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The Fate of Polychlorinated Biphenyls in Karstic Soil

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ABSTRACT: During the Croatian Homeland war in 1991, the capacitor batteries of the Zadar electric power substation (TS 110/35 kV) were damaged, resulting in the severe pollution of the soil with polychlorinated biphenyls (PCBs). Due to porosity of karstic soil PCBs represent great environmental and human health risks that need some action. The polluted soil was collected and an experimental field was formed. This paper reports the behaviour of PCBs in karstic soil over an extended period of time under field conditions. Vertical movement of PCBs through the soil profiles was also observed. The soil was sampled four times. The initial median levels of Aroclor 1248 in the surface soil layer were 76.5 µg g^{-1}. The levels of PCB in the soil layers collected after initial stage were quite variable. In general, PCB patterns were dominated by low-chlorinated homologue groups (<5 Cl groups). The dominant indicator PCB congeners initially present in the soil were PCB 28 and PCB 52. At the end of the experiment, in surface soil layer, the levels of PCB 28 decreased significantly (38%), while the levels of PCB 52 decreased at a smallier rate with time (15%). In the observed time periods the levels of higher PCBs (n>6) were relatively stable. The results show that the total PCB concentration in the soil around the roots significantly dropped by 36% while in the deeper soil layer decreased for 18%.

Key words: PCBs, Karstic soil, Field site, War, Croatia

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of compounds previously used in transformers, capacitors, paints, and other industrial appliances. The excellent properties of PCBs for industrial use also make it hazardous to the environment (Erickson, 2001). Due to their hydrophobicity and lipophilicity, they accumulate in soils, sediments, and in the fatty tissues of living organisms and also they biomagnify in higher trophic levels of the food chains (Valle *et al.*, 2005; Holoubek *et al.*, 2009). Therefore, PCBs constitute a substantial environmental and health risk for plants, animals and humans (Petrik *et al.*, 2006). Industrial use of PCBs has been restricted since mid 1970s, but many old equipments filled with PCBs are still in service today. Thus one route via which PCBs enter soils is by accidental spills of PCB-contaminated fluids associated with transformers and large capacitors (Picer and Holoubek, 2003).

The fate of PCBs in soil is complex. Physico-chemical properties of PCBs in conjunction with the environmental factors play an important roles in transport of PCBs in soil. The composition of the soil and its texture can also influence the sorption of PCBs. Therefore, once deposited to the soil the PCBs will be subject to various partitioning, degradation and transport processes, which also will control their vertical distribution in the soil (Cousins *et al.*, 1999; Li *et al.*, 2003). Under environmental conditions, biological degradation of PCBs is extremely slow (Borja *et al.*, 2005).

Environmental pollution by warfare in the area of former Yugoslavia was recognized by the experts of the EU Fifth Framework Programme and the project “APOPSBAL” (APOPSBAL, 2005), investigating the levels and fate of PCBs in the various environmental matrices was approved. Zadar is a city in Croatia on the Adriatic Sea. The capacitor batteries of the Zadar electric power substation were damaged by the war in the 1990s and PCB-containing oil was spilled into the soil. The analysis of soil samples collected around the TS Zadar showed substantial levels of PCBs (Picer *et al.*, 2004b). The soil was excavated from the heavily contaminated area around the damaged capacitor and a experimental field was created to investigate the behavior of PCBs and their natural attenuation (Picer *et al.*, 2004c). Although there are numerous data about the behavior of PCBs in artificially contaminated soil

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*Corresponding author E-mail: vhodak@irb.hr under laboratory conditions however laboratory studies do not always relate directly to field conditions (effects of weather, climate, biological diversity). Field studies may be used to overcome this problem. We previously showed that transport of PCBs with leachate water from contaminated soil was negligible (Hodak Kobasić *et al.*, 2008). This paper reports the PCBs behaviour in karstic (limestone) “weathered” soil through 38 months under field conditions. Vertical movement of PCBs through the soil profiles was also observed in this study.

