

## Possibility of elimination of polychlorinated biphenyls from liquid media by sorption onto low-density polyethylene packaging material

BOŽENA SKLÁRŠOVÁ – PETER ŠIMKO – PETER ŠIMON – BEATA DROBNÁ

### Summary

Polar (water) and non-polar (rapeseed oil) media were spiked with six polychlorinated biphenyls (PCB), filled into low-density polyethylene (LDPE) cylindrical receptacles and the PCB concentrations were followed within 72 h. It was found that PCB concentration in water decreased considerably during the experiments due to the adsorption of PCB onto the walls of the receptacles. By using of the experimental data, diffusion and the distribution coefficients were obtained for all studied compounds for polar water using a kinetic equation. Comparing LDPE surface and the surface of monomolecular PCB film to be calculated on the base of difference between initial and infinite PCB concentrations as well as surface PCB molecule sizes, it was deduced that the mechanism of PCB removal can be characterized either as monomolecular adsorption combined with subsequent diffusion into LDPE, or as two-layer molecular adsorption. Regarding rapeseed oil, it was found that LDPE was not an efficient material for removal of PCB from this medium because PCB concentrations remained at a constant level during the experiment, probably due to stronger interactions oil-PCB in comparison to LDPE-PCB interactions.

### Keywords

polychlorinated biphenyls; low-density polyethylene; adsorption; diffusion; elimination of contaminants

Polychlorinated biphenyls (PCB) are a group of 209 man-made organic chemicals containing carbon, hydrogen and differing amounts of chlorine atoms. The commercial production of PCB started in 1929 but their use had been banned or severely restricted in many countries since the 1970s and 80s because of serious risks to human health and the environment. PCB have been used in a wide range of products such as polymers, paints, and adhesives. Since PCB are resistant to acids and bases as well as to heat, they have mainly been used in electric equipment as heat transfer fluids, or lubricants, respectively. PCB were first detected in environmental samples in 1966 [1]. PCB can persist in the environment and accumulate in animal tissue and along the food chain. A human organism may be exposed to PCB by ingestion of contaminated food and water or by inhalation of contaminated air. PCB have been shown to cause cancer as well as a number of serious non-cancer

health effects in animals, including effects on the immune system, reproductive system, nervous system, endocrine system, more frequent infections, and skin changes, particularly rashes and chloracne. Their harmful effects to man are well documented in a number of reviews [2-6]. Therefore, protection of the food chain against PCB penetration is an important topic of current science and technology. Adsorption of organic contaminants on polymer packaging materials is a promising way of reducing the contents of organic contaminant in foods [7-10]. On the basis of these interactions, concentrations of polycyclic aromatic hydrocarbons (PAH) in a liquid smoke flavour stored in low density polyethylene (LDPE) bottles were lowered by two orders of magnitude during 14 days. As found, the rate-limiting step was the diffusion in the liquid medium. PAH were primarily adsorbed on the LDPE surface, with subsequent diffusion into the bulk of the polymer, which intensified the

**Božena Skláršová, Peter Šimko**, VÚP Food Research Institute, Priemyselná 4, P. O. Box 25, SK – 824 75 Bratislava 26, Slovakia.

**Peter Šimon**, Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, SK – 812 37 Bratislava, Slovakia.

**Beata Drobňá**, Department of Toxic Organic Pollutants, Research Base of the Slovak Medical University, Slovak Medical University, Limbová 12, SK – 833 03 Bratislava, Slovakia.

*Correspondence author:*

Peter Šimko, tel.: 00 421 2 55574622, e-mail: peter.simko@vup.sk

effectiveness of the removal process [11]. Recently, PCB were partially removed from polar media by adsorption onto polyethylene terephthalate and polystyrene. Therefore, the aim of this work was to study the possibilities of PCB removal from water as a polar medium, and from rapeseed oil as a non-polar medium, by adsorption onto LDPE plastic material.

## MATERIALS AND METHODS

### *Rapeseed oil*

Commercially available rapeseed oil was produced by Palma-Tumys (Bratislava, Slovakia) and purchased in a local market in Bratislava. The oils were packed in PET bottles with a volume of 4 l.

### *LDPE receptacles*

LDPE flasks with i.d of 45 mm and 68 mm, respectively, were purchased from Čechvalab (Bratislava, Slovakia).

