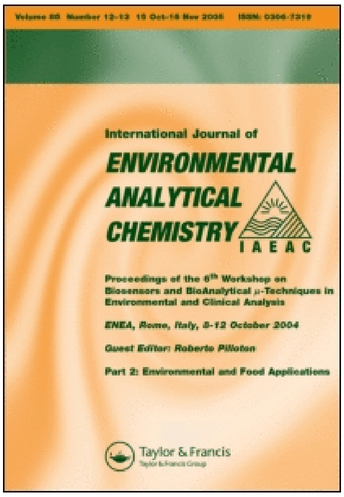

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Baseline Studies of the Global Pollution VIII: The Complex Pattern of C_1–C_4 Organohalogens in Continental and Marine Background Air†

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Adsorption sampling on Tenax GC combined with thermal desorption and cold trap injection allows the analysis of 2–500 liters of air as a single sample. The separation by high resolution gas chromatography and electron capture detection reveals a complex pattern of baseline pollution of C_1–C_4 organohalogens in clean continental and marine air. Air samples from the Azores and from the Madeira Archipelago—above and below the trade-wind inversion—give similar patterns of pollution.

KEY WORDS: Global pollution; air pollutants; C_1–C_4 organohalogens; capillary gas chromatography; North Atlantic.

INTRODUCTION

A series of investigations has been started to give a detailed qualitative and quantitative analysis of the global baseline pollution of organochlorine compounds covering the C_1- to C_{26}-range.[1] A global background of some of the most common C_1/C_2 organohalogens (Table I) is well established.[2,3] Sources, life times

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TABLE I

U.S. production in 1980 and background concentration of C_1/C_2 organohalogens in the lower troposphere

Compound	Mol. wt.	U.S. production in 1980 in 1000 t	Continental air		Marine air	
			ppt(V/V)	ng/Nm^3	ppt(V/V)	ng/Nm^3
CH_3Cl	48.5	164	569[7]	1230	1260[8]	2730
CH_2Cl_2	85	256	36[7]	137	35[7]	133
$CHCl_3$	119.5	160	9[7]	48	40[8]	210
					29[10]	156
					14[8b]	75
CCl_4	154	322	122[7]	840	128[8]	880
			103[9]	708		
			144[6]	990		
CF_2Cl_2 (F12)	121	134	228[7]	1230	207[8]	1120
			300[6]	1620	274[10]	1480
$CFCl_3$ (F11)	137.5	72	130[7]	800	123[8]	755
			160[6]	980	161[10]	988
CH_3Br	95	n.a.	15[8]	64	93[8]	390
			5[8b]	21	15[8b]	64
CH_2Cl-CH_2Cl	98	5039	—	—	—	—
CH_3-CCl_3	133.5	314	95[7]	570	117[10]	697
			128[6]	760	113[8b]	673
CCl_3-CCl_3	237	—	—	—	7[8b]	74
CF_2Cl-$CFCl_2$ (F113)	187.5	n.a.	21[7]	180	13[10]	109
$CHCl=CCl_2$	131.5	121	20[7]	120	16[8b]	94
$CCl_2=CCl_2$	166	347	31[11]	230	56[10]	420
					40[8b]	300

n.a. = not available.

and transport pathways of these molecules are of particular interest.[2,3,4] While the unsaturated ethene derivatives have atmospheric life times in the range of hours to days, for the methane and ethane derivatives life times from 5 up to 75 years have been estimated.[5] The background concentrations reflect these differences in stability (Table I). The increase per year in troposphere concentration has been estimated recently: CF_2Cl_2, 20 pptv; $CFCl_3$, 12 pptv; CCl_4, 4 pptv; and CH_3CCl_3, 15 pptv.[6]

Improved enrichment and injection techniques, which allow the analysis of up to 100–500 liters (130–650 grams) of air as a single probe by high resolution gas chromatography (GC) with electron capture detection (ECD), reveal a far more complex pattern of low-boiling organohalogens in continental as well as marine background air than previously found.

