

## CONFERENCE PAPER

**PERSISTENT,  
BIOACCUMULATIVE, AND  
TOXIC COMPOUNDS IN  
CENTRAL AND EASTERN  
EUROPE – HOT SPOTS****IVAN HOLOUBEK, ANTON KOČAN, IRENA  
HOLOUBKOVA, KLARA HILSCHEVA,  
JIRI KOHOUTEK, JERZY FALANDYSZ,  
AND OTT ROOTS***Recetox-Tocoen & Associates*

Received November 2000

The sources and environmental levels of the PBTs in the countries of Central and Eastern Europe are broadly described. Most of the countries in the region produce and/or formulate pesticides. The pesticide registration is a primary requirement for import, production and distribution. The special attention must be given to unwanted pesticides. The problem of unwanted and expired pesticides pose the greatest danger to the natural environment and people which is brought about by the use of chemicals in agriculture in CEE countries. Countries still have not solve the problem of safety storage for PBTs and other chemicals classified as poisons and they have no special sites or facilities for destruction of these chemicals. This region has very specific problems of environmental pollution, which are the results of the recent wars. Destruction of industrial facilities and spilling of chemicals have the worst effect for the environment (Bosnia and Herzegovina, Croatia, Serbia and Montenegro).

*Key words:*  
environmental pollution, organochlorine pesticides,  
PCBs, POPs, transboundary pollution

**O**rganic substances that are persistent, bioaccumulative, and possess toxic characteristics likely to cause adverse human health or environmental effects are called PBTs (persistent, bioaccumulative, and toxic substances). In this context, »substance« means a single chemical species, or a number of chemical species, which form a specific group by virtue of (a) having similar properties and being emitted together into the

environment or (b) forming a mixture normally marketed as a single product. Depending on their mobility in the environment, PBTs could be of local, regional or global concern (1).

A subclass of PBTs called POPs (persistent organic pollutants) is a group of compounds which are prone to long-range atmospheric transport and deposition (1, 2). The global extent of POP pollution became apparent with their detection in areas such as the Arctic, where they have never been used or produced, at levels posing risks to both wildlife (3) and humans (4).

The UN-ECE initiative, which started within the UN-ECE region (comprising Eastern and Western Europe, Canada, and the USA) in 1992, prepared the Protocol on POPs (2). The Protocol includes 16 POPs and its main objective is to control, reduce, or eliminate discharges, emissions, and losses of POPs. Beside the UN-ECE initiative, a similar programme of the United Nations Environment Programme (UNEP) started in the co-operation with the International Forum for Chemical Safety (IFCS) (5) which included 12 POPs.

The expert groups of both international bodies call for new data on exposure and fate assessment. Especially for data which are available for a particular region, as they should be used in the assessment process. International experts strongly recommend to study the fate and distribution of selected chemicals in different regions using compartment mass balance models which must be verified by the real measured data. The most serious data gap for the prediction of environmental behaviour are degradation rates and their regional variability based on specific transport conditions. More data need to be collected in this area. The main topic of further research are the deposition/emission processes, transformation processes, and bioavailability of POPs and PBTs in terrestrial ecosystems (1).

## PBT COMPOUNDS

The sources and environmental levels of PBTs in the countries of Central and Eastern Europe have broadly been described by *Holoubek and co-workers* (6). The first complex description of the state of environmental pollution with PBT types of compounds in Central and Eastern European countries (CEECs) was prepared by *Heinisch and co-workers* (7). Heinisch and his co-workers continued that investigation and published many other reports such as the three-volume comparison study of the situation in Germany, mainly in Bavaria, and the new countries including the Czech Republic (8–10).

This region has very specific problems of environmental pollution, which are the results of the recent wars. The destruction of industrial facilities and spilling of chemicals have had the worst effect for the environment in Bosnia and Herzegovina, Croatia, Serbia, and Montenegro. Furthermore, the bizarre usage of transformer oil as a diesel fuel and anti-lice shampoo containing lindane against pests in gardens seems to have been inevitable (11). Beside the above mentioned sources of contamination in Bosnia and Herzegovina, a specific problem was the so-called pharmaceutical waste. During the war, huge amounts of drugs were received by those countries as humani-

tarian aid. Part of those drugs had already expired when they arrived, while others were not used for various reasons. The total waste drugs according to the WHO estimation are 800 t. The major part is still not adequately treated in Bosnia and Herzegovina. Disposal such as through incineration and legal and illegal dumps can be the source of environmental contamination, including the one by PBT compounds.

Most countries in the region produce and/or formulate pesticides. Pesticide registration is a primary requirement for import, production, and distribution. During the period of centralised economy in this region, the import was monopolised by relevant state bodies. By the end of the 80s, many private companies and minor distributors were involved in import and distribution of pesticides.

Special attention must be given to unwanted pesticides. Unwanted and expired pesticides pose the greatest danger to the environment and people. Many countries still have not solved the problem of safe storage for pesticides and other chemicals classified as poisons and they have no information concerning the quantity of pesticide and chemical (e.g. PCBs) waste. Many CEE countries have no special sites for dangerous materials or incinerators in which these types of chemicals could be safely burnt.