### *PCB*

PCB congeners:

- PCB 28 (2,4,4'-trichlorbiphenyl);
- PCB 52 (2,2',5,5'-tetrachlorbiphenyl);
- PCB 101 (2,2',4,5,5'-pentachlorbiphenyl);
- PCB 103 (2,2',4,5',6-pentachlorbiphenyl);
- PCB 138 (2,2',3,4,4',5'-hexachlorbiphenyl);
- PCB 153 (2,2',4,4',5,5'-hexachlorbiphenyl);
- PCB 174 (2,2',3,3',4,5,6'-heptachlorbiphenyl);
- PCB 180 (2,2',3,4,4',5,5'-heptachlorbiphenyl)

were purchased from Labservice (Spišská Nová Ves, Slovakia) each with the concentration of 100 µg.ml<sup>-1</sup> in hexane.

### *Solvents*

Methanol, dichloromethane and hexane of analytical grade were purchased from Merck, Darmstadt, Germany. The solvents were rectified just before use in a distillation apparatus.

### *Other chemicals and materials*

Anhydrous Na<sub>2</sub>SO<sub>4</sub>, alumina, Florisil, silica gel and H<sub>2</sub>SO<sub>4</sub> were also purchased from Merck.

## Experiment

### *Water*

Distilled water was spiked with six PCB congeners solutions diluted in acetone to obtain final concentration in water between 1–7 µg.l<sup>-1</sup>. Then, water was heated to 40 °C for 1 h and occasionally shaken to evaporate the residual acetone. After cooling to 19.0 °C, water was sampled for initial PCB concentration. Then, LDPE flasks were filled

with the water and placed into a foam polystyrene box to protect them from light and to keep the constant temperature of 19.2 °C. The temperature was monitored and recorded by thermometer Logger S 0121 (Comet System, Rožnov pod Radhoštěm, Czech Republic).

The samples for analysis were taken after 1; 3; 5; 7; 11; 24; 72 h. To maintain the same static conditions, a new set of receptacles was taken for each analysis.

### *Rapeseed oil*

An amount of 100 g of rapeseed oil was spiked with six PCB congeners in hexane in 2 l volume glass flask and the solvent was left to evaporate spontaneously. The oil was stirred occasionally to accelerate the evaporation of the solvent. Then, roughly 900 g of oil was added and the flask content was stirred thoroughly. At this stage, the oil was sampled to determine the initial PCB concentration. Then, LDPE flasks were filled with the spiked oil and placed into a polystyrene box to protect them from light and to keep a constant temperature of 18.2 °C. The samples for analysis were taken after 1; 3; 5; 7; 11; 24; 72 h. To maintain the same static conditions, a new set of receptacles was taken for each analysis.

## Sample preparation

### *Water*

A volume of 5 ml of water was extracted with hexane for four times. Hexane layers were combined, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated until nearly dryness. The remaining solvent was evaporated at room temperature just before analysis. The residuum was dissolved in a known volume of standard solution of PCB 103 and analysed by GC.

### *Rapeseed oil*

A known amount of the standard solution of PCB 174 was added to rapeseed oil (approx. 0.100 g) and weighted to the nearest 0.001 g to determine the extraction recovery. The sample was dissolved in 1 ml of hexane and cleaned up in the combined Florisil-silica gel column (0.5 g Florisil, 1 g 44% H<sub>2</sub>SO<sub>4</sub> on silica gel, 0.5 g Florisil and 1 g anhydrous Na<sub>2</sub>SO<sub>4</sub>). The column was eluted with 10 ml of 10% (v/v) dichloromethane in *n*-hexane. The eluate was evaporated to about 0.5–1 ml and transferred by a Pasteur pipette into a vial. Evaporation continued under nitrogen until nearly dry. The remaining solvent was evaporated at room temperature just before analysis. The residuum was dissolved in a known volume of the sampling standard solution of PCB 103 and analysed by GC.

