Fresenius J Anal Chem (1990) 336:193–200

Fresenius' Journal of Analytical Chemistry

Studies of the global baseline pollution XIII*

C_6-C_{14} Organohalogens (α- and g-HCH, HCB, PCB, 4,4′-DDT, 4,4′-DDE, cis- and trans-chlordane, trans-nonachlor, anisols) in the lower troposphere of the southern Indian Ocean

R. Wittlinger and K. Ballschmiter

Department of Analytical Chemistry and Environmental Chemistry, University of Ulm, D-7900 Ulm, Federal Republic of Germany

Summary. High-volume air sampling by adsorption on silica gel on the island Rèunion (21° S, 56° E) in the southern Indian Ocean was done for analyzing typical southern hemisphere air for semivolatile organohalogens such as α-hexachlorocyclohexane (13) and g-hexachlorocyclohexane (406), hexachlorobenzene (7), polychlorobiphenyls [PCB 28 (3.2); PCB 52 (4.9) PCB 101 (6.0); PCB 138 (5.0); PCB 153 (5.0); PCB 180 (1.5)], 4,4′-DDT (8), 4,4′-DDE (19), cis- (4) and trans-chlordane (9), trans-nonachlor (3) and heptachloroepoxide (6) in the lower troposphere. The values in parenthesis are mean concentrations in picogram per m^3 air. Local input and long range transport could be distinguished in most cases. The 2,4-, 2,6-, 2,4,5-, 2,4,6-, the tetra- and pentachloro-congeners of the chloroanisoles (phenylmethyl-ethers) were detected. 2,3,5,6-Tetrachloro-1,4-dimethoxy-benzene was found in the 100–280 pg/m^3 range, while 2,4,6-tribromoanisol was detected in the 8–30 pg/m^3 range together with traces of 2,4- and 2,6-dibromoanisole. The sources and the fate of the latter compounds are not yet understood, since both anthropogenic emissions and biogenic origin are possible.

The ratios of the concentrations in the southern and northern hemisphere (south/north ratio) of the semivolatile organochlorine compounds are discussed. The south/north ratio ranges from 0.05 to 0.09 for HCB and α-HCH, respectively, to 0.74 for the PCBs and 0.9 for g-HCH, to 3 for 4,4′-DDE and up to 8 for 4,4′-DDT. This indicates that there is no significant interhemispheric exchange for compounds such as HCB and α-HCH in the atmosphere, and as a consequence the same must be true for other semivolatile compounds.

1 Introduction

The major industrial nations and the main part of the global population are concentrated in the northern hemisphere. Their input of persistent anthropogenic organic chemicals – xenobiotics – into the environment can be traced to applications of agrochemicals, to traffic and energy production, to inadequate means of industrial production and waste disposal or simply to widespread diffuse use patterns of organic compounds. In the southern hemisphere direct input of the xenobiotics into the environment is mainly a result of pesticide use for crop protection or health care programs for humans and animals. It is less well correlated with industrial production in all its aspects. Interhemispheric exchange is the second major source for xenobiotics in the southern hemisphere.

Local input, hemispheric long range transport in the air, the Indian Ocean and interhemispheric exchange are the three main sources one has to discuss for the island Rèunion in the southern Indian Ocean. This island is, in terms of the global mass flow in the atmosphere and the oceans, a counterpart to Madeira and Tenerife in the northern hemisphere. The former islands have been used by us to characterize the baseline situation at the edge of the west wind belt and the beginning of the trade winds over the North Atlantic [1–3].

The air reaching the island Rèunion (21° S, 56° E), which lies east of Madagascar in the beginning of the south east tradewinds of the southern Indian Ocean, originates from descending air of the southern Headly cell as well as from the circumpolar westwind drift. The surface currents of the western part of the south Indian Ocean are characterized by southbound streams originating from the westbound South Equatorial Stream which has its sources at the west coast of Australia [4–6]. Thus, if local input can be excluded, a baseline situation characterized by southern hemispheric long-range transport only in both the atmosphere and the hydrosphere is presented at Rèunion.

While the global distribution pattern is increasingly understood for the volatile C_1/C_2-halocarbons [2, 7, 8], the semivolatile halogenated C_6/C_{14}-compounds are less well investigated (Table 1). As their physico-chemical properties do not favor aero- or aquo-accumulation, their concentrations in the readily exchanged global compartments, the atmosphere and the oceans, are in the picogram/m^3 or nanogram/m^3 range, respectively. Within our program of global baseline studies, we are increasingly focussing on the semivolatile compounds in air [9] and ocean water [3, 10]. They can help us to understand the correlation of the chemical structure and global transport phenomena which includes the study of the global dynamics of anthropogenic compounds [11]. The range of physico-chemical properties

