

PCB AMOUNTS AND ENVIRONMENTAL CONTAMINATION IN CENTRAL AND EASTERN EUROPE

Holoubek Ivan, Klanova Jana
RECETOX, Masaryk University, Brno, Czech Republic
National POPs Centre CR
Central and Eastern European Regional POPs Centre
Kamenice 126/6, 625 00 Brno, Czech Republic; holoubek@recetox.muni.cz; <http://recetox.muni.cz>

Abstract

The problems of polychlorinated biphenyls in the region of the Central and Eastern Europe is presented and the results of national PCBs inventories and the regional environmental trends of PCBs are mentioned. PCBs were produced in region and very broadly applied. In many countries are still used in transformers and capacitors. Environmental levels are also very high in some cases. Based on the Stockholm Convention measures, CEE countries realized the actual inventory of PCBs in equipments, wastes and also the inventory of contaminated sites.

Sources and production of PCBs in CEE countries

The global production of PCBs has been estimated to be in the order of 1.7 million tones.¹ The summary of available POPs including PCBs information was presented by RECETOX in 2000.² PCBs were also produced as Delor (Delotherm, Hydeler) by Chemko Strážské in the former Czechoslovakia, in eastern Slovakia (Michalovce District) from 1959 to 1984. The production of Delor 106 was started in 1959 for use in a paint factory. In 1967 and 1968, the production of Delors 103 and 105 was initiated for use in transformers and capacitors. Delor 103 was used as a dielectric fluid in capacitors and Delor 105 was used in transformers manufactured in the Czech Republic. It has been estimated that Chemko produced 21,500 metric tons of PCBs. About 46% of the PCBs were exported to the former East Germany³ whereas the rest was used in the territory of former Czechoslovakia.

PCB formulations may be currently used only in the closed systems and they are gradually replaced. Currently, waste landfills is considered to be the most relevant source of environmental pollution by PCBs in these countries. Estimated contribution of applied paint to total PCB pollution within Slovakia is about 5 % and that of industrial and municipal waste incinerators is 9 %.

It was recently rather unknown that Poland had its two own technical PCB formulations - Chlorofen, which is similar in appearance and composition to Aroclor 1262, and Tarnol, which is similar to Aroclor 1254.³ Tarnol, which was also called Chlorowany bifenyl, was a low chlorinated technical PCB formulation manufactured between the years 1971 and 1976 by the company Zakłady Azotowe in Moscie near the city of Tarnow in southern-east Poland.^{4,5} The mixture is in its physical appearance and properties similar to well known foreign technical PCB mixtures such as Aroclor 1248, Clophen A 40, Phenoclor DP-4, Fenchlor 42 or Kanechlor 400. Tarnol was a product of the "anti import philosophy", which was on the agenda of the government in the 1970s. The total quantity of manufactured Tarnol was in 679 tonnes. Chlorofen was a highly chlorinated (63.6% Cl) PCBs formulation manufactured in the town of Ząbkowice Śląskie in southern Poland. The mixture was a light to dark-brown sticky and viscous resin mainly composed of PCB congeners with 5 to 9 chlorine atoms that comprised 99.55% of total PCBs.

Industrialised countries such as USA and Western European countries have some legislative measures for controlling the flux of PCBs in the environment. One important aspect is control of PCBs sources such as transformers, capacitors, electric motors etc. The materials containing more than 50 µg.g⁻¹ are subject to some regulations. These regulations are adopted in CEE countries. Since 1993, in Poland the waste oils containing PCBs were included on the list of hazardous substances, but to the present days the flux of these pollutants was not a subject of any regulation.⁶ Recently available data⁷ have indicated that in national power plant installations about 1 400 tons of transformers and capacitors oils are used. However, unknown is even estimated

amount of the waste industrial oils (transformers, capacitors, motors etc.) occurred in the trade. An assessed percentage of PCB contaminated equipment is following: transformers (0.38 %), capacitors (35 - 50 %), other electromagnetic equipment (25 - 50 %). An assessed amount of PCB contaminated oil/capacitors/other electromagnetic equipment is up to 10 000 tonnes⁵. Determination the levels of PCBs in the random samples of waste motor and transformer oils collected from different regions of Poland showed that these concentrations in the most of samples did not exceed the limit value of 50 µg.g⁻¹.⁶