MATERIALS & METHODS

The study took place on the location of the TS Zadar. This area has an mediterranean climate. July and August are the hottest months, with an average high temperature around 30 °C. The experimental field included six soil plots. Each plot was 3 m long by 1 m wide in size. Two-hundred grams of soil samples at various depths from each plot were collected using the three point sampling method. Soil was sampled manually using a stainless steel spatula and core sampler. The samples were stored at 4 °C until time of analysis. The soil type was classified as clay loam and the soil was humus-rich. The pH value of the soil in the study area was mildly alkaline. The particle distribution indicated that the soil contained lot of the particles under 0.002 mm. The first soil sampling was performed in July 2003. Second soil sampling was performed in December 2003. Samples were taken from the soil surface (depth of 0-5 cm). The other two soil samplings were done in June 2005 and in September 2006. The analytical results of soil samples were also used to study the PCBs transportation in vertical direction. Soil samples were taken from the surface layer, deepest layer (10-15 cm) and also around the plant roots. In June 2005, samples were collected also from the middle layer (5-10 cm). The soil inside plots gradually became naturally colonised with different types of grasses and weeds.

The soil samples were air dried and sifted through a 2 mm sieve. Ten grams of soil were placed in a Dionex standard 11 ml stainless steel cell and extracted three times with hexane/acetone mixture (1:1) using an automated extraction system (Dionex ASE 200). The ASE extraction parameters were 100 °C, 14 MPa, 5 min of heating and 10 min of static time. After the extraction, the cell was flushed with solvent (60%) and purged with nitrogen. Extract was collected in vials with teflon septa. The analytical method used to purify the obtained extracts included filtration through a column of Na_2SO_4 anhydrous. The resultant eluate was concentrated to about 1 ml with a rotary evaporator and further cleaned up using 5% deactivated alumina. All chemicals used were of analytical and chromatographic grade. The PCB concentration of the contaminated soil was determined by capillary gas chromatography (GC) with electron capture detection (ECD) containing a cell plated with 63 Ni and were quantified using an HP Chemstation by confirming the peaks. The carrier gas was nitrogen. The column used was high resolution glass capillary HP-5 (cross-linked 5% phenyl methyl siloxane), 30 m × 320 μm × 0.25 μm film thickness.

The PCB concentrations were quantified in comparison with the corresponding external standard calibration solution which was injected into the GC before sample injection. The standard PCB mixture (SRM 1493, NIST) used for the GC-ECD analysis of the individual PCBs. PCBs in mixture ranged from lower chlorinated PCBs to higher chlorinated PCBs and included: PCB 8, PCB 18, PCB 28, PCB 44, PCB 52, PCB 66, PCB 77, PCB 101, PCB 105, PCB 118, PCB 128, PCB 138, PCB 153, PCB170, PCB 180, PCB 187, PCB 195, PCB 206 and PCB 209. The detection limit for the PCBs in the soil was 0.01 μg g^{-1}. One blank sample was carried out during each batch of the experiment to evaluate any contamination during the analysis. The mass of each individual PCB in the blanks was insignificant relative to that of the soil samples. Detailed descriptions of the analytical procedure for PCBs were described earlier (Picer and Ahel, 1978; Picer, 2000; Hodak Kobasić *et al*., 2008). All PCB concentrations were reported on a dry weight basis (dw) and were the median of six replicate analyses. Statistical analysis of the results was performed in SigmaStat for Windows (version 2.03) using non-parametric statistics (Kruskal-Wallis test at significance level 0.05, 0.01 or 0.001) and post-hoc Dunnov test ($p<0.05$). Graphs were generated in Statistica for Windows (version 6.0). Fig. 1, 2 and 4 show box plots, with the median, the interquartile range, the outliers (between 1.5 and 3 box lengths) and extreme values (more than 3 box lengths) of the PCBs. On the figures, the letters (a, b, c) represent the homogenous groups given by the comparison of medians with the post-hoc Dunn test ($P<0.05$).

