Characterization of Polychlorinated Biphenyl Distribution in the Marine Environment[1]

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Introduction. Polychlorinated biphenyls ($C_{12}Cl_nH_{10-n}$ with n = 1, 2 . . . 10) originate as commercially prepared mixtures of controlled chlorobiphenyl content. However, once released in the environment, their original distribution pattern is altered as a result of specific physicochemical interactions with the various media of the receiving system. This distribution behavior has been observed during recent field investigations conducted in a number of coastal and estuarine regions (PAVLOU *et al.* 1974). Since there is experimental evidence that toxicity is homolog dependent (DEXTER and PAVLOU 1972; HAMMOND 1972) it is apparent that the transport and bioaccumulation characteristics of the individual homologs should be an important factor in assessing biological perturbations to an ecosystem receiving a substantial input of these compounds.

Other investigators have also noted distribution changes in marine samples, (ZITKO *et al.* 1972; VIETH 1972; RISEBROUGH *et al.* 1972; GIAM *et al.* 1973) but the data has been generally reduced to total PCB, rather than component concentrations, primarily due to the difficulties inherent in the analysis of individual components. The commonly employed method of quantitation by electron capture gas chromatography (EC/GC) provides little distribution information since results are obtained from total integrated spectral comparisons with commercially available mixtures such as the Aroclor series. ROTE and MURPHY (1971) have improved the data analysis by separating the spectra into regions corresponding to the isomers of the same chlorine content, but failed to recognize the high variability in response for isomeric chlorobiphenyls (ZITKO *et al.* 1971). WEBB and MCCALL (1973) provide a method for determining individual component responses but the technique requires microcoulometric detection capability which limits the analytical sensitivity.

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[1] Contribution No. XXXX of the Department of Oceanography, University of Washington. This work was supported by the U.S. Environmental Protection Agency, Grant No. R-800362.

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Bulletin of Environmental Contamination & Toxicology,
Vol. 16, No. 4

With the above considerations in mind, we have developed a modified gas chromatographic spectral analysis technique based on the determination of the individual component responses. This technique is similar to that proposed by UGAWA *et al.* (1973) but provides a more rapid assessment of residue concentrations with little, if any, loss in precision. We are currently implementing this method to characterize the spatial and phase distribution of polychlorinated biphenyls in the marine environment. This paper presents a detailed description of the computational framework together with typical standardization results.

Computational Framework. Since all chlorobiphenyls show nearly the same molar response on a flame ionization detector (FID) (ALBRO and FISHBEIN 1972; UGAWA *et al.* 1973), the relative peak area of a given spectral component to the total area of the mixture is proportional to its mole fraction. If the degree of chlorination of the component is known, a mass corrected response can be obtained. The mass fraction of each component, F_i, is then expressed as:

$$F_i = \frac{A_i M_i}{\Sigma_i (A_i M_i)} \qquad (1)$$

where A_i is the peak area in cm^2 and M_i is the molecular weight in g/mole of the i<u>th</u> component.

Applying this analysis to a standard chlorobiphenyl mixture, one can generate a series of F_i values corresponding to the individual components of that standard. Thus, for any known mass of standard, m_t, and the appropriate F_i, the specific mass of component i can be determined from

$$m_i = m_t F_i \qquad (2)$$

If the same standard is chromatographed under identical conditions, but with EC detection, similar component separation will be obtained but with different response characteristics. The corresponding EC response, R_i, is then simply expressed as:

$$R_i = A_i'/m_i \qquad \text{in units of } cm^2\ g^{-1} \qquad (3)$$

where A_i' refers to the area in the EC trace. Once an R_i value has been determined from the analyses of the standard, its corresponding m_i in an unknown sample can be easily obtained from relation (3).

Although F_i is only internally consistent and independent of the absolute FID response, R_i is governed by the operational parameters which affect A_i'. Therefore, the calibration utility of R_i is limited since simultaneous injections of standards would be required with each unknown. This shortcoming can be overcome by calculating the response of each component relative to an operationally convenient external standard. We define this relative response as the sensitivity ratio

$$S_i = R_i/R_{st} \tag{4}$$

where R_{st} refers to the EC response of the external standard.