There has been no PCBs production in the other countries of the region. PCBs can still be found in many closed systems, dumps and environmental matrixes in all the countries in the region. For example, in Croatia in 1997, more than 2 000 tonnes of PCBs oils from various countries were imported.⁸ Part of PCBs amounts from various countries of the region was exported to the France for destruction. Part of PCBs amount used in the region, was liquidated legally, and part probably illegally during the period of main economic changes in these countries in the early 1990s. Unknown part of total used amount of PCBs is still in the various environmental compartments.

The use of PCBs in Slovenia increased after 1960, when an ISKRA condenser factory was built in Semic, Bela Krajina (about 80 km south-east from Capitol Ljubljana).⁹ 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 3 700 tons with a PCBs waste rate of 8 - 9 % in the form of waste impregnates, condensers, etc. By 1974, 130 tons of waste containing around 70 tons of pure PCBs were dumped at various waste sites within five km round the factory. After 1975 waste impregnates were collected and sent to France for treatment (170 t), whereas smaller waste condensers were still disposed of at local waste site. Measurements in 1982 showed very high concentration of PCBs in the environmental compartments (air, water and sediments), as well as in food and in animal and human tissues.¹⁰

Actual PCBs inventory in the CEE region

The recent inventory of PCBs in Slovakia¹¹ gave the following actual PCBs equation in this country: PCBs (Wastes from production - 1 606 t) + PCBs (Products - 4 071 t) = PCBs (Still used - 960 t) + PCBs (Liquidated - 368 t) + PCBs (Disposed - 1 605 t) + PCBs (Rest - 2 744 t)

In Croatia, there are 405 users of 22 532 PCBs capacitors and 293 users of PCBs transformers (Sinovcevic, 1998). The most important source of PCB information are the national POPs inventories and the National implementation plans which every country including the countries of CEE region developed and adopted from 2004 as a part of the implementation of the Stockholm Convention. The overview of PCB inventories in some selected countries of the CEE region are presented in Table 1.¹² The data are presented from the countries where the results were presented. From the rest of region te data are not available or under development.

Regional background PCBs levels and trends

Persistent organic pollutants have been monitored using the integrated monitoring approach in all environmental matrices in the Kosetice observatory since 1988. This facility of the Czech Hydrometeorological Institute located in the southern part of the Czech Republic serves as a Central European background monitoring station for the purpose of various national and international (EMEP, GAW) monitoring programmes.^{13,14} Long-term trends in the levels of persistent organic pollutants in the ambient air and wet deposition were assessed.

Although the ambient air and wet deposition measurements have been carried on since 1988 in the Kosetice observatory, only POP data from the last ten years (1996-2005) were used for the evaluation of the long-term trends. The main reason is a comparability of the results; the same sampling frequency as well as the same sampling and analytical techniques were employed during this period.

The annual medians of PCBs also indicate a general decreasing trend interrupted with two periods of higher concentrations (Fig. 1): 1997-1998 and 2000-2001. There are significantly elevated summer maxima of PCB concentrations in 1997 and 1998 (maxima 390 pg m⁻³ and 337 pg m⁻³ for the sum of 7 PCB congeners in 1997

and 1998, respectively). In contrast, summer maxima between 2000 and 2001 were lower (167 pg m^{-3} and 246 pg m^{-3}) but due to the higher winter minima (52 pg m^{-3} - same as in 1998), the annual medians remained quite high. Interestingly, in the 2000-2001 periods there was also significant fraction of particle associated PCBs (Fig. 4).

