Polychlorinated biphenyls (PCBs) Contamination of Soil in a Former Soviet Army Base in Poland

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Abstract

Soil samples were collected in 1994 from various sites in a former Soviet army base (FSAB) localised near the town of Świnoujście in the north-western corner of Poland to investigate possible contamination with PCBs. The concentrations of PCB in FSAB soil ranged from 32 ng/g to 3400 ng/g, with a mean of 900 ng/g and median 260 ng/g dry wt, and the background concentration for the various types of soil in the northern part of Poland ranged between 2.3 and 38 ng/g dry wt.

Key words: polychlorinated biphenyls, PCBs, soil, pollution, army ground base

Introduction

Polychlorinated biphenyls (PCBs) are of concern in the environment because of their toxicity, high stability and resistance to degradation. Soil acts in part as a temporal sink for persistent organohalogenated compounds, and the rates of their removal from soil are dependent largely on the presence of some bacteria and/or lower fungi [1,2], soil type and condition, climate and composition of contaminating mixture. PCBs are complex mixture and a lower chlorinated PCB members are usually more prone both for degradation by microbes as well as volatilisation from the soil than higher chlorine substituted congeners [3]. Most of the atmospherically deposited PCBs are sorbed by the organic fraction of the soil and are retained in a top layer, and in the case of the spill those chemicals are able to migrate vertically and horizontally in the soil profile [4-6].

The former Soviet Union has two own PCB formulations: Trichlorodiphenyl and Sovol. The chlorine content of Trichlorodiphenyl is 41%, and number of chlorine atoms per biphenyl molecule is 3, while Sovol contains 53% of chlorine and 5 chlorine atoms per biphenyl molecule, on the average [7].

Elevated concentrations of PCBs in soil in a former U.S. air base grounds in Vietnam imply on the military activities of the allied forces during the Second Indochina War as a source of the contamination with those substances [8], what have prompt us to investigate the possibility of contamination with PCBs of soil in a randomly selected one of the former Soviet army base grounds in Poland. In this study are reported data on occurrence of PCBs in a top layer of soil taken in a former Soviet army base ground localised near the town of Świnoujście in Poland.

Experimental Methods

A soil samples were collected from seven sites in a former Soviet army base (Figure 1) and an additional sample was taken from a roadside in nearby town of Świnoujście in July 1994. A 5-cm surface layers of soil were taken and subjected for chemical analysis. The soil samples were taken with a vertical corer, packed in clean polyethylene bags and until further laboratory analysis kept under temperature-controlled condition. In the laboratory the soils were air-dried, ground, sieved with 32 a mesh (0.5 mm) and kept in closed glasses at a temperature of -20°C.

A soil sample (50 g) was taken in a 500-ml stoppered Erlenmeyer flask, a hexane-washed water (30 ml) was added and kept for 30 minutes to wet the soil. The sample was extracted in triplicate with 150 ml acetone for one hour by a shaker. The combined supernatant was transferred into a 3-litre separatory funnel containing 200 ml of hexane and 1300 ml of hexane-washed water, and the funnel was shaken for 10 min. The hexane extract was further washed three times with haxane-washed water, dried with anhydrous sodium sulphate, concentrated to 5 ml using a Kuderna-Danish (K-D) concentrator and then a stream of nitrogen gas, subjected to clean-up with 2 ml of concentrated nitric acid, washed three times with hexane-washed water, and then fractionated on Florisil column. The fraction 1, eluted with 60 ml of hexane, contained PCBs and *p,p'*-DDE, and fraction 2, eluted with 150 ml of 20% dichloromethane in hexane, contained organochlorine pecticides.

After concentration (4 ml) of hexane extract using a K-D and nitrogen gas, the final PCBs determination was achieved using capillary column gas chromatography (Hewlett Packard 5890 Series II) with ^{63}Ni electron capture detection (GC/ECD). The DB-1 fused silica capillary column (30 m x 0.25 mm x 0.25μm) was operated under temperature programmed condition, starting from 160°C in isothermal for 4 minutes, then increase at rate 2°C per minute until 240°C and hold for 20 minutes. The carrier gas was helium (2 ml/min) and make up gas was nitrogen (60 ml/min). The PCB content of the sample was calculated by adding the concentrations of the individually resolved peaks of different PCB isomers and congeners. An equivalent mixture of Kanechlor 300, 400, 500 and 600 of known composition and concentration of chlorobiphenyl congeners was used as a standard.

