kJ·mol⁻¹. The difference suggests a higher affinity of OC to soils than that corresponding to simple adsorption mechanisms.

* Corresponding author phone: 34 93 4006122; fax: 34 93 2045904; e-mail: jgoqam@cid.csic.es.

Introduction

Polychlorinated biphenyls (PCBs), DDTs, hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), and other organochlorine compounds (OCs) remain in the environment, despite their discontinued use in most countries as a consequence of their high chemical stability, hydrophobic properties, and low volatility. These properties also determine their selective accumulation in specific ecosystems such as those in cold areas. Thus, part of the OCs released in the northern temperate areas, where they were used most intensively, accumulated at high latitudes (1–3) or at high mountain sites (4). This transfer involves a reversal of the common pollutant dilution trend upon release into the environment. This mechanism, called the global distillation effect (3, 5, 6), encompasses the concentration of these compounds from diffuse pollution to environmental cold sites as a consequence of condensation.

However, this mechanism, and its relevance for OC transfer, has only been considered in ecosystems at high latitudes (1–3) or, recently, in high mountains of temperate areas (4). A global understanding of the distribution pattern of these compounds also requires the inclusion of low latitude regions.

In the present paper, a mountain system in the subtropical Atlantic Ocean (28°N 16°W; Teide, Tenerife, Canary Islands; Figure 1) is considered. This area is characterized by a stable temperature inversion year-round that separates air masses of lower altitude (below 1000 m) from the free troposphere (above 1800 m). These conditions result from the descent branch of the Hadley cell at this latitude. They involve a different meteorological situation from that in mountain systems of temperate areas (4) where the vertical structure of the atmosphere is less stable and changes depending on season and local weather episodes.

The distribution patterns of PCBs, DDTs, HCHs, HCB, and pentachlorobenzene in the soils of this mountain system are considered. Soils constitute the main compartment for the accumulation of OC in the dry environments of these regions. To the best of our knowledge, this is the first study considering the distribution of OC in mountains of low latitude areas.

Materials and Methods

Meteorological Data. The average atmospheric temperature profiles were obtained after summarizing the hour-to-hour long-term climatic records stored at Izaña (Spanish National Institute of Meteorology (INM)).

Materials. Residue analysis *n*-hexane, dichloromethane, isooctane, methanol, and acetone were from Merck (Darmstadt, Germany). Anhydrous sodium sulfate for analysis and powdered copper (size <63 μm) were also from Merck. Neutral aluminum oxide type 507C was from Fluka AG (Buchs, Switzerland). Cellulose extraction cartridges were from Whatman Ltd. (Maidstone, U.K.). Aluminum foil was rinsed with acetone and allowed to dry at ambient temperature prior to use. The purity of the solvents was checked by gas chromatography-electron capture detection (GC-ECD). No significant peaks should be detected for acceptance. Aluminum oxide, sodium sulfate, and cellulose cartridges were cleaned by Soxhlet extraction with dichloromethane/methanol (2:1, v/v) for 24 h before use. The purity of the cleaned reagents was checked by ultrasonic extraction with *n*-hexane/dichloromethane (4:1; 3 × 20 mL), with a concentration of 50 μL and analysis by GC-ECD. No interferences were detected. Sodium sulfate and aluminum oxide were

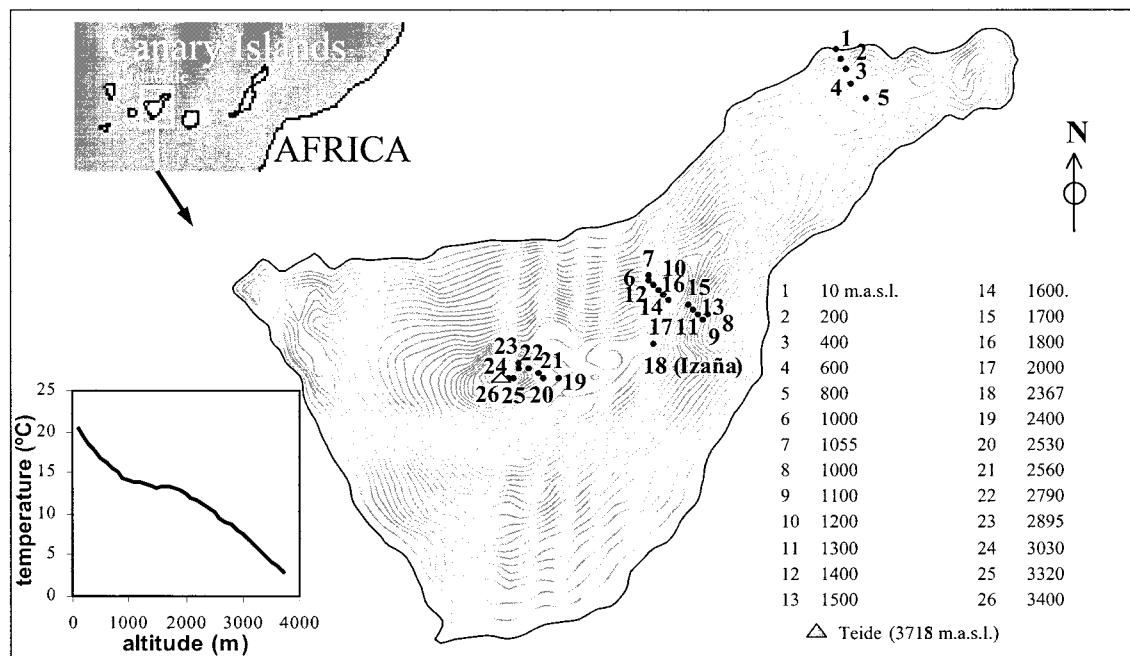


FIGURE 1. Distribution of the soil samples collected in Tenerife Island. The inset indicates the average altitude temperature gradient defining a stable atmospheric inversion layer throughout the year.

