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DETERMINATION OF TOXIC EQUIVALENTS (TEQ) FOR POLYCHLORINATED BIPHENYLS (PCBs) IN SEDIMENTS AND SURFACE WATER (EAST SLOVAKIA)

Marek DRIMAL[1], Karol BALOG[2] & Judita TOMAŠKINOVÁ[1]
[1]*Faculty of Natural Sciences, Matej Bel University, Tajovského 40, 97556 Banská Bystrica, Slovakia.*
marek.drimal@umb.sk; judita.tomaskinova@umb.sk
[2]*Faculty of Materials Science and Technology in Trnava, Paulínska 19, 91724 Trnava, Slovakia; karol.balog@stuba.sk*

Abstract: Contamination of the environmental compartments by polychlorinated biphenyls (PCBs) is mater of great concern. Strážske area in East Slovakia is known as one of the largest contaminated areas by polychlorinated biphenyls in Europe. The objective of this work is to investigate the distribution of 12 dioxin – like PCB congeners, in accordance of World Health Organization in water and sediment samples, to determine the most abundant congeners and to define Toxic Equivalency Factors (TEF) and Toxic Equivalent Concentrations (TEQ). The most abundant PCB congeners in sediments were PCB 123 2.1 $mg.kg^{-1}$ and PCB 126 1.4 $mg.kg^{-1}$, in surface water PCB 126 28.4 $ng.l^{-1}$ and PCB 167 27.11 $ng.l^{-1}$. Total TEQ for the most polluted sediment was 41958 $pg.g^{-1}$ and for surface water 2.86 $ng.l^{-1.}$ The standard TEF values of World Health Organisation for sediments and soils are 0.00003 $mg.kg^{-1}$ (PCB 123), 0.1 $mg.kg^{-1}$ (PCB 126). A guideline of TEF for measured PCB in surface water is 0.0001 $ng.l^{-1}$ (PCB 126). Is it possible to consider these values as aim for site cleaning. This study indicates recommendation for next analyses in more places, especially considering the sediments samples. TEQ values can be used as relative measures between different abiotic samples, e.g. sediment and soil, to prioritize remedial actions.

Keywords: polychlorinated biphenyls, sediment, surface water, toxic equivalency factor (TEF), toxic equivalents (TEQ)

1. INTRODUCTION

PCBs are a class of chemical compounds in which 2–10 chlorine atoms are attached to the biphenyl molecule. The 209 possible compounds are called congeners. PCBs can also be categorized by degree of chlorination. The term “homolog” is used to refer to all PCBs with the same number of chlorines (e.g., trichlorobiphenyls). Homologs with different substitution patterns are referred to as isomers (ATSDR, 2000).

PCBs are a group of synthetic organic chemicals that can cause a number of different harmful effects. There are no known natural sources of PCBs in the environment. PCBs are either oily liquids or solids and are colorless to light yellow. Some PCBs are volatile and may exist as a vapor in air. They have no known smell or taste. PCBs enter the environment as mixtures containing a variety of individual chlorinated biphenyl components, known as congeners, as well as impurities. Because the health effects of environmental mixtures of PCBs are difficult to evaluate, most of the information in this toxicological profile is about seven types of PCB mixtures that were commercially produced (ATSDR, 2000). The mixtures are well known in USA as Aroclor joined with specified number.

PCBs are group of organic chemicals characterized by their persistence, bioaccumulation and bioapmplification in biota, high level of toxicity, and wide range of transport (Pennington, 2001; Sapozhnikova et al., 2004).

PCBs were for long time considered to be a miracle compound. Due to their fire-proof properties, they have probably saved many lives and construction work easier due to the effect as plasticizer and added durability. The total global production was approximately 1.5 million tons. It has been calculated that 48% of the produced PCBs were used for transformer oils, 21% for small capacitors, 10% for other closed systems (heat transfer fluids, hydraulic fluids, liquid filled cables and circuit breakers) and approximately 21% for open systems as paints, pesticides (Andersson et al., 2015).

