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Application of different criteria for the assessment of arable soil pollution with PAHs

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The level of contamination in arable soils from rural and urbanised areas in Poland was evaluated using three different systems which consisted of the Dutch standard regarding Σ10PAHs, Polish regulations concerning 9 PAH compounds (sum and individual compounds) and the Polish (IUNG) proposition based on the Σ13PAHs amount normalised to OM content. The median contents of the Σ9PAHs, Σ10PAHs, and the Σ13PAHs were 260 $\mu g \cdot kg^{-1}$, 289 $\mu g \cdot kg^{-1}$, and 350 $\mu g \cdot kg^{-1}$, respectively. Regardless on the applied criteria, no less than 90% of the soils can be classified as unpolluted. Elevated amounts of PAHs occurred mainly in soils from areas with a strong industrial influence.

Key words: PAHs, soil quality criteria, soil contamination

INTRODUCTION

Arable soils that are responsible for crop production are of great importance for food safety, but also for animal and human health (Jensen, Mesman, 2007; Maliszewska-Kordybach, 1999; Oleszczuk, Pranagal, 2007). Food production is one of the main soil functions as specified in the Soil Thematic Strategy for Soil Protection[1] which emphasises the importance of the soil and the need of its protection. The document specified eight main soil threats: erosion, decline in organic matter, local and diffuse contamination, sealing, compaction, a decline in biodiversity, salinisation, floods, and landslides. Contamination can generate direct and indirect risks for most functions of the soil. The contaminants of special concern include, among others, polycyclic aromatic hydrocarbons (PAHs) exhibiting strong toxic, carcinogenic and mutagenic properties (Cai et al., 2007; Jensen, Mesman, 2007; Maliszewska-Kordybach, 2007; Wilcke, 2000), hazardous to soil's organisms and humans (Maliszewska-Kordybach, 2003). Thus, proper evaluation of the state of soil contaminated with PAHs and related risks are of great importance (Bucheli et al., 2004; Jensen, Mesman, 2007; Maliszewska-Kordybach, 2007).

There are two approaches to the assessment of hazards related to soil contamination: human and ecological risk assessment or the application of formal soil quality criteria (very often in the form of regulations). The first approach demands scientific expertise and wider knowledge and is recommended by scientific institutions, while the environment protection and administration services limit, in practice, their opinion to the application of relevant regulations (usually national ones). However, the attitudes to the policies, standards, and regulations regarding soil quality criteria (SQC) for PAHs differ significantly (Maliszewska-Kordybach, 2007).

The aim of the study was to evaluate the similarities and differences in the application of three different assessment systems of agricultural soils exposed to PAHs. Polish arable soils were chosen as an example.

MATERIALS AND METHODS

The data set included 216 soil samples collected in 2005 from the upper layer of arable lands in Poland. The distribution of sampling points was aimed to reflect different geographical regions, various soil properties, and diverse exposure of soils to pollution sources, with a special reference to the areas of the highest exposition to anthropogenic pressure.

The soil's physicochemical characteristic included basic soil properties such as particle size distribution, soil organic matter content and pH. The distribution of the soil particle size was established by the aerometric method (PN-R-04032, 1998[2]). Organic carbon (C_{org}) content was determined by sulfochromic

[1] COM(2006) 231 final. Communication from the Commission of the Council, the European Parliament, the European Economic and Social Committee, and the Committee of the Regions. Thematic Strategy for Soil Protection. 22 September 2006. Brussels, 2006.

[2] PN-R-04032. Soils and mineral soil materials. Soil sampling and determination of particle size distribution in mineral soil material. 1998 (in Polish).

oxidation of organic carbon (PN-ISO 14235, 2003[3]) followed by titration of the excess $K_2Cr_2O_7$ with $FeSO_4(NH_4)_2SO_4 \cdot 6\ H_2O$. Organic matter content (OM) was calculated on the basis of the relationship OM = 1.724*C_{org}. The pH was measured potentiometrically in 1 : 2.5 (m/V) suspension of soil in 1 mol · l^{-1} KCl solution (PN-ISO 10390, 1997[4]).

Analysis of PAHs in the samples from 2005 comprised 16 individual PAHs (US EPA List) (Table 1). Three other sub-groups were selected: Σ13PAH – according to the IUNG (Instytut Uprawy Nawożenia i Gleboznawstwa) classification (Terelak et al., 2008), Σ9PAH – according to Polish regulation (Dz. U., 2002[5]) and Σ10PAH – according to Dutch regulations[6] (Table 1).