### GC analysis

Analyses were performed on a gas chromatograph 6890N (Agilent Technologies, Palo Alto, California, USA) equipped with an electron capture detector, using a capillary GC column DB-5, 60 m, 0.25 mm (i.d.), 0.25  $\mu\text{m}$  film thickness (J&W Scientific, Folsom, California, USA), using the splitless technique with a temperature programme as follows: isothermal at 110  $^{\circ}\text{C}$  for 1.5 min, then temperature elevation to 200  $^{\circ}\text{C}$  at 30  $^{\circ}\text{C}\cdot\text{min}^{-1}$ , hold for 0.2 min, then temperature elevation to 300  $^{\circ}\text{C}$  at 2.5  $^{\circ}\text{C}\cdot\text{min}^{-1}$ . Helium was used as a carrier gas with a constant flow rate of 0.8  $\text{ml}\cdot\text{min}^{-1}$ .

## RESULTS AND DISCUSSION

At first, the experiment was carried out with the spiked water filled in LDPE receptacles. Concentrations of PCB started to decrease immediately after filling the receptacles in the studied system (Fig. 1). The observed dependences of PCB concentrations versus time were treated using the kinetic equation (1), which was derived for the diffusion of PAH in non-stirred liquids placed into cylindrically-shaped receptacles [7]:

$$c_t = c_{\infty} + (c_0 - c_{\infty}) \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} \exp[-D \alpha_n^2 t] \quad (1)$$

where  $c_0$  is the initial concentration of PCB in water,  $c_t$  is the concentration of PCB in the medium at time  $t$ , and  $c_{\infty}$  is the concentration of PCB corresponding to infinite time (equilibrium),  $a$  is the radius of the cylinder,  $\alpha_n$  are the roots of the zero-order first-kind Bessel function, and  $D$  is the diffusion coefficient of PCB in water. The parameters  $c_{\infty}$ ,  $c_t$  and  $D$  were obtained by the non-linear least

squares method by minimizing the sum of squares of differences between the PCB concentrations measured experimentally and those calculated by equation (1). The values of minimized parameters are listed in Tab. 1.

The extent of PCB removal can be characterized by the distribution coefficient expressed by the formula

$$\beta = \frac{c_0 - c_{\infty}}{c_{\infty}} \quad (2)$$

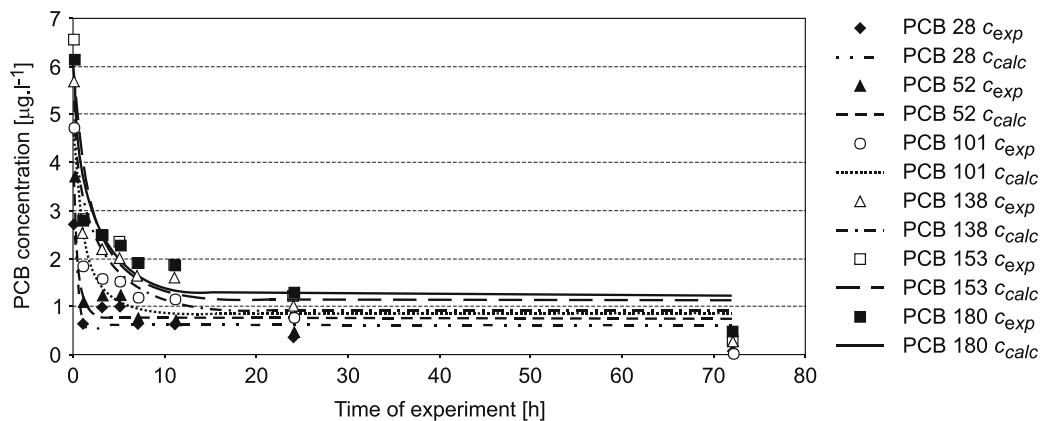
**Tab. 1.** Values of the identified model parameters, diffusion and distribution coefficients of PCB congeners in water – LDPE system.

	LDPE			
	$c_{\infty}$ [ $\mu\text{g}\cdot\text{l}^{-1}$ ]	$c_t$ [ $\mu\text{g}\cdot\text{l}^{-1}$ ]	$D$ [ $\text{cm}^2\cdot\text{h}^{-1}$ ]	$\beta$
PCB-28	0.61	2.12	3.62	3.490
PCB-52	0.73	3.02	1.42	4.119
PCB-101	0.83	3.76	0.44	4.528
PCB-138	0.92	4.40	0.25	4.767
PCB-153	0.97	5.27	0.26	5.433
PCB-180	1.22	4.58	0.26	3.764

**Tab. 2.** Comparison of identified model parameters and average distribution coefficients of PCB in water – “plastics” systems.