RESULTS & DISCUSSION

In the examined soil samples significantly higher contents of the lower-chlorinated PCBs was noticed. The obtained profiles can be associated with the use of commercial mixture Aroclor 1248 in condenser oil and therefore the levels of the total PCBs are expressed in equivalents of Aroclor 1248. Results for the sum of the seven PCBs (ΣPCB_7; IUPAC numbers PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180) are also shown. These PCBs also known as indicator PCBs and potentially represent all PCBs, since they are ubiquitous in all environmental compartments. The proportions of the various PCB congeners in the soil samples differed significantly. Moreover, congeners containing 3–4 chlorine atoms (PCB28 and PCB52) were more abundant than 5–7 chlorine congeners (PCB101, PCB118, PCB153, PCB138 and PCB180). During the experiment, the soil was sampled four times. The first soil sampling was performed in July 2003 (zero time). The initial levels of PCB in the soil collected from plots were relatively homogenous. Total PCB levels expressed as Aroclor 1248 were in range of 71.0 to 77.9 µg g^{-1}, whereas the levels of ΣPCB_7 were in range of 15.87 to 17.36 µg g^{-1} (Picer *et al*., 2004). Five months later the levels of PCBs in the surface soil layer were quite variable (Aroclor 1248 were in range of 51.5 to 83.8 µg g^{-1}, whereas the levels of ΣPCB_7 were in range of 10.06 to 15.1 µg g^{-1}). Two soil samplings were done after the different type of Mediterranean grasses and weeds had grown. The PCB levels for those sampling periods are expressed as the median of soil samples from the six plots and all the results are expressed in dry weight. In this study we monitored the temporal variability of PCBs in the soil. During the research period of 38 months the levels of Aroclor 1248 and ΣPCB_7 were decreased approximately 46% and 29% respectively (Fig. 1). Kruskal-Wallis test confirmed that exists statistically significant differences in levels of PCB between four observed groups of data ($p<0.001$), i.e. for different times of sampling. Furthermore, post-hoc Dunnov test (at the significance level $p<0.05$) also was determined statistical significant differences. PCB loss from the soil layer is calculated as the differences between the median measured in individual samplings and expressed in percentages. The relative distribution of indicator congeners (present in ΣPCB_7) in soil samples during sampling campaigns was as follows: PCB28 > PCB52 > PCB101 > PCB118 > PCB138 > PCB153 > PCB180.

The dominant PCB congeners initially present in the soil were PCB 28 (trichlorobiphenyl) and PCB 52 (tetrachlorobiphenyl) (Fig. 2). During a 38-month experiment under natural conditions the median of trichlorobiphenyls decreased for approximately 42%, while the median of tetrachlorobiphenyls dropped by 40% (for that results were responsibled PCB 44 and PCB 66). Trichlorobiphenyls referred in this study is the sum of PCB18 and PCB28 while tetrachlorobiphenyls is the sum of the PCB44, PCB 52 and PCB 66. The various reduction of PCBs in the soil within observed time, suggested that the individual homologous groups of PCB behave very differently. Most of the lower chlorinated congeners showed significant decreases in the long term while higher chlorinated congeners were more persistant (Saba *et al*., 2011). Rates of decrease slowed in the period from June 2005 (23rd month) to September 2006 (38th month). Abiotic mechanisms such as volatilization can contribute to the natural attenuation of the lighter PCBs and they can be transported to the atmosphere (Wania, 2003). The rate of volatilization can slows as the age of the spill increases (Kastanek *et al*., 1999).