activated overnight at 400 and 120 °C, respectively. Copper was activated by sonication with 35.5% hydrochloric acid (3 × 3 mL) and then rinsed several times with Milli-Q water to a 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).

Pentachlorobenzene, HCB, α -HCH, γ -HCH, δ -HCH, 4,4'-DDE, 4,4'-DDT, and the PCB congeners no. 18, 28, 30, 52, 70, 90, 101, 105, 110, 118, 123, 132, 138, 149, 153, 158, 160, 180, 194, 199, and 209 were from Cromlab (Barcelona, Catalonia, Spain). Standard mixtures in isoctane were prepared with these compounds for instrumental calibration. Surrogate solutions of PCB congeners no. 30 and 209 were prepared for recovery calculation. 1,2,3,4-Tetrachloronaphthalene (TCN) and octachloronaphthalene (OCN) were from Dr. Ehrenstorfer (Augsburg, Germany). These compounds were used for the preparation of surrogate solutions for the assessment of instrument stability.

Sampling. Fresh surface litter was removed prior to sample collection. Surface soils (upper 5 cm) between 10 and 2500 m above sea level (a.s.l.) were collected with a soil corer provided by Lancaster University. Samples above 2500 m, very stony, were sampled with a small shovel and sieved through 500 μ m. The samples were wrapped in aluminum foil, packed into heat-sealed polyester bags (Kapak corporation, Minneapolis, MN), and stored at 4 °C until analysis.

Sample Extraction. About 50 g of fresh soil were mixed with 25–50 g of anhydrous sodium sulfate for water removal. The mixtures were then introduced into Whatman Soxhlet cellulose thimbles, spiked with PCB congeners no. 30 and 209, and extracted with hexane/dichloromethane (4:1) for 18 h. All extracts were first concentrated by rotary vacuum evaporation to 3–5 mL and subsequently further dehydrated by elution through anhydrous sodium sulfate. After rotary vacuum evaporation to ~0.5 mL, the extracts were fractionated by column chromatography using 2 g of neutral alumina. OCs were obtained by elution with 8 mL of hexane/dichloromethane (9:1). Subsequently, activated copper (~1 g) was added to the eluate for the removal of sulfur-containing compounds. This copper powder was removed by filtration through glass wool and rinsed with *n*-hexane. Elution solvent

and rinses were concentrated to 50 μ L in isoctane after rotary vacuum and nitrogen stream evaporation.

Instrumental Analysis. The extracts were injected into a Hewlett-Packard 5890 Series II GC-ECD (Palo Alto, CA). An HP-5 fused silica capillary column (50 m length, 0.25 mm i.d., 0.25 μ m film thickness) coated with 5% phenyl 95% methylpolysiloxane was used for the analyses. The oven temperature program started at 100 °C (holding time 1 min), increased to 120 °C at 20 °C/min, to 240 °C at 4 °C/min (holding time 12 min), and finally to 300 °C at 4 °C/min (holding time 10 min). Injector and detector temperatures were 280 and 310 °C, respectively. Helium and nitrogen were used as the carrier (0.33 mL/min) and makeup (60 mL/min) gases, respectively. Compound identification was confirmed by GC coupled to mass spectrometry in the chemical ionization mode and negative ion recording (Fisons 8000 series, mass selective detector 800 series; ThermoQuest, Manchester, U.K.).

Quantification. Solutions of TCN and OCN were added to the vials prior to injection. Calibration curves (detector response vs amount injected) were performed for each compound to be quantified. The range of linearity of the detector was evaluated from the curves generated by representation of detector signal/amount injected versus the amount injected. All measurements were performed in the ranges of linearity found for each compound. In some cases, the samples were rediluted and reinjected for fitting within the linear range of the instrument. The quantitative data were corrected for surrogate recoveries.

Statistical analysis was performed with SPSS 8.0 for Windows 5.1. Normal distributions were tested with the Kolmogorov–Smirnov test. The correlation analysis was performed with the least-squares method. Significance was set at $p < 0.05$.

