PROBLEMS OF ADSORPTION IN ANALYSIS OF PCBs IN PLANTS GROWING ON EXPERIMENTAL REMEDIATION FIELDS

Hodak Kobasic V, Calic V, Picer M
[1]Institute "Rudjer Boskovic", Bijenicka 54, 10000 Zagreb, Croatia

Introduction

Polychlorinated biphenyls (PCBs) are xenobiotics with pronounced persistence and tendency for bioaccumulation in a food chain. Therefore, PCBs present great danger for both environment and human health, even when they are present in extremely low concentrations.[1] To clean up the polluted environment, phytoremediation can be used because it is one of the environment friendly methods which uses green plants to degrade or prevent further spreading of various contaminants.[2,3] During the war in Croatia, one capacitor battery of the Electrical Transformer Station in Zadar (ETS) was hit by a rocket. The oil containing PCBs was spilt over the surrounding area.[4] Our phytoremediation research field was located near the ETS and composed of ten plots.[5] After one year of planting, many different plant species (mainly weeds) were grown in soil contaminated with PCBs. In the literature available, we have not found any data about PCB residues adsorbed on plant surfaces. Furthermore, even the data about cleaning plants before their analysis for PCBs were very scarce. [6,7] This study was conducted to determine the level of PCBs adsorbed on plants and their roots surfaces.

Materials and Methods

Twelve lysimeters were set on four plots consisted of homogenized soil polluted with PCBs. In June 2005, the soil samples were taken in three depths from each lysimeter (surface layer, middle layer, deeper layer and also from around the roots of the plants) in order to investigate distribution of PCBs.[8] The plots were left to grow naturally. At the same time, different plant species, mainly different sorts of weeds, were grown and some of them were taken out from the particular lysimeters for analysis (Table 1).

Table 1. The experimental plots in which the different plant species were grown and composed samples for analysis

PLOT	LYSIMETER	SAMPLE	PLANT
Plot No1	Lysimeter 2	Sample 1	Dittrichia viscosa Sonchus sp. Mentha sp.
Plot No2	Lysimeter 4	Sample 2	Lolium perenne (Perennial ryegrass) Sonchus arvensis (Perennial sowthistle)
	Lysimeter 5	Sample 3	Myosurus minimus (Mousetail) Agropyron elongatum (Tall wheatgrass)
Plot No3	Lysimeter 7	Sample 4	Arenaria sp. Vicia sp. Gramineae
Plot No4	Lysimeter 11	Sample 5	Arenaria sp. Sonchus arvensis (Perennial sowthistle) Myosurus minimus (Mousetail) Dittrichia viscosa
	Lysimeter 12	Sample 6	Avena barbata (Slender wild oats) Sonchus arvensis (Perennial sowthistle) Desmazeria rigida

Every sample for the further study was composed of several plant species. The roots were cleaned of soil by shaking. The plants were divided into the shoot and the root and also analysed separately. The roots were carefully washed with tap water to remove the visible traces of soil before analyses. The shoots were not cleaned with tap water because there was no noticeable soil present on them. Both the shoots and the roots were air-dried and than cut out on equal parts. After they had been transferred into the glass flasks, tap water was added into

each flask and the samples were shaken. The process was repeated one more time. Water rinses were combined and filtered. After filtration, the solid particles were extracted from the filter paper using an ultrasonic bath (two times for half an hour with an equal mixture of hexane: acetone). Before extraction, NaCl was added to the filtrate phase of the water rinses to satiate the solutions. PCBs were extracted from the filtrate phase by liquid/liquid partitioning with the addition of 30 ml of hexane. After rinsing with water had been completed, the shoots and the roots were air dried and then the second rinsing was performed on the same sample but with hexane (three times using new volumes of hexane). Volume of hexane depends on the amounts of rinsed plants. It was between 20 to 40 ml. All hexane rinses were collected into the same flask. Analytical methods used for the analysis of the extracts included filtration through a column of Na_2SO_4 anh. The extracts were also purified using an aluminium oxide column. The samples were analysed with a gas chromatogram equipped with an electron capture detector. A detailed description of the analytical methods used can be found in our papers which have been published previously.[9,10,11]

