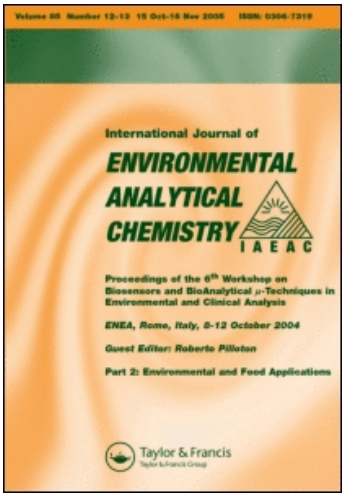

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article De Alencastro, L. F. , Prelaz, V. and Tarradellas, J.(1985) 'An Improved Quantitation Method Used to Determine the Origin of PCBs in Wastewaters: The Index of Similarity', International Journal of Environmental Analytical Chemistry, 22: 3, 183 — 201
To link to this Article: DOI: 10.1080/03067318508076421
URL: http://dx.doi.org/10.1080/03067318508076421

Intern. J. Environ. Anal. Chem., 1985, Vol. 22, pp. 183–201
0306-7319/85/2204-0183 $18.50/0

Printed in Great Britain

An Improved Quantitation Method Used to Determine the Origin of PCBs in Wastewaters: The Index of Similarity†

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(*Received March 25, 1985; in final form May 8, 1985*)

Wastewaters contain PCBs which become concentrated in the sewage sludge issuing from water treatment plants. This can create problems when sludge is used as agricultural fertilizer. The origin of these PCBs was investigated by studying the wastewaters in the sewer networks of three Swiss towns. To do this, methods of extraction and purification of the samples and chromatographic conditions were such as to obtain good resolution of the various PCBs components, despite the complexity of the matrix and the low concentration of PCBs (between 0.02 and 1.2 μg/l). Particular care was taken of the quantitative analysis stage which was carried out by pattern comparison in each sample of 36 individual monitoring components. This quantitation method allows one to follow the variations of the different types of PCBs as a function of socio-professional activities and time. A numerical representation of the notion of fingerprint of PCBs is proposed: the index of similarity. Statistical treatment of this index allows one to increase the reliability of the statements about the sources of PCBs. A practical example is presented.

KEY WORDS: Wastewater, PCBs, sludge, agricultural fertilizer, index of similarity.

†Presented at the 14th Annual Symposium on the Analytical Chemistry of Pollutants, November 21–23, 1984, Barcelona, Spain.

INTRODUCTION

In spite of numerous regulations against PCBs, sewage sludges still present, in Switzerland, relatively high concentrations of these pollutants,[1] creating an environmental risk when these sludges are utilized in agriculture.[2] This is the result of the general presence of PCBs in municipal wastewaters.[3] To reduce the presence of these pollutants it is necessary to determine their main sources in municipal sewer networks as a function of time and socio-professional activities. For this purpose, the presence of PCBs in wastewaters from sewer networks and treatment plants of some towns in Switzerland was investigated. As regards other multi-component micropollutants, for example, polychlorodibenzodioxins, the results obtained by the analytical methodology are greatly improved using a quantitation based on single components which gives a fingerprint of the pollutants and could, in some cases, allow us to determine their sources.

EXPERIMENTAL

Analytical methods

Analytical methods were previously described by de Alencastro and Tarradellas.[3] All glassware was washed with acetone and *n*-hexane. Reagents utilized were "pesticide grade". Samples were analysed as soon as possible after sampling to avoid losses by adsorption on the glass walls. About 1 liter of raw wastewater, non-filtered, was extracted using a magnetic stirrer, during 15 min each time,[4] with 3×50 ml of a mixture of 15% methylene chloride in *n*-hexane.[5] After decantation in a separatory funnel, the organic phases are concentrated and sulfur is removed by metallic mercury. Interferences are eliminated by Florisil chromatography.[6]

A Perkin–Elmer Sigma 3 B chromatograph, with an electron-capture ^{63}Ni detector at 325°C, N_2 as carrier gas and the injection made at 265°C in the split mode, was used with two types of column and oven conditions:

— fused silica column (30 m, i.d.: 0.25 mm) coated with SPB-5 bonded phase from Supelco, oven temp.: 110°C up to 265°C, ramp rate: 2°C/min;

— fused silica column (50 m, i.d.: 0.25 mm) coated with SE 30, oven temp.: 140°C up to 255°C, ramp rate: 2.5°C/min.

Quantitation of total PCBs

In order to determine the concentration of total PCBs in the water samples, we used a set of 36 pure components which represents 68% of the concentration of total PCBs present in a mixture of Aroclors 1242 + 1254 + 1260 (1:1:1).

These pure components are presented in Table I. The range of concentrations of the injected sample in which the detector can be considered as linear for all these components is defined, and the concentration of the extract of the sample is adjusted to fall into this range.

