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IDENTIFICATION OF DIOXINS IN FOREST SOIL

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Abstract. The study aimed to determine the level of contamination by dioxins of the forest soil samples collected from two sites not adjacent to potential sources of industrial pollution. The results were compared with the data on soils from the Warsaw area and from non-contaminated areas (natural background). Chemical analyses showed that the amount of dioxins contained in the forest soils was 0.48 and 4.70 $ng \cdot kg^{-1}$, respectively. These values correspond with those characteristic of the natural background (1.0−5.0 $ng \cdot kg^{-1}$ soil), suggesting that dioxins have not accumulated in the forest soils and thus do not pose any threat to the living organisms.

Key words: dioxins, TEQ, forest soil, contamination

INTRODUCTION

The scientific and technological progress makes it possible to improve the accuracy of environmental research and to observe changes in the natural environment. This allows a faster response to undesirable changes and enables prevention of environmental threats and pollution. Due to the advances in chemical analytical techniques, chemical compounds can be detected in very low concentrations. Apart from such compounds as carbon dioxide, nitrogen oxide, etc., which are released to the atmosphere, water and soil in high concentrations, there are also some groups of chemical compounds, among them dioxins, having a very low concentration but causing a major environmental hazard.

Dioxins are relatively little known chloroorganic and aromatic compounds whose molecules show a high thermal stability and chemical resistance to oxidation and biological degradation. Dioxins comprise three groups of compounds that co-occur and have similar toxic properties and common sources, namely polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) [Grochowalski and Chrząszcz 1997]. These compounds are formed as by-products of human activity or as a result of natural processes on the Earth [Poszyler--Adamska i Czerniak 2006]. The main anthropogenic sources of dioxins are plants in

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which chlorine-containing communal, hospital and industrial wastes are incinerated and where technological regimes are not carefully followed [Grochowalski 2000]; fires and explosions of big transformers that contain polychlorinated biphenyls as compounds ameliorating cooling properties (local pollution); and various chemical plants (especially paper mills and herbicide-producing plants) [Standberd et al. 1998, Bergqvist et al. 1999]. In the production of some pesticides and herbicides, a side reaction occurs in which two molecules of chlorophenolate condense to produce one molecule of PCDD. Yet another source of dioxins is the car industry. As shown by Marklund [1987], PCDDs and PCDFs are emitted when lead gasoline with the addition of chlorine hydrocarbon as a scavenger of free radicals is used. The natural sources of dioxins include volcanic eruptions, forest fires, and storms with lightning. Some microorganisms, e.g. the soil fungus *Penicillium*, produce 2,4-dichlorophenol. Some other soil organisms, such as the fungus *Phanerochaete chyrosporium* (which can decompose DDT, too) and the soil bacteria *Pseudomonas*, are able to decompose dioxins without being adversely affected.

The PCDDs/PCDFs contents of soil have been on the increase since the first half of the 20th century. The concentration of dioxins in the soil depends on various factors such as the power of PCDDs/PCDFs adsorption on small soil particles, the kind of soil, its humidity, percolation degree**,** and pH value. The deposition of these compounds in upper soil layers depends also on the degree of dilution connected with the blending of different layers due to erosion or human activity. Dioxins move vertically as a result of the saturation of sorption places, migration of organic solvents, and ground works. Usually, PCDDs/PCDFs reach the depth of 15−30 cm but in a sandy soil they can migrate to deeper layers, especially aquifers [Helling et al. 1973]**.**

Balance of the main matter-conversion processes in a forest ecosystem is the precondition for its permanent existence. Each significant change in chemical balance disturbs homeostasis and the quantitative and qualitative succession of individual components of flora and fauna, thus causing degradation to the forest environment. It is therefore necessary to investigate the factors that contribute to such changes.

The present study was aimed at evaluating the degree of contamination by dioxins of forest soils in the areas not neighbouring on the sources of industrial pollutant emissions.