The potential risk is linked with storage of unused PBT pesticides. In this respect, Poland has evidenced the storage over 10,000 t of unused pesticides (mixture of different pesticides including different PBT compounds). The situation is probably very similar in many other CEE countries. These were identified as possible hot spots in the region.

#### *Polycyclic aromatic hydrocarbons (PAHs)*

The main sources of polycyclic aromatic hydrocarbons (PAHs) in the region are thermal plants and district heating, waste incineration, road traffic and some industrial technologies (e. g. high-temperature coal carbonation, catalytic cracking of crude oil, and aluminium production).

A limited amount of non-carcinogenic PAHs (naphthalene, anthracene, phenanthrene, pyrene, and carbazole) is produced industrially in pure form (DEZA Valašské Meziříčí, Czech Republic). They usually serve as the material for synthesis of dyes, pesticides, and pharmaceuticals (12).

The major sources of PAHs in the Czech Republic (CR) are PAH production and their use as intermediates, production of carbon black, metallurgy, production and use of coke, asphalt, and coal tars, catalytic cracking, heat coal conversion processes, waste waters, landfills, combustion of wastes and fossil fuels, cement production in dry or wet process kilns, petroleum refineries, crematoria, forest fires, and smoking. The situation in other CEE countries is very similar. The annual emissions of PAHs in the former Czechoslovakia were estimated to about 215 t (13) or 378 t (14).

One of the major PAH sources in the Czech Republic are coal-fired stations burning mainly the lower quality brown coal. The coal used in the Czech Republic has in some cases low heat capacity, high content of water and ash, and the sulphur content that can be over 2% (brown coal from northwest Bohemia). The estimated average emission factor of ?SPAHs in Czech power plants (45  $\mu\text{g}/\text{kg}$  with the range 25–60  $\mu\text{g}/\text{kg}$ ) is practically identical with the value of 42  $\mu\text{g}/\text{kg}$  found in the UK (15). The annual emission of 1,381 kg (765–1,842 kg/year) represents approximately one third of the amount emitted in the UK.

Among different kinds of coal, sorted brown coal with the average heating capacity of 18 MJ/kg, is mostly used in heating of Czech residential buildings. Sorted black coal, coke, and brown or black coal briquettes are combusted less often. The estimated emission factor of S?PAHs of 2–50 mg/kg for residential heating with brown coal is comparable with the value of 56.4 mg/kg (15) and the range of 1.8–30 mg/kg reported in the UK (IEA, 1993) and with the range of 3–70 mg/kg found in the Netherlands (16).

The estimated emission of PAHs from residential heating is about 560 t/year. Assuming that the emission caused by residential heating accounts for about 80% of the annual PAH emissions, the estimation for the Czech Republic would be approximately 700 t/year. This value corresponds to the sum of individual major increments (annual emissions from coal-fired stations, residential heating, PAHs and carbon production, and coke production) which is approximately 735 t/year.

Hungary showed a decreasing trend in total annual PAH emissions from 137.1 kt in 1980 to 61.7 kt in 1996. The crucial point was the shutting down of coke production in 1993 (17).

#### *Organochlorine pesticides (OCPs)*

Most countries in the region produce and/or formulate pesticides (18, 19). Many countries lack the required experience, and a large part of the farming population has insufficient education and training in protection of plants (20).

Pesticide concentrations in the Danube and its tributaries show significant differences between the Danube basin countries in the number and types of detected pesticides (18). The cumulative number of analysed pesticides was 76, but the residues were found of only 36 pesticides. The most frequently detected are organochlorine compounds and triazines. DDT and metabolites, HCH and isomers, and atrazine and metabolites were found in more than 50% of all samples.

Special attention must be given to unwanted pesticides. Unwanted and expired pesticides pose the greatest danger to the natural environment and people. The amount of unwanted pesticides in Poland is estimated to 60,000 t – about 10,000 t in tombs, another 25,000 t in storehouses, and about 25,000 t at private farms (21). The inventory of banned organochlorine pesticides in stocks in Bulgaria in 1996 showed about 35 t, which is a relatively high quantity for the small territory such as Bulgaria (20).

The potential risk is linked with the storage of unused PBT pesticides. In this respect, Poland has evidenced the storage of more than 10,000 t of unused pesticides (a mixture of different pesticides including other PBT compounds). The situation is probably very similar in many other CEE countries (22). These were identified as possible hot spots in the region.

In some countries of the region (such as Bulgaria) it was recognised that concentrations of PBT pesticides decreased in environment to such levels that no further systematic monitoring is needed (20). That is not true for Albania (23) or Romania (18, 19, 24) where relatively high concentrations are still measured in water and sediments (DDT and other chlorinated pesticides). In the Slovak Republic, the measured data have shown high exposure to hexachlorobenzene (HCB) from an unknown source, which resulted critically high concentrations of that compound in human tissue (22, 25–27).

