RADIATION DEGRADATION OF POLYCHLORINATED BIPHENYLS

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1. Introduction

Polychlorinated biphenyls (PCBs) were produced commercially all over the world in specific PCB congener mixtures (e.g. Aroclor, Delor, Delotherm, Hydelor, etc). They had a wide range of use, because of very good chemical and physical properties (i.a. transformer and capacitator liquids, etc). The density, boiling point and hydrophobicity of PCBs increase with the degree of chlorination. High molecular weights and boiling points lead to a viscous fluid with low flammability that can tolerate high temperatures without substantial chemical degradation. One of the areas of PCB production was also in Eastern Slovakia, in the town Strážske in Michalovce district. The location is considered as one of the most contaminated territories with PCBs in Central Europe. Content of PCBs was detected in the entire environment. The producer was the chemical company Chemko Strážske. Sediments in Strážske channel flowing from the company area react as an environmental reservoir, which have accumulated the contaminants and releases them to the water. The content of PCBs in sediment is usually around 5 $\mu g \cdot kg^{-1}$, but in contaminated area (Petrovce nad Laborcom) is the amount of 6 PCB congeners 15000 $\mu g \cdot kg^{-1}$ [1], which is critical. Due to the fact that Strážske channel flows into the river Laborec, which flows into the lake Zemplínska Šírava water reservoir. PCB congeners were found in very high levels in bottom sediments of the reservoir. The highest level of PCBs was found in 2003 (1630 $\mu g \cdot kg^{-1}$), than in 1999 and 2005 (450 $\mu g \cdot kg^{-1}$) and in 2007 (690 $\mu g \cdot kg^{-1}$) [1]. During the monitoring experiment, 10 sediment samples were analysed for PCBs (PCB 28, 52, 77, 81, 202, 229, 126, 138, 153, 169 and 180). These congeners have negative effect on human health (i.e. cancer, neurotoxic effects, reproduction problems) [1].

2. Radiation degradation of PCBs and chemical pretreatment

Radiation remediation of PCBs with electron beam and a chemical pretreatment is new environment-friendly technology, which has not been used very often till now. The basic principle is that the electrons interact with matter at high energies predominantly by elastic

scattering. For 5 MeV electrons, electron energy loss is predominantly through collisions with bound electrons. It is not possible to determine the increase in chloride ion concentration in the liquid phase because sediment is rich in chloride. Therefore, only the change in PCB concentration is determined. Scavenging of electrons (e_{aq}^-) (Eq.1, 2) by the protons formed upon radiolysis is prevented by the use of the carbonate buffer, which keeps the solution at pH > 7. Other compounds present in the sediment, which may react with e_{aq}^- are metal ions. Competition reactions for hydrated electron (with k= reaction speed constant):

$$e_{aq}^- + O_2 \rightarrow O_2^- \qquad k = 1.9 \cdot 10^{10}\ dm^3 \cdot mol^{-1} \cdot s^{-1} \qquad (1)$$

$$e_{aq}^- + H_3O^+ \rightarrow H^\cdot + H_2O \qquad k = 2.3 \cdot 10^{10}\ dm^3 \cdot mol^{-1} \cdot s^{-1} \quad [2] \qquad (2)$$

The hydrated electron was shown to be the main radiolytic species responsible for the dechlorination of PCBs. In heterogeneous marine sediment-water system, there are competition reactions for the hydrated electron between PCBs, metal ions, pesticides, organic matter. The chemical changes in PCBs primarily occur through secondary reactions of radiolytic species with PCBs. Hydroxyl radicals and hydrogen atoms react with PCBs via addition to the phenyl rings, producing various isomeric PCB adduct radicals. As the irradiation proceeds, the fraction of e_{aq}^- reacting with PCBs decreases as PCBs are converted to lower chlorinated PCB congeners and biphenyl. PCBs, that remain in association with or within the sediment phase may undergo dechlorination by thermalized electrons that may be formed at particle sites [3].

3. Experiment

Sediments from Strážsky channel were used for PCBs determination. The total content of PCB (congeners 28, 52, 101, 105, 118, 138, 153, 156 and 180) determined in non-irradiated sample was 1842.69 $ng \cdot g^{-1}$. 20 g of wet sediment were mixed with 10 % (w/v) of K_2CO_3. The mixture was homogenized and 5 % (w/v) $CuSO_4 \cdot 5\ H_2O$ powder was added and let to dissolve. Prepared samples were irradiated by linear electron accelerator with scanning beam UELR-5-1S at the University Centre of Electron Accelerators of the SMU in Trenčín. Applied doses were: 0, 100, 300, 500 and 700 kGy. Determination of PCB in sediment was performed at the Department of Toxic Organic Pollutants of the SMU in Bratislava. Isotope-dillution method by using of ^{13}C-labeled standard solution was used. About 0,15 g of dried homogenized irradiated sediment was Soxhlet extracted with toluene (8 hours). An 1/50 aliquot of the extract was applied on multi-layer silica column (44 % sulphuric acid/potassium hydroxide/silver nitrate on activated silica gel). The PCB extract was carefully concentrated and after dilution coupled with high-resolution mass spectrometry (HRGC).

4. Results

Radiation techniques for degradation of PCBs have not been used widely. During irradiation process the hydrated electrons were produced, which were responsible for the dechlorination of PCBs. But in heterogeneous marine sediment-water system, it was necessary to use co-solvent ($CuSO_4 \cdot 5\ H_2O$), which could scavenge water molecules presented in marine samples. $CuSO_4 \cdot 5\ H_2O$ scavenged water, which is competitive to PCBs

during irradiation process. Addition of K_2CO_3 caused pH~10, which was important to keep reaction balance and prevent Cl^- anions from conversion to Cl_2. PCB congeners 28, 52, 101, 105, 118, 138, 153, 156 and 180 were determined in samples from Strážske channel. The total amount of PCBs was decreasing with increasing doses (Fig.1), at 700 kGy the amount of PCBs decreased by 45.7 %. The measurement showed, that during irradiation process, the amount of higher chlorinated biphenyls was decreasing, but on the other hand the amount of lower chlorinated PCBs was increasing (Fig.3). This phenomenon was caused by gradual changing of higher chlorinated PCBs to lower ones.

