Bromochloromethoxybenzenes in the Marine Troposphere of the Atlantic Ocean: A Group of Organohalogens with Mixed Biogenic and Anthropogenic Origin

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Halogenated methoxybenzenes (anisoles) are ubiquitous organics in the environment, although they are not produced in technical quantities. To elucidate the sources of the various halogented anisoles in the marine troposphere, their concentrations were measured in air from the Eastern Atlantic Ocean between 40° N and 57° S during the north-south transect ANT XI/1 of the German RV *Polarstern*. A typical pattern of eight congeners was observed. It consisted of 2,4,6-trichloro-, 2,3,4,6-tetrachloro-, pentachloro-, 2,4-dibromo-, 2,6-dibromo-, 2,4,6-tribromo-, and two unidentified dibromochloroanisoles. The meridional concentration profiles, the comparison of the patterns of the relative concentrations of bromo- and chloroanisoles, as well as principal component analysis of the concentrations of the halogenated anisoles indicate an anthropogenic origin for the chloroanisoles and a biogenic origin for the bromoanisoles. The pattern of the chloroanisoles differs for the two hemispheres. It seems to reflect the global pollution with chlorophenols which have a maximum of anthropogenic input in the Northern Hemisphere. The pattern of the bromoanisoles is characterized by regional biogenic sources, which leads to high concentrations of bromoanisoles south of 20° N in contrast to low concentrations of chloroanisoles in this part of the Atlantic Ocean.

Introduction

Halogenated methoxybenzenes (halogenated anisoles) appear to be ubiquitous organics not only in air but in the total environment. Several members of the three classes of 19 chloro-, 19 bromo-, and 96 bromochloroanisoles have been detected in air (*1*−*3*), in drinking water (*4, 5*) and in river water (*6*), in freshwater fish (*7*−*10*) and in marine fish (*11*), in oysters (*12*), in earthworms and in the soil of a closed sawmill (*13*), in paddy soil and rice plants (*14, 15*), in the soil of a coniferous wood (*16*), in sediments (*11*), and in effluents of a wastewater treatment plant with a biological treatment basin (*17*).

Despite this prevalence of the halogenated anisoles in the environment, their specific sources are mostly unknown. The halogenated anisoles are not produced or used in technical quantities. However, anisoles are formed by microorganisms (*18*−*20*), plants (*14*), fungi (*21*), and animals (*22*) through O-biomethylation of phenol and the respective halogenated phenols.

Chlorophenols are widely used as fungicides (*23*); however, they can also be produced by microbial metabolism of the halogenated benzenes (*24, 25*). An indirect anthropogenic input of chlorophenols is the bleaching process of pulp mills with chlorine (*26*−*28*) and the chlorination of water (*4, 29*). Bromophenols are used as fumigants (*30*) and are also formed in the chlorination of water, if bromide ions are present (*31, 32*). Thus, halogenated anisoles have to be discussed as metabolites of halogenated phenols as precursors which are deriving from anthropogenic sources.

In addition to the anthropogenic origin of the halogenated anisoles, biogenic sources may also exist. Halometabolites are well-known in nature, and many chlorinated and brominated phenolic compounds were detected in plants and animals (*33*−*41*). Methylhalides are formed by methylhalide transferases (*42*−*44*), whereas more complex halometabolites are formed by haloperoxidases (*45*). Moreover, halogenated phenols are products of the reaction of haloperoxidases with humic substances in soil, lakes, rivers, oceans, and sediments (*36, 39, 46*−*50*).

As a result of the high concentrations of halide ions, the oceans are an ideal environment for the production of halometabolites. However, life is distributed very inhomogeneously in the oceans. This is due to the dependence of animals on phytoplankton as a direct or indirect source of nourishment. The ability of phytoplankton to form organic carbon compounds by assimilating carbon dioxide with the help of light and micro nutritives is called primary production (*51*). Areas with a high primary production rate (measured in grams of organically bound carbon per area and time) are abundant with marine life. Such areas are located at the west coast off the continents where upwelling cold water rich with nutritives emerges to the surface. Very low primary production rates are found in the open ocean (*52, 53*). Therefore, a biogenic release of halogenated anisoles into the ocean water and finally into the air as the result of biohalogenation or microbial metabolism should be dependent on the rate of primary production.

To investigate the origin of the halogenated anisoles in the troposphere, air samples were collected during a north-south transect of the German RV *Polarstern*, where several zones with different primary production rates were passed at least 200 sea miles off the coast. Thus the influence of continental anthropogenic sources is minimized. In this paper, concentrations and patterns of halogenated anisoles in air samples were determined and analyzed. The results were correlated with the regional primary production rate and the origin of the sampled air masses indicated by calculated trajectories. Conclusions were drawn on a biogenic or anthropogenic origin of the halogenated anisoles in the lower troposphere of the Atlantic Ocean.

