Article 2.

DEPOSITION OF SEMI-VOLATILE ORGANOCHLORINE COMPOUNDS IN THE FREE TROPOSPHERE OF THE EASTERN NORTH ATLANTIC OCEAN

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Deposition of Semi-Volatile Organochlorine Compounds in the Free Troposphere of the Eastern North Atlantic Ocean

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Deposition samples were taken at a height of 2367 m above sea level (m.a.s.l.) on the Island of Tenerife from May 1999 until July 2000 and analysed for 19 polychlorinated biphenyl (PCB) congeners, hexachlorobenzene (HCB), hexachlorocyclohexanes (HCH) and DDTs. This site is located above the inversion layer, so samples represent background concentrations of the free troposphere. The average deposition fluxes of HCB, total HCH, DDTs and PCBs were 86, 400, 110 and 780 ng m^{-2} yr^{-1}, respectively, being lower than those reported at sea level in continental or marine areas. All compounds are generally found in higher abundance in the wet precipitation samples. However, these samples only represent a fraction, e.g. 33%, of the total deposition load. Annual mass balance calculations show that wet precipitation is essentially responsible for the deposition of the low molecular weight OC whereas dry deposition accounts for more than 50% of the higher molecular weight PCBs. © 2001 Elsevier Science Ltd. All rights reserved.

Introduction

Several studies show that semi-volatile xenobiotic organochlorine compounds (OCs) are global pollutants found in sites where they were never produced nor used (Atlas and Giam, 1981; Ballschmitter, 1992; Iwata *et al.*, 1993). For instance, irrespective of the regulations that have drastically decreased the production of polychlorobiphenyls (PCBs), the atmospheric concentrations of these compounds in remote locations have not decreased or have decreased very little since 1970s (Panchin and Hites, 1994; Baker and Eisenreich, 1990). They are also resistant to biological, chemical and physical breakdown and tend to accumulate in organic materials (Erickson, 1997). This persistence is a cause of concern since some PCB congeners are likely to cause toxic effects at present concentration levels (Hooper *et al.*, 1990; Muir *et al.*, 1988; Porta *et al.*, 1999). Likewise, hexachlorobenzene (HCB) and DDTs are toxic and tend to bioaccumulate (Grimalt *et al.*, 1994; Porta *et al.*, 1999). Some hexachlorocyclohexanes (HCHs) have also this capacity for bioaccumulation and are potentially toxic.

The atmosphere seems to be the most important way for the distribution of OCs on a global scale, including transport to the marine system (Duce *et al.*, 1991; Ballschmitter, 1992; Iwata *et al.*, 1993; Tolosa *et al.*, 1997). Its large volume and the high speed at which air masses can move afford a high capacity for transport over long distances. However, one major question to be elucidated is the role of high altitude air masses, free from the influence of ground OC inputs, in the transport of these compounds and its significance for the marine environment. To this end, the study of OC atmospheric deposition fluxes in the free ocean troposphere provides a major clue for the understanding of the significance of long-range air transport to seawaters.

For this purpose, the present paper reports the deposition fluxes of these compounds at 2367 m.a.s.l. in Izaña (Tenerife, Canary Islands). This site is representative of the subtropical region of the northeastern North Atlantic Ocean. In this region (30°N), the descendent branch of the Hadley cell produces strong subsident circulation in the middle and low troposphere (Fig. 1). This circulation causes a dry and dynamically stable troposphere, inhibiting convective phenomena. At sea level the circulation is dominated by the trade-wind systems (NE-winds) which transport relatively humid and cool air from middle latitudes. A temperature inversion, characterized by a typical stratocumulus cloud layer between 1400 and 1800 m.a.s.l., separates both air masses obstructing vertical exchange (Wells, 1997).

The sampling site considered in this study was situated above the inversion layer with a predominant wind direction from the NW (direct ocean inputs). The
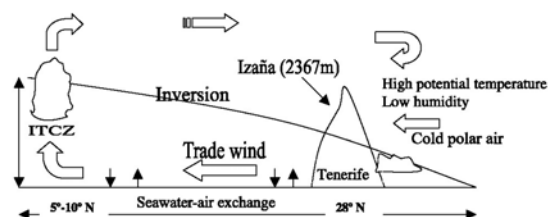
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Fig. 1 General air circulation in the subtropical marine troposphere.

studied samples are representative of the free troposphere, not being affected from local and regional pollution sources.