TABLE I

The 36 pure PCB-components used to determine the PCB concentration in the samples and to determine the sets of components well adapted for establishing the "index of similarity".

IUPC No.		IUPAC No.	
8	2,4′	138	2,3,4,2′,4′,5′
18	2,5,2′	141	2,3,4,5,2′,5′
28	2,4,4′	149	2,4,5,2′,3′,6′
44	2,3,2′,5′	151	2,3,5,6,2′,5′
52	2,5,2′,5′	153	2,4,5,2′,4′,5′
60	2,3,4,4′	170	2,3,4,5,2′,3′,4′
64	2,3,6,4′	171	2,3,4,6,2′,3′,4′
70	2,5,3′,4′	172	2,3,4,5,2′,3′,5′
84	2,3,6,2′,3′	174	2,3,4,5,2′,3′,6′
87	2,3,4,2′,5′	177	2,3,5,6,2′,3′,4′
92	2,3,5,2′,5′	180	2,3,4,5,2′,4′,5′
99	2,4,5,2′,4′	183	2,3,4,6,2′,4′,5′
101	2,4,5,2′,5′	185	2,3,4,5,6,2′,5′
105	2,3,4,3′,4′	187	2,3,5,6,2′,4′,5′
110	2,3,6,3′,4′	194	2,3,4,5,2′,3′,4′,5′
118	2,4,5,3′,4′	196	2,3,4,5,2′,3′,4′,6′
128	2,3,4,2′,3′,4′	201	2,3,4,5,2′,3′,5′,6′
135	2,3,5,2′,3′,6′	209	2,3,4,5,6,2′,3′,4′,5′,6′

The concentration of each of these 36 components is calculated for the sample extract using the areas, and the total PCB concentration to be taken into account is obtained by the formula:

$$[\text{PCBs}] = \frac{100}{68} \times \sum_{i=0}^{36} c^i$$

with: c^i, concentration of component i in the sample.

The limitations of this method lie mainly in the fact that different components could be present in the same peak. In fact, however good the resolution of the gas chromatograph, a peak in an environmental sample or even in a commercial mixture, is considered as being only one of these components, whereas it generally represents a mixture of different components in which the component of interest is predominant.[7] For example, some cases where overlapping between components occurs are:

— components 28 and 31
— components 105 and 153
— components 118 and 149
— components 156 and 171.

To reduce the risk of errors it is necessary to use different types of column and chromatographic conditions.

Quantitation of these particular components by pattern comparison of the height instead of the area can also, in some cases, reduce this error.

Results based on total PCB quantitation

This quantitation method for total PCBs was applied to the wastewaters of three Swiss towns. Some of these results have already been published,[3] the range of PCB concentrations found being shown in Table II:

TABLE II

Characteristics of the wastewaters considered.

Town	Hydraulic population equivalent	Range of PCB concentration found in wastewaters ($\mu g \cdot l^{-1}$)
Morges (VD)	28,000	0.02–0.23
Fribourg (FR)	75,000	0.04–1.20
Bienne (BE)	142,000	0.14–0.50

These results show an order of concentration of PCBs similar to those found in other studies, like those published about wastewaters of towns in Wisconsin (1974),[8] towns in Ontario (1974)[9] and in the region of Oxford (U.K.) in 1980.[10]

In addition to these overall results, the use of a quantitation method based on single components allowed us, over a period of time, to follow the relative importance, of the different types of PCB as a function of their degree of chlorination. For example, Figure 1 shows the evolution, over 24 hours, of six different groups of PCBs in the inlet wastewater of the treatment plant of the city of Fribourg.

In this figure, one can observe that during the night lightly chlorinated PCBs are predominant, and heavily chlorinated absent. In our point of view, heavily chlorinated PCBs are more bonded to suspended matter than lightly chlorinated ones, and the suspended matter is immobilized during the night by decantation in the sewer due to the low water-flow.

Need for a qualitative index of the aspect of PCB chromatograms

The previous comments allow us to suggest that examination of single components of PCBs in wastewater, and also in environmental samples, could give information about the different sources of these pollutants. This point is clearly illustrated in Figure 2, which shows the chromatogram aspects of PCBs extracted from wastewaters at the same moment in two different districts of the town of Fribourg. The aspects of the PCBs extracted are noticeably different.

To compare these different fingerprints, it can, in some cases, be useful to employ a graphic representation. Using a desk-computer (Hewlett–Packard 9845B), we have built a programme which gives a graphic representation of the spread of six different groups of PCBs. The computer divides the 36 components, presented below, into these six groups as a function of their degree of chlorination. The sum of the concentrations of the components of each group is calculated and the particular spread of each group represents the ratio of this concentration to the total concentration of the 36 components. Figure 3 shows the graphic representation given by the computer from the chromatograms of Figure 2.

