Intern. J. Environ. Anal. Chem., Vol. 57, pp. 33-52
Reprints available directly from the publisher
Photocopying permitted by license only

PATTERN ANALYSIS OF POLYCHLORINATED BIPHENYLS (PCB) IN MARINE AIR OF THE ATLANTIC OCEAN

J. SCHREITMÜLLER, M. VIGNERON†, R. BACHER‡ and
K. BALLSCHMITER*

*Department of Analytical and Environmental Chemistry, University of Ulm,
Albert-Einstein-Allee 11, D-89069 Ulm-Donau, Germany*

(Received, 23 August 1993; in final form, 10 January 1994)

The patterns of polychlorinated biphenyls (PCB) in marine air samples of the North- and the South Atlantic were compared to each other by a congener ratio correlation, by the similarity index, which was calculated by two different algorithms, and by principal component analysis (PCA). The calculations were done on the basis of the following fourteen PCB congeners: the trichlorobiphenyls PCB 28, PCB 31, the tetrachlorobiphenyls PCB 44, PCB 49. PCB 52, the pentachlorobiphenyls PCB 87, PCB 101, PCB 110, PCB 118, the hexachlorobiphenyls PCB 138, PCB 149, PCB 151, PCB 153 and the heptachlorobiphenyl PCB 180. The three methods gave basically the same results. The use of only the seven indicator PCB congeners 28, 52, 101, 118, 138, 153 and 180 did not alter the pattern classification of the samples.

There exists a typical marine clean-air PCB pattern in the lower troposphere of the Atlantic Ocean between 40° North and 40° South, which apparently reflects the air/sea water equilibrium. This marine clean-air pattern is significantly different from a pattern of marine air samples influenced by continental air masses coming in from Europe or South America. This influence is marked by an increase of the levels of the higher chlorinated congeners.

The PCB patterns in continental air samples from western Europe and the Great Lakes region in North America differ in their portion of lower chlorinated congeners.

KEY WORDS: Pattern classification, similarity index, principal component analysis, polychlorinated biphenyls (PCB), marine air samples, air/sea exchange.

INTRODUCTION

Modern analytical chemistry creates in many cases either as the result of high resolution in separation or of high sensitivity in detection a broad spectrum of complex informations

---

†Institute de Chimie et de Physique Industrielles, Lyon, France

‡Present address: PTRL Europe, Helmholtz-Str., D-89069 Ulm, Germany

*To whom correspondence should be adressed

Partly presented at DIOXIN '92, 12th International Symposium on Chlorinated Dioxins and Related Compounds, 24–28 August 1992, Tampere, Finland

Chemometrical techniques are increasingly an important part of the evaluation and presentation of such analytical data. Various mathematical tools are available to structure or to correlate the gathered informations. Correlation analysis, display methods as principal component analysis (PCA) and other approaches as cluster analysis are becoming standard procedures in the assessment of complex data sets. Reviews of the application of chemometrics in data treatment are found the literature[1-8].

Capillary gas chromatography combined with appropriate detectors gives in terms of resolution and selectivity a depth of information which is often neglected or even overlooked. Pattern correlation techniques can be specifically helpful to interprete the information obtained in environmental chemistry using high resolution chromatography of complex mixtures. Chemical classes of complex mixtures found in the environment are the polychlorinated biphenyls (PCBs) (209 congeners), polychlorinated naphthalenes (75 congeners), polychlorinated diphenyl ethers (209 congeners), polychlorinated dibenzofurans (PCDF) (135 congeners), polychlorinated dibenzo-p-dioxins (PCDD) (75 congeners), polychlorinated camphenes (Toxaphen) (>150 congeners), the tetrachlorinated benzyltoluenes (95 isomers), the alkyl substituted arenes and thioarenes and others. These groups of compounds can be often mixtures in themselves and will develop a "fingerprint", which depends on the input by different sources and on the environmental fate of the individual congeners in terms of abiotic and/or biotic degradation and intercompartimental distribution[9]. Comparisons between congener profiles of PCDDs and PCDFs in atmospheric samples and the correlation to their possible sources have been carried out previously also using principal component analysis[10-13].

The levels of the individual PCB congeners in air relaxate from the original terrestrian input towards an equilibrium between output from the atmosphere and re-input from the marine surface during long-range transport in the marine atmosphere as depicted in Figure 1.

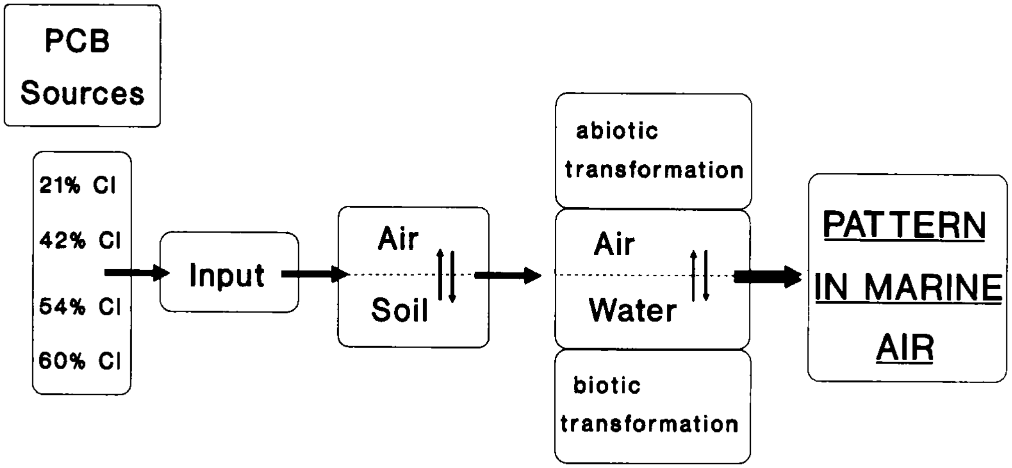

Figure 1 Fate of the polychlorinated biphenyls during the transport from sources, which are characterized by technical mixtures with different chlorine contents, to the marine atmosphere. During this transport several processes contribute to a distinct PCB pattern in air.

The fluxes of the compounds, often discussed only as an average sum, are governed by the physical properties of the individual congeners and their respective partition coefficients, which differ quite substantially for the different degrees of chlorination. Next the geophysical parameters in the lower troposphere and at the air/surface water interface including the microlayer will influence the distribution of the individual congeners.

This should lead to different PCB patterns in marine air at source-near and source-distant locations and in continental air, which is in equilibrium with a terrestrian surface. Levels and pattern of PCBs in marine air have recently reported by Iwata *et al.*[14]. The authors observed a relatively high portion of lower chlorinated congeners in air of high latitude oceans, as the Bering Sea and the Southern Ocean, and discussed the dependence of the pattern from the gas/water partition coefficients.

To characterize the PCB pattern in marine air we quantified the following fourteen PCB congeners in air samples of the Atlantic Ocean (see Table 1): the trichlorobiphenyls PCB 28, PCB 31, the tetrachlorobiphenyls PCB 44, PCB 49. PCB 52, the pentachlorobiphenyls PCB 87, PCB 101, PCB 110, PCB 118, the hexachlorobiphenyls PCB 138, PCB 149, PCB 151, PCB 153 and the heptachlorobiphenyl PCB 180. These fourteen congeners cover a wide range of chlorination, they differ in the substitution pattern and have widely divergent physical properties, which means, that they can be considered as representatives for a respective group of congeners in the various technical PCB mixtures. Altogether these fourteen congeners represent about 40% of the sum of all PCB congeners in a 1:1:1 mixture of the technical mixtures Aroclor 1242, 1254 and 1260.