---

* *Part XII:* Fresenius Z Anal Chem (1988) 330:524–526

** *Present address:* BASF, Ludwigshafen, Federal Republic of Germany

Offprint requests to: K. Ballschmiter

Table 1. Concentrations of semivolatile organohalogens in air of the tradewinds of the southern hemisphere and near the equator. All measurements were done on cruises. Values in picogram/m^3

Sampling location	Bidleman et al. [31] 1°S–5°N 53°–95°E Equator South of India	Tanabe et al. [29] 9°–46°S 110°–124°E 151°–155°E South of Japan	Tanabe et al. [29][a] 20°–40°S 50°–57°E South of Mauritius	Kawano et al. [30][a] 45°–64°S 110°–120°E South of Australia
Year	1976	1981	1982	1983/84
α-HCH	>300	42–160	–	–
g-HCH	156	52–370	–	–
Sum of HCH		100–510	50–250	–
Sum of chlordane[+]	<3–3.9	–	–	4.8–7.5
4,4′-DDT	4.7–16	97–330	–	–
4,4′-DDE	–	16– 62	–	–
Sum of DDT	–	160–540	50–300	8.4–11
Sum of PCB (3–10 chlorine atoms)	–	–	200–250	–

Sampling location	Atlas et al. [33] (40°S, 170°E) New Zealand	Atlas et al. [33] (14°S, 170°W) American Samoa
Year	1984	1984
Pentachloroanisole	2.1 ± 0.8	9.0 ± 3.9
2,3,5,6-Tetrachloro-1,4-dimethoxybenzene	13.4 ± 6.7	6.2 ± 1.6
2,3,6-Tribromoanisole	18 ± 5	19 ± 10

[a] Values are taken from graphic plots
[b] Two samples near Australia showed higher concentrations
[c] Sum of chlordane = cis-chlordane + trans-chlordane + trans-nonachlor
– No values reported

as well as their structural characteristics are much wider spread for the semivolatile compounds than those of the volatile C_1/C_2-halocarbons, even if hexachloroethane is included in the latter group.

2 Experimental

2.1 *Air sampling procedure, separation, detection and quantitation*

We used an effective and simple way of high volume sampling of organics in air by adsorption on silica gel (100 g, 0.2–0.5 mm) [9] instead of on the otherwise widely used polyurethane foam plugs. Contamination control, sample transport and sample preparation, chromatographic pre-separation and clean-up, the mode of final gas-chromatographic separation, detection and quantitation are described in a previous paper [9]. To minimize any interferences from the laboratory environment, sample extraction and presentation was accomplished in a clean room of a residence home. Final separation and detection was done by HRGC/ECD and HRGC/MSD, quantitation by HRGC/ECD [9]. High resolution gas-chromatography was done in both cases on a SE 54 coated 50 m × 0.20 mm fused silica capillary, 0.33 μm film, "ultra no. 2" (Hewlett Packard, Palo Alto, USA).

The lower chlorinated anisoles are surely not completely retained by the adsorptive air-sampling on 100 g silica gel, as their boiling points are close to those of the corresponding chlorobenzenes, no quantitations were made. The 2,4,6-tribomoanisole has a boiling point close to the pentachlorobenzene, the collection efficiancy should be similar to that compound.

The separationof 2,3,4,6- and 2,3,5,6-tetrachloroanisole was not possible on SE 54 capillary columns, but can be achieved on the more polar OV 1701 capillary columns (30 m × 0.25 mm, film 0.15 μm. DB 1701, temperature program 3 min isothermal at 80° C, then 3° C/min to 280° C).

The peak produced by the coeluting pentachloroanisole and 2,3,5,6-tetrachloro-1,4-dimethoxybenzene could be evaluated by mass-selective detection [HRGC (SE 54)/MSD]. 2,3,5,6-Tetrachloro-1,4-dimethoxybenzene is the main compound of the signal.

2.2 *Meteorological conditions and sampling locations at Réunion*

2.2.1 General meteorological conditions

The meterological conditions at and around Réunion during the sampling period were visually observed and augmented by the local weather reports as well as photographs from the satellite "Meteosat 2".

During the whole sampling period in March 1986 air currents from the south-east and of high humidity predominated. The temperatures were between 25° C and 35° C, and short, but intense showers of rain, including cloudbursts, characterized the tropical climate. Sampling conditions and times of sampling are cited in detail in Table 2.

