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PCB POLLUTION OF THE KARSTIC ENVIRONMENT (KRUPA RIVER, SLOVENIA)

ONESNAŽENJE KRAŠKE REKE KRUPE S PCB-JI

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S. Polič & H. Leskovšek & M. Horvat: Onesnaženje kraške reke Krupe s PCBji

Problem onesnaženja reke Krupe s polikloriranimi bifenili (PCB) je še zlasti pereč zaradi zakraselosti terena in mešanja podtalnice s prenikujočimi površinskimi vodami. Onesnaženost Krupe s PCB in usodo le-the smo nazadnje zasledovali v obdobju 1995-1998 v okviru programa "okoljske remediacije", ki se je začel izvajati leta 1984. Določili smo koncentracijo PCB v zraku, vodi, rečnem sedimentu in tleh; uporabili smo preprost dvofazni fugativnostni model porazdelitve, ki je zadovoljivo opisal dolgoročni trend spreminjanja koncentracije polutanta. Določili smo celokupni snovni tok PCB na meji voda/zrak (0,3 ng/m^{2}s). Prikazana je situacija in trendi gibanja nivoja onesnaženja po 10 letih remediacije in kvantitativno določena emisija PCB iz podzemnega dela toka Krupe v izvir. Primerjava koncentracij PCB v vodi v letih 1986 do 1988 in 1995 do 1998 kaže trend upadanja (s povprečno 380 ng/l na povprečno 100 ng/l). Emisijski snovni tok na meji voda/zrak vzdolž celotnega toka Krupe (2,6 km) znaša 200 do 500 g/leto, kar je približno desetina začetne vrednosti, ko se je remediacija začela.
Ključne besede: krasoslovje, hidrogeologija, onesnaženje s PCB, transport, emisija, Slovenija, Bela Krajina, Krupa.

Abstract UDC: 556.3.054(497.4)

S. Polič & H. Leskovšek & M. Horvat: PCB Pollution of the Karstic Environment (Krupa River, Slovenia)

The PCB (Polychlorinated biphenyls) pollution problems in Krupa River are related to sinking surficial streams that mix with the regional groundwater supply, thus endangering the quality of the groundwater reservoirs. The last state of contamination with PCBs and their fate and exposure in the polluted environment were studied in the period 1995 to 1998 within the Remedial Environmental Programme that began in 1984. The concentrations of PCBs in the environmental compartments (air, water, sediment, and soil) of the Krupa were determined. A simple two-compartment (air/water) fugacity mass balance model was applied to these figures, and yielded a reasonable simulation of long-term trends in concentration. The net flux of PCBs from water to air was determined (0.3 ng/m^{2}s). Research into levels of pollution in the Krupa area showed the situation and trends regarding pollution after ten years of remedial measures, and produced a quantitative assessment of the emission of PCBs from the underground catchment area of the source of the river. Comparisons between PCB concentrations in the polluted water measured from 1986 to 1988 and the concentrations measured in 1995 to 1997 show a decreasing trend (i.e. from a mean of 380 ng/l to a mean of 100 ng/l in the Krupa's water). The emission flux of PCBs from water to air for the entire River Krupa (2.6 km long) was estimated at 200 to500 g/year, i.e. approximately one-tenth of the figure at the time the remedial measure was initiated.
Key words: karstology, hydrogeology, PCB pollution, transport, emission, Slovenia, Bela Krajina, Krupa River.

INTRODUCTION

Because of their low cost, their insulating capacity and their non-flammable nature polychlorinated biphenyls (PCBs) have been widely used as coolants and lubricants, particularly in dielectric fluids in capacitors and transformers, in heat transfer and hydraulic systems, pigments, plasticisers, carbonless copying papers, electromagnets, and components in cutting oils. PCBs have been marketed under different names: Aroclor, Clophen, Pyralen, Kenneclor, Santotherm, etc. In recent years their widespread use, their distribution, persistence and accumulation in the environment and several incidents causing serious health problems among humans and animals has given rise to great concern (Waid, 1986, Murty, 1986).