Table 1 Concentrations of 14 polychlorinated biphenyl congeners in the boundary layer of the Atlantic Ocean atmosphere (all values in pg/m^3) (a)

Sample-No.		*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*13*	*14*
mean latitude [°]		46	41	32	27	12	2	-9	-27	-31	-38	-46	16.5	16.5
mean longitude [°]		-12	-18	-24	-26	-29	-29	-31	-40	-44	-51	-59	-23	-23
PCB 28	2,4,4′	4.1	1.3	5.9	7.5	5.4	10.0	7.6	4.9	3.4	4.1	2.6	1.5	1.7
PCB 31	2,4′,5′	6.7	1.9	9.4	11.8	7.1	18.0	8.6	6.8	4.3	5.6	4.2	2.6	2.3
PCB 44	2,2′,3,5′	8.8	1.5	7.2	(e)	7.6	13.0	(e)	8.3	5.5	(e)	4.3	1.7	2.9
PCB 49	2,2′,4,5′	4.0	1.2	6.0	(e)	5.4	9.0	(e)	5.1	3.4	(e)	2.5	1.2	1.9
PCB 52	2,2′,5,5′	16.3	5.0	21.2	36.9	19.3	35.0	41.3	18.1	14.4	14.6	11.7	5.3	6.9
PCB 87	2,2′,3,4,5′	2.9	≤0.3	2.5	5.5	2.9	4.0	4.2	3.0	1.7	2.1	6.3	≤0.6	1.3
PCB 101	2,2′,4,5,5	14.6	3.0	14.7	22.8	14.4	21.0	24.4	16.2	9.8	12.1	28.4	3.2	6.4
PCB 110	2,3,3′,4′,6	6.6	1.3	4.3	6.8	4.9	8.0	8.3	6.6	3.1	4.0	14.5	1.2	2.6
PCB 118	2,3′,4,4′,5	3	≤0.5	1.5	3	2	3	2.5	3	1	2	9	≤0.5	1.3
PCB 138(b)	2,2′,3,4,4′,5	8	1	2	4	4.5	4	4.5	11	2.5	3	21	1	2
PCB 149	2,2′,3,4′,5′,6	11	2	4.5	(e)	5.5	8.5	9.5	9.5	4	6	21.5	2	3.5
PCB 151	2,2′,3,5,5′,6	3	≤0.7	2.5	(e)	2.5	3.5	4.5	3.5	2	2.5	7.5	≤0.5	1.5
PCB 153	2,2′,4,4′,5,5′	6	1	2	3.5	4	4	4.5	9	2.5	3	18	1	2
PCB 180	2,2′,3,4,4′,5,5′	1.5	<0.2	<0.2	≤0.5	1	1	≤0.5	3	≤0.5	≤0.5	5.5	≤0.2	≤0.4
PCB (Σ7) (c)		54	12	48	78	51	78	85	65	34	39	96	13	21
total PCB (d)		214	48	190	313	202	312	341	261	136	157	385	52	84

(a) ranges of mean deviation of mean values: *mean ≤1 pg/m^3: ≥20 %; mean <10 pg/m^3*: 8-10%; *mean >10 pg/m^3*: 3-7%

(b) PCB 138 includes PCB 163, which contributes to about 16% to the peak of PCB 138 in the technical mixture Aroclor 1254 (21)

(c) Σ7 includes the seven indicator PCBs: 28, 52, 101, 118, 138, 153, 180; if values were below limit of detection (LOD), 50% of LOD are included in the sum

(d) total PCB = (Σ7) x 4

(e) not determined

Different studies have been previously carried out to characterize the pattern of polychlorinated biphenyls (PCB) in various matrices by a principal component analysis (PCA) and by the soft independent modelling of class analogy (SIMCA), which is one of several linear cluster analysis techniques[15–19].

Three different approaches of pattern classification are applied here to characterize the PCB pattern in the marine air samples: a congener ratio correlation, the similarity index, which was calculated by two different algorithms, and the principal component analysis. In addition to comparing the results of these three approaches we tried to elaborate to what extent the seven indicator PCB congeners PCBs 28, 52, 101, 118, 138, 153 and 180 are representative of PCB occurrence, or whether more congeners have to be used for such a pattern classification.

EXPERIMENTAL SECTION

High volume air samples (500–1000 m^3) were collected using pre-cleaned silica gel as adsorbent during a north/south cruise on the german research vessel "Polarstern" (cruise ANT IX/1) across the Atlantic Ocean from Germany to Chile in fall 1990 (Figure 2: samples 1–11). In addition two air samples were collected in March 1992 on the Capo Verde islands in the Trade Wind region of the northern Atlantic Ocean (Figure 2: samples 13 and 14). The details of the sampling procedure, the meteorological and hydrospheric parameters related to the samples and the sample preparation steps are given in reference 20. The sampling locations and the results are summarized in Table 1[20].

In addition, the PCB pattern of continental air samples from the Great Lakes district in the US (Green Bay, Lake Michigan)[22], from Ontario[23] and from Ulm, Southern Germany[24] were included in the pattern classification (Table 2). From these studies only the seven indicator congeners PCB 28, 52, 101, 118, 138, 153 and 180 are taken into consideration. Partly, values for some of these congeners were reported as sums of groups of congeners. In these cases we corrected the portion of these congeners in the sum as they occur in the most likely technical PCB mixture, which may underly the observed PCB patterns in air.

DATA SET TREATMENT

The indicator congener ratio classification

As a first approach we correlated the ratios of the congeners pentachlorobiphenyl PCB 101 (2,2′,4,5,5′-Cl_5B) to trichlorobiphenyl PCB 28 (2,4,4′-Cl_3B) and tetrachlorobiphenyl PCB 52 (2,2′,5,5′-Cl_4B) to hexachlorobiphenyl PCB 153 (2,2′,4,4′,5,5′-Cl_6B) of the air samples. The four congeners are major and representative components in the technical PCB mixtures of a defined mean degree of chlorination[25,26]: PCB 28 is one of the most important congeners in the technical mixtures containing 21% chlorine (Cl), PCB 52 has a high portion in those mixtures containing 42% Cl, PCB 101 has the highest portion in the mixtures with 54% Cl

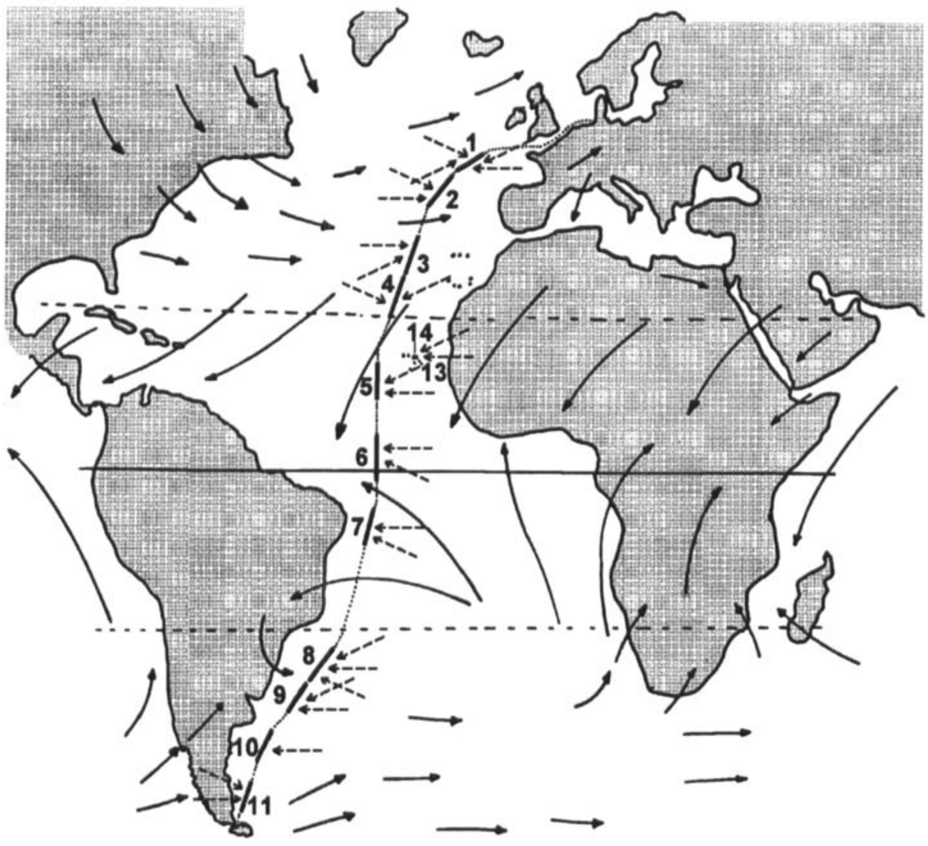

Figure 2 Air sampling locations on the cruise ANT IX/1 of RV "Polarstern" from Germany to Chile (numbers 1–11) and on the Capo Verde Islands (numbers 13 and 14). The actual wind directions during sampling are marked with dotted arrows. In addition, the main tropospheric air movements as part of the global circulation are indicated by strong lines.

and PCB 153 is the most abundant congener in the mixtures with 60% Cl. Therefore they can be taken to characterize an input of such technical PCB mixtures. The PCBs 28 and 52 are increased in marine air, PCB 101 is dominant in all marine air samples and PCB 153 is clearly associated with terrestrian air samples collected in central Europe (Table 2).