Many pesticides from the UN-ECE list of POPs have never been used in many countries from the region (aldrin, chlordane, mirex, heptachlor, and toxaphen). These were banned or restricted in several countries of the region, as well as in some other countries in the world. Hungary was among the first in the world to ban or severely restrict chlorinated pesticides, that is, as early as 1966 (22).

DDT is no longer used in many countries, including the CEE countries. It was banned in the Czech part of the former Czechoslovakia in 1974 and in the Slovak part in 1976. However, it is still used in some African, Asian, and South American states as a cheap and efficient insecticide. Some countries in the region have inventories of use and import of pesticides. For example, in 1997 Croatia imported more than 503 t of pesticides containing PBTs as active substances (22). Estonia was one of the first countries in the Baltics to ban chlorinated pesticides (in 1968) (28). In 1957, 226 tons of pesticides, mainly DDT and lindane were used in Estonia. As pests do not reproduce in cold climates as much as in warm climates, the usage of pesticides in Estonia did not exceed 0.7–1.0 kg per ha in mid 60s (among them, 0.03–0.06 kg per ha were chlorinated pesticides).

The distribution of DDT, DDE, DDD, DDMU, HCH isomers as well as the PCB congeners in aquatic and terrestrial ecosystems suggest input (i.e. the perpetrator) as well as date of the process. *Heinisch and Kettrup* (29) demonstrated it on the distribution pattern of DDT metabolites after their massive application in forests of the German Democratic Republic (GDR) in 1983/4 and compared it with earlier applications and with the distribution pattern of HCH isomers in the surroundings of factories or as consequences of lindane applications.

The situation in the former GDR is not discussed in this report, but that application influenced the contamination levels in the former Czechoslovakia and the described approaches serve as a very useful tool to interpret the history and the state of contamination. The comparison of the levels of contamination was published in the Report of IOC GSF, Neuherberg, Germany (8–10).

More than 20 years after the severe restrictions of DDT worldwide, increased contamination levels can still be found in different matrices. A simple substance distribution pattern of the DDT parent substance and metabolites is able to suggest the source. We will describe two examples.

In 1983/4, 260,000 ha of forests of the former GDR were treated with high amounts of DDT/lindane preparations using aircrafts to combat the black-arched moth (*Lymanthria monacha*). Before that, in 1975, a gradual ban of DDT was passed, which mainly worked well. The levels of  $\Sigma$ DDTs and the percentage of the parent substance DDT usually decreased after their banning. The decrease in the former GDR from 1976 to 1982 had one simple reason – until 1992 no new DDT was imported into the region.

In 1984 and 1985 not only the  $\Sigma$ DDTs concentrations increased in many observed matrices and commodities, but also the percentage of the parent substance DDT. This suggested a new DDT input in the region from 1983. The impact was detectable not only in the region where it was used, but also throughout the former GDR and former Czechoslovakia, and now 15 years later in the Czech Republic.

For example the DDT levels in the herring matrix from waters around the Isle of Rügen were elevated and in 1986, the observed value of DDT in herrings reached the maximum as a result of transport up to the Baltic Sea with a time-lag effect. After a

sharp decrease in  $\Sigma$ DDT contamination values and in the percentage of the parent substance DDT between 1971 and 1985, there was a sharp increase in 1986, especially in the percentage of the parent substance DDT.

In the south-east GDR – the district of Chemnitz (the former Karl-Marx-Stadt) received about 10% of DDT/lindane preparations used for combating *Lymanthria monacha* in 1982–1985 – there was apparently a drift leading to »co-treatments« of the North-Bavarian border areas. In 1983 and 1984, the used amounts of DDTs were 120 and 480 t, respectively. Using the analysis of kidney fat of deer and red deer in 1985, Hecht found clear gradual loads of  $\Sigma$ DDTs from the north to the south in 1996 (7).

Other border-crossing co-treatments have been registered in the former Czechoslovakia. Table 1 describes higher levels  $\Sigma$ DDT residues with high percentages of DDT in soil samples from the boundary mountain Krušné hory (Erzgebirge Moun-

Table 1  $\Sigma$ DDTs and percentages of the parent substance DDT in soil samples from the Czech Republic (ng/g). Sampling took place in 1995 (6, 44)

Sampling site	DDT	DDE	DDD	$\Sigma$ DDTs	% DDT in $\Sigma$ DDTs*	References
Mumlava, Krkonoše, 1 190 m	33	8	n/a	41	80	(44)
Pudlava, Krkonoše, 1 140 m	179	70	n/a	249	72	
Pašerácký chodníček, 1 310 m	99	36	n/a	135	73	
Jedlová, Lužické hory, 710 m	302	84	n/a	386	78	
Lesná, Krušné hory, 800 m	2,390	795	n/a	3,185	75	
Načetín, Krušné hory, 710 m	4,013	1,164	n/a	5,177	78	
Ústí nad Labem (M)	1,133	1	1	1,135	100	(6)
Teplice (M)	1,207	146	256	1,609	75 (89)	
Karlovy Vary	398	122	36	556	72 (77)	
Sokolov (M)	522	209	40	771	68 (71)	
Cheb (M)	264	167	25	456	58 (61)	
Kladno (M)	63	53	7	123	51 (54)	
Praha (M)	1,044	1,054	1	2,099	49 (50)	
Mníšek pod Brdy (M)	651	245	4	900	72 (73)	
Příbram (M)	28	31	1	60	47 (47)	
Boubín, Šumava, 1995	11	7	n/a	18	61	(44)
Český Krumlov, M, 1995	1	1	1	3	33 (50)	(6)
Prachatice, M, 1995	1	1	1	3	33 (50)	
Košetice, 1995	0.2	9	0.2	1.3	15	