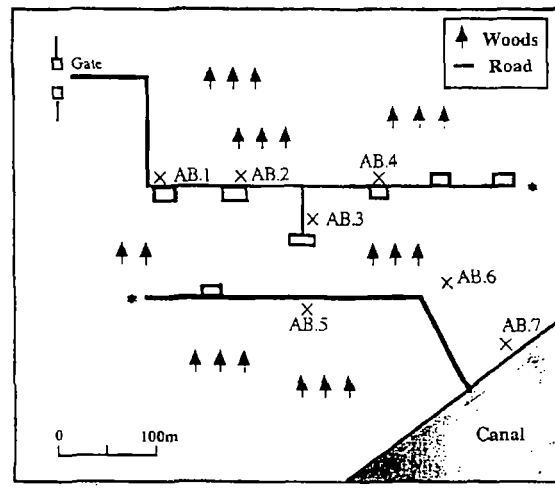

Figure 1. Sampling sites (x) of soil in a former Soviet army base near Świnoujście.

A Hewlett-Packard 5890 Series (GC) USA coupled with JEOL JMS GC Mate (MS) Japan system was operated at resolution 1,000 in the quantification/confirmation of PCB congeners. A fused silica column (30 m x 0.25 mm i.d.) coated with DB-1 and helium as the carrier gas was operated in temperature programmed conditions (splitless injection at 70°C, isothermal for 1 min, 20°C per min to 180°C, isothermal for 1 min, 2°C per min to 260°C, isothermal for 2 min). M^+ and $(M + 2)^+$ ions were monitored at *m/z* 222.0003 and 223.9975 for dichlorobiphenyl, *m/z* 255.9613 and 257.9585 for trichlorobiphenyl, *m/z* 289.9224 and 291.919 for tetrachlorobiphenyl, *m/z* 325.8805 and 327.8776 for pentachlorobiphenyl, *m/z* 359.8415 and 361.8385 for hexachlorobiphenyl, *m/z* 393.8025 and 395.7995 for heptachlorobiphenyl, and *m/z* 427.7635 and 429.7606 for octachlorobiphenyl.

Results and Discussion

There is no data available on the type and amounts of the technical PCBs potentially used by the former Soviet Army in their bases in Poland. The technical PCB formulations, including two produced in the former Soviet Union, *i.e.* Sovol and Trichlorodiphenyl, were mainly used as dielectric fluids in electrical equipment such as the transformers and large capacitors. Nevertheless, various miscellaneous and disperse uses of PCBs in equipment other then the transformers and capacitors was also possible, and such products can still be in service.

The production of Trichlorodiphenyl was ceased in the former Soviet Union in the late 1980s, and in the case of Sovol a produced volume was only reduced in a recent years to *ca.* 500 tones annually [7].

A detailed study of the Sovol and Trichlorodiphenyl has indicated that those two technical mixtures differ largely in their PCB congeners and homologues composition [7,9,10]. The Sovol formulation, which is a highly chlorinated PCB mixture fairly similar to Aroclor 1254, contains mainly penta- (53 %), tetra- (23 %) and hexachlorobiphenyls (22 %), and was used both in closed (transformers and capacitors) and open systems (wire insulators, sealing materials and plasticizers) [7,9,10]. The Trichlorodiphenyl mixture is composed mainly of tri- (49 %), tetra- (32 %), di- (14 %) and pentachlorodiphenyls (4 %), and was used as a dielectric fluid in closed systems [7].

The GC/MSD chromatogram of PCBs in a highly contaminated (3400 ng/g) with those substances soil sample collected from the former Soviet army base shows a very similar pattern of chlorobiphenyl congeners to that of the Sovol mixture (Figure 2). Also other the FSAB soil samples examined showed composition of PCB congeners more or less similar to that of the Sovol mixture. The available published data on chlorobiphenyl composition of the Sovol mixture differ slightly, and most abundant congeners are such as: 2,3',4,4',5-P_5CB (PCB IUPAC No. 118), 2,3,3',4',6-P_5CB/3,3',4,4'-T_4CB (No. 110/77), 2,2',3,4,4',5'-/2,3,3',4,5,6-H_5CB (No. 138/160), 2,2',3,4',5-/2,2',4,5,5'-P_5CB (No. 90/101), 2,3,3',4,4'-P_5CB (No. 105) and 2,3',4,4'-T_4CB /2,2',3,5',6-P_5CB (No. 66/95) or 3,3',5,5'-T_4CB/2,2',3,5',6-P_5CB (80/95), while 2,2',3,4,4',5,5'-H_5CB (No. 180) is a minor constituent [7,9,10].

Six of totally seven samples of soil collected from the FSAB (Figure 3) were apparently contaminated with PCBs, and most of them were highly contaminated. The mean concentration of PCBs in those soil samples was 900 ng/g on a dry weight basis, and up to 3400 ng/g was found. An elevated concentration of PCBs, *i.e.* 230 ng/g dry weight, was detected also in roadside soil in the town of Świnoujście, a site quite close to the investigated FSAB.

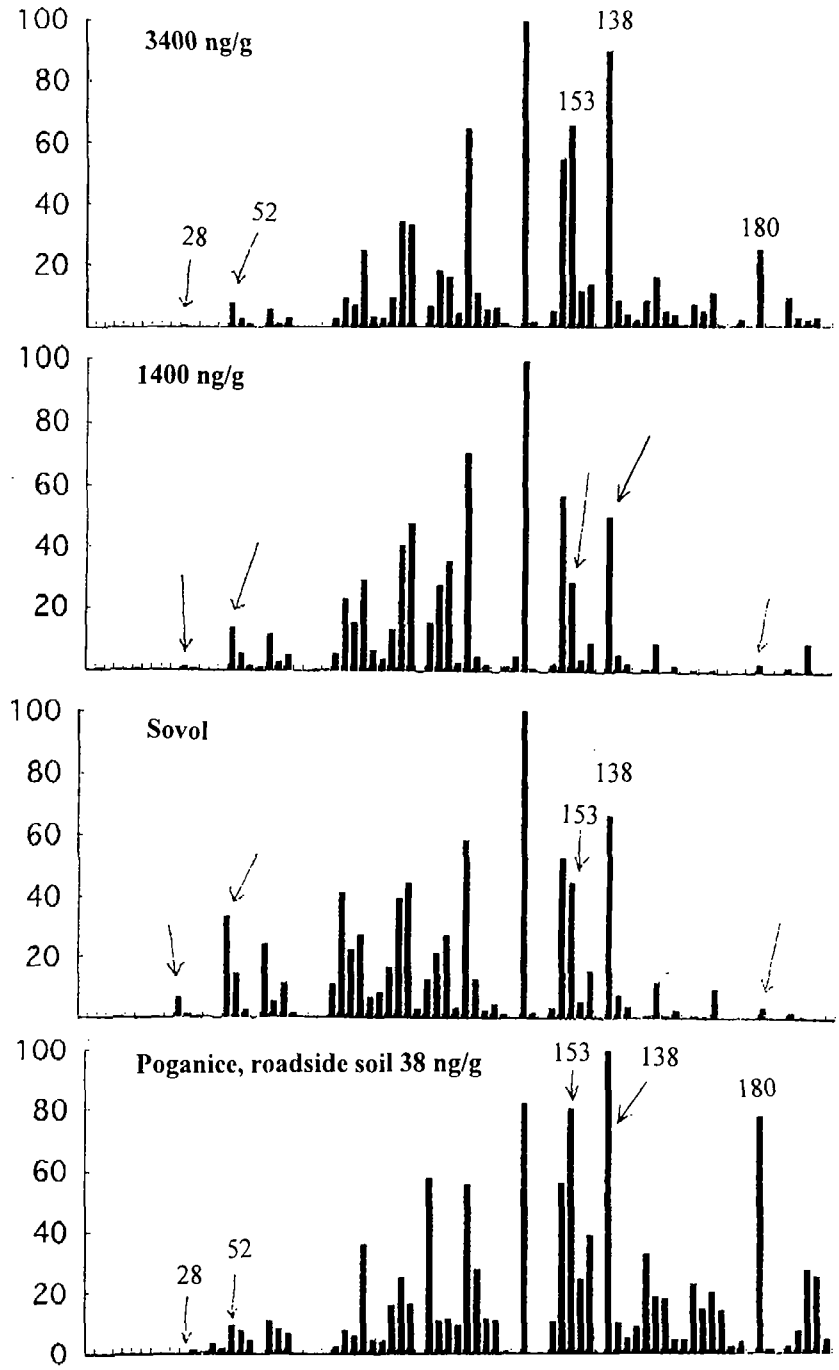

Figure 2. Normalised GC/MS chromatograms of PCBs in two soil samples from the former Soviet army base, the Sovol mixture and a control roadside soil from Poganice (Northern Poland).

The background concentration of PCBs in various types of soil collected in the northern part of Poland ranged between 2.3 and 38 ng/g dry weight, and for agricultural soil it was between 2.3 and 8.9 ng/g. Suprisingly, a highly chlorinated PCB member, such as 2,2',3,4,4',5,5'-H_7CB (No. 180), is one of the most contributing congeners in a GC/MSD chromatogram of background soil (Figure 2), as well as in the samples of other reference soils, including a roadside soil collected in town of Świnoujście.

2,2',3,4,4',5,5'-H_7CB is a dominating PCB constituent (17.21 %) in Chlorofen, a highly chlorinated technical PCB mixture produced in the past in Poland [11]. Because Chlorofen was designed as a lubricant in hydraulic systems in mining equipment, it has to be cleared whether a relatively high proportion of chlorobiphenyl no. 180 found in the reference soils is mainly due to contamination with Chlorofen or to other factors such as physical conditions and ageing or its relative resistence to microbial degradation when compared to lower chlorinated members.

The samples of soil collected from the former Soviet army base apart to high load of PCBs, when compared to reference soils from the northern part of Poland (Figure 2), remained much less contaminated with chlorobiphenyl no 180. A roadside soil collected from the town of Świnoujście at site localised a few kilometres from the FSAB, which was also relatively highly contaminated with PCBs, showed much different distribution of chlorobiphenyl congeners with relatively greater content of higher chlorinated members when compared to the FSAB soils.

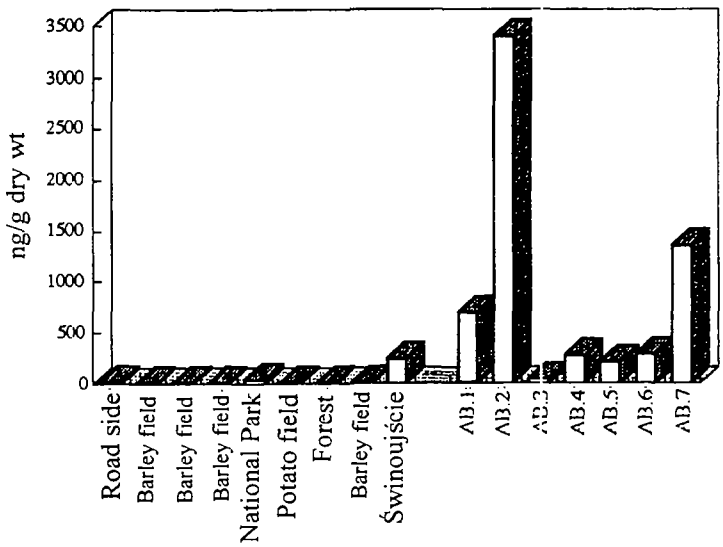

Figure 3. The concentrations of PCBs in soil from various sites in the northern part of Poland and a former Soviet army base (AB 1-7).

Acknowledgments

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