Analysis of Halogenated Methoxybenzenes and Hexachlorobenzene (HCB) in the Picogram m^{-3} Range in Marine Air

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Summary

Halogenated methoxybenzenes (halogenated anisoles) and hexachlorobenzene (HCB) have been analyzed in marine air samples from the lower troposphere of the East Atlantic Ocean, taken on the German research vessel `Polarstern' during two cruises in 1993 and 1994, and in air samples from the North Pacific Ocean (1995). The high-volume sampling method, sample preparation and analysis by HRGC-ECD and HRGC-MSD-SIM are described. The effectiveness of a new graphitized-carbon-covered silica sorbent (ANGI-Sorb B) for the sampling of semi-volatiles is demonstrated. Eight congeners of the halogenated anisoles and HCB were detected in almost all marine air samples. The concentrations of the chloroanisoles, which show a distinct north–south inter-hemispherical gradient, were between 0.2 and 145 pg m^{-3}; for the bromoanisoles concentrations were between 0.2 and 42 pg m^{-3}. Only a weak inter-hemispheric gradient was observed for HCB at levels of 10–40 pg m^{-3}. Levels of HCB were approximately 100 pg m^{-3} in continentally influenced air. Biogenic and indirect anthropogenic sources of the halogenated anisoles are discussed.

Introduction

The halogenated methoxybenzenes seem to be ubiquitous in the environment. Several of the 134 congeners of the bromo-, chloro- and bromochloromethoxybenzenes (hereafter denoted bromo-chloro-anisoles), which consist of 19 chloroanisoles, 19 bromoanisoles and 96 mixed bromochloroanisoles, have been detected in marine [1] and fresh-water [2–4] fish, in oysters [5], in the effluents [6] and atmospheres [7] of municipal waste water biological treatment plants, and in marine air [8, 9]. Despite the ubiquity of the bromo-chloro-anisoles in the environment, their main sources are not yet known. Although halogenated anisoles are not produced and/or used in technical quantities as were the polychlorinated biphenyls (PCB), the concentrations of the two groups of compounds in the environment are similar.

One possible source is biomethylation of the respective halogenated phenols by microorganisms [10–12]. Chlorinated phenols, e.g. tetrachloro- and pentachlorophenol, are widely used as biocides [13] and are formed in the pulp mill bleaching process [14–16] and during the chlorination of water [17]. Chlorophenols are, moreover, metabolites of other anthropogenic precursors, e.g. chlorobenzenes [18, 19]. The chloroanisoles can be considered as atmospheric indicators of the general pollution of the environment with halogenated phenols and benzenes. A further pathway to halogenated anisoles is the halogenation of phenols and halophenols, or other suitable precursor compounds by haloperoxidase enzymes. Especially in the marine environment many natural brominated compounds are synthesized in this way, e.g. by marine worms [20–22].

Like the halogenated anisoles, chlorobenzenes are ubiquitous in the environment yet unsolved problems in sampling and sample clean-up have restricted the global monitoring of these relatively volatile compounds. Hexachlorobenzene (HCB) has been found in the atmosphere [8, 23] and in several biological samples, e.g. in leaves [24] and in marine mammals at the top of the marine food chain [4, 25, 26]. The environmental input of

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HCB is complex and diffuse and not very well understood. HCB has been used as a fungicide and is a technical by-product of chlorination processes [27]. HCB is, furthermore, formed in combustion processes, e.g. in municipal waste incineration plants [28].

Experimental

The systematic congener number used for the bromo-chloro-anisoles, and their substitution pattern, accord with those given by Führer et al [7].

The physico-chemical properties of the bromo-chloro-anisoles and of the chlorobenzenes are very similar. Both groups are semivolatile organic compounds with vapor pressures of the pure liquid at 25 °CC between 0.37 Pa (pentachloroanisole, A19) and 90 Pa (2,6-dichloroanisole, A7) [29]. Pentabromoanisole (3×10^{-4} Pa, A38) is substantially less volatile. Its vapor pressure is comparable with those of the less chlorinated PCBs.

The solubility in water of the chloroanisoles decreases from 5.37 mol m^{-3} (2-chloroanisole, Al) to 1.78×10^{-3} mol m^{-3} (pentachloroanisole, A19). The aqueous solubility of pentabromoanisole (A38; 7.6×10^{-4} mol m^{-3}) is in the range of the solubility of the PCBs [29]. The Henry's law constant describes air–water distribution for solutes in water. Air is the environmental compartment preferred by the compounds, which have a Henry's law constant > 20 Pa m^3 mol^{-1} [30]. The Henry's constants of haloanisoles are in this range [29], therefore will, like the chlorobenzenes, be found mainly in the atmosphere.

The extremely low concentrations of these compounds in marine air require an effective enrichment method. Although silica gel or Florisil are commonly used as sorbents for high-volume sampling of semivolatile compounds such as the HCHs and the PCBs [31], because these sorbents are deactivated by humidity their activity and capacity are not sufficient for quantitative sampling of more volatile nonpolar semi-volatile organics including the HCB. Initially, therefore, we used a mixture of silica gel 60 and ENVI-Carb, a graphitized carbon black available from Supelco. This sorbent mixture proved to be suitable for sampling halogenated anisoles in the atmosphere above a municipal waste-water treatment plant [7]. Next a specifically designed sorbent (ANGI-Sorb B) with variable carbon content was tested; this carbon-covered silica gel is custom-synthesized by pyrolysis in our laboratory [32].

High-Volume Sampling of Marine Air

The high-volume sampling method is based on that described by Wittlinger et al. [33]. Air was pumped by a large turbine pump through a stainless-steel sieve filled with two layers of a sorbent separated by a glass fiber filter. The upper sorbent layer was a mixture of 100 g silica gel 60 (30–70 mesh) and 5 % *w/w* ENVI-Carb (120–200 mesh) or 136 g of a mixture of ANGI-Sorb 5B (carbon content 0.7 %) and ANGI-Sorb 10B (carbon content 1.6 %). The mesh size of the ANGI-Sorb was 35–70 mesh in both cases. Breakthrough was monitored by use of the second sorbent layer, 100 g silica gel 60 containing 1 % *w/w* ENVI-Carb or 198 g ANGI-Sorb 2.5B (carbon content 0.3 %). Air particulates were collected by placing a glass fiber filter (collection efficiency > 99.97 % for oil droplets > 1 μm) on top of the upper sorbent layer. The cleaning of the silica gel 60, of the ENVI-Carb and of the glass fiber filters before sampling is described elsewhere [7]. The carbon-covered silica gel ANGI-Sorb B was cleaned by successive Soxhlet extraction with hexane and acetone. The residual solvent was removed by evaporation at 90 °CC and 100 hPa.

Air (100–400 m^3) was sampled at a flow rate between 15 and 20 m^3 h^{-1} when using silica gel 60–ENVI-Carb or at a flow rate of 30 m^3 h^{-1} when using ANGI-Sorb B. After sampling the sorbents were transferred to glass flasks, which were flame-sealed to enable air-tight long-term storage of the samples.

Sample Preparation

Extraction of the Sorbents

The sorbents were extracted by Soxhlet extraction for 24 h with 200–250 mL high purity dichloromethane or diethyl ether, in a glass-metal-only clean bench, previously tested for contamination. All further steps of the sample preparation were performed in the glass-metal-only clean bench equipped with charcoal air-filters.

Before extraction each sorbent layer was spiked with 5–40 ng 2,4,6-trichlorophenyl ethyl ether (TCPE-C2) and 2,4,6-trichloro-*n*-octyl ether (TCPE-C8) as internal standards and retention-time markers. Approximately 2 mL hexane was added to the extract as a keeper. The extract was then slowly concentrated to approximately 0.5 mL by rotary evaporation at 35–38 °CC and at atmospheric pressure. The relatively high vapor pressures of the halogenated anisoles prohibits working at reduced pressure.

Sample Clean-up and Group Pre-separation by NPLC

Clean-up and group pre-separation were performed using activated Florisil previously cleaned by heating at 600 °C for 24 h. Before use it was kept at 130 °C for at least 12 h and used directly after removal from the oven. A water-cooled column was packed with 3 g Florisil in pentane, topped with 0.6 g Na_2SO_4 and cleaned with 50 mL pentane. The sample solution, which must be free from CH_2Cl_2 or diethyl ether, was added to the top. Three fractions with increasing polarity were subsequently eluted. The first fraction (19 mL pentane; eluate LC1) contained the non-polar alkanes, most of the polychlorobiphenyls (PCB), and a small portion of the chlorobenzenes. The halogenated anisoles elute in the second fraction (pentane–CH_2Cl_2, 4:1; 35 mL or, as an alternative, pentane–diethyl ether, 3:1; 36 mL; eluate

Table I. Conditions used for gas chromatography.