PCBs are synthetic organic compounds (209 possible isomers) of high physical, chemical and biological stability, and persist for long periods in a contaminated environment: they are undegradable (xenobiotics, Hutzinger et al., 1974). They are biotoxically active compounds, and in animals and people cause acute and chronic damage to the skin, liver and lungs. In addition they cause metabolic disorders and disturbances to the action of the endocrine system, and are associated with loss of bodyweight and immuno-sensitivity. They are mutagenic and teratogenic, and are suspected to be carcinogenic (Safe, 1984). PCB toxicity is principally dependent on the level of chlorination, the position of the substituted chlorine on the biphenyl, and the stereochemical structure (Tanabe et al., 1987). The toxicity of individual PCB isomers is defined in relation to the most toxic halogenated aromatic compound TCDD (2,3,7,8-tetrachloro-p-dioxin): the figure for the most toxic isomers ranges from 0.001 do 0.1(Safe, 1992).

There was an increase in use of PCBs in Slovenia after l960, when Iskra built a condenser factory at Semič in Bela Krajina (about 80 km southeast of the capital Ljubljana and 100 km east of Trieste). PCBs were introduced into the production process in 1962 (before 1970 Clophen A-50 and A-30 were supplied by the German Company Bayer, from l970 to 1985 Pyralen 1500 was supplied by Prodelec of France). Iskra's total consumption of PCBs between 1962 and 1985 was about 3.7 million kg, with a PCB waste rate of 8 to 9 per cent in the form of waste impregnates, condensers, etc. By l974, 130,000 kg of waste containing around 70,000 kg of pure PCBs had been dumped at various waste sites within 5 km of the factory. After 1975 waste impregnates were collected and sent to France for processing (170,000 kg), but smaller waste condensers were still disposed of at a local waste site (Polič, 1997).

Initial GC-MS analysis in l983 showed a very high concentration of PCBs in environmental compartments (water, air, sediments, Medved et al., 1984, Jan & Tratnik, 1985), and in food, animal, and human tissues. PCB levels were particularly high in the River Krupa.

The source of the Krupa has a mean flow rate of 3 to 5 m^3/s and is situated in typical karstic terrain about 3 km south of the condenser factory. The water rises to the surface in strong karstic springs from underneath steep overhanging rock faces, in a unique green-coloured dammed pool. The hinterland area is karstic, with numerous fractures in various directions, and a total catchment area of 140 to 170 km^2. The river has a relatively small drop in altitude as it flows 2600 m through a gorge 30 m deep into the River Lahinja. Together with its source and the surrounding environment the Krupa is an exceptional piece of natural and cultural heritage, and has been classified among the most important heritage in the country, being proclaimed a site of outstanding natural significance in 1997. In addition the Krupa's source is the largest in Bela Krajina and is thus the

most important future source of drinking water for the Bela Krajina region. The region is relatively densely populated, and the major settlements lie right along the Krupa gorge.

REMEDIAL PROGRAMME

In view of the high level of pollution found in the environment of the Iskra factory and in the Krupa river, Slovenian authorities and research institutes began a PCB remedial programme in 1984, encompassing a waste disposal project, an environmental monitoring programme, and health research (Poliočˇ, 1997, Polič & Kontič, 1987).

In early 1985 Iskra was forced to cease its production of PCB condensers. Analysis of PCB concentrations in waste sites showed very high soil contamination levels of up to 50g of PCB per kg of dry matter. It was established that some 6000 m^3 of contaminated subsoil required decontamination. A study of possible PCB waste treatment (disposal) technologies was carried out, with final disposal of the contaminated subsoil in a storage facility for PCB wastes chosen as the best available solution (Ackerman, 1983). In 1986 a concrete watertight storage facility was built and filled with 6000 m^3 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 and a drainage system in the sand with control shafts under the container and a half-metre protective layer of clay below it.

In 1984 an environmental monitoring programme, including extensive sample analysis in environmental compartments under threat (soil, sediments, water, air) and in foodstuffs and living organisms (milk, eggs, meat, fruit, vegetables, fish), was initiated (Table 1).