Quality Control. Procedural blanks were performed with each set of nine samples to check for possible impurities. Recoveries of PCB congeners no. 30 and 209 averaged 70% and 95%, respectively. Replicate analysis of soil samples gave dispersion errors lower than 16%. The detection limits ranged between 0.5 and 70 pg. The analytical methods were validated by replicate ($n = 4$) analysis of the reference sample BCR 536

TABLE 1. Characteristics of the Sampling Sites and Soils in Teide

site number ^a	altitude (m a.s.l.) ^b	N ^c	T (°C)	soil type	vegetation	land use	TOC ^d (mg/g dw)
1	10	3	20	sandy entisol		agriculture	3.9
2	200	3	19	sandy entisol	tabaibas, holly tree	scrub	36
3	400	3	18	sandy entisol	tabaibas, holly tree	scrub	36.5
4	600	3	16	sandy entisol	tabaibas, holly tree	agriculture	17
5	800	3	15	inceptisol	laurisilva, GM ^e	agriculture	51
6	1000	3	14	inceptisol	laurisilva, GM ^e	woodland	320
7	1055	4	14	inceptisol	pine	agriculture	120
8	1000	2	14	inceptisol	pine	agriculture	64
9	1100	2	14	inceptisol	pine	woodland	16
10	1200	3	14	inceptisol	pine, eucalyptus, GM ^e	agriculture	43
11	1300	2	14	inceptisol	pine	woodland	0.5
12	1400	3	13	inceptisol	pine	woodland	11
13	1500	2	13	inceptisol	pine	woodland	4.3
14	1600	3	13	inceptisol	pine	woodland	120
15	1700	2	13	inceptisol	pine	woodland	15
16	1800	3	13	inceptisol	broom	woodland	7.3
17	2000	3	12	pumice stone entisol	pine, broom	woodland	26
18	2367	3	11	pumice stone entisol	broom	scrub	16
19	2400	2	11	pumice stone entisol			0.7
20	2530	2	10	pumice stone entisol			0.5
21	2560	2	9.3	pumice stone entisol			1.5
22	2790	2	8.6	pumice stone entisol			1.2
23	2895	2	8.1	pumice stone entisol			3.1
24	3030	2	7.5	pumice stone entisol			1.6
25	3320	2	5.6	pumice stone entisol			0.5
26	3400	2	4.9	pumice stone entisol			0.7

^a Site number as described in Figure 1. ^b Meters above sea level. ^c Number of samples analyzed in each site. ^d Total organic content. ^e Green Mount is the sum of beech tree, moor, and scrub.

(Community Bureau of Reference, Brussels, Belgium). The results obtained were in agreement with the certified values.

In addition, an intercalibration exercise for the analysis of PCB congeners no. 18, 28, 52, 70, 101, 105, 110, 118, 123, 132, 149, 153, 138, 158 + 160, 180, 194, and 199 in soil samples was organized within the scope of the Global Mass Balance of Semivolatile Organic Compounds (GLOBAL-SOC) project. This exercise was participated by the Institute of Applied Environmental Research (University of Stockholm, Sweden), Institute for Marine Research (University of Kiel, Germany), Environmental Science Department (Lancaster University, U.K.), Environmental Chemical Processes Laboratory (University of Crete, Greece), Norsk Institutt for Luftforskning (Norway), and our group. Replicates of two soil samples were distributed among these teams for analysis. Accuracy, repeatability, and reproducibility values were satisfactory.

Total Organic Carbon (TOC). TOC determination was performed by flash combustion at 1025 °C and thermic conductivity detection with a CHNS elemental analyzer EA1108 (ThermoQuest). Limit of detection was 0.1%.

Results and Discussion

Atmospheric Conditions at Teide. The meteorological conditions in the subtropical North-Eastern Atlantic area 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 (7). This circulation results in a dry and dynamically stable free troposphere, inhibiting convective processes. A stable temperature inversion separates the air masses below and above the boundary layer (between 1000 and 1800 m; Figure 1). The annual average temperatures of the sites considered for study situated below, at, and above the boundary layer range between 13.5 and 20 °C, 13.5 and 12.5 °C, and 12 and 5 °C. This inversion is stable throughout the year, obstructs vertical motions, and generates a typical stratocumulus sea-cloud between 900 and 2000 m.

At sea level, the circulation is dominated by the Trade-winds (NE winds), which transport relatively humid and cool air from middle latitudes.

Soils Description and Sampling. Soils were collected at various altitudes, ranging from sea level up to 3400 m. The samples collected above 1000 m encompassed both the northern and southern sides of the mountain edge (Figure 1). Replicates were taken at each altitude and site ($n = 2$ or 3). These were distributed in areas around 50 m². The soils of Tenerife Island are derived from volcanic and basalt ash. They can be classified into three groups which are distributed by altitude: sandy entisols (10–800 m), inceptisols (800–2000 m), and pumice stone entisols (2000–3400 m) (8). Agricultural activities are performed in the lower altitude regions mostly below 1000 m, in the region below inversion layer, and in some sites up to 1300 m (Table 1). Inceptisols have, in general, higher TOC.