We used a similar approach to measure the extent of photolysis of PCB congeners in the air samples by correlating the mono-ortho substitued (PCBs 28, 31, 118) to the trio-ortho substituted congeners (PCBs 149, 151)[27]. Both groups of congeners differ significantly in their photolysis rates and characterize therefore this degradation reaction.

Table 2 Concentrations of the seven indicator PCB congeners in air samples from different locations (all values in pg/m^3)

Sample No.	*15*	*16*	*17*	*18*	*19*	*20*	
Location *latitude, longitude*	*Green Bay, Lake Michigan* *45°N, 87°W*	*Green Bay, Lake Michigan* *45°N, 87°W*	*Green Bay, Lake Michigan* *45°N, 87°W*	*Green Bay, Lake Michigan* *45°N, 87°W*	*Green Bay, Lake Michigan* *45°N, 87°W*	*Green Bay, Lake Michigan* *45°N, 87°W*	*O* *40°*
code in ref.	*Northern Bay* *(a)* *mean values over 5 samples*	*Central Bay* *(a)* *mean values over 6 samples*	*Southern Bay* *(a)* *mean values over 9 samples*	*UWGB* *(a)* *mean values over 25 samples*	*PEN* *(a)* *mean values over 6 samples*	*FAY* *(a)* *mean values over 4 samples*	*mean v* *143*
PCB 28	26.8 (d)	29.7 (d)	115.5 (d)	26.5 (d)	32.3 (d)	11.6 (d)	
PCB 52	19.6	22.1	69.5	17.6	18.6	20.5	
PCB 101	9.3	10.8	20.2	10.2	9.1	15.8	
PCB 118	2.7	3.4	7.0	2.3	3.8	3.8	
PCB 138	4.4 (e)	4.6 (e)	7.7 (e)	4.6 (e)	2.1 (e)	6.4 (e)	2
PCB 153	3.7 (f)	3.6 (f)	7.1 (f)	4.3 (f)	4.0 (f)	5.3 (f)	
PCB 180	2.1	1.2	3.9	2.5	1.1	4.3	

Sample No.	*22*	*23*	*24*	*25*	*26*	*27*
Location *latitude, longitude*	*Ulm, Germany* *48°N, 10°E*	*Ulm, Germany* *48°N, 10°E*	*Ulm, Germany* *48°N, 10°E*	*Ulm, Germany* *48°N, 10°E*	*Ulm, Germany* *48°N, 10°E*	*Ulm, Germany* *48°N, 10°E*
code in ref.	*A1* *(c)*	*A2* *(c)*	*A3* *(c)*	*B1* *(c)*	*B2* *(c)*	*B3* *(c)*
PCB 28	36	68	19	5	4	5
PCB 52	230	88	23	7	7	9
PCB 101	230	96	24	27	10	10
PCB 118	68	29	6	7	3	2
PCB 138	110 (e)	52 (e)	12 (e)	15 (e)	7 (e)	6 (e)
PCB 153	130	73	16	21	8	7
PCB 180	27	13	2	2	8	1

(a) ref. (22)

(b) ref. (23)

(c) ref. (24)

(d) values given in ref. (22) for PCB 28 include PCB 31; a portion of 58% is taken as the value for PCB 28, according the composition of Aroclor 1016 and Arocl as listed in ref. (26)

(e) the values for PCB 138 include PCB 163, as the stationary phases used for quantitation were of the 95% methyl, 5% phenyl type, which don't separate these two cong

(f) values given in ref. (22) for PCB 153 include PCB 105 and PCB 132; a portion of 48% is taken as the value for PCB 153, according the composition of Aroclo listed in ref. (26)

The similarity index classification

The similarity index (SI) was calculated by two algorithms. Both methods classify a pattern with respect to a reference pattern, which has to be set. The PCB pattern of air sample 3, collected over the North Atlantic (32°N 24°W)—Table 1—, was chosen as a reference for marine air, while the PCB pattern of air sample 25 (Table 2) from central Europe collected in a rural area in the vicinity of the city of Ulm[24] was taken as a reference for a source-distant terrestrian PCB pattern in air.

The first approach to calculate the similarity index is known as the correlation coefficient (equation (1)). It will be refered as method CC:

$$SI = \sum_i (c_{nx}^i \, c_{ny}^1) \,/\, \sqrt{\sum_i (c_{nx}^i)^2} \, \sqrt{\sum_i (c_{ny}^i)^2} \tag{1}$$

x: reference sample; y: training sample; c_{nx}, c_{ny}: normalized concentration of congener i

In a first step only the seven indicator PCB congeners PCBs 28, 52, 101, 118, 138, 153 and 180 were taken into consideration. These congeners are often reported in environmental samples by other authors because they are the major compounds of the technical PCB mixtures and reflect the various degrees of chlorination. In this case the data sets were normalized to the sum of seven congeners, having the value 1. If the statistical treatment was extended to all 14 quantified congeners the normalization was made over the sum of 14 congeners. In this case four out of 15 marine air samples could not be taken into consideration, because some congeners could not be quantified in these samples due to a coelution with other unidentified compounds.

As the normalized concentrations of the congeners varied within one order of magnitude, no transformation of the data was carried out.

A SI value of 0.85 is set for high similarity, whereas samples with an index >0.95 are defined as having a very high similarity. This method has formerly been applied for the pattern analysis of PCB pollution[28].

Another algorithm to calculate a similarity index (equation (2)) is described by de Alencastro *et al.*[29]. This algorithm makes a different normalization procedure of the data as compared to the correlation coefficient. This approach will be refered as method AL:

$$SI = \sum_i \left(\frac{c_x^i}{\sum_i (c_x^i)} \bullet s_i \right) \tag{2}$$

$$s_i = c_{ny}^i \,/\, c_x^i, \; if \; (c_{ny}^i \le c_x^i) \tag{2a}$$

$$s_i = c_x^i \,/\, c_{ny}^i, \; if \; (c_{ny}^i > c_x^i) \tag{2b}$$

x: reference sample; y: training sample; c_x, c_y: not normalized concentration of congener i; c_{nx}, c_{ny}: normalized concentration of congener i

The principal component analysis classification

The degree of similarity of the PCB pattern is more clearly and independently elaborated by a PCA approach. The calculations were carried out with a public domain software[30]. The normalized values of the seven indicator congeners and in a second run of all fourteen congeners were used to calculate the correlation matrix. The degree of similarity of various patterns is given by the distance of the data points projected onto the plane defined by the first two principal components.