Materials and Methods

Samples were taken at Izaña Meteorological Observatory (28° 18′N; 16° 29′W), on top of a tower of 15 m height. Atmospheric deposition was collected in stainless steel reservoirs ($\emptyset = 24$ cm, $A = 452.4$ cm^2) using a Model ARS 1010 sampler (MTX, Italy). Each sampling period encompassed approximately two weeks. After this time the reservoirs were carefully rinsed with Milli Q water in three successive steps and the rinses were collected together. Blanks were taken before each sampling. Both samples and blanks were filtered with pre-weighted glass microfibre filters (GFF) (Whatman, Maidstone, England (4.7 cm)). These filters were previously cleaned by ashing at 400°C for 24 h. After filtration the dissolved phase was extracted using Empore extraction C-18 disks (3M Empore, Harbor City, USA). Vacuum was used to increase the speed of filtration/extraction. PCB congeners #30 and #209 were introduced in both GFF and C-18 disks as internal standards before sample introduction. Then, the GFFs and C-18 disks were wrapped in aluminium foil, placed in polyester bags and stored at −20°C. These bags were introduced in portable refrigerators for air transport to Barcelona (approximately 2 days) where they were kept at 4°C.

The C-18 disks were successively extracted with methanol, cyclohexane and dichloromethane (5 ml each). Sample handling is described in detail elsewhere (Carrera et al., 1998). Briefly, GFFs were Soxhlet extracted for 24 h in 100 ml of hexane:dichloromethane (DCM) (Merck, Darmstadt, Germany) (4:1 v/v), respectively. This extract was vacuum evaporated to 1 ml.

All samples and blanks were cleaned up with 2 g of alumina (aluminium oxide Fluka Type 507C, Fluxa AG, Switzerland) and 8 ml of hexane:DCM (9:1 v/v) (Merck, Darmstadt, Germany). The collected volume was vacuum evaporated to 1 ml and further concentrated to 50 μl in isooctane (Merck, Darmstadt, Germany) under a gentle stream of nitrogen. Tetrachloronaphthalene and octachloronaphthalene were added as internal standards before instrumental analysis for correction of possible instabilities.

The extracts were analysed by gas chromatography with electron capture detection (GC–ECD; Hewlett–Packard 5890) using a 50 m DB-5 column (J&W; id. 0.25 mm; film thickness 0.25 μm). The oven program started at 100°C for one min, increased to 150°C at 15°C/min and then to 240°C at 4°C/min holding this temperature for 12 min. Then, it was increased to 300°C at a rate of 4°C/min with a final holding time of 10 min. The detector and injector temperatures were 310°C and 250°C, respectively.

The 19 PCB congeners considered for study are representative of the total congeners present in higher abundance in environmental samples. These compounds and their respective mean blank values (pg) are as follows: #18 (0.16), #28 (0.05), #52 (0.14), #70 (0.15); #90 + #101 (0.23), #105 + #132 (0.13), #110 (0.17), #118 (0.07), #123 + #149 (0.07), #138 (0.13), #153 (0.08), #158 + #160 (0.012), #180 (0.03), #199 (0.001), #194 (0.0025). The HCH isomers considered for study, α-, β- and γ-, are also those currently found in higher abundance in environmental samples, their respective mean blank values were 0.09, 0.01 and 0.18 pg, respectively. No β-HCH was measured above detection limit (0.01 pg) in any of the samples. Blank values for pp′-DDE and pp′-DDT were 0.1 and 0.005 pg, respectively. The reported values have been subtracted for blank values in all cases.

Results and Discussion

Thirteen atmospheric deposition samples were collected during the sampling period, from 20 May 1999 until 4 July 2000, each encompassing about 15–25 days (Table 1). These deposition samples involve 234 days of collection. Over one year period (20 May 1999–19 May 2000) they represent 213 days, 58% of total. Dry and wet precipitation was collected in four samples (69 days, 33% of total sampling time) and only dry deposition in the rest. The collection time covered by these two types of samples is representative of the annual wet and dry periods at the sampling site.

Higher fluxes of organochlorine pesticides and PCBs are collected in the periods of wet and dry deposition than in the period of dry deposition only (Tables 1 and 2). The differences are very significant for HCHs, with increases of more than one order of magnitude for both α- and γ-isomers in the wet + dry period. The increase in pp′-DDE flux in wet + dry deposition is also near one order of magnitude higher than in dry deposition conditions. HCB and pp′-DDT increased 5 and 3.2 times in the wet + dry deposition samples, respectively. Although both series of data are not coincident in time, these strong differences are likely related to the different ways of deposition of the pesticides from the atmospheric pool. In fact, the atmospheric concentrations measured during the time of study at Izaña do not reflect major differences between the two periods.