Results and Discussion

Six plant samples from the area of the Zadar ETS were used in this study. Every sample was composed of few different plants. The experiments included rinsing plants first with water and then with hexane, followed by determination of target analytes in both rinses. After rinsing with water, we estimated distribution of total PCBs within particular samples to contain Aroclor 1248 equivalents. Concentrations of both the shoots and the roots are reported separately and calculated on a dry weight. The water rinses were filtered because of relatively large quantity of particular substances had rinsed from the shoot and root surfaces during the process of shaking. The levels of Aroclor 1248 in the filtrate phase of root samples ranged from 156 ng g^{-1} to 932 ng g^{-1} while in the solid phase ranged from 475 ng g^{-1} to 1293 ng g^{-1}. The water rinses of shoots contained lower levels of PCBs. The dissipation of the Aroclor 1248 was very similar between filtrate and solid phase of shoot samples and ranged from 16 ng g^{-1} to 276 ng g^{-1} (Figure 1).

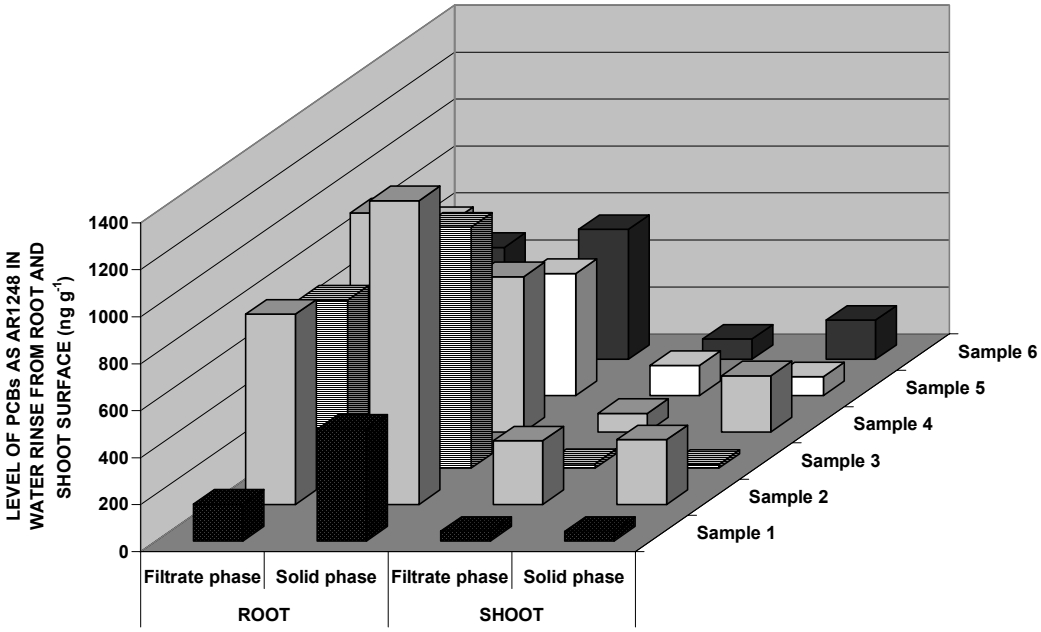

Figure 1. Level of total PCBs expressed as Aroclor 1248 in particular water rinses from root and shoot

Determined levels of PCBs were detected in all rinses (Figure 2). The results obtained with rinsing were expressed as the equivalents of Aroclor 1248 and the sum of the 7 key PCBs herein referred to as ΣPCB_7 (IUPAC No: PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180). The level of PCBs in the water and hexane rinses was expressed as the arithmetic means with standard deviations of six samples.