(M) – maximal value from 5–60 samples

\* number without parantheses – original number of *Heinisch and Kettrup* (8);

in parantheses –  $\Sigma$ DDTs=DDT+DDE, same values for all samples from various authors (6, 8, 44)

tains), Krkonoše Mountains, Lužické hory and in the north-east Bohemian cities of Ústí nad Labem, Teplice, and Karlovy Vary. These levels decreased from the former GDR towards the inner parts of the Czech Republic (Prague, Kladno, Příbram, South Bohemia, and the south border Šumava Mountains). The trend is evident in the levels of  $\Sigma$ DDTs, and mainly the percentages of the parent substance markedly decrease, which means the SDDT residues were of older origin. Especially low were the  $\Sigma$ DDT

residues and the percentage of the parent substance in the south of the Czech Republic, in Šumava Mountains, in the towns of Český Krumlov, Prachatice, and in the area of TOCOEN/CHMI regional background observatory Košetice.

The total amount of the technical DDTs used in Poland from 1974 to 1980 was 48,152 t and the annual rate was up to 3,881 t. HCB was imported and used in Poland as fungicide and the application rates were relatively small (the total import was 187.6 t between 1962 and 1972) (29).

The soil contamination by hexachlorocyclohexane and consequently the HCH cumulation in agricultural products were of great interest due to their long persistence in our ecosystem (30). In the Slovak Republic, hexachlorocyclohexane was synthesised in the former CHZJD factory in Bratislava. During the years 1956–1966 the factory produced more than 13,000 t of g-HCH. Some additional raw HCH was imported from the former Yugoslavia. After isolation of the gamma isomer, it was formulated into different pesticides in same factory. The produced pesticides were partly intended for domestic use. A very rough estimate of the annual consumption of lindane-containing pesticides in the Slovak Republic was about 1 t/year. That amount gradually decreased. Lindane-based formulations also dropped. For instance, the List of Permitted Pesticides for 1972 quoted 11 pesticides on the basis of lindane. Those were insecticides for the most important crops (potatoes, beet roots, rapeseeds, and hops), staining agents for treating seeds of cereals, maize, legumes, sugar beet, cucumber, cotton, hemp, rapeseed, water melon, soil desinsectants for growing beet roots, sugar beet, cereals, maize, tobacco, hops, young fruit, trees and vines, and fumigant.

The application of all these pesticides was possible only with some restrictive precautions. The wide and systematic utilisation of lindane containing insecticides was banned in 1974. The year 1992 was the last to see permitted use of lindane seed treating agents, such as formulations Lindane WP 80 for rapeseed and Lindane 50/35 WP for flax and hemp seeds. The List of Permitted Pesticides for 1993 included a new lindane-containing pesticide Emdenit, intended for controlling pine insects, but only for two years.

HCB had been used worldwide as a fungicide for agricultural purposes since 1915. That compound was also registered in Poland and sold as a fungicide under the trade name »Sniciotox«. Around 1980 HCB became unpopular and finally was withdrawn from agriculture in Poland (31).

Pentachlorobenzene (PeCBz) is a substrate used for the synthesis of the fungicide pentachloronitrobenzene (PeCNBz) and, apart from this application, it has not found any other special application. Pentachlorobenzene, like HCB, is a technical impurity in some chemical formulations (up to 0.06% in technical formulation of HCB, and was also found in technical formulation of PCNBz). Another source of environmental pollution with HCB and PCBz are high temperature processes such as municipal solid waste incineration. All theoretically possible congeners of chlorobenzene were identified in flue gas and fly ash from the municipal solid waste incinerators, and the contribution of PCBz and HCB was up to 50% and 13%, respectively. Hexachlorobenzene is highly persistent under environmental conditions. Nevertheless, depending on the environmental matrix, HCB slowly undergoes abiotic (photochemical) and biotic degradation (it is mainly metabolised by bacteria and lower fungi in soil and sediments as well as by man and animals). Pentachlorobenzene is an intermediate product of metabolism of HCB and lindane (g-HCH).

### Polychlorinated biphenyls (PCBs)

In the former Czechoslovakia, PCBs were manufactured in a chemical plant in eastern Slovakia under the commercial name Delor from 1959 to 1984. From the total 21,482 t produced (and about 1,600 t of PCB wastes), 46% was exported and the rest was intended for the home market. In both the Czech Republic and Slovakia, PCB formulations may currently be used only in closed systems and they are being gradually replaced. Currently, waste landfills are considered to be the most relevant source of environmental pollution by PCBs in these countries. The estimated contribution of applied paint to total PCB pollution in Slovakia is about 5% and that of industrial and municipal waste incinerators 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 (32).