TABLE 1

Deposition fluxes of organochlorine pesticides in the free troposphere of the eastern Atlantic Ocean.[a]

Sampling start	Sampling days	α-HCH	HCB	γ-HCH	pp'-DDE	pp'-DDT
Dry deposition						
20 May 1999	15 (6)[b]	1.1	12	7.7	24	88
7 June 1999	15 (7)	1.9	11	8.5	23	32
24 June 1999	15 (–)	1.5	120	41	0.9	37
13 July 1999	14 (3)	6.1	18	6.6	11.5	30
30 July 1999	18 (7)	0.5	11	2.4	0	4.8
3 December 1999	17 (14)	54	35	130	47	9
10 January 2000	21 (7)	31	63	48	8.6	7
15 March 2000	21 (11)	13	3.5	61	37	27
14 June 2000	21 (–)	4	86	81	24	11
Mean		13	40	43	20	27
SD		18	41	43	16	26
Dry and wet deposition						
14 September 1999	15 (18)	210	89	630	140	47
9 October 1999	25 (13)	130	180	570	280	110
11 November 1999	14 (13)	680	390	1700	72	93
15 February 2000	15 (170)	110	190	880	130	100
Mean		280	210	950	160	87
SD		270	130	520	88	28
Total						
Mean		95	92	320	61	46
SD		190	110	510	80	38
%(dry + wet)/(dry + wet + dry only)		96	84	96	88	76

[a] The values are reported in ng m^{-2} yr^{-1} after normalization of the flux collected during the sampling period (ng m^{-2}) to annual values.
[b] Total deposition (mg) collected during the sampling period (– not available).

Since all these organochlorine compounds are essentially found in the gas phase (unpublished results), their increased deposition in the presence of water precipitation is probably influenced by their Henry constants (Ballschmitter and Wittlinger, 1991). Thus, the partitioning between gas phase and water dissolution is related to these constants (Wania, 1998). Accordingly, α-HCH and γ-HCH, the compounds with lowest Henry constants, 1.1 and 1 Pa m^3 mol^{-1}, exhibit highest deposition as wet + dry materials.

The fluxes observed for HCHs are significantly lower than those reported in south Norway, 2000–4000 ng m^{-2} yr^{-1} and 10 000–35 000 ng m^{-2} yr^{-1} for α-HCH and γ-HCH, respectively (Wania and Haugen, 1999) or Saskatchewan, 119 000 ng m^{-2} yr^{-1} for γ-HCH (Waite *et al.*, 1999). They are also lower than the estimated (by calculation) average deposition over the North Atlantic, 4200 ng m^{-2} yr^{-1} for the summed HCH (Duce *et al.*, 1991). The proportion between α and γ-isomers (1:3) is similar to that found in rural central Europe (1:3; Wittlinger and Ballschmitter, 1987). α-HCH dominates over γ-HCH in more remote locations such as the eastern Arctic or the North Pacific Oceans, (2:1 and 17:1, respectively; Harner *et al.*, 1999; Atlas and Giam, 1981). The difference between very remote locations and sites receiving air masses from industrialized areas is attributed to the former use of HCH as insecticides in the form of technical mixtures containing high proportions of the α-isomer whereas, at present, only pure lindane (γ-HCH) is used (Harner *et al.*, 1999). The HCH mixtures used in the past still dominate the composition in remote areas, e.g. due to revolatilization effects,

whereas the γ-isomer dominates the HCH composition in industrialized areas (Harner *et al.*, 1999).

HCB also exhibits lower values than those measured in the Mediterranean Sea, 240 ng m^{-2} yr^{-1} (Villeneuve and Cattini, 1986) or estimated over the North Atlantic, 310 ng m^{-2} yr^{-1} (Duce *et al.*, 1991). The summed DDT fluxes are also lower than those calculated as likely average deposition over the North Atlantic, 280 ng m^{-2} yr^{-1} (Duce *et al.*, 1991).

The average PCB fluxes are also lower than those reported elsewhere. Deposition values of 1400–7300 ng m^{-2} yr^{-1} are reported inland or near polluted sites such as Chesapeake Bay, Lakes Superior, Michigan, or near Wisconsin or Saskatchewan (Leister and Baker, 1994; Swackhamer and Armstrong, 1986; Franz *et al.*, 1991; Swackhamer *et al.*, 1988). The deposition values of Izaña are also lower or range in the lower end of those reported in marine areas such as the Swedish west coast (500–2300 ng m^{-2} yr^{-1}; Brorström-Lundén, 1998), Enewetak Atoll (North Pacific; 200–3000 ng m^{-2} yr^{-1}; Atlas and Giam, 1981) or those calculated as average deposition over the North Atlantic (1800 ng m^{-2} yr^{-1}, Duce *et al.*, 1991).