1.1. WHO approach for evaluation PCB toxicity

PCB contamination might be described through different ways. One significant possibility is based on identifying a subset of PCB molecules as having toxicological properties comparable to chlorinated dibenzo-p-dioxins. According to approach provided by the World Health Organization (WHO) (Van den Berg et al., 2006). The health risk of these 12 dioxin-like PCB congeners can be related to 2.3,7,8-tetrachIorodibenzo-p-dioxin (2.3.7.8-TCDD) through a Toxicity Equivalency Factor (TEF). By multiplying the concentration of each of the 12 PCB congeners by its own TEF, one can derive the Toxicity Equivalents concentration (TEQ) of 2.3.7.8-TCDD that would represent an identical health risk. If each of the 12 PCB congener's TEQs are added together, one can calculate the concentration equivalent of 2.3.7.8-TCDD for the entire PCB mixture. These calculations are shown as equations (Eq. 1) and (Eq. 2).

Individual PCB congener concentration x TEF = congener 2.3.7.8-TCDD TEQ (1)

Sum of all 12 (congener TEQ) = (2.3.7.8-TCDD TEQ) (2)

Table 1. Toxicity equivalency factors for selected congeners of PCB

Dioxin- like PCB congener	**TEF**
PCB 77	0.0001
PCB 81	0.0003
PCB 105	0.00003
PCB 114	0.00003
PCB 118	0.00003
PCB 123	0.00003
PCB 126	0.1
PCB 156	0.00003
PCB 157	0.00003
PCB 167	0.00003
PCB 169	0.03
PCB 189	0.00003

TEF values, in combination with chemical residue data can be used to calculate toxic equivalents (TEQ) concentration in various environmental samples, including animal tissues, soil, sediment and water. TEFs and TEQs are then used for risk characterization and management purposes, e.g. to help prioritize areas of concern for cleaning up. TEQ values can be used as relative measures between different abiotic samples, e.g. sediment and soil, to prioritize remedial actions (Van den Berg et al., 1998).

1.2. History of investigated locality

Environmental burden MI (012)/Strážske - Chemko – a discharge channel (registered in the Environmental Burden Information System under the number - ISEZ - SK/EZ/MI/494) is located in the Košice region, district Michalovce and occupies cadastral area of the town Strážske and a village Voľa (Fig. 1).

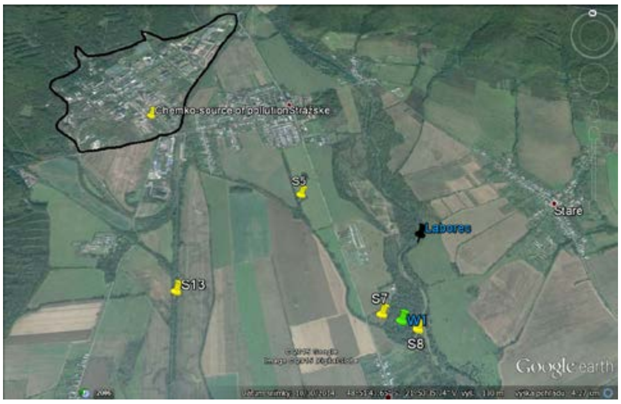

Figure 1. Location of sampling places

Pollution in the discharge channel Strážske has been mainly occurred due to industrial production and handling with PCB compounds and also from the production of basic organic and inorganic chemicals used for the further chemical industries.

Chemical production in Strážske, currently known as Chemko Strážske, started in 1952 with the construction of a factory producing the explosives and intermediate products destined for military and civil purposes. The production program was extended to the production of polychlorinated biphenyls (PCBs) in 1959. During the years 1959-1984, a total production reached a value of over 21,000 tonnes, half of which was mainly exported to Eastern Europe. There was always produced a mixture of polychlorinated biphenyls (PCBs) under the commercial designation Delor©, Hydelor© a Deloterm©.

One of the pollution sources of the environmental compartments in Laborecka floodplain is the discharge channel Strážské, into which was water diversion from WWTP Chemko. Its length from a border area of Chemko Strážske to the outfall into the river Laborec is 4,000 m. It is approximately 10-15 m wide and 2.5 to 3 m deep. This is a potential source of contamination of PCBs in the surrounding area.

The task of the presented research is to define a toxic potential of the environmental compartments - sediments and water.

2. MATERIALS AND METHODS

2.1. Sample collection

A total of 12 samples of bottom sediment were taken from the discharge channel Strážske, discharge channel Duša and its right-bank tributary and Laborec. Values of several congeners crossing the detection limit were identifying in the case of four sampling places.