RESULTS

On the basis of accurate and relevant data sets one can correlate different sources of emissions to a given immission. One can also quantify the changes of patterns of pollutants as the result of abiotic or biotic transformations indicated by their decreasing similarity. The same approach can be used to describe the results of the geophysical transport phenomena in long-range transport of chemical compounds in the atmosphere and in the oceans. Changes

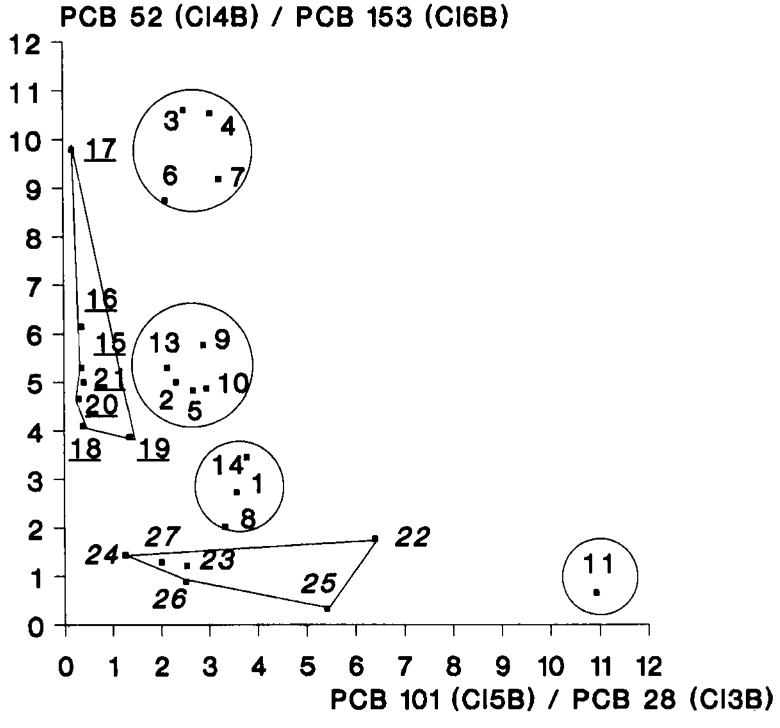

Figure 3 Correlation of the ratios of PCB 101 to PCB 28 and PCB 52 to PCB 153 in the air samples. The origin of the samples is indicated by numbers (see Tables 1 and 2). Underlined numbers indicate samples from North America (15–21), italic numbers indicate samples from Germany (22–27).

in the similarity can thus help firstly to categorize and secondly to quantify changes in the composition of complex mixtures in air.

The indicator congener ratio classification

The results are presented in Figure 3. The marine air samples 3, 4, 6 and 7 and the marine air samples 2, 5, 9, 10 and 13 form two groups. The marine air samples 1, 8 and 14 can be taken as a third cluster, leaving the sample 11 way out. The continental air samples from Europe and the Great Lakes region do not overlap. The air samples 15–21 from the USA and Canada form a group which is indicative of a dominance of the lower chlorinated biphenyls as given by low values on the x-axis and higher values on the y-axis. The contrary is observed for the air samples 22–27 from central Europe . A simple explanation would be a difference in the input of the PCB types used in the past and now in both regions (see 5.3).

Table 3 Similarity-indices of PCB pattern in marine air samples

	reference: sample 3				*reference: sample 25*	
Sample No.	*SI CC (7 congeners)*	*SI CC (14 congeners)*	*SIAL (7 congeners)*	*SI AL (14 congeners)*	*SICC (7 congeners)*	*SI AL (7 congeners)*
3	1	1	1	1	0.63	0.47
6	1.00	0.99	0.93	0.90	0.62	0.47
4	1.00	(a)	0.91	(a)	0.62	0.48
9	1.00	0.99	0.89	0.87	0.68	0.53
7	0.99	(a)	0.89	(a)	0.61	0.48
5	0.99	0.99	0.86	0.86	0.72	0.56
13	0.99	0.99	0.86	0.86	0.67	0.51
10	0.99	(a)	0.85	(a)	0.73	0.58
2	0.99	0.98	0.84	0.80	0.68	0.52
14	0.97	0.96	0.78	0.75	0.79	0.65
1	0.94	0.92	0.70	0.70	0.83	0.68
8	0.90	0.90	0.65	0.69	0.86	0.69
11	0.68	0.67	0.47	0.44	0.98	0.80
20	0.95	(a)	0.69	(a)	0.74	0.51
21	0.85	(a)	0.59	(a)	0.53	0.36
16	0.79	(a)	0.56	(a)	0.50	0.35
15	0.78	(a)	0.55	(a)	0.50	0.34
18	0.77	(a)	0.53	(a)	0.53	0.37
17	0.68	(a)	0.51	(a)	0.36	0.23
19	0.71	(a)	0.50	(a)	0.45	0.32
27	0.86	(a)	0.64	(a)	0.91	0.71
22	0.90	(a)	0.63	(a)	0.88	0.73
24	0.87	(a)	0.59	(a)	0.86	0.64
23	0.85	(a)	0.57	(a)	0.89	0.67
26	0.71	(a)	0.48	(a)	0.89	0.69
25	0.63	(a)	0.47	(a)	1	1

(a) no value; not all 14 congeners have been determined

The similarity index classification

The results of calculating the similarity index of air samples 1–27 with sample 3 and sample 25, respectively, as the reference using equations (1) and (2) are presented in Table 3.

Although the two methods qualitatively agree in their results, the SI-values obtained by method AL differ among each other more than the correlation coefficients. Especially when the patterns have a very high similarity (SI > 0.95, method CC; SI > 0.85, method AL), slight differences are indicated more clearly by method AL than by the correlation coefficient. The correlation coefficient (equation (1)) can be helpful to quantify on a course level the dissimilarities, whereas the AL-algorithm (equation (2)) allows a more detailed differentiation of rather similar sets of data.

According to the method AL the air samples 2, 4, 5, 6, 7, 9, 10 and 13 have a very high similarity to the marine air reference sample 3, whereas the samples 1, 8, 11 and 14 differ more or less in their similarity indices to this reference (Table 3). If the PCB pattern of the continental air sample 25 is taken as a reference, a reversed classification in terms of the SI values is observed (Table 3).

If all 14 PCB congeners instead of only the seven indicator congeners are taken into account, the results are not significantly different (Table 3). Again the samples 1, 8, 11 and 14 clearly differ in their similarity indices from the pattern of reference sample 3. The seven indicator congeners obviously provide already the basic information not only for a discussion of the origin of polychlorinated biphenyls but also for the comparison of PCB patterns of air samples. Alencastro *et al.*[29] could prove the same for PCBs in wastewater from treatment plants.

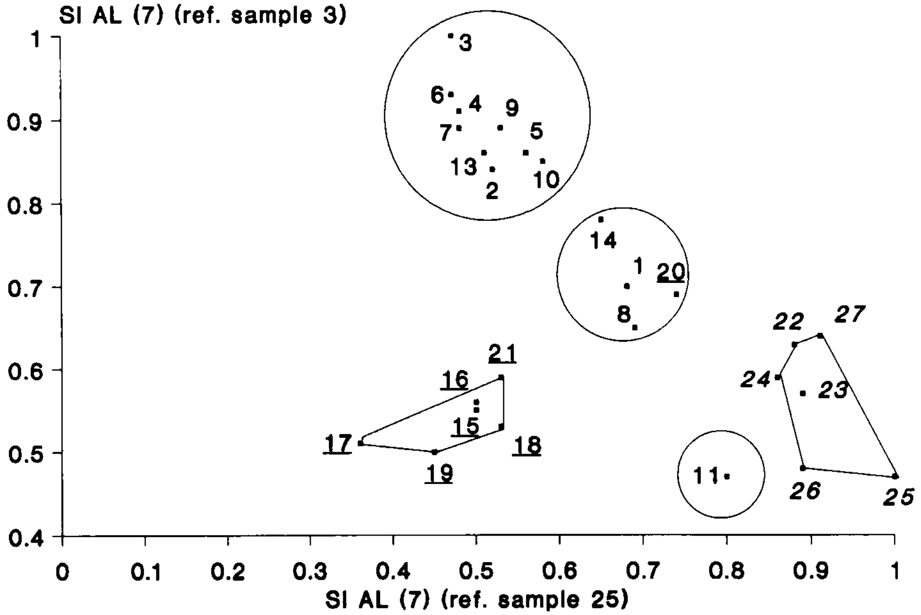

Figure 4 Correlation of the similarity-indices (calculated from the seven indicator congeners with method AL) of the PCB pattern of the air samples with respect to reference sample 3 and reference sample 25.

Figure 4 depicts the correlation of the SI values obtained by method AL (equation (2)) based on seven congeners using sample 3 (marine clean air) and sample 25 (european continental air) as references. The clustering of the air samples is rather similar as obtained by the indicator congener ratio approach. This underlines that the levels of the PCBs 28, 52, 101 and 153 characterize to a high extent the observed PCB pattern in air.

The principal component analysis classification

If the calculations for the PCA are carried out with only the seven indicator congeners, almost the whole variation (>94%) in the data set given by the marine air samples is described by the first two principal components (PC 1: 77.7%, PC 2: 16.4%). The resulting data points are projected into the plane defined by these two principle component axis (Figure 5). The contributions of the first two principal components (PC 1: 77.1%, PC 2: 11.7%) and the relative positioning of the data points does not change distinctly, if all fourteen PCB congeners are taken as the data basis (Figure 6).

