NEW METHODS FOR THE CHARACTERIZATION OF THE COMPOSITION OF ENVIRONMENTAL PCB MIXTURES

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ABSTRACT

The great abundance of data received from isomer specific determinations of environmental PCB mixtures leads to complex results which are not readily compared and understood. Two methods facilitating the interpretation of these data are presented and examples regarding PCB mixtures of various species of wildlife animals are given which demonstrate the usefulness of these procedures.

INTRODUCTION

Mixtures of Polychlorinated Biphenyls (PCB) in environmental samples may be quite different from technical PCB mixtures (Aroclor, Clophen etc.). The examination of the former is done by isomer specific determinations which produce a great abundance of data consisting of the concentrations or fractions of a great number of congeners. These data are too complex to be readily understood or to be easily compared by univariate statistical methods, and, therefore, data reduction seems neccessary in order to characterize environmental PCB mixtures.

PARAMETERS OF METABOLIZATION

For this purpose, pattern recognition methods (1) or multiple regression analyses (2) were applied. These methods lead to modelling of environmental PCB mixtures by (a) technical mixture(s). However, environmental PCB mixtures, especially those of wildlife animals, are too different from those of technical origin to be described properly in this way (1). Here, parameters of metabolization are described that serve as a measure for differences between an environmental and an arbitrary standard PCB mixture. This method extensively makes use of the fact that, at first glance, higher metabolized differ from lower metabolized PCB mixtures by their greater fractions of the congeners with higher degrees of chlorination (3, see fig. 1). The first pa-

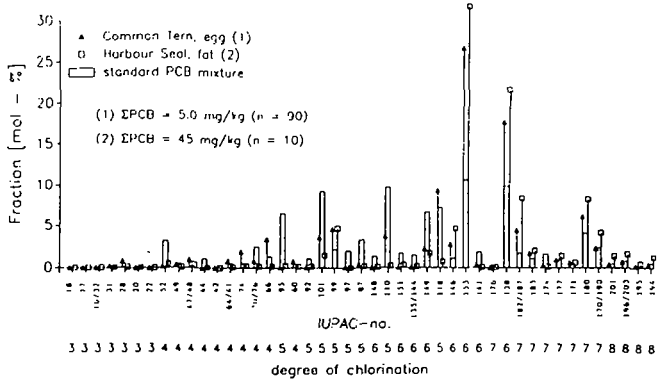

Figure 1. PCB mixture in Common Tern and Harbour Seal compared with the standard mixture (Aroclor 1254 : Clophen A 60 = 1:1 w/w); IUPAC-no. see (4).

rameter is derived from the sum of all positive fraction differences d between the environmental and the standard mixture (or all absolute values of the negative fraction differences) over all observed congeners:

$$S = \sum_{i=1}^{k} |d_i| /2$$ (migration sum), with k = number of observed congeners,

that describes the change of the fractions during the course of metabolization (3). The second parameter describes the distance the fraction differences had migrated along the scale of chlorine numbers and is calculated by

$$D = \sum_{i=1}^{k} (d_i \cdot a_i) /S$$ (migration distance),

with a_i = number of chlorines in congener i (degree of chlorination).

It can be shown that the product of both parameters is the difference of the mean wheighted degrees of chlorination between environmental and standard PCB mixture (3):

$G = D \cdot S$ (degree of metabolization).

Plotting S against D the resulting graphical presentation of G allows an easy comparison of the degrees of metabolization between various wildlife animals (fig. 2a) showing the PCB mixtures of birds of prey and of Harbour Seals being highly and those of fisheating birds being less metabolized. The extent of variation of the congener distribution depends on the species; the Common Tern has much greater a variation than the Peregrine Falcon (fig. 2b). In nearly all animals examined so far the variation of the total PCB concentration is greater than that of the PCB composition (fig. 2b).

STABILITIES OF THE PHENYL COMPONENTS OF PCB CONGENERS

The parameters of metabolization do not provide information about the congeners involved. This information may be largely preserved when the phenyl moieties are considered seperately. In this way, the contribution of the left and right ring towards the stability in environmental compartments may be evalu-

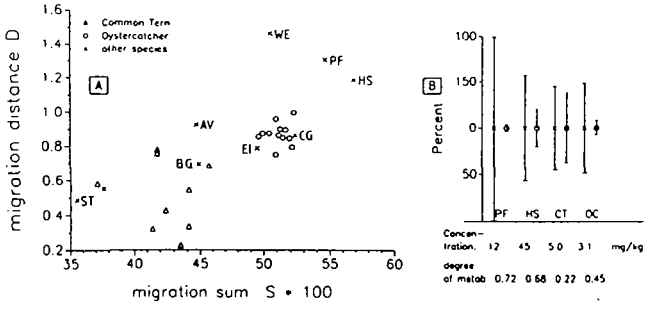

Figure 2. A: Metabolization plot of Common Tern (CT, Sterna hirundo, 9 locations of the German Bight, each n=10), Oystercatcher (OC, Haematopus ostralegus, 12 locations of the German Bight, each n=10), PF=Peregrine Falcon (Falco peregrinus, n=11), WE=White-tailed Eagle (Haliaetus albicilla, n=4); all others n=10, HS=Harbour Seal (Phoca vitulina), ST=Sandwich Tern (Sterna sandvicensis), AV=Avocet (Recurvirostra avosetta), BG=Black-headed Gull (Larus ridibundus), EI=Eider (Somateria molissima), CG=Common Gull (Larus canus);
B: concentration (X) and degree of metabolization G (O) as well as their relative standard deviations.