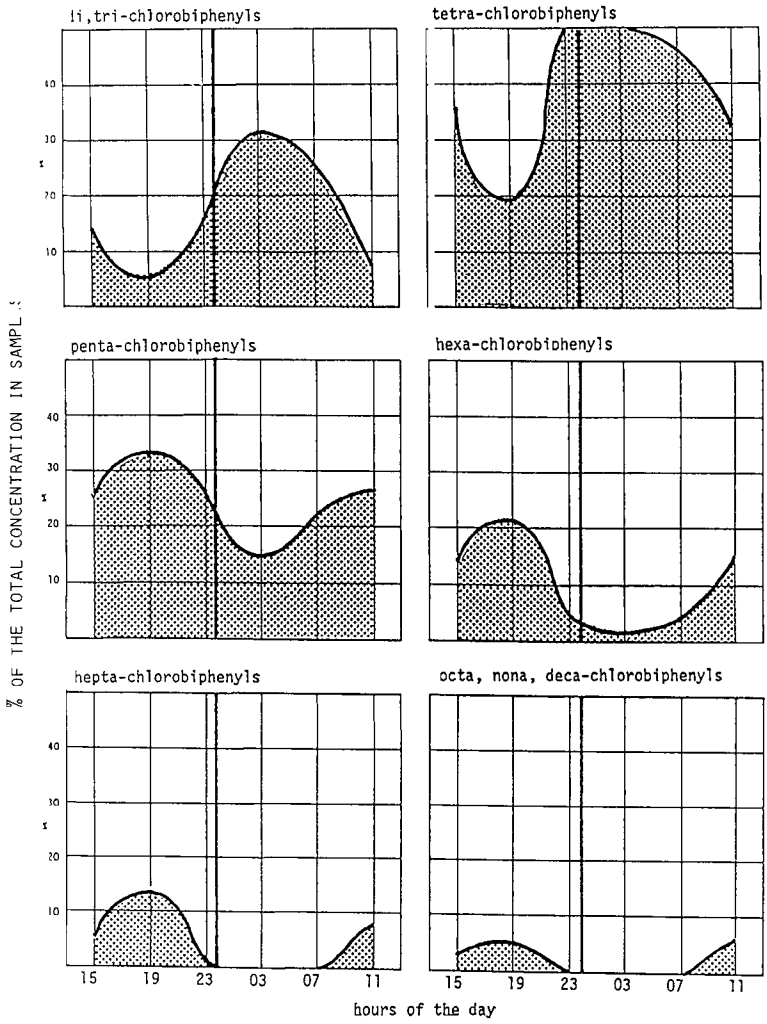

FIGURE 1 Typical relative variation during a day of the 36 components of PCBs divided into 6 groups.

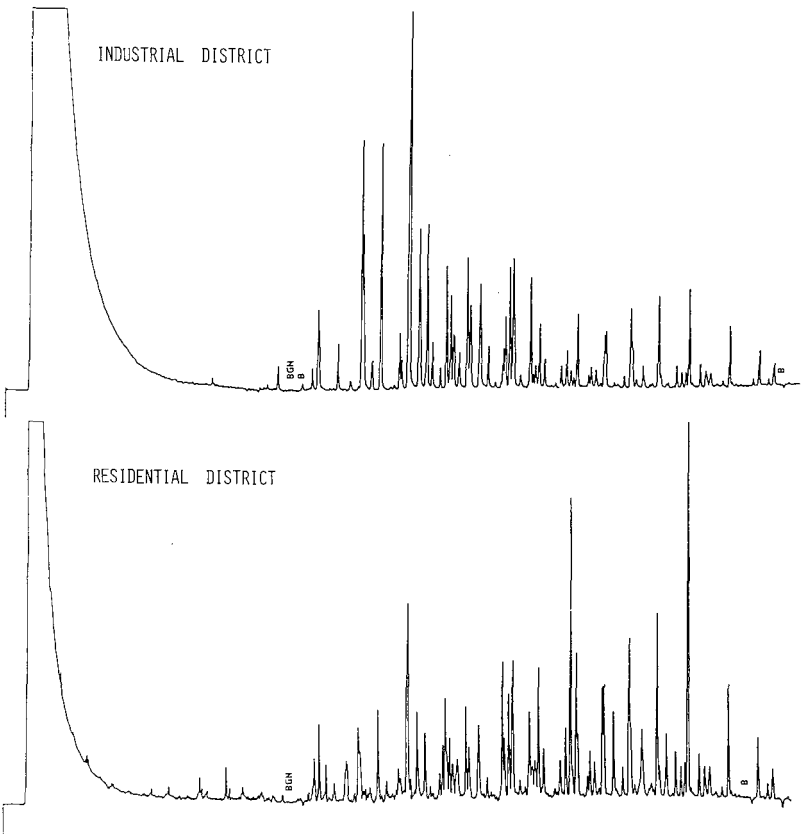

FIGURE 2 Chromatograms of PCB in wastewater from two different districts in the city of Fribourg, Switzerland.

This method allows us to have a simple and immediate graphic representation of the fingerprint of the PCBs extracted from a sample, but is, however, a limited tool to give utilizable results. In fact we need a numerical representation of the notion of fingerprint, since we have to be able to apply mathematical and statistical methods before giving any acceptable explanation of the differences and variations that we observe in the aspect of PCBs. This is the reason why we have developed the notion of "index of similarity".

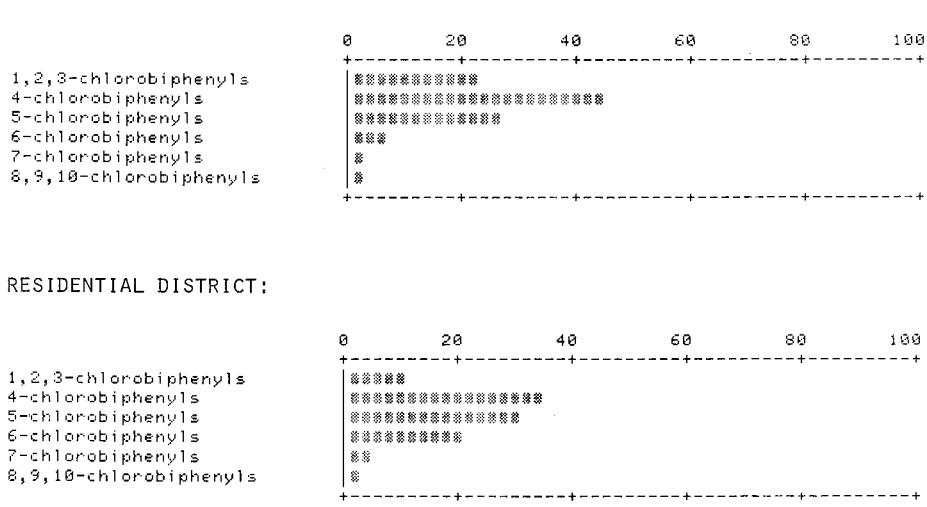

FIGURE 3 Computerized graphic representation of the fingerprints of the PCBs of the chromatograms which are represented in Figure 2.

INDEX OF SIMILARITY

Definition

The index of similarity, S, should allow us to give a numerical value to the difference between two extracts of PCBs. It will depend on the number n of individual components of PCBs chosen for this purpose.

The concentration of component i is calculated in the two extracts using a pure component as standard:

— c_A^i, is the concentration of component i in extract A;

— c_B^i, is the concentration of component i in extract B.

The "real concentration" of each sample is defined as the sum of the concentrations of the n components:

— real concentration of A: $C_A = \sum_{i=1}^{n} c_A^i$;

— real concentration of B: $C_B = \sum_{i=1}^{n} c_B^i$.

To establish a relationship between the aspects of samples A and B we have to standardize their concentrations.

If, for example, we consider sample A as a reference, we can establish the "normalized concentration" of each component in B, weighing its real concentration by the ratio between real concentration of A and real concentration of B:

$$c_{nB}^i = \frac{C_A}{C_B} \cdot C_B^i.$$

The sum of the normalized concentrations of the n components in B is to be equal to the sum of the real concentrations of the components in A.

$$\sum_{i=1}^{n} c_{nB}^i = \sum_{i=1}^{n} c_A^i = C_A.$$

The particular similarity of each component, s_i, is defined by the ratio, between its real concentration in A and its normalized concentration in B, with the weaker concentration always being in the numerator:

— if: $c_{nB}^i \leqq c_A^i$; $\quad s_i = \frac{c_{nB}^i}{c_A^i}$

— if: $c_{nB}^i > c_A^i$; $\quad s_i = \frac{c_A^i}{c_{nB}^i}$.

The particular similarity, s_i, of each component is consequently always inferior or equal to one:

$$0 \leqq si \leqq 1.$$

The "index of similarity", S, between the two samples is the sum of the particular similarities of the n components, balanced by the relative importance of each component in the sample of reference.

This relative importance is defined by the ratio between the concentration of the component and the total concentration of the n components in A.

$$S = \sum_{i=1}^{n} \frac{c_A}{C_A} \cdot s_i \qquad 0 \leqq S \leqq 1$$

This definition means that if the n PCB components are present in an identical relative concentration in samples A and B:

$$S = 1.$$

If each of the PCB components is present in one sample, but absent in the other:

$$S = 0.$$

Choice of the components

The sensitivity of the index of similarity will depend largely on the choice of the n components. With a view to determining the most adequate components, to give maximum sensitivity to this index with a minimum number of components, we tested four sets of 6, 8, 12 and 18 components. Table III shows the composition of these four sets of individual components.