With the PCA classification the samples 1, 8, 11 and 14 can be distinguished again from the samples 2, 3, 4, 5, 6, 7, 9, 10 and 13.

We also compared the PCB patterns of the marine air samples with the patterns of terrestrian air samples originating from North America (samples 15–21) and Germany (samples 22–27). Figure 7 depicts the positioning of the data points based on the seven indicator congeners (Tables 1 and 2) in the PC1-PC2-plane. The marine air samples 2, 3, 4,

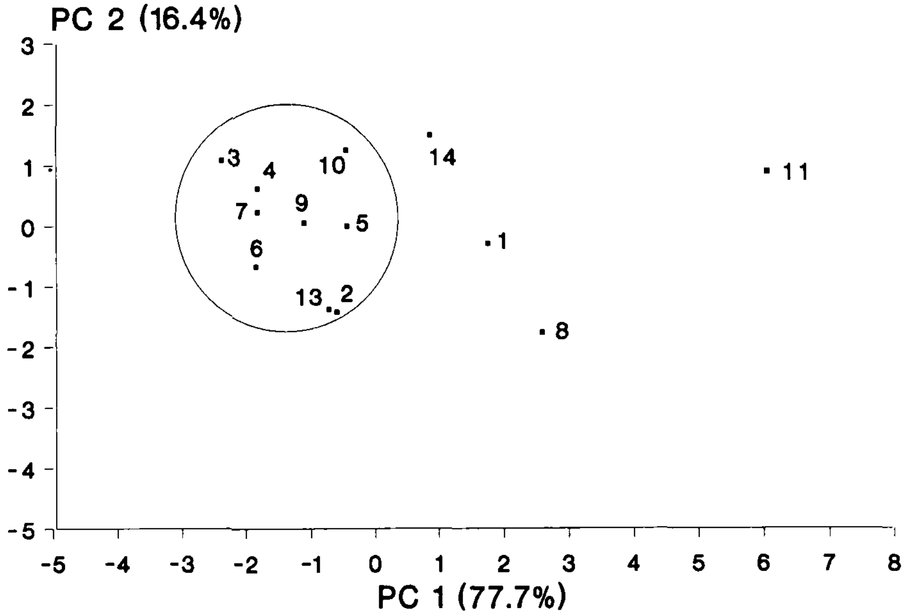

Figure 5 Principal component analysis of the PCB patterns (based on 7 indicator congeners) of the marine air samples: the data points were projected into the plane defined by the first two principal component axis.

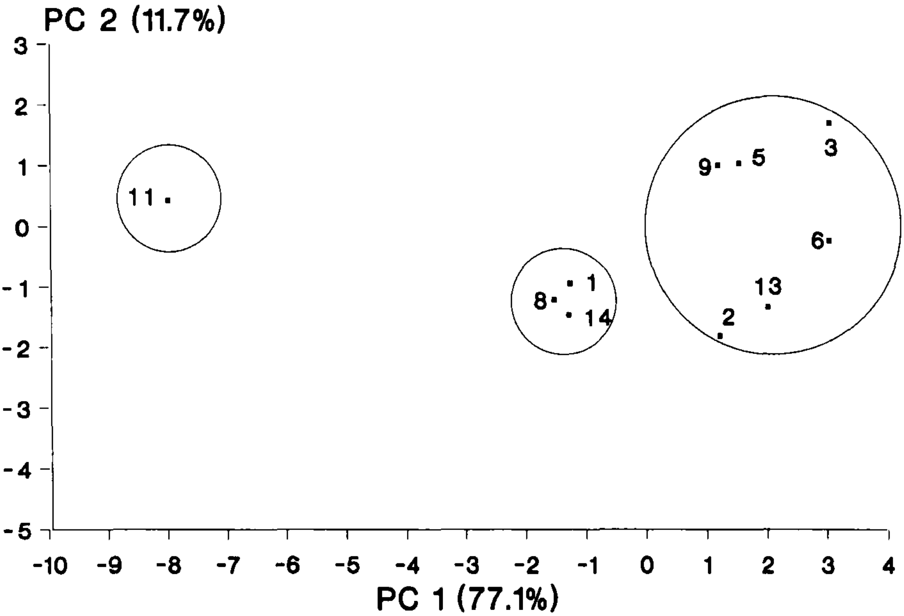

Figure 6 Principal component analysis of the PCB patterns (based on 14 congeners) of the marine air samples: the data points were projected into the plane defined by the first two principal component axis.

5, 6, 7, 9, 10 and 13 again form a cluster, which is clearly distant from the terrestrian air samples. The marine air samples 1, 8 and 14 are partly similar to terrestrian air samples from Europe. The marine air sample 11, collected near the coast of South Patagonia, is strongly distinct from the other marine air samples, as already indicated by the congener ratio approach and the similarity index.

The above results indicate that a marine clean-air PCB pattern exists—represented by the air samples 2, 3, 4, 5, 6, 7, 9, 10, 13—, which extends over the North- and the South Atlantic between 40°N and 40°S. The PCB patterns of the marine air samples 1, 8, 11 and 14 clearly differ from this marine clean-air pattern. These air parcels apparently are partly influenced by continental air masses.

The change of the PCB pattern at 46°N 12°W (sample 1) can definitely be traced back to the specific meteorological situation during sampling: an extended high pressure system over Europe led to the input of continental air masses as seen by the easterly wind at sampling route 1 (Figure 2). A high content of the insecticide γ-HCH[27], also determined in the sampling region of sample 1, is a further indicator of continental air masses. Another region in the northern hemisphere, where continental air masses were encountered was around 8°N and 12°N. These air masses presumably coming from North-West Africa (Figure 2) were indicated by elevated levels of the cyclodiene insecticide endosulfan[27], which is applied in regions affected by the Tse-Tse fly. However these continental air masses were not indicated by a clear change of the PCB pattern. Only the air sample 14, taken on the Capo Verde islands, differs slightly in its PCB pattern from the other air samples in this region. The

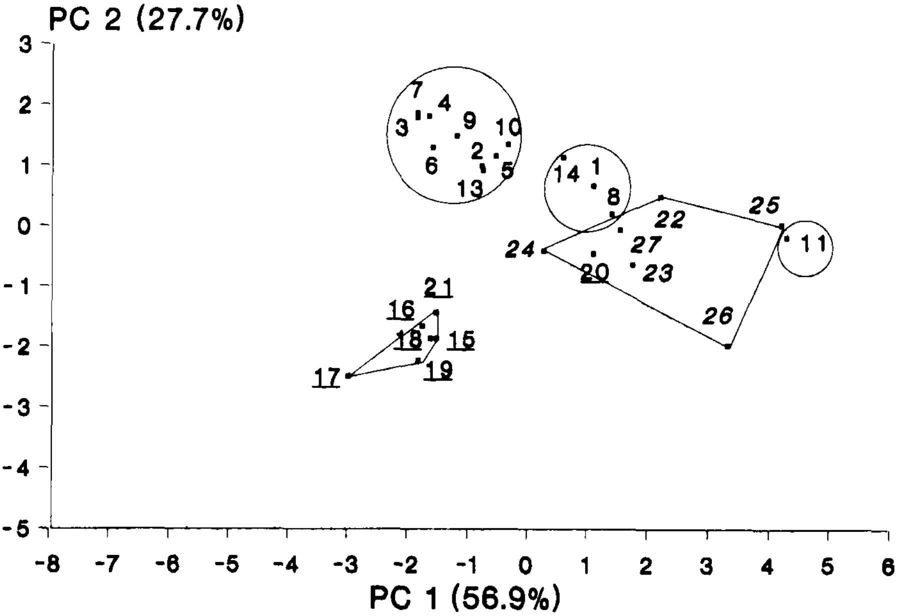

Figure 7 Principal component analysis of the PCB patterns (based on 7 indicator congeners) of the marine and the continental air samples: the data points were projected into the plane defined by the first two principal component axis. Underlined numbers indicate samples from North America (15–21), italic numbers indicate samples from Germany (22–27).

change of the PCB pattern in air sample 8 in the South Atlantic also should have their origin in an input of continental air masses. Strong westerly winds in this region during the days before sampling[31] support this conclusion, despite the easterly winds at sampling position 8 (Figure 2). The air sample 11 (46°S 60°W) was influenced by air masses from South Patagonia (Figure 2). The oil hauling plants and other industries at Patagonia could be the reason for the elevated levels of the higher chlorinated congeners (Table 2), which caused the strong change of the PCB pattern. A rise of the contents of hexachlorobenzene in the samples 8 and 11 was also observed[27].

