ENVIRONMENTAL TRANSPORT AND FATE

HALOGENATED METHYL-PHENYL ETHERS (HMPE; HALOGENATED ANISOLES) IN THE MARINE TROPOSPHERE AND IN THE SURFACE WATER OF THE ATLANTIC OCEAN – AN INDICATOR OF THE GLOBAL LOAD OF ANTHROPOGENIC AND BIOGENIC HALOPHENOLS

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Introduction

Several members of the group of halogenated methyl-phenyl ethers (HMPE) - halogenated anisoles - that consists of 19 chloroanisoles, 19 bromoanisoles and 96 bromo-chloroanisoles, respectively, have been detected in the marine atmosphere[1-4], in marine and freshwater fish[5], in marine algae[6], in effluents of municipal waste water treatment plants[7] and in sediments[8]. The lower chlorinated congeners are responsible for the musty odor of some waters. The so-called cork taste of vines is assigned to the presence of elevated levels of 2,4,6-trichloroanisole[9].

Halogenated methyl-phenyl-ethers (anisoles) appear to be ubiquitous organics in the environment. Up to now no definite primary anthropogenic sources for the halogenated anisoles are known. Chlorinated anisoles are not produced and/or used in technical quantities. However, methyl-phenyl ethers are formed by many microorganisms by biomethylation of the respective phenols. Thus, among others, chlorophenols may be easily biotransformed into chlorinated anisoles[10]. The chlorophenols can either be direct anthropogenic emissions like the tetrachlorophenols, the pentachlorophenol and the chloromethylphenols (cresols) or they are enzymatically formed from anthropogenic precursors like chlorobenzenes[11].

Precursors of the bromoanisoles are bromophenols, which are well known halometabolites in nature[12]. 2,4,6-Tribromophenol (P33) is the main product of the reaction of bromoperoxidases with humic substances. Increased atmospheric concentrations of halogenated anisoles in the lower pg/m^3 range can generally be found in marine areas with high biological activity. Former measurements in air from the Eastern Atlantic Ocean showed a typical pattern of HMPEs of eight congeners[4]. In this study we present pattern and levels of HMPEs in air and water samples taken simultaneously during a cruise with the German RV "Polarstern" in the Northern and the Southern Atlantic Ocean (ANT XVII/1).

Methods and Materials

The air sampling method, the sample preparation and the clean-up of the air samples by HRGC have been described in detail before [3,12]. Therefore, only a brief overview of the procedure is given here. The air samples were taken by the high-volume sampling method during a cruise with the German RV "Polarstern" (cruise leg ANT XVII/1) from Bremerhaven (Germany) to Capetown (South Africa) in December 1999/ January 2000 as marked in the map. The air sampling was carried out on custom made carbon covered titania[13]. A water sampling method has been developed that allows the solid-phase extraction of organic compounds from large volumes of filtered seawater (up to 300 L) on the polymeric styrene-divinylbenzene sorbent LiChrolut EN. Recovery studies carried out for the

ENVIRONMENTAL TRANSPORT AND FATE

halogenated anisoles revealed good performance of the method. The solid-phase extraction was carried out in specially designed glass cartridges with a diameter of 40 mm filled with 5 g LiChrolut EN at a flowrate of 500 ml/min. The sorbent was soxhlet extracted with 100 mL of dichloromethane (nanograde).

A clean-up step was done by normal phase liquid chromatography (NP-LC) using silica. The sampling locations are shown in the map of the cruise leg (Shortcuts: air: carbon covered titania (MBL), water: LiChrolut EN (SW)). All sample extracts were analysed after concentration by HRGC-MSD-SIM on a DB-5ms column (J&W Sientific) for all 134 congeners of the bromo-chloro-anisoles.

Results and Discussion

The group of the bromo-chloro-anisoles (HMPEs) consists of 134 congeners. In order to simplify the discussion of this complex mixture, each congener was given a systematic congener number[3]. Table 1 summarises the concentrations of the halogenated anisoles in the lower troposphere and in the surface water of the Eastern Atlantic Ocean. Ten congeners were detected in almost all water and air samples: 2,6-dichloroanisole (A7), 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), pentabromoanisole (A38), 2,4-dibromo-6-chloroanisole (A83) and 2,6-dibromo-4-chloroanisole (A88). These ten congeners represent the basic global pattern and are referred to as indicator congeners of the HMPEs. Chloro- and bromoanisoles have to be discussed separately as their origin differs.

The chloroanisoles show an interhemispherical concentration gradient typical for anthropogenic compounds with production and release into the environment in the industrialised northern hemisphere. The concentrations of the chloroanisoles in air are up to 25times higher in the northern hemisphere than in the southern part. It is striking that only chloroanisoles are detected in the marine air that can be assigned to metabolites of chlorophenols for which many anthropogenic processes are known. The same pattern is given in the analyzed water samples. A major interhemispherical exchange for the surface water of the Atlantic Ocean is only from the south to the north[14]. This might explain why the concentrations of the chloroanisoles especially the concentration of 2,4,6-trichlorophenyl-methyl-ether decreases moving southward. This clearly indicates the high input of chlorophenols in the northern industrialised hemisphere.

