SOIL CONTAMINATION BY PCBs AND PAHs RELATED TO THE PAINT INDUSTRY

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Abstract

Polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are both persistent, bioaccumulative, and toxic organic pollutants with aromatic structures and similar environmental behaviour. They accumulate in soil and sediments, and bioaccumulate in living organisms, leading to long-term ecological and human health risks. Unlike PCBs which have been used in industry for a long time, PAHs were not intentionally produced or used. An important global source of PCBs and PAHs is their unintentional formation during the manufacture of paints, dyes, adhesives, and pigments. The present study focuses on soil contamination with PCBs and PAHs potentially originating from paint use. Soil samples were collected from 18 points located in the proximity of paint factories. Gas chromatography with electron capture detector was used to determine the PCBs content and liquid chromatography with UV-VIS detection was used for PAHs determination. The results show that PCB 52 is present at concentrations reaching the alert threshold, which may be attributed to its formation as an unintended by-product during pigment manufacturing. Among the PAHs, fluoranthene and pyrene have the highest concentrations.

Key words: PAHs, paints, PCBs, soil

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of organochlorine compounds that comprise 209 possible chemical formulas with 1 to 10 chlorine atoms in the molecules (Stringer & Johnston, 2001). Of these, 150 have been identified in the environment (Jones et al., 1991). Because of their lipophilicity, toxicity, bioaccumulation in food chains, and resistance to chemical and biological degradation, PCBs have been globally banned under the Stockholm Convention on Persistent Organic Pollutants (POPs). PCBs are included in Annex A (Elimination) of the Convention, meaning countries are obligated to eliminate their production and use. At present, the two main sources of PCB pollution are industrial production and combustion processes. Although the production, processing, distribution, and use of PCBs have been banned in many countries since 1985, the complete elimination of existing PCB stocks and all PCB-contaminated equipment remains challenging, and our country has requested a derogation in this respect. Thus, this operation must be done in an ecologically rational manner (without danger to human health and the environment), the financial effort required to replace this equipment being considerable. As a result, there are still activities that can generate PCB waste and lead to soil contamination: accidental generation of PCBs, recycling operations.

Another important source of PCBs worldwide is the production of paints, dyes, adhesives and pigments. There are studies that demonstrate environmental pollution from these products (Jartun et al., 2009).

The total PCB content in some paint samples can be substantial, with concentrations as high as 919 mg/kg reported in azo pigments (Hannah et al, 2022). Recent studies have found high levels of PCBs in pigments, indicating that this may be a noteworthy environmental concern (Anezaki et al., 2015).

Pigments are materials which are used as colorants in paints and other products and are generally insoluble in the medium in which they are applied (Herbst and Hunger, 2004). A variety of different pigments have been associated with by-product PCBs including; azo pigments, phthalocyanine pigments, diketopyrrolopyrrole pigments, dioxazine pigments, and titanium dioxide (Vorkamp, 2016).

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds composed of multiple fused benzene rings, formed mainly by incomplete combustion of organic materials such as coal, oil, wood, or gasoline. They are persistent, lipophilic, and bioaccumulative, meaning they can remain in the environment for long periods and build up in the fatty tissues of living organisms.

PAHs are also toxic and potentially carcinogenic, with compounds like benzo[a]pyrene classified by the IARC as carcinogenic to humans. Major environmental sources include vehicle exhaust, industrial emissions, tobacco smoke, and soot.

Unlike PCBs, PAHs have not been intentionally produced or used. They have not been manufactured for an economic purpose. However, certain technical mixtures (e.g. tars, heavy mineral oils, bitumen) naturally contain PAHs — and these mixtures have been used for various industrial purposes (Srogi, 2007). So, the manufacture of paints and pigments can be a source of PAHs. For example, carbon black, a very common pigment in paints, inks and plastics, is a significant source of PAHs. There are studies that demonstrate the presence of PAHs in black carbon thus explaining that the source of PAHs pollution can be the tire industry (Bucheli et al., 2004).

MATERIALS AND METHODS

Soil sampling

Soil samples were collected from 18 locations (S1-S18) situated in the proximity of paint, varnish, and primer factories from Prahova, Brașov, and Ilfov counties.

Average soil samples were obtained by mixing 5 samples collected from the corners and center of a 5 x 5 m^2 area. When field conditions allowed, the soil sampling was done around the factory (figure 1).

Figure 1. Sampling points around a paint factory in Brașov County

Soil physicochemical properties

Soil properties were analysed using standard methods:

- pH: potentiometric method (SR-7184-13)
- Organic Carbon (C, %): wet oxidation method (Walkley-Black, STAS 7184/21-82)
- Total nitrogen (N, %): Kjeldahl method (STAS 7184/2-85)
- Mobile Phosphorus (PAL, mg/kg): Egner-Riehm-Domingo method (STAS 7184/19-82)
- Mobile potassium (KAL, mg/kg): Egner-Riehm-Domingo method (STAS 7184/18-80)

- Electrical Conductivity (EC, μS/cm): aqueous extract and conductometric method (STAS 7184/7-87)

The chemical properties of the studied soils are summarized in the Table 1.