HRGC-ECD	
Gas chromatograph:	HP 5890 Series II (Hewlett-Packard)
Injector:	On column, temperature programmed (3° above oven temperature) Autosampler, on column
Detector:	^{63}Ni ECD, T = 300 °C
Make-up gas:	Ar–CH$_4$ (90:10; Linde), flow 40 mL min^{-1}
Stationary phase:	CP-Sil 2, 55 m, 0.25 mm i.d., film thickness 0.25 μm (Chrompack)
Carrier gas:	Nitrogen 5.0 (Linde)
Pressure program:	30 kPa (0.1 min), 100 kpa min^{-1}, 71 kPa, 4 kpa min^{-1}, 79 kPa, 1 kpa min^{-1}, 98 kPa
Temperature program:	40 °C (0.5 min), 100° min^{-1}, 100 °C, 4° min^{-1}, 240 °C (30 min)
HRGC-MSD-SIM	
Gas chromatograph:	HP 5890 (Hewlett-Packard)
Injector:	On column
Detector:	MSD HP 5970,(Hewlett-Packard)
Stationary phase 1	DB 1701, 30 m, 0.25 mm i.d., film thickness 0.25 μm (J&W Scientific)
Carrier gas:	Helium 4.6, 150 kPa, (Linde)
Temperature program	50 °C (3 min), 20° min^{-1}, 80 °C, 2.5° min^{-1}, 230 °C (1 min), 20° min^{-1}, 290 °C, 10 min
Stationary phase 2	HP Ultra 2, 50 m, 0.2 mm i.d, film thickness 0.33 μm (Hewlett-Packard)
Carrier gas:	Helium 4.6, 186 kPa (Linde)
Temperature program:	50 °C (3 min), 10° min^{-1}, 130 °C, 1.5° min^{-1}, 250 °C (10 min), 10 ° min^{-1}, 270 °C, 10 min

LC2). More polar compounds were eluted in the third fraction (20 mL CH$_2$Cl$_2$ or diethyl ether; eluate LC3). Sometimes the more polar dimethoxybenzenes, which normally elute in eluate LC2, can be found in this third fraction. In air samples originating from urban regions, long-chain alkyl nitrates, a group of compounds known to contribute significantly to the nitrogen oxides in air, are present at much higher concentrations than are the halogenated anisoles [34, 35]. As the alkyl nitrates are also eluted in the second eluate (LC2) further separation by HPLC on a special graphitized carbon is necessary to avoid interferences in subsequent capillary gas chromatography [7]. Because alkyl nitrate concentrations in marine air samples were very low there were no interferences with the analysis of the halogenated anisoles by HRGC-ECD and this additional separation step could, therefore, be omitted.

The pentane–diethyl ethyl (3:1) eluate (LC2) was slowly concentrated on a rotary evaporator using 500 μL hexane as keeper. The final volume of hexane was measured by weighing. This concentrate was analyzed by HRGC-ECD and HRGC-MSD-SIM.

The sample preparation method described above was originally developed for the analysis of urban air samples from a waste-water treatment plant [7]. Although concentrations of the haloanisoles are lower by an order of magnitude or more in marine air, the same protocol is applicable. As marine air is much cleaner than urban air, the general background of organic micro constituents of the samples is less complex, which enables simplified sample clean-up and group pre-separation.

Gas Chromatography

The halogenated anisoles can be detected by ECD or by MSD. The advantage of MSD is its higher selectivity and its substantially lower detection limits for the lower halogenated congeners. It is, moreover, possible to identify congeners of the bromo-chloro-anisoles, for which no reference substances are available, by their typical bromo or chloro isotope pattern. Although no determination of the substitution pattern is possible, the degree of halogenation can be determined.

Two non-polar stationary phases were selected, CP-Sil 2 (Chrompack, 55 m, 0.25 mm i.d., film thickness 0.1 μm) and HP Ultra 2 (Hewlett-Packard, 50 m, 0.2 mm i.d., film thickness 0.33 μm) for detection by ECD and MSD, respectively. For reasons of verification an additional analysis of the samples was performed on the polar phase DB 1701 (J & W Scientific, 30 m, 0.25 mm i.d., film thickness 0.25 μm), with detection by MSD. The gas-chromatographic conditions are given in Table I.

In HRGC-ECD analysis compound identification was achieved by comparison of the retention time with those of reference substances and by comparing retention relative to that of pentachloroanisole (A19) as the standard. Pentachloroanisole was present in all air samples. The relative retention on several stationary phases has been published by Führer et al [7]. The retention indices of several halogenated anisoles were also determined relative to the *n*-alkyltrichloroacetates (ATA). As the *n*-alkanes, proposed as the basis for the calculation of retention indices by Kováts [36] are not detectable by ECD, the ATA were introduced as an ECD-active homologous series by Neu et al. [37]. The temperature-programmed retention indices of selected halogenated

Table II. Retention indices of halogenated anisoles and benzenes on CP-Sil 2 relative to the homologous series of ATA (I^T (C7-trichloroacetate) = 1400). Pressure program: 30 kPa (0.1 min), 100 kPa min^{-1}, 110 kPa. Temperature program: 40 °C (3 min), 20 ° min^{-1}, 80 °C, 2 ° min^{-1}, 240 °C (45 min).

Compound	Symbol	I^T_X
Chloroanisoles		
2,3-Cl_2	(A4)	1273.5
2,4-Cl_2	(A5)	1249.9
2,5-Cl_2	(A6)	1239.4
2,6-Cl_2	(A7)	1116.6
3,4-Cl_2	(A8)	1245.9
3,5-Cl_2	(A9)	1229.1
2,3,4-Cl_3	(A10)	1463.2
2,3,5-Cl_3	(A11)	1425.7
2,3,6-Cl_3	(A12)	1343.8
2,4,5-Cl_3	(A13)	1420.3
2,4,6-Cl_3	(A14)	1322.5
3,4,5-Cl_3	(A15)	1437.1
2,3,4,5-Cl_4	(A16)	1629.4
2,3,4,6-Cl_4	(A17)	1519.9
2,3,5,6-Cl_4	(A18)	1516.3
2,3,4,5,6-Cl_5	(A19)	1719.4
Bromoanisoles		
2-Br	(A20)	1116.6
3-Br	(A21)	1100.0
4-Br	(A22)	1116.6
2,4-Br_2	(A24)	1448.2
2,6-Br_2	(A26)	1351.3
2,3,4-Br_3 / [a)]	(A29) /	
2,3,4-Br_3 /	(A31) /	
2,4,5-Br_3	(A32)	1726.5
2,3,4-Br_3 /	(A29) /	
2,3,4-Br_3 /	(A31) /	
2,4,5-Br_3	(A32)	1782.1
2,4,6-Br_3	(A33)	1633.2
2,3,4,5,6-Br_5*	(A38)	(2498)
Bromochloroanisoles		
2-Br-4-Cl	(A40)	1344.7
2-Br-6-Cl	(A42)	1245.4
4-Br-2-Cl	(A46)	1351.2
2-Br-3,5-Cl_2 /	(A50) /	
4-Br-3,5-Cl_2	(A61)	1541.3
2-Br-4,6-Cl_2	(A53)	1420.5
3-Br-2,4-Cl_2 /	(A54) /	1444.5 /
3-Br-2,6-Cl_2 /	(A56) /	1517.7 /
5-Br-2,4-Cl_2	(A63)	1566.9
Bromochloroanisoles (continued)		
4-Br-2,3-Cl_2 /	(A58) /	
6-Br-2,3-Cl_2	(A64)	1568.2
4-Br-2,6-Cl_2	(A60)	1426.7
3-Br-2,4,6-Cl_3	(A69)	1626.9
3-Br-2,5,6-Cl_3	(A70) /	
4-Br-2,3,6-Cl_3	(A72)	1627.8
6-Br-2,3,4-Cl_3	(A74)	1622.7
4-Br-2,3,5,6-Cl_4	(A77)	1836.1
2,4-Br_2-4-Cl /	(A81) /	
2,4-Br_2-5-Cl /	(A82) /	
2,6-Br_2-3-Cl	(A87)	1623.8
2,4-Br_2-3-Cl /	(A81) /	
2,4-Br_2-5-Cl /	(A82) /	
2,6-Br_2-3-Cl	(A87)	1671.1
2,6-Br_2-4-Cl	(A88)	1524.0
2,4-Br_2-3,5-Cl_2	(A97) /	
2,6-Br_2-3,5-Cl_2	(A103)	1846.7
2,4-Br_2-5,6-Cl_2	(A99)	1734.3
2,4,6-Br_3-3-Cl	(A124)	1846.5
Dimethoxybenzenes		
TCDMB		1680.0
Chlorobenzenes		
1,2-Cl_2		1006.5
1,3-Cl_2		988.1
1,4-Cl_2		989.0
1,2,3-Cl_3		1196.8
1,2,4-Cl_3		1173.6
1,3,5-Cl_3		1150.7
1,2,3,4-Cl_4		1375.3
1,2,3,5-Cl_4		1348.4
1,2,4,5-Cl_4		1348.5
1,2,3,4,5-Cl_5		1545.9
1,2,3,4,5,6-Cl_6		1747.5
Bromobenzenes		
Br		895.1
1,4-Br_2		1189.5
Bromochlorobenzenes		
1-Br-4-Cl		1086.9

*Because pentabromoanisole (A38) elutes in the isothermal section of the temperature program its I^T value was extrapolated.