Concentrations of Organochlorine Compounds. The concentrations in the soil samples collected at Tenerife are generally low. Total PCB range between 0.04 and 9.2 ng·g⁻¹ (mean, 1.2 ng·g⁻¹; Table 2). All concentrations refer to dry weight unless otherwise stated. These values are low in comparison to those reported in the industrial areas of Austria (6.4–95 ng·g⁻¹; 9) and Poland (4.6–3400 ng·g⁻¹; 10); in rural sites of the U.K. and Norway (1.2–2000 ng·g⁻¹; 11–14), Germany (8.4–59 ng·g⁻¹; 15), and Brasil (27–49 ng·g⁻¹; 16); or in the woodland regions of Norway (5.3–30 ng·g⁻¹; 17) and the United States (7.5–250 ng·g⁻¹; 18). PCB concentrations similar to those found in Tenerife have been reported in the woodland regions of Germany (0.2–4.8 ng·g⁻¹; 19), Austria (0.2–7.5 ng·g⁻¹; 20), and the rural areas of Thailand (1.1–6.2 ng·g⁻¹; 21). Total DDTs (4,4'-DDE + 4,4'-DDT) range between 0.01 and 40 ng·g⁻¹ (mean, 5.4 ng·g⁻¹; Table 2), which is lower than the concentrations reported for industrial/urban areas from Germany (500–400 000 ng·g⁻¹; 22) and Poland (8.6–2400 ng·g⁻¹; 10) or in the woodland regions of the United States (2.1–270 ng·g⁻¹; 18) but in the same order of the woodland regions from Austria (<22 ng·g⁻¹; 20). Total HCH,

TABLE 2. Average Concentration Values of the Organochlorine Compounds Found in the Soils from Teide

compound	below the inversion layer (10–1000 m a.s.l.)	at the inversion layer (1000–1800 m a.s.l.)	above the inversion layer (1800–3400 m a.s.l.)	total (10–3400 m a.s.l.)
pentachlorobenzene	22 (16) ^a	78 (76)	9.6 (16)	41 (59)
HCB	470 (780)	450 (650)	72 (60)	310 (550)
α-HCH	35 (32)	120 (180)	5.5 (8.4)	59 (120)
γ-HCH	130 (120)	53 (120)	5.6 (6.2)	49 (100)
δ-HCH	0.75 (1.6)	3.1 (3.8)	0.1 (0.19)	1.5 (2.9)
4,4'-DDE	890 (830)	7500 (11000)	170 (300)	3400 (7900)
4,4'-DDT	960 (1200)	4200 (6100)	81 (74)	2000 (4300)
PCB no. 18	17 (16)	90 (150)	8.1 (10)	44 (100)
PCB no. 28	49 (20)	83 (93)	22 (31)	53 (68)
PCB no. 52	58 (44)	190 (180)	44 (41)	110 (140)
PCB no. 70	41 (38)	160 (140)	33 (28)	89 (110)
PCB no. 101 + 90	70 (81)	280 (300)	63 (81)	160 (230)
PCB no. 110	85 (72)	530 (890)	35 (55)	250 (610)
PCB no. 123 + 149	52 (37)	140 (180)	25 (37)	77 (130)
PCB no. 118	43 (40)	120 (140)	19 (21)	64 (100)
PCB no. 153	50 (31)	140 (220)	17 (23)	74 (150)
PCB no. 105 + 132	60 (51)	88 (96)	12 (23)	53 (74)
PCB no. 138	95 (59)	200 (300)	28 (43)	110 (210)
PCB no. 158 + 160	20 (6.7)	34 (72)	3.6 (4.7)	20 (48)
PCB no. 180	130 (250)	92 (190)	6.5 (11)	66 (170)
PCB no. 199	4.2 (3.3)	25 (63)	0.41 (0.53)	12 (42)

^a Units in pg/g dry weight. Standard deviation is indicated between brackets.

0.001–1 ng·g⁻¹ (mean, 0.11 ng·g⁻¹; Table 2), are also low (e.g., concentrations reported in the urban/industrial areas of Poland range between 0.36 and 110 ng·g⁻¹ (10) and for the woodland regions of Austria (0.6–6.6; 20)). HCB concentrations, 0.01–3.2 ng·g⁻¹ (mean, 0.31 ng·g⁻¹; Table 2), are lower than the soil concentrations reported in the urban/industrial areas of Germany (100–1300 ng·g⁻¹; 22) and Poland (0.19–30 ng·g⁻¹; 10) but in the same order as those in the woodland regions of Austria (<1.9 ng·g⁻¹; 20). These low concentrations suggest the absence of major pollution sources in Tenerife Island. Obviously, site-specific pollution processes may have affected the soils analyzed, but their effect has not lead to major inputs of OCs as compared to the literature data.

These concentrations are also much lower than those reported for total PCBs and DDTs in mountain soils located near industrial sites such as the Giant Mountains (Czech–Polish border), where concentration ranges of 5–140 ng·g⁻¹ and 20–5100 ng·g⁻¹, respectively, have been found (23, 24). The concentrations of HCB in the soils of Tenerife and the Giant Mountains are more similar, 0.47–48 ng·g⁻¹ in this last case (23, 24).

In view of the low influence of possible specific pollution sites, the observed concentrations may be evaluated for their altitude distribution. For this purpose, considering the stable vertical structure of the atmosphere in the area, samples may be grouped as those below, at, and above the altitude range in which the inversion layer is defined (Table 2). The average values corresponding to these three groups show a common trend for nearly all OCs. The highest concentrations are found in the section at the inversion layer, and those situated above this boundary show the lowest. This trend is observed for all compounds either those related to agricultural or industrial applications. γ-HCH is the only exception, showing significantly higher average values at the section below the inversion layer, 130 pg·g⁻¹ (Table 2). Considering that this compound is still used as a pesticide, this deviation perhaps reflects the influence of agricultural applications.