Table 2. Location, time and meteorological conditions of air sampling on Réunion using silica gel as adsorbent

Sample number	1	2	3	4	5	6	7
Location	A	B	B	B	B	B	B
Date	20.3.87	14.3.87	20.3.87	21.3.87	21.3.87	22.3.87	22.3.87
Begin of sampling	12.30	24.00	23.45	10.45	20.00	7.00	21.00
Period h	8	8	8.45	9.15	11	14	12
Flux (m^3/h)	60	60	60	60	60	60	60
Sample volume (m^3)	220[a]	540	550	630	600	840	720
Meteorological conditions							
Temperature (°C)	29	31	26	32	26	32	26
Precipitation	yes (1 h)	no	yes (little)	no	no	yes (very little)	no
Wind	South East 25 to 40 km/h	during all sampling periods (0–10 km/h) winds from different directions					
Traffic on coastal road	no streets	little	little	little	little	much	little
Remarks			[b]				

[a] The amount sampled was 440 m^3, but the equivalent of 220 m^3 only was analyzed

[b] A lot of seaweed on the beach during sampling of number 3

2.2.2 Sampling locations at Réunion

The sampling locations on the island were selected in such a way as to exclude major local input from traffic or by dwellings. On the other hand, in certain experiments we tried to uncover the influence of the island as a general source of xenobiotics.

Sampling location A. Location A was situated on the nearly uninhabited east coast of Réunion on a rocky steep coast about 10 m above sea level. During sampling winds (25–40 km/h) from the east, coming in from the open ocean were recorded (sample 1). The influence of local sources of the island can be considered as minimized at this sampling location. Only substances with sources in the open ocean or which are stable enough to be transported over long distances in the air can be expected here. The baseline pollution of the south-east tradewinds of the south Indian Ocean will be represented by the sample 1.

Sampling location B. Location B was situated on the west-coast of the island Réunion, 10 m away from the borderline of a lagoon, which has a depth of about 1–1.5 m. The lagoon is separated from the open ocean by a coral reef 200 m away from the coast. Tides changed the depth of the water in the lagoon. The general winds from the south-east were superimposed by local winds from changing directions. During day-time the land is heated up by solar radiation, during night-time it cools down, whereas the ocean shows nearly stable temperatures. The local air flow followed these temperature gradients. Air samples taken at night can contain input of local sources on the island (samples 2, 3, 5 and 7) whereas long range transport as well as local input from the lagoon will be mainly found in the air samples taken during the day (samples 4 and 6). The samples 3–7 were taken one week after sample 2.

3 Results

Table 3 summarizes the values measured for all the air samples. The results are discussed in detail in the following.

3.1 Halogenated aromatic compounds

3.1.1 Hexachlorobenzene (HCB)

The concentrations of hexachlorobenzene in air amounted to values between 4 and 60 pg/m^3 (Table 3). The spreading of the values indicates an inhomogenous distribution of HCB around Réunion. This makes local sources on the island likely. A baseline concentration of 7 ± 3 pg/m^3 can be calculated from the four low-level values for HCB which is taken as representative for the air over the southern Indian Ocean (Table 3).

3.1.2 Polychlorobiphenyls (PCB)

All air-samples collected at Réunion contained polychlorobiphenyls (PCB) with 3 to 7 chlorine atoms. The mean concentrations of the principal congeners PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 varied between 3.2 and 6 pg/m^3, PCB 180 1.5 pg/m^3 as determined by HRGC/ECD (Table 3). The concentrations of the six PCB in sample 2 could be verified by HRGC/MSD (range 3.3 to 8.3 pg/m^3, Table 3). The sum of the six PCB congeners amounts to between 15 and 35 with a mean of 26 pg/m^3. These results make local sources of significance for the PCB unlikely.

For the quantitation of total PCB in sample 2 it was assumed that the MSD gives the same response for PCB congeners with the same degree of chlorination. Sample 2 was additionally examined by HRGC/MSD for the isomer-specific distribution of the PCB congeners with 3 to 6 chlorine-atoms [9, 12]. The results reveal that the isomer-specific pattern of PCB in air coming in from the sea cannot be represented by a single technical mixture. The sum of three mixtures, PCB 42% chlorine (Aroclor 1242, Clophen A30), PCB 54% chlorine (Aroclor 1254, Clophen A50), and PCB 60% chlorine (Aroclor 1260, Clophen A60) is needed to characterize the isomer-specific distribution of PCB in the lower troposphere. In contrast to earlier results from air samples collected in a city in central Europe, where the

Table 3. Concentrations of chlorinated cyclocarbons in air samples collected March 1986 at Réunion, Southern Indic Ocean. All values in picogram/m^3