Table 1: Typical PCB concentration levels in the polluted environment of the Krupa river (1982 to 1992) (Ackerman, 1983, Jan & Tratnik, 1988, Jan et al., 1988, Zupančič-Kralj et al., 1992, Zupančič-Kralj et al., 1992a, Zupančič-Kralj & Jan, 1994).
Tabela 1: Koncentracija PCB v onesnaženi reki Krupi v letih 1982 do 1992 (Ackerman, 1983, Jan & Tratnik, 1988, Jan et al., 1988, Zupančič-Kralj et al., 1992, Zupančič-Kralj et al., 1992a, Zupančič-Kralj & Jan, 1994).

Sample	Levels	Standards
air	1 to 10 µg/m3	1 µg/m3 [a]
water	100 to 1000 ng/l	1 ng/l [b]
sediment	10 to 800 mg/kg	-
milk	1 to 5 mg/kg	1.5 mg/kg (fat) [c]
eggs	1 to 10 mg/kg	0.3 mg/kg (total volume)
fish	1 to 200 mg/kg	2.0 mg/kg (edible part)
poultry	1 to 20 mg/kg	3.0 mg/kg (fat)
human (adipose tissue)	1 to 10 mg/kg	-

[a] NIOSH - National Institute of Occ. Saf. and Health (USA)
[b] EPA - Environmental Protection Agency (USA)
[c] FDA - Food and Drug Administration (USA)

Sampling sites locations on Krupa river.
Lokacija vzorčevalnih mest na Krupi.

STUDY AREA, SAMPLING AND CHEMICAL ANALYSIS

Research into the levels of pollution in the Krupa area conducted between 1995 and 1998 showed the situation and trends regarding pollution after ten years of remedial measures, and led to a quantitative assessment of the emission of PCBs from the underground catchment area of the source of the river (Polič, 1997). In the experimental phase of the research (Polič & Leskovšek, 1996, Leskovšek et al., 1996, Leskovšek et al., 1996a) the authors focused on measuring PCBs in air samples taken from above the water surface of the Krupa and water samples taken at the same time, which, using a thermodynamic model of the distribution and transport (Liss & Slater, 1974, Mackay & Paterson, 1981, Mackay et al., 1983, Mackay & Paterson, 1983, Mackay & Paterson, 1986) of PCBs between various environmental compartments, yielded a quantitative assessment of the evaporation (flux) of PCBs from the Krupa, and of aerogenic transport and ecological loading on the Krupa gorge. In addition, samples taken from contaminated river sediment and soils in the immediate vicinity of the Krupa were also analysed.

Air and water samples were taken at two sampling sites in the middle of the river flow at the source (Site I) and about 1200 m downstream (Site II) during two two-week periods in the spring, autumn and summer of 1995 to 1997, after heavy rains and at the beginning of a longer period of dry, stable weather. During sampling the water flow rate was measured, and the automatic meteorological measuring station (AMES - Jozef Stefan Institute, Ljubljana) provided data of water and air temperature, humidity, atmospheric pressure, and wind speed and direction at the middle of the flow of the Krupa.

The contaminated air was sampled daily at a height of 50 to 150 cm above the surface of the Krupa by pumping the air over glass ampules filled with polyurethane foam. The air was pumped using membrane pumps over a period of about 24 or 48 hours at a flow rate of 2 to 3 m^3/h. The PCBs were concentrated in the adsorbent polyurethane foam under the standard procedure (ASTMD 4861-91). The polyurethane plugs were deep-frozen until analysis. In parallel with the daily air samples water samples were taken daily from the active section of the flow just under the surface of the Krupa, using sampling floats. The samples were taken using a single sampling and placed in analytically clean 2.5-l laboratory flasks, which were stored in a refrigerator until analysis. Sediment samples were taken from the deep sediment on the river bed (about 3 m) where the effect of the flow was at its lowest. During sampling special sampling tubes were used (35 mm in diameter) which made it possible to take a section of the sediment by hand to a depth of 30 to 50 cm (done by a diver using an aqualung) without mixing the strata. The section of sediment was divided into 1-cm slices in the laboratory. The individual slices were air dried, homogenised and sieved (particle size 150 mm) and was frozen until analysis.