The levels of low-volatile compounds such as higher chlorinated biphenyls decreased in upper soil layer at a very small rate with time and their levels at the beginning and at the end of the experiment were within a range of 1.37 µg g^{-1} and 1.16 µg g^{-1} for pentachlorinated biphenyls, and between 0.15 µg g^{-1} and 0.11 µg g^{-1} for heptachlorinated biphenyls. The hexachlorinated biphenyls contents in the soils was not significantly decreased during the experiment ($p>0.05$) possibly due its slow rates of desorption from organic matter in soil and thus its resistance to degradation. However this reduced bioavailability can

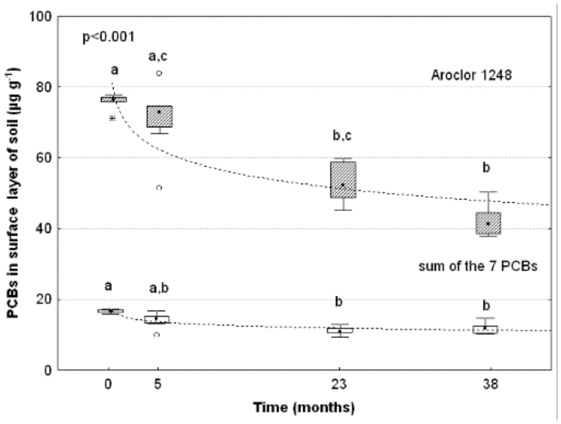

Fig. 1. Levels of PCBs (µg g^{-1}) in surface layer of soil (since July 2003 to September 2006).
Boxes indicate the range between the 25th and 75th percentiles. The dark circle inside box indicate the median value, the circle outside box indicate the outliers and * is extreme value.

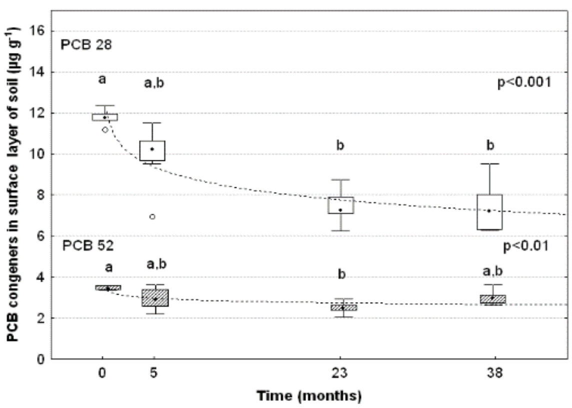

Fig. 2. Levels of PCB 28 and PCB 52 (µg g^{-1}) in surface soil layer (since July 2003 to September 2006).
The statistical definition of the boxes is described in the caption of Fig.1.

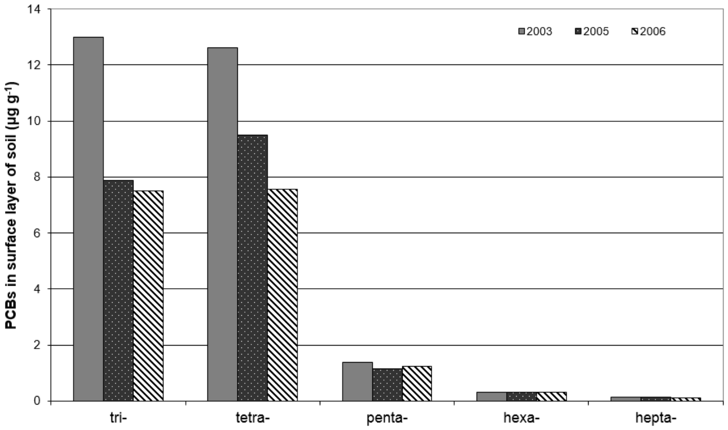

Fig. 3. Levels of PCB homologues (µg g^{-1}) in the surface soil layer

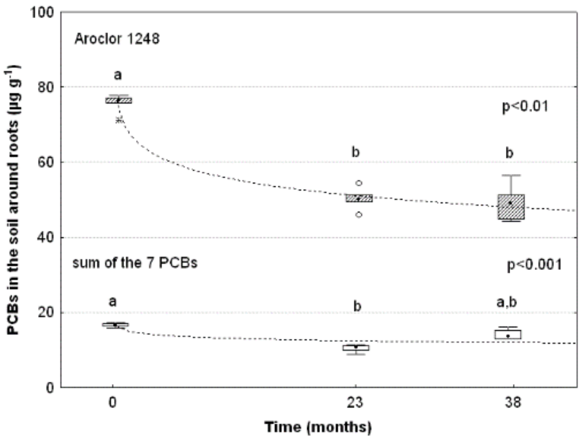

Fig. 4. Levels of PCBs (µg g^{-1}) in the soil around roots. The statistical definition of the boxes is described in the caption of Fig.1.