	$c_{\infty}$ [ $\mu\text{g}\cdot\text{l}^{-1}$ ]	$c_t$ [ $\mu\text{g}\cdot\text{l}^{-1}$ ]	$\beta$
PET*	9.65	11.98	1.24
PS*	4.42	17.32	3.92
LDPE	1.06	27.75	4.35

\* values from SKLÁRŠOVÁ et al. [10].



**Fig. 1.** Changes in PCB concentration in water stored in LDPE flasks. Experimentally obtained data vs calculated data using kinetic equation of adsorption (1).

**Tab. 3.** Surface area of PCB molecules and area of PCB monolayer on polymer surface.

Compound	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180	Total
Surface area [nm <sup>2</sup> ]	2.634	2.741	2.886	3.014	3.031	3.159	
Molar mass [g.mol <sup>-1</sup> ]	257.559	292.008	326.457	360.906	360.906	395.355	
PET coverage* [%]	2.9	2.6	4.1	6.2	7.2	7.4	30.4
PS coverage* [%]	2.8	4.6	7.0	11.6	12.6	14.1	52.7
LDPE coverage [%]	14.7	19.2	22.5	25.0	29.8	24.8	136.0

\* values from SKLÁRŠOVÁ et al. [10].

The higher is the value of  $\beta$ , the greater part of PCB is removed from water at reaching the equilibrium. The values of  $\beta$  are listed in Tab. 1, average  $\beta$  is given in Tab. 2. It is clear that the value of  $\beta$  for LDPE is higher than the corresponding values for PET and PS [10]. This implies a higher affinity of PCB to LDPE in comparison with PET and PS, respectively. A comparison of “total PCB area” to contact area of the polymer receptacles is based on the calculation of the monomolecular film formed from PCB molecules, when the surfaces of congener molecules were calculated using the Savol programme (Tripos, St. Louis, Missouri, USA) and they are summarized in Tab. 3.

Extent of coverage of the polymer surface was calculated from differences between initial and equilibrium PCB concentrations in water using the modified formula derived in [12]

$$C = \frac{N_A a (c_0 - c_\infty) S}{2M} \quad (3)$$

where  $C$  is extent of coverage by PCB film on polymer surfaces,  $M$  is the molar mass of PCB,  $N_A$  is the Avogadro number,  $S$  is the surface of PCB congener molecule calculated by the Savol program, and the other symbols have the same meaning as above. Results showed that the area of LDPE to

be covered by PCB adsorbed onto the polymer surface is equal to 136% of the total LDPE area. This value indicates that the removal of PCB from water could be classified either as monomolecular adsorption combined with subsequent diffusion into LDPE, or as two-layer molecular adsorption.

Different situation was observed in the case of rapeseed oil, where the concentrations at the beginning of experiment decreased only slightly, exhibiting oscillations with a subsequent return to the original concentrations (Fig. 2). This indicates that the affinity interactions between oil and PCB are much stronger than the interactions between the polymers and PCB. For this reason, LDPE is applicable to eliminate PCB from polar aqueous media, but not from rapeseed oil. The fact that LDPE can considerably lower PCB concentrations in foods may be exploited to protect the consumer from exposition to these hazardous compounds

## CONCLUSIONS

1. PCB concentration in water filled into LDPE receptacles decreases considerably due to affinity interactions between PCB and the surface of the polymer.