Sample number	1	4	6	3	5	7	2	Mean
Day/Night	Day	Day	Day	Night	Night	Night	Night	*(Low level)*
Rain	(1 h)	no	little	little	no	no	no	
Location	A	B	B	B	B	B	B	
Wind from	sea	lagoon	lagoon	land	land	land	land	
Hexachlorobenzene								
(HCB)	12	*58*	*33*	4	*23*	9	4	7
Polychlorobiphenyls								
PCB 28 (2,4,4′)	3	2	4	2	4	4	4 (3.3)[a]	3.2
PCB 52 (2,2′,5,5′)	4	(8)[b]	3	3	3	6 (7.1)	4.9	
PCB 101 (2,2′,4,5,5′)	6	8	5	4	5	4	8 (8.1)	6.0
PCB 138 (2,2′,3,4,4′,5′)	9	4	3	3	2	3	8 (8.3)	5.0
PCB 153 (2,2′,4,4′,5,5′)	7	5	4	3	3	3	7 (8.3)	5.0
PCB 180 (2,2′,3,4,4′,5,5′)	4	1	1	0.2	0.7	1	3 (3.6)	1.5
Sum PCB (28 – 180)	33	28	22	15	18	18	35 (39)	26
Sum PCB (all congeners)	–	–	–	–	–	–	– (125)[a]	
Hexachlorocyclohexanes								
α-HCH	6	10	19	12	9	41	21	13
g-HCH	370	320	530	*1400*	*1100*	*1400*	*1600*	406
Chlordane								
cis-Chlordane	4	3	4	4	4	6	4	4
trans-Chlordane	6	8	8	9	10	10	*19*	9
trans-Nonachlor	4	2	3	3	2	2	4	3
Sum chlordane	14	13	15	16	16	18	*27*	15
Heptachloroepoxide	4	5	6	6	5	7	7	6
DDT								
4,4′-DDT	6	6	6	7	6	10	13	8
4,4′-DDE	18	7	13	34	21	20	20	19
Halogenated anisoles								
2,4,6-Tribromo-anisole	8	21	30	12	11	17	8	15
2,3,5,6-Tetrachloro-1,4-Dimethoxybenzene	20	130	220	150	210	280	180	195 (20)

[a] Values in bracket were determined by HRGC/MSD
[b] The peak of PCB 52 was unresolved. PCB 52 = PCB 101 was assumed
[c] The value also contains a small, unresolved quantity of pentachloroanisole
The italic values were not used for calculating the "low level mean"

distribution between the gaseous phase and the particle phase was found to be correlated with the vapor pressure [9], a detailed analysis of the individual congeners revealed no significant differences in the relative distribution of the PCB isomers within a group of chloro-homologues between air sample 2 and a composite technical mixture of PCB 42%, 54% and 60% chlorine (1:1:1). Only the tetra- and pentachlorobiphenyls exhibited a very slight enrichment of the more volatile congeners. This behaviour can be expected, when low levels of particulate surface per volume and elevated temperatures are given. No indication of a structure specific photodegradation could be found.

The amounts of 125 pg total PCB per cubic meter of air of the trade winds of the southern hemisphere, represented by the air samples from Réunion, is near to the level of 168 pg total PCB/m^3 (range 124 – 230) of the mean PCB pollution found for baseline air samples in the northern hemisphere (Table 4).

3.2 Chlorinated insecticides

3.2.1 Hexachlorocyclohexane (HCH) isomers

In the air at Réunion, both the α- and g-isomer of hexachlorocyclohexane (α-HCH, g-HCH) were detected, with a clear dominance of g-HCH. Two groups of samples with different levels of g-HCH could be distinguished (Table 3). Air samples of marine origin (samples 1, 4 and 6) gave levels of 6 – 19 pg/m^3 for α-HCH and 300 – 500 pg/m^3 for g-HCH. These samples should reflect the upper level of the baseline pollution of the lower troposphere in this region of the south Indian Ocean. Air samples clearly influenced by local sources, such as the samples 2, 3, 5 and 7, gave a level of 1100 – 1600 pg/m^3 for g-HCH while the level of α-HCH was the same as for the previous samples. The latter samples were taken at location B during night with air descending from the mountains. These facts indicate that there is a local input of g-HCH as "Lindane". All samples gave alpha to

Table 4. Baseline values and South/North ratio of semivolatile organochlorine compounds in lower troposphere southern Indian Ocean (Réunion), Central Europe (Ulm, FRG) [9], North Atlantic [16] and North Pacific Ocean [16]. All values in picogram/m^3

	Réunion (S)	Ulm (N) (a)	North Atlantic (b)	Enewetak Atoll (N) (c)	S/N ratio		
					(a)	(b)	(c)
Hexachlorobenzene	*7*	*120*	*150*	*100*	*0.06*	*0.05*	*0.07*
Hexachlorocyclohexanes							
α-HCH	13	150	390	250	0.09	0.03	0.05
g-HCH	406	(430)[b]	[a]	15	(0.94)	–	27
α/g-HCH	0.03		[a]	17	–	–	–
Chlordane (cis + trans)	13	[a]	[a]	13	–	–	1
Polychlorobiphenyls							
PCB 28	3	5	[a]	[a]	0.60	–	–
PCB 52	5	8	[a]	[a]	0.63	–	–
PCB 101	6	15	[a]	[a]	0.38	–	–
PCB 118	[a]	4	[a]	[a]	–	–	–
PCB 138	5	10	[a]	[a]	0.50	–	–
PCB 153	5	12	[a]	[a]	0.42	–	–
PCB 180	1.5	4	[a]	[a]	0.38	–	–
ΣPCB (28–180)	26	53	[a]	[a]	0.49	–	–
PCB (3–9)	125	168	[a]	[a]	0.74	–	–
DDT							
4,4′-DDT	8	1	[a]	[a]	8	–	–
4,4′-DDE	19	6	6	3	3.2	3.2	6.3
DDE/DDT	2.3	6	–	–	–	–	–

[a] No value given

[b] This value may be influenced by regional applications. At rainy weather a value of 180 pg/m^3 was measured for g-HCH

gamma ratios from 1:30 to 1:100, corresponding to the composition of "Lindane" (>99% g-HCH).