Combining relations (3) and (4), the injected mass of each component in a sample can be determined as follows:

$$m_i = \frac{A_i'}{S_i R_{st}} \tag{5}$$

A_i' is now the peak area of the i<u>th</u> component in the sample. The mass of all chlorobiphenyls of a given chlorine substitution, m_N , can then be calculated from the sum of all component masses of the same chlorine content. Hence,

$$m_N = (\sum_i m_i)_N \tag{6}$$

where N refers to the degree of chlorination. The corresponding sample concentration can be easily computed as:

$$C_N = \frac{m_N}{LP} \tag{7}$$

where L is the volume fraction of the sample extract injected in the GC and P is the quantity of sample extracted.

It can be seen from the above considerations that from measured areas and the appropriate sensitivity ratios, one can determine directly the N-CB abundance in any environmental sample.

Experimental. All analyses were performed on a Tracor MT-220 gas chromatograph equipped with both flame ionization and ^{63}Ni-electron capture detectors. A 6' x 2 mm ID pyrex column was packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcon AW-DMCS and operated isothermally at 160°C. The carrier gases were N_2 and a 5% methane/95% argon mixture for the FI and EC analyses, respectively. Peak areas were recorded on a Westronics MT-22 strip chart recorder and were measured by planimetry.

F_i and S_i determinations were made with standard solutions of Aroclors 1242, 1254, and 1260 together with p,p'-DDE as an external standard. Molecular weights of the component peaks were identified by GCMS in a Finnigan Model 1013 GCMS at the U.S. EPA Region-X laboratories. In cases of insufficient resolution or small peak areas, adjacent peaks were combined and treated as one.

Results and Discussion. Figure 1 shows a chromatogram of the mixed standards typical of those generated in this study.

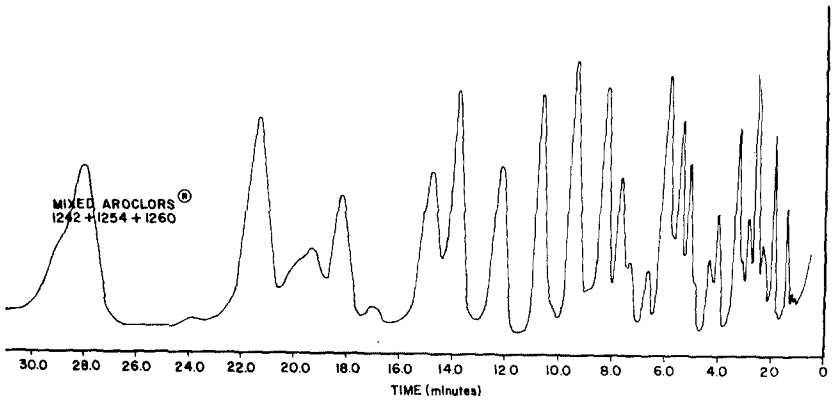

Figure 1. Typical 1.5% OV-17/1.95% OV-210 (SP-2250/SP-2401) column chromatogram of mixed Aroclor standards.

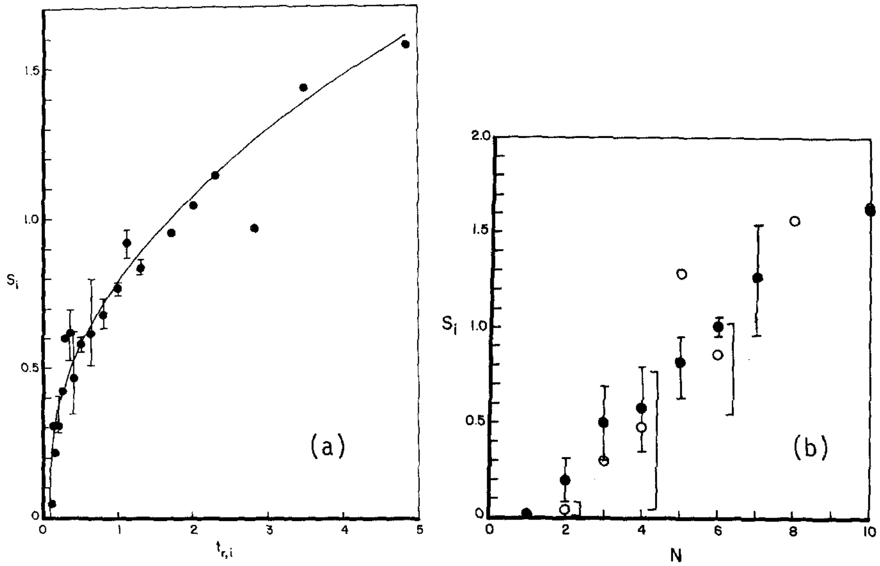

Figure 2. Plots of averaged sensitivity ratios, S_i, versus (a) relative retention time, $t_{r,i}$, and (b) the chlorine number, N, observed in this study, ●, and reported by Zitko et al., (1971), o. The vertical brackets indicate the ranges of S_i observed (offset for Zitko's data).