Table 1. The main chemical properties of the analyzed soils

Chemical properties of the analysed soil sample (N=20)	Range
pH	5.85 – 7.85
C (%)	0.97 - 6.21
N (%)	0.150 - 0.509
EC (μS/cm)	30.2 - 312
P (mg/kg)	16.34 - 271.2
K (mg/kg)	148-500

It can be seen that:
- The pH varies from moderately acidic (5.85) to slightly alkaline (7.85);
- The electrical conductivity is closely correlated with the total salt content and has very low values. A good soil EC level would be somewhere above 200 µS/cm and below 1200 µS/cm. An EC level below 200 indicates a lack of nutrients available to plants and could possibly indicate a sterile soil with little microbial activity. An EC above 1200 µS/cm may indicate too much fertilizer or too many salts due to lack of drainage.
- Organic carbon varies between 0.97 and 6.21% indicating low and medium supply.
- Nitrogen content varies between 0.150% (good supply) and 0.509% (high).
- Mobile phosphorus content varies between 30 mg/kg (low) and 185 mg/kg (very high).
- Potassium content varies between 148 mg/kg (medium) and 500 mg/kg (very high).

PCBs are analysed from soil according to the standards set forth in the European Standards (EN 17322:2022). To extract these compounds from soil, a Soxhlet extractor and a mixture of hexane and acetone (in a 1:1 ratio) were employed.

The extract is washed with water for chromatography to remove acetone and it is passed through anhydrous sodium sulphate. If necessary to remove the sulphur, copper powder can be used.

The analysis focused on seven indicator polychlorinated biphenyls (PCBs), specifically PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, and PCB 180, as specified in Order 756/1997.

PCBs were measured using an Agilent gas chromatograph (GC), an instrument that separates chemical mixtures, equipped with an electron capture detector (ECD), which is highly sensitive to PCBs. The separation was conducted on a long and narrow capillary column (30 meters in length, 0.32 millimeters in diameter, and 0.25 millimeters in thickness), equipped with a nonpolar stationary phase (DB-5). This approach proved effective in differentiating and resolving the diverse isomeric structures of polychlorinated biphenyls.

PAHs are analysed from soil according to the standards set forth in the European Standards (SR EN 17503:2022). To extract these compounds from soil, an automated Soxhlet extractor and a mixture of hexane and acetone (in a 1:1 ratio) were employed.

The determination of PAHs was performed on a Knauer ultrahigh pressure liquid chromatograph (UHPLC) with UV-VIS detection, at 254 nm.

In accordance with Order 756/1997, the following priority PAHs are to be quantified: anthracene, pyren, benzoanthracene, benzopyrene, benzofluoranthene (with izomers b and k), chrysene, fluoranthene, indeno(1,2,3)pyren, naphthalene, and phenanthrene.

The pair consisting of benzo[ghi*]*perylene and indeno(1,2,3) pyrene cannot be determined with UV-VIS detector.

The separation of the other compounds was performed with a C18 column (2.1 mm x 100 mm x 1.8 mm) operated at 40°C. The mobile phase is composed of water and acetonitrile.

RESULTS AND DISCUSSIONS

PCBs content in soil

The total concentration of PCB compounds ranges from 0.001 mg/kg to 0.028 mg/kg, with an average of 0.01 mg/kg. The highest concentrations were recorded in soil samples S5, S8 (belonging to a paint factory) and S18, located near an emulsion station from Bucharest (Figure 2). At these points, the total concentrations exceed the normal threshold value (<0.01 mg/kg), but remain below the alert threshold (0.25 mg/kg).

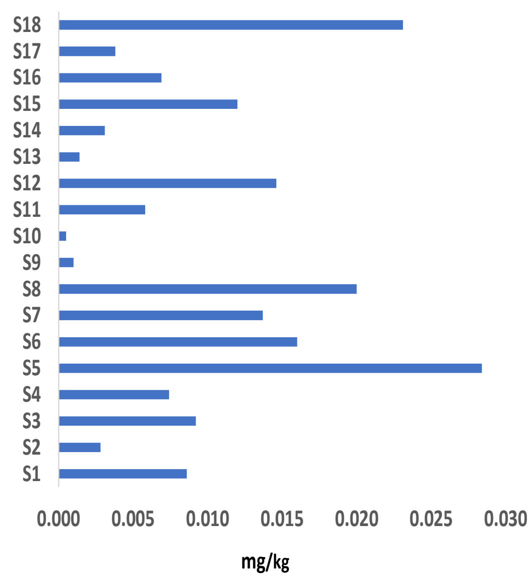

Figure 2. The total content of PCB compounds in soils situated in the proximity of the paint factories

Regarding the profile of the 7 congeners in soil, all isomers except PCB 52 have normal concentrations or only slightly exceed the upper limit of the normal values according with Order 756/1997 (Table 2). In contrast, for PCB 52, 16% of the analyzed samples reach the alert threshold (Figure 3).

Soil contamination with PCB 52 is possible because this congener is present in pigments used in the preparation of paints (Anh et al, 2021).