[a)] If the exact substitution pattern of an anisole is not known, all possible congeners are stated and separated by '/'.

anisoles, calculated by the method of Fischer et al. [38], are listed in Table II. The retention indices range from 1100 to 2500 index units (2,6-dichloroanisole (A7), 1116.6; pentabromoanisole (A38), 2498).

Detection Limits

In HRGC-ECD analysis the limits of detection of the chlorinated anisoles in 1 m^3 of air range from 10 pg m^{-3} (dichloroanisoles) to 0.6 pg m^{-3} (pentachloroanisole). The ECD response to the monochloroanisoles is too low for a detection by ECD at the trace level. The limits of detection of the bromoanisoles are in the range 100 pg m^{-3} (monobromoanisoles) to 2 pg m^{-3}.

Quantitation in HRGC-ECD and -MSD was performed by the internal standard method. TCPE-C2 was used for calculation of the concentration of the anisoles eluting before this compound and TCPE-C8 was used for the anisoles eluting after TCPE-C2.

The ion-selective mass spectrometric detection of the halogenated anisoles is based on signals originating from the compounds' molecular ions. Compounds were identified by comparison of retention times with those of reference substances and verification of the relative intensities of the molecular ions. By means of the relative intensities of the molecular ions and their elution in the correct retention time window, several halogenated anisoles (e.g. some dibromo- and five tribromoanisoles,

Table III. Recoveries of halogenated anisoles (%) after Soxhlet extraction of silica gel 60–ENVI-Carb with dichloromethane or diethyl ether.

Compound	Symbol	Extraction with CH_2Cl_2	Extraction with diethyl ether
Chloroanisoles			
2,3-Cl_2	(A4)	130	73
2,6-Cl_2	(A7)	86	82
3,5-Cl_2	(A9)	87	86
2,3,4-Cl_3	(A10)	111	60
2,3,6-Cl_3	(A12)	98	72
2,4,5-Cl_3	(A13)	103	63
2,4,6-Cl_3	(A14)	90	73
2,3,4,5-Cl_4	(A16)	105	90
2,3,5,6-Cl_4	(A18)	100	82
2,3,4,5,6-Cl_5	(A19)	197	91
Bromoanisoles			
2-Br	(A20)	79	82
3-Br	(A21)	91	82
4-Br	(A22)	86	82
2,4-Br_2	(A24)	100	89
2,4,6-Br_3	(A33)	128	90
2,4,6-Cl_3-Phenyl ether			
TCPE-C2			87
TCPE-C8			118

2,4,6-tribromoanisole, and the three tetrabromoanisoles), for which no reference substances were available, could be identified. The substitution pattern of these bromoanisoles was derived from order of elution of the corresponding chloroanisoles. The molecular ions and their relative intensities for the halogenated anisoles are published elsewhere [7]. In HRGC-MSD-SIM analysis the limits of detection of the chloroanisoles in 10-m^3 air samples were in the range 0.1 pg m^{-3} (monochloroanisoles) and 0.2 pg m^{-3} (pentachloroanisole).

The limits of detection of the bromoanisoles were in the range 0.1 pg m^{-3} (monobromoanisoles) and 0.5 pg m^{-3} (pentabromoanisole). Reference substances were available for all quantified compounds except 2,5-dibromo- (A25), 3,4-dibromo- (A27) and 3,5-dibromoanisole (A28), the five tribromoanisoles (A29–A34), 2,4,6-tribromoanisole (A33), and the tetrabromoanisoles (A35–A37). The values for the tetrabromoanisoles were calculated as the mean of the response factors for 2,4,6-tribromoanisole (A33) and pentabromoanisole (A38). The mean response for 2,4- (A24) and 2,6-dibromoanisole (A26) and that for 2,4,6-tribromoanisole were used for quantitation of the di- and tribromoanisoles, respectively,. Blanks were detected for pentachloroanisole (A19, 80 pg) and HCB (114 pg).

Recovery Experiments

Charcoal and carbonaceous sorbents in general are well known for the difficulty of recovering the adsorbed analytes in satisfactory quantities in the sample preparation step. The recoveries of the halogenated anisoles during sample preparation were, therefore, determined by spiking 100 g of the sorbent mixture silica gel 60–5 % *w/w* ENVI-Carb with a known amount (50–4182 ng) of several halogenated anisoles. The sorbent was deactivated by addition of distilled water previously pre-extracted with hexane. In this way a water content of approximately 50 % was achieved; this is typical of adsorbent used to sample of marine air. The spiked sorbent samples were extracted with CH_2Cl_2 or with diethyl ether in a Soxhlet apparatus and the extracts were handled further as described above. A comparison of the extraction efficiency of CH_2Cl_2 and of diethyl ether is given in Table III.

Recoveries were better with CH_2Cl_2 than with diethyl ether. The latter recovered only 60 % of 2,3,4-trichloro- (A10) and 2,4,5-trichloroanisole (A13) but recoveries of the other congeners were satisfactory (72–118 %). Better recoveries with CH_2Cl_2 were at the expense of frequent problems with the purity of the solvent, expensive waste disposal, and the environmental impact of halogenated solvents. In contrast, diethyl ether can easily be highly purified by distillation over sodium. Diethyl ether was, therefore, used for extraction of the samples, except for samples FP 25 and FP 39.

Effectiveness of ANGI-Sorb B for Sampling Semi-Volatiles in Air

The suitability of the new sorbent ANGI-Sorb B for high-volume-sampling of halogenated anisoles and benzenes was tested by taking air samples in parallel on ANGI-Sorb B (ANI 7) and on silica gel 60–ENVI-Carb (ANI 8). Both air samples were taken from a ship in the northern Monterey Bay near Santa Cruz (California, USA). The sampling conditions are given in Table IV. Both types of sorbent were treated identically, accord-

Table IV. Sampling conditions for the air samples taken on silica gel–ENVI-Carb and on ANGI-Sorb B in the Monterey Bay near Santa Cruz (California, USA).

Sample	ANI 7 ANGI-Sorb B	ANI 8 Silica gel- ENVI-Carb
Date	25.8.95	25.8.95
Air temperature (°C)	15	15
Air pressure (hPa)	1010	1010
Sorbent layer 1	136 g (ANGI-Sorb B5 + ANGI-Sorb B10)	105 g (5% ENVI-Carb)
Sorbent layer 2	198 g (ANGI-Sorb B2,5)	101 g (1% ENVI-Carb)
Sample volume (m^3)	275	162
Mean flow (m^3 h^{-1})	30	20
Water content of the sorbent after sampling (%)		
Sorbent layer 1	28	53
Sorbent layer 2	8	52

Table V. Comparison of the two sorbents silica gel–ENVI-Carb and ANGI-Sorb B for the analysis of halogenated anisoles and of HCB in air by high-volume sampling. The concentration in air and the amount of breakthrough in the second sorbent layer are given.

	Concentration in air (pg m^{-3})		Breakthrough on second sorbent layer (%)[a]	
	Silica gel + 5% ENVI-Carb	ANGI-Sorb B	Silica gel + 5% ENVI-Carb	ANGI-Sorb B
Chloroanisoles				
2,6-Cl_2 (A7)	34	26	13	8
2,4,6-Cl_3 (A14)	113	103	16	8
2,3,4,6-Cl_4 (A17)	9	26	0	13
2,3,4,5,6-Cl_5 (A19)	31	26	15	13
Bromoanisoles				
2,4-Br_2 (A24)	13	14	8	8
2,6-Br_2 (A26)	14	12	17	9
2,4,6-Br_3 (A33)	53	54	10	13
Chlorobenzenes HCB	86	100[b]	15	18

[a] Percentage of the amount detected in the first sorbent layer, where the amount in the first sorbent layer = 100%.
[b] LC1 + LC2.

ing to the methodology described above. The concentration of the halogenated anisoles and of hexachlorobenzene (HCB) and the amounts of breakthrough detected are compared in Table V. Figure 1 depicts the HRGC-ECD chromatograms of fraction LC2 from both samples.

Although sampling on the newly developed material ANGI-Sorb B was performed at a 50 % higher flow rate (30 m^3 h^{-1}, compared with 20 m^3 h^{-1}) and a 70 % greater volume of air (275 m^3 compared with 162 m^3) was pumped through the sorbent, the breakthrough of the higher halogenated benzenes and methoxybenzenes is comparable on both types of sorbent. The breakthrough is in the range 10–15 % of the amount detected in the first sorbent layer. For the lower halogenated congeners even better adsorption properties were observed for the ANGI-Sorb B. Whereas the breakthrough on silica gel 60–ENVI-Carb is 8–17 % for 2,6-dichloro- (A7), 2,4,6-trichloro- (A14), 2,4-dibromo- (A24), and 2,6-dibromoanisoles (A26), these compounds are better retained on ANGI-Sorb B, for which the breakthrough is only 8 %. The correspondence of the concentration of the analytes in both samples underlines that recoveries from the two kinds of sorbent must be comparable. ANGI-Sorb B is even more suitable for the sampling of non-polar semi-volatiles than the sorbent mixture silica gel 60–ENVI-Carb. With ANGI-Sorb B it should be possible to sample halogenated benzenes and methoxybenzenes even under critical conditions of high temperatures and high humidity, conditions typically encountered in the tropics. Larger amounts of air can, moreover, be sampled; this is an advantage in areas where the atmospheric concentrations of the analytes are extremely low.

A further advantage of ANGI-Sorb B is the homogeneity of the sorbent. The sorbent mixture silica gel 60–ENVI-Carb combines hydrophilic and hydrophobic properties, which leads to a partial separation and the formation of ENVI-Carb pellets at high humidity; this results in reduced adsorption efficiency at the ENVI-

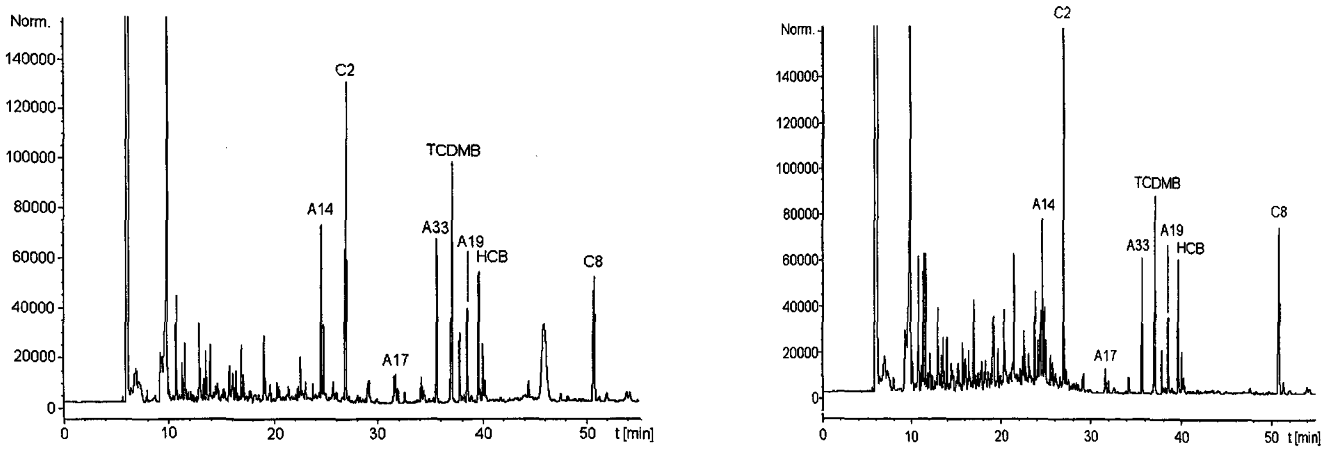

Figure 1

HRGC-ECD chromatograms of the LC2 fractions of marine air samples ANI 7 (ANGI-Sorb B) (a) and ANI 8 (silica gel 60–ENVI-Carb) (b); stationary phase: CP-Sil 2; C2: 2,4,6-trichlorophenyl ethyl ether; C8: 2,4,6-trichlorophenyl octyl ether; TCDMB: tetrachloro-1,4-dimethoxybenzene.

Carb-free spots. Because of the hydrophobic character of ANGI-Sorb B, there is less adsorption of water, which deactivates the silica gel 60. The handling of ANGI-Sorb B at the sampling site is, moreover, much easier, as no mixing of sorbents is necessary. Although the purification of new ANGI-Sorb B is more complicated, it is easier to recycle than the mixture of silica gel 60 and ENVI-Carb. These considerations show ANGI-Sorb B to be a very good choice for the analysis of semi-volatiles in air by high-volume sampling.

Collection of Marine Air Samples in the Atlantic Ocean

The air samples (FP 21–FP 39) were taken on cruise leg ANT XI/1 of the German research vessel (RV) 'Polarstern' from Bremerhaven (Germany) to Capetown (South Africa) in October–November 1993. Only sample CARBO 2 was taken on the cruise leg ANT XI/5 (Capetown–Rotterdam, Netherlands) in May–June 1994. The sampling locations are depicted in Figure 2, which also presents the trajectories of the sampled air masses, as calculated by the meteorologist on board the ship. All relevant meteorological and hydrological data were measured every 5 s and averaged over a period of 10 min by the data system of the research vessel. A selection of the data is given in Table VI.

The sampling location was on the upper-most deck of the RV 'Polarstern', approximately 20 m above sea level. Precautions were taken to prevent contamination of the samples by exhaust from the vessel. The mixture of silica gel 60 and ENVI-Carb was used as sorbent. In the first sorbent layer (100 g) the ENVI-Carb content was 5 % *w*/*w* and in the second layer (100 g) 1 % ENVI-Carb was added. 140–400 m^3 of air were sampled at a flow of 15–20 m^3 h^{-1}. The observed breakthrough did not exceed 25 % of the amount detected in the first sorbent layer. In all cases the amounts measured in the two layers were summed.

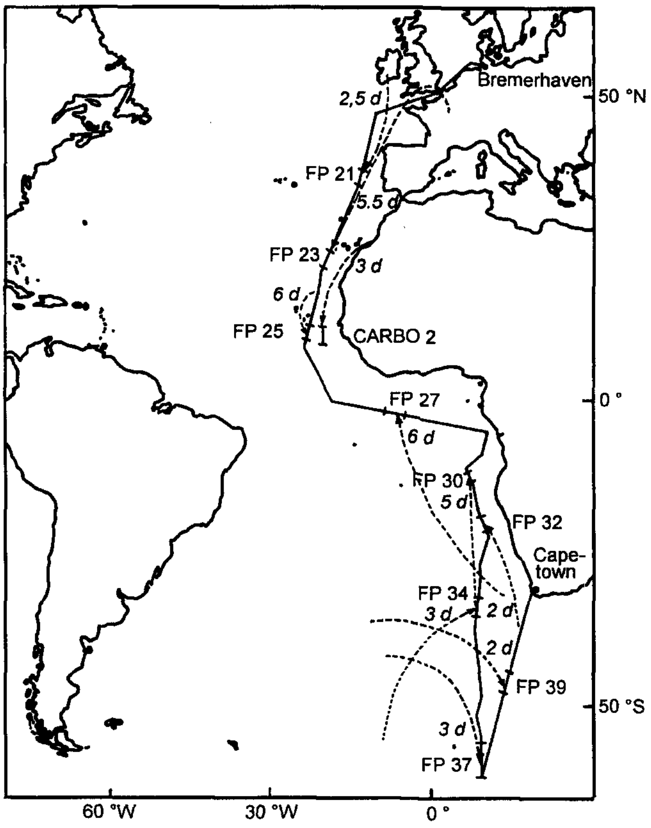

Figure 2

Sampling locations of the air samples during the cruises of the RV 'Polarstern' across the Atlantic Ocean. Air samples FP 21-FP 39 are from cruise leg ANT XI/1 (October–November 1993) from Germany to South Africa, sample CARBO 2 is from cruise leg ANT XI/5 (May–June 1994) from South Africa to Germany. —: route of the RV 'Polarstern'; - - -: trajectories of the sampled air masses and period of calculation.

The samples originating from the North Pacific Ocean (ANI 7 and ANI 8) were sampled as described above. The sampling location is shown in Figure 3.

Table VI. Meteorological parameters related to the air samples. The mean value is given in brackets.