Experimental Section

Air Sampling, Sample Preparation, and Analysis. The sampling method, sample preparation, cleanup, and analysis

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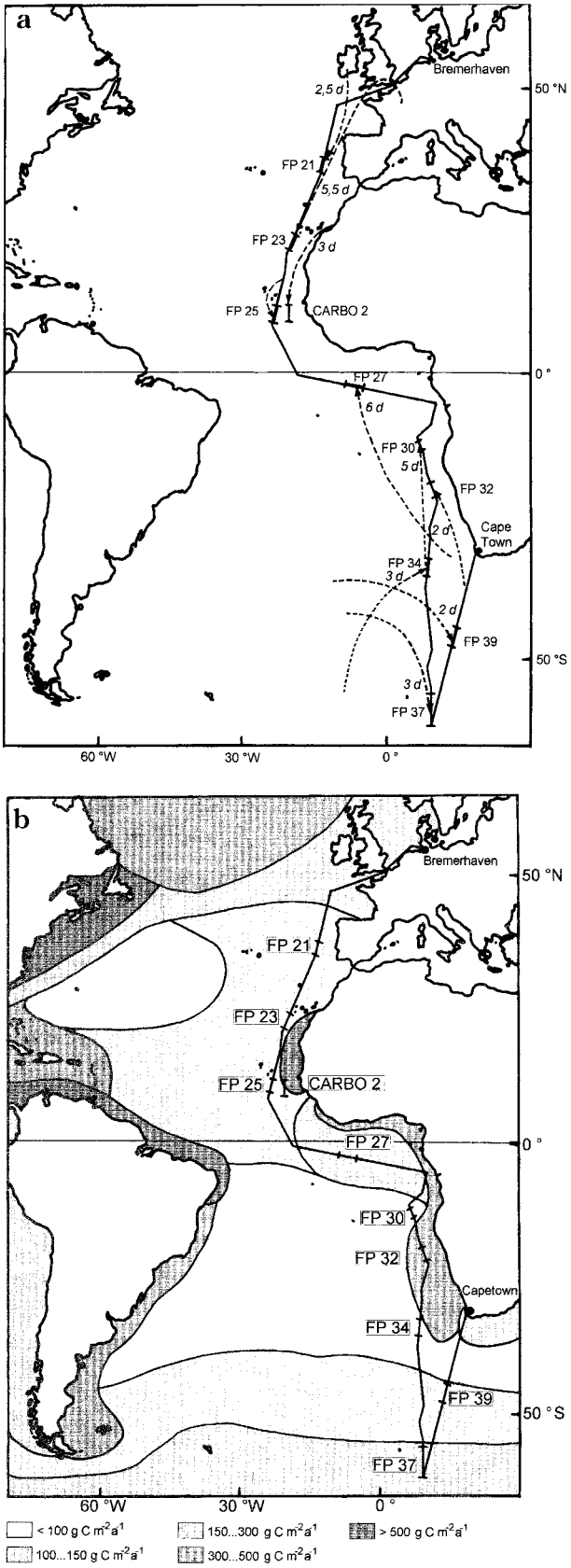


FIGURE 1. Sampling locations of the air samples during the cruises of the RV *Polarstern* (—) across the Atlantic Ocean and the trajectories (- - -) of the sampled air masses in days (a), and the annual rate of primary production in g of organically bound carbon m^{-2} a^{-1} (*53*) (b).

TABLE 1. Sampling Locations and Volume of Air Sampled

sample	date	location	sample volume (m^3)
ANT XI/1			
FP 21	10/22−23/93	40.3° N 14.4° W	358
		37.7° N 13.8° W	
FP 23	10/25−26/93	27.0° N 18.2° W	292
		24.4° N 20.2° W	
FP 27	11/3−4/93	2.3° S 8.2° W	255
		2.9° S 5.1° W	
FP 30	11/9−10/93	13.4° S 6.4° E	287
		15.9° S 7.4° E	
FP 32	11/11−12/93	22.0° S 9.1° E	293
		25.0° S 10.3° E	
FP 34	11/15/93	36.1° S 8.2° E	212
		38.0° S 8.0° E	
FP 37	11/19−20/93	53.6° S 9.1° E	306
		57.4° S 9.2° E	
FP 39	11/23−24/93	47.5° S 13.6° E	400
		44.6° S 14.7° E	
ANT XI/5			
CARBO 2	6/3/94	11.1° N 21.5° W	138
		13.6° N 21.5° W	

by high resolution gas chromatography (HRGC) have been previously described in detail including the evaluation of the analytical methodology in terms of reproducibility and accuracy (*3, 54*). Therefore, only a brief overview of the procedure is given in this paper. The air samples (FP 21−FP 39) were collected in a manner similar to that reported in ref *55* using a high-volume sampling during a cruise of the German RV *Polarstern* (cruise leg ANT XI/1) from Bremerhaven (Germany) to Capetown (South Africa) in October/November 1993 (Figure 1a). One air sample originates from a later cruise (cruise leg ANT XI/5) from Capetown to Rotterdam (The Netherlands) in May/June 1994 (Figure 1). A specially designed mixture of silica gel 60 and ENVI-Carb (5% w/w), a graphitized carbon black, was used as sorbent (*3, 54*). The air was sampled at a flow rate between 15 and 20 m^3 h^{-1}.

To prevent local contamination the sampling was accomplished windward on the upper-most deck of the ship. The samples were stored and transported in airtight flame-sealed glass flasks that were resealed right after the sampling. Sample preparation was performed in a laboratory designed for extreme organic trace analysis using a "metal/glass only" clean-bench equipped with charcoal air filters (*55*). All solvents and chemicals were tested for their purity before use (*3, 54*).

The sorbent was Soxhlet extracted with either dichloromethane (CH_2Cl_2) or diethyl ether (Et_2O). A cleanup and group preseparation was done by normal phase liquid chromatography (NP-LC) using activated Florisil. Three subsequent fractions with increasing polarity (LC 1, pentane/LC 2, pentane/CH_2Cl_2 4:1 or pentane/Et_2O 3:1; LC 3, CH_2Cl_2 or Et_2O) were eluted. The halogenated anisoles elute in the second fraction LC 2, which was then analyzed by high-resolution gas chromatography with mass selective detection in the single-ion mode (HRGC−MSD−SIM) with two stationary phases differing in polarity (CP-Sil 2, Chrompack; DB 1701, J&W Scientific) for all 134 possible congeners of the bromochloroanisoles (*3, 54*).

Sampling Locations and Related Meteorological and Hydrological Data. Figure 1a depicts the sampling regions and the 2−6 day trajectories of the sampled air masses. The trajectories were calculated by the meteorologist on board the RV *Polarstern*. The exact sampling locations are given in Table 1.The north−south transects of the RV *Polarstern* are ideal cruises to study the possible biogenic or anthropogenic origin of compounds regarding a hemispheric point of view. Cruise leg ANT XI/1 started in the west-wind belt

TABLE 2. Concentration of Halogenated Anisoles in the Lower Troposphere of the Atlantic Ocean[a]

		Northern Hemisphere[b]			Southern Hemisphere[b]					
	congener	39 ° N FP 21	26 ° N FP 23	13 ° N CARBO 2	3 ° S FP 27	15 ° S FP 30	24 ° S FP 32	37 ° S FP 34	46 ° S FP 39	56 ° S FP 37
Cl-anisoles										
2,4,6-Cl_3	A14	145	27	20	2.9	1.9	7.5	5.1	nd	7.2
2,3,4,5-Cl_4	A16	i	nd	i	i	i	0.7	i	nd	i
2,3,4,6-Cl_4	A17	11	1.0	1.8	1.2	0.7	1.3	1.0	nd	nd
2,3,4,5,6-Cl_5[c]	A19	12	1.8	2.4	3.3	1.3	1.3	5.3	(0.2)	5
Br-anisoles										
2,4-Br_2	A24	6.4	0.2	7	2.5	1.0	2.1	0.4	nd	0.5
2,6-Br_2	A26	2.6	0.4	3.6	0.9	0.9	0.8	0.5	nd	0.5
2,4,6-Br_3	A33	30	4.3	42	28	4.9	11	4.0	0.5	3.4
2,3,4,5-Br_4	A35	nd	nd	nd	nd	nd	0.8	nd	nd	0.4
2,3,4,6- Br_4	A36	nd	nd	nd	nd	nd	1.2	nd	nd	0.4
2,3,5,6-Br_4	A37	nd	nd	nd	nd	nd	1.1	nd	nd	0.4
2,3,4,5,6-Br_5	A38	nd	nd	nd	0.8	nd	5.7	nd	nd	1.3
Br−Cl-anisoles										
Br_2Cl isomers detected		2	2	2	2	2	2	nd	nd	nd

[a] Concentration in pg m^{-3}; nd, not detected; LOD < 0.1 pg m^{-3}; i, detection was not possible due to interferences. [b] Mean latitude. [c] Blank: 0.2−0.5 pg m^{-3}.

of the Northern Hemisphere (sample FP 21), representing the pollution of the densely populated and industrialized countries. In the north−east tradewind region air samples FP 23 and CARBO 2 were collected. The intertropical convergence zone (ITCZ) near the equator, where both trade wind systems meet in a cyclonic system of uprising air, is an effective barrier for a tropospheric transport of molecules from the northern to the Southern Hemisphere. In the significantly less industrialized Southern Hemisphere, the south-east tradewinds (samples FP 27, FP 30, and FP 32) and the southern west-wind belt (samples FP 34, FP 37, and FP 39) were sampled. The southern west-wind belt with its high wind speeds and frequent cyclones is characterized by air coming in from the South Pacific. One sample (sample FP 25) was influenced by air masses of the Cape Verde Islands and showed extremely high concentrations of halogenated anisoles (*3, 54*). In this case no differentiation between anthropogenic and biogenic sources was possible and the results of this sample are excluded from the discussion in this paper.

Several different zones of primary production were crossed by the RV *Polarstern* during the north−south transect. In Figure 1b the generalized primary production rates are shown, according to data from Longhurst et al. (*53*), which were obtained by satellite radiometer data. As the biogenic production of halogenated anisoles must be dependent on primary production, samples from different regions should differ in concentrations and pattern of halogenated anisoles. Samples FP 23, FP 32, and CARBO 2 were taken in the upwelling zones off the coasts of North and South Africa, regions known for their high primary production rates. Air sample FP 34, on the contrary, derives from a region with a very low primary production rate.

Results and Discussion

The group of the bromochloroanisoles consists of 134 congeners. To simplify the discussion of this complex mixture, each congener was given a systematic congener number (*3*). Table 2 summarizes the concentrations of the halogenated anisoles in the lower troposphere of the eastern Atlantic Ocean. The overall uncertainty of the values of Table 2 is ±10−15% relative. For pentachloroanisole a blank was observed with a total amount of 80 pg. Based on sampled air volumes of 140−400 m^3 this blank relates to concentrations between 0.2 and 0.5 pg m^{-3} in air.

Halogenated Anisoles in the Troposphere of the Eastern Atlantic Ocean. Only few of the 134 theoretically possible halogenated anisole congeners are present in marine air. Eight congeners were detected in almost every sample: 2,4,6-trichloroanisole (A14), 2,3,4,6-tetrachloroanisole (A17), pentachloroanisole (A19), 2,4-dibromoanisole (A24), 2,6-dibromoanisole (A26), 2,4,6-tribromoanisole (A33), and two dibromochloroanisoles with unknown substitution patterns. Most likely they have a 2,4,6-substitution pattern corresponding to the 2,4,6-tribromoanisole. These eight congeners represent the basic global pattern and therefore are referred to as indicator congeners. Chloro- and bromoanisoles have to be discussed separately as their origin differs.

Chloroanisoles in the Troposphere of the Eastern Atlantic Ocean. *Meridional Concentration Profiles of the Chloroanisoles.* The highest concentrations of chloroanisoles are found in the Northern Hemisphere. Heading south the concentrations decline and remain at relatively constant and low values in the Southern Hemisphere. South of 30° S the concentrations of pentachloroanisole (A19) and 2,4,6-trichloroanisole (A33) increase slightly (Figure 2a,b,c).

Samples FP 23 and FP 39 show very low concentrations of halogenated anisoles. The trajectory of the sampled air masses of sample FP 23 reveals a major input of air from the Sahara Desert. Such a decline in the meridional concentration profile has already been observed before for the polychlorinated biphenyls (PCB) (*56*). In contrast to the other air samples, the trajectory of sample FP 39 represents only the last 2 days. No calculation of a longer period was possible because of several cyclones during this period of time. The general mass flow in the lower atmosphere in the FP 39 sample region indicates at least a partial input of air from Antarctica.

The Pattern of the Chloroanisoles in the Lower Troposphere of the Eastern Atlantic Ocean: Principal Component Analysis and a Comparison of Relative Concentrations. A principal component analysis of the concentrations of the three chloroanisoles using a public domain software (*57*) was performed and is depicted in Figure 3a. The contents of the three compounds were normalized to their sum, and the calculations were carried out with the correlation matrix. The degree of similarity of various patterns is given by the distance of data points projected onto the plane defined by the first two principal components. Two clusters of samples are obtained by this classification. One cluster is formed by the air samples of the Northern Hemisphere (FP 21, FP 23, and CARBO 2) and one sample of the Southern Hemisphere (FP 32); the second cluster consists of the samples of the Southern Hemisphere (FP 27, FP 30, FP 34, and FP 37), except

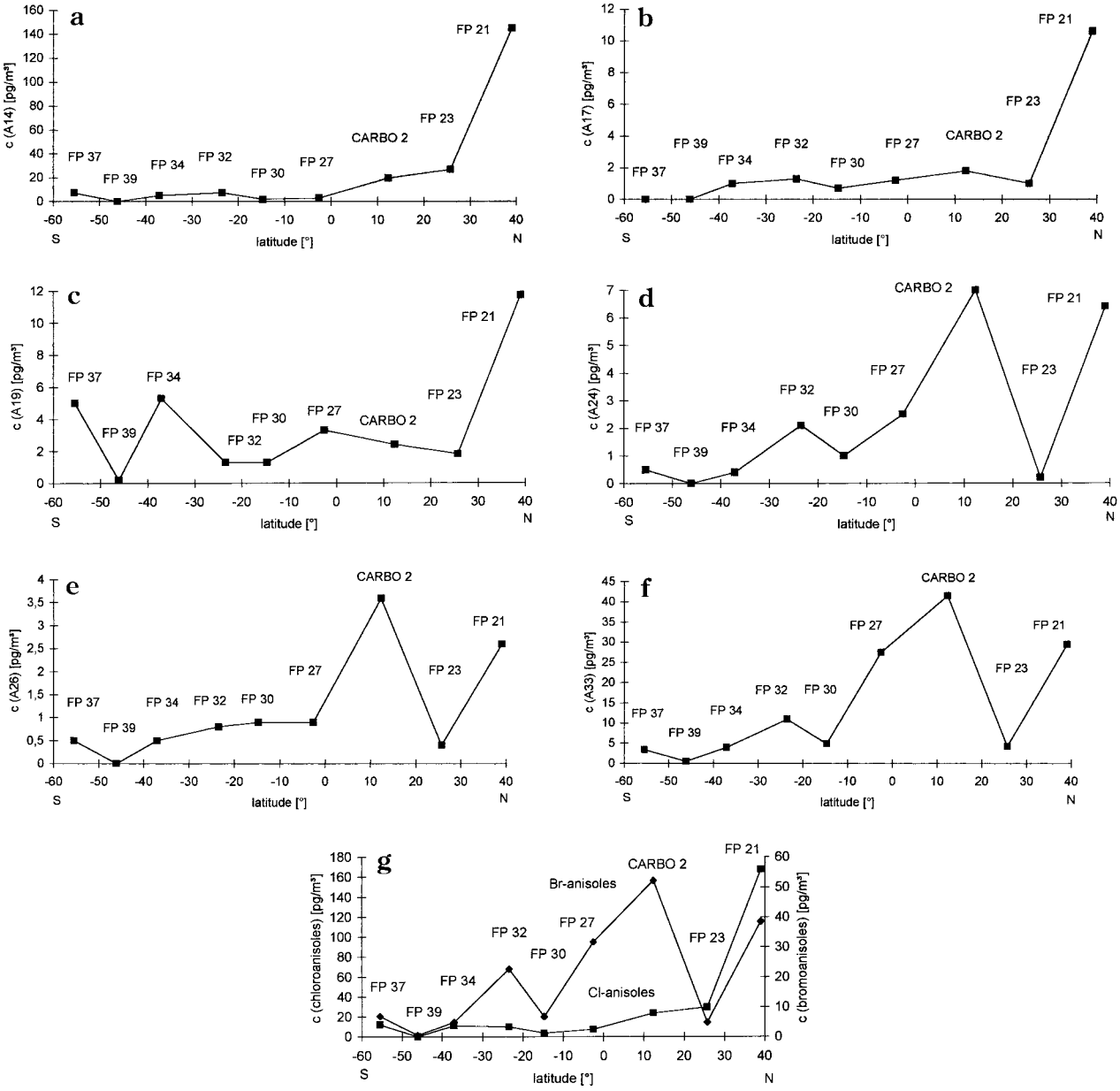


FIGURE 2. Meridional atmospheric concentration profiles of the chloroanisoles, 2,4,6-trichloro- (A14), 2,3,4,6-tetrachloro- (A17), and pentachloroanisole (A19), in air samples (parts a b, and c), of the bromoanisoles, 2,4-dibromo- (A24), 2,6-dibromo (A26), and 2,4,6-tribromo (A33), (parts d, e, and f), and of the sums of the concentrations of the chloroanisoles (-■-) and of the bromoanisoles (-◆-) (part g) in the troposphere of the East Atlantic Ocean.

for sample FP 39. Sample FP 39 is exceptional, because only pentachloroanisole (A19) was detectable.

The splitting of the air samples into two clusters is mainly given by the relative amounts of 2,4,6-trichloro- (A14) and pentachloroanisole (A19) (Figure 3b). In the Northern Hemisphere 2,4,6-trichloroanisole amounts to more than 80% of the concentration of all chloroanisoles, whereas the contribution of pentachloroanisole is less than 10%. The pattern of the samples of the Southern Hemisphere is completely different. The portion of 2,4,6-trichloroanisole (A14) is smaller than 60%; however, the portion of pentachloroanisole amounts to more than 33%. This means that the A14/A19 ratio is larger than 5 in the north and smaller than 2 in the south. In sample FP 32, north of Capetown, the A14/A19 ratio (5.7) resembles more the samples of the Northern Hemisphere.

Discussion of the Pattern of the Chloroanisoles. The clear differentiation in a northern and a southern pattern of chloroanisoles leads to the conclusion that the chloroanisoles are most likely of anthropogenic origin. The chloroanisoles show an interhemispherical concentration gradient typical for anthropogenic compounds, which are released into the environment in the industrialized, Northern Hemisphere and hardly ever pass the intertropical convergence zone (ITCZ). The north to south gradient is 16:1 for 2,4,6-trichloroanisole, 6:1 for 2,3,4,6-tetrachloroanisole, 2:1 for pentachloroanisole (A19), and 10:1 for the sum of the chloroanisoles.

It is interesting that only those chloroanisoles are detected in the marine air that can be assigned to metabolites of chlorophenols for which many anthropogenic processes are known. Pentachlorophenol (P19) is widely used as a biocide and 2,3,4,6-tetrachlorophenol (P17) is its main byproduct. The other main sources of chlorophenols are chlorination processes, as the bleaching of pulp (*6, 26, 28, 58, 59*) and the chlorination of drinking water (*4, 26, 29*). In all these processes 2,4,6-trichlorophenol is the main reaction product, as a further chlorination in meta position is difficult. The high concentrations of chloroanisoles in sample FP 21 may

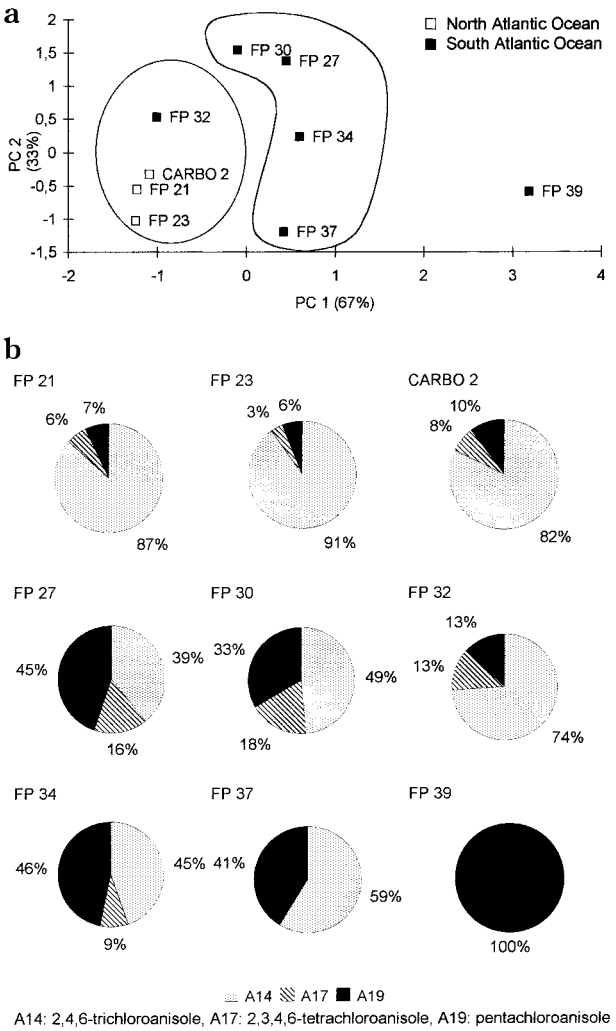


FIGURE 3. (a) Principal component analysis of the normalized concentrations of the chloroanisoles in air samples FP 21−FP 39 (ANT XI/1) and CARBO 2 (ANT XI/5): the data points were projected into the plane defined by the first two principal component axes. (b) Relative concentration of the chloroanisoles, 2,4,6-trichloro- (A14), 2,3,4,6-tetrachloro- (A17), and pentachloroanisole (A19), in air samples; 100% is sum of the concentrations of the chloroanisoles.

be due to a major input of chlorophenols by the pulp mill industry in the United States and in Canada, the world's largest producers of pulp (*60*), into the water masses of the Gulf Stream. Another source of chloroanisoles could be contaminated air from Western Europe. The main source of 2,4,6-trichloroanisole in sample FP 32 is probably the chlorination of drinking water in South Africa, the closest industrialized country in this region. Sample FP 32 resembles in its pattern of chloroanisoles the pattern of the samples from the Northern Hemisphere.

The minimum of the chloroanisole concentration near the equator, however, is remarkable. Increased concentrations should be observed there due to an increased outgassing as a result of the higher water and air temperatures. Such an effect can be seen, for example for the polychlorinated biphenyls (PCB) (*61*). A possible explanation for the different behavior of the chloroanisoles is the increased abiotic degradation of these compounds by photolysis and reaction with hydroxyl radicals. Between 30° N and 30° S insolation is especially high and the mean concentration of OH radicals is twice as high as in higher latitudes (*62*).

No degradation rates with hydroxyl radicals were available in the literature for the halogenated anisoles. However, the

TABLE 3. Rate Constants for Reaction with OH Radicals in Air at 295−298 K

	$k_{OH} \times 10^{-12}$ (cm^3 molecule^{-1} s^{-1})
benzene[a]	1.45
toluene[a]	6.03
anisole[a]	14.1
chlorobenzene[a]	0.67
o-/*p*-chlorotoluene[a]	2.4
1,2-dichlorobenzene[a]	0.42
1,3-dichlorobenzene[a]	0.72
1,4-dichlorobenzene[a]	0.32
1,2,4-trichlorobenzene[a]	0.5
hexachlorobenzene[b]	0.02

[a] Ref *63*. [b] Ref *64*.

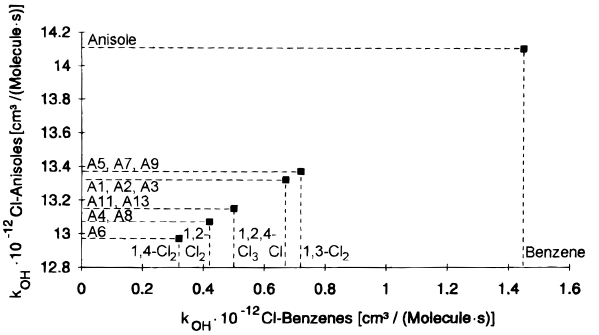


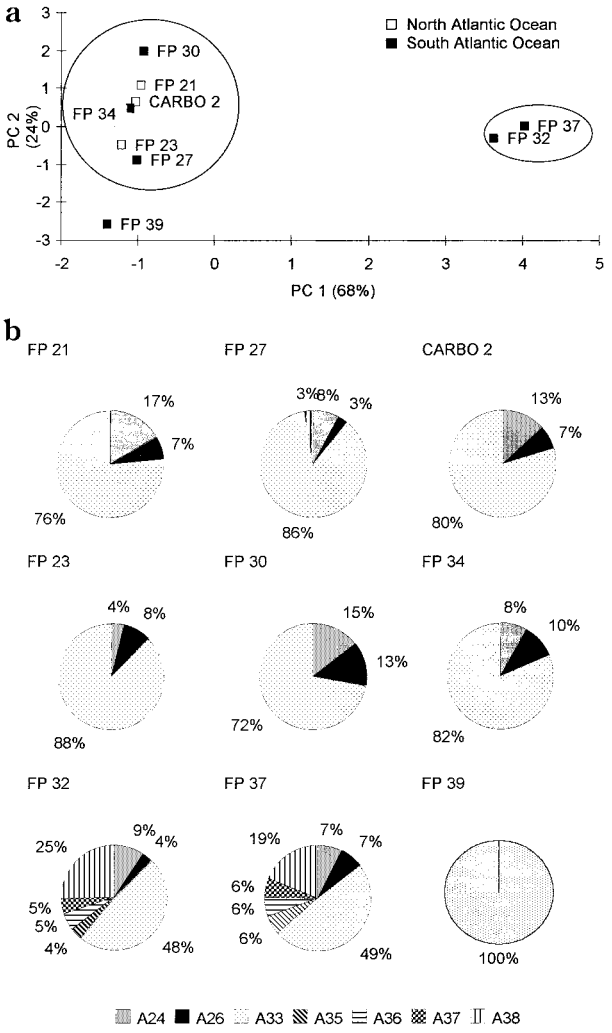
FIGURE 4. Approximation of reaction rate constants of chloroanisoles with hydroxyl radicals (k_{OH}) based on the reaction rate constants (k_{OH}) of benzene, anisole, and chlorobenzenes.

reaction rate constant of the halogenated anisoles should be higher than that of the halogenated benzenes, toluenes, or the PCBs (Table 3) (*63*, *64*). On the basis of the reaction rate constant k_{OH} of the chlorobenzenes, benzene, and anisole, the reaction rate constant k_{OH} of the chloroanisoles was approximated (Figure 4). The reaction rate constant k_{OH} of the mono- to trichloroanisoles should be in the range 13×10^{-12} cm^3 molecule^{-1} s^{-1}, which corresponds to a lifetime τ_{OH} of about 20 h in the tropics (C_{OH}: 10.2×10^5 radicals/per cm^3). Higher chlorinated congeners should be less susceptible to a degradation by hydroxyl radicals, corresponding to the chlorobenzenes. The concentration profile of the chloroanisoles agrees with these considerations. The decline in concentration of 2,4,6-trichloroanisole (A14) is more pronounced than for the higher chlorinated congeners.