Two types of hexachlorocyclohexane (HCH) are used as an insecticide. Technical HCH (benzene hexachloride, BHC) contains 55–70% α-HCH, 10–15% g-HCH and other chlorinated compounds. Only the g-HCH reveals a remarkable insecticidal activity and is therefore used in a purified form of HCH ("Lindane", >99% g-isomer). A world-wide trend toward the g-HCH (Lindane) is known. Nevertheless, in the northern hemisphere a prevalence of technical HCH (BHC) can be observed, as major production lines – 200000 tons per year [13] – are installed for this product. India alone uses about 20000 tons of BHC per year for public health programs since 1978 [14]. The pattern of the HCH isomers in the Caspian Sea with a dominance of α-HCH clearly indicates a widespread use of BHC in areas surrounding this landlocked water mass [15]. At the Enewetak Atoll in the North Pacific Ocean (12° N, 162° E) the concentrations in air were: α-HCH = 250 pg/m^3; g-HCH = 15 pg/m^3 and in rain: α-HCH 3110 pg/l; g-HCH = 510 pg/l [16]. The ratio of alpha and gamma HCH in the water column of the North Atlantic is different depending on whether the water masses originate in the northern or in the southern hemisphere [10]. This supports the conclusion that there is a typical hemispheric difference in the composition of the HCH-products used. Field investigations of the factors influencing the distribution of the HCH isomers in BHC-20-treated soil clearly indicated that the removal from the soil was in the order alpha > gamma > delta ≫ beta HCH [17]. These investigations also proved that BHC has been applied to sugar cane fields in Australia at least locally for the last two decades.

3.2.2 4,4′-DDT and 4,4′-DDE

The concentrations of 4,4′-DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)-ethane) in air samples 1 and 3–7 from Réunion are nearly the same (Table 3). In contrast to the insecticide g-HCH, no differences between sampling location A and B and between day and night at place B could be observed. A local input can thus be excluded for 4,4′-DDT. The concentration of 4,4′-DDT in air amounted to 6–13 pg/m^3. A mean of 8 pg/m^3 can be considered to be the baseline concentration for 4,4′-DDT around Réunion and is therefore typical for the air over the south Indian Ocean.

DDT is still an important insecticide, even though its use is restricted or has even ceased in several western countries. There is no indication that the general use of the cheap insecticide DDT has been abandoned. Although DDT was banned as early as 1972 in the USA, more than 37000 pounds of DDT were still used in 1975–1977 for forest insect control programs by the U.S. Department of Agriculture [18]. It is known that 4,4′-DDT is continuously being used in anti-malaria campaigns in East Africa. In India about 10000 tons of DDT were used per year from 1977/78 till 1982/83 for public health programs [14]. More recent figures are not available. Large amounts of DDT are transported into the Caspian Sea as revealed by the accumulation of even the 2,4′-isomer in fish eggs [15]. In global terms the continued use of DDT is a fact despite the well propagated restrictions in some western countries and despite the development of DDT-resistant strains of the malaria mosquitoes. About 2 millions deaths per years caused by Malaria tropica are counted in the eighties [19]. Recent numbers for new malaria infections are given by the WHO [19]. In Africa the number of new cases is estimated to be 300000000, in Asia 170000000 and in Latin America 150000000.

4,4′-DDT is not stable under environmental conditions. It undergoes biotic or abiotic degradation to several products. The most important and stable transformation product is 4,4′-DDE. This compound could be found in all air samples from Réunion. The concentrations of 4,4′-DDE in air had a mean value of 19 pg/m^3 and ranges from 7 – 34 pg/m^3. The 4,4′-DDE values were slightly higher in air samples collected at night with winds descending from the mountains (samples 2, 3, 5, 7) which may be taken as an indication of a former use of 4,4′-DDT on Réunion. 4,4′-DDD, the typical transformation product produced by algae and effectively accumulated by fish could not be detected in air.

3.2.3 Technical chlordane

Technical chlordane, a cyclodiene insecticide, is used worldwide for special applications e.g. in termite control. The technical mixture has been analyzed recently in detail by capillary gas chromatography and mass selective detection [20]. It is a mixture composed of several major compounds and isomers thereof. This report examines only the three main components of technical chlordane, namely cis-chlordane, trans-chlordane and trans-nonachlor.