Sample	Date Humidity	Location	Sample volume (mL)	Air temperature (°C)	Air pressure (hPa)	Wind direction; wind velocity (m s^{-1})	(%)
ANT XI/1							
FP 21	22–23.10.1993	40.3 °N 14.4°W... 37.7 °N 13.8°W	358	14.6...15.9 (15.1)	1018...1023 (1021)	NNE ... NE; 9...11 N; 9...10	65
FP 23	25–26.10.1993	27.0°N 18.2°W... 24.4°N 20.2°W	292	21.0...21.8 (21.3)	1014...1016 (1015)	NE; 3	64
FP 25	28–29.10.1993	14.5°N 22.8°W... 11.3°N 23.6°W	227	24.9...28.1 (26.0)	1013...1015 (1014)	NNW...NNE; 3...8	84
FP 27	3–4.11.1993	2.3°S 8.2°W... 2.9°S 5.1°W	255	24.7...25.7 (25.3)	1013...1016 (1015)	S...SSE; 3...8	88
FP 30	9–10.11.1993	13.4°S 6.4°E... 15.9°S 7.4°E	287	19.2...20.5 (19.9)	1013...1015 (1014)	S...SSW; 3...9	73
	11–12.11.1993	22.0°S 9.1°E... 25.0°S 10.30E	293	16.6...17.7 (17.0)	1017...1019 (1018)	SSE; 10	73
FP 34	15.11.1993	36.1°S 8.2°E... 38.0°S 8.0°E	212	11.7...13.1 (12.3)	1015...1017 (1016)	W...NW; 11...15	63
FP 37	19–20.11.1993	53.6°S 9.1°E... 57.4°S 9.2°E	306	- 0.1...1.4 (0.6)	1010...1013 (1012)	NW... N; 6...9	98
FP 39	23–24.11.1993	47.5°S 13.6°E... 44.6°S 14.7°E	400	4.1...9.0 (6.4)	1014...1017 (1016)	NW; 9...13	86
ANT XI/5							
CARBO 2	3.6.1994	11.1 °N 21.5 °W... 13.6 °N 21.5 °W	138	2 2.6...24.4 (23.4)	1012...1015 (1014)		74

Results and Discussion

Concentration of Bromo-chloro-anisoles and of HCB in Air of the East Atlantic Ocean

Table VII summarizes results from measurement of halogenated methoxybenzene and of HCB levels in the lower troposphere of the Eastern Atlantic Ocean. Figure 4 shows the HRGC-MSD-SIM chromatograms obtained from sample FP 32, taken as a typical example of air of the oceanic troposphere.

Only a few of the 134 theoretically possible bromo-chloro-anisole congeners were present in the air samples from the Atlantic Ocean. Of the chloroanisoles only 2,4,6-trichloro- (A14), 2,3,4,6-tetrachloro- (A17) and pentachloroanisole (A19) were detected. The concentrations were in the range 0.2–145 pg m^{-3}. Three congeners of the bromoanisoles (2,4-dibromo- (A24), 2,6-dibromo- (A26) and 2,4,6-tribromoanisole (A33)) were present in almost all samples. All three possible tetrabromoanisoles (2,3,4,5-tetrabromo- (A35), 2,3,4,6-tetrabromo- (A36), 2,3,5,6-tetrabromoanisole (A37)) and pentabromoanisole (A38) were detectable in samples FP 32 and FP 37. Pentabromoanisole (A38) was also present in sample FP 27. The concentrations of the bromoanisoles were in the range 0.2–42 pg m^{-3}. Although 96 mixed halogenated anisoles are possible in theory, these congeners are rarely found in the marine troposphere. Two dibromomonochloroanisole isomers were detected in samples to the north of 25°S. These isomers

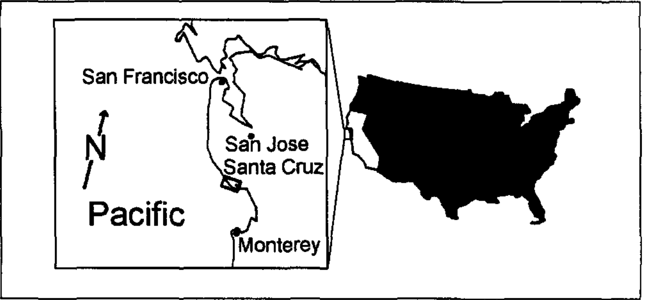

Figure 3
Sampling location of samples ANI 7 and ANI 8.

Table VII. Concentration (pg m^{-3}) of halogenated anisoles and of HCB in the lower troposphere of the Atlantic Ocean

Compound	Symbol	Mean latitude, northern hemisphere				Mean latitude, southern hemisphere					
		39°N FP 21	26°N FP 23	13°N FP 25	13°N CARBO2	3°S FP 27	15°S FP 30	24°S FP 32	37°S FP 34	46°S FP 39	56°S FP 37
Chloroanisoles											
2-Cl	A1	n.d.[a]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-Cl	A2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Cl	A3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,3-Cl_2	A4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4-Cl_2	A5	n.d.	n.d.	9871+[b]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,5-Cl_2	A6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-Cl_2	A7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3,4-Cl_2	A8	n.d.	n.d.	651+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3,5-Cl_2	A9	n.d.	n.d.	1513+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,4-Cl_3	A10	n.d.	n.d.	90+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,5-Cl_3	A11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,6-Cl_3	A12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,5-Cl_3	A13	n.d.	n.d.	197+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-Cl_3	A14	145	27	44	20	2.9	1.9	7.5	5.1	n.d.	7.2
3,4,5-Cl_3	A15	n.d.	n.d.	99000+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,4,5-Cl_4	A16	[c]	n.d.	15100+	[c]	[c]	[c]	0.7	[c]	n.d.	[c]
2,3,4,6-Cl_4	A17	11	1.0	n.d.	1.8	1.2	0.7	1.3	1.0	n.d.	n.d.
2,3,5,6-Cl_4	A18	n.d.	n.d.	679+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,4,5,6-Cl_5[d]	A19	12	1.8	386+	2.4	3.3	1.3	1.3	5.3	0.2	5
Bromoanisoles											
2-Br	A20	n.d.	n.d.	36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3-Br	A21	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Br	A22	n.d.	n.d.	28+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4-Br_2	A24	6.4	0.2	2310+	7	2.5	1.0	2.1	0.4	n.d.	0.5
2,5-Br_2	A25*	n.d.	n.d.	149+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,6-Br_2	A26	2.6	0.4	n.d.	3.6	0.9	0.9	0.8	0.5	n.d.	0.5
3,4-Br_2	A27*	n.d.	n.d.	138+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3,5-Br_2	A28*	n.d.	n.d.	198+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,4-Br_3	A29*	n.d.	nd.	100+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,5-Br_3	A30*	n.d.	n.d.	733+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,6-Br_3	A31*	n.d.	n.d.	118+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,5-Br_3	A32*	n.d.	n.d.	1601+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4,6-Br_3	A33	30	4.3	386+	42	28	4.9	11	4.0	0.5	3.4
3,4,5-Br_3	A34*	n.d.	n.d.	310+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,3,4,5-Br_4	A35*	n.d.	n.d.	1164+	n.d.	n.d.	n.d.	0.8	n.d.	n.d.	0.4
2,3,4,6-Br_4	A36*	n.d.	n.d.	1008+	n.d.	n.d.	n.d.	1.2	n.d.	n.d.	0.4
2,3,5,6-Br_4	A37*	n.d.	n.d.	725+	n.d.	n.d.	n.d.	1.1	n.d.	n.d.	0.4
2,3,4,5,6-Br_5	A38	n.d.	n.d.	612+	n.d.	0.8	n.d.	5.7	n.d.	n.d.	1.3
Bromochloroanisoles											
2-Br-4-Cl	A40	n.d.	n.d.	500000+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Br_2Cl	–	21	21	11	21	21	21	21	n.d.	n.d.	n.d.
Chlorobenzenes HCB[e]	–	35	19	97	36	32	28	44	17	9	33

[a] Not detected. [b] Minimum concentration. [c] Detection was not possible, because of interferences. [d] Blank 80 pg. [e] Blank 114 pg.

were not present in samples taken at more southerly latitudes.

Obviously the presence of 2,4,6-trichloro- (A14), 2,3,4,6-tetrachloro- (A17), pentachloro- (A19), 2,4-dibromo- (A24), 2,6-dibromo- (A26) and 2,4,6-tribromoanisole (A33), and of the two unidentified dibromomonochloroanisoles is typical of marine air. These anisoles can be referred to as indicator congeners in marine air.

The concentrations of the halogenated anisoles found in sample FP 25 were completely different from those in all the other samples of marine air analyzed. Only minimum contents can be given, because of complete breakthrough of almost all compounds. Obviously the capacity of the sorbent was not efficient enough for the concentrations of halogenated anisoles found in this sample of marine air. Besides very high concentrations of the chloro- (up to 99 ng m^{-3}) and the bromoanisoles (up to 2310 pg m^{-3}) several congeners were detected which are not present in the other marine air samples: 2,4-dichloro- (A5), 3,4-dichloro- (A8), 3,5-dichloro- (A9), 2,3,4-trichloro- (A10), 2,4,5-trichloro- (A13), 3,4,5-tri-

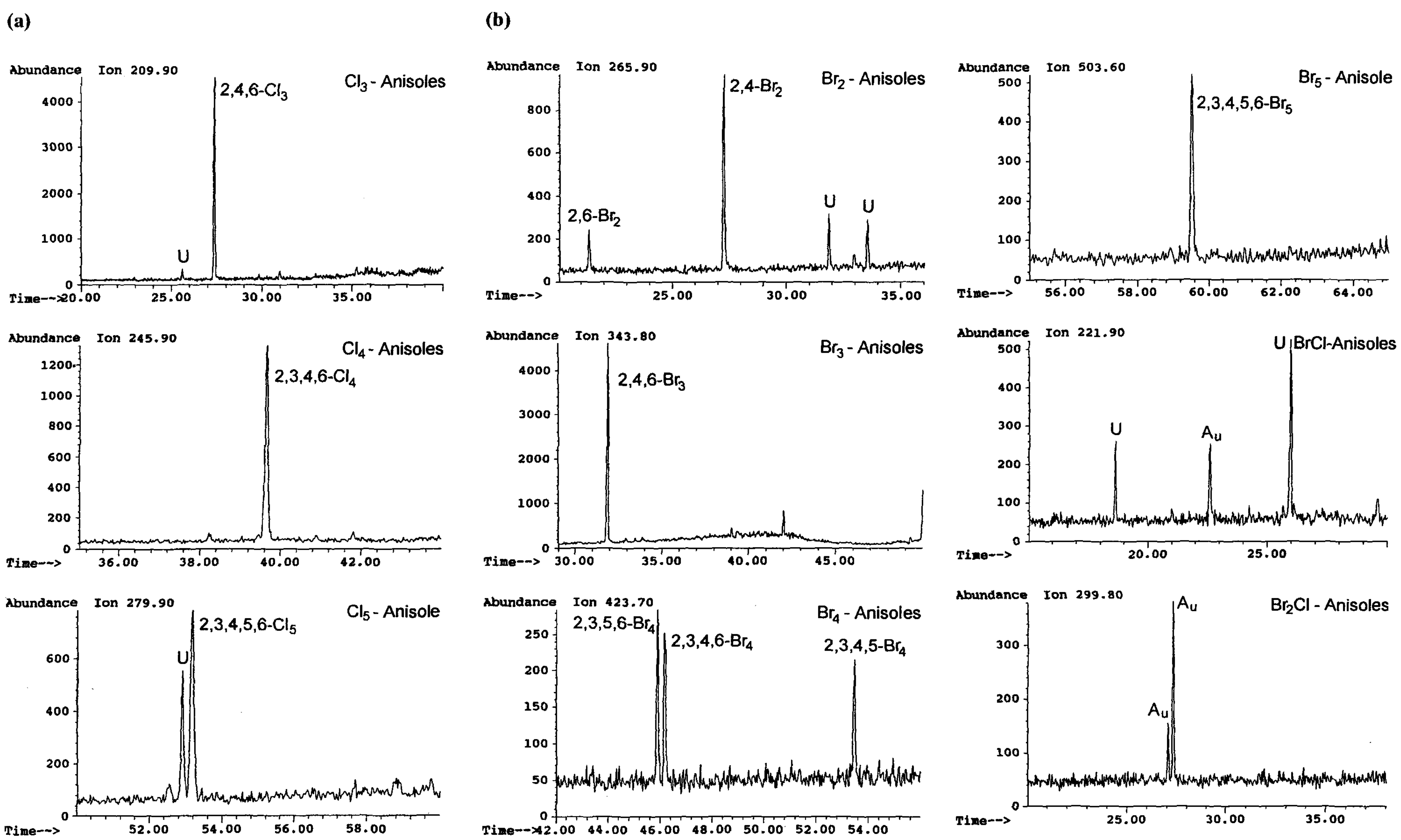

Figure 4
HRGC-MSD-SIM-chromatograms of sample FP 32 (24°S 10°E). U: unknown, Au: anisole congener with unknown substitution pattern. (a) Chloroanisoles. HP Ultra 2 (50 m, 0.2 mm i.d., 0.33 µm film), He (186 kPa), 50 °C (3 min), 10° min^{-1}, 130 °C, 1.5° min^{-1}, 250°C (10 min), 10° min^{-1}, 270 °C, 10 min. (b) Bromoanisoles and mixed halogenated anisoles. DB 1701 (30 m, 0.25 mm i.d., 0.25 µm film), He (156 kPa), 50 °C (3 min), 20° min^{-1}, 80 °C, 2.5° min^{-1}, 230 °C (1 min), 20° min^{-1}, 290 °C, 10 min.

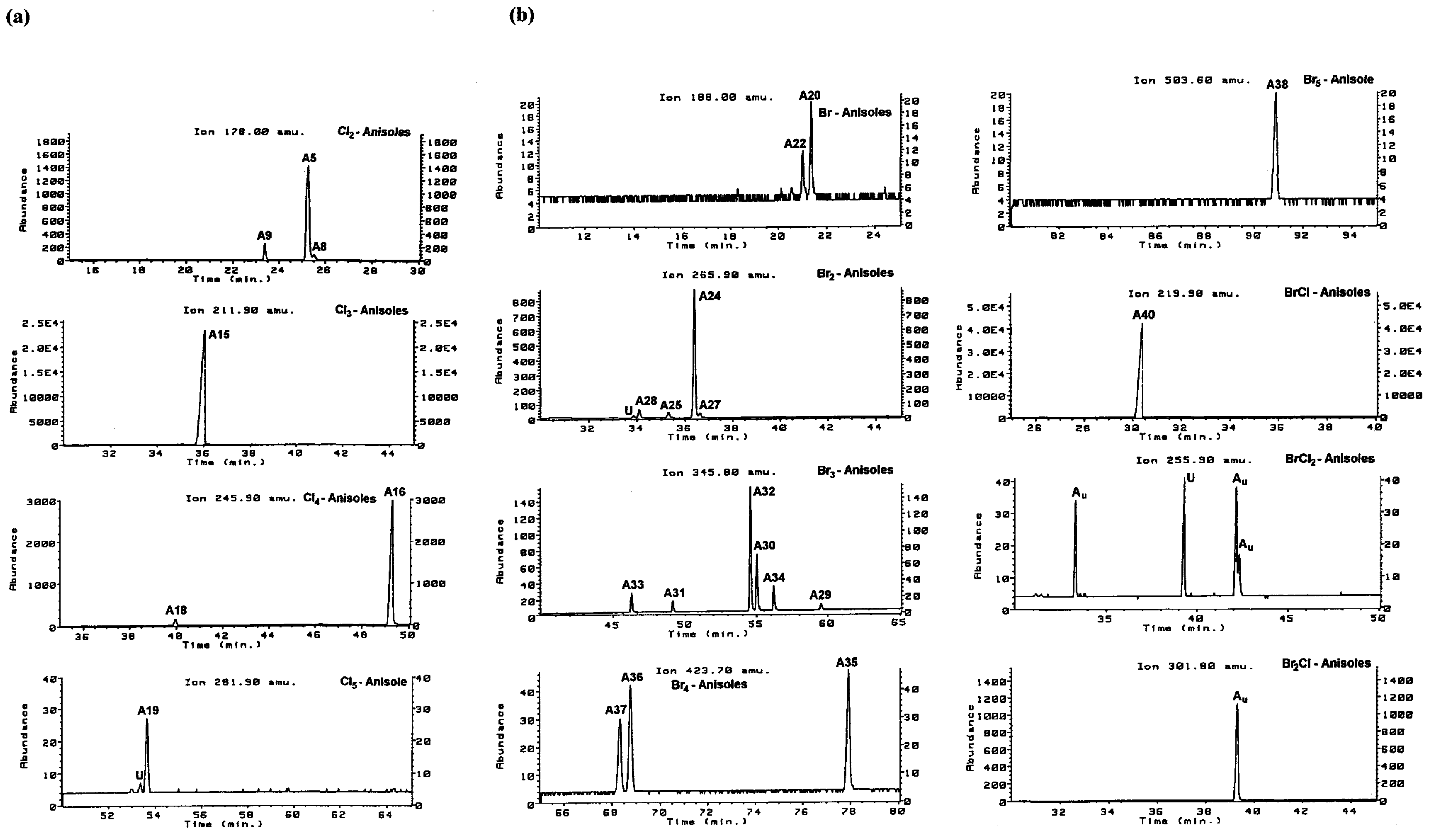

Figure 5
HRGC-MSD-SIM-chromatograms of sample FP 25 (13 ° N 23 ° W). U: unknown, Au: anisole congener with unknown substitution pattern. (a) Chloroanisoles. HP Ultra 2 (50 m, 0.2 mm i.d., 0.33 µm film), He (186 kPa), 50 °C (3 min), 10° min^{-1}, 130 °C, 1.5° min^{-1}, 250 °C (10 min), 10° min^{-1}, 270 °C, 10 min. (b) Bromo- and bromochloroanisoles.