Biogenic Production of Chloroanisoles. In regions with a high primary production the probability that microorganisms with the capability of O-methylating phenols are present is higher as compared to other regions. Such an elevated O-biomethylation rate may be responsible for the increase of the concentrations of 2,4,6-trichloro- (A14) and pentachloroanisole (A19) south to 35° S. Measurements of the chlorophyll a content in the surface water gave elevated levels in this region (*65*).

In regions with a high primary production the probability of the existence of species capable of biohalogenation will also be increased. In contrast to the bromoanisoles, a biogenic contribution of chlorophenols, and thus of chloroanisoles, by biohalogenation is worth mentioning but appears unlikely as up to now only one species of green algae is known which possesses a chloroperoxidase (*66*, *67*).

Bromoanisoles in the Troposphere of the Eastern Atlantic Ocean. *Meridional Concentration Profile of the Bromoanisoles.* In Figure 2b the north-south concentration profile of the bromoanisoles is shown. The profiles of the two dibromoanisoles (2,4-dibromo- (A24) and 2,6-dibro-



A24: 2,4-dibromoanisole; A26: 2,6-dibromoanisole; A33: 2,4,6-tribromoanisole; A35: 2,3,4,5-tetrabromoanisole; A36: 2,3,4,6-tetrabromoanisole; A37: 2,3,5,6-tetrabromoanisole; A38: pentabromoanisole

FIGURE 5. (a) Principal component analysis of the normalized concentrations of the bromoanisoles in air samples FP 21−FP 39 (ANT XI/1) and CARBO 2 (ANT XI/5): the data points were projected into the plane defined by the first two principal component axes. (b) Relative concentration of the bromoanisoles, 2,4-dibromo- (A24), 2,6-dibromo (A24), 2,4,6-tribromo (A33), 2,3,4,5- (A35), 2,3,4,6- (A36), 2,3,5,6-tetrachromo- (A37), and pentabromoanisole (A38) in air samples; 100% is sum of the concentrations of the bromoanisoles.

moanisole (A26)) and of 2,4,6-tribromoanisole (A33) are very similar. Striking are concentration maxima in samples FP 21 and CARBO 2 (ANT XI/5) from the Northern Hemisphere and relatively high amounts in samples FP 27, FP 30, and FP 32 from the Southern Hemisphere. Samples FP 23 and FP 39 show very low concentrations of bromoanisoles, which is probably due to a dilution of the air with clean air from the Sahara Desert or from Antarctica, respectively, as discussed before.

The Pattern of the Bromoanisoles in the Lower Troposphere of the Eastern Atlantic Ocean: Principal Component Analysis and a Comparison of Relative Concentrations. Figure 5a depicts the result of a principal component analysis of the normalized concentration of seven bromoanisole congeners: 2,4- (A24), 2,6-dibromo- (A26), 2,4,6-tribromo- (A33), 2,3,4,5- (A35), 2,3,4,6- (A36), 2,3,5,6-tetrabromo- (A37), and pentabromoanisole (A38). Three different clusters of samples can be observed. One cluster (sample FP 32 and FP 37) is due to the tetrabromoanisoles, detectable only in these two samples of the Southern Hemisphere, and to the existence of pentabromoanisole. The second cluster is formed by the samples FP 21, FP 23, and CARBO 2 (Northern Hemisphere) and FP 27, FP 30, and FP 34 (Southern Hemisphere). Sample FP 39 differs from the other samples, because only 2,4,6-tribromoanisole was detected. No differentiation into samples from the northern or the Southern Hemisphere is observed, which is contrary to the pattern of the chloroanisoles.

Besides the occurrence of tetrabromoanisoles (portion of 4−6%) and pentabromoanisole (A38) in samples FP 32 and FP 37, the pattern of the relative concentrations of the bromoanisoles (Figure 5b) reveals differences in the portion of 2,4,6-tribromoanisole (A33) in samples FP 32 (48%) and FP 37 (49%), respectively, compared to the other samples with a portion of 72−88%. The pattern of the relative concentration of the other samples is relatively similar. Small differences are due to the detection of pentabromoanisole (A38) in sample FP 27 and to higher concentrations of bromoanisoles in samples FP 21, CARBO 2, and FP 27 compared to samples FP 23, FP 30, and FP 34. Moreover, the ratio of 2,6-dibromo- (A26) to 2,4-dibromoanisole (A24) is interesting. 2,4-Dibromoanisole (A24) is dominant in samples FP 21, CARBO 2, and FP 27, whereas the amounts of 2,4-dibromoanisole (A24) and 2,6-dibromoanisole (A26) are almost equal in samples FP 30 and FP 34. In sample FP 23 the concentration of 2,6-dibromoanisole (A26) is even higher than that of 2,4-dibromoanisole (A24).