For the purpose of determining PAHs in soils, twenty grams of soil material were extracted with 125 ml of CH_2Cl_2 in a Soxtec apparatus (Bűchi, B-811) and cleaned up on glass minicolumns (1 × 20 cm) filled with 1 g of silica gel suspended in dichloromethane. The PAHs were eluted with 5 ml of a mixture of CH_2Cl_2 / n-hexane (2 : 3 v/v) and then evaporated to a volume of approximately 1 ml prior to analysis, using an Agilent 6890N gas chromatograph equipped with an Agilent 5973 Network mass spectrometer (70 eV) and an Agilent 7683 B series autosampler. The resolution of PAH compounds was achieved with a DB-5 MS-DG column at a constant helium flow of 30 cm · s^{-1}. MS (mass spectrometer) detection was based on the selected ion monitoring (SIM) system of appropriate primary and secondary ions according to ISO 18287[7]. Four deuteriated PAHs (D_{10}-fluorene, D_{10}-fenanthrene, D_{12}-chryzene and D_{12}-perylene) were used as internal standards for the quantification of target PAH compounds. The method detection limit (MDL) for individual PAHs was in the range of 0.6–2 µg · kg^{-1}. Quality control included solvent blank samples carried through all procedures and analysis of a certified reference material (sandy loam soil CRM131) every 20 samples.

RESULTS AND DISCUSSION

The properties of soils under study, to a great extent, represented by *Luvisols* (34.3%), *Cambisols* (31%), and *Arenosols* (13.4%), were typical of Poland. They were mostly acidic soils, and 75% of them exhibited a pH value of <5.9 and 25% <4.6 (data not shown), with a low content of organic matter (OM in 75% of soils was <2.06%), and 75% of soil samples were characterised by the fraction <0.02 mm content <36.5% with a great contribution (47.3%) of sandy soils (fraction <0.02 mm content <20%).

The median concentrations of the selected PAH groups comprising from 9 to 13 PAHs were within the limits of 260–350 µg · kg^{-1}, but their concentrations in individual samples varied distinctly (standard deviations from 517 µg · kg^{-1} to 749 µg · kg^{-1}, respectively). The content of Σ13PAHs was within 68–7114 µg · kg^{-1}, while the Σ9PAHs varied from 48 to 4852 µg · kg^{-1}. The highest maximum concentrations were noted for phenanthrene, fluoranthene and pyrene, with the average content of 51 µg · kg^{-1}, 47 µg · kg^{-1} and 43 µg · kg^{-1}, respectively. The average contribution of those hydrocarbons to Σ16PAH were 12–14%. The concentration of the most carcinogenic benzo[a]pyrene (BP), which is suggested to be indicative of the carcinogenicity of Σ16PAH (Wilcke, 2000), varied widely from 6 to 615 µg · kg^{-1}.

Table 1. **Polycyclic aromatic hydrocarbons included in the studies and classification systems applied for Polish arable soils**

Classification	PAHs															
	NP	AP	AC	FN	PH	AT	FL	PR	BA	CH	BF	BK	BP	DA	IP	BR
Σ16P US EPA	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Σ13PAH IUNG	–	–	–	+	+	+	+	+	+	+	+	+	+	+	+	+
Σ9PAH Polish regulations	+	–	–	–	+	+	+	–	+	+	+	–	+	–	–	+
Σ10PAH Dutch regulations	+	–	–	–	+	+	+	–	+	+	–	+	+	–	+	+

NP (naphthalene), AP (acenaphtylene); AC (acenaphtene); FN (fluorene); PH (phenanthrene); AT (anthracene); FL (fluoranthene); PR (pyrene); BA (benzo[a]anthracene); CH (chrysene); BF (benzo[b]fluoroanthene); BK (benzo[k]fluoroanthene); BP (benzo[a]pyrene); DA (dibenzo[a,h]anthracene); IP (indeno[1,2,3-cd]pyrene); BR (benzo[g,h,i]perylene).

Comparing the obtained data with the literature, it should be stressed that only a half of the investigated soils were collected from areas not exposed to a direct influence of pollution sources. Overall, the results are in agreement with other data reported in the literature for the top layer of soils from non-industrial areas. Maliszewska-Kordybach (2003) established the average content of 13 PAHs in agricultural soils from the Pulawy region, Poland, to be 196 µg · kg^{-1}. In the same area, Oleszczuk and Pragnal (2007) reported the content of 16 PAHs in different types of arable soils as 105–290 µg · kg^{-1}. Lichtfouse et al. (2005) showed that the content of 10 PAHs in soil from an experimental crop field in Bordeaux was 123 µg · kg^{-1}, while Bucheli et al. (2004) reported the content of 16 PAHs in Swiss soils to be 50–619 µg · kg^{-1}.

