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ACCOUNTING FOR PCBs IN THE CONTINENTAL SHELF SEDIMENTS AS PART OF A GLOBAL BUDGET FOR PCBs: TOWARD PREDICTIONS OF GLOBAL ENVIRONMENTAL LONGEVITIES

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Introduction

The expected environmental residence time should be one of the key elements in risk assessment of persistent organic pollutants (POPs). A quantitative understanding of the integrated interactions of persistent organic pollutants (POPs) with large-scale biogeochemical processes is required for predicting their global removal rates and thus environmental longevity. Due to their persistence, high ecotoxicity, and well-known span of physico-chemical properties, the notorious polychlorinated biphenyls (PCBs) serve well as POP model compounds. Persistent contaminants of semivolatile and hydrophobic nature such as the PCBs are found throughout the global biogeosphere. However, it is distressing that, after over three decades of research[1], we still cannot answer the question: which sink process dominates the large-scale fate of PCBs, and by inference many other POPs, and approximately how large is this sink?

The environmental pool of PCBs is dynamically recycled and partition between the major environmental media in response to the physico-chemical properties of the individual compounds. Because of their large organic-matter inventories, sediments and soils would be expected to constitute the largest environmental reservoirs of POPs due to the generally low vapor pressure and water solubility of the substances. Hence, because PCBs are continuously seeking to equilibrate between the different reservoirs, a permanent loss process of PCBs occurring in any one reservoir will be reflected also in the PCB inventory of the others. While PCBs are dynamically partitioning between the atmosphere-ocean-sediment/soil reservoirs, the net or permanent environmental sinks of PCBs are (*i*) burial to deeper layers of soils and sediments (*ii*) reaction with hydroxy radical in the atmosphere, and (*iii*) export to deep ocean water masses (removal on 100 yr time scale)[2,3].

Progress in elucidating the rate of these global environmental sink processes holds the key to estimate the "global cleaning time" and thus developing the capacity to predict at what rates the concentration of these compounds will decrease in various ecosystems and regions. The joint objective of the EU research project (GLOBAL-SOC) was to establish the global environmental residence times for POP model compounds of different physico-chemical properties (trichloro to heptachlorobiphenyls). Special emphasis will in this talk be placed on the role of the continental margin sediments as this compartment is still overlooked in other present-day large-scale POP fate models.

Methods

The recyclable PCB inventory and sink fluxes were calculated based on data from the troposphere (n=407), the ocean (n=224), continental margin sediments (n=2170), and soils (n = 207). The sampling locations for the different matrices are shown in Fig. 1.

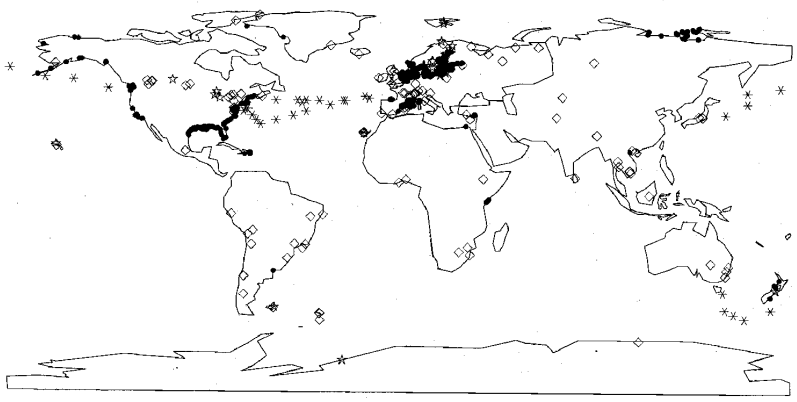

Fig. 1. Locations for the global PCB sampling program (filled circles = shelf sediments, open diamonds = soils, open stars = troposphere; and snowflakes = ocean samples).

Chemical analysis: followed common procedures of the research field, with minor differences between the GLOBAL-SOC laboratories. Generally, samples were organic solvent extracted, cleaned-up with SiO_2 and/or prep-HPLC, and analysed with gas chromatography- high resolution mass spectrometry or electron capture detector. Intercomparison quality tests gave a mean interlaboratory relative standard deviation of 28 % and the deviation appeared to be random. The risk of a systematic interlaboratory error affecting the results was therefore considered negligible. Methods were assured against contamination and loss of analyte.

Statistics: In a set of samples collected randomly, i. e. with no bias towards populated and possibly contaminated areas, a log-normal distribution can be expected[4]. In such a case an average value should be used to estimate the inventory[5]. However, to represent a "typical" concentration the median value is obviously preferable.