Tarnol, also called Chlorowany bifenyl, was a low chlorinated technical PCB formulation manufactured between 1971 and 1976 by the company Zakłady Azotowe in Moszce near the city of Tarnów in south-east Poland (31, 33). The mixture is similar in its physical appearance and properties to the well-known foreign technical PCB mixtures such as Aroclor 1248, Clophen A 40, Phenoclor DP-4, Fenchlor 42, or Kanechlor 400. Tarnol was the product of the »anti-import philosophy«, which was of the government agendas in the 1970s. The total quantity of manufactured Tarnol is 679 t. Tarnol was a colourless clear liquid of density 1.45–1.47 g/ml at 20 °C. The chlorobiphenyl isomer and congener composition of Tarnol are unknown in detail. According to the manufacturer, this mixture was composed mainly of trichlorobiphenyls with di-, tetra- and pentachlorobiphenyls as minor constituents. Nevertheless, the composition of Tarnol was not confirmed using the capillary gas chromatography and low/high resolution mass spectrometry (HRGC-LR/HRMS) for analysis. No official data on the use of the Tarnol were released – it seems that it was used exclusively as dielectric fluid mainly for transformers, but its use as a dielectric in capacitors is also likely.

Chlorofen was a highly chlorinated (63.6% Cl) PCBs formulation manufactured in the town of Zabkowice Śląskie in the south of Poland. The mixture was a light to dark-brown sticky and viscous resin mainly composed of PCB congeners with 5–9 chlorine atoms that comprised 99.55% of total PCBs. The average number of Cl per biphenyl molecule in Chlorofen is 7.3 and the average molecular weight is 405.4. Chlorofen contains at least 59 PCB congeners with the major components such as PCBs nos. 153 of hexa-, 176, 180 and 187 of hepta-, 194, 195, 198, 201/196 of octa-, and 206 of nonachlorobiphenyls.

Industrialised countries such as the USA and Western European countries have some legislative measures to control the flux of PCBs in the environment. One important aspect is control of PCB sources such as transformers, capacitors, and electric motors. The materials containing more than 50 µg/g are subject to regulations. These regulations have been adopted by the CEE countries. In Poland, the waste oils containing PCBs have been included on the list of hazardous substances since 1993, but the flux of these pollutants has not been the subject of any regulation to the present day (34). Recent data (35) indicate that the national power plants use about 1,400 t of transformer and capacitor oils. However, the amount of the waste industrial oils (transformers, capacitors, motors etc.) cannot even be estimated. An assessed per-



centage of PCB-contaminated equipment is: transformers (0.38%), capacitors (35–50%), and other electromagnetic equipment (25–50%). An assessed amount of PCB contaminated oil/capacitors/other electromagnetic equipment is up to 10,000 t (31). The determination of PCB levels in random samples of waste motor and transformer oil collected from different regions in Poland showed that these concentrations did not exceed the limit value of 50  $\mu\text{g/g}$  in most samples (34).

Although other countries of the region did not produce PCBs, they can still be found in many closed systems, dumps, and environmental matrixes. For example, Croatia imported more than 2,000 t of PCB oils from various countries in 1997 (36).

A part of PCB amounts from various countries of the region was exported to France for destruction. Part of the PCB amount was destroyed legally and a part probably illegally during the period of main economic changes in the early 1990s. Unknown amounts of PCBs are still in various environmental compartments. The recent inventory of PCBs in Slovakia (37) gave the following actual PCB equation for this country:

PCBs (wastes from production – 1,606 t)+PCBs (products – 4,071 t)=PCBs (still used – 960 t)+PCBs (eliminated – 368 t) + PCBs (disposed – 1,605 t) + PCBs (rest – 2,744 t).

In Croatia, there are 405 users of 22,532 PCB capacitors and 293 users of PCB transformers (36).

The use of PCBs in Slovenia increased after 1960, when ISKRA condenser factory was built in Semič, Bela Krajina (about 80 km south-east from the capital Ljubljana) (38). PCBs were introduced into the production process in 1962 (until 1970 Clophen A-50 and A-30 supplied by Bayer, the former Federal Republic of Germany, and between 1970 and 1985 Pyralen 1500 supplied by Prodelec, France). The consumption of PCBs by ISKRA in 1962–1985 totalled about 3,700 t with a PCB waste rate of 8–9% in the form of waste impregnates, condensers, and so on. By 1974, 130 t of waste containing about 70 t of pure PCBs were dumped on various waste sites within five km from 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 sites. Measurements in 1982 showed very high concentrations of PCBs in environment (air, water, sediments) as well as in food and in animal and human tissues (39).

#### *Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs)*

The main sources in the region of PCDDs/Fs, mainly by-products of chemical industry, are typical for industrialised countries: production of chlorophenols and their derivatives (former Czechoslovakia, USSR, GDR, Poland, probably Romania), processes using chlorinated catalysts and solvents used such as pulp and paper production, bleaching based on chlorine treatment, metallurgy, where metal chlorides are used, magnesium production, metal scrap recycling, municipal, hospital, hazardous, and industrial waste incineration; solid fossil fuel combustion (coal, wood, peat), internal-combustion engine operation, leaded petrol use with the addition of chlorinated compounds; dry distillation (dry cleaning), and fires (forest, agriculture).