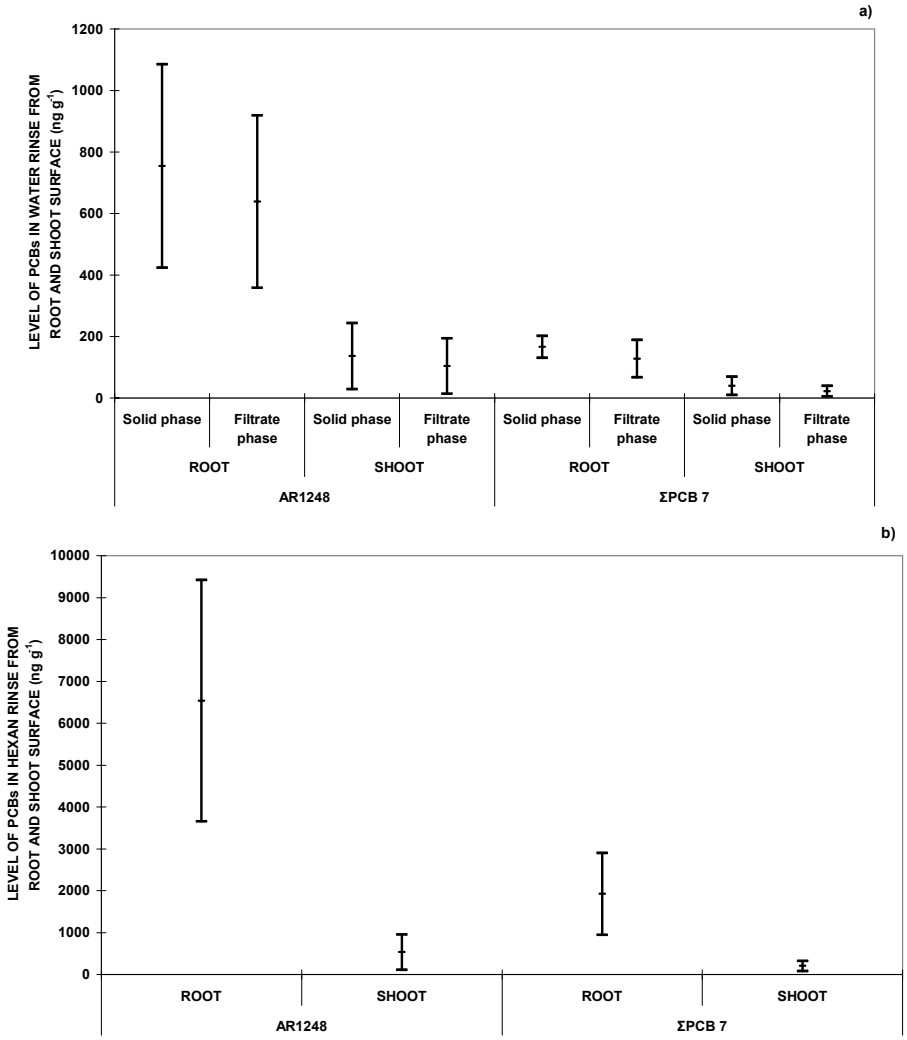

Figure 2. Level of PCBs expressed as the equivalents of Aroclor 1248 and the sum of the 7 key PCBs (average followed by the standard deviations) in particular rinses from root and shoot surface

As shown on figure 2a, the levels of total PCBs and ΣPCB_7 were very similar in solid and filtrate phases of the roots and the shoots, but these results indicate that significantly higher levels of Aroclor 1248 (about 697 ng g^{-1}) and ΣPCB_7 (about 147 ng g^{-1}) were rinsed with water from the surface of the roots as compared with about 219 ng g^{-1} of Aroclor 1248 and about 54 ng g^{-1} of ΣPCB_7 from the surface of the shoots. Experiment with hexane rinsing was performed to determine if any level of PCBs remained after water rinsing or had they been completely washed off the surfaces of the shoots and the roots. According to the results, it was shown that a significant level of PCBs also existed in hexane rinses. Level of Aroclor 1248 in hexane rinse from the root's surface was 6537 ± 2881 ng g^{-1} and it was about five times higher than the level of Aroclor 1248 in water rinse (sum of solid and filtrate phase was about 1393 ng g^{-1}). It can be noticed that higher level of ΣPCB_7 was obtained in hexane rinse from the root's surface also (1924 ± 977 ng g^{-1}) as compared with those in water rinse (sum of solid and filtrate phase was about 295 ng g^{-1}). Hexane rinse from the shoot's surface had significantly lower level of total PCBs (531 ± 423 ng g^{-1}) and ΣPCB_7 (202 ± 124 ng g^{-1}) in comparison with the level of PCBs which was rinsed from the root's surface. Concentration of PCBs in soil was expressed as the arithmetic means of data obtained from six lysimeters. The lysimeters on which previously mentioned plants were grown and analysed are taken into account. The soil in the surface layer had slightly higher levels of Aroclor 1248 (51.8

± 8 μg g^{-1}) as compared with 48.5 ± 4 μg g^{-1} in the soil around the roots. There was no significant correlation between concentration of PCBs in soil and their residues from the plants' surfaces.