Shelf Sediments: A database was constructed largely based on a global literature search for PCBs in marine continental margin sediments. Obviously, since the data was based on tallying mostly already published records the sampling locations and applied analytical techniques could not be influenced. This most certainly lead to some inherent bias in the raw data set, which it was necessary to consider in the subsequent data analysis. The criteria for entry of data into the database were a transparent description of sampling location, sampling technique, sample handling and analytical methodology. Modelling was performed on the database when it consisted of entries of PCB concentrations for 4214 sediment samples. The subsequent modelling required input of estimates at the individual congener level. In addition to the directly reported individual congener concentrations, concentrations of the individual target congeners could be estimated for several other reporting forms (only 2170 data points were found useful in the end). The position of each datum relative the coastline of the Digital Chart of the World (DCW®) was checked in the GIS software Geomedia®. Since the original sediment sampling is likely to have been biased toward near-urban shelf sediments as opposed to the vast remote regions of the global continental shelf, the data was divided for modelling into three groups with respect to distance to presumed urban source regions. The data were classified as local, regional or remote accordingly to if their distance was less than 1 km, between 1 and 10 km or more than 10 km to the nearest population centre as defined by DCW® data in Geomedia®. More details is found in ref. 6.

Results and Discussion

There are large inter-congener differences in environmental fate. The most important recyclable pools for PCBs in the environment are the continental shelves[6] and the soils[7], with total amounts of individual congeners of the order 1000 ton. The Remote shelf areas are quantitatively much more important than all the local hot-spots (Fig. 2). The Remote sub-basin of the North Atlantic contains approximately half of the global shelf sediment inventory for most of the PCB congeners studied (e.g., for PCB52 in Fig. 2). The vast Arctic shelf contains only a few per cent of the global shelf inventory of PCBs.

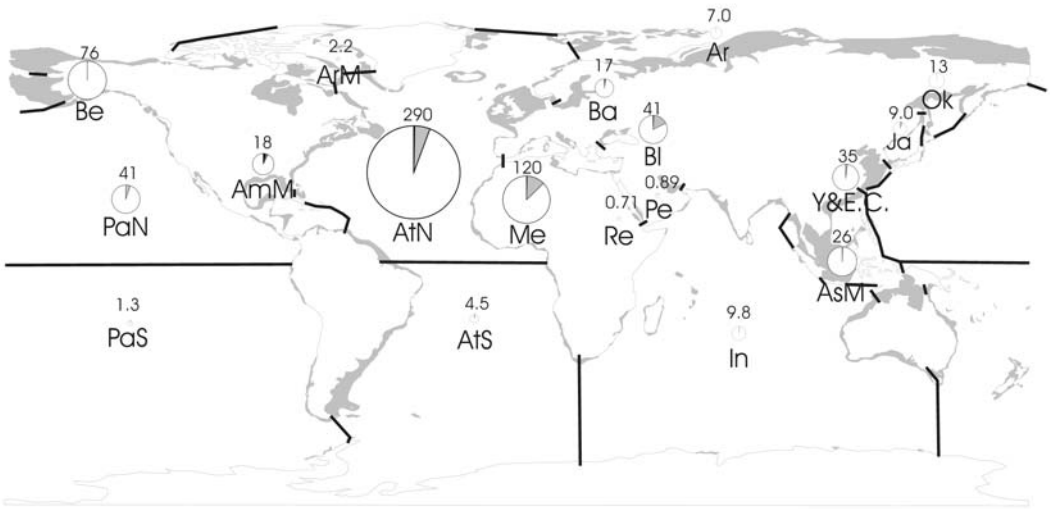

Fig. 1. *Inventories (metric ton) in the ocean shelf sediments for PCB52 partitioned between the different basins (areal extents of each basin are indicated with thick black lines). The diameters of the pie charts are proportional to the total inventory in each basin (listed above pie chart). The contribution of each sub-basin class to the total inventory is indicated by the size of the pie slices as white (remote), grey (regional), and black (local). It is evident that the Remote shelf sediments on Earth host the vast majority of shelf sedimentary PCBs. The grey-marked zone of the continental margins represent the extent of the 0-200 m depth continental shelf as defined by the General Bathymetric Chart of the Ocean (GEBCO®).*

The global shelf inventories represent 1-6% of the global industrial production of PCBs[8]. For the heavier congeners, over 50% of the PCBs projected to have been cumulatively released to the environment are accounted for in these marine sediments. The global shelf burial fluxes were estimated to be on the order of 8-24 ton/yr each for the eight major congeners investigated. Tropospheric reaction with the hydroxy radical appears to be the dominant environmental sink for lighter PCBs whereas burial in continental shelf sediments and export to the deep ocean is the most important removal mechanisms for more hydrophobic congeners. The permanent removal into deeper shelf sediments of PCB153 and PCB180 suggests that the global environmental mean residence times of these pollutants are on the order of 50-100 years. Hence, even after production and direct releases have been halted, we may expect to be exposed to such persistent pollutants for decades and centuries to come.

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