EXPERIMENTAL

The control of any contamination during sampling, sample transport and storage, sample injection and analysis has been the basic requirement of this type of background pollution measurement. The sampling was done by adsorption and precleaned Tenax GC .[12,13] The introduction of the micropollutants into the GC system was done by thermal desorption followed by a cold trap (liquid N_2) collection prior to the injection by a sudden (1–2 sec) temperature rise (Fig. 1). The separation was achieved on a 50 m fused silica capillary, stationary phase OV-1, film thickness 0.17 μm. The gas chromatograph was temperature-programmed from −10 to 200°C, with a heating rate of 3.0°C per min, model Dani 6800. The detector

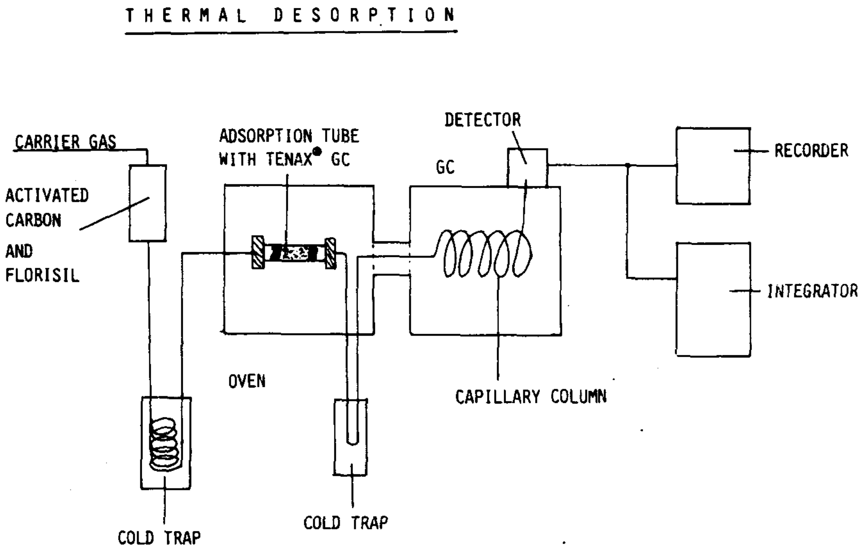

FIGURE 1. Experimental set up for thermal desorption and cold trap injection.

was a frequency-modulated ECD. The detector signal was simultaneously recorded by a two-stage mV recorder and a Spectra Physics Integrator 4100.

The experimental set-up allowed a defined and reproducible GC temperature and flow control, which gave the basis for highly reproducible retention index measurements for all compounds of the complex mixtures. The retention indices were based on the homologous series of n-alkanes using CH_2Cl_2, $CHCl_3$, CH_3CCl_3, CCl_4, tetrachloroethene and the C_1–C_{18} alkyl trichloroacetates[14] as external reference compounds with ECD response. The identification was done by comparison with authentic reference compounds, which were introduced into the separation system in the same way as for the real samples in order to ensure reproducibility in retention characteristics.

RESULTS AND DISCUSSION

The blank for the analytical procedure can be seen in Fig. 2. Qualitative and quantitative results for continental background air and marine background air below and above the trade-wind inversion (Madeira) and from the Azores High (Sao Miguel, Azores) are summarized in Table II and Figs. 3–6.

The Madeira island was chosen because access to the prevailing north-easterly winds above the trade-wind inversion is conveniently gained at the mountain Pico Arieiro at a height of 1800 m. In spring there is a rather stable inversion at 700–1100 m above sea level, which separates the two different air masses of the boundary layer, and with its clouds acts as a cover for the local emissions from the island itself. Air collected at the Pico Arieiro, Madeira, is seen in Fig. 3.