[3] PN-ISO 14235. Soil quality – determination of organic carbon in soil by sulfochromic oxidation. 2003.

[4] PN-ISO 10390. Soil quality – determination of pH. 1997.

[5] Dz. U. Nr. 165, poz. 1359. Regulation of the Minister of the Environment on the standards of the soil and ground quality. 2002 (in Polish).

[6] VROM. Circular on Target Values and Intervention values for Soil Remediation. Ministry of Housing, Spatial Planning and Environment, The Netherlands. 2000.

[7] ISO 18287. Soil quality – determination of polycyclic aromatic hydrocarbons (PAH) – Gas chromatographic method with mass spectrometric detection (GC-MS). 2006.

Similar levels of PAHs in surface soils from non-polluted regions have been recently reported for China; 22–1256 μg · kg^{-1} with a mean value of 318 μg · kg^{-1} for Σ16PAHs in agricultural soils (Hao et al., 2007), 8.6–3881 μg · kg^{-1} of Σ15PAHs in soils from the Yangtze River Delta (Ping et al., 2007) and 160–3700 μg · kg^{-1} for Σ16PAHs in vegetable fields in the Pearl River Delta (Cai et al., 2007).

To evaluate the pollution status of Polish agricultural soils, three different systems were applied: two Polish and one Dutch. All classifications are related to the content of PAHs in the upper layer of soil.

The first classification (Institute of Soil Science and Plant Cultivation – IUNG system) includes six classes of soil contamination (Terelak et al., 2008) (Table 3). The system refers to soil properties, and the OM content is accounted for. The threshold values correspond to the Σ13PAH normalised to soil with OM = 2.0% (representing the standard Polish soil). Normalisation is not applied to soils with OM < 2.0%. According to the IUNG system, 76% of soils can be classified as uncontaminated (including 22% characterised by the PAH content below the background level of 200 μg · kg^{-1}). Weakly contaminated soils (Σ13PAH / OM in the limits of 600–1000 μg · kg^{-1}) constituted 14%, and only 10% were qualified as contaminated (Σ13PAH / OM >1000 μg · kg^{-1}) (Figure).

The second classification is based on a Polish regulation (Dz. U., 2002), where only two classes of soils are distinguished

Table 2. **Statistical evaluation of the content of selected PAHs groups**

PAHs	Median	SD	Lower quartile	Upper quartile
	(μg · kg^{-1})			
Σ16	395	767	256	694
Σ13	350	749	215	592
Σ10	289	579	186	501
Σ9	260	517	168	467

Table 3. **Three classification systems applied to Polish arable soils**

IUNG system	Polish regulations	Dutch regulations
Limit values (μg · kg^{-1})		
Σ13PAH	Σ9PAH	Σ10PAH
< 200 NCb	>1 000 NC	>1 000 NC
200–600 NCe	< 1 000 C	1 000–40 000 CS
600–1000 CW		>40 000 CSi
1 000–5 000 C	Each of individual 8PAHs <100 BP <30 NC	
5 000–10 000 CH	Each of individual 8PAHs >100 BP >30 C	
>10 000 CVH		

NCb – not contaminated (background value); NCe – not contaminated (elevated value); CW – contaminated weakly (need of further investigation); C – contaminated; CH – contaminated highly; CVH – contaminated very highly; CS – contaminated slightly; CSi – contaminated seriously (intervention value); BP (benzo[a]pyrene).

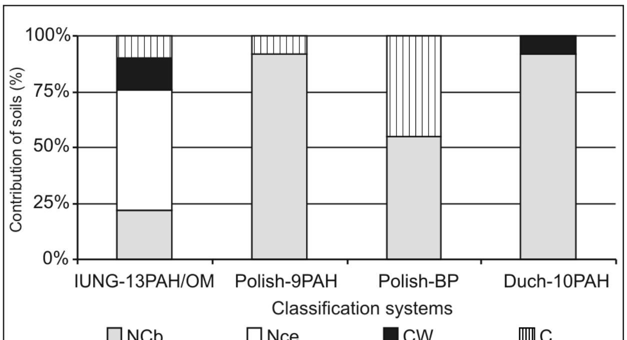
(uncontaminated and contaminated – Table 3) with a threshold value for Σ9PAH in agricultural soils of 1000 μg · kg^{-1}. Additionally, threshold values for each of the nine individual PAHs (Table 1) are established on the levels of 100 μg · kg^{-1}, besides BP (limit value of 30 μg · kg^{-1}). Application of the Σ9PAH criterion indicates an 8% contribution of contaminated soils in all data set.