DISCUSSION

The PCB congener profile of the marine clean-air pattern

Figure 8 depicts a typical marine clean-air pattern of the PCBs and other trace constituents detected by electron capture detection (ECD) (sample 3), as compared to a sample of marine air (sample 11) (Figure 9), which is significantly influenced by an input of continental air masses.

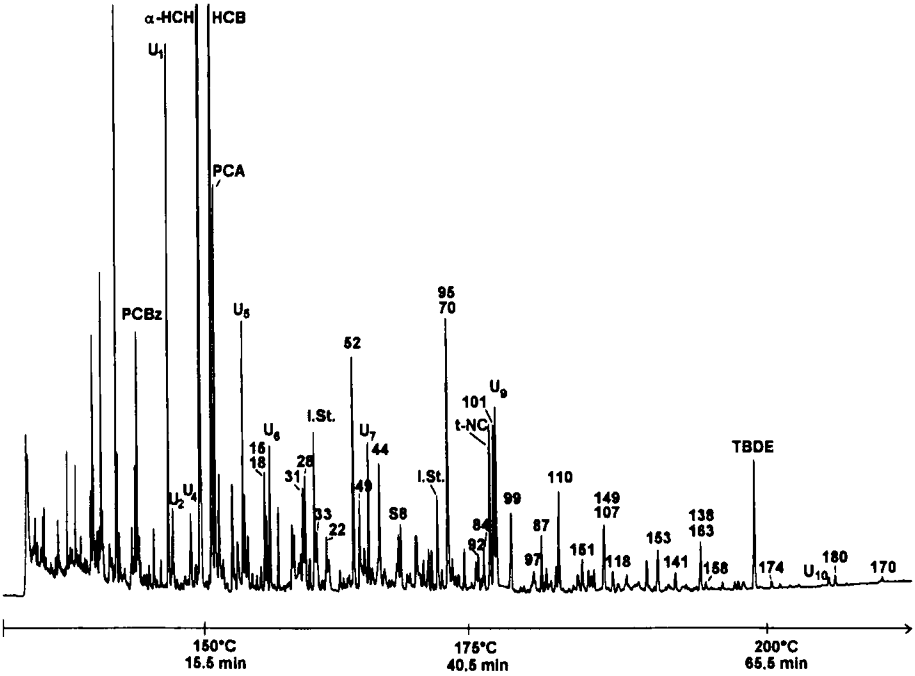

Figure 8 Capillary gas chromatogramm (column: CP-Sil 8 + 10% C 18), detected by ECD, of marine air sample 3 (32°N, 24°W), aliquot: 7.5 m^3. In addition to the signals of the PCB congeners (marked by the PCB-numbers), peaks of other major compounds are marked: PCBz (pentachlorobenzene), PCA (pentachloroanisole), HCB (hexachlorobenzene), S8 (sulfur), I.St. (internal standard), t-NC (trans-Nonachlor), TBDE (tetrabromodiphenylether), U (unidentified compounds).

A comparison of the congener levels in the marine clean-air reference pattern (sample 3) and the PCB pattern of air samples influenced by continental air (sample 1 and 11) (Figure 10) reveals, that the concentrations of higher chlorinated congeners in marine clean-air are decreased according to their decreasing vapor pressure[32] as reported before[33,34]. This decrease could be a result of the selective adsorption of higher chlorinated congeners to atmospheric particles due to their lower vapour pressures and the output of these particles primarily by wet deposition. It follows, that the pattern in air with increasing distance from the source is more and more enriched with the lower chlorinated congeners.

The other possibility is the output by gas dry deposition. Due to the trend of the gas/water partition coefficients K_{gw} towards lower values with increasing degree of chlorination[35], the rate constant of the output from the air by gas dry deposition is lower for the higher chlorinated congeners. This means, that the gas/water equilibrium of the lower chlorinated congeners adjusts more rapidly leading to a greater flux of these congeners across the air/sea boundary layer at source-near locations[14,36]. It would at least temporarily enhance the relative portion of the higher chlorinated congeners in air as compared to source-nearer air masses. Sample 11 might be be an example for this effect.

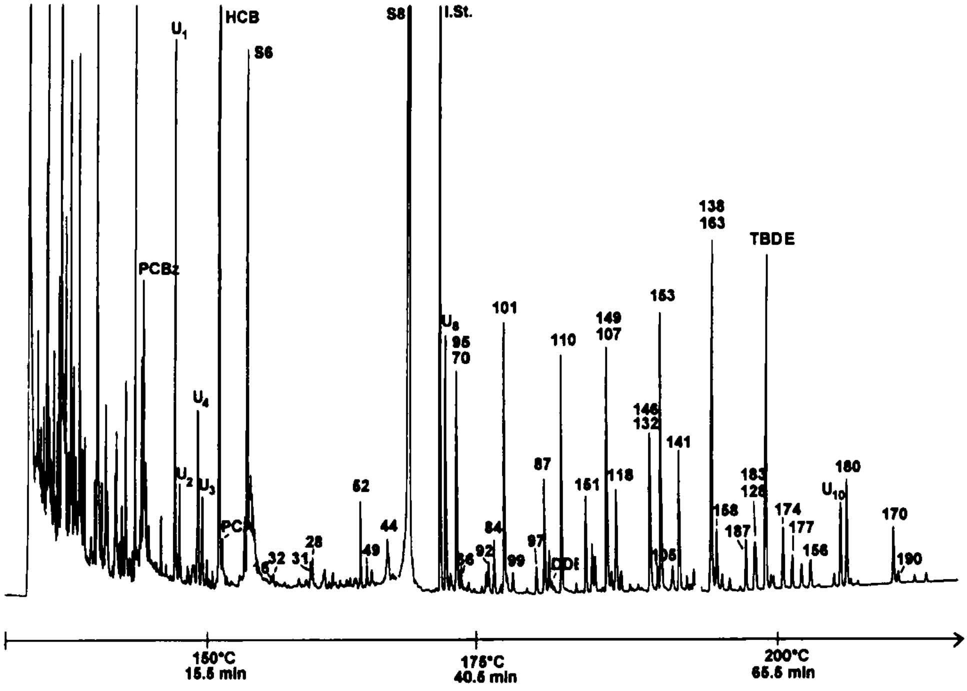

Figure 9 Capillary gas chromatogramm (column: CP-Sil 8 + 10% C 18), detected by ECD, of marine air sample 11 (46°N, 59°W), aliquot: 5 m^3. In addition to the signals of the PCB congeners (marked by the PCB-numbers), peaks of other major compounds are marked: PCBz (pentachlorobenzene), PCA (pentachloroanisole), HCB (hexachlorobenzene), S6 and S8 (sulfur), I.St. (internal standard), DDE (4,4'-DDE), TBDE (tetrabromodiphenylether), U (unidentified compounds).

For source distant air another effect appears to dominate. The lower K_{gw} values of the higher chlorinated congeners lead to a greater absorption of these congeners by the surface water, until the distribution equilibrium between surface water and the lower troposphere is achieved. As a result, the equilibrium will favour the occurrence of the lower chlorinated congeners in air. As a third possibility dilution effects by air masses originally lower in or preferably depleted of higher chlorinated congeners (input pattern, photolysis in air, adsorption effects in water) could be the reason for the changes of the PCB pattern.

The south-north course of the levels of PCBs and the pattern type in marine air

Figure 11 summarizes the meridional course of the PCB levels in marine air given by the sum of seven indicator congeners (Table 1) and the variation of the pattern in air indicated by the similarity index calculated by method AL (seven congeners) against reference sample 3. The PCB pattern in air is only partly dependent from the PCB level in air. The reason is that the sources of PCBs to the Atlantic Ocean atmosphere have a quite distinct PCB pattern.