Adsorption of Organochlorine Compounds to Organic Matter. The common distribution pattern of most OCs in Tenerife points to a dominant process, independent of pollutant origin, as responsible for its occurrence in the mountain soils after release into the environment. Correlation of the concentrations observed at each site (Figure 1) with soil organic matter (Table 1) show high coefficients, r^2 ,

TABLE 3. Slopes and Linear Regression Coefficients for the Correlation of log(OC) vs log(TOC) and log(OC/TOC) versus 1/T

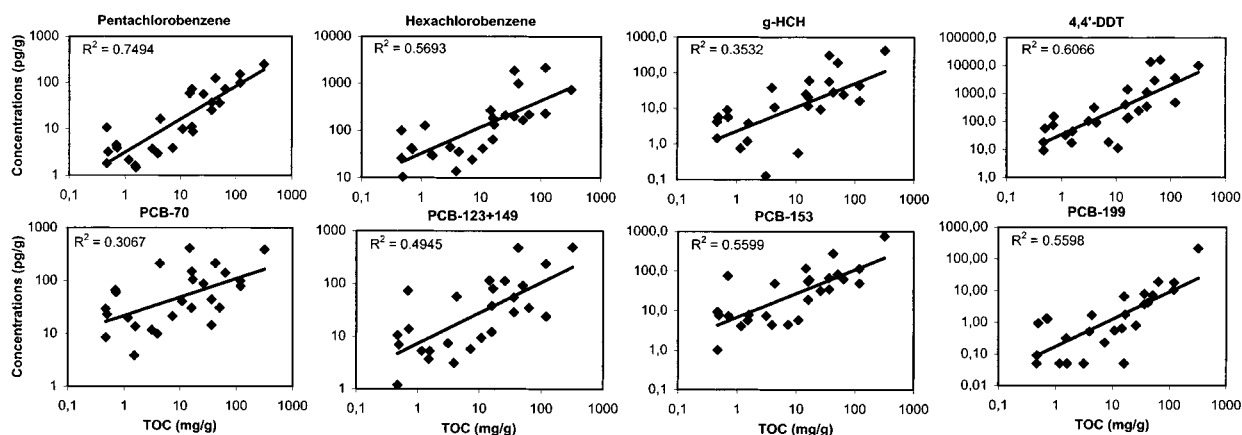
compound	log(OC) vs log(TOC)		log(OC/TOC) vs 1/T	
	slope	r^2	slope	r^2
pentachlorobenzene	0.71	0.7494	6500	0.4194
HCB	0.56	0.5693	8200	0.4173
α-HCH	0.79	0.6765	^a	0.0847
γ-HCH	0.67	0.3532		0.0083
δ-HCH	0.68	0.2268	6300	0.1309
4,4'-DDE	1.0	0.5810		0.0004
4,4'-DDT	0.89	0.6066		0.0538
PCB no. 18	0.46	0.2864	8300	0.2713
PCB no. 28	0.49	0.5187	5200	0.1862
PCB no. 52	0.26	0.1828	11000	0.4351
PCB no. 70	0.35	0.3067	10000	0.4308
PCB no. 101 + 90	0.35	0.1184	12000	0.3814
PCB no. 110	0.59	0.3688	8100	0.2950
PCB no. 123 + 149	0.58	0.4945	8400	0.4493
PCB no. 118	0.54	0.2969	8800	0.2809
PCB no. 153	0.60	0.5599	8200	0.4618
PCB no. 105 + 132	0.76	0.5601	4200	0.1253
PCB no. 138	0.75	0.5891	6200	0.3028
PCB no. 158 + 160	0.58	0.3799	5200	0.1118
PCB no. 180	1.2	0.6681		0.0467
PCB no. 199	0.86	0.5598	6200	0.2069

^a Slopes are not given when the correlation was not significant.

between 0.3 and 0.75 in most cases (Table 3). Both OC and TOC concentrations were log-transformed before correlation in order to have normal distributed variables according to the Kolmogorov–Smirnov test. The good agreement between the regression lines and experimental data is illustrated in Figure 2 for some compounds.

Soil organic matter is generally considered as a preferential site for the sorption of hydrophobic pollutants (25, 26). The good correlation between log(OC) and log(TOC) suggests that the geographical distribution pattern of these compounds is in steady-state, in equilibrium with soil properties. Atmospheric transport is an efficient mechanism for OC redistribution between contaminated and pristine soils (27). The observed geographical distributions of OC in Tenerife, in equilibrium with soil properties, indicate that punctual pollution episodes have already been smeared out into diffuse