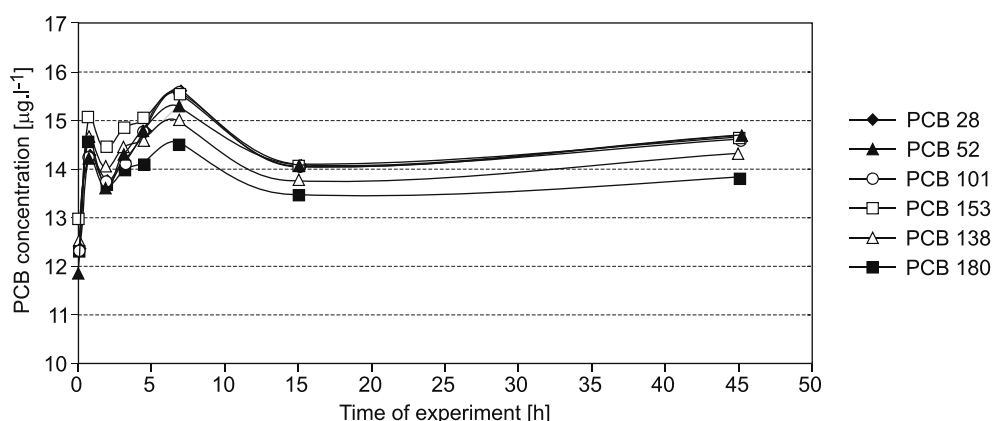


Fig. 2. Changes in PCB concentration in rapeseed oil stored in LDPE flasks.

2. The interactions between PCB and the polymer can be classified either as monomolecular adsorption combined with subsequent diffusion into LDPE, or as two-layer molecular adsorption.
3. The values of diffusion coefficients obtained enable to predict the rate of PCB elimination at any time of the interaction; the values of distribution coefficients characterize the extent of the removal of PCB congeners.
4. LDPE is a suitable material for an efficient removal of PCB from polar aqueous media.
5. LDPE is not applicable for elimination of PCB from rapeseed oil as a non-polar matrix.

#### Acknowledgement

This work was supported by Science and Technology Assistance Agency of Slovak Republic under the contract No. APVT-27-002204.

#### REFERENCES

1. Jensen, S.: Report of a new chemical hazard. *New Scientist*, 32, 1966, pp. 116.
2. IARC Monographs on the evaluation of the carcinogenic risk of chemicals to humans. Vol. 18. Polychlorinated biphenyls and polybrominated biphenyls. Lyon : International Agency for Research on Cancer, 1978, 140 pp. ISBN 92 832 1218 5.
3. IARC Monographs on the evaluation of the carcinogenic risk of chemicals to humans. Supplement 7. Overall evaluation of carcinogenicity: An updating of IARC monographs, Vol 1 to 42. Lyon : International Agency for Research on Cancer, 1987. 440 pp. ISBN 92 832 1411 0.
4. Fuoco, R. – Ceccarini, A: Polychlorobiphenyl residues. In: Nollet, L. M. L. (Ed.): *Handbook of food analysis*. New York, Basel : Marcel Dekker, 2004, pp. 331–336.
5. Kimbrough, R. D.: Human health effects of polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs). *Annual Review of Pharmacology and Toxicology*, 27, 1987, pp. 87–111.
6. Masuda, Y.: Health effects of polychlorinated biphenyls and related compounds. *Journal of Health Science*, 49, 2003, pp. 333–336.
7. Šimko, P. – Šimon, P. – Khunová, V. – Bruncková, B. – Drdák M.: Kinetics of polycyclic aromatic hydrocarbons sorption from liquid smoke flavour into low density polyethylene packaging. *Food Chemistry*, 50, 1994, pp. 65–68.
8. Skláršová, B. – Šimko, P. – Šimon, P. – Belajová, E.: Diffusion and adsorption of BaP from vegetable oils onto polyethylene terephthalate and low density polyethylene package. *Journal of Food and Nutrition Research*, 45, 2006, pp. 12–16.
9. Šimko, P. – Kolek, E. – Skláršová, B. – Šimon, P.: Removal of benzene from water by adsorption on polymer materials. *Journal of Food and Nutrition Research*, 45, 2006, pp. 179–182.
10. Skláršová, B. – Šimko, P. – Šimon, P. – Drobná, B.: Removal of polychlorinated biphenyls from water by sorption onto polymers. *Journal of Food and Nutrition Research*, 46, 2007, pp. 128–133.
11. Šimko, P. – Šimon, P. – Khunová, V.: Removal of polycyclic aromatic hydrocarbons from water by migration into polyethylene. *Food Chemistry*, 64, 1999, pp. 157–161.
12. Šimko, P. – Šimon, P. – Belajová, E.: Lowering of concentration of polycyclic aromatic hydrocarbons in liquid media by sorption into polyethylene terephthalate – a model study. *European Food Research and Technology*, 219, 2004, pp. 273–276.

Received 4 June 2008; revised 10 August 2008; accepted 15 August 2008.