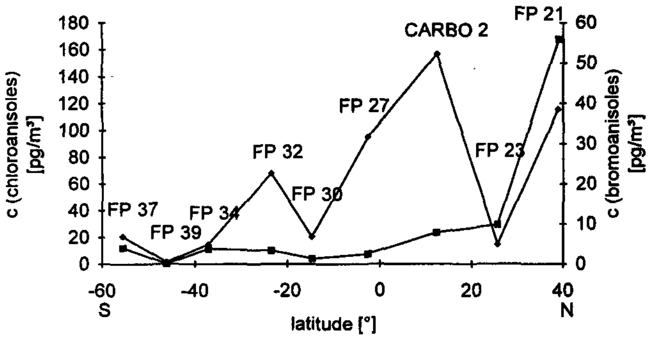

Figure 6
Meridional profile of the sum of the chloroanisole and the bromoanisole concentrations. ■: chloroanisoles, ◆: bromoanisoles

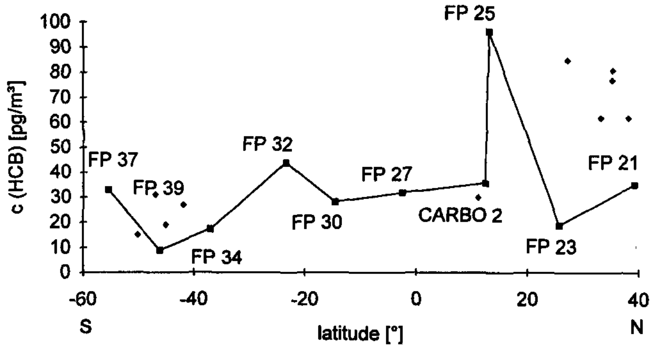

Figure 7
Meridional profile of the HCB concentration on three cruises with the RV 'Polarstern' across the Atlantic Ocean. ◆: cruise leg ANT IX/4 [35], ■: cruise leg ANT XI/1 plus sample CARBO 2 from cruise leg ANT XI/5.

chloro- (A15), 2,3,4,5-tetrachloro- (A16), 2-bromo- (A20), 4-bromo- (A22), 2,5-dibromo- (A25), 3,4-dibromo- (A27), 3,5-dibromoanisole (A28), all five tribromoanisole isomers, 2,4,6-tribromoanisole (A33), 2-bromo-4-chloroanisole (A40), and three monobromodichloro isomers. Surprisingly 2,3,4,6-tetrachloro- (A17), 2,6-dibromo- (A26), and one of the dibromomonochloro isomers, which are among the typical indicator congeners of marine air as discussed above, were not present in sample FP 25.

Especially striking is the presence of 17 of the 19 possible bromoanisoles; many of these bromoanisoles have not previously been found in air. This specific pattern of halogenated anisoles in sample FP 25 is probably a result of local anthropogenic and/or biogenic input from the Cape Verde Islands. The trajectory of the sampled air masses shows that the air was influenced by the islands. A possible anthropogenic influence is underlined by the relatively high concentration of HCB. The unique presence of 17 bromoanisoles, for which no major anthropogenic sources are known, indicates a biogenic influence on the sampled air masses. Because of the exceptional pattern of sample FP 25, its HRGC-MSD-SIM chromatograms are given in Figure 5.

HCB was detected in all the air samples. With the exception of sample FP 25, in which the highest HCB concentration (97 pg m^{-3}) was found, the range of concentrations was 10–40 pg m^{-3}.

Concentration of Bromo-chloro-anisoles and of HCB in air of the North Pacific Ocean

The concentrations of halogenated anisoles in the air of the North Pacific Ocean are higher those in the marine air of the Eastern Atlantic Ocean. This is probably because of the coastal sampling area in the Monterey Bay, whereas the samples of the Atlantic Ocean were taken far away from the coast. The concentrations are in range 13 pg m^{-3} (dibromoanisoles) and 108 pg m^{-3} (2,4,6-trichloroanisole, A14). The patterns of halogenated anisoles above the Atlantic and North Pacific Oceans are very similar. The typical eight indicator congeners were detectable in both types of sample. A difference, besides the higher concentrations, is the presence of 2,6-dichloroanisole (A7) in the air samples of the Monterey Bay. This congener was also detectable in air samples taken above the biological treatment basin of a wastewater treatment plant [7]. 2,6-Dichloroanisole (A7) probably arises from waste water from Santa Cruz and nearby industry, discharged into the Monterey Bay.

The concentration of HCB (100 pg m^{-3}) is comparable with that detected in sample FP 25. This is a further hint of a probable anthropogenic influence on the air masses sampled in FP 25.

Meridional Concentration Profiles of the Bromo-chloro-anisoles of the Lower Troposphere of the Eastern Atlantic Ocean

Figure 6 presents the meridional concentration profile of the sum of the chloroanisoles and of the sum of the bromoanisoles. The highest chloroanisole concentrations were detected in the most northern sample (FP 21; 39°N. Going south, the concentration of the chloroanisoles decreases and remains relatively constant at a low concentration level. In two samples, FP 23 and FP 39, the concentration of the chloroanisoles is extremely low. The study of the trajectories showed that the air of these samples was probably diluted with clean air from the Sahara (FP 23) or from Antarctica (FP 39). The chloroanisoles show a clear inter-hemispherical concentration gradient of 9.8:1 from north to south. Normally, one can observe an inter-hemispherical concentration gradient for anthropogenic compounds with a tropospherical lifetime less than a year, as the intertropical convergence zone (ITCZ) is an effective barrier to fast exchange of the air masses. The northern hemisphere is much more industrialized than the southern hemisphere and the input of pollutants is therefore much higher in the northern hemisphere.

Meridional Concentration Profile of HCB of the Lower Troposphere of the East Atlantic Ocean

Figure 7 depicts the meridional concentration profile of HCB in the troposphere of the East Atlantic; the concentrations of HCB in air samples taken in May–June 1991 during the cruise leg ANT IX/4 from Capetown (South Africa) to Bremerhaven (Germany) are also included in the figure [39]. The HCB concentration seems to be relatively constant in the southern hemisphere. In the northern hemisphere the concentration in samples taken in 1991 is somewhat higher than that in samples taken two and a half years later. If only the samples of cruise legs ANT XI/1 and XI/5, without sample FP 25 (which shows extraordinarily high concentrations of halogenated anisoles and a high HCB value) are considered, no inter-hemispherical concentration gradient of HCB is observable. Homogenous distribution of HCB in the two hemispheres is also indicated by analysis of leaves [24]. The slightly higher levels in the samples from the northern hemisphere of cruise leg ANT IX/4 can be explained by the partial influence of continental air masses [39–41].

The environmental anthropogenic input of HCB is complex and diffuse. Reduced environmental input of HCB in the northern hemisphere combined with a relatively high life-time is possibly an explanation of the absence of an inter-hemispherical concentration gradient and the homogenous distribution of the compound in the troposphere of the Atlantic Ocean.

Conclusions

The analysis of non-polar semi-volatiles present at very low concentrations in air is difficult, as these compounds require high-volume-sampling. A new graphitized carbon-covered silica gel (ANGI-Sorb B) has therefore been tested as sorbent and compared with a silica gel 60–ENVI-Carb sorbent mixture, which has previously been found to be suitable. Parallel sampling with the two kinds of sorbent indicated even better adsorptivity of ANGI-Sorb B for the lower halogenated congeners of the haloanisoles and comparable efficiency for the higher halogenated congeners. It is, moreover, possible to sample larger volumes of air and at higher flows. Although desorption is often a problem using carbonaceous sorbents, the recoveries of the halogenated anisoles from ANGI-Sorb B are comparable with those from the silica gel 60–ENVI-Carb mixture.