Figure 2a shows a plot of S_i, averaged at a given retention time, as a function of relative retention time, $t_{r,i}$; both quantities are normalized to p,p'-DDE. S_i initially increases rapidly with increasing $t_{r,i}$ and approaches a maximum at longer retention times.

The validity of using the average S_i values was verified by quantitating single and mixed Aroclor standards. A summary of the data is shown in Table I. It can be seen that in all cases the total mass (Σm_i) determined from the S_i analyses agreed well ($\pm 6\%$) with the actual m_t value.

TABLE I

Comparisons of actual and calculated mass values for single and mixed Aroclor standards, in units of 10^{-10} g

Standard	$m_{t,}$ injected	Σm_i [a]	$\%\Delta$ [b]
1242	2.06	1.97	-4.6
1254	2.57	2.58	+0.2
1260	2.28	2.26	-0.8
1242 + 1254	3.25	3.36	+3.1
1242 + 1260	3.07	3.24	+5.5
1254 + 1260	2.89	2.98	+3.1
1242 + 1248 + 1260	4.65	4.92	+5.8

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[a] Determined from the averaged S_i value at a given $t_{r,i}$

[b] $\%\Delta = (m_{t,\,inj} - \Sigma m_i) \,/\, m_{t,inj} \times 100$

The change of S_i as a function of chlorine number, N, is shown in Figure 2b together with ZITKO's (1971) data. The agreement is good, even though only a few of the isomers used by ZITKO have been observed in commercial mixtures. It should be noted that the apparent S_i maximum depicted by the decachlorobiphenyl is pragmatic and does not correspond to the theoretical value that can be obtained from collision theory (SULLIVAN 1973). Nevertheless, the linear dependence of S_i on N is consistent with the capture rate constant behavior reported by SULLIVAN.

In summary, the spectral analysis technique presented in this paper is uniquely advantageous in describing environmental chlorobiphenyl distributions. It is based on easily determined empirical parameters, can be readily tailored to most laboratory systems, and can effectively remove the ambiguities in chlorobiphenyl quantitation.

References

ALBRO, P.W. and L. FISHBEIN: J. Chromatogr. 69, 273 (1972).

DEXTER, R.N. and S.P. PAVLOU: Journées Étud. Pollutiones, 155, Athens, CIESM (1972).

GIAM, C.S., M.K. WONG, A.R. HANKS, W.M. SACKETT and R.L. RICHARDSON: Bull. Environ. Contam. Toxicol. 9, 376 (1973).

HAMMOND, A.L.: Science 175, 155 (1972).

PAVLOU, S.P., R.N. DEXTER and J.R. CLAYTON, in Proceedings of the International Conference on Transport of Persistent Chemicals in Aquatic Ecosystems, May 1-3, Ottawa, Ontario, Canada (1974).

RISEBROUGH, R.W., V. VREELAND, G.R. HARVEY, H.P. MIKLAS and G.M. CARMIGNANI: Bull. Environ. Contam. Toxicol. 9, 376 (1972).

ROTE, J.W. and P.G. MURPHY: Bull. Environ. Contam. Toxicol. 6, 377 (1971).

SULLIVAN, J.J.: J. Chromatogr. 89, 9 (1973).

UGAWA, M., A, NAKAMURA and T. KASHIMOTO: New methods in environmental chemistry and toxicology, Proceedings of the International Symposium, Susono, Japan, 1973; F. Coulston, F. Korte and M. Groto, eds., International Academic Printing Co., Tokyo, Japan 1973.

VIETH, G.D.: Environ. Health Perspect. No. 1, 51 (1972).

WEBB, R.G. and A.C. MCCALL: J. Chromatogr. Sci. 11 366 (1973).

ZITKO, V., O. HUTZINGER and S. SAFE: Bull. Environ. Contam. Toxicol. 6, 160 (1971).

ZITKO, V., O. HUTZINGER and P.M.K. CHOI: Environ. Health Perspect. No. 1, 47 (1972).