Despite the two decades of worldwide interest and intensive studies of PCDDs/Fs, there are practically no data available on these compounds in environmental

matrices in the CEE countries. Limited information exist in the Czech Republic, Slovakia, Poland, Slovenia, whereas other countries lack information altogether (40).

The knowledge of sources of environmental pollution and emission rates of PCDDs/Fs in Poland is also described as extremely limited (41). In the past, some technical products potentially contaminated with dioxins were used. For example, a popular wood preservative of the Xylamit series contained technical pentachlorophenol (similar products were also seen in the former Czechoslovakia), and Masc grzybobójcza (fungicidal ointment) contained waste products of the distillation of technical chlorophenols and was used for technical purposes. Technical pentachlorophenol (e.g. Antox), and herbicides such as 2,4-D; 2,4-DP; MCPA, MCPP, and Dicamba were also used in the past in Poland. Some efforts have been undertaken to elucidate the status of PCDDs/Fs in some of those formulations. However, detailed composition and concentrations of contaminating dioxin residues remain unknown.

#### *Polychlorinated naphthalenes (PCNs)*

Virtually nothing is known about the type and quantity of PCNs potentially manufactured in the CEE countries. From PCB formulations produced in the former Czechoslovakia and USSR, we can roughly assess a 0.0067% content of PCNs in the PCB mixtures. In the case of the former Czechoslovakia, we can guess the potential release into the environment of about 1.6 t of PCNs during between 1959 and 1984, and secondary inputs a year after the ban (from disposals, combustion, incinerators, contaminated soils, and sediments).

1-chloronaphthalene was utilised in Xylamits, a popular wood (and other purpose) preservative widely applied in the past in Poland and also containing technical pentachlorophenol together with waste products of chlorophenol distillation and other substances (42).

2-chloronaphthalene was produced and used as a solvent in Poland (43). It is possible that in the chemical plant in Tarnów-Moscice in southern Poland (the manufacturer of the technical PCB formulation Tarnol) some higher chlorinated naphthalenes were produced on a small scale in the past (1930–1950?).

**Acknowledgement** This paper was produced as part of the following projects: TOCOEN (Toxic Organic COMpounds in the ENvironment), BETWEEN (The relationships BETWEEN environmental levels of pollutants and their biological effects), and research projects which are funded by the Ministry of Education, Czech Republic ENVIRONMENT – CARCINOGENESIS – ONCOLOGY (CEZJ071400003).

## REFERENCES

1. Walack HW, Bakker DJ, Brandt I, Brostrom-Lundén E, Brouwer A, Bull KR, et al. Controlling persistent organic pollutants – what next? *Environ Toxicol Pharmacol* 1998;6:143–75.
2. UN-ECE. Draft Protocol to the Convention on Long-range Air Pollution on Persistent Organic Pollutants (EB.AIR/1998/2), The Convention on Long-range Transboundary Air Pollution. United Nations Economic and Social Council, Economic Commission for Europe, 1998.