also be used for remediation purposes, since immobilization of these compounds reduces the environmental impact. Whereas, the initial levels of higher chlorinated PCBs were significantly lower in relation to the levels of trichlorobiphenyls and tetrachlorobiphenyls, therefore their levels insignificantly changed the total mass balance of loss of PCBs from the soil surface (Fig. 3).

Fig. 4. shows the levels of PCBs in the soil around the roots of native vegetation cover since July 2005 to September 2006 in comparison with the initial period. The analysis showed that total PCBs were significantly dropped by about 36%.

PCB compound profiles on a mass per mass basis have been calculated at different soil depths (vertical soil profile). The PCB level expressed here is the median of the PCB measurements in the soil samples taken from six plots. Figs 5a and b presents the levels of PCBs (µg g^{-1}) at various depths of the soil during sampling in June 2005 and in September 2006.

The PCB concentrations in the soil during sampling in June 2005 showed minimal values at the surface and increasing values with sampling depth but those differences were statistically insignificant ($p>0.05$). Detailed analysis was performed to explore if exist differences in the distribution of the individual PCB congeners. The most abundant PCB congeners were PCB 28 > PCB 66 > PCB 52 > PCB 44 > PCB 18 >PCB 101. Statistically significant differences were observed only for PCB 28 and PCB 18. The levels of PCBs were higher in the middle and deepest layer of soil. Differences in levels of Aroclor 1248 between various soil layers were statistically significant ($p<0.01$).

Fig. 6 presents the more detailed illustration of distribution for particular congeners at the vertical profile of soil during sampling in September 2006. Levels of PCBs were significantly higher in the deepest layer of soil than in surface (for example, levels of PCB 28, PCB 52 and PCB 101 were higher for about 25-35%). The most possible mechanism which defines the such distribution may be connected with the evaporates of less hydrophobic congeners of PCBs from the surface layer of soil. Furthermore, PCBs can also be transported downward in association with solid material . Although at the beginning of our research (July 2003) a relatively good homogeneity of the levels of PCBs in the soil was attained, through time and under realistic field conditions a significantly more unbalanced distribution of the pollutants occurred. In environmental conditions numerous factors affect the spatial variability of the concentration of pollutants in soil, such as soil structure, organic ingredients of the soil, moisture levels and microbes activity. Namely, through time, these factors also vary, which can add to the uneven distribution of pollutants (Cousins *et al.*, 1999a; Gerhardt *et al.*, 2009).

The PCB congener specific pattern in the studied soil samples corresponds to the usage of Aroclor 1248.

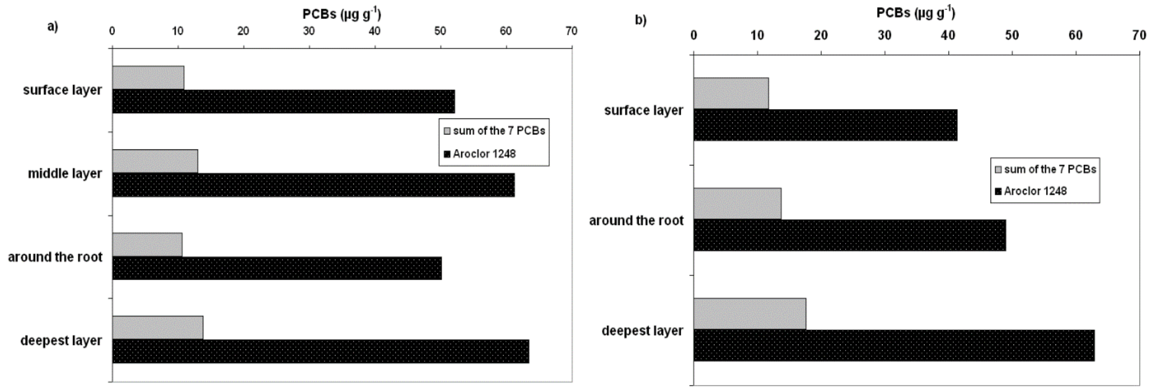

Fig. 5. a) PCBs distribution in the different depth soils during sampling campaign in June 2005. b) during sampling campaign in September 2006

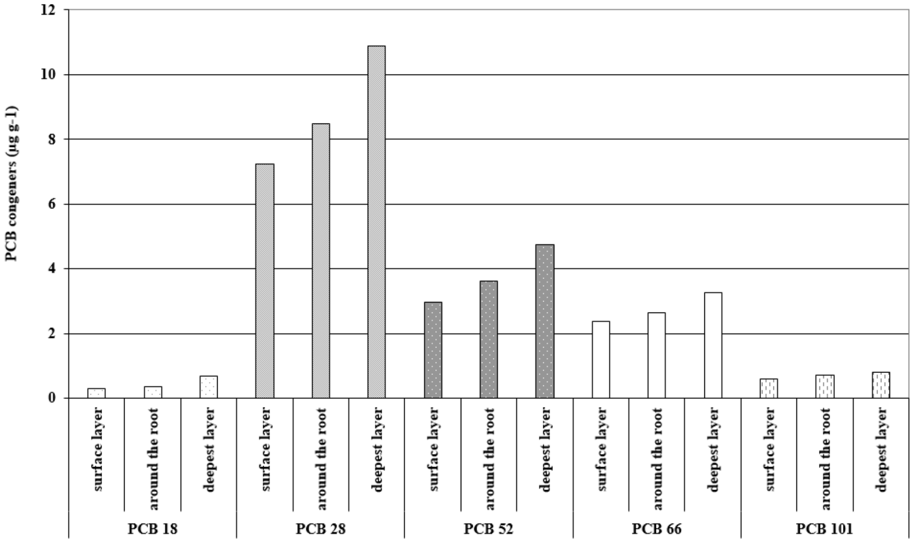

Fig. 6. Levels and vertical distribution of PCB congeners (µg g^{-1}) at various depths of the soil during sampling in September 2006

In the original mixture Aroclor 1248, the highest level is found in tetrachlorobiphenyls (49%), followed by pentachlorobiphenyls (27%), trichlorobiphenyls (22%), hexachlorobiphenyls (2%) and dichlorobiphenyls (1%) (Brinkman and Kok, 1980). After being put in the environment that composition could change significantly. Therefore, we took into consideration that the soil at the TS Zadar was already polluted with PCBs in 1991, while the trials started in the field in 2003, i.e. 12 years after the pollution occurred.

The analysis of homogenous groups of PCBs at various depths of the soil provides information about the main mechanisms of their transport in the soil. Complex mixture of many congeners has not uniform diffusivity thus the pattern of PCB congener distribution can be change with the sampling depth. PCBs with fewer chlorines can completely biodegrade. In this study PCBs with low number of chlorines decreased more than the PCBs with a high content of chlorines. Doick *et al*. (2005) studied the behaviour of PCB 28 and PCB 52 in soil. A noticeable loss of PCBs from the surface soil layer did not differ in the case of these two congeners.

