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Review

Polychlorinated Biphenyls (PCBs) in the Bio-geochemistry of Oceans

Narayanan Kannan*

SSRI, KORDI, 391 Jangbuk-ri, Jangmok-myon, Geoje 656-830, Korea

Abstract Polychlorinated biphenyls (PCBs) are anthropogenic contaminants found globally in water, ice, soil, air and sediment. Modern analytical techniques allow us to determine these chemicals in environmental matrices at parts per trillion levels or lower. Environmental forensic on PCBs opens up new avenues of investigation such as transport and fate of water masses in oceans, sedimentation, onset of primary production, migration of marine mammals, their population distribution and pharmacokinetics of drugs inside organisms. By virtue of persistence, bioaccumulation, bioconcentration and structure-activity relationship PCBs emerge as unconventional chemical tracers of new sort.

Key words : PCBs, tracers, environmental forensic, sea water, suspended particulate matter, sediment, anthropogenic contaminants, TEQs, risk assessment, metabolic slope.

Introduction

Apart from the traditional tracers of ocean chemistry that help to understand the ocean process such as salinity, temperature, sigma-t, oxygen-18/16 ratios, phosphate, ammonia, silicate, nitrate, dissolved oxygen, iodine-129 concentrations, and chlorophyll *a*, a new class of tracers emerged in recent years that complements traditional oceanographic investigations. Those are the man made industrial chemicals that are widely used in agriculture, aquaculture, and public sanitation and in consumer products. Several of these chemicals are found to be persistent, bioaccumulative, toxic and trans-boundary (in transport) in nature. By virtue of these physico-chemical properties these chemicals are suggested as tracers along with conventional isotopic tracers that have long half lives. Once absorbed to an organic phase the anthropogenic chemicals are long lasting, less biodegradable and persistent - qualities that are useful as tracers.

Among the several hundred organic anthropogenic chemicals that are introduced in to the global ecosystems polychlorinated biphenyls (PCBs) are well characterized as model substances for the class of persistent organic pollutants [5,6,13,15,19]. Since they accumulate readily in biological tissues such as fatty blubber, PCBs could reveal the migration [14] of oceanic wildlife such as whales, their distribution [6] and nursing behavior [1]. PCBs are widely used in understanding the trophic transfer of accumulative chemicals [9]. Fugacity models based on physico chemical properties of PCBs are widely used in understanding the global transfer of these chemicals and the dynamics behind this transfer [22]. Deep water sampling devices developed in recent years when applied for PCB studies help to understand ocean circulation [15]. The structure biological activity relationship based on the inherent planar and globular nature of PCBs help to understand the phase I and phase II metabolism, the enzyme induction and ultimately the *in-vitro* and *in-vivo* toxicity [4,11].

PCBs reveal biological productivity

Since the principle source of PCBs are commercial mixtures [12] their signature in an environmental matrix is often compared with the composition of commercial mixtures. While it helps to trace the point source of these contaminants, the signature often changes in the environ-

* Corresponding author
Phone: +82-55-639-8675, Fax: +82-55-639-8689
E-mail: nkannan@kordi.re.kr

ment due to weathering. However, it is still possible to identify the point source (as composition varies among mixtures) and in addition, it may reveal relationship among various environmental matrices. For example, PCBs enter the sea via atmosphere and reside in solution before being absorbed by suspended particulate matter (SPM), which in turn settles down at the bottom for burial or resuspension. Thus, accurate analysis of PCBs in water (solution), SPM and sediment reveal this transport. An attempt was made in Oder estuary in Northern Germany to understand this relationship (Fig. 1).

The overall pattern of PCBs in SPM and sediment revealed, in consistent with previous observations [8], a pattern that is similar to the pentachloro mixture (A50). This also reveals the fact that the environmental contamination of PCBs to River Oder comes from Germany and not from Poland as the composition of Chlorofen does not match SPM or sediment. PCB composition in SPM matches closely with sediment revealing their close relationship as described above. On the other hand, if we compare a similar PCA plot including data from solution (water), then the PCB pattern in water differs significantly from SPM as the portioning behavior of individual congeners between water and SPM/sediment differs (Fig. 2).