3. Barrie LA, Gregor D, Hargrave B, Lake R, Muir D, Shearer R, et al. Arctic contaminants: sources, occurrence and pathways. *Sci Total Environ* 1992;122: 1–74.
4. Mulvad G, Pederson HS, Hansen JC, Dewaily E, Jul E, Pedersen MB, et al. Exposure of Greenlandic Inuit to organochlorines and heavy metals through the marine food-chain: an international study. *Sci Total Environ* 1996;186:137–9.
5. UNEP Survey on sources of POPs [report]. IFCS expert meeting on POPs. 17–19 June 1996; Manila, Philippines. Geneva: UNEP; 1996.
6. Holoubek I, Kočan A, Holoubková I, Hilscherová K, Kohoutek J, Falandysz J, et al. Persistent, Bioaccumulative and Toxic Chemicals in the Central and Eastern European Countries – State-of-the-Art Report. The 2<sup>nd</sup> version. Brno: RECETOX - TOCOEN & Associates; 2000. TOCOEN report No. 150a.
7. Heinisch E, Kettrup A, Wenzel-Klein B, editors. Schadstoffatlas Osteuropa. Ökologisch-chemische und okotoxikologische Fallstudien über organische Spurenstoffe und Schwermetalle in Ost-Mitteleuropa. Ecomed, Landsberg/Lech; 1994.
8. Heinisch E, Kettrup A, Holoubek I, Matousek J, Podlesakova E, Hecht H, et al. Persistente organische Verbindungen in Nahrungsketten 7 von Bayern und Tschechien. Teil 1: Terrestrische Systeme. GSF-Berichte 10/97. Munich: 1997.
9. Heinisch E, Kettrup A, Holoubek I, Langstädtler M, Podlesakova E, Svobodova Z, et al. Persistente organische Verbindungen in Nahrungsketten 7 von Bayern und Tschechien. Teil 2. Aquatische Systeme. GSF-Berichte 11/97. Munich: 1997.
10. Heinisch E, Kettrup A, Holoubek I, Wenzel S. Persistente organische Verbindungen in Nahrungsketten 7 von Bayern und Tschechien. Teil 3: Persistente organische Verbindungen in Unteren Teil der Troposphäre in Bayern und Tschechien – Zusammenhänge von Emission und Kontamination. GSF-Berichte 12/97. Munich: 1997.
11. Knezevic A, Sober M. Treatment of medical waste in Bosnia and Herzegovina. In: UNEP/IFCS; 1998: 175–86.
12. Holoubek I, Čáslavský J, Nondek L, Kočan A, Pokorný B, Leníček J, et al. The compilation of emission factors of persistent organic pollutants in Czech and Slovak Republics. Brno: Canada and Masaryk University; 1993. Report of AXYS Ltd.
13. Warmenhoven JP, Duiser JA, de Leu LT, Veldt C. The contribution of the input from the atmosphere to the contamination of the North Sea and the Dutch Wadden Sea. 1989.TNO Report No. R 89/394A,
14. Holoubek I, Čáslavský J, Korínek P, Kohoutek J, Štaffová K, Hrdlička A, et al. Project TOCOEN. Fate of selected organic pollutants in the environment. Part XXVII. Main sources, emission factors and input of PAHs in Czech Republic. *Polycyclic Aromatic Compounds* 1996;9:151–7.
15. Wild SR, Jones KC. Polynuclear aromatic hydrocarbons in the UK environment: A preliminary source inventory and budget. *Environ Pollut* 1995;88:91–105.
16. Duiser JA, Veldt C. Emissions into the atmosphere of polyaromatic hydrocarbons, polychlorinated biphenyls, lindane and hexachlorobenzene in Europe. TNO Environmental and Energy Research. 1989. January 1989 TNO Report No. 89-036.
17. Kovacs G. Monitoring and releases of POPs in Hungary. In: UNEP/IFCS; 1998: p. 234–46.
18. Environmental Programme for the Danube River Basin: Danube Regional Pesticide Study. Final Report. CITY OF PUBLICATION: PUBLISHER; 1997. April 1997 PHARE report No. ZZ911/0106.
19. Bratanová Z, Kovačičová J, Gopina G. A review of existing data on the occurrence of pesticides in water of the River Danube and its tributaries. *Fresenius Envir Bull* 1998;7:495–501.
20. Tasheva M. Persistent organic pesticides in Bulgaria. In: UNEP/IFCS; 1998: p. 279–82.
21. Stobiecki S. The problem of unwanted pesticides in Poland. In: UNEP/IFCS; 1998: p. 283–4.
22. UNEP GEF PDF-B. Regionally based assessment of persistent toxic substances [draft report]. 1<sup>st</sup> Scientific and Technical Evaluation Workshop on Persistent Manufactured Chemicals Produced for Non-agricultural Applications, Persistent Toxic and Persistent Unintentional By-products of Industrial and Combustion Processes; 11–15 January 1999; Geneva, Switzerland.
23. Kosta K. The trend of POP pollution in the Albanian Adriatic Coast. Case study PCBs (1992–1996). In: UNEP/IFCS; 1998:101–6.