Concentrations of HMPEs in pg/m^3 (MBL) and ng/m^3 (SW)A long-range transport of chlorophenols in seawater is also limited due to the permanent transformation to chloroanisoles by O-methylating bacteria. Due to their Kgw distribution coefficient, the formed HMPEs tend to be transferred into the atmosphere. A long-range transport of the chlorinated anisoles in the atmosphere is however unlikely. Their estimated lifetime τ_{OH} is of about 40 hours for the temperate climates with an average C_{OH} of $5*10^5$ (molecules/cm^3) and an lifetime τ_{OH} of about 20 hours for the tropics with an average C_{OH} of $10,2*10^5$ (molecules/cm^3)[15]. K_{OH} of HMPEs has been estimated to be in the range of 12-$14*10^{-12}$ (cm^3/molecules*s)[16]. An additional yet unknown degradation by photolysis has also to be accounted for.

The pattern of the bromoanisoles differs remarkably from the pattern of the chloroanisoles. The occurrence of bromoanisoles in water samples is coupled to the primary production rate. Known regions with high primary production rate are upwelling zones off the west coast of Africa, where strong local, biogenic sources of bromophenols and thus bromoanisoles are assumed.

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. Whereas a minimum of the concentration of chloroanisoles is observed, the bromoanisoles show a distinct maximum in this region. The bromoanisoles are definitely more susceptible to a degradation by photolysis and by reaction with hydroxyl radicals than the chloroanisoles. In fact, the concentrations of

ENVIRONMENTAL TRANSPORT AND FATE

Table 1. Concentrations of halogenated anisoles in the air of the marine boundary layer (MBL) in pg/m^3 and in the surface water (SW) in ng/m^3 of the Atlantic Ocean

		SW 1	MBL 1	SW 2	MBL 2	SW3	MBL 3	MBL 4	MBL 5	SW 4
Mean latitude		45°N	42°N	25°N	15°N	4°S	24°S			
Anisole	**Substitution**									
7	**2,6-Cl$_2$**	5,0	62	9,7	16	5,4	n.d.	3,4	5,2	4,5
14	**2,4,6-Cl$_3$**	29	243	25	37	11	33	3,2	11	n.d.
16	**2,3,4,5-Cl$_4$**	21	n.d.	7,7	n.d.	91	n.d.	n.d.	n.d.	2,9
17	**2,3,4,6-Cl$_4$**	3,3	1,4	5,3	n.d.	6,0	2,6	n.d.	0,1	6,0
18	**2,3,5,6-Cl$_4$**	2,3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
19	**2,3,4,5,6-Cl$_5$**	41	7,2	16	8,5	221	12	0,5	0,4	17
20	**2-Br**	n.d.	2,2	4,8	0,4	1,4	n.d.	0,2	0,4	2,1
21	**3-Br**	n.d.	n.d.	13	n.d.	4,6	n.d.	0,1	0,1	5,2
22	**4-Br**	n.d.	3,6	7,7	0,5	3,4	n.d.	0,3	0,5	2,9
24	**2,4-Br$_2$**	22	16	192	8,3	50	17	6,0	6,2	27
26	**2,6-Br$_2$**	4,3	2,9	4,3	2,1	5,3	6,2	0,6	1,2	2,8
33	**2,4,6-Br$_3$**	142	22	200	16	124	69	15	11	44
38	**2,3,4,5,6-Br$_5$**	1,4	0,2	8,0	0,2	8,7	0,3	n.d	n.d.	1,8
83	**2,4-Br$_2$-6-Cl**	4,9	1,9	6,0	2,0	1,9	5,7	1,7	1,6	1,9
88	**2,6-Br$_2$-4-Cl**	2,8	0,9	3,4	0,8	1,1	2,5	0,6	0,7	0,8
	Br-Cl	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
	Br-Cl$_2$	(1)	(1)	(1)	(1)				(2)	(2)

(n.d.: not detected; LOD < 0,1 pg/m^3 (TS); LOD < 0,1 ng/m^3 (PP); (number of yet unidentified HMPE congeners))

the brominated anisoles reach a maximum in the region, where increased abiotic degradation of the halogenated anisoles by photolysis and reaction with hydroxyl radicals takes place. This can only be explained by the higher formation rate of the bromoanisoles in this region.

The analyzed mixed dibromo-chloro-anisoles (A83, A88) can be halometabolites of species capable of chlorinating and brominating or being formed by a light-induced change of halogens in tribromoanisoles[17].

K_{GW}-values can be calculated where air and water samples were taken simultaneously. These K_{GW}-values are 10 to 70 times (mean value 39) lower than values calculated from the Henry's constants reported before[18]. This leads to the assumption, that the Atlantic Ocean surface water is always oversaturated relativ to the air. The imbalance is enhanced by the rather fast OH-degradation of the halogenated anisoles in air. The Atlantic Ocean surface water can be seen as a strong source of halogenated anisoles and the occurrence is a rather local to regional phenomenon.

The different patterns of chloro- and bromoanisoles in the troposphere and in the surface water of the eastern Atlantic Ocean point out that mainly anthropogenic sources are responsible for the occurrence of chloroanisoles in the marine environment.

ENVIRONMENTAL TRANSPORT AND FATE

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