The SPM in the Baltic Sea is derived principally from autotrophic phytoplankton, herbivorous zooplankton, carnivorous zooplankton, heterotrophic microorganisms, bacteria, flagellates, fungi, organic detritus, remains and faeces of pelagic organisms [16] indicating a close link with primary productivity that occurs usually in spring and summer months in the Baltic [20]. This fact can be derived from the analysis of PCBs in solution and SPM from cruises in the Baltic Sea during winter and

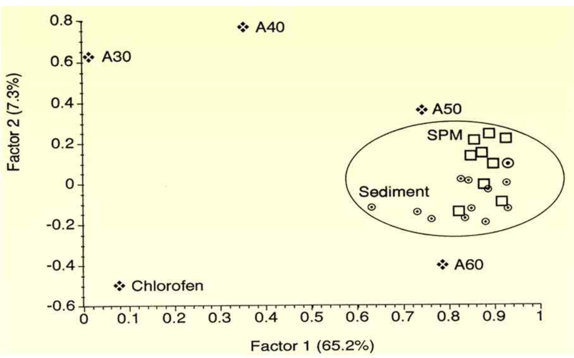

Fig. 1. Principle component analyses (PCA) plot of PCBs in SPM and sediment from Oder estuary. A30, 40, 50 and 60 denote German PCB mixtures, viz. Clophen. Chlorofen is a commercial product from Poland.

spring (Fig. 3 and 4).

The distribution coefficient (Kd) of PCBs between solution and particles was calculated from PCB data in solution and SPM. A comparison was made with

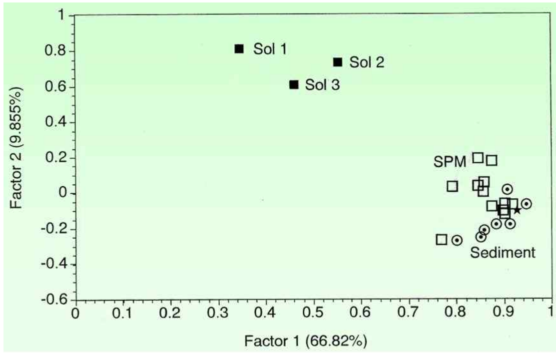

Fig. 2. Principle component analyses (PCA) plot of PCBs in solution (water), SPM and sediment from Oder estuary.

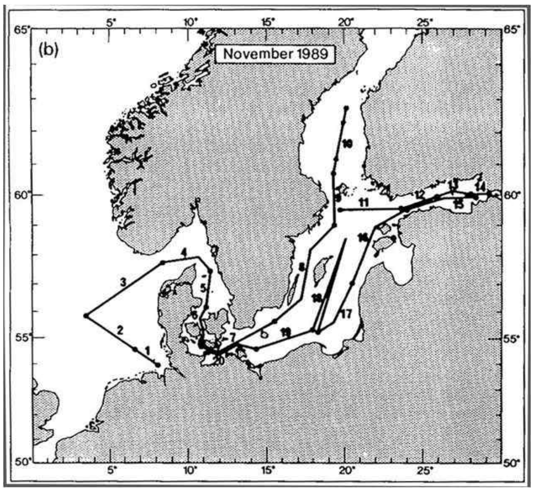

Fig. 3. Winter cruise transect in the Baltic.

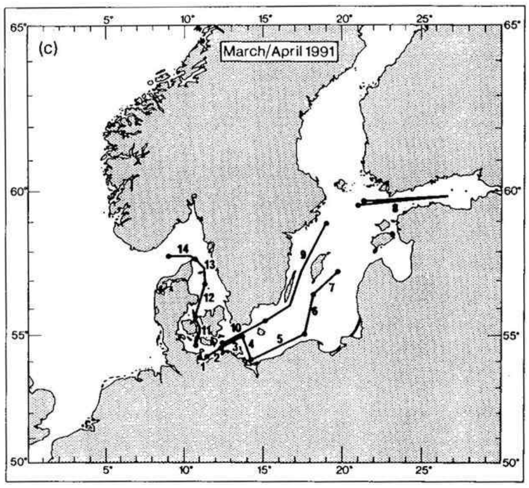

Fig. 4. Spring cruise transect in the Baltic.

similar values derived at steady state condition in a laboratory experiment [7]. When they were plotted together (Fig. 5) and observed several interesting facts emerged. For example, the winter plot revealed that Kd values for all transects in the Baltic were below the expected plot indicating that there was hardly any mass of SPM in the water. This means otherwise that biological productivity in the Baltic has not started yet. On the other hand, similar plots derived from spring cruise revealed a different story (Fig. 6).