The first set of 6 components includes those which are noted as highly characteristic of environmental samples by Tuinstra *et al.*[11] and are proposed for regulation in the Federal Republic of Germany. Among these components only no. 138 is considered as an AHH activity inducer.[12]

The set of 8 components was obtained by:

- eliminating from the previous set the component 153, which in most cases is difficult to distinguish from component 105;
- eliminating component 52 and considering components 18 and 60 which are more characteristic of commercial lightly chlorinated PCBs (i.e. Aroclors 1232, 1242, Clophen A30, A40 and Prodelec DP4);
- considering two important pentachlorobiphenyls, components 95 and 110.

TABLE III

Characterization of the four different sets of individual components utilized in calculating the index of similarity.

IUPAC no.		Percentage of mixture Aroclors 1242 +1254 +1260 (1:1:1)[a]	Percentage of mixture Clophens A40 +A50 +A60 (1:1:1)[b]	Percentage of mixture[c] Clophens A30 +A60 (1:1)[c]
Set of 6 components				
28	2,4,4′	3.5	1.5	4.1
52	2,5,2′,5′	2.0	5.6	1.5
101	2,4,5,2′,5′	2.6	4.6	2.9
153	2,4,5,2′,4′,5′	4.8	4.4	4.9
138	2,3,4,2′,4′,5′	5.4	6.5	5.7
180	2,3,4,5,2′,4′,5′	4.5	4.3	3.5
Total		22.8	26.0	22.6
Set of 8 components				
18	2,5,2′	1.3[b]	1.3	6.2
28	2,4,4′	3.5	1.5	4.1
95	2,3,6,2′,5′	2.3[b]	2.3	2.1
60	2,3,4,4′	1.8[b]	1.8	0.7
101	2,4,5,2′,5′	2.6	4.6	2.9
110	2,3,6,3′,4′	6.4	5.5	2.3[b]
138	2,3,4,2′,4′,5′	5.4	6.5	5.8
180	2,3,4,5,2′,4′,5′	4.5	3.4	3.5
Total		27.8	26.9	27.6
set of 12 components				
8	2,4′	0.1[b]	0.1	3.1
18	2,5,2′	1.3[b]	1.3	6.2
28	2,4,4′	3.5	1.5	4.1
95	2,3,6,2′,5′	2.3[b]	2.3	2.1
60	2,3,4,4′	1.8[b]	1.8	0.7
101	2,4,5,2′,5′	2.6	4.6	2.9
110	2,3,6,3′,4′	6.4	5.5	2.3[b]
149	2,4,5,2′,3′,6′	4.0	4.7	5.1[b]
138	2,3,4,2′,4′,5′	5.4	6.5	5.8
180	2,3,4,5,2′,4′,5′	4.5	3.4	3.5
201	2,3,5,6,2′,3′,5′,6′	0.8	0.3	0.7
194	2,3,4,5,2′,3′,4′,5′	0.4[b]	0.4	0.7[b]
Total		33.1	32.4	37.2

TABLE III (continued)

IUPAC no.		Percentage of mixture Aroclors 1242 +1254 +1260 (1:1:1)[a]	Percentage of mixture Clophens A40 +A50 +A60 (1:1:1)[b]	Percentage of mixture Clophens A30 +A60 (1:1)[c]
Set of 18 components				
8	2,4′	0.1[b]	0.1	3.1[b]
18	2,5,2′	1.3[b]	1.3	6.2
28	2,4,4′	3.5	1.5	4.1
52	2,5,2′,5′	2.0	5.6	1.5
44	2,3,2′,5′	1.0	3,6	1.1
64	2,3,6,4′	1.1	1.1[a]	0.1
95	2,3,6,2′,5′	2.3[b]	2.3	2.1
60	2,3,4,4′	1.8[b]	1.8	0.7
101	2,4,5,2′,5′	2.6	4.6	2.9
110	2,3,6,3′,4′	6.4	5.5	2.3[b]
149	2,4,5,2′,3′,6′	4.0	4.7	5.1[b]
153	2,4,5,2′,4′,5′	4.8	4.4	4.9
138	2,3,4,2′,4′,5′	5.4	6.5	5.8
187	2,3,5,6,2′,4′,5′	1.4[b]	1.4	1.0
174	2,3,4,5,2′,3′,6′	1.7[b]	1.7	0.9
180	2,3,4,5,2′,4′,5′	4.5	3.4	3.5
170	2,3,4,5,2′,3′,4′	4.5	2.1	1.9
194	2,3,4,5,2′,3′,4′,5′	0.4[b]	0.4	0.7
Total		48.8	52.0	47.9

[a]According to authors.
[b]According to Ref. 13.
[c]According to Ref. 14.