Most of contaminated soils, independently of the evaluation system, were concentrated in the proximity of cities and industrial towns in Poland (Warszawa, Krakow, Katowice, Szczecin, Płock, Nowa Huta), or were situated close to local industrial sites. The highest contamination corresponded to the highly industrialised and urbanised areas of Upper Silesia, partially influenced by emissions from the Czech Republic. There were also a few samples with a relatively high content of PAHs found in rural areas and in other regions of the country, with no defined pollution sources, which suggests accidental point contamination.

According to the Polish regulation, nearly half of the samples (45%) should be classified as contaminated with BP (Figure). It should be stressed that the BP threshold value of 30 μg · kg^{-1} (Dz. U., 2002) used in the Polish regulation is extremely strict as compared to the BP limit value of 100 μg · kg^{-1} used as a criterion in Denmark (Jensen, Mesman, 2007). If the latter criterion (100 μg · kg^{-1}) is applied, then only 8% of Polish arable soils exhibit elevated BP levels. This corresponds very well to evaluations based on the sum of PAHs (groups "contaminated" according the IUNG system and Polish regulations).

The Dutch system includes two limit values: the background level (Σ10PAHs of 1000 μg · kg^{-1}) and the level when remediation action has to be undertaken (intervention value: Σ10PAHs of 40 000 μg · kg^{-1}). This classification, similarly as the IUNG proposition, takes into account the soil properties (organic matter content). The values given in the Dutch regulations are meant for standard soils, with 10% of OM. For both PAH limit values no soil type correction is used for soils with an organic matter content of up to 10% and above 30%. Hence, the Dutch limit values were applied without any correction in the assessment of Polish soils, because in none of the soil samples organic matter content exceeded 10%.

According to this system, 92% of the soil samples have PAH concentrations at background levels (Σ10PAHs ≤1000 μg · kg^{-1}),



NCb – not contaminated (background value); NCe – not contaminated (elevated value); CW – contaminated weakly (need of further investigation); C – contaminated.

Figure. Contamination level of arable soils in Poland with PAHs (2005 data) according to three classification systems and only 8% of soils may need further investigations (Σ10PAHs >1000 μg · kg^{-1}) (Figure). None of the samples exhibited a PAH content over intervention value (Σ10PAHs > 40000 μg · kg^{-1}).

CONCLUSIONS

The presented data indicate a low level of contamination of Polish arable soils with PAHs. All three systems of evaluation of soil contamination with PAHs, although based on different approaches, led to a similar conclusion that no less than 90% of soils can be considered as uncontaminated, taking into account the total content of PAHs (13, 10 or 9 compounds). In this light, the Polish regulation criterion of BP content (<30 μg · kg^{-1}) indicating a much higher level of contamination reaching 45% of the data set seems to be too strict and suggests further considerations / improvements in this area.

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SKIRTINGŲ KRITERIJŲ TAIKYMAS ĮVERTINTI DIRBAMŲ DIRVOŽEMIŲ UŽTARŠĄ PAA

Santrauka
Tyrinėta dirbamų dirvožemių užtarša policikliniais aromatiniais angliavandeniliais (PAA) Lenkijos kaimo ir miesto vietovėse taikant tris vertinimo sistemas: olandiškąjį standartą, apimantį Σ10PAA, lenkiškąjį standartą, apimantį Σ9PAA (suminė užtarša ir užtarša pavieniais teršalais), ir lenkiškąjį IUNG standartą, apimantį Σ13PAA bei suderintą su organinės medžiagos kiekiu. 216 dirvožemio ėminių Σ16PAA kiekis atitiko 80–7264 μg · kg^{-1} koncentraciją, kurios vidutinis rodiklis – 395 μg · kg^{-1}. Didžiausią PAA kiekį dirvožemiuose lėmė industrijos poveikis. Vidutinės koncentracijos, esant Σ13PAA, Σ9PAA ir Σ10PAA, buvo atitinkamai 350, 260 ir 289 μg · kg^{-1}. Pagal taikytus standartus, ne mažiau kaip 90% dirvožemio ėminių galima vertinti kaip neužterštus.

Raktažodžiai: PAA, dirvožemio kokybės kriterijus, dirvožemio užterštumas