A suitable place for the analysis of the marine boundary layer below the trade-wind inversion is found at Porto Santo, a small island north of Madeira, where local influences can be definitely excluded. Its population (about 2000 inhabitants) is living mainly at the southerly lee-side of the island. This allows a locally undistributed access to the north-easterly winds close to sea level by collecting at the edge of the rocky north coast of the island. Two air samples are presented from Porto Santo, one with 4.72 liter (Fig. 4)

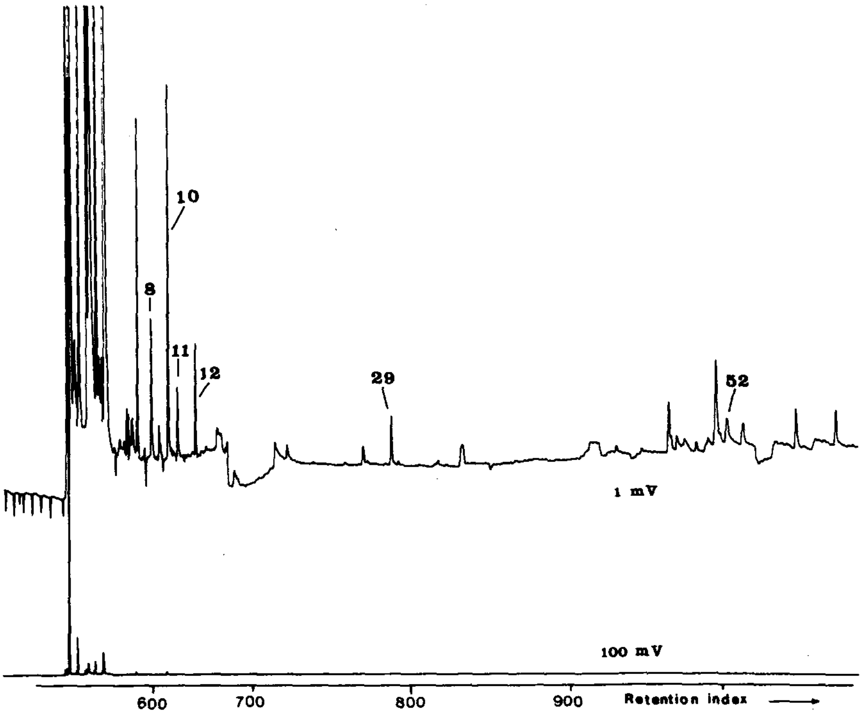

FIGURE 2. Blank value of sampling tube of Tenax GC. Identified peaks (in Figs. 2–6): 8, chloroform; 10, 1,2-dichloroethane; 11, 1,1,1-trichloroethane; 12, carbon tetrachloride; 18, trichloroethene; 29, tetrachloroethene; 32, 1,1,1,2-tetrachloroethane.

TABLE II

Background concentration of major C_1 and C_2 halocarbons in continental and marine clean air in 1982

	Hochgrat German Alps, 1860 m[a]		Pico Arieiro Madeira, 1810 m[b]		Porto Santo Madeira, 100 m[c]		Sao Miguel Azores, 510 m[d]	
Compound	pptv	ng/Nm^3	pptv	ng/Nm^3	pptv	ng/Nm^3	pptv	ng/Nm^3
$HCCl_3$	19	103	19	100	21	110	13	68
CCl_4	80	550	103	710	95	650	106	730
CH_3-CCl_3	86	510	139	830	148	880	138	820
$CHCl=CCl_2$	6	35	<2	<13	13	76	<5	<30
$CCl_2=CCl_2$	15	110	9	66	26	190	13	99

[a] The seventh day of a continuous inversion above Southern Germany, Jan. 1982, wind SSE, mean of 4 samples.
[b] Above the trade-wind inversion at 700–1100 m, March 1982, wind ESE, mean of 2 samples.
[c] Below the trade-wind inversion at 700–1100 m, March 1982, wind NNE, mean of 3 samples.
[d] June 1982, wind NNW, mean of 3 samples.