Discussion of the Pattern of Bromoanisoles in the Troposphere of the Eastern Atlantic Ocean. The pattern of the bromoanisoles differs remarkably from the pattern of the chloroanisoles. In contrast to the chloroanisoles (10:1) only a small interhemispherical concentration gradient of 3:1 of the sum of the bromoanisoles is observed. The bromoanisoles are much more susceptible to a degradation by photolysis and reaction with hydroxyl radicals than the chloroanisoles. Therefore, a distinct interhemispheric gradient should be observed, if a major anthropogenic input in the Northern Hemisphere would exist. Another indicator for a mainly biogenic origin of the bromoanisoles is the high concentration of bromoanisoles detected in sample CARBO 2, whereas the concentration of the chloroanisoles is not increased.

Precursors of the bromoanisoles are bromophenols, which are well-known halometabolites in nature. 2,4,6-Tribromophenol (P33) is the main product of the reaction of bromoperoxidases with humic substances (*46, 49*). Several plants and animals synthesize bromophenols and bromophenol derivatives (*33, 34, 38, 68, 69*). 2,4-Dibromo- (P24) and 2,4,6-tribromophenol (P33) are halometabolites of *Lanice conchilega* (*70*). Altogether 15 different bromophenols and polybrominated diphenyl ethers, with up to 6 bromo-substituents, were detected in sponges of the Indo Pacific Ocean (*71*). Some marine organisms produce bromophenols even in high amounts. *Arenicola cristata* has a content of 2,6-dibromophenol (P26) of 6.3 mg (g of wet weight)$^{-1}$ (*72*).

Bromophenols and derivatives are also used as fumigants (*30, 73, 74*). Furthermore, bromophenols are formed during chlorination of drinking water, if high amounts of bromide are present (*31, 32*). Bromo-containing compounds are more unstable to photolysis than chloro-containing compounds, which makes a long-range transport for bromoanisoles more unlikely (*75, 76*). Figure 6 clearly indicates that the wavelength of the absorption maximum of the brominated congeners is shifted to higher values than that of the chlorinated congeners.

Regions with a high annual primary production rate are the upwelling zones off the west coast of Africa. Samples FP 23, FP 27, FP 30, FP 32, and CARBO 2 were all collected in these regions, of which samples FP 27, FP 32, and CARBO 2 show high amounts of bromoanisoles. Especially the region near the Cape Verde Islands seems to be highly productive

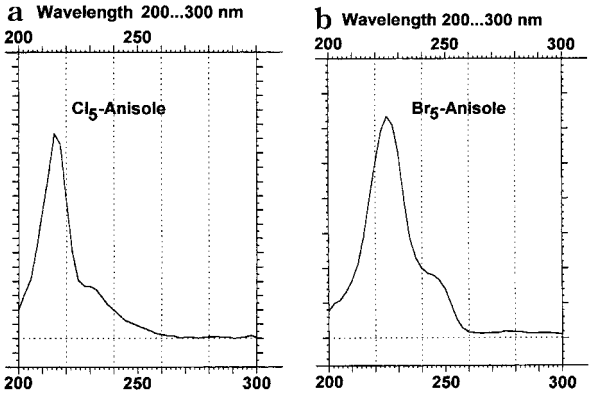


FIGURE 6. UV spectra of (a) pentachloro- (A19) and (b) pentabromoanisole (A38).

with bromo-metabolites. During cruise leg ANT III/4 a distinct increase from less than 1 to 4.5 and 14 pptv in the levels of dibromo- and of tribromomethane, respectively, was observed at 7° N 16° W (*77*−*79*).

Besides the rate of primary production the kind of biota prevalent is also important. Not all marine species are able to synthesize bromophenols, nor is the ability to brominate, for example in the meta position, or the permeability of membranes for bromide equal for all species. It has been reported that some algae are known to be capable of concentrating bromide 35-fold from ocean water and to reduce chloride to half of the concentration in ocean water, simultaneously (*80*). Although not known yet, it may be possible that special bromoperoxidases exist, which prefer bromination in meta position. A regio-selective chlorination in a meta position with the help of a chloroperoxidase was detected in the bacterium *Pseudomonas pyrrocinia* (*45*). Thus, local peculiarities may lead to point sources of tetrabromoanisoles (A35, A36, A37) and pentabromoanisole (A38). Changes in plankton species may also be responsible for the disappearance of the two dibromochloroanisole indicator congeners in samples FP 34, FP 37, and FP 39, which were collected south of sample FP 32 (25° S 10° E). In all other samples these mixed halogenated anisoles are present. These dibromochloroanisoles can be halometabolites of species capable of chlorinating and brominating or may be formed by a light-induced change of halogens in tribromoanisoles (*75*, *76*).

A comparison of the meridional concentration profile of the sum of the chloroanisoles with the profile of the sum of the bromoanisoles shows a striking difference for low latitudes (Figure 2g). Whereas a minimum of the concentration of chloroanisoles is observed, the bromoanisoles show a distinct maximum in this region. The decline of chloroanisoles can explained by an abiotic degradation in the atmosphere. This should also hold for the bromoanisoles. Elevated temperatures of the water phase cause a shift of the air−water partition coefficient K_{GW} in favor of the air phase, which will lead to higher concentrations of bromoanisoles in the troposphere. In addition, strong local biogenic sources of bromophenols and thus bromoanisoles may be assumed. The different patterns of chloro- and bromoanisoles in the troposphere of the eastern Atlantic Ocean lead to the conclusion that mainly anthropogenic sources are responsible for the occurrence of chloroanisoles in the marine environment, whereas bromoanisoles are most probably mainly of biogenic origin in the marine environment.

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