MATHEMATICAL MODELING OF HUMAN DIETARY EXPOSURE TO POLYCHLORINATED BIPHENYLS

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Introduction

Polychlorinated biphenyls are a family of 209 compounds made up of attached benzene rings with varying numbers and locations of chlorine atoms. PCBs are characterized by their low flammability, low electrical conductivity, high resistance to thermal breakdown and to other chemical agents, and high degree of chemical stability. These qualities make them effective coolants, lubricants, and insulators[1]. The physical attributes that make PCBs useful in industry also make them a serious health threat to workers, wildlife, and communities[2,3]. PCBs' environmental persistence and long-range transport properties facilitate their movement to all environmental compartments. PCBs continue to enter the groundwater, soils, and atmosphere from multiple sources including old industrial equipment, recycled oil and materials, chemical manufacturing, landfills, and incineration of industrial and municipal waste. Even so-called "closed" industrial systems can release large amounts of PCBs. Until recently it was believed that there were no natural sources of PCBs. However, PCBs not associated with anthropogenic activities were identified in ash from volcanic eruptions, and subunits of PCBs have also been identified as components of glycoproteins[4].

Understanding how the chemical behaves in the environment provides information on possible effects on human health and allows for the risk to humans and the environment to be assessed. In order to assess the behavior of a chemical, the intrinsic properties and emission patterns of the chemical must be known. Due to the persistence of POPs, and their tendency to bioaccumulate and biomagnify, almost undetectable concentrations in the abiotic environment have the potential under certain conditions to result in significant exposure levels for organisms at higher trophic levels, e.g. humans (with biomagnification factors greater than 10^7 in some cases)[5]. PCBs concentrate in the food web and bioaccumulate in the fatty tissue of wildlife and people. Virtually everyone has PCBs in their bodies.

In order to understand distribution and transformations of PCBs in the environment, we need, besides their basic physical characteristics, additional information on their environmental behaviour and reactions. Even a good knowledge of physical and chemical properties of these persistent industrial substances does not enable precise distribution of PCBs over the Earth since such a global experiment was performed only once, and because it is complex, long-lasting, unplanned, subject to changes, and practically impossible to reconstruct. Thus, for complete understanding of distribution phenomena it is necessary to combine results of monitoring and field studies with the mathematical models, which are substitutes for the controlled experiment that cannot be performed in the natural systems.

Methods and Materials

Postulation of the mathematical model

In this paper a mathematical model for human dietary exposure to polychlorinated biphenyls is postulated, based on the calculation of human exposure factors to PCBs via different members of the terrestrial food chain (Eq. 1):[6]

$$e_{total} = \int_{t_1}^{t_2} e_i dt = \int_{t_1}^{t_2} F_i \cdot c_i dt \qquad [1]$$

where: e_{total} – total human exposure to a contaminant, e_i – human exposure to contaminants from the foodstuff *i*,F_i – exposure factor of humans to a contaminant from a foodstuff *i*,c_i – contaminant concentration in a foodstuff *i*,$(t_2$-$t_1)$ – time interval of the exposure.

If concentration of PCBs in all foodstuffs is considered constant over a period of one day,

$$e_{total} = \sum_i e_i = \sum_i F_i \cdot c_i \qquad [2]$$

expression [1] can be transformed into:

Required input data:

- PCBs concentrations in atmosphere and soil;
- *Physical and chemical properties of PCBs* (density, solubility, partition coefficients, Henry's constant, runoff constant, factors of the uptake of PCBs by plants and animals, biotransfer factors of PCBs into meat $BTF_{(z)}$, specifically into beef - $BTF_{(g)}$, pork - $BTF_{(s)}$, and chicken - $BTF_{(p)}$, milk - $BTF_{(m)}$, and eggs - $BTF_{(j)}$)
- *Meteorological parameters of the environment* (average daily precipitation, average annual temperature);
- *Physiological characteristics of plants, animals and humans* (annual plant inventory, intake of air and food by animals and humans).

Model output includes:

- *Fa/v* – human exposure factor (HEF) to atmospheric contaminants via foodstuffs of plant origin (grains, fruits and vegetables)
- *Ft/v* – HEF to soil contaminants via plants
- *Fv/g, Fv/s, Fv/p* – HEFs to contaminants in vegetation via beef, pork and chicken (respectively)
- *Fm/g* – HEF to contaminants in cow's milk
- *Fj/p* – HEF to contaminants in eggs.
- *Total average daily exposure* of humans to PCBs

Experimental

In order to evaluate the proposed mathematical model, content of total PCBs was determined in samples of plants, beef, pork, chicken, cow's milk and eggs taken from 6 localities in the city of Novi Sad, and also in soil. Samples of foodstuffs were extracted with the n-hexane for 8 hours in the Soxhlett apparatus. Soil samples were extracted for 24 hours with the mixtureof n-hexane:acetone (1:1) on the mechanical shaker. After filtration and cleanup with concentrated sulfuric acid, content of PCB residues was determined by gas chromatography (GC/ECD), with the following parameters: Instrument: HP 6890 GC; Detector: ECD; Capillary column-HP-5% Phenyl-Methyl Siloxane; Applied method: EPA 625.