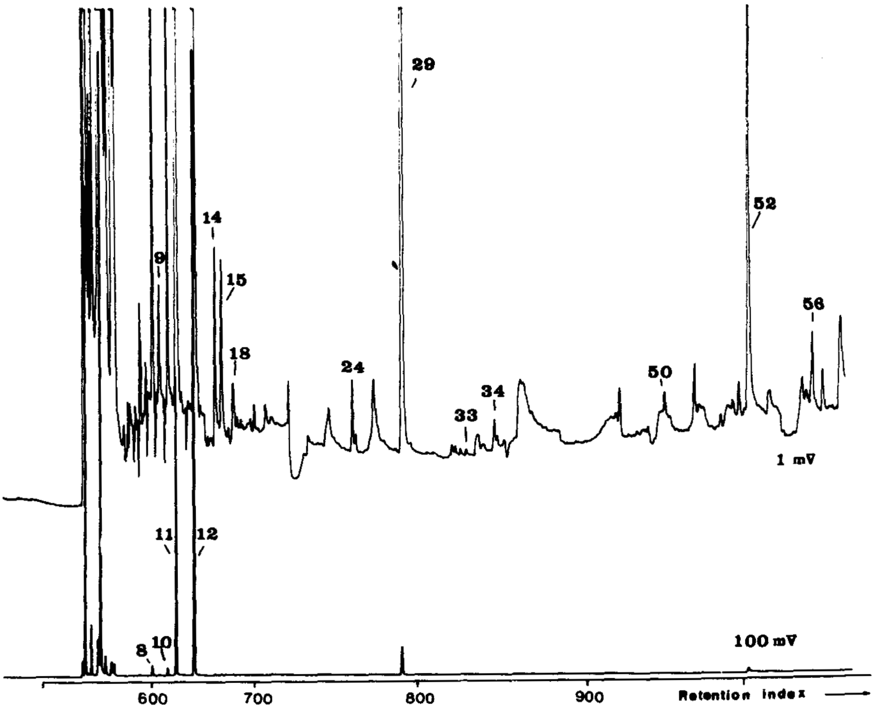

FIGURE 3. Air sample from Pico Arierio, Madeira, 1810 m; 13.3.1982, 17.10–18.10; sampling volume: 2.83 l; Tenax GC: 250 mg; weather conditions: wind ESE, temperature: 10°C, sunny, clouds at 800–1100 m.

and one with 108 liters (Fig. 6). The latter sample exemplifies the extremely complex background pattern of C_1–C_4 organochlorine compounds in the lower nanogram per cubic meter range found in clean marine air.

As air sampling at the Madeira Archipelago does not insure the exclusion of recent input (2–4 days) from the European and African continents (Portugal, South Spain, Maroc) we have collected air samples at the west coast (luff-side) of the island Sao Miguel, the Azores. The prevailing winds at the Azores blow from the west. Any major input into the boundary layer can only come from the sea itself or from the North American continent. Figure 5 exemplifies the background pollution by organohalogens found in the air masses