For example, Kd values of transects where primary production has started showed values much higher than the expected plot indicating the availability of considerable SPM mass. On the other hand, those values from transects, which are mostly in the northern Baltic, showed lower values than the expected plot, indicating that primary production has not yet begun in those sectors. These are clear indications that PCB data if used judicially can reveal the occurrence of primary production in aquatic systems and can also reveal the transportation path of those materials.

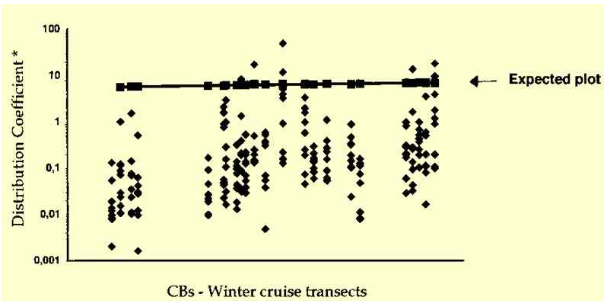

Fig. 5. Plot showing the distribution coefficient (Kd) of PCBs derived from their concentration in solution and SPM obtained during winter cruise in the Baltic in 1989. Each dot is a PCB congener and every row indicates a transect in the Baltic. The expected plot is derived from laboratory experiments [7].

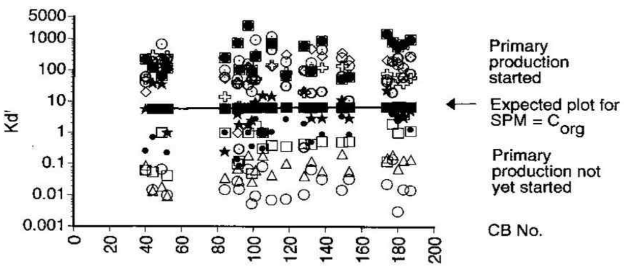

Fig. 6. Plot showing the distribution coefficient (Kd) of PCBs derived from their concentration in solution and SPM obtained during spring cruise in the Baltic in 1991. Each dot is a PCB congener and every row indicates a transect in the Baltic. The expected plot is derived from laboratory experiments [7].

PCBs reveal under water currents and movement of water masses

Sensitive measurement of PCBs in deep waters of East Sea using German techniques supports a Korean model developed from conventional oceanographic measurements. In 1995, a joint scientific cruise between IFM, Germany and NIRE, Japan was planned in the Japanese waters of East Sea. During this cruise a high volume, deep water sampler devised in Germany was experimented [15]. It was possible to collect several 100 liters of water from depths ranging from 50 m to 3000 m at one of the deepest points of the East Sea (viz. Seribesi trough with 3500 m depth). Fig. 7 shows the sampling tracks and vertical sampling sites in the East Sea and Pacific Ocean.

The usual vertical profile of PCB concentrations among world oceans is typified in Fig. 8 derived from an experiment in the Atlantic Ocean (47°N, 20°W). Thus the concentration decreases systematically from surface to bottom. On the other hand, the vertical profile in the East Sea was quite unique as shown in Fig. 9. The levels at the bottom water points showed considerable fluctuation indicating either under water currents