The samples corresponding to combined dry and wet deposition involve higher atmospheric inputs of nearly all organochlorine compounds analysed (Fig. 2). However, over the whole year period, these samples only constitute about 33% of the total collection days. This rate is close to the annual percentage of wet precipitation days at Izaña Observatory. A deposition mass balance over a whole year period can therefore be estimated. The samples collected between 20 May 1999 and

TABLE 2

Atmospheric input fluxes (ng m^{-2} yr^{-1}) of polychlorobiphenyls in the free troposphere of the eastern Atlantic Ocean.[a]

Sampling start[b]	#18[c]	#28	#52	#70	#90 + 101	#110	#149 + 123	#118	#153	#105 + 132	#138	#160 + 158	#180	#199	#194	Total
Dry deposition																
20 May 1999	0	0	0	225	35	58	160	29	232	80	204	39	190	0	19	1300
7 June 1999	28	41	54	30	360	190	78	44	5	110	71	11	14	0	7	1000
24 June 1999	190	46	0	0	79	43	52	0	56	88	33	23	4	7	4	630
13 July 1999	69	57	180	41	150	77	53	37	6	61	46	19	5	0	5	810
30 July 1999	1	13	25	0	6	0	7	0	4	11	0	4	2	0	0	73
3 December 1999	75	91	150	38	0	9	7	8	6	13	36	0	0	0	0	440
10 January 2000	53	0	20	0	0	0	16	0	6	0	23	0	0	0	0	120
15 March 2000	0	0	0	18	130	200	19	3	48	41	57	0	14	0	0	550
14 June 2000	0	0	0	44	170	260	16	3	13	20	25	0	0	2	0	550
Mean	51	31	63	45	100	90	42	15	38	52	53	11	25	2	3	620
SD	61	32	82	66	110	92	48	17	71	40	56	13	58	4	6	370
Dry and wet deposition																
14 September 1999	230	110	250	96	93	84	18	42	92	340	34	18	19	10	0	1400
9 October 1999	170	87	180	55	180	130	120	46	86	46	41	46	32	7	0	1200
11 November 1999	160	100	345	74	140	53	46	88	39	47	27	4	75	34	33	1300
15 February 2000	210	88	120	73	170	240	110	130	55	120	84	10	87	0	0	1500
Mean	180	92	210	67	170	140	93	87	60	70	51	20	65	14	8.2	1300
SD	28	9	120	11	20	95	41	41	24	41	30	23	29	18	20	140
Total																
Mean	80	45	98	50	120	100	53	32	43	56	52	13	34	5	6	790
SD	77	39	110	58	100	92	50	39	63	39	50	15	55	10	12	450
% (dry + wet)/(dry + wet + dry only)	78	75	77	60	63	61	69	85	61	57	49	65	72	71	92	68

[a] These fluxes are normalized to annual values like the values reported in Table 1.
[b] Sampling periods as in Table 1.
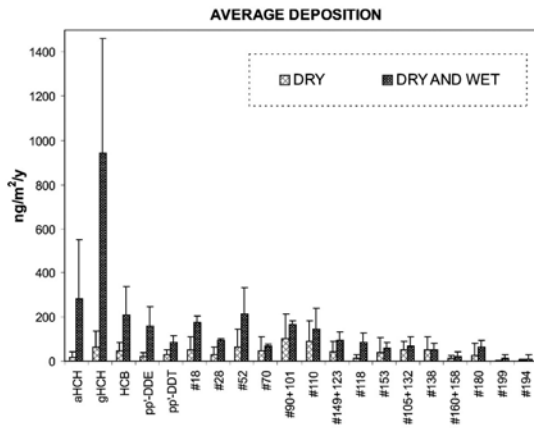[c] IUPAC congener numbers.

Fig. 2 Composition of the organochlorine pesticides and polychlorobiphenyl congeners in dry only and wet + dry deposition collected at Izaña Observatory. Interval bars indicate standard deviation. Numbers in abscissas refer to IUPAC PCB congener numbers. The flux values have been calculated by referencing the compound amounts deposited during the sampling time intervals to a whole year.

5 April 2000 (Tables 1 and 2), nearly an annual time interval, have been selected for calculation. The total load of organochlorine compounds represented by these samples shows that dry deposition is important for the incorporation of the higher molecular weight congeners (Fig. 3). In contrast, the proportion of organochlorine pesticides, particularly HCHs, and even low molecular weight PCBs, e.g. #18, #28, #52, is small in this mode of atmospheric precipitation.