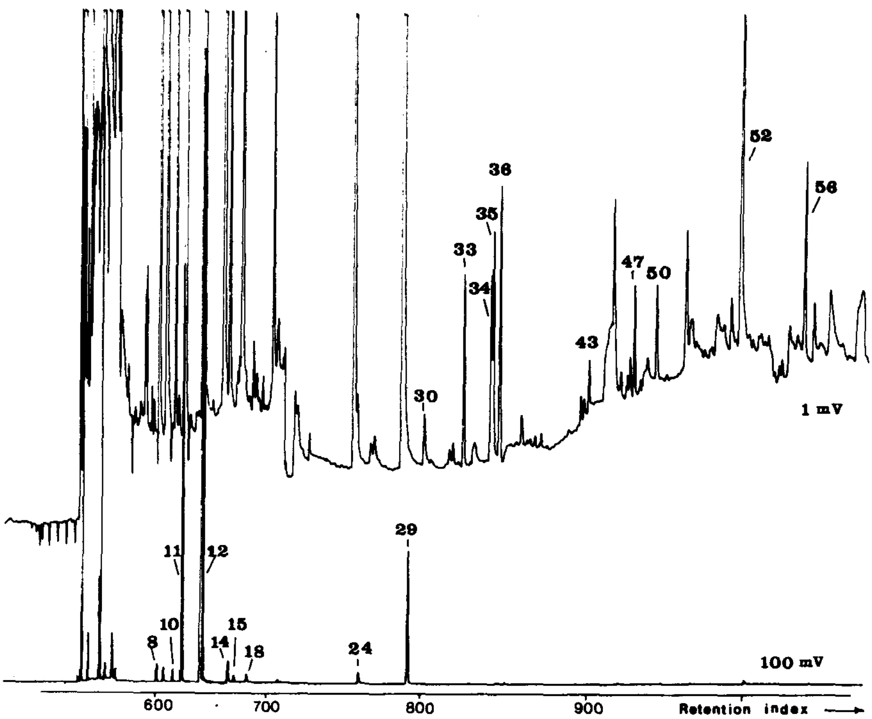

FIGURE 4. Air sample from north coast of Porto Santo, Madeira Archipelago, 100 m; 16.3.1982, 10.40–12.20; sampling volume: 4.72 l; Tenax GC: 250 mg; weather conditions: wind NNE; 35 km/h: 7/8 clouds at 800 m; relative humidity 72%, temperature 15°C; air pressure: 1.011 bar.

hitting the Azores and which can be considered as a well-mixed mean of background air.

A detailed comparison and identification of the compounds found in the three types of air masses above the North Alantic in under progress.[15] It can be stated already that there are no basic differences in the pattern of the complex marine background pollution. This opens the questions of sources, sinks, life times and routes of degradation for these molecules, besides the questions of environmental impact of these ubiquitous molecules.

On comparison of the results of Table II with former measurements in Table I baseline concentrations of 10–20 pptv for chloroform ($CHCl_3$) and similar low concentrations of <2–10 pptv

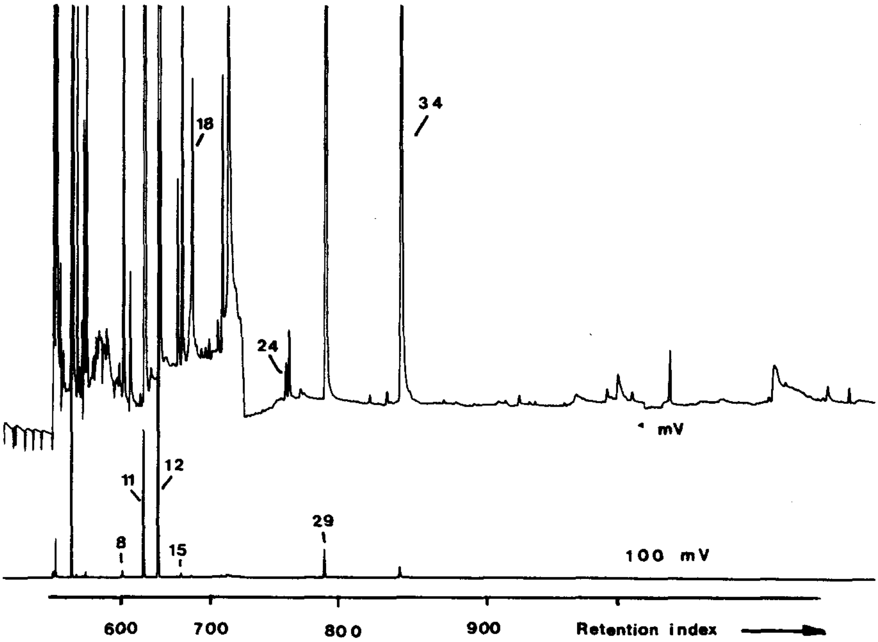

FIGURE 5. Air sample from north-east Coast of Sao Miguel, Azores, 30 m; 16.6.1982, 15.15–16.10; sampling volume: 1.94 l; Tenax GC: 250 mg; weather conditions: wind NNW; 10 km/h; 1/2 clouds sunny, relative humidity 52%; temperature 21°C; air pressure: 1.000 bar.

for trichloroethene ($CHCl=CCl_2$) and <7–20 pptv for tetrachloroethene ($CCl_2=CCl_2$) seem likely. These values are a result of an effective degradation mechanism in the troposphere.