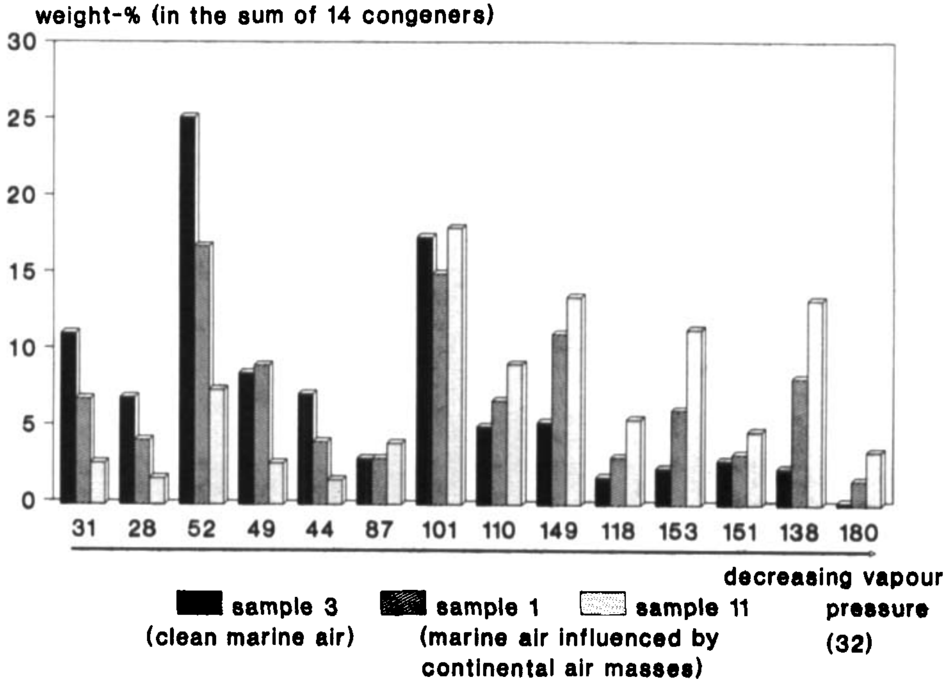

Figure 10 Comparison of the PCB patterns of a marine clean-air sample and air samples influenced by continental air masses. The PCB congeners are ordered by decreasing vapour pressures (from ref. 32).

One source is the input of air masses from continental areas having a pattern with increased concentrations of the higher chlorinated congeners. This leads to the observed pattern changes and rather high PCB contents in the air samples 1, 8 and 11.

The constancy of the PCB pattern in the marine clean-air samples over the Atlantic between 40° North and 40°South inspite changing absolute concentrations suggests that the levels of the single congeners in marine clean-air are determined by a process, which is common to all congeners and which also is congener specific. Such a process is an equilibrium between the atmosphere and the upper water layer. The surface water acts as both the sink and the source for the PCB congeners.

The parameter regulating the strength of this source is the water temperature by influencing the magnitude of the gas/water partition coefficient K_{gw} and the active PCB concentration. The correlation of the levels of the lower chlorinated congeners in air of the South Atlantic with the water temperature and thus with the temperature depending gas/water partition coefficient K_{gw} supports this assumption[20]. The constancy of the PCB pattern in the air samples between 40° North and 40° South furthermore suggests, that an air/water equilibrium does not alter the PCB pattern. This requests that the temperature dependance of K_{gw} within the considered temperature range (surface water: about 14°C at sample 10 to about 29°C at sample 7) must be in the same range for all the considered PCB congeners. Theoretical considerations[37] and experimental results[38] support this conclusion. The latter

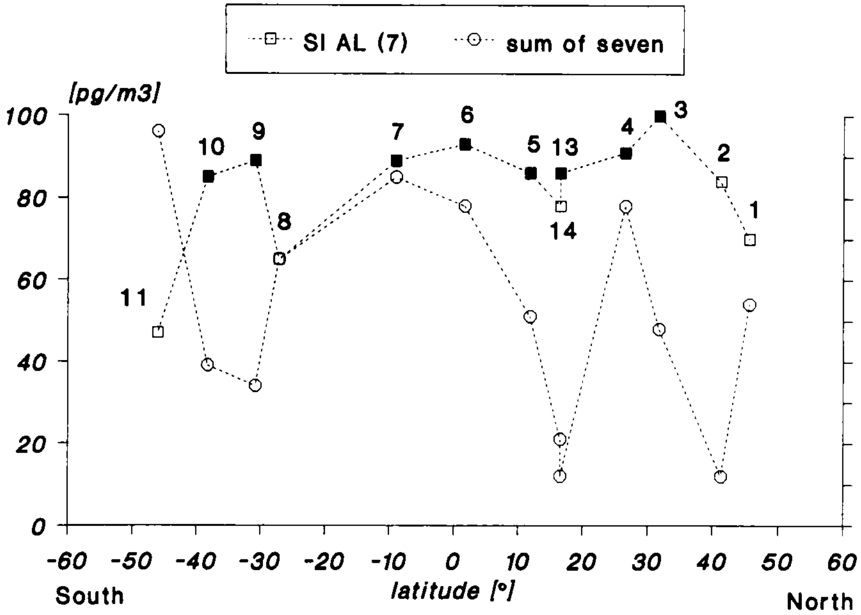

Figure 11 Level of the sum of the seven indicator congeners in air samples 1–14 from the tropospheric boundary layer of the Atlantic Ocean. In addition the similarity indices of the samples with respect to reference sample 3 (calculated with method AL, based on 7 indicator congeners) are given. Filled boxes indicate samples with SI-values ≥0.85.

study reports a difference of only about 10% for the temperature dependance of K_{gw} of the technical PCB mixtures Aroclor 1242 (42% Cl) and 1260 (60% Cl) in the temperature range discussed here.

In ocean areas with higher water temperatures the gas/water equilibrium is strongly shifted to the gaseous side by the enhanced evaporation of PCBs. The air samples 3, 4, 6 and 7 originate from subtropical and tropical areas, they therefore give increased values for the sum of PCBs. The air samples 5, 13 and 14 from warm water regions giving relatively low PCB levels are probably "diluted" air masses with low PCB levels originating from North-West Africa. Easterly winds were prevailing during the sampling (Figure 2). The extended desert regions in North-West Africa with "burnt out" descending air of the subtropical high system and only a few isolated cities as point sources for PCBs could be the reason for these low level PCB air masses. Unknown variables in the context are the PCB content of the upwelling deep sea water at the west coast of Africa and the "relaxation time" of the air/surface water equilibrium. The constancy of the marine clean-air PCB pattern proves furthermore that a slow but preferential output of higher chlorinated PCBs via particles during long-range transport of the PCBs in air is unlikely. The decrease of the higher chlorinated congeners—present in increased amounts only when the marine air is influenced by a substantial input of continental air masses—must be a relatively fast process and of regional dimensions only.

Comparison of PCBs in continental air and marine air

While the PCB pattern in marine clean-air is rather constant, the pattern in continental air samples change stronger in samples even from the same locations (Figure 7). More surprizing is a general difference between the patterns collected in North America and Germany. The reason is most probably the difference in the production and thus use patterns of the technical PCB mixtures. The production of PCBs in U.S.A. was dominated by mixtures with the lower chlorinated congeners, like Aroclor 1242 and since 1972 like Aroclor 1016[39]. This should lead to higher values of dichlorinated and trichlorinated congeners in the samples from North America, as indicated by rather high contents of PCBs 18 and 28[22,23,40]. In 1977 the mostly used technical mixtures in Germany contained 54% weight-% chlorine, but still in 1983 the higher chlorinated congeners were applied at a considerable amount[41]. Air samples from Europe often contained a substantial portion of the higher chlorinated congeners[24,42]. The PCB pattern in air sample 1 describing air masses originating from Europe indicates this possible difference in the application pattern. The greater similarity of the PCB patterns in air samples 8 and 11, apparently influenced by continental air masses from South America, to the patterns of the European air samples also indicates that in these regions technical PCB mixtures with greater portions of the higher chlorinated congeners are applied.