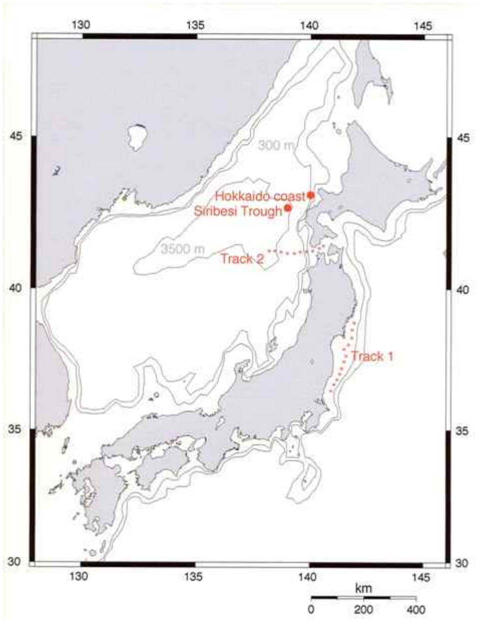

Fig. 7. Map showing surface water sampling tracks (1 & 2) and deep water sampling points (Siribesi trough and Hokkaido coast) in the Pacific Ocean and in the East Sea.

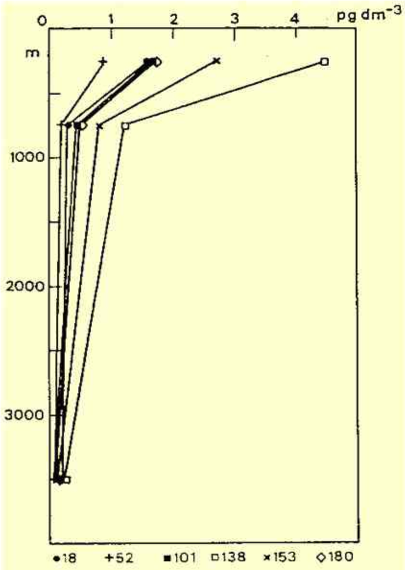

Fig. 8. Typical vertical profile of PCB concentration (numbers at the bottom indicate PCB congeners measured) in water column (samples from Atlantic Ocean).

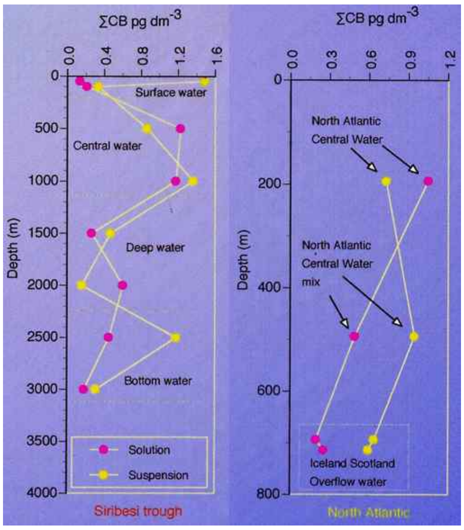

Fig. 9. Vertical profiles of PCBs in East Sea (left) and the North Atlantic (right).

or water masses. In fact, a similar observation in the North Sea [18] earlier suggested the presence of different water masses as shown in the right side of the figure 9. Hence, the data from the East Sea was further analyzed using PCA as shown in Fig.10. This clearly shows the existence of several water masses in the East Sea.

The naming of the water masses follows a scheme devised by Kang et.al. [10] as shown in Fig. 11. Accordingly, four water masses were identified namely, 1.surface water, 2.central water, 3.deep water, and

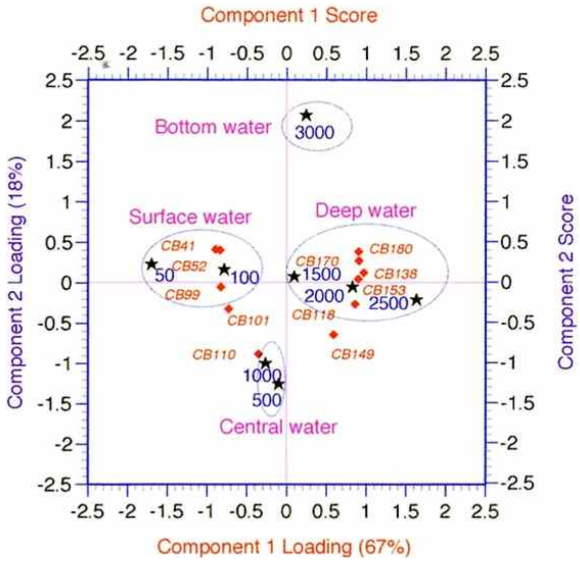

Fig. 10. A biplot of PCA analysis derived from PCB data (solution) of vertical samples at the East Sea.