Results and Discussion

Within the mathematical modeling of human dietary exposure to PCBs the following expressions for HEFs were obtained:

$$F_{a/v} = \frac{U_v \cdot c_v}{c_a} = U_v \cdot \frac{\left(0,259(\rho - 1,29) + P \cdot b \cdot K_{c/w}\right) \cdot L + \frac{K_{c/w} \cdot RT}{H}}{G \cdot M} \cdot \omega_i \qquad [3]$$

$$F_{t/v} = U_{vp} \cdot K_{vp/t} \cdot k_{sm} \cdot \omega_{vp} + U_c \cdot K_{c/t} \cdot k_{sm} \cdot \omega_c \qquad [4]$$

$$F_{v/z} = \sum_i U_{z_i} \cdot \left(\frac{U_a \cdot a}{TM_z} + \frac{U_v}{TM_z} \cdot BTF_i\right) \cdot \omega_i \qquad [5]$$

$$F_{m(g)} = U_m \cdot U_g \cdot \left(\frac{U_a \cdot a}{TM_z} + \frac{U_v}{TM_z} \cdot BTF_{(g)}\right) \cdot BTF_{(m)} \qquad [6]$$

$$F_{j(p)} = U_j \cdot U_p \cdot \left(\frac{U_a \cdot a}{TM_z} + \frac{U_v}{TM_z} \cdot BTF_{(p)}\right) \cdot BTF_{(j)} \qquad [7]$$

where: U_v, U_{vp}, U_c, U_z, U_m, U_g, U_j, U_p – average human daily intake of foodstuffs (total vegetation, fruits and vegetables, grains, total meat, milk, beef, eggs and chicken, respectively) in g/kg day; U_a – average air intake by domestic animals used in human diet, in m^3/day; ρ - density of PCBs, in kg/m^3; P – average daily precipitation rate, in 1/m day; b – runoff constant; $K_{c/w}$ – cuticle-water partition coefficient for PCBs; L – exposed leaf area; H – Henry's constant for PCBs; T – average annual temperature; G – removal constant for PCBs from exposed plant area; M – annual inventory of plants; $K_{vp/t}$ and $K_{c/t}$ – partition coefficient of PCBs between soil and fruits and vegetables, or grains; ω_{vp}, ω_c – fraction of fruits and vegetables, and grains, in the total dauly intake of plant food; k_{sm} – dry mass/fresh mass ratio for plant food; TM – body mass of the animal used in human diet.

The proposed model enables calculation of biotransfer factors of PCBs from different members of the food chain, based on the interpolation of the literature experimental data for 12 persistent organic pollutants. These values are listed in Table 1.

Table 1. Parameters used for PCBs in calculation of human exposure factors

Mean density	ρ= 1400 kg/m3*
Henry's constant	H = 0.02*
Partition coefficient octanol/water	log Ko/w =6.97*
Partition coefficient vegetation/soil	Kvp/t = 0.029**
Partition coefficient cuticle/water	Kc/w = 0.359**
Biotransfer factor from plants into beef	BTF(g) =0.079**
Biotransfer factor from plants into pork	BTF(s) =6.026**
Biotransfer factor from plants into chicken	BTF(p) =66.069**
Biotransfer factor from beef into milk	BTF(m) =0.00681**
Biotransfer factor from chicken into eggs	BTF(j) =74.131**

*literature data, ** values calculated using the proposed model

In calculation of the theoretical concentrations of PCBs in plants, beef, pork, chicken, cow's milk and eggs, the equations [3-7] were used. Since there is no domestic legislative, which requires determination of PCB content in the atmosphere as a measure of air quality, maximal allowed concentrations in air were used, according to the EU regulations[7]. Concentration of PCBs in atmosphere and in soil (determined experimentally) were as follows: c_a = 5e-10 mg/m^3, c_s = 0.05 mg/kg.

Comparison of PCBs concentrations determined experimentally in foodstuff samples by gas chromatography, and calculated values are represented in Figure 1.

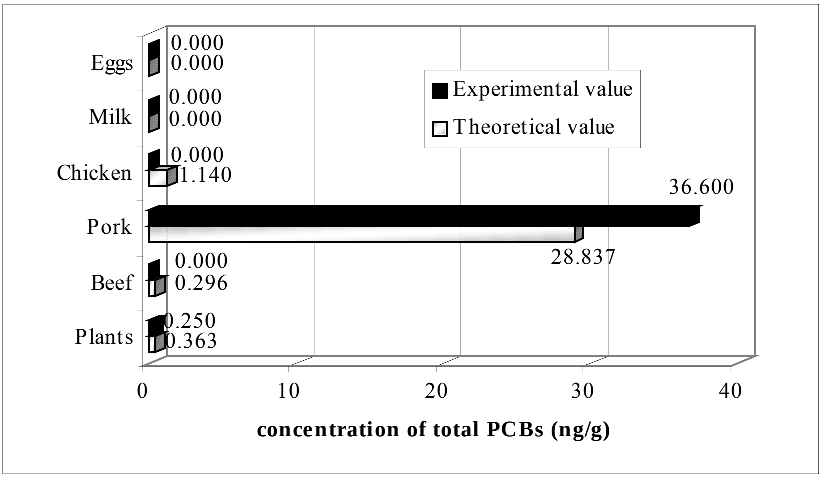

Fig. 1. Correlation between theoretical (calculated) and experimentally determined concentrations of total PCBs in samples of foodstuffs

Comparison of calculated and experimentally determined concentrations of contaminant concentrations in vegetation show that correlation between them is excellent. Higher theoretical values can be explained by the probably lower actual atmospheric concentrations of given pollutants than maximally allowed concentrations in air.

On the basis of postulated model and experimental values for the atmospheric and soil concentration of PCBs it is possible to calculate the average daily exposure of a human organism to these ubiquitous environmental toxicants, which represent a constant threat to human health due to various chronic, developmental and genetic effects. Proposed model is the contribution to the development of exposure analysis, which is a part of a complex process of risk assessment, which gains its importance in the current situation of rapid development of industry and technology and the existence of innumerable anthropogenic hazardous chemicals.

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