Table 1: The overview of PCB inventories in some selected countries of the CEE region

| Country | Number of transformer [pieces] | Content of oil with potential PCB contents [t] | Revealed levels of PCBs [$\mu\text{g.kg}^{-1}$] | Number of capacitors [pieces] | Potential content of PCB [t] |
|--|--------------------------------|--|---|-------------------------------|------------------------------|
| Armenia | 3 582 | 18 654.3 | 11.0 – 24.3 | | |
| Bulgaria | 41 | 1 642.1 | > 50 | 2 415 | 7.9 |
| | 158 | 327.2 | > 500 | | |
| Croatia | 3 045 | 728.7 | | 22 859 | 655.7 |
| Czech Republic | 125 (confirmed content) | 288.3 | | 24 403 | 180.3 |
| | 1 398 (potential content) | 2 302.6 | | 2 914 | 29.2 |
| Total number of equipments with confirm content of PCBs – 20 535 with 497.3 t of PCBs | | | | | |
| Total number of equipments with potential content of PCBs – 9 072 with 3 487.4 t of PCBs | | | | | |
| Latvia | 34 | 230 | | 4 282 | 30 |
| Montenegro | 77 | | 0.2 – 930 | | |
| Poland | 3 500 | 3 000 | | 7 620 | |
| Romania | 50 030 (out of use) | 510 358.1 | | | |
| | 94 237 (under use) | 1 911 820.1 | | | |
| Serbia | 46 | 34.7 | | 4 500 | 30 |
| Slovakia | 406 | 82 | | 30 426 | 170 |

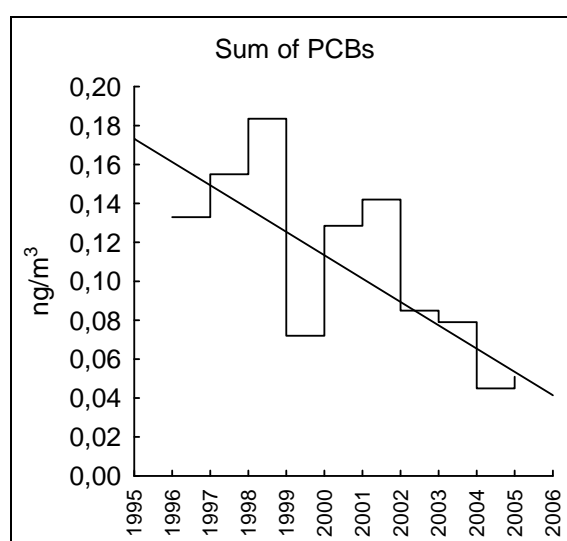
On the contrary, high summer maxima were observed in 2002 and 2003 (366 pg m^{-3} for the sum of 7 congeners) but due to the low winter levels, it was not reflected in the annual medians. These fluctuations in the annual medians of PCBs may reflect the major flood events in the Czech Republic in 1997 and 2002. A large area of central and southern Moravia (to the east from Kosetice) was flooded in 1997, including the industrial and agricultural facilities where various chemicals were stored. The floods were followed by extremely hot summer therefore those chemicals could evaporate from impacted areas and be a subject of the atmospheric transport. Similarly, the central part of Bohemia (to the west from Kosetice, Prague included) was flooded in 2002. Several large chemical enterprises located to the north of Prague were severely damaged and variety of chemicals escaped to the surface waters and was distributed with the flood. One of the effects of floods is a re-distribution of the old burdens from the river sediments to the surface layers of the soils that were flooded. Semi-volatile persistent organic compounds can easily re-evaporate from these top soil levels during the warm season. This is probably the source of elevated atmospheric concentration of chlorinated POPs in the years following these disasters.

Intensive research of POPs contamination was performed in the former Yugoslavia during the period of 2002-2005.^{15,16} Persistent organic pollutants (POPs) spilled into the environment as a result of damaged industrial and military targets, natural resources, and infrastructure during the Balkan wars still pose a problem several years later. The aim of the project APOPSBAL was to investigate an extent to which the residents of former Yugoslavia were/are exposed to elevated levels of POPs as a consequence of the wars. The atmospheric as well as the soil levels of PCBs, OCPs and PAHs were determined in Croatia, Serbia, Bosnia and Herzegovina during five high volume air sampling campaigns in 2003 and 2004. A considerable contamination of several sites was detected (PCB concentrations in the atmosphere ranged between 67 pg m^{-3} and 40 ng m^{-3} for the sum of 7 indicator congeners) and the levels were reported.

Results of this project show highly uneven distribution of PCBs in the atmosphere of former Yugoslavian countries indicating the presence of strong point sources of pollution. While PCB levels in residential and background areas of the studied region are comparable with other countries in Europe (UNEP, 2002a), the sites

preliminary suggested for investigation as potentially contaminated with PCBs were confirmed to be a source of considerable air pollution. Additional sources of pollution were identified as well. This is not surprising considering that industrial facilities and power stations were the common targets of military operations during the wars. Since many of damaged transformers and capacitors were originally filled with PCB mixtures, their leakage into the soils and industrial grounds became the major source of PCB contamination in the region. Several facilities where the situation reached the point of ecological disaster were remediated several months after the war operations (Zastava factory in Kragujevac, Serbia where more than 3000 l of Pyralene was spilled) (APOPSBAL, 2005). It was confirmed that countries of former Yugoslavia affected by the wars still require attention and coordinated support to estimate the real status of the contamination and its environmental influence. Identification and survey of local sources, stocks, and reservoirs of PCBs should be the first priority and a substantial part of any monitoring program. Seasonally and spatially resolved monitoring information is also needed to assess the fate and the transport of chemicals and to suggest appropriate solutions.^{15,16}

Figure 1: Time related trends of POPs in Air, (PUF + QUARTZ); the line represents estimated trend



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References

- Holoubek I. et al: Regionally Based Assessment of Persistent Toxic Substance - European Regional Report. UNEP Chemicals. Number of project: GF/CP/4030-00-20, Number of subproject: GF/XG/4030-00-86, November 2002, 147 p.
- Holoubek I, Kočan A, Holoubková I, Hilscherová K, Kohoutek J, Falandysz J, Roots O. Persistent, Bioaccumulative and Toxic Chemicals in the Central and Eastern European Countries - State-of-the-Art Report. The 2nd version. TOCOEN REPORT No. 150a, květen 2000. RECETOX - TOCOEN & Associates, Brno, Czech Republic. Internet: <http://recetox.chemi.muni.cz/>.
- Kocan, A., Petrik, J., Drobna, B., Chovancova, J. *Chemosphere* 1994; 29:2315.
- Falandysz J., Yamashita N., Tanabe S., Tatsukawa R. Composition of PCB isomers and congeners in technical Chlorofen formulation produced in Poland, 305-312, W Environmental Analytical Chemistry of PCBs. J. Albaiges (red.). Current topics in environmental and toxicological chemistry, Gordon and Breach Science Publishers, 1993, Singapore.
- Falandysz J. *Organohal. Compds.* 2000.
- Lulek J, *Organohal. Compds.*, 1996; 28:267.
- Gurgacz W. Waste oils and dioxins. 1st Symposium Dioxin-Human-Environment, Krakow, Poland, 14-26, 1994
- Sinovec R. POPs management in the Republic of Croatia. In: UNEP/IFCS, 213-230, 1998.
- Polic S, Kontic B. Report on PCBs remediation in Bela Krajina. World Conference on Hazardous Waste, Budapest, Hungary, 925-929, 1987.
- Polic S, Leskovsek H. *Organohal. Compds.* 1996; 28:35.
- Kocan A, Petrik J, Chovancova J, Jursa S, Drobna B. *Organohal. Compds.* 1999; 43, 105-109.
- National implementation plans of the Stockholm Convention implementation in the mentioned countries

13. Holoubek I, Klánová J, Jarkovský J, Kohoutek J. *J. Environ. Monitoring*. Submitted.
14. Holoubek I, Klánová J, Jarkovský J, Kubík V, Helešic J. *J. Environ. Monitoring*. Submitted.
15. Klánová J, Kohoutek J, Kostrhounová R, Holoubek I. *Environ. Intern*. Submitted
16. Klánová J, Kohoutek J, Čupr P, Holoubek I. *Environ. Intern*. Submitted