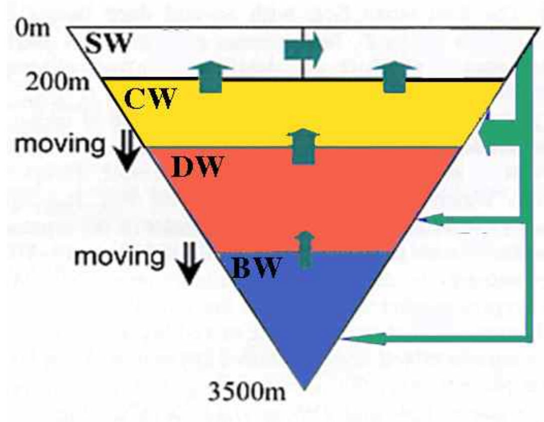

Fig. 11. Water masses in the East Sea. A scheme devised by Kang et al. [18].

4.bottom water. Based on their moving-boundary box model (MBBM), the water masses move over time causing currents and mixing. This is seen clearly in Fig.9 as the vertical profile of PCBs was not smooth as expected. The drastic fluctuation in the concentration is thus explained by the MBBM. This is another excellent example of using PCB data for understanding the physical oceanography of Oceans.

PCBs reveal population distribution

Individual chlorinated biphenyls were determined in blubber samples of 40 harbour porpoises (*Phocoena phocoena*) of different age and sex from the North Sea, the Baltic Sea and Greenland coastal waters [6].

Specimens were collected from the German coast of Schleswig-Holstein and Mecklenburg-Vorpommern and from the west coast of Greenland as shown in Fig. 12.

Subcutaneous blubber samples were taken from behind the dorsal fin. PCBs are known to accumulate in the fatty blubber tissue of marine mammals [14]. Congener specific analysis was carried out using high resolution techniques, including two dimensional gas chromatography [6]. The complex data obtained from 40 samples were normalized for PCA analysis and results plotted in Fig. 13. In this biplot of principal components 1 and 2 were derived from correlation matrix of mol% contributions of PCBs in the blubber tissue of male and female immature as well as male mature harbour porpoises from the Baltic Sea (B), North Sea (N) and Arctic waters (A). The CB numbers represent the loadings and B, N, A represent the scores. It is observable from this plot that the North Sea and Baltic Sea populations were distinctly separate from the Arctic population on the basis of levels and compositions of these contaminants. Read [17] notes that the population structure of harbour porpoises in the north-eastern Atlantic and North Pacific is complex and not well understood. In a genetic study, Andersen et al. [2] found that harbour porpoises from West Greenland, the Norwegian West coast, Ireland, the British North Sea, the Danish North Sea and the inland waters of Denmark (IDW) are all genetically distinguishable from each other.

A number of studies found differences between Baltic Sea and North Sea animals, although comparison of studies is difficult because sampling areas and methods differed notably. In such a complex biological situation, studies using PCBs throw some light on the population structure of marine wildlife which complements genetic studies.

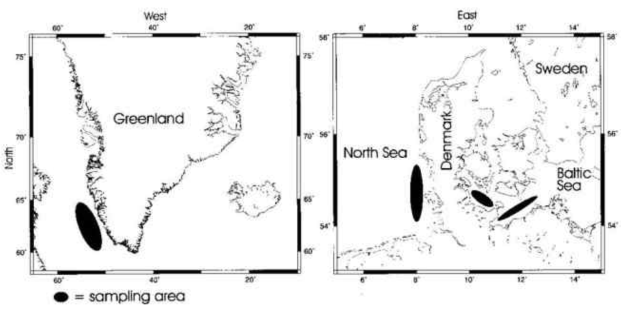

Fig. 12. Sampling locations in the Baltic Sea, North Sea and Arctic waters.