MATERIAL AND METHODS

The study was based on two forest ranges distant from the sources of chemical contaminants, i.e. the Orchówek Forest Range (Gniezno Forest District) and the Czarnylas Forest Range (Antonin Forest District). Soil was sampled in November 2005 from under pine stands of age class II at a depth of 0.3 m.

Due to very high levels of humus compounds in the soil it was necessary to modify analytical methods for determining the concentration of dioxins. The samples were prepared according to procedures based on liquid-solid extraction and multistage liquid chromatography. Analyses were conducted in the certified Laboratories for Trace Organic Analysis of the Cracow University of Technology, using gas chromatography combined with mass spectrometry with double fragmentation of the particle tested (Finnigan MAT

GCQ and GC/MS/MS equipment). The recovery of the analyte was calculated on the basis of standards labelled prior to extraction by isotopes ^{13}C-PCDD and ^{13}C-PCDF. The calculated detection limit was 0.002 ng in 1 kg of sample. The analytical techniques were in accordance with the EPA Method 1613 [1990] and with laboratory procedures [Grochowalski 2000].

Among 210 congeners, those with positions 2, 3, 7 and 8 in the molecule substituted with chlorine atoms were determined. To establish the potential toxicity of soil samples, seventeen most toxic PCDD/PCDF congeners were considered. The level of sample toxicity was expressed as a toxic equivalent (TEQ) computed on the basis of analytical results on the mass concentration of the congeners. The numerical value of TEQ is the sum of the values of partial parameters each of which was obtained by multiplying the mass concentration of an individual congener by its toxicity equivalency factor (TEF):

$$TEQ = \sum_{i=1}^{i=17} (m_i \cdot TEF_i)$$

where:

TEQ − International Toxic Equivalent of a sample (in mass units, usually ng or pg) − only for PCDDs/PCDFs,

m_i − mass of the *i*-th congener of PCDD/ PCDF (ng),

TEF_i − International Toxicity Equivalency Factor for the *i*-th congener of PCDD/PCDF, in relation to the toxicity of 2,3,7,8-TCDD (the most toxic dioxin).

According to the WHO recommendations of 1998, the TEF value for the most toxic 2,3,7,8-TCDD was assumed to be 1, and the values for the least toxic PCDDs/PCDFs, i.e. OCDD and PCDF, were 0.0001.

RESULTS AND DISCUSSION

The representative analytical results were tabulated. The table shows the contents of 17 congeners determined for forest soils from two forest ranges, and the values of TEF in standard units.

The total level of PCDDs and PCDFs congeners in the soil samples from the Gniezno Forest District was low (0.4832 ng-PCDD/F-TEQ · kg^{-1} soil). The samples from the Antonin Forest District had a ten times higher dioxin content (4.7063 ng-PCDD/F-TEQ · kg^{-1} soil). To compare, the dioxin contamination levels found by Grochowalski in industrialised areas in the years 1997−2000 were 10.0−20.0 ng-TEQ · kg^{-1} soil in the surface layer [Grochowalski and Chrząszcz 1997, Grochowalski 2000]. In Krakow, in the areas where household wastes are incinerated, the dioxin contents reached up to 850 ng-TEQ · kg^{-1}, whereas in unpolluted areas (e.g. the Tatra National Park or Magurski National Park) they ranged from 1 to 5 ng-TEQ · kg^{-1}. The latter values correspond with those for the natural background that have resulted from the natural chemical processes taking place on the Earth for millions of years, and can serve as a reference for comparing environmental

samples. Research carried out by Fiedorov and Miasojedov [1990] established the admissible levels of TCDDs as dependent on the land-use pattern. According to them, the dioxin contents should not exceed 10 ng-TEQ · kg^{-1} for agricultural areas, 50 ng-TEQ · kg^{-1} − for non-agricultural areas, and 250 ng-TEQ · kg^{-1} − for industrial areas. Our values were comprised within the above limits, which suggests that dioxins have not accumulated in the forest soils studied.

Further research is needed to determine the directions of migration, and to understand the processes of biodegradