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Letters to Editor

Data on the Manufacture, Use, Inventory and Disposal of Polychlorinated Biphenyls (PCBs) in Poland

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Abstract

In Poland there were originally manufactured two technical PCB formulations of moderate (40%) and high (63.6%) chlorine content. A moderate chlorinated PCB mixture called Tarnol (or Chlorowany bifenyl) was synthesized in 1971-1976 and used as dielectric oil in home manufactured transformers, while the highly chlorinated mixture Chlorofen was used as a lubricant and hydraulic fluid mainly in mining equipment. There is no data available indicating when materials and products containing PCBs appeared for the first time in Poland. In Poland there were also originally manufactured two PCN formulations of low (mono-chloronaphthalene) and high (tri- to octachloronaphthalene) chlorine content. Due to historical reasons some materials and equipment containing PCB/PCT/PCN could reach the present country's territory before 1945, *i.e.* at the same time when they were available in neighbouring Germany. Some foreign technical PCB mixtures as well as materials, products and equipment containing PCBs were imported from abroad after 1945. After World War II PCN formulations were synthesized in Poland. There is not yet a whole country-based register of materials, products and equipment containing PCBs, PCTs and/or PCNs. Nevertheless, some preliminary inventory work was done in the mid - 1990s and includes the public electric power supply sector. It has been assessed that roughly 35-50% of capacitors and 1 % of transformers still in use in Poland contain PCBs. An assessed total amount of PCB contaminated oil in stock or service is up to 17500 t, *i.e.* 3500-5000 t in capacitors, 3000 t in transformers, and 8000-9500 t in other electromagnetic equipment such as breaker switches, choking coils, measuring transformers, starters, voltage regulators or other machinery. The up-to-date facilities for safe disposal of PCB wastes are non-existant in Poland. Over the past two years a strategy for management of hazardous wastes has been developed and includes development of the facilities for thermal decomposition. According to schedule, environmentally safe PCB waste treatment facilities have to be installed before 2010.

Keywords: hazardous substances, hazardous waste, disposal, inventory, PCBs, PCTs, PCNs

Introduction

Polychlorinated biphenyls (PCBs) are an important group of persistent organic pollutants (POPs) exhibiting significant toxicity and of widespread occurrence in the environment [1, 2]. They represent a class of inert industrial chemicals with physical appearance ranging from transparent and mobile liquids to viscous or hard yellowish and brown-coloured resins with excellent dielectric properties, which are inflammable and compatible with

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many organic substances. Polychlorinated biphenyls were developed and introduced in 1929 as a substitute for polychlorinated naphthalenes (PCNs) already in existence since 1910 at the market but were too hazardous for humans and accidentally exposed cattle. Chloronaphthalene congeners are largely planar compounds [3-6]. These chemicals are the earliest group of man-made dioxin-like compounds for which human beings and wildlife were exposed due to their large industrial production, widespread use and leaching into the environment [7]. Polychlorinated naphthalenes, biphenyls and terphenyls (PCTs) found numerous and largely similar industrial applications. Around 50% of the amount of technical mixtures of PCBs produced world-wide were utilized as capacitor and transformer insulating oils, while the remaining part has found diverse use in hundreds of applications [8]. A large percentage of the capacitors and a small percentage of transformers still in service world-wide contain PCBs as a dielectric medium and have to be safely replaced [9]. Additionally, nearly in every industrially developed country PCB-contaminated waste dielectric oil and other PCB-contaminated substances are in storage awaiting environmentally safe disposal [10]. A recent case study [11] has identified that even technical mixtures of PCNs, which are historically older industrial chemicals than PCBs, could be used and found at industrial sites in economically highly developed countries even in 1989.

The Directive on disposal of PCBs and PCTs [12] is a law which obligates member states of the European Union to manage environmentally safe elimination of PCB/PCT by the end of 2010. The EU associated countries in Central and Eastern Europe have to implement in their national legal orders the bulk of EU environmental legislation, including specific requirements on hazardous waste management as regards PCBs and PCTs.

Data Collection

The data in this study have been gathered from the scientific literature search, collection of the background documents from the manufacturing companies, interviews and direct contacts with persons engaged in the industry as well as research and governmental organisations.

Results and Discussion

The exact date of introduction of technical formulations of PCNs, PCBs and PCTs, and specific materials, products or equipment containing these compounds into common practice in Poland is not known. Technical PCN formulations were produced worldwide from around 1910 and are an example of the earliest known class of popular synthetic dielectric insulating materials and resins, which were widely used in the past in industry. These compounds were manufactured in neighbouring countries like Germany and were commercially available under the trade names Nibren Wax, Perna Wax and Basileum. Some of the materials, products and electrical equipment made in Germany and containing PCB/PCT/PCN were also available in Poland, at least during the Second World War and thereafter. Two technical formulations of PCN were synthesized in Poland from 1936. 2-Chloronaphthalene was manufactured in the amount of 15 tons, while a higher chlorinated mixture named Woskol (tri- to octachloronaphthalene) was manufactured in the amount of 9 tons per annum. 2-Chloronaphthalene was used as a substrate in dye production and in the pharmaceutical industry, as a plasticizer and for the manufacture of insecticides, and also as a solvent, *e.g.* in widely used wood and other purpose impregnating agents of the Xylamit series. Woskol was primarily used for cable insulation. Polychlorinated naphthalenes were identified recently as technical impurities in a Polish PCB mixture [13]. Poland has produced two technical PCB mixtures, namely Tarnol and Chlorofen, and there is no data indicating that PCTs were synthesized. The residues of PCTs were identified in gulls from the Polish coast of the Baltic Sea but were not detected in fish-eating birds from the Gulf of Gdansk in the 1980s [14, 15].

Polish PCB Formulations

Poland has its own two technical PCB mixtures. Tarnol, which is also called Chlorowany bifenyl, is a moderately chlorinated technical PCB formulation manufactured in 1971-1976 by the chemical company Zaklady Azotowe in Moscice near the city of Tarnow in southeastern Poland. The mixture *(ca.* 40% Cl *per* biphenyl molecule) in its physical appearance and properties is similar to well known foreign technical PCB formulations such as Aroclor 1248, Clophen A 40, Phenoclor DP-4, Fenchlor 42 or Kanechlor 400. Tarnol is a product of the anti-import policy, which was on the agenda of the government in the 1970s. The total quantity of manufactured Tarnol was 679 tons. It is a colourless clear liquid of density 1.45-1.47 g/ml at 20°C. Chlorobiphenyl isomer and congener composition of Tarnol is unknown. According to the data released by the manufacturer of Tarnol, the mixture is composed mainly of trichlorobiphenyls with di-, tetra- and pentachlorobiphenyls as minor constituents. Nevertheless, the chlorobiphenyl composition of Tarnol was not confirmed by capillary gas chromatography and mass spectrometry (HRGC-MS) for analysis. Till now no official data on the use of Tarnol were released. It appears that Tarnol was used exclusively as a dielectric fluid for domestically manufactured transformers, but the use as a dielectric in capacitors could also be possible.

Chlorofen is a highly chlorinated (63.6% Cl) PCB formulation manufactured in Z^bkowice near Bedzin in southern Poland. The mixture is a light to dark-brown sticky and viscous resin composed mainly of PCB congeners with 5 to 9 chlorine atoms that comprise 99.55% of total PCBs. The average number of CI 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 [16]. Chlorofen was used as a lubricant and hydraulic fluid in mining equipment.

In the past, manufacture and landfill of PCB containing wastes lead to highly elevated contamination of the environment adjacent to such facilities and caused high risks to human. Various abiotic and biotic environmental matrices collected world-wide at sites less or more distant from production facilities and nearby landfills of PCBs still contain great concentrations of this hazardous substance. For example, it was recently discovered that the human body burden of PCBs of the inhabitants of the Michalovice District (Slovakia), which is where technical PCB formulations of the Delor series were manufactured in 1959-1984 by the Chemko chemical factory in the town of Strazske, are much greater than in Slovakia's other districts. Fourteen years after the manufacture of Delors was stopped the neighbourhood adjacent to the Chemko facility is highly polluted, at least with PCBs [17]. In another example, PCBs at highly elevated concentrations were quantified in sediments from the local creek and drainage ditches as well as in soil samples collected from the various sites located in a neighbourhood adjacent to the main PCB production facility in Annison, Alabama, USA (manufactured from 1930 until the early 1970's) and nearby landfills which contained buried PCB wastes. Even in 1997-1998 soil samples from sites far from the facility contained PCBs up to 2810 mg/kg, while human blood concentrations in 1999 were up to 2100 $\mu g/dm^3$ [18]. In Poland there is no data available on degree of contamination by PCBs of the environment close to the manufacturing or former landfill/disposal sites of these compounds.

Imported PCB Formulations

Some foreign PCB mixtures were also imported to Poland before 1971 because of the demand for the home manufacture of the capacitors and transformers. The PCB mixtures such as Sovol (former Soviet Union) and Delor (former Czechoslovakia) were imported but other formulations were also possible and Clophen (Germany), Phenoclor (Italy) and Pyralene (France) are likely candidates. Demand for PCB dielectric oil for the manufacture of capacitors was assessed to be approximately 100 tons annually in the late 1960s [19].

Use

Home-produced and imported PCB mixtures were used mainly as dielectric fluid in capacitors, transformers and other electromagnetic equipment, lubricants in mining industry, and hydraulic fluids and heat exchange fluids. Capacitors of various type, size and origin are in use in Poland. In addition to domestic products, they were also imported from the former East Germany, Soviet Union, Romania, Hungary, Czechoslovakia, Italy, France, Finland and Sweden. The capacity of the capacitors in service is approximately between 1 and 50 litres. There has been no requirement to possess a register of capacitors or their movement at any level of organization (company and institution or local, district and national administration). The total number of capacitors with capacity greater than 5 litres (assuming 25 L on average) in use or stored is roughly estimated to be around 400,000, while the amount of impregnating material contained is around 10,000 tons. Approximately 40% of capacitors in use in Poland contain cooling material of unknown origin or composition. The estimated percentage of capacitors with impregnating material containing PCBs is 35-50%. Thus, the total quantity of dielectric cooling material composed of PCBs is assessed to be roughly 3500-5000 tones.

Transformers of various type, size and origin are in use in practically every industrial enterprise in Poland. In addition to transformers that were made locally they were also imported from the former East Germany, West Germany, Soviet Union, Czechoslovakia and Yugoslavia. Less than 1.0% of transformers have been assessed to contain PCB dielectric fluid. There is no information available on the number of transformers produced and designated for domestic use. There is no data on the number of transformers refilled (exchange of PCB contaminated dielectric fluid for PCB-free oil) and removed from service, amount of oil recovered, and their method of disposal or those units which were destroyed. The current estimate of the total number of transformers in Poland is 285,000 and the corresponding amount of oil in use or stored is 300,000 tons.

The total number of the other electromagnetic equipment such as breaker switches, choking coils, measuring transformers, starters, voltage regulators and other machinery which may contain PCBs in use in industry, and the total amount of PCB-contaminated dielectric oil is highly uncertain. This is assumed to be approximately 50,000 units of such electromagnetic equipment (around 5500 tons of oil; 25% of units may contain PCB-contaminated oil). The total amount of dielectric oil with PCBs contained in capacitors, transformers and other electromagnetic equipment is assessed of 8000 to 9500 tons (Table 1).

Table 1. An assessment of the amount of PCBs available for disposal in Poland.

Name of the equipment	PCBs contaminated equipment (%)	Estimated amount of PCB contaminated oil (tones)
Capacitors	35-50	3500-5000
Transformers	1%	3000
Other equipment		8000-9500
Total		Up to 17500

Inventory and Disposal

There is no national register or inventory of the amounts and fluxes of technical PCB/PCT/PCN formulations produced, imported and utilised in Poland as well

as of the materials, products, equipment or waste containing these chemicals. Nevertheless, some preliminary works were conducted in the mid 1900s [19]. There are examples of both bad and good practice as regards the management and disposal of PCB contaminated oil and equipment (capacitors, transformers) removed from the service or scrubbed. Large transformers, especially those owned by the state Power Grid Companies, are inventoried and subjected to internal company inspection and control measures, and those in service are generally in good condition. Randomly collected soil samples at a few "transformer stations" inspected in the former Gdansk Voyevodeship in northern Poland [20] did not contain PCB concentrations above a background level. Ambient air, surface water (Vistula River) and surface sediment in Poland showed low concentrations of PCBs [21, 22], and also in most of the soil samples [23]. A relatively elevated PCB contamination in some of the sediment and soil samples were found at highly industrialized sites in southern Poland [24].

There is a lack of rules regarding equipment storage for outdated equipment containing PCBs or used dielectric fluid containing PCBs. Nevertheless, there are examples where outdated or scrapped capacitors are gathered and kept in dry condition in enclosed spaces or closed outdoors under an umbrella roof, and used transformer oil contaminated with PCBs is also stored in closed vessels in dry condition in separate areas.

There are a few examples where used PCB dielectric oil has been treated at collection facilities similar to mineral oils and subsequently mixed with used-mineral oils for further regeneration [19]. A randomly selected six samples of used mineral oil contained PCBs at concentrations between 2.9 and 53 mg/kg (median 36 mg/kg), while in six samples of used transformer oils, concentrations were between 2.3 and 31 mg/kg (median 4.3 mg/kg) [25]. There were also cases noted when outdated transformers were decommissioned under uncontrolled conditions, while transformer and capacitor oil and materials incinerated in open conditions or in unauthorized (i.e. dioxin emissions) hazardous waste incinerators. Legislative action on the management and safe disposal of PCB materials, equipment and wastes is expected to be introduced in Poland. Waste substances, products and equipment containing or contaminated with PCBs are hazardous waste. Over the past few years a strategy for management of hazardous waste has been developed, and in Poland the problem of waste contaminated with PCBs cannot be separated from the broader problem of hazardous waste management. It is anticipated that the introduction (in force from late 1999) of two national regulations [26, 27] regarding safe use of electrical equipment containing PCBs will assist in establishing proper decontamination practice.

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