The sum of these three compounds in air of Réunion amounted to 13 – 27 pg/m^3 with 17 pg/m^3 as the mean. The three compounds gave mean values of 4, 10 and 3 pg/m^3 for cis-chlordane, trans-chlordane and trans-nonachlor, respectively. The rather constant level makes relevant sources for this insecticide on the island unlikely. The values measured can be taken as baseline levels of long range transport over the south Indian Ocean.

Heptachloroepoxide, another cyclodiene insecticide, was measured at levels between 4 and 7 pg/m^3 in air. Dieldrin could be detected but was not quantified.

3.2.4 Polychlorocamphene – toxaphene

Though toxaphene is found as a globally spread pollutant accumulated by e.g. fish [21] it could not definitely be detected in air samples from Réunion.

3.3 Halogenated methyl-phenyl-ethers (anisoles)

3.3.1 Chloro-anisoles

In the air samples collected on Réunion several halogenated methyl-phenyl-ethers (anisoles) were found. The following chloroanisoles have been detected by HRGC (SE 54) MSD: 2,4-dichloro-, 2,6-dichloro-, 2,4,5-trichloro-, 2,4,6-trichloro-, 2,3,4,5-tetrachloro-, 2,3,4,6-tetrachloro- and for 2,3,5,6-tetrachloro- and pentachloro-anisole. Remarkable is the prevalence of 2,4-, 2,6-, and 2,4,6-substitution patterns. Because of the relative high volatility of some congeners, no quantification was made. The levels are in the 2 – 20 pg/m^3 range.

Plants and microorganisms are known to synthesize some halogenated phenols and methylate the phenolic hydroxy-group. Because no biotic sources and no technical production are known for pentachloroanisole, the biotransformation of pentachlorophenol is the most likely source of airborne pentachloroanisole [22, 23]. Pentachlorophenol itself is used as an effective fungicide, but it is also formed as other chlorophenols in municipal waste incineration plants as a result of the incomplete combustion of de novo formed chlorobenzenes [24]. The biodegradation of hexachlorobenzene (HCB) and g-hexachlorocyclohexane (g-HCH) can also lead to pentachlorophenol [23].

3.3.2 2,3,5,6-Tetrachloro-1,4-dimethoxybenzene

2,3,5,6-Tetrachloro-1,4-dimethoxybenzene is the main component of the chromatographic peak being composed of this compound and pentachloroanisol as evaluated by HRGC (SE 54)/NSD. The amounts of 2,3,5,6-tetrachloro-1,4-dimethoxybenzene in air, measured by HRGC/ECD, varied between 100 and 280 pg/m^3, except for sample 1, were 20 pg/m^3 were measured.

2,3,5,6-Tetrachloro-1,4-dimethoxybenzene has previously been isolated from the rotten wood fungus *Fomes fastuosus lev*, collected in India [25]. It has been reported to be present also in other species of the same family of fungi [26]. It could also result from the biotransformation of pentachloronitrobenzene (quintozene, a soil fungicide), pentachloroanisole, pentachlorophenol or even g-hexachlorocyclohexane (g-HCH) [22, 23]. An assignment to a definite source is not possible at the moment. The low value for sample 1 (120 pg/m^3) may indicate that the major source for 2,3,5,6-tetrachloro-1,4-dimethoxybenzene is on the island itself. An explanation would be the former use of pentachlorophenol on the island or the biotransformation of g-hexachlorocyclohexane. 2,5-Dichloro-1,4-dimethoxybenzene (chloroneb) is used as a systemic fungicide. The tetrachloro-congener could be a by-product, though this will be an unlikely source.

3.3.3 Bromo-anisoles

2,4,6-Tribomoanisole (2,4,6-tribromophenyl-methyl-ether) in air on Réunion gave a mean value of 15 pg/m^3 and a range of 8 to 30 pg/m^3. It is the only isomer of the *tribromo*anisoles detected. Traces of 2,4- and 2,6-*dibromo*anisole could be detected by GC/MSD. The occurrence of 2,4,6-tribromoanisole in sample 1 (Table 3), which basically represents air from the open ocean, points to the ubiquity of this substance. Emissions from incineration processes, like the use of bromoethane or 1,2-dibromo-ethane as additives in leaded gasoline [27], waste incineration [28] and a former use as flame-retardant, have to be discussed as anthropogenic sources of 2,4,6-tribromophenol, which is the likely parent compound of 2,4,6-tribromoanisole. So far none of these sources can be identified as the major one.

The ease of photodegradation of bromoanisoles nearly excludes any long-range transport of anthropogenic emissions and makes a biogenic source most likely for the tradewind region at Réunion. The slightly increased values of samples 4 and 6 (Table 3) may indicate that the lagoon, including the corral reef, can be seen as such a source. Bromophenol derivatives are not uncommon in marine biochemistry.

4 Discussion

Several authors have reported the occurrence of some of the xenobiotics investigated in this paper (Table 1). In March

1982 Tanabe et al. analyzed chlorinated hydrocarbons in air samples some 100 km away from Réunion [Mauritius Island (20°S, 57°E)] [29]. Total PCB amounted to 200 pg/m^3, compared to 125 pg/m^3 in this report. The sum of HCH amounted to 250 pg/m^3 on that cruise. This also agrees well with this work: sum of α- and g-HCH: 330 – 520 pg/m^3. However α-HCH was reported to be the most abundant isomer, whereas in our 1986 air samples from Réunion the gamma-isomer strongly dominates.

Kawano et al. in 1983/84 detected organochlorine insecticides near Australia at relatively high levels [30]. Further south (45° – 64°S, 110° – 120°E) they determined the sum of chlordane (4.8 – 7.5 pg/m^3) and the sum of DDT (8.4 – 11 pg/m^3) on the same cruise. Their values agree well with those of this report (Table 4).

Bidleman et al. in 1976 measured 4,4′-DDT, chlordane and HCH in air on a cruise near the equator [31]. The values of the sample from the most southern point (0.5°S – 5°N, 53 – 85°E) for 4,4′-DDT (4.7 – 16 pg/m^3) and chlordane (cis + trans = <3 – 5.4 pg/m^3) are at the same level with those of this report. α-HCH was reported to be the dominating HCH-isomer.

Cis- and trans-chlordane have been detected in arctic air in concentrations of 1.5 and 1.0 pg/m^3, respectively [32]. Trans-nonachlor was found at a level of 1.3 pg/m^3. The level at Réunion was higher by a factor of three to ten. This may be due to a broader range of applications in the tropics than in the moderate and cold climate of the northern westwind belt region or due to a more effective atmospheric deposition in the cold regions.

Atlas et al. describe the occurrence of three halogenated anisoles in the marine air of the lower troposphere of both hemispheres [33]. Sampling locations were at New Zealand, Texas (USA), and American Samoa. The reported concentrations of 2,4,6-tribromoanisole and pentachloroanisole in the southern hemisphere are in the same order of magnitude as in this report, only 2,3,5,6-tetrachloro-1,4-dimethoxybenzene was reported to be a factor of ten lower, compared to this report. As the class of halogenated anisoles is detectable in the lower troposphere of Réunion (south Indian Ocean), New Zealand, American Samoa, Texas (USA) and Central Europe one may conclude, that these substances are ubiquitous in the lower troposphere of both hemispheres.

The measurements at Réunion clearly indicate that α-HCH (South/North = S/N ratio = 0.09), HCB (S/N ratio = 0.06) and PCB (S/N ratio = 0.49/0.74) exhibit lower, while 4,4′-DDT (S/N ratio = 8) and 4,4′-DDE (S/N = 3.2) give higher concentrations compared with air samples of the westerlies of the northern hemisphere [9]. Baseline levels for both hemispheres are summarizes in Table 4.

The results also prove that the assumption of a gamma-HCH to alpha-HCH isomerization [34] is only minor or not valid at all for the atmosphere. The results furthermore prove that in the troposphere there is no significant interhemispheric crossing to the south for both α-HCH and hexachlorobenzene. The photochemical lifetimes in the troposphere would allow such a hemispheric equilibration. The atmospheric residence time has to include both chemical and physical scavanging processes [35]. For hexachloroethane a tropospheric south/north ratio of 0.85 has been determined [2]. Interhemispheric crossing in the hydrosphere, e.g. in the Atlantic Ocean, has been proved for gamma-hexachlorocyclohexane [10].

5 Conclusions

Compared with the production figures, the estimated amounts of the semivolatile organohalogens in the troposphere are very small. Most of the environmental load of the semivolatile organohalogens has to be looked for in the other environmental compartments, namely water, biota, soil or sediment. The troposphere will, however, act as an important and fast transport medium within the hemispheres, though an interhemispheric exchange seems to be excluded or very slow at least for the semivolatile organohalogens. Extrapolation of the findings for α-hexachlorocyclohexane and hexachlorobenzene requires that other semivolatile compounds, such as the PCB or the compounds of the DDT and cyclodiene-group, do not cross the equator via the atmosphere either. Junge discussed the interhemispheric exchange of trace gases and clearly defined the conditions of the widely accepted value 0.9 – 1.0 years for for the hemispheric exchange times [35].

The halogenated methyl phenyl ethers seems to be ubiquitous in the lower troposphere. The preference of the 2,4-, 2,6-, 2,4,5- and 2,4,6-substitution pattern for this class of components is remarkable. The corresponding phenols seem to be the parent compounds. Different sources are possible, ranging from combustion related input to biogenic halogenation of phenol substances.

Acknowledgement. The authors acknowedge the support (R. W.) for this research project provided by the LGFG of Baden-Württemberg. Dr. U. Reuter is gratefully acknowledged for assistance during the expedition to Réunion.