There are studies showing the presence of PCB 52 in consumer products which were treated with azo red, orange and yellow pigments (Guo et al., 2014).

Table 2. Concentration range of the seven PCB congeners

Congener	Concentration range (µg/kg)
PCB 28	Slq* - 0,8
PCB 52	Slq - 1,5
PCB 101	Slq - 1,3
PCB 118	Slq - 0,7
PCB 138	Slq - 2,4
PCB 153	Slq - 2,4
PCB 180	Slq - 2,6

*- below the limit of quantification (1µg/kg)

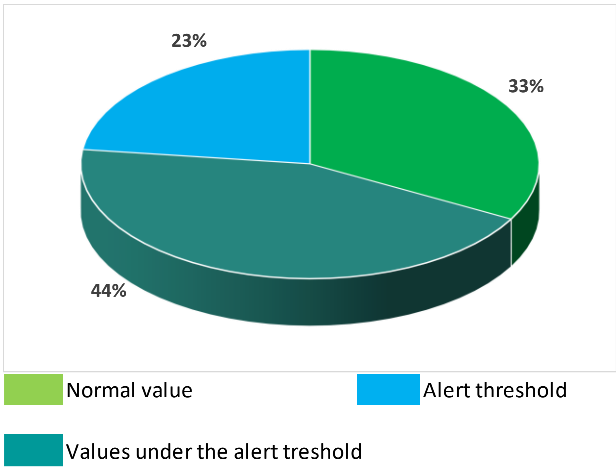

Figure 3. Distribution of soil samples collected from the vicinity of paint factories according to the degree of PCB 52 loading

PCB 52 can be formed unintentionally during the synthesis of azo pigments. In this process more than ten common intermediates and starting materials—such as chlorinated anilines and chlorinated benzidines—can potentially undergo side reactions leading to the formation of PCBs, especially PCB 11 and PCB 52 (Hu & Hornbuckle, 2010).

PAHs content in soil

The total concentration of polycyclic aromatic hydrocarbons in soils collected from proximity of paint, dye, adhesive, and pigment factories ranges between 0.046 mg/kg and 2.347 mg/kg with an average of 0.223 mg/kg. According to Order 756/1997,

the normal values of the total concentration of PAH in soil must be less than 0.1 mg/kg, which means that in the case of the results obtained in this study, 36.8% exceed this threshold, the rest being normal values.
In 1996 Maliszewska-Kordybach proposed 4 classes of PAH contamination, which are still used today:

- < 0.2 mg/kg – unpolluted soils
- 0.2 mg/kg – 0,6 mg/kg – slightly polluted soils
- 0.6 mg/kg – 1 mg/kg – moderately polluted soils
- > 1 mg/kg – highly polluted soils

According to this classification, the soil 2.347 mg/kg PAHs is highly polluted.
Regarding the compounds profile, it can be seen in Figure 4 that the decreasing order of concentration in the studied soils is: fluoranthene > pyrene > benzo(b)fluoranthene > chrysene > benzo(a)anthracene > benzo(a)pyrene > naphthalene > fluorene > anthracene = phenanthrene.

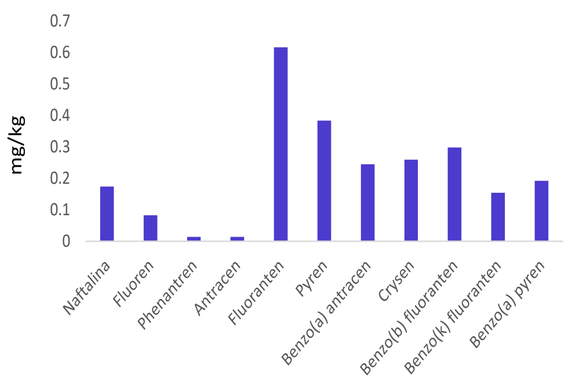

Figure 4. Concentration of individual PAH compounds in soils harvested from the vicinity of paint factories

Phenanthrene and pyrene, the two PAHs with the highest concentration, can appear as unintended products in the paint industry.
They occur mainly as impurities from:

- carbon black used as a pigment in paints and inks;
- unpurified mineral solvents or mineral oils used in production;
- thermal processes (e.g. sintering or incomplete combustion of organic materials) (Abdel-Shaty și Mansour, 2016).

CONCLUSIONS

PCBs can result as unintentionally products in pigments and paints manufactory. The total concentration of PCBs in soil samples collected from the proximity of paint, varnish, and primer factories located in the counties of Prahova, Brașov, and Ilfov ranges from 0,001 mg/kg to 0,028 mg/kg.
Of the seven congeners, the highest concentration, which reaches the alert threshold, is PCB 52.
Soil contamination with PCB 52 is possible because this congener can be formed in azo red, orange and yellow pigments used in the preparation of paints.
The total concentration of polycyclic aromatic hydrocarbons in soils collected from proximity of paint, dye, adhesive, and pigment factories ranges between 0.046 mg/kg and 2.347 mg/kg with an average of 0.223 mg/kg.
Phenanthrene and pyrene have the highest concentrations. These compounds can occur as unintended byproducts from carbon black which is used as a pigment in the paint industry.

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