The set of 12 components was obtained from the previous set by adding the four following components:

— component 8, characteristic of very lightly chlorinated commercial mixtures;
— an additional hexachlorobiphenyl, component 149;
— two important octochlorobiphenyl components 194 and 201.

The set of 18 components was obtained using all the components of the previous sets, replacing component 201 by component 170,

which is an important heptachlorobiphenyl in terms of concentration in commercial mixtures and which is also considered as an AHH activity inducer[12] and adding the four other most important components of our 36 previous pure components: 44, 64, 187 and 174.

The percentage composition in commercial mixtures of these different sets as shown in Table III was calculated using our own pure components and also feature the results published by Duinker *et al.*,[13] and Schulte *et al.*[14]

The sensitivity of the index of similarity given by these four sets can be tested by comparing the index of similarity of different commercial mixtures of PCBs, in our case Aroclors, with respect to one of them chosen as reference: in the present case Aroclor 1248 which is the Aroclor containing the greatest range of components. The results are shown in Figure 4.

It can be seen that the set of 6 components displays little sensitivity. In particular it is unable to differentiate between Aroclors 1232 and 1242, and the differentiation between Aroclors 1260 and 1262 is poor. The differentiation obtained with the set of 18 components is very good, and that obtained with the sets of 8 and 12 components is quite acceptable. These remarks mean that, in most cases, the use of the set of 6 components does not allow one to differentiate between the fingerprints of two PCB extracts. The set of 18 components would be best for calculating the index of similarity but necessitates a long calculation time. Consequently, for our further studies we have utilized only the sets of 8 or 12 components.

Example of the use of the index of similarity

In the following example we have applied the use of the index of similarity to state with precision the importance of the wastewater from a particular factory, suspected of utilizing PCBs, with respect to the total PCB content in the wastewater treatment plant of the city of Fribourg.

Figure 5 represents the variation over 10 summer weeks, in 1983, of the water flow, PCBs concentration and PCBs flow in the inlet wastewaters of this treatment plant. The sample representing one week was obtained by mixing ten samples of 200 ml, drawn each

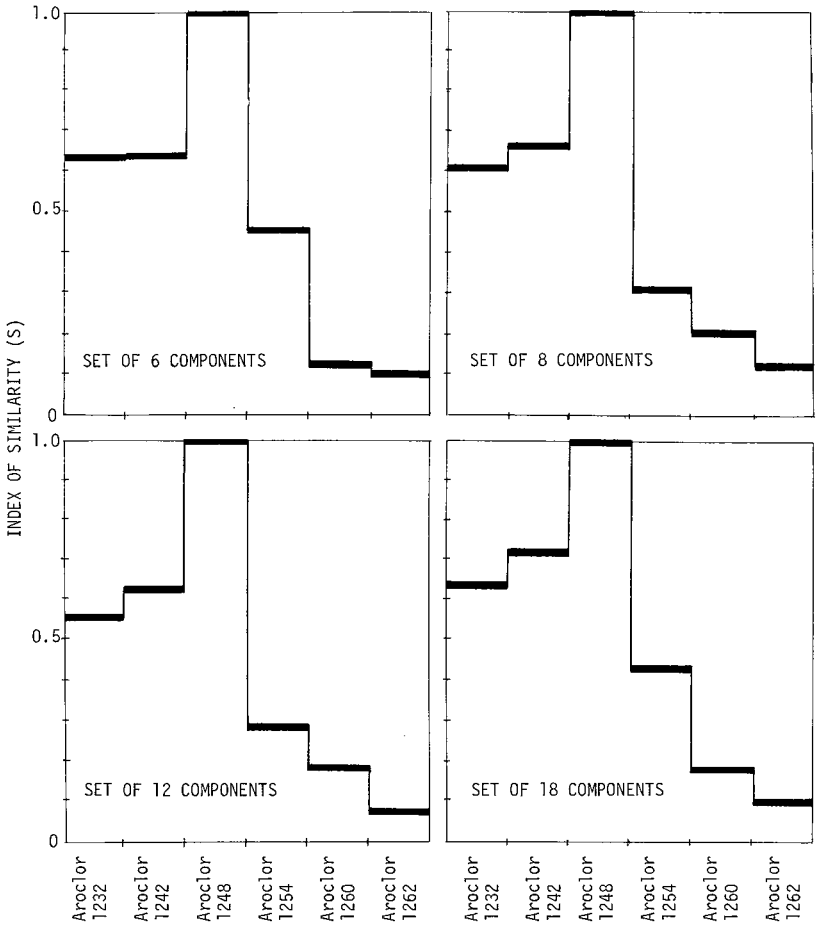

FIGURE 4 Index of similarity (S) of some Aroclors vs. Aroclor 1248 as a function of the four different sets of individual components.