To establish and determine the clean up and remediation levels for PCB mixture, the toxic equivalency factor (TEF) was used and then the toxic equivalent (TEQ) was determined according to Eq.3 (with c_n – concentration of the individual congener in the mixture).

$$TEQ = \Sigma\, c_n * TEF_n \qquad (3)$$

The TEF values are given only for few selected PCB congeners, also called dioxin-like PCBs (DL-PCBs: 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189), because they present higher risk for human health. On the basis of extensive evidence of a mechanism of dioxin-like PCB carcinogenesis identical to that of 2,3,7,8-tetrachloro dibenzo-p-dioxin. PCBs were in 2013 also classified by Internation Agency for Research on Cancer (IARC) in Group 1, as carcinogenic to humans [4]. Fig. 2 shows that the concentrations of PCBs 105, 118 and 156 in sediment samples were decreasing with increasing dose and at the dose 700 kGy the TEQ value fell down by 22.3 %.

This experiment referred to the fact that irradiation and presence of co-solvent decreased the level of PCBs, even the most toxic ones. We can expect even better efficiency in PCBs degradation, if we improve the geometry of irradiation by using Petri dishes instead of test-tubes.

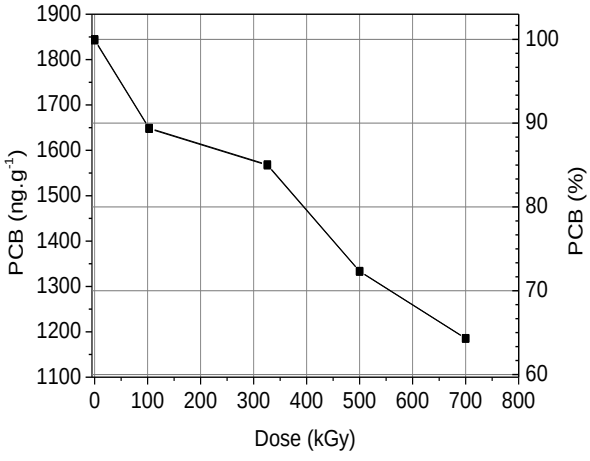

Fig.1 *The total amount of PCBs (28, 52, 101, 105, 118, 138, 153, 156 and 180) in sediment samples with increasing dose.*

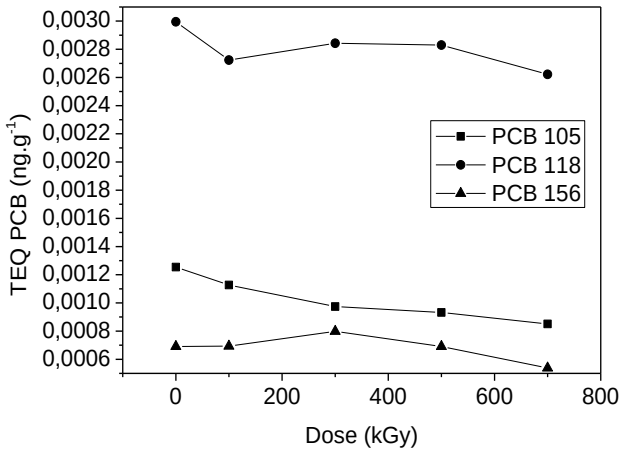

Fig.2 *Decreasing level of the toxic equivalent (TEQ) with increasing dose.*

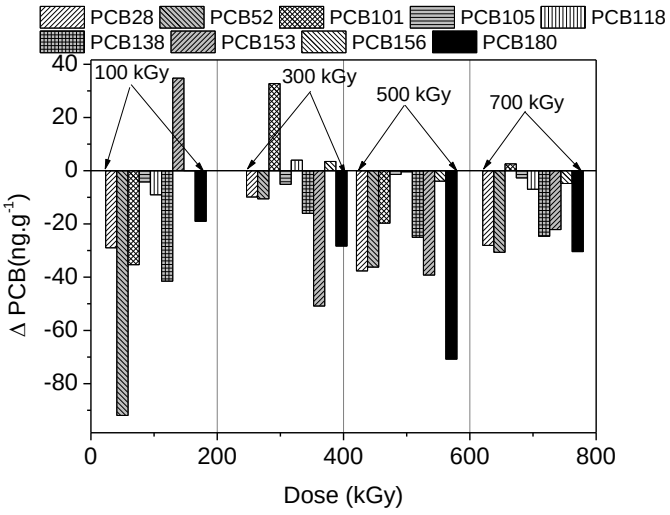

Fig. 3 *Variation of PCB concentration (calculated as its value after irradiation by given dose minus concentration before radiation treatment) as a function of applied dose.*

5. Conclusion

This study was based on the fact that the situation with PCBs in Slovakia is alarming. The effect of irradiation on PCBs is well known, but it is crucial to select appropriate co-solvent. We assume that a more suitable co-solvent can provide more effective conversion of PCBs (>90 %). Our results shown that $CuSO_4 \cdot 5\ H_2O$ provide 64 % conversion of PCBs. $CuSO_4 \cdot 5\ H_2O$ behaves as a water scavenger, but the ideal co-solvent should easily transfer H^- anion to replace Cl^- anions in PCBs.

Acknowledgement

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