CONCENTRATIONS OF ORGANOCHLORINE COMPOUNDS vs TOTAL ORGANIC CARBON (TOC) IN SOIL



CONCENTRATIONS OF ORGANOCHLORINE COMPOUNDS NORMALIZED TO SOIL TOC vs 1/TEMPERATURE

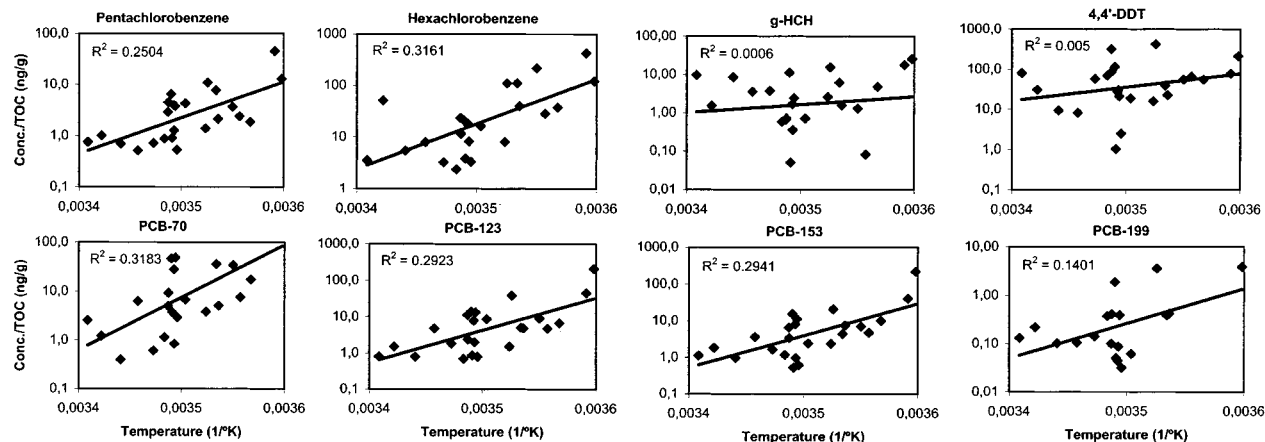


FIGURE 2. Correlation plots for the concentrations of organochlorine compounds versus total organic content in log scale (top) and versus reciprocal of temperature (K; bottom).

pollution within the soil system. This effect can also be evidenced in other areas upon re-examination of data previously reported in the literature. High PCB concentrations from soils collected in 1950–1965 in agricultural regions of the U.K. did not show any correlation with TOC (11). However, PCB analysis of soils from the same sites collected in 1993 showed a general decrease of PCB and then a good log(OC) versus log(TOC) correlation (28).

These steady-state conditions may also be encountered in urban OC-polluted soils (e.g., as evidenced by recalculation of the dataset reported from urban soils of Bangkok (29)). In the case of Tenerife, the high log(OC) versus log(TOC) correlation coefficients indicate that the atmospheric exchange of OCs between polluted and pristine soils has already been completed to equilibrium and that possible recent pollution episodes have not been so significant as to move the OC distribution from steady state. The atmospheric transfer of OC has occurred beyond the restriction for convective transport because of the atmospheric inversion layer. Long-range transported OCs through the free troposphere may also have contributed to the overall burden of these pollutants. In any case, the good correlation along the soils collected between 10 and 3400 m suggests an overall equilibrium.

In general, OC with a lower vapor pressure and a higher octanol–water coefficient tend to accumulate in soils versus in the atmosphere (30). Soil/air distributions of OC have shown a dependence from the octanol–air coefficient (K_{OA}) (31–32). A linear dependence between the slopes of the log(OC) versus log(TOC) and K_{OA} is observed in the soils of

Tenerife (Figure 3). K_{OA} for the PCBs have been calculated

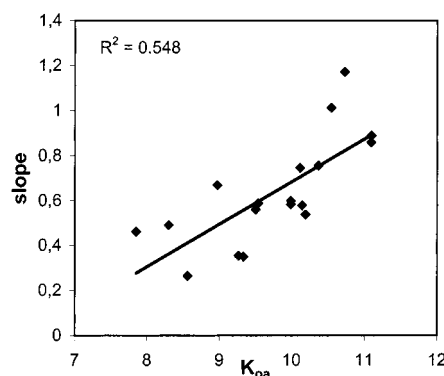


FIGURE 3. Correlation plot for the slopes obtained from curve fitting of the concentrations of organochlorine compounds versus total organic content (reported in Table 3) and octanol–air partition coefficients (K_{OA}) in log scale.

from the vapor pressures reported by Falconer and Bidleman (33) which were transformed into the octanol–air constants using the equations of Harner and Bidleman (34). K_{OA} for the other OC were obtained from the values reported by Finizio et al. (35). An r^2 value of 0.548 is observed for the correlation between slopes and K_{OA} when α -HCH is not included. Inclusion of this compound gives r^2 coefficients of 0.3696. α -HCH deviates from the general trend because it exhibits a higher slope than that expected for its lower K_{OA} value. In

any case, both correlation coefficients are significant, indicating that an important proportion of the variance of the distribution of OC in Tenerife soils (55% or 37% when α -HCH is included) depends from their K_{OA} and soil TOC.

Concentrations of Organochlorine Compounds and Ambient Air Temperature. Because K_{OA} is defined at constant temperature, the strong dependence of the $\Delta \log(\text{OC})/\Delta \log(\text{TOC})$ slopes from this constant suggest a dependence from temperature. This dependence can be tested with the Tenerife samples because each altitude represents a defined mean annual air temperature due to the stable conditions of the inversion layer all along the year (Table 1; Figure 1).

One method for testing this possible temperature dependence is the linear correlation between the log-transformed OC soil/air concentrations and the reciprocal of the mean annual air temperature in K (Figure 2; Table 3). In this case, soil concentrations should be normalized to TOC in view of the strong relationship between OC and TOC, as previously described. When the air concentrations near all sampling sites are similar, the correlation can be simplified by only considering OC soil concentrations (normalized to TOC in this case) and reciprocal of temperature. In the stable atmospheric inversion system characteristic of Tenerife, air OC concentrations above and below the mixing layer exhibit a rather constant factor, being 2 times higher below (van Drooge, personal communication). To equilibrate this difference in the correlation, the soil concentrations of OC in the samples situated at 2000 m and above have been multiplied by 2.