working day (Monday to Friday) at 9 a.m. and 4 p.m. In this figure one can observe a high input of PCBs into the treatment plant during the week of 11 to 17 July and, more especially, an important decrease during the two weeks of 1 to 14 August, exactly the two vacation weeks of the factory suspected of utilizing PCBs. Using the index of similarity allowed us to confirm the relationship between

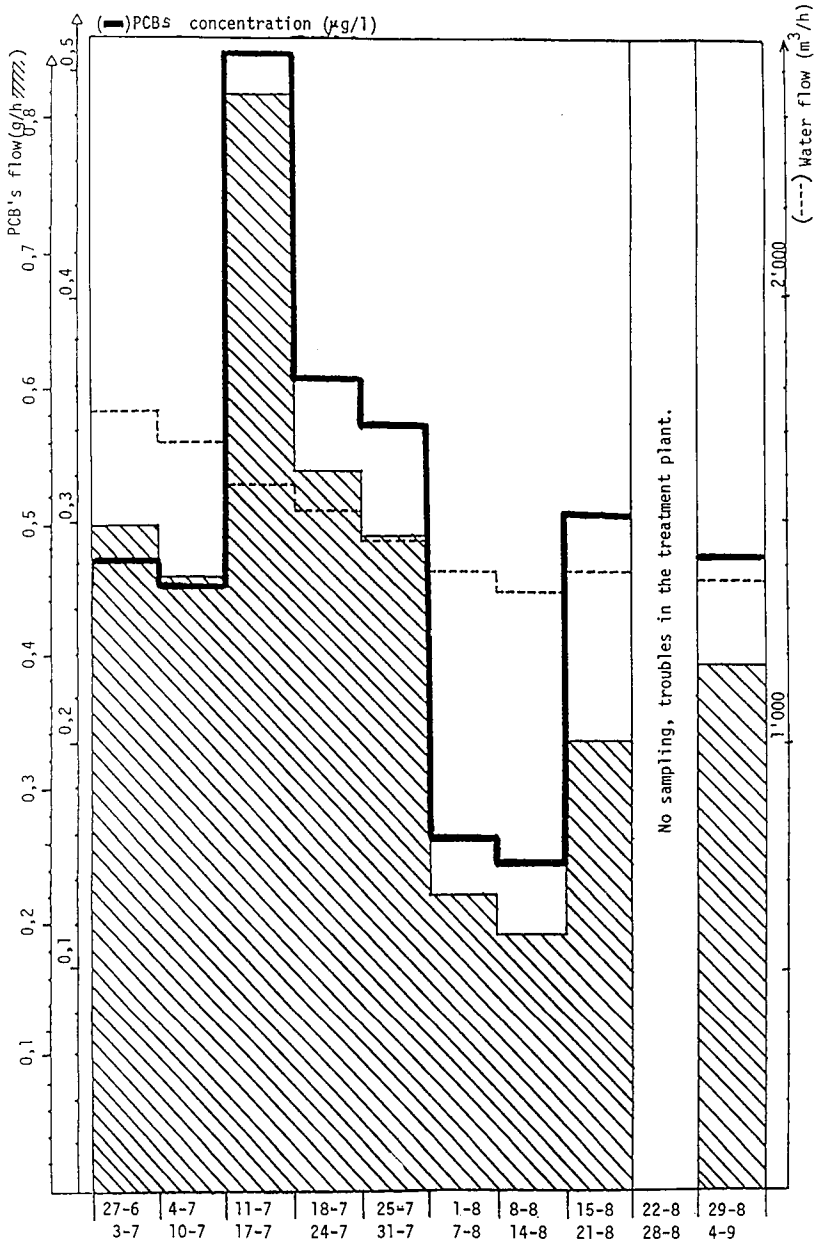

FIGURE 5 Variation of water flow and of PCBs flow and concentration in the inlet wastewater of a treatment plant.

the decrease in PCBs into the treatment plant and the factory vacation.

For the same period we calculated the index of similarity of the PCBs extracted from the inlet wastewater of the treatment plant with respect to the PCBs extracted from different samples drawn at random over many working days in one year from the wastewaters of the factory and of a residential district.

Figures 6 and 7 show the results obtained.