ated, and instead of 209 congeners only 20 different phenyl rings have to be monitored resulting in a considerable data reduction. This procedure presupposes the sufficient representation of the PCB congeners by their phenyl rings, i.e. the contribution of the interaction between the phenyl moieties in respect to the stabilities of the congeners must be small. It can be shown that in environmental PCB mixtures about 80 % of the variation of the congener stabilities is determined by their ring stabilities (5). Thus, the interaction between the phenyl moieties is small. However, differences between species exist.

The congener stability q_i is defined by the quotient of the fraction of congener i in the environmental and that of the same congener in the standard PCB mixture (see fig. 1) and can be predicted by the ring stability values α_j and $\alpha_{j'}$ ($1 \leq j \leq 20$, j=index):
$q_i = \alpha_j \cdot \alpha_{j'} \cdot \tau_i$, where τ_i is a congener specific factor which represents the fraction of the stability of congener i depending merely on the interaction of its rings. The estimation of the ring stability values α_j of 13 phenyl ring structures by 45 congeners (in some cases of 14 phenyl rings by 52 congeners) is done by transforming the multiplicative model into a linear additive model and by performing a least squares estimation which maximizes the correlation between the sum of the logarithms of the α_j-estimators and q_i-values, or minimizes the estimators of the τ_i-values. The correlation coefficient ($r \geq 0.9$) is a measure for the determination (in terms of logarithms) of the congener stabilities q_i by the estimated ring stability values α_j.

Fig. 3 shows great differences between the the ring stability values within the phenyl ring structures of the same degree of chlorination. The ring stability value diagram of the White-tailed Eagle shows that phenyl rings with adjacent hydrogen atoms in m- and p-position (chlorine substitution in 2-;

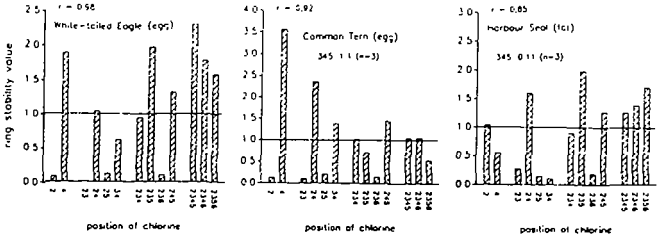

Figure 3. Ring stability values in 3 species of wildlife animals. The lines drawn parallel to the x-achsis with a distance of 1 roughly seperate the rings with relatively high a stability from those with lower ones. r = coefficient of correlation (see text).

2,3-; 2,5-; and 2,3,6-position) are highly metabolized. Those with adjacent hydrogen atoms in o- and m-position (chlorine substitution in 4-; 2,4-; 3,4-; and 2,3,4-position) are less and those without any adjacent chlorine atoms (chlorine substitution in 2,3,5-; 2,4,5-position and all structures with the degree of chlorination 4) are least metabolized. The different stabilities of the phenyl rings unsubstituted in 3,4- and 2,3-position may be best explained by the different accessabilities of these positions to the microsomal P-450 dependent oxigenases which biotransform xenobiotics via epoxids.

The ring stability value diagrams of the other fisheating species resemble that of the White-tailed Eagle (fig. 3). There are only minor but interesting deviations. The Common Tern exhibits the phenyl ring substituted in the 2,3,5-positions (no adjacent hydrogens) being no more stable than the one with 2,3,4-substitution (adjacent hydrogens in a less accessable position).

An important aspect is the fact that in Harbour Seals the biotransformation of the 3,4- and 3,4,5-substituted phenyl rings is enhanced. Phenyl rings of this structure are found in the highly toxic coplanar non-ortho and in the somewhat less toxic mono-ortho congeners. It is difficult to recognize this toxicologically important fact by the display shown in fig. 1. This result is important because the non-ortho PCB congeners are difficult to determine.

The procedure shown here offers the possibility of reducing the complex patterns of environmental PCB mixtures into those of a few relevant phenyl ring structures. Additionally, valuable information about toxicological properties of environmental PCB mixtures may be obtained by monitoring only those congeners with phenyl rings chlorinated in 3,4- and 3,4,5-positions which are easily determinable.

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