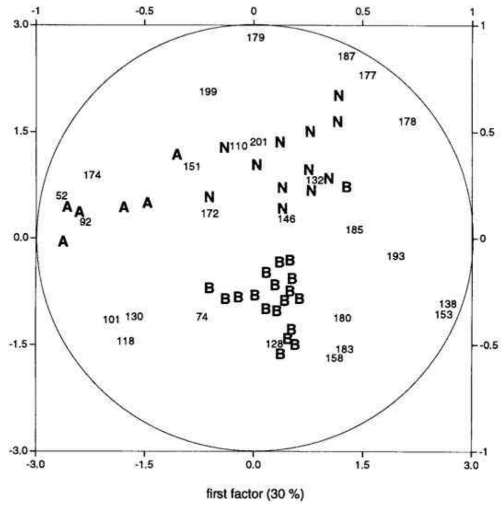

Fig. 13. Biplot of PCB loadings and scores revealing the nature of population distribution.

PCBs reveal physiological stress in animals

One possible mechanism by which PCBs may interfere with physiological function of animals, including humans is their ability to mimic natural hormones. This is achieved through the physicochemical properties encoded in the PCB molecular structure and the responses they evoke in biological systems. These physicochemical properties determine the molecular reactivities of PCBs and are responsible for their recognition at biological receptors, as well as for triggering molecular mechanisms that lead to tissue response. For example, if vicinal atoms are present in the *meta* and *para* positions with overlapping covalent radii at two *ortho*-Cl then it is highly improbable that this molecule will attain planar configuration. On the other hand, if a PCB congener exists with vicinal H atoms in the *ortho* and *meta* positions and non-overlapping covalent radii for *ortho*-Cl, i.e. when chlorine atoms do not oppose each other and this configuration causes a much lower energy barrier for attaining planar configuration [4]. Thus, "Coplanarity" of PCB phenyl rings and "laterality" of chlorine atoms are important structural features determining specific binding behavior with proteins and certain toxic responses in biological systems. The structure-activity-relationship for the metabolism of PCBs depends on the presence of vicinal Hs in *m,p* positions (substrates for cytochrome P450 IIB) or *o,m* positions (substrates for cytochrome P450 IA). The number of *ortho*-Cls affects metabolism: cytochrome P450 IA and IIB isozymes show a high affinity for planar and globular molecules, respectively [4]. There is a qualitative difference among the animal species in metabolizing PCBs. Seals show PB-type activity [3]. The situation for cetaceans is less clear.

Kannan et al. [13] described a model to explain the compositional similarities and differences in PCBs in members of marine food chains. Four groups of PCBs were distinguished based on the presence/absence of vicinal H-atoms in *o,m* and/ or *m,p* vicinal H-atoms, according to structure-activity relations for their biotransformation by cytochrome P-450 IA and IIB isozymes. Contents of PCBs (X) in the test sample were transformed into molar X/153 ratios (CB-153 is persistent) and plotted against X/153 ratios in a sample with least metabolic ability such as diatom, for example. For each metabolic group, a linear plot results. Their slopes indicate relative metabolic efficiencies of cytochrome P-450 isozymes.

This way of representation (Fig. 14) indicates PB-type enzyme activity in harbor porpoise (Schweinswal) and herring (Hering) which was not known before. Thus metabolic slopes of PCBs can be used as environmental stress indicators by comparison of slopes in a selected organism in areas with different degrees of contamination.

PCBs and risk assessment

The most popular method of assessing the 'potential' toxicity of dioxins and dioxin- like compounds (that include several classess of PCBs) is by using the so called Toxic Equivalents (TEQs) [21]. For example, TEQs were calculated using PCBs, Polychlorinated dibenzo dixions (PCDDs) and Polychlorinated dibenzofurans (PCDFs) concentrations in harbour porpoise collected in the Arctic, North Sea and Baltic Sea waters (Fig. 15). In a typical way, TEQs for toxic PCBs are far higher than PCDDs and PCDFs. Though TEQ is a useful tool for environmental managers to get a glimpse of 'potential toxic' stress in a particular ecosystem, metabolic slope-derived representation offers more clear picture of the metabolic stress in an organism in that ecosystem. For example, harbour porpoises in the Baltic Sea shows signs of mixed function oxidase (MFO) enzyme induction of both types, namely PB-type and MC-type in equal proportion (Fig. 16).