With respect to the PCBs from the factory, the index of similarity of the PCBs entering the treatment plant:

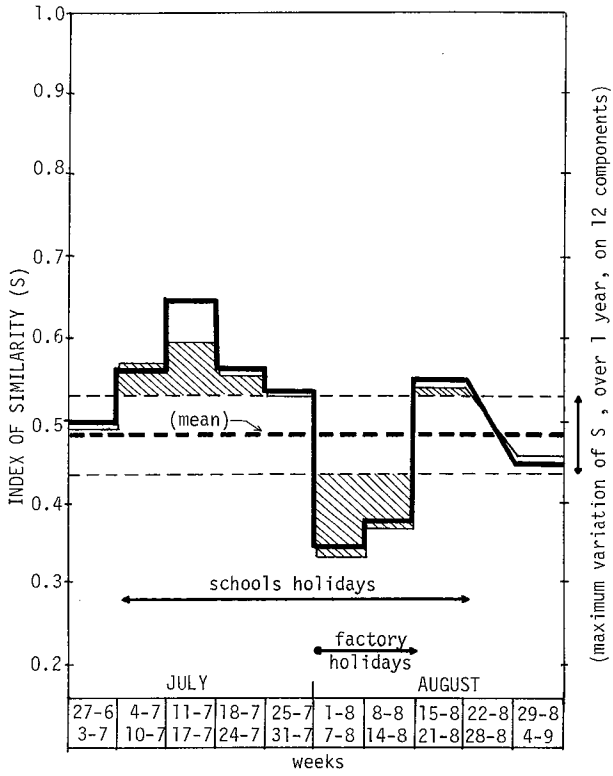

FIGURE 6 Index of similarity (S) of the inlet PCBs in the wastewater treatment plant of Fribourg, as a function of PCBs in the wastewaters of a factory assumed to utilize PCBs. (——): S, calculated with the set of 8 components; (——): S, calculated with the set of 12 components).

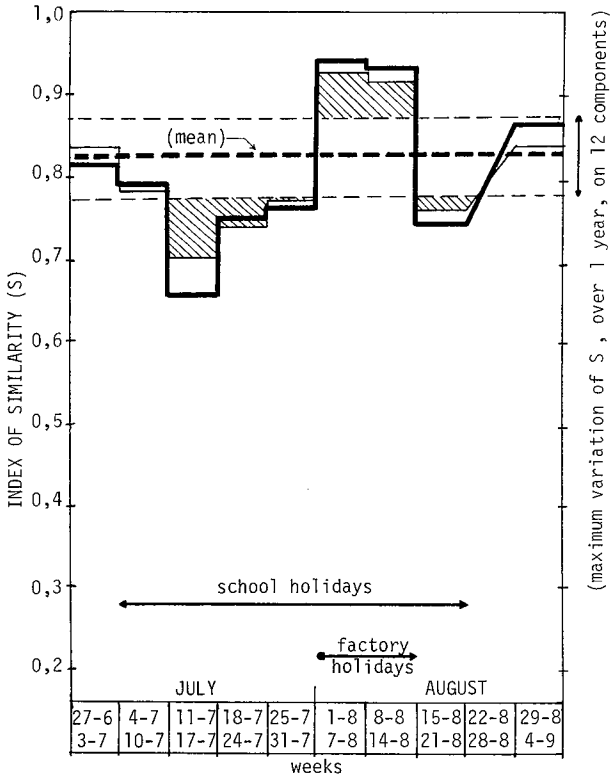

FIGURE 7 Index of similarity (S) of the inlet PCBs in the wastewater treatment plant of Fribourg, as a function of PCBs in the wastewaters of a residential district. (——): S, calculated with the set of 8 components; (——): S, calculated with the set of 12 components.

— increases in a significant way (during the school vacation period) when part of the population leaves the city. But the factory continues to function (weeks: 4 to 31 July and 15 to 21 August).
— decreases in a most significant way during the factory holiday period (1 to 14 August).

The index of similarity with respect to the PCBs from a residential district has a variation exactly opposed to this to such a point that, during the factory holiday period, we can say that the inlet wastewater to the treatment plant is purely residential wastewater.

Analysing these results, we are able to employ the word "significant" since the variations in the index of similarity S are higher or lower than the maximum deviation statistically observed in values obtained over one year.

CONCLUSIONS

In spite of the fact that the use of single components for the quantitation of PCBs necessitates great care and attention as regards:

- the purification stage;
- the use of high resolution chromatography;
- the employment of calibration curves or the adaption of the concentration of the sample injected to the range of linearity of all the components used in the quantitation;
- computerized calculations.

This method has the great advantage that it allows one to go beyond the passive stage of the single concentration of total products.

In fact the use of the index of similarity allows a more dynamic dimension to be given to the results. The present paper has tried to demonstrate the interest offered by this notion and the fact that it can be applied, in the case of PCBs, with a limited number of components (8 or 12).

The possibility of linking the aspect of chromatograms obtained from other multi-component products with specific sources of emission has already been noted, particularly for dioxins and dibenzofurans.[15] Application of the index of similarity could also be helpful in those cases.

Finally, use of the index of similarity allows one to treat, mathematically and statistically, a numerical representation of the notion of the fingerprint of multi-component pollutants, and consequently increases the reliability of the statements that one can make about the sources of these products.

Acknowledgements

Part of the researchs presented in this paper was supported by the Swiss Federal Board for the Environment Protection and the European Communities Scientific Program COST 68 ter.

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