PCBs were extracted from the solid samples and the polyurethane foam using two procedures: ultrasonic extraction and supercritical fluid extraction (SFE, Standard Methods 8000). The PCBs from the 2.5-litre water samples were pre-concentrated on a solid C18 adsorbent (500 mg) using a standard solid phase extraction procedure (Water Analysis, Organic Micropollutants, Hewlett-Packard 5962-6216E, 2/94, Extraction Methods Separcol W1, Anapron) and were then washed out of the microcolumn using acetone or hexane. All the extracts were concentrated to a volume of 500 µl and were frozen until analysis. The extracted PCB samples were analysed using HP 6890 GC/MSD and GC/ECD instruments. Low concentrations of PCBs in the extract samples (below 1 ng/µl) were analysed using gas chromatography with a mass-selective detector (GC/MSD (TIC,

SIM), Leskovšek et al., 1996, Leskovšek et al., 1996a). Individual PCB isomers were identified during the gas chromatography analysis using a standard mixture of Clophen A40 and Aroclor 1242.

RESULTS AND DISCUSSION

The PCB concentrations in the air above the surface of the River Krupa measured in different seasonal cycles at the source (Site I) and a point 1.2 km downstream (Per Mill, Site II) show seasonal and daily fluctuation. The fluctuation is the result of the rapidly changing conditions in

Table 2: PCB concentrations in the air above the surface of the Krupa river at Site II (1.2 km downstream of the source) in 1-metre and 2-metre belts (Samples II.1. and II.2.) and in flux from the surface covered (II.2.), 14 to 27 July 1996.*
Tabela 2: Koncentracije PCB v zraku nad rečno gladino na točki II (1,2 km od izvira) v 1 in 2 m pasu (vzorca II.1. in II.2.) in snovni tok skozi pokrito površino (II.2.) med 14. in 27. julijem 1996.*

Sample Site II 1 km downstream	**Date and time of start of sampling**	**Sampling time air sampled [h]**	**Volume of conc. in air [m^3]**	**PCB [ng/m^3]**
II.1. - 1	16.7., 10^{20}	24 h	55.030	216.1
II.1. - 2	17.7., 10^{40}	20 h 40 min	43.530	46.6
II.1. - 3	18.7., 7^{40}	25 h 50 min	53.360	238.5
II.1. - 4	19.7., 10^{00}	23 h 30 min	58.000	77.4
II.1. - 5	20.7., 10^{00}	23 h	52.770	19.7
II.1. - 6	21.7., 9^{30}	24 h	54.160	286.0
II.1. - 7	22.7., 10^{00}	23 h 20 min	52.570	31.2
II.1. - 8	23.7., 9^{40}	24 h	59.200	138.7
II.1. - 9	24.7., 10^{30}	23 h 50 min	50.840	130.0
II.1. -10	25.7., 10^{25}	23 h	47.830	108.3
II.1. -11	26.7., 10^{00}	24 h 20 min	57.490	59.9
II.2. - 1	16.7., 10^{20}	24 h	51.050	55.8
II.2. - 3	18.7., 7^{40}	25 h 50 min	49.060	133.4
II.2. - 5	20.7., 10^{00}	23 h	54.820	65.0
II.2. - 7	22.7., 10^{00}	23 h 20 min	51.440	59.4
II.2. - 9	24.7., 10^{30}	23 h 50 min	50.550	93.4
II.2*. - 2*	17.7., 10^{40}	20 h 40 min	50.810	52.8
II.2*. - 4*	19.7., 10^{00}	23 h 30 min	52.180	120.0
II.2*. - 6*	21.7., 9^{30}	24 h	46.510	144.9
II.2*. - 8*	23.7., 9^{40}	24 h	49.820	57.3
II.2*. -10*	25.7., 10^{25}	23 h	57.890	154.6
II.2*. -11*	26.7., 10^{00}	24 h 20 min	59.710	54.8

the Krupa such as: emission of PCBs, transport of suspended sediment along the river and concentration changes in the air in the gorge. The average daily PCB concentrations in the air between the sample sites, i.e. between the source of the Krupa and Per Mill, show less fluctuation.