Taking into account the annual wet precipitation rate, the results outlined in Fig. 3 show a scenario dominated by low deposition fluxes of organochlorine pesticides
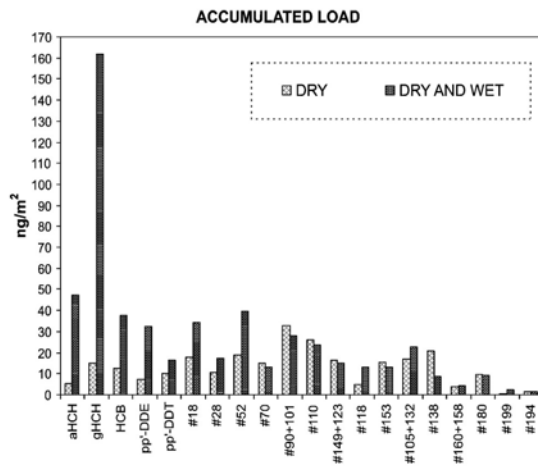

Fig. 3 Accumulated load of organochlorine compounds in the samples collected between 20 May 1999 and 19 May 2000 at Izaña Observatory. The days included in the collection periods represent 58% of the whole year. See Table 3 for scaling to one year cycle. Numbers in abscissas refer to IUPAC PCB congener numbers.

TABLE 3

Annual deposition fluxes (ng m^{-2} yr^{-1}) of organochlorine pesticides and polychlorobiphenyls calculated from mass balance integration of the input fluxes recorded in the samples collected over one year period (20 May 1999–5 April 2000) in the free troposphere of the eastern Atlantic Ocean.

Deposition type	α-HCH	γ-HCH	HCB	pp'-DDE	pp'-DDT	#18ᵃ	#28	#52	#70	#90 + 101	#110	#149 + 123	#118	#153	#105 + 132	#138	#160 + 158	#180	#199	#194	Total
Dry	9.5	26	21	12	17	31	18	32	26	57	45	28	8.5	27	29	35	6.6	16	0.46	2.4	360
% of total	10	9.3	24	18	37	34	37	32	54	54	52	52	27	55	43	70	47	50	11	46	46
Dry and wet	82	280	65	56	29	59	30	68	22	48	41	25	23	22	39	15	7.3	16	3.8	2.8	420
% of total	90	90	76	82	63	66	63	68	46	46	48	46	74	45	57	30	52	50	90	54	54
Total	91	310	86	68	46	90	48	100	48	105	86	54	31	49	68	50	14	32	4.2	5.2	780

ᵃ IUPAC congener numbers.

and PCBs. In association with the fall of dry particles, all compounds are incorporated at about similar fluxes, between 5 and 32 ng m^2, in this deposition mode (10 and 65 ng m^{-2} yr^{-1}, if these results are scaled to annual deposition, Table 3). In addition to this baseline flux, wet + dry deposition episodes involve high inputs of the lower molecular weight compounds, in the order of 20–48 ng m^{-2} (35–80 ng m^{-2} yr^{-1}, Table 3) for most compounds, and 162 ng m^{-2} for γ–HCH (280 ng m^{-2} yr^{-1}, Table 3), overcoming the dry deposition inputs.

This mass balance involves that 90% of HCH are incorporated as consequence of the sparse wet precipitation events. 76% and 82% of HCB and pp'-DDE are incorporated to the earth/sea surface by mediation of these wet episodes. Another group of compounds, pp'-DDT and PCBs #18, #28 and #52, exhibit an association to wet episodes of about 60% of the total load. Finally, these wet episodes are responsible of about 40–50% of the atmospheric higher molecular weight PCB, e.g. #70 or higher.

Conclusion

The average deposition fluxes of HCB, total HCH, DDTs and PCBs in the free troposphere (2367 m.a.s.l.) of the eastern North Atlantic Ocean are 86, 400, 110 and 780 ng m^{-2} yr^{-1}. These values are lower than those measured at sea level in rural or industrial continental sites or in marine areas. These lower fluxes represent the net input of long-range transported OC to the ocean region whereas those measured at sea level likely reflect contributions after volatilization of those present in soils, water or local pollution sources. To this end, the isomeric composition of HCH is coincident with that observed in rural sites of central Europe (α/γ ratio 1:3). No β-HCH has been found. Comparison of the compounds present in dry only or dry + wet deposition shows the preferential association of all compounds to wet precipitation. However, when considering the annual frequency of wet deposition events, deposition associated to this precipitation mode appears to be specifically relevant for low molecular weight OC, particularly HCHs. In contrast, dry deposition seems to be responsible for a background atmospheric precipitation of similar fluxes, within a range of 10 and 65 ng m^{-2} yr^{-1}, for all compounds.

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