Calculation of the correlation coefficients after consideration of all of these factors shows that they are significant ($p < 0.05$) in most cases (e.g., pentachlorobenzene, HCB, and most PCBs (Table 3)). About 18–46% of the variance of their TOC-normalized concentrations depends on the average air temperature. Higher TOC-normalized concentrations are observed at higher altitudes, in the sites located further away from human influence (Table 1). The distribution trend of these compounds is, again, consistent with aforementioned steady-state conditions in which anthropogenic influence from local specific sites is not significant.

In contrast, the correlation coefficients are not significant for the HCHs, DDTs, and some PCB congeners (105 + 132, 158 + 160, and 180). In the case of the pesticides, the lack of correlation is due to too high of values at a higher temperature (Figure 2). Because these sites are those situated at a lower altitude, in the area of agricultural activity (Table 1), it is possible that small local anthropogenic inputs may distort the correlation. As indicated previously, the altitudinal distribution of γ -HCH deviates from the general trend showing higher concentrations below the inversion layer. Evaluation of the variance of the TOC-normalized concentrations of all OC by principal component analysis show the lack of influence of land use or soil type on PCB levels but not in the case of the pesticides. In any case, these inputs may not be so relevant as for deviating significantly the stronger correlation between OC and TOC concentrations, as discussed previously.

In contrast, the lack of correlation of some PCB congeners is difficult to interpret because most PCBs are correlated to temperature. In any case, another aspect to be considered is whether the temperature range represented by Tenerife soils (15.1 °C) is sufficient for the observation of temperature-related trends. Laboratory experiments for testing the linear dependence between $\log(K_{OA})$ and reciprocal of temperature have typically been performed over larger temperature ranges (e.g., 55 °C (36) or 40 °C (34)).

Further assessment on the environmental significance of these observed correlations between TOC-normalized concentrations and the reciprocal of temperature can be obtained by the calculation of the pseudo-enthalpies from the slopes

($\Delta H = SR \ln(10)$; S = slope of the regression line, $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $\ln(10) = 2.303$). Most values range between 120 and 160 $\text{kJ} \cdot \text{mol}^{-1}$, although higher values are also found for some compounds (Table 3). These field constants are higher than the enthalpies of phase change from octanol–air calculated in laboratory experiments, 66–93 $\text{kJ} \cdot \text{mol}^{-1}$ (35). A comparison of both types of values must be done with caution. The field series correspond to different sites from which a constant annual average air temperature is assumed, whereas the octanol–air values were obtained from laboratory systems in which temperatures are fixed by experimental design. Furthermore, deviations from linearity of some field data points may also have significant influence on the overall slope values. The comparison between both datasets is, therefore, only done on a tentative basis.

With these constraints in mind, the high difference between air–soil and octanol–air constants must be considered, namely, when considering that similar plots involving the log-transformed partial pressure of PCB congeners versus the reciprocal of temperature give rise to enthalpies that are lower than the theoretical octanol–air values (37). The high air–soil enthalpies observed from the Tenerife soil dataset probably provides evidence for the occurrence of sorption effects other than simple linear adsorption, which tend to increase the retention of these compounds in soil organic matter. The higher enthalpies observed from the field data indicate that the intensity of these effects is also related to ambient temperature, being more relevant at low values.

Acknowledgments

Roser Chaler and Rosa Mas (Department of Environmental Chemistry, CSIC) are acknowledged for technical assistance in instrumental analysis. Financial support from the European Union (GLOBAL-SOC Project No. ENV4-CT97-0638) is acknowledged. A.R. thanks a Ph.D. fellowship from CIRIT (Generalitat de Catalunya). We thank Parque Nacional del Teide permission for sampling in Las Cañadas del Teide.