During the summer period (8 to 15 July 1995) the daily PCB concentrations at the source of the Krupa (Site I) ranged from 20 to 60 ng/m^3 (11 samples with an average of about 40 ng/m^3), while those 1.2 km downstream (Site II) ranged from 25 to 90 ng/m^3 (12 samples with an average of about 65 ng/m^3). The figures for the autumn period (25 October to 2 November 1995) were 1 to 30 ng/m^3 (11 samples with an average of about 10 ng/m^3) for Site I and 1 to 30 ng/m^3 (12 samples with an average of about 5 ng/m^3). In the next summer period (14 to 27 July 1996) samples were only taken at Site II. The concentrations of PCBs in the air (at various heights above the surface and in flux from the surface covered) show huge daily fluctuation, particularly in the one-metre band just above the surface.

The daily concentrations in the first one-metre band ranged from 20 to 285 ng/m^3 (with an average of about 120 ng/m^3) and those in the two-metre band ranged from 55 to 130 ng/m^3 (with an average of about 80 ng/m^3). The concentrations of PCBs in flux from the river surface covered also show substantial daily fluctuation, ranging from 50 to 155 ng/m^3 (with an average of about 100 ng/m^3).

PCB concentrations in the water in the active section of the Krupa in the summer period (8 to 15 July1995) ranged from 205 to 65 ng/l (and fell daily). A relatively rapid drop in the concentration of PCBs in the water from 13.5 to 8.5 m^3/s was observed after a long period of rain. In the autumn period (25 October to 2 November 1995) the concentrations in the water ranged from 75 to 15 ng/l. There was also a noticeable drop in the concentrations linked with a fall in the flow rate from 2.6 to 1.9m^3/s. In the summer period (14 to 27 July 1996) the PCB concentrations in the water show a closer link to the drop in flow rate. During the ten-day measurement period the concentration fell from 220 to 40 ng/l, while the flow rate fell from 7.5 to 4 m^3/s in the same period following the rain (Figure 1).

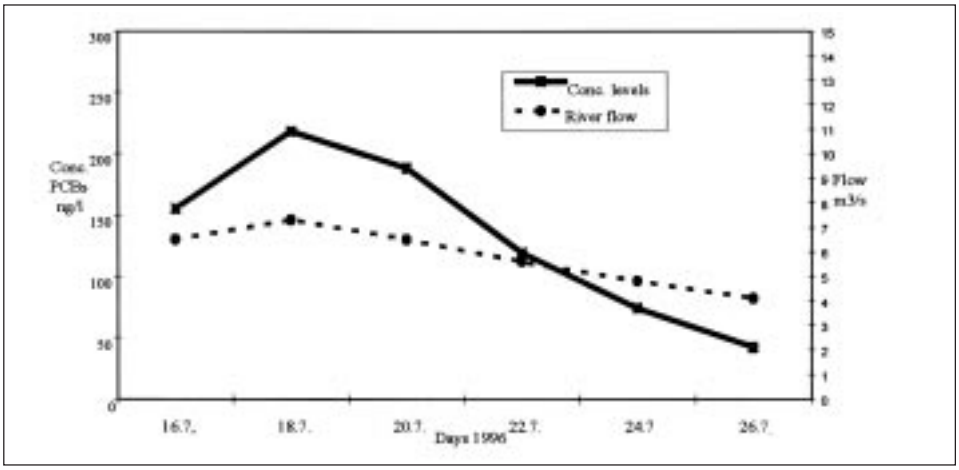

Fig. 1: Drop in PCB concentration (ng/l) in Krupa water and fall in flow rate (m^3/s) over the same period of measurement, 14 to 27 July 1996.
Sl. 1: Padanje koncentracije PCB (ng/l) v Krupi in padec toka (m3/s) v obdobju 14.-27.7.1996.

A comparison of all the measurements of PCB concentrations in water in the Krupa in the ten years (1986 to 1996) after the remedial measures shows a fall in the level of PCB pollution (Table 3).

Table 3: Mean values of PCB concentration measured in Krupa water (by monitoring period), 1986 to 1996.
Tabela 3: Srednje koncentracije PCB v Krupi v opazovanlem obdobju 1986-1996.