CONCLUSIONS

Three methods of classification of the PCB pattern in air samples with increasing sophistication in the mathematics including the principal component analysis (PCA) gave basically the same results. There exists a typical marine clean-air PCB pattern which can be differentiated from continental air patterns observed in central Europe and the Great Lakes region in North America. The constancy of the marine clean-air pattern between 40° North and 40° South of the Atlantic Ocean and the independence of the pattern from the PCB levels in air leads to the conclusion that the pattern is regulated by a common process which will be the surface-water/air exchange. While in the PCB pattern in the air over the Great Lakes an elevated level of lower chlorinated PCBs is a feature, continental air from central Europe is characterized by increased levels of the higher chlorinated PCBs.

Acknowledgements

This work has been financially supported by the German Science Foundation (DFG-Ba 371 11-2).

We gratefully acknowledge the support by the Government of the Republic of Capo Verde and its Embassy in Germany. We thank the Captain and the Crew of the "FS Polarstern" for their support of our work during the cruises ANT IX/1 and ANT IX/4. We thank the "Alfred-Wegener-Institut für Meeres-und Polarforschung", Bremerhaven, Germany, for the support. Support for our expedition to Capo Verde by the airline "Condor" is also acknowledged.

References

1. B.R. Kowalski (ed.), *Chemometrics, Theory and Application* (ACS Symposium Series, No. 52, American Chemical Society, Washington, 1977).
2. H. Späth (ed.), *Cluster Analyse—Algorithmen zur Objektklassifizierung und Datenreduktion* (R. Oldenburg Verlag, München, 1977). *Fallstudien Cluster Analysen* (R. Oldenburg Verlag, München, 1977).
3. C. Albano, W. Dunn, U. Edlund, E. Johansson, B. Norden, M. Sjöström, and S. Wold, *Anal. Chim. Acta*, **103**, 429–443, (1978).
4. S. Wold, C. Albano, W.J. Dunn, U. Edlund, K. Esbensen, P. Geladi, S. Hellberg, E. Johansson, W. Lindberg, and M. Sjöström, In: *Chemometrics, Mathematics and Statistics in Chemistry* (B.R. Kowalski, ed.) (D. Reidel, Dordrecht, 1984), pp. 17–95
5. D.L. Massart, and L. Kaufman (eds.), *The interpretation of analytical chemical data by the use of cluster analysis* (Chemical Analysis, Vol. 65) (J. Wiley, New York, 1983).
6. D.L. Massart, B.G.M. Vandeginste, S.N. Deming, Y. Michotte, and L. Kaufman (eds.), *Chemometrics: A Textbook* (Data Handling in Science and Technology, Vol. 2) (Elsevier, Amsterdam, 1988).
7. J. Devillers, and W. Karcher (eds.) *Applied Multivariate Analysis in SAR and Environmental Studies* (Kluwer Academic, Dordrecht, 1991).
8. M.H. Feinberg, and C.J. Ducauze, *Fresenius J. Anal. Chem.*, **339**, 604–607, (1991).
9. K. Ballschmiter, *Angew. Chem.* **104**, 501–528, (1992), *Angew. Chem. Int. Ed. Engl.*, **31**, 487–515 (1992)
10. I.M. Czuczwa, and R. Hites, *Environ. Sci. Technol.*, **20**, 195–200 (1986)
11. R.M. Smith, P.W. O'Keefe, K.M. Aldons, H. Valente, S.P. Connor, and R.J. Donelly, *Environ. Sci. Technol.*, **24**, 1502, (1990).
12. S. Marklund, M. Tykslind, R. Andersson, K. Ljung, and C. Rappe, *Chemosphere*, **23**, 1359–1364, (1991)
13. M. Tykslind, J. Füngmark, S. Marklund, A. Lindskog, L. Thaning, and C. Rappe, submitted for publication.
14. H. Iwata, S. Tanabe, N. Sakai, and R. Tatsukawa, *Environ. Sci. Technol.*, **27**, 1080–1098, (1993).
15. T.R. Schwartz, D.L. Stalling, and C.L. Rice, *Environ. Sci. Technol.*, **21**, 72–76, (1987).
16. T.R. Schwartz, and D.L. Stalling, *Arch. Environ. Cont. Tox.*, **20**, 183–199, (1991).
17. F.I. Onuska, and S. Davies, *Intern. J. Environ. Anal. Chem.*, **43**, 137–150, (1991).
18. E. Storr-Hansen, and H. Spliid, *Arch. Environ. Cont. Tox.*, **24**, 44–59, (1993)
19. D.C.G. Muir, M.D. Segstro, P.M. Welbourn, D. Toom, S.J. Eisenreich, C.R. Macdonald, and D.M. Whelpdale, *Environ. Sci. Technol.*, **27**, 1201–1210, (1993).
20. J. Schreitmüller, and K. Ballschmiter, submitted for publication.
21. J. de Boer, and Q.T. Dao, *J High Res Chrom.*, **14**, 593–596, (1991).
22. K.C. Hornbuckle, D.R. Achman, and S.J. Eisenreich, *Environ. Sci. Technol.*, **27**, 87–98, (1993).
23. R.M. Hoff, D.C.G. Muir, and N.P. Grift, *Environ. Sci. Technol.*, **26**, 266–275, (1992).
24. R. Wittlinger, and K. Ballschmiter, *Chemosphere*, **16**, 2497–2513, (1987).
25. K. Ballschmiter, In: *Analytiker Taschenbuch* (W. Fresenius, H. Günzler, W. Huber, H. Kelker, J. Lüderwald, G. Tölg, and H. Wisser, eds.) (Springer Verlag, Berlin, 1987), Vol. 7, pp. 393–432.
26. D.E. Schulz, G. Petrick, and J.C. Duinker, *Environ. Sci. Technol.*, **23**, 852–859 (1989).
27. J. Schreitmüller, and K. Ballschmiter, unpublished results.
28. H. Buchert, and K. Ballschmiter, *Fresenius Z. Anal. Chem.*, **320**, 707–709, (1985), H. Buchert, Dr. rer. nat. Thesis (University of Ulm, 1984).
29. L.F. de Alencastro, V. Prelaz, and J. Tarradellas, *Intern. J. Environ. Anal. Chem.*, **22**, 183–201, (1985).
30. G.C. Cash, and J.J. Breen, *Chemosphere*, **24**, 1607–1623, (1992).
31. Meteorological Office of RV "Polarstern": Weather Reports (1990).
32. R.C. Fischer, R. Wittlinger, and K. Ballschmiter, *Fresenius. J. Anal. Chem.*, **342**, 421–425 (1992).
33. E. Atlas, T.F. Bidleman, and C.S. Giam, In: *PCBs and the Environment* (J. S. Waid, ed.) (CRC Press, Boca Raton, 1986), Vol. I, pp. 79–100.
34. S. Tanabe, and R. Tatsukawa, In: *PCBs and the Environment* (J.S. Waid, ed.) (CRC Press, Boca Raton, 1986), Vol. I, pp. 143–161.
35. S. Brunner, E. Hornung, H. Santl, E. Wolff, O.G. Piringer, J. Altschuh, and R. Brüggemann, *Environ. Sci. Technol.*, **24**, 1751–1754, (1990).
36. D.R. Achman, K.C. Hornbuckle, and S.J. Eisenreich, *Environ. Sci. Technol.*, **27**, 75–87, (1993).
37. R.P. Schwarzenbach, P.M. Gschwend, and D.M. Imboden (eds), *Environmental Organic Chemistry*, (Wiley Interscience, New York, 1993), p. 114f.
38. L.P. Burkhard, D.E. Armstrong, and A.W. Andren, *Environ. Sci. Technol.*, **19**, 590–596, (1985).

39. P. de Voogt, and U.A.T. Brinkmann, In: *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products* (R.D. Kimbrough and A.A. Jensen, eds.) (Elsevier, Amsterdam, 1989), pp. 3–43.
40. M.H. Hermanson, and R.A. Hites, *Environ. Sci. Technol.*, **23**, 1253–1258, (1989).
41. Bundesgesundheitsamt, Umweltbundesamt, *Polychlorierte Biphenyle (PCB)* (H. Lorenz, and G. Neumaier, eds.) (MMV Medizin Verlag, Munich, 1983).
42. P. Larsson, and L. Okla, *Atmos. Environ.*, **23**, 1699–1711, (1989).