The half-life in soil is 10.9 years for PCB 28 and 11.2 years for PCB 52. Numerous studies indicate that adding plants to experiments positively influences the rate of removal of xenobiotics from samples, although the paths of decomposition alone, as well as the mechanisms for regulation of these processes have not been completely clarified yet (Ryslava *et al*., 2003; Chekol *et al*., 2004; Demnerová *et al*., 2005). The drop of levels of PCB in the soil around plants roots was noticed in the cases of both observed parameters (Aroclor 1248, the sum of 7 PCBs). Although a decrease in the level of lower congeners was more pronounced, it was significant also for higher congeners. This points to the possible role of the plants secondary metabolites. It is believed that secondary metabolites may act as natural inducers of enzyme systems of bacteria needed for decomposition of PCBs (Singer *et al*., 2003; Luo *et al*., 2007). It was shown that the secondary plant metabolites may affect greater bioavailability of PCB to bacteria (White *et al*., 2006). The study of the distribution of PCBs in the vertical soil profile 38 months after the field was formed showed that in the surface layer the levels of PCBs were significantly lower than in deeper layers. Such a distribution can be the result of several different processes. For a decrease in the level of PCBs in the surface layer, the evaporation of PCBs into atmosphere is important firstly, whereas the movement of PCBs in the gaseous phase towards the lower layers of soil is minimal (Moeckel at al., 2009). For the vertical transport of PCBs towards deeper layers of soil transport in sorbed forms, helped by the process of bioturbation, and in dissolved form with leachate water is important. The movement of particles through the soil profile could depend on the properties of the soil and on the diameter of particles (Müller-Lemans and van Dorp, 1996).

Direct measurements to estimate the loss by evaporation were not done, but some experiments with biological decomposition made on the same soil pattern indicated that such losses should not be pronounced at temperatures lower than 30°C (Petrić, 2011). However, it should be emphasized that the air and soil temperatures in the summer months in the open field at the transformer station Zadar are frequently significantly higher than 30°C and a lot more intense evaporation of PCBs can be expected then. Observations in the vicinity of the damaged transformer station Zadar confirmed that the levels of PCB in the air were significantly more elevated than at the control locations, suggesting volatilization as a weathering process for lightly chlorinated PCBs (Picer *et al*., 2004a, Klanova *et al*., 2007). On the basis of that we can conclude that evaporation has to be included when considering mechanisms which contribute to the removal of PCBs from the field. Furthermore, the results of the research (Petrić, 2011) indicate that the autochthonous bacterial population from the polluted soil of the TS Zadar is not active in the decomposition of PCBs when the corresponding inducers for the activation of enzyme system are not present. By adding secondary plant metabolites (carvone, tannin) a lot better decomposition of PCB was attained and they were evaluated therefore as efficient inducers for application in the environment. The research mentioned indicates that the presence of the native plant cover in the experimental field of the TS Zadar might affect positively the microbiological decomposition of PCBs. The following scientific paper will be focused on detailed plant uptake.

CONCLUSIONS

By intensive mixing in the mixer of the soil used to form the field, a relatively good homogeneity was attained regarding the distribution of PCB in the soil of the experimental system (Picer *et al*., 2004c). This fact enabled, through the monitoring of the changes of levels of PCBs in soil, an insight could be obtained about the degree and main mechanisms of their removal. The decrease of the level of PCBs in the surface layer of the soil was significantly greater statistically than in deeper layers. Also, minor but systematic differences were noticed in the distribution of the tri- and tetrachlorobiphenyls (PCB 18, PCB 28 and PCB 52) in relation to pentachlorobiphenyls (PCB 101) in the vertical profile, with a smaller ratio of lower congeners determined in the surface layer. This pointed to a mild but significant selectivity of the processes that affected the distribution of PCBs. The most probable processes that could have contributed to the changes observed are evaporation, flushing of leachate water, biological decomposition and phytoextraction. All these processes resulted in the preferential removal of lower congeners and perhaps in the depletion of their ratio in the surface layer.

In the soil around plants roots a decrease in the level of PCBs was observed. That decrease was the most pronounced for lower congeners, but was significant also for higher congeners. It was postulated that the observed decrease of PCB might be the result of weathering process which can occur by physical weathering and the microbiological decomposition prompted by mutual activity of secondary plant metabolites and autochthonous bacteria in the soil.

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