Monitoring period	Number of samples	Mean PCB concentration (ng/l)
1986 to 1988	27	~380
1989 to 1991	30	~230
1992 to 1994	10	~120
1995 to 1996	20	~100

The highest concentrations of PCBs in the water (over 1000 ng/l) were measured during the period after the excavation of the factory waste depot in June 1986, which shows the direct link between PCB emissions in the area of the transformer factory and pollution of the Krupa's water. The subsequent high concentrations in the water also indicate the strong leaching of PCBs by rainwater from the contaminated zone underground and from the wider area of ground contaminated aerogenically. The last measurements, carried out between 1995 and 1997, indicate that the emission of PCBs from underground has fallen since the remedial work on the waste site, even after heavier precipitation in the catchment area (during which time the Krupa's flow increased). PCB concentrations in the water of the Krupa grew to approximately 200 ng/l, but dropped very rapidly as the flow rate fell. This indicates that PCB emissions from underground occur mainly through the transport of polluted sediment and suspended particles during periods of heavy flow. The contaminated sediment is transferred along the course of the Krupa, while there is relatively rapid desorption and resuspension of PCBs from the "active" sediment, and transport of the more soluble and volatile isomers to the water phase and air above the Krupa. This mechanism (Liss & Slater, 1974, Mackay & Paterson, 1981, 1983, 1986, Mackay et al., 1983) is confirmed by the measurements of PCBs in silt flats in the water (considerably high values), the measurements of PCBs in the air above the water surface, and a histogram of the river sediment with a strongly polluted upper stratum. The change in the concentrations of PCBs in the water indicates a general dependence on the flow-rate of the Krupa (Fig. 1). The estimate of the amount of PCBs emitted at the source of the river between 1995 and 1997 was 5 to 10 kg/year, a load one-fifth of that a decade before, after the remedial work.

The average daily concentrations of PCBs in the layer of air above the surface of the Krupa was in the range of 1 to 10 ng/m^3, 10 to 50 ng/m^3 and 50 to 100 ng/m^3 during different cycles of measurement. The large daily fluctuation of the concentrations in air was a result of complex competitive interphase and phase transport and partition processes in the Krupa and the air above the surface of the river (Mackay et al., 1983, Mackay & Paterson, 1983, 1986, Jeremaison et al., 1994, Harner et al., 1995) such as: sediment and suspended particles↔water↔air, transfer of sediment along the river and resuspension and desorption of PCBs into the water phase, changing speeds of the diffusive-advective transport of PCBs through the water phase and the outer layer of the water

surface, and diffusive-advective transport of PCBs in the air above the water in the Krupa gorge. Calculation of the flux from the surface of the Krupa using measurements of PCB concentrations in the air above the water surface gives an average value of about 0.3 ng/m^{2}s, which is in good agreement with the fugacity model (Mackayy & Paterson, 1981, Mackay et al., 1983). The estimated aerogenic emission along the whole of the river course through the Krupa gorge between 1995 and 1997 was between 200 and 500 g/year, which is assessed as being one-tenth of the figure during the era of high pollution ten years earlier.

CONCLUSIONS

Prior to 1983 the River Krupa was the only suitable source of water for regional exploitation. No use was made of the water because of the high content of polychlorinated biphenyls (PCBs) in the water and the sediment. Later hydrological research has pointed towards the possible use of deep underground karstic waters in the Krupa catchment area. It was found that the PCB load was much reduced after the ecological remedial work, as less and less contaminated sediment was being washed into the Krupa from underground. The most recent research into the air above the surface of the Krupa indicates that the load on the area owing to emission is one-tenth of the level ten years before. In comparison with emissions of PCBs into the air during the era of highest production at the condenser factory in Semič (100 kg/year between 1970 and 1985) PCB emissions into the air along the entire River Krupa are now less than one-hundredth of the former level.

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ONESNAŽENJE KRAŠKE REKE KRUPE S PCB-JI

Povzetek

Problematika preprečevanja onesnaženosti podtalnice in sanacije le-te na kraškem terenu je bistveno bolj kompleksna kot na nekraškem terenu, kjer so zadrževalni časi vode v vodonosnikih daljši in so ti tudi bolje definirani. Zato je tehnologija čiščenja onesnaženih kraških podtalnic nujno drugačna in zahteva večjo inovativnost. Na področju kraške reke Krupe obstaja problem onesnaženja s polikloriranimi bifenili (PCB). Onesnaženi površinski tokovi - ponikalnice se mešajo s podtalnico, ki je vir pitne vode za to področje, tako da je ogrožen celotni sistem podtalnice.