S5 – discharge channel from the wastewater treatment plant

S7 – the place above the discharge channel confluence to the river Laborec

S8 – the place at the discharge channel confluence and river Laborec

S13 - right-bank nameless tributary of Duša

Sampling of surface water was carried out from Laborec, its own discharge channel and its tributaries, from Duša and its right-bank tributary. In total, 54 samples of surface water were taken. For representative evaluation was used sampling place at the confluence of the discharge channel to the river Laborec. Value of several congeners crossing the detection limit was identifying in one sample (Fig. 1). According to standard procedures, for statistical calculations was applied the value of 50% detection limit.

2.2. Sample analysis

EPA 525.2 (surface water samples) - Gas chromatography/mass spectrometry (GC/MS) system. Organic compound analyses, internal standards, and surrogates are extracted from a water sample by passing 1 L of sample water through a cartridge or disk containing a solid matrix with a chemically bonded C18 organic phase (liquid-solid extraction, LSE). The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a high resolution fused silica capillary column of a gas chromatography/mass spectrometry (GC/MS) system.

STN EN15308 (sediments samples) Characterization of waste. Determination of selected polychlorinated biphenyls (PCBs) in solid waste by using capillary gas chromatography with electron capture or mass spectrometric detection.

3. RESULTS AND DISCUSSION

The analysis of PCBs in sediments and water shows specific proportion of PCB congeners. The most abundant congener in the case of sediments is PCB 123 (samples S7, S8, S13) and PCB 81(sample S5) (Table 2; Fig. 2).

Evaluation the PCB contamination of surface waters has been interest of the environmental and health risks relevant PCBs present for the human population living near polluted channel. We indicate the highest values in case of PCB 126 (28.4 ng.l^{-1}) and relatively equal values of PCB 167 (27.88 ng.l^{-1}), PCB 127 (27.11 ng.l^{-1}) and PCB 105 (26.3 ng.l^{-1}). These values were used for health risk assessment of near-living population.

Several studies indicate the PCB concentration measured in surface water. A few studies were conducted in Great Lakes (USA). It was found that Lake Erie had the highest degree of contamination with total PCB concentration ranging from 0.2 to 1.6 ng.l^{-1} (Anderson et al., 1999). Other studies indicate PCB values in rivers. Total PCB concentrations studied from 1990 to 1991 in the Saginaw River ranged from 11 to 31 ng.l^{-1} (Verbrugge et al., 1995).

Table 2. Concentration of PCB congeners in sediment and surface water

Cong.	Surface water (W15) (ng.l^{-1})	Sediment (S5) (mg.kg^{-1})	Sediment (S7) (mg.kg^{-1})	Sediment (S8) (mg.kg^{-1})	Sediment (S13) (mg.kg^{-1})
PCB 77	0.50	0.0025	0.0025	0.0025	0.1090
PCB 81	0.50	0.1010	0.0025	0.0025	0.1100
PCB 105	26.30	0.0450	0.5330	0.0025	0.0870
PCB 114	0.50	0.0025	0.0025	0.0025	0.0025
PCB 118	26.30	0.0025	0.0025	0.0025	0.0025
PCB 123	27.11	0.0550	1.5560	2.1620	0.1050
PCB 126	28.40	0.0200	0.4180	1.4150	0.0130
PCB 156	0.50	0.0025	0.0025	0.0025	0.0025
PCB 157	0.50	0.0025	0.0025	0.0025	0.0025
PCB 167	27.88	0.0300	0.5640	0.9420	0.0260
PCB 169	0.50	0.0080	0.0025	0.0025	0.0025
PCB 189	0.50	0.0025	0.0780	0.2250	0.0060

½ limit of detection

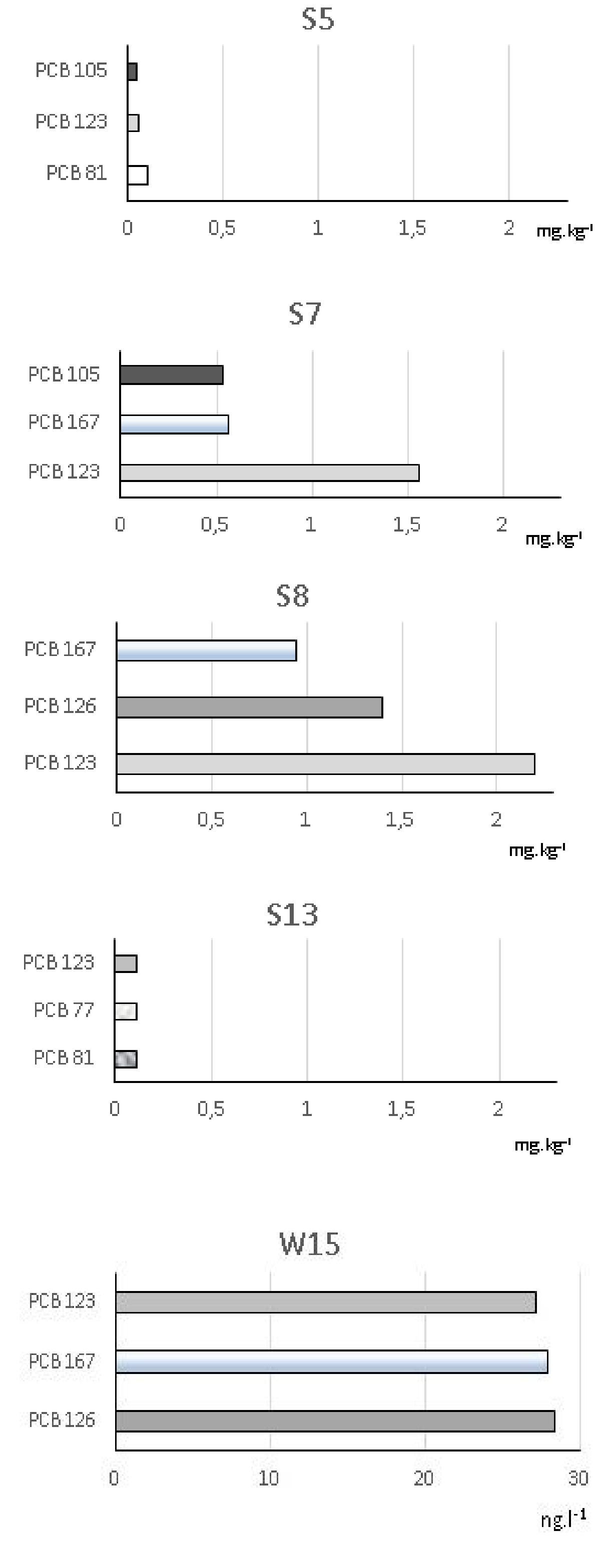

Figure 2. Outputs of the most abundant PCB congeners in analysed samples

Although PCBs are widely found in surface waters, their low solubility generally prevents them from reaching high concentration especially in groundwater (EPA, 1980b). However, under extreme conditions, such as at hazardous waste sites, PCB contamination of groundwater can occur (ATSDR, 2000). The study conducted in river Chenab (Pakistan) shows outputs of analyses of 32 PCB congeners in water. PCB concentration ranged between 0.2 and 28ng.l^{-1}, respectively, where tetra chloro PCB and tri chloro PCB dominated over other congeners (Mahmood et al., 2014).

Research of Necibi et al., (2015) shows output of PCB analysis in surface water in Bizerte Lagoon (Tunisia). The average concentration of PCB range was between 3 and 10ng.l^{-1}. The predominant PCB congeners were PCB 28 (0.2-1.4ng.l^{-1}) and PCB 52 (0.8-3.5 ng.l^{-1}).

A serious problem should be connected with extreme atmospheric conditions as storms, especially in time of flood situations. In a literature review a lot of articles containing information on urban storm water quality. Makepeace et al., (1995) reported that total PCB concentration in urban storm water ranged from 27 to 1100 ng.l^{-1}. A maximum total PCB concentration of 15000 ng.l^{-1} was detected in surface water samples from the St. Lawrence River downstream from Superfund site (General Motors Foundry Division) (ATSDR, 1995)

PCB levels in sediment varies are depending on source of contamination and also on temporal changes in Superfund Place. We found specific composition of congeners (three with the highest values) at each sampling sites (4) in discharge channel (Fig. 2). The most abundant congeners are PCB 123 (22-2162ng.g^{-1}), PCB 126 (13-1415ng.g-^{1}), PCB 167 (26-942ng.g^{-1}), PCB 105 (2.5-533 ng.$g^{-1)}$, PCB 81 (2.5-110 ng.g^{-1}), and PCB 77 (2.5-109 ng.g^{-1}).

Mahmood et al., (2014) investigated concentration levels, spatial distribution pattern sediments samples from two tributaries of river Chenab (Pakistan). PCB concentration in sediment ranged between 0.8-60 ng.g^{-1}. Kampire et al., (2015) published outputs of PCB analysis in sediments at Port Elizabeth Harbour (South Africa). The total PCB concentration ranged from 0.56 to 2.35ng.g^{-1}.

Surface sediments were analyzed for PCBs from Lake Ontario from 1982 to 1986 (Oliver et al., 1989). Concentration decreased from1300—1900 ng.g^{-1} in 1982/83 to 80-290 ng.g^{-1} in 1985/86. Researchers determined that the percentage of lower chlorinated congeners (tri to penta) decreased with depth, while hexachlorobiphenyls remained fairly constant throughout and the concentration of highly chlorinated congeners increased with depth (ATSDR, 1995).

Determination of TEF and TEQ

We calculate TEF values in accordance of Eq. 1 and Eq. 2 in Introduction. Table 3 shows outputs of calculation. Highest values of TEQ were determined in place S8 141676 pg.g^{-1} equal to 141.7 ng.g^{-1} (Table 3).

Table 3. Outpust of toxic equivalency factor and toxic equivalency concentration calculation.

Cong./TEF	**Surface water (W15) ($ng.l^{-1}$)**	**Sediment (S5) ($pg.g^{-1}$)**	**Sediment (S7) ($pg.g^{-1}$)**	**Sediment (S8) ($pg.g^{-1}$)**	**Sediment (S13) ($pg.g^{-1}$)**
PCB 77	0.00005	0.25	0.25	0.25	10.9
PCB 81	0.00015	30.3	0.75	0.75	33
PCB 105	0.00079	1.35	15.99	0.075	2.61
PCB 114	0.00002	0.075	0.075	0.075	0.075
PCB 118	0.00079	0.075	0.075	0.075	0,075
PCB 123	0.00081	1.65	46.68	64.86	3.150
PCB 126	2.84	2000	41800	141500	1300
PCB 156	0.00002	0.075	0.075	0.075	0.075
PCB 157	0.00002	0.075	0.075	0.075	0.075
PCB 167	0.00084	0.9	16,92	28.26	0.780
PCB 169	0.015	240	75	75	75
PCB 189	0.00002	0.075	2.34	6.75	0,18
TEQ=$\sum TEF_{cong.}$	2.86	2274.83	41958.23	141676.25	1425.92

Sediments were analyzed for non-ortho and mono-ortho-chlorine substituted PCBs in Kentucky Lake (USA). TEQs (calculated using WHO-TEFs proposed in 1998) indicated that sediments from Kentucky Dam Tailwater are 0.3 pg. g^{-1} dry wt) (Loganathan et al., 2001).

TEQ for sediment calculated at contaminated areas in Europe for mixture of polychlorinated dibenzo-p-dioxin, polychlorinated dibenzofuran and coplanare PCB were in Finland 80000 $pg.g^{-1}$, Germany 1500 $pg.g^{-1}$, Netherlands 4000 $pg.g^{-1}$ and UK 7410 $pg.g^{-1}$ (EU DG Environment, 1999).

Forty-five marine sediments from the Catalonian coast were analyzed for non-ortho and mono-ortho chlorine substituted PCB congeners. Total toxicity equivalent (TEQ) values were calculated using the toxicity equivalent factors (TEFs) proposed by WHO for dioxin-like PCBs. These levels ranged between 0.03 and 24.8 $pg.g^{-1}$ (Eljarat et al., 2001).

Polish authors evaluate quality of water as effluent from wastewater treatment plant. In case of three types of effluent were found to have similar TEQ values, ranging from 0.31 to 0.37 $pg.l^{-1}$ (Urbaniak & Kiedrzynska, 2015).

4. CONCLUSIONS

The present study has showed data on the levels of dioxin-like PCB congeners in surface water and sediments along the Strážske discharge channel which is situated in industrial area well known with production of pesticides and PCB products. This area belongs to national register of old environmental burdens localities. The findings of this study indicate that there is still the place with a high level of organic pollution in Slovakia with strong need to establish a reliable system of monitoring polychlorinated biphenyls and other organochlorine compounds not only in channel's body but also in Laborec River. The PCB levels were higher in sediment than in surface water. In general PCB 123 is the most abundant PCB in sediment and PCB 126 in surface water.

For relevant human health and environmental risk assessment is necessary to have actual and appropriate amount of data.

A further investigation is needed on levels of PCB in biota, mammalian body especially. Research of local produced meat and eggs in households along the channel and near Laborec River may show very interesting results.

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