For this type of sorbent, recoveries were determined by spiking. Use of CH_2Cl_2 or diethyl ether as solvent in Soxhlet extraction resulted in recoveries between 72 and 118 %. As marine air samples are cleaner than urban air samples, for which the method was originally developed, it was possible to omit an additional clean-up step by HPLC on a graphitized carbon phase to separate the interfering long-chain alkyl nitrates from the halogenated anisoles. Identification and quantitation was performed by HRGC-ECD and HRGC-MSD-SIM analysis.

The results obtained from 10 marine air samples taken on cruise leg ANT XI/1 (Bremerhaven–Capetown, autumn 1993) and ANT XI/5 (Capetown–Rotterdam, spring 1994) of the German research vessel 'Polarstern' and two samples from the North Pacific Ocean (Monterey Bay near Santa Cruz, summer 1995) are presented. Eight typical indicator congeners of the halogenated anisoles are detectable in marine air from both oceans. These are 2,4,6-trichloro-(A14), 2,3,4,6-tetrachloro-(A17), pentachloro- (A19), 2,4-dibromo- (A24), 2,6-dibromo- (A26), and 2,4,6-tribromoanisole (A33) and two dibromomonochloroanisole isomers. The concentrations of the halogenated anisoles are in the range 0.2–145 pg m^{-3}. Concentrations are generally higher in the samples from the Monterey Bay, as result of sampling in a coastal area. One sample from the East Atlantic Ocean (FP 25) shows a completely different pattern of halogenated anisoles. The concentrations are much higher (up to 99 ng m^{-3} for 3,4,5-trichloroanisole and 2310 pg m^{-3} for 2,4-dibromoanisole) and several congeners (17 of the possible 19 bromoanisoles) are detectable only in this sample of marine air. This extraordinary pattern of halogenated anisoles is probably a result of anthropogenic and/or biogenic influences from the Cape Verde Islands.

Hexachlorobenzene (HCB) was detected in all marine air samples. Concentrations were in the range 10–40 pg m^{-3} . Anthropogenic influence on the air masses sampled in the North Pacific Ocean and near the Cape Verde Islands is demonstrated by elevated HCB concentrations of about 100 pg m^{-3}.

For the chloroanisoles a clear inter-hemispherical concentration gradient is observable; this is typical of compounds of continuing anthropogenic origin. Although there are many anthropogenic sources of HCB, the compound seems to be distributed relatively homogeneously in the northern and in the southern hemispheres. No significant inter-hemispherical concentration gradient of HCB is observable, which could be explained by a low environmental input of HCB in the northern hemisphere combined with a long atmospheric residence time.

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References

[1] *I. Watanabe, T. Kashimoto, R. Tatsukawa*, Arch. Environ. Contam. Toxicol. **12**, 615 (1983).

[2] *R. Jaffe, R. A. Hites*, J. Great Lakes Res. **12**, 63 (1986).

[3] *J. Paasivirta, J. Tarhanen, B. Juvonen*, Chemosphere **16**, 1787 (1987).

[4] *C. J. Schmitt, J. L. Zajicek, P. H. Peterman*, Arch. Environ. Contam. Toxicol. **19**, 748 (1990).

[5] *T. Miyazaki, S. Kaneko, S. Horn, T. Yamagishi*, Bull. Environ. Contam. Toxicol. **26**, 577 (1981).

[6] *H. Shiraishi, A. Otsuki*, Res. Rep. Natl. Inst. Environ. Stud. Jpn **79**, 83 (1985).

[7] *U. Führer, A. Deißler, K. Ballschmiter*, Fresenius J. Anal. Chem. **354**, 333 (1996).

[8] *R. Wittlinger, K. Ballschmiter*, Fresenius J. Anal. Chem. **336**, 193 (1990).

[9] *E. Atlas, K. Sullivan, C. S. Giam*, Atmos. Environ. **20**, 1217 (1986).

[10] *A. H. Neilson, A.-S. Allard, P.-A. Hynning, M. Remberger, L. Landner*, Appl. Environ. Microbiol. **45**, 774 (1983).

[11] *M. Remberger, A.-S. Allard, A. H. Neilson*, Appl. Environ. Microbiol. **51**, 552 (1986).

[12] *T. Suzuki*, J. Pesticide Sci. **8**, 419 (1983).

[13] *J. Paasivirta, J. Särkkä, T. Leskijärvi, A. Roos*, Chemosphere **9**, 441 (1980).

[14] *J. Paasivirta, J. Knuutinen, J. Tarhanen, T. Kuokkanen, K. Surma-Aho, R. Paukku, H. Kääriäinen, M. Lahtiperä, A. Veijanen*, Water Sci. Technol. **15**, 97 (1983).

[15] *A. H. Neilson, A.-S. Allard, P.-A. Hynning, M. Remberger*, Environ. Sci. Technol. **28**, 278 (1994).

[16] *L. R. Suntio, W. Y. Shiu, D. Mackay*, Chemosphere **17**, 1249 (1988).

[17] *S. Karlsson, S. Kaugare, A. Grimvall, H. Boron, R. Sävenhed*, Water Sci. Technol. **31**, 99 (1995).

[18] *K. Ballschmiter, Ch. Unglert, P. Heizmann*, Angew. Chem. Int. Ed. **16**, 645 (1977).

[19] *K. Ballschmiter, Ch. Scholz*, Chemosphere **9**, 457 (1980).

[20] *S. A. Woodin, M. D. Walla, D. E. Lincoln*, J. Exp. Mar. Biol. Ecol. **107**, 209 (1987).

[21] *T. Higa, J. P. Scheuer*, in D. J. Faulkner, W. H. Fenical (eds), Marine Natural Products Chemistry. Constituents of the Hemichordate *Ptychodera flava laysanica*, Plenum Press, New York, 1977, 35-43.

[22] *T. Higa, S. Sakemi*, J. Chem. Ecol. **9**, 495 (1983).

[23] *R. M. Hoff, D. C. G. Muir, N. P. Grill*, Environ. Sci. Technol. **26**, 266 (1992).

[24] *D. Calamari, E. Bacci, S. Focardi, C. Gaggi, M. Morosini, M. Vigli*, Environ. Sci. Technol. **25**,1489 (1991).

[25] *S. Mössner*, Dissertation: 'Isomeren- und enantiomerenspezifische Bestimmung von schwerflüchtigen Organochlorverbindungen in Meeressäugetieren: Transformation – Transport – Verbleib', University of Ulm, 1995.

[26] *M. Zell, K. Ballschmiter*, Fresenius' Z. Anal. Chem. **300**, 387 (1980).

[27] 'Hexachlorbenzol', BUA-Stoffbericht 119, BUA Beratergremium für umweltrelevante Altstoffe der Gesellschaft Deutscher Chemiker, ed., VCH, Weinheim (1993).

[28] *K. Ballschmiter, W. Schafer, H. Buchert*, Fresenius' Z. Anal. Chem. **326**, 253 (1987).

[29] *U. Führer*, Dissertation: 'Analytik und Vorkommen der Bromchloranisole (Bromchlormethoxybenzole) in der Umwelt', University of Ulm, 1996.

[30] *K. Ballschmiter*, Angew. Chem. Int. Ed. **31**, 487 (1992).

[31] *R. M. Wittlinger*, Dissertation: 'Herkunft, Vorkommen und Verbleib von weniger flüchtigen Organohalogenen in der unteren Troposphäre', University of Ulm, 1988.

[32] *A. Deißler*, Dissertation: 'Entwicklung von Kohleadsorbentien und ihre analytische Anwendung', University of Ulm, 1996.

[33] *R. Wittlinger, K. Ballschmiter*, Chemosphere **16**,2497 (1987).

[34] *O. Luxenhofer, K. Ballschmiter*, Fresenius J. Anal. Chem. **350**, 395 (1994).

[35] *O. Luxenhofer, E. Schneider, K. Ballschmiter*, Fresenius J. Anal. Chem. **350**, 384 (1994).

[36] *H. Kováts*, Helv. Chim. Acta **41**, 1915 (1958).

[37] *H. J. Neu, M. Zell, K. Ballschmiter*, Fresenius' Z. Anal. Chem. **293**, 193 (1978).

[38] *R. C. Fischer, R. Wittlinger, K. Ballschmiter*, Fresenius J. Anal. Chem. **342**, 421 (1992).

[39] *J. Schreitmüller*, Dissertation: 'Verteilung schwerflüchtiger Organohalogenverbindungen in der Troposphäre und Hydrosphere des Atlantischen Ozeans', University of Ulm, 1993.

[40] *J. Schreitmüller, K. Ballschmiter*, Fresenius J. Anal. Chem. **348**, 226 (1994).

[41] *J. Schreitmüller, K. Ballschmiter*, Environ. Sci. Technol. **28**, 207 (1995).

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