The levels for tetrachloromethane (CCl_4) and 1,1,1-trichloroethane (CH_3–CCl_3) found in clean air are about 10–50 times higher. The concentration ranges for these compounds, CCl_4 (80–106 pptv) and CH_3–CCl_3 (86–148 pptv), in clean air cannot be explained yet, but agree with the levels of 103–128 pptv for CCl_4 and 95–117 pptv for CH_3–CCl_3 found by other authors (Table I). Very recent results for the free troposphere over Western Europe give ranges of 122–155 pptv for CCl_4 and 120–170 pptv for CH_3–CCl_3.[6] One explanation would be that the long-range mixing processes are less effective than is generally assumed. It seems unlikely that a limited

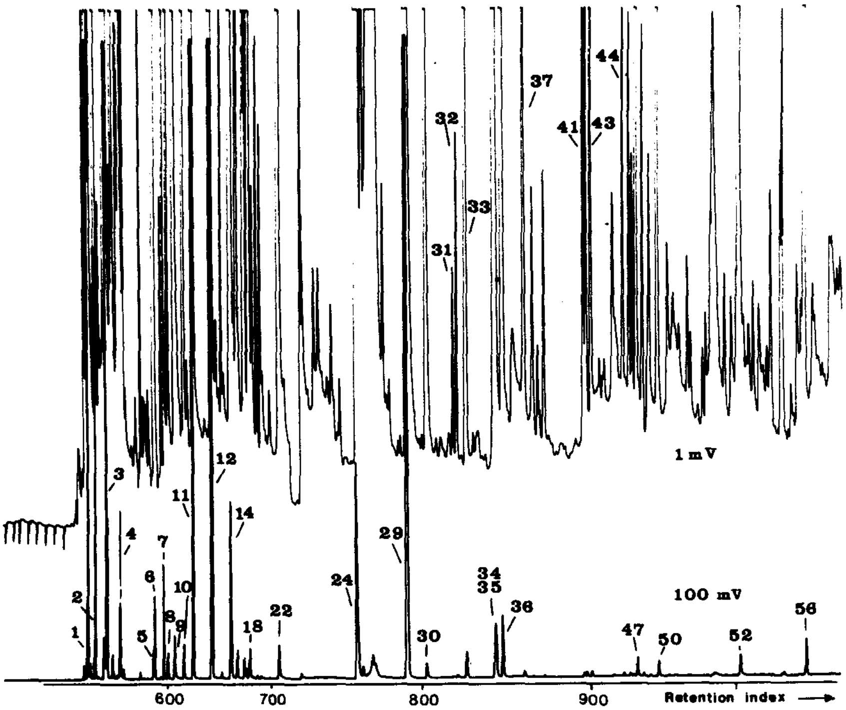

FIGURE 6. Air sample from north coast of Porto Santo, Madeira Archipelago; 100 m; 16.3.1982; 10.30–14.20; sampling volume: 108 l; Tenax 250 mg; weather conditions: see Fig. 4.

accuracy of the analytical procedures alone is the reason for the ranges of ±(10–15)% relative.

The complexity of the pattern of not yet identified C_2- to C_4-halocarbons is found in continental as well as in marine clean air indicating a type of molecules stable to environmental degradation (Fig. 6). The sources for this complex pattern seem to be all kinds of burning processes including heating and traffic.[15]

Acknowledgements

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