References

1. Kirschmer P, Ballschmiter K (1983) Int J Environ Anal Chem 14:275 – 284
2. Class T, Ballschmiter K (1987) Fresenius Z Anal Chem 327:198 – 204
3. Krämer W, Buchert H, Reuter U, Biscoito M, Maul DC, LeGrand G, Ballschmiter K (1984) Chemosphere 13:1255 – 1267
4. Gierhoff-Emden HG (1983) Geographie des Meeres – Ozeane und Küsten, Teil 1. de Gruyter, Berlin, pp 647 – 650
5. Blüthgen J, Weischet W (1980) Allgemeine Klimageographie, 3. Aufl. de Gruyter, Berlin, pp 522 – 551
6. Liljequist GH, Cehak K (1979) Allgemeine Meteorologie. Vieweg, Braunschweig, pp 281 – 310
7. Dervent RG, Eggleton AEJ (1981) Quart JR Met Soc 107:242 – 251
8. Khahil MAK, Rasmussen RA (1985) Modelling chemical transport and mass balances in the atmosphere. In: Brock Neely W, Blau GE (eds) Environmental exposure from chemicals, vol II. CRC Press, Boca Raton, pp 21 – 54
9. Wittlinger R, Ballschmiter K (1987) Chemosphere 16:2497 – 2513; Wittlinger R (1988) Ph. D. Thesis, Ulm
10. Krämer W, Ballschmiter K (1988) Fresenius Z Anal Chem 330:524 – 526; Krämer W (1987) Ph. D. Thesis, Ulm
11. Ballschmiter K (1979) Nachr Chem Tech Lab 27:542 – 546; (1985) Nachr Chem Tech Lab 33:206 – 208; (1987) Wiss Fortschr 37:111 – 113
12. Ballschmiter K, Schäfer W, Buchert H (1987) Fresenius Z Anal Chem 326:253 – 257
13. Deutsche Forschungsgemeinschaft (1983) Hexachlorcyclohexan als Schadstoff in Lebensmitteln. Verlag Chemie, Weinheim, pp 14 – 17
14. Krishna Murti CR, Dikshith TSS (1982) Application of biodegradable pesticides in India. In: Matsumara F, Krishna Murti

CR (eds) Biodegradation of pesticides. Plenum Press, New York, pp 257–301
15. Ballschmiter K, Buchert H, Scholz B, Zell M (1983) Fresenius Z Anal Chem 316:242–246
16. Atlas E, Giam CS (1980) Science 211:163–165
17. Chessells MI, Hawker DW, Conell DW, Papajcsik IA (1988) Chemosphere 17:1741–1749
18. Crisp CE (1982) Biodegradable insecticides in forestry. In: Matsumura F, Krishna Murti CR (eds) Biodegradation of pesticides. Plenum Press, New Yok, pp 157–191
19. Anonymous (1989) Parasitology Today 5:39; Gratz NR (1985) J An Mosq Control Assoc 1:273–278
20. Buchert H, Class T, Ballschmiter K (1989) Fresenius Z Anal Chem 333:211–217
21. Zell M, Ballschmiter K (1980) Fresenius Z Anal Chem 300:387–402
22. Ranga Roa R (ed) (1978) Pentachlorophenol. Plenum Press, New York, pp 67–197
23. Gesellschaft Deutscher Chemiker (1985) Beraterprogramm Umweltrelevante Altstoffe, BUA-Stoffbericht "Pentachlorphenol". VCH, Weinheim, pp 31–63
24. Ballschmiter K, Braunmiller J, Niemczyk R, Swerer M (1988) Chemosphere 17:995–1005
25. Singh P, Rangaswami S (1966) Tetrahedron Lett 1229–1231
26. Butruille D, Dominguez XA (1972) Tetrahedron Lett 211–212
27. Müller MD, Buser HR (1986) Environ Sci Technol 20:1151–1157
28. Ballschmiter K, Niemczyk R (1987) (unpublished results)
29. Tanabe S, Tatsukawa R, Kawano M, Hidaka H (1982) J Oceanogr Soc Jap 38:317; Tanabe S, Hidaka H, Tatsukawa R (1983) Chemosphere 12:277
30. Kawano M, Tanaba S, Inone T, Tatsukawa R (1985) Trans Tokyo Univ Fish 6:69
31. Bidleman TF, Leonard R (1982) Atmos Environ 16:1099
32. Hoff RM, Chan KW (1986) Chemosphere 15:449–452
33. Atlas E, Sullivan K, Giam CS (1986) Atoms Environ 20:1217; Chang LW, Atlas E, Giam CS (1985) Int J Environ Anal Chem 19:145
34. Oehme M, Mano S (1984) Fresenius Z Anal Chem 319:141–149
35. Czeplak G, Junge CE (1974) Adv Geophys 18:57–72

Received September 5, 1989; revised October 19, 1989