Literature Cited

- (1) Simonich, S. L.; Hites, R. A. *Science* **1995**, *269*, 1851–1854.
- (2) Iwata, H.; Tanabe, S.; Sakal, N.; Tatsukawa, R. *Environ. Sci. Technol.* **1993**, *27*, 1080–1098.
- (3) Wania, F.; Mackay, D. *Environ. Sci. Technol.* **1996**, *30*, 390A–396A.
- (4) Grimalt, J. O.; Fernandez, P.; Berdié, L.; Vilanova, R. M.; Catalan, J.; Psenner, R.; Hofer, R.; Appleby, P. G.; Rosseland, B. O.; Lien, L.; Massabuau, J. C.; Battarbee, R. W. *Environ. Sci. Technol.* **2001**, *35*, 2690–2697.
- (5) Wania, F.; Mackay, D. *Environ. Sci. Technol.* **1995**, *160/161*, 211–232.
- (6) Muir, D. C. G.; Ford, C. A.; Grift, N. P.; Metner, D. A.; Lockhart, W. L. *Arch. Environ. Contam. Toxicol.* **1990**, *19*, 530–542.
- (7) Wells, N. *The Atmosphere and Ocean: A physical Introduction*, 2nd ed.; Wiley: New York, 1991.
- (8) Fernández-Caldas, E.; Tejedor-Salguero, M.; Quantin, P. *Suelos de Regiones Volcánicas. Tenerife. Vol IV*; Colección Viera y Clavijo: Tenerife, Spain, 1982.
- (9) Weiss, P.; Riss, A.; Gschmeidler, E.; Schentz, H. *Chemosphere* **1994**, *29*, 2223–2236.
- (10) Falandysz, J.; Brudnawska, B.; Kawano, M.; Wakimoto, T. *Arch. Environ. Contam. Toxicol.* **2001**, *40*, 173–178.
- (11) Lead, W. A.; Steinnes, E.; Bacon, J. R.; Jones, K. C. *Sci. Total Environ.* **1997**, *196*, 229–236.
- (12) Sanders, G.; Jones, K. C.; Hamilton-Taylor, J. *Environ. Pollut.* **1995**, *89*, 17–25.
- (13) Alcock, R. E.; Johnston, A. E.; McGrath, S. P.; Berrow, M. L.; Jones, K. C. *Environ. Sci. Technol.* **1993**, *27*, 1918–1923.
- (14) Creaser, C. S.; Fernandes, A. R.; Harrad, S. J.; Hurst, T.; Cox, E. A. *Chemosphere* **1989**, *19*, 1457–1466.
- (15) Wilcke, W.; Zech, W. *Z. Pflanzenernähr. Bodenkd.* **1998**, *161*, 289–295.
- (16) Wilcke, W.; Lillienfein, J.; do Carmo Lima, S.; Zech, W. *J. Plant Nutr. Soil Sci.* **1999**, *162*, 539–548.
- (17) Calamari, D.; Bacci, E.; Focardi, S.; Gaggi, C.; Morosini, M.; Vighi, M. *Environ. Sci. Technol.* **1991**, *25*, 1489.

- (18) Smith, W. H.; Hale, R. C.; Greaves, J.; Hugget, R. J. *Environ. Sci. Technol.* **1993**, *27*, 2244–2246.
- (19) Krauss, M.; Wilcke, W.; Zech, W. *Environ. Pollut.* **2000**, *110*, 79–88.
- (20) Weiss, P.; Lorbeer, G.; Scharf, S. *Organohalogen Compd.* **1998**, *39*, 381–384.
- (21) Thao, V. D.; Kawano, M.; Tatsukawa, R. *Environ. Pollut.* **1993**, *81*, 61–71.
- (22) Wilken, M.; Walkow, F.; Jager, E.; Zeschmar-Lahl, B. *Chemosphere* **1994**, *29*, 2237–2252.
- (23) Holoubek, I.; Caslavsky, J.; Vancura, R.; Kocan, A.; Chovancova, J.; Petrik, J.; Drobna, B.; Cudlin, P.; Triska, J. *Toxicol. Environ. Chem.* **1994**, *45*, 189–197.
- (24) Holoubek, I.; Triska, J.; Cudlin, P.; Caslavsky, J.; Karl-Werner, S.; Kettrup, A.; Kohoutek, J.; Cupr, P.; Schneiderova, E. *Toxicol. Environ. Chem.* **1998**, *66*, 17–25.
- (25) Pignatello, J. J. *Adv. Colloid Interface Sci.* **1998**, *76–77*, 445–467.
- (26) Marschner, B. *J. Plant Nutr. Soil Sci.* **1999**, *162*, 1–14.
- (27) Jones, K. C.; Johnston, A. E.; McGrath S. P. *Int. J. Environ. Anal. Chem.* **1995**, *59*, 167–178.
- (28) Lead, W. A.; Steinnes, E.; Bacon, J. R.; Jones, K. C. *Sci. Total Environ.* **1997**, *193*, 229–236.
- (29) Wilcke, W.; Müller, S.; Kanchanakool, N.; Niamskul, C.; Zech, W. *Aust. J. Soil Res.* **1999**, *37*, 245–254.
- (30) Pichler, M.; Guggenberger, G.; Hartmann, R.; Zech, W. *Environ. Sci. Pollut. Res. Int.* **1996**, *3*, 24–29.
- (31) Jones, K. C.; Stratford, J. A.; Tidridge, P.; Waterhouse, K. S.; Johnston, A. E. *Environ. Pollut.* **1989**, *56*, 337–342.
- (32) Cousins, I. T.; McLachlan, M.; Jones, K. C. *Environ. Sci. Technol.* **1998**, *32*, 2734–2739.
- (33) Falconer, R. L.; Bidleman, T. F. *Atmos. Environ.* **1994**, *28*, 547–554.
- (34) Harner, T.; Bidleman, T. F. *J. Chem. Eng. Data* **1996**, *41*, 895–899.
- (35) Finizio, A.; Mackay, D.; Bidleman, T.; Harner, T. *Atmos. Environ.* **1997**, *31*, 2289–2296.
- (36) Hippelein, M.; McLachlan, M. *Environ. Sci. Technol.* **2000**, *34*, 3521–3526.
- (37) Hoff, R. M.; Brice, K. A.; Halsall, C. J. *Environ. Sci. Technol.* **1998**, *32*, 1793–1798.

Received for review October 24, 2001. Revised manuscript received January 31, 2002. Accepted February 6, 2002.

ES010272H