24. Toader C, Chitimiea S. The fate of some persistent organic pesticides in a particular Romanian aquatic ecosystem. In: UNEP/IFCS; 1998: p. 309-314.
25. Kocan A, Petrik J, Chovancova J, Drobna B, Uhrinova H, Holoubek I, et al. [The ambient air pollution by emissions of persistent organic pollutants in the Slovak Republic, in Slovak]. Bratislava: Slovak Hydrometeorological Institute; 1994. November 1994 report.
26. Kocan A, Ursinyova M, Reichertova E, Hladikova V, Petrik J, Chovancova J, et al. Occurrence of selected toxic and carcinogenic organic and inorganic compounds in ambient air in selected locations of the Slovak Republic. Bratislava: Institute of Preventive and Clinical Medicine. June 1996 report. Project no. PHARE EC/93/AIR/22.
27. Kocan A, Patterson DG, Petrik J, Chovancova J, Needham LL, Barr JR, et al. Polyhalogenated dibenzp-p-dioxins, dibenzofurans, biphenyls, and dioxin-like PCBs in the human population of the Slovak Republic: an analysis and health risk assessment. Bratislava: US-Slovak Science and Technology Program; 1998. Final report. Project No. 94023.
28. Roots O. Toxic chloroorganic compounds in the ecosystem of the Baltic Sea. Tallinn: Estonian Environment Information Centre; 1996.
29. Dabrowski J, Silowiecki A, Heinisch E, Wenzel-Klein S. Anwendung chloroorganischer Pestizide und hieraus entstehende ökologische-chemische und okotoxikologische Folgen. In: Heinisch E, Kettrup A, Wenzel-Klein S, editors. Schadstoffatlas Osteuropa. Ökologisch-chemische und okotoxikologische Fallstudien über organische Spurenstoffe und Schwermetalle in Ost-Mitteuropa. Ecomed, Landsberg/Lech. 1994. p. 19–24.
30. Schlosserova J. Evaluation of hexachlorocyclohexane residues in different localities of the Slovak Republic. In: International HCH and halogenated pesticides. Forum; 1993. p. 122-129.
31. Falandysz J. Manufacture, use, inventory and disposal of polychlorinated biphenyls (PCBs) in Poland. *Organohalogen Compounds* 2000;46:345–8.
32. Falandysz J. Polychlorinated naphthalenes: an environmental update. *Environ Pollut* 1998;101: 77–90.
33. Falandysz J, Yamashita N, Tanabe S, Tatsukawa R. Composition of PCB isomers and congeners in technical Chlorofen formulation produced in Poland. In: Albaigés J, editor. Environmental analytical chemistry of PCBs.. Current topics in environmental and toxicological chemistry. Vol. 16. Singapore: Gordon and Breach Science Publishers; 1993. p. 305–12.
34. Lulek J. Determination of polychlorinated biphenyls in waste motor and transformer oils. *Organohalogen Compounds* 1996;28: 267–70.
35. Gurgacz W. Waste oils and dioxins. 1st Szmpozium Dioxin/Human?Environment 1994; Kraków, Poland. 1994. p. 14–26.
36. Sinovčević R. POPs management in the Republic of Croatia. In: UNEP/IFCS; 1998: p. 213–30.
37. Kocan A, Petrik J, Drobna B, Chovancova J, Jursa S, Pavuk M, et al. The environmental and human load in the area contaminated with polychlorinated biphenyls. Bratislava: Ministry of the Environment; 1999.
38. Polič S, Leskovšek H. Fate and transport of polychlorinated biphenyls (PCBs) between water and atmosphere of the polluted Krupa River in Slovenia. *Organohalogen Compounds* 1996;28:35–8.
39. Polič S, Kontič B. Report on PCBs remediation in Bela Krajina. World Conference on Hazardous Waste; 1987; Budapest, Hungary. 1987 p. 925–9.
40. Fiedler H. Dioxin and furan inventories. National and regional emissions of PCDD/PCDF. UNEP Chemicals. Geneva, Switzerland 1999.
41. Falandysz J, Florek A, Strandberg L, Strandberg B, Berqvist PA, Rappe C. PCDDs and PCDFs in biota from the Southern part of the Baltic Sea. *Organohalogen Compounds* 1997;32:167–71.
- 42) Falandysz J, Strandberg L, Berqvist PA, Kulp SE, Strandberg B, Rappe C. Polychlorinated naphthalenes in sediment and biota from the Gdansk Basin. *Baltic Sea. Environ Sci Technol* 1996;30:3266–74.
43. Falandysz J, Strandberg B, Strandberg L, Berqvist PA, Rappe C. Concentrations and spatial distribution of chlordanes and some other cyclodiene pesticides in Baltic plankton. *Sci Tot Environ* 1998;215:253–8.
44. Holoubek I, Triska J, Cudlín P, Čáslavský J, Schramm KW, Kettrup A, et al. Project TOCOEN (Toxic Organic Compounds in the ENvironment). Part XXXI. The occurrence of POPs in high-mountain ecosystems of the Czech Republic. *Toxicol Environ Chem* 1996;66:17–25.

*Sažetak*

**PERZISTENTNI, BIOAKUMULATIVNI I TOKSIČNI SPOJEVI U ZEMLJAMA SREDNJE I ISTOČNE EUROPE - KRITIČNA MJESTA**

U radu su iscrpno opisani izvori i razine u okolišu perzistentnih bioakumulativnih i toksičnih spojeva (PBTs) u zemljama srednje i istočne Europe. U većini zemalja te regije proizvode se i/ili formuliraju pesticidi. Registracija pesticida osnovni je uvjet za uvoz, proizvodnju i distribuciju. Posebna pozornost mora se posvetiti nepoželjnim pesticidima. Nepoželjni pesticidi i oni kojima je istekao rok upotrebe najveća su opasnost za okoliš i ljude, uzrokovana primjenom kemijskih sredstava u poljoprivredi u zemljama srednje i istočne Europe. U većini zemalja još nije riješen problem sigurnosti skladištenja PBTs-a i ostalih kemikalija klasificiranih kao otrovi, a također nema posebnih mjesta ni uređaja za uništavanje takvih kemikalija. Ova regija ima i specifičan problem onečišćenja okoliša kao posljedicu nedavnog rata. Razaranje industrijskih postrojenja i rasipanje kemikalija ima najgori učinak na okoliš (Bosna i Hercegovina, Hrvatska, Srbija i Makedonija).

*Ključne riječi:*

onečišćenje okoliša, organoklorovi pesticidi, PCB, perzistentni spojevi, prekogranična onečišćenja

Requests for reprints:

Ivan Holoubek, Ph. D.  
Recetox, Department of Environmental Chemistry and Ecotoxicology  
Veslarská 230B, 63700 Brno, Czech Republic