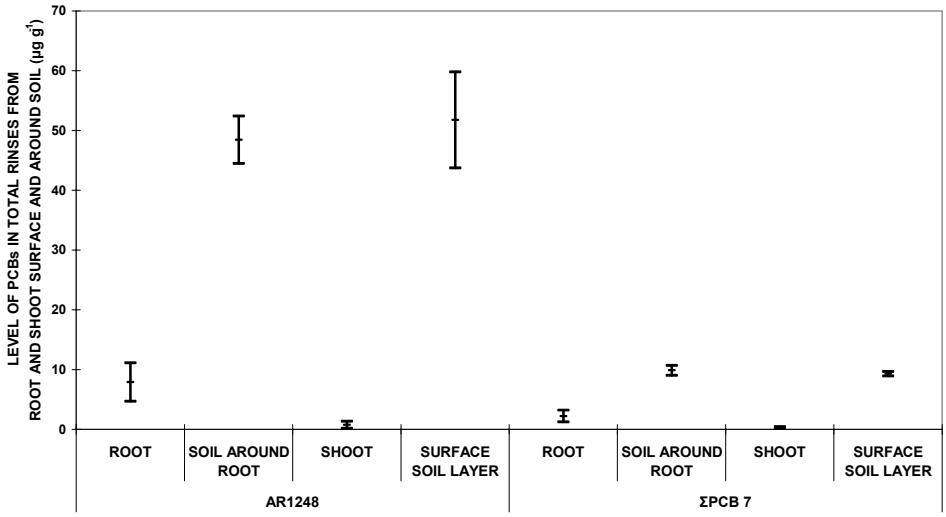

Figure 3. Total level of rinsed PCBs obtained by water and hexane rinses and PCBs level in the soils where the plants were grown

Significant amounts of PCBs remained absorbed on the surface of the roots in spite of the fact that the roots had previously been washed with tap water. The level of PCB residues in rinses was 7.9 ± 3.2 μg g^{-1}, expressed as Aroclor 1248, whereas the level of ΣPCB_7 was 2.2 ± 1 μg g^{-1}. Total PCB rinses of shoots were significantly lower in comparison with PCB rinses of roots and contained 0.8 ± 0.6 μg g^{-1} of Aroclor 1248. Considering these results, it is reasonable to suggest that all traces of contaminated soil must be carefully removed from the plants surface before starting the analysis of the plants. Otherwise the analysis can lead to a false result.

Acknowledgements
The authors express their gratitude to the Ministry of Science, Education and Sports of Republic Croatia for their financial support. This work has been carried out as part of the Contract ICA2- CT-2002-10007 (APOPSBAL) between the European Union and the Rudjer Boskovic Institute, Zagreb, Croatia.

References

1. Cousins IT, Mclachlan MS, Jones KC. *Environ Sci Technol* 1998; 32: 2734–40.
2. Schnoor JL, Licht LA, McCutcheon SC, Wolfe NL, Carriera LH. *Environ Sci Technol.* 1995; 29: 318–323.
3. Macek T, Mackova M, Kas J. *Biotechnol Adv.* 2000; 18: 23–34.
4. Picer M, Picer N, Hodak Kobasić V. *Organohalogen Comp* 2003;62:472-475.
5. Picer M, Tarnik T, Picer N, Kovač T. *Fres Environ Bull* 2004; 13(12B): 1487-1492.
6. Tesema C, Lester RV, Rufus LC. *Environ Int.* 2004; 30: 799–804.
7. Zohair A, Salim AB, Soyibo AA, Beck AJ. *Chemosphere* 2006; 63: 541-553.
8. Hodak Kobasić V, Čalić V, Tarnik T, Picer M, Franetović M. European conference on Industrial Pollution and Sustainable Development, Maribor, Slovenia, 2005; 36-48.
9. Picer, M. *Croat. Chem. Acta* 2000; 73(1): 123-186.
10. Picer M, Picer N. *Wat. Res*. 1995; 29: 2707-2719.
11. Hodak Kobasić V, Čalić, V, Tarnik T, Picer M, Šangulin J, Franetović M. *Organohalogen Comp* 2005; 67: 1932-1936.