PCB predstavlja 209 izomer sintetičnih organskih spojin z veliko molsko maso, ki so kemijsko in biološko zelo stabilne - nerazgradljive (ksenobiotične). Gre za aktivne biotoksične spojine, ki povzročajo akutne in kronične poškodbe kože, jeter in pljuč pri živalih in ljudeh. Povzročajo tudi motnje metabolizma, endokrinega in imunskega sistema. So mutagene in teratogene, sumijo tudi, da so karcinogene. Toksičnost PCB je predvsem odvisna od stopnje kloriranosti, mesta substitucije klora na bifenilu in stereokemične strukture.

Tovarna kondenzatorjev v Semiču (Bela Krajina, okrog 80 km JV od Ljubljane) je od leta 1962 do 1984 z izpusti onesnažila zaledje reke Krupe, ki teče okrog 3 km južno od tovarne; je tipična kraška reka s pretokom 3 do 5 m^3/s. Zanjo je značilen močan kraški izvir pod previsno steno. Zaledje je kraško, razpokano, zbirno področje meri 140 do 170 km^2. Področje je razmeroma gosto naseljeno, predvsem kmetijsko (vinogradništvo), v manjši meri industrializirano. Okolica izvira Krupe predstavlja izjemen primer naravne in klturne dediščine v Sloveniji in je bila leta 1997 uvrščena med najpomembnejše naravne spomenike. Gre za najbolj izdaten izvir v Beli Krajini in predstavlja najpomembnejši potencialni vir pitne vode za to območje. Zaradi onesnaženosti s PCB vode iz reke, kakor tudi studencev in črpališč, ne uporabljajo

Zaradi visokih koncentracij PCB v reki Krupi in njeni okolici se je leta 1984 začel izvajati sanacijski program, ki je vključeval konstrukcijo odlagališča odpadkov, obsežno okoljsko in zdravstveno študijo ter vzpostavitev rednega monitoringa. V obdobju 1982 - 1992 so koncentracije PCB v okolju Krupe znašale v zraku od 1 do 10 mg/m^3, v vodi 100 do 1000 ng/l, v sedimentu 10 do 800 mg/kg, v jajcih (celokupen volumen) 1 do 10 mg/kg, v užitnih delih rib 1 do 200 mg/kg, v maščobi perutnine 1 do 20 mg/kg in v maščobnem tkivu ljudi 1 do 10 mg.

Zadnje raziskave onesnaženosti in izpostavljenosti okolice Krupe PCB ter usode le-teh v okolju so bile opravljene v letih 1995 do 1998 in sodijo v sanacijski program, začet leta 1984. Določili smo koncentracije PCB v zraku, vodi, rečnem sedimentu in tleh v okolici reke Krupe. Koncentracije PCB v zraku, izmerjene v več desetdnevnih vzorčevanjih nad gladino Krupe, so znašale 20 - 60 ng/m^3, 25 - 90 ng/m^3, 1-30 ng/m^3, 20 - 285 ng/m^3in 55 - 140 ng/m^3. Koncentracije PCB v vodi so bile 65 - 205 ng/l, 15 - 75 ng/l in 40 - 220 ng/l, v rečnem sedimentu 23 - 185 mg/kg in v tleh 0,5 - 38,5 mg/kg. Eksperimentalne podatke in dolgoročni trend njihovega spreminjanja dobro opišemo s preprostim dvofaznim fugativnostnim modelom porazdelitve. Celokupen snovni tok PCB na meji voda/zrak znaša 0,3 ng/m^3s. Na osnovi meritev koncentracij in analize njihovega spreminjanja s časom tekom desetletne sanacije smo izdelali kvantitativno oceno emisije PCB iz podzemlja v območje izvira Krupe. Primerjava koncentracij PCB v vodi, izmerjenih v letih 1986-1988 in 1995-1998 kaže trend upadanja (s 380 ng/l na 100 ng/l). Emisijski snovni tok iz vode v zrak vzdolž 2,6 km toka Krupe znaša 200 do 500 g/leto, kar je približno desetkrat manj kot pred začetkom sanacije.