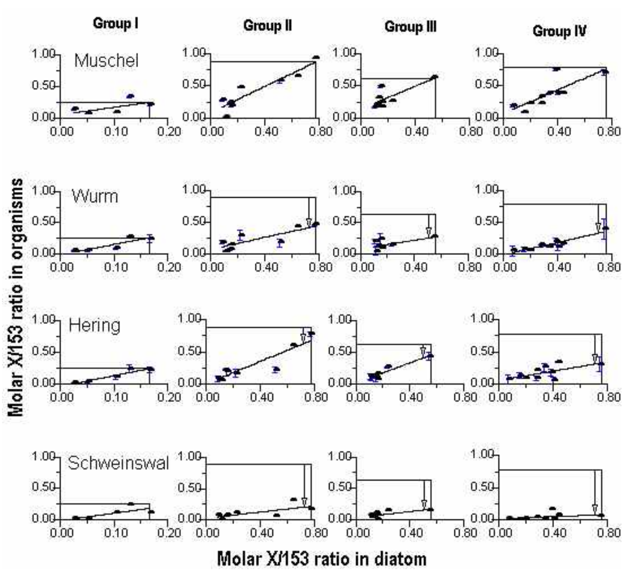

Fig. 14. Metabolic slopes [1] were derived from PCB data in organisms occupying a food chain.

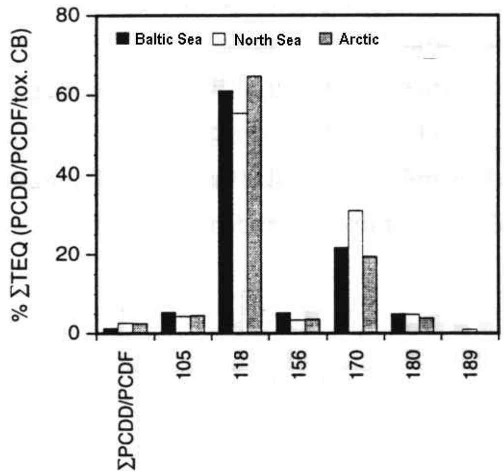

Fig. 15. TEQs of PCDDs, PCDFs and PCBs (represented as individual congeners) in harbor porpoise.

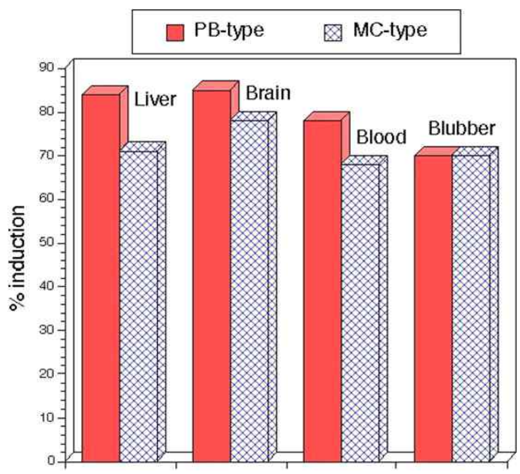

Fig. 16. Metabolic stress indicators in harbor porpoise from the Baltic Sea. PB-type induction represents P-450 IIB isozymes; MC-type induction represents P-450 IA isozymes

This is important as TEQs are essentially based on the levels of non-*ortho* and mono-*ortho* PCBs that induce MC-type isozymes. Fig.16 clearly shows that the induction of MFOs (both types) is prevalent in harbour porpoise indicating metabolism of several PCBs including non-*ortho* congeners as they are excellent substrates for these enzymes. This is one of the reason why it is hard to find non-*ortho* PCBs in many organisms. In this way, a representation as in Fig. 16 will account for both measreable and non-measreable congeners of PCBs in a holistic way.

It is reviewed in this article that PCBs when measured accurately in sea water, SPM, sediments and in organisms, are useful chemicals in revealing biological productivity, movement of water masses, transport of particles, biological stress and in ecological risk assessment.

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