Fate and Transport of Polychlorinated Biphenyls (PCBs) between Water and Atmosphere of the Polluted Krupa River in Slovenia

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1. Introduction

Polychlorinated biphenyls (PCBs) have been widely used because of their low cost, insulting capacity and their non-flammable nature as coolants and lubricants, particularly in dielectric fluids in capacitors and transformers, as well as in heat transfer and hydraulic systems, pigments, plasticisers, carbonless copying papers, electromagnets, components in cutting oils, and others. PCBs have been marketed under different names: Aroclor, Clophen, Pyralen, Kenneclor, Santotherm, etc¹⁾. In recent years, the widespread use, distribution, persistence and accumulation in the environment, and several incidents causing serious health problems in humans and animals gave rise to great concern^{2),3)}. The use of PCBs in Republic of Slovenia increased after 1960, when an ISKRA condenser factory was built in Semič, Bela Krajina (about 80 km south-east from capital Ljubliana). PCBs were introduced into the production process in 1962 (until 1970 Clophen A-50 and A-30 supplied by Bayer, FRG and between 1970 and 1985 Pyralen 1500 supplied by Prodelec, France). The consumption of PCBs by ISKRA in period 1962 - 1985 totalled about 3.7 million kilograms with a PCB waste rate of 8-9 per cent in the form of waste impregnates, condensers, etc. By 1974, 130000 kilograms of waste containing around 70000 kg of pure PCBs were dumped at various waste sites within five kilometres round the factory. After 1975 waste impregnates were collected and sent to France for treatment (170000 kg), whereas smaller waste condensers were still disposed of at a local waste site. First GC-MS analysis in 1982 showed very high concentration of PCBs in the compartments of the environment (water, air, sediments), as well as in food and in animal and human tissues. PCB level were particularly high in the nearly 3 km long Krupa river⁴⁾. The source of Krupa river with mean flow of 4 m³/s is situated in a typical Karstic terrain about 2 kilometres from the factory.

2. Remediation Programme

In view of the high pollution level found in the environment of the ISKRA factory and the Krupa river, the Slovene authorities and research institutes started in 1984 a PCB remediation programme: waste disposal project, environmental monitoring programme, and health researches.^{4),5)}

In early 1985 ISKRA had to stop its production of PCB condensers. The analyses of PCB concentrations in waste sites showed very high soil contamination levels of up to 50g of PCB per kilogram of dry weight. It was established that some 6000 m³ of contaminated subsoil should be decontaminated. A study of possible PCB waste treatment (disposal) technologies was carried out and a final disposal of the contaminated subsoil in a storage facility for PCB wastes was chosen as the

optimal available solution.⁶⁾ In 1986, a concrete watertight storage facility was built and filled with 6000 m³ of highly contaminated subsoil and wastes. The final storage facility was built according to maximum safety standards: a watertight concrete container, seismic criteria, a double control and monitoring system with a draining system in sand with control shafts under the container and a half-metre protection layer of clay below it.

In 1984, an environmental monitoring programme containing an extensive sample analysis in potentially threatened environmental compartment (soil, sediments, water, air), in food and living organisms (milk, eggs, meat, fruit, vegetables, fish), etc. was initiated. Some typical values, of PCB concentrations in the polluted area are shown in Table 1 (Analyses of PCBs were performed by GC-ECD and GC-MS (SIM)).⁵⁾

Standards	Conc.level
lng/l	10 - 1200 ng/l
/	2- 800 mg/kg
1µg/m ³ ^b	1- 60 μg/m ³
1,5 mg/kg (fat) ^c	0,6- 4,0 mg/kg
0,3 mg/kg (total volume)	0,1- 6,0 mg/kg
2,0 mg/kg (edible par:)	1- 120 mg/kg - (72 % > 2 mg/k
	$\frac{lng/l^{a}}{l\mu g/m^{3}}$ $\frac{1,5 mg/kg (fat)^{c}}{0,3 mg/kg (total volume)}$

^a EPA - Environmental Protection Agency U.S.

^b NIOSH - National Institute of Occ. Saf. and Health U.S.

[°] FDA - Food and Drug Administration U.S.

3. Transport of PCBs between Water and Atmosphere

A comparison of PCB concentrations in samples before and after decontamination in a 10 -year period (1984-1994) shows a slow decrease in these concentrations in air, soil and food, confirming the effectiveness of the remediation measures, namely the elimination of gros PCB emissions in the environment ^{5),7)}

But still the highest concentrations of PCBs have been confirmed by measurements made in the region around the river Krupa recently. Also the measurements have shown (Figure 1.) an increase of PCB concentrations in soil in the NE Krupa area which is the most common direction of the wind blowing(intense deposition).

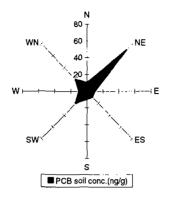
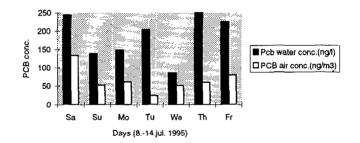
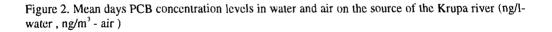


Figure 1. Mean PCB concentrations in polluted soil within 1 km around the source of Krupa river (ng/g-dry)

A comprehensive model has been developed describing the dominant volatilisation process i.e. waterair exchange process of PCBs at water surfaces.^{8,9,1,00,111,12} Figures 2. illustrate a typical concentration pattern measured in 1995 simultaneous on the source of the Krupa river in water and in the air 1 m above the river surface (high flux of PCBs into atmosphere).





Sediment samples were taken in 1995 the deepest section of the river source where disturbances of the water column are minimal.¹³⁾ Results of PCB concentrations in sediment show a clear histogram of the river pollution, giving $< 0.1 \ \mu g \ PCB/g$ between 30 - 34 cm of sediment layer, about $\ \mu g \ PCB/g$ between 8-8 cm and over 160 $\ \mu g/g$ between 0-1 cm.

4. References

¹⁾Report on Protection of the Environment by Control of PCB (Polychlorinated Biphenyls), OECD, ENV/CHEM/81.2 (1st Revision), Paris, Nov. 1981.

- ²⁾ Waid J.S.: PCBs and Environment. CRC Press, Inc., Boca Raton, Florida, U.S., 1986
- ³⁾ Murty A.S.: Toxicity of Pesticides to Fish. CRC Press, Inc., Boca Raton, Florida, U.S., 1986
- ⁴⁾ Polič S. and B. Kontić (1987): Report on PCB Remediation in Eela Krajina. Word Confer. on Hazardous Waste, Budapest, 925 929.
- ⁵⁾ Polič S.: Reports on PCB Remediation and monitoring program in Bela Krajina (Slovenia) 1983-1993. Personal communication, Jožef Stefan Insitute, University of Ljubljana, Slovenia, 1986, 1993.
- ⁶⁾ Ackerman D.G.: Destruction and Disposal of PCBs by Thermal and Non.Thermal Methods. Noyes Data Corporation, Park Ridge, New Yersey, U.S., 1983.
- ⁷⁾ Brumen S, M. Medved, E Vončina and J.Jan (1989): Case of Polychlorinated Biphenyl Contamination of Water and Sediment in The Slovenian Karst Region. Chemosphere 13 (12).
- ⁸⁾ Neely W.B. and G.E. Blau: Environmental Exposure from Chemicals. CRC Press, Inc., Boca Raton, Florida, U.S., 1985.
- ⁹⁾ Mackay D. and S. Paterson (1982): Fugacity revisited. Environ. Sci. Technol. 16, 654 A- 660 A
- ¹⁰⁾ Mackay D. and S. Paterson (1986): Model Describing the Rates of Transfer Processes of Organic Chemicals between Atmosphere and Water. Environ. Sci. Techaol. 20, 810-816.
- ¹¹⁾ Mackay D. and S. Paterson (1991): Evaluating the Multimedia Fate of Organic Chemicals: A Level III Fugacity Model. Environ. Sci. Technol. 25, 427- 436.
- ¹²⁾ Harner T., D. Mackay and K.C. Jones (1995): Model of the Long-Term Exchange of PCBs between Soil and the Atmosphere in the Southern U.K.. Environ. Sci. Technol., 29, 1200 1209.
- ¹³⁾ Leskovšek H., M. Šusteršič, L.Z. Kralj and J. Marsel (1996): The Determination of PCBs in River Sediment from a Polluted Region. Personal communication. Jozef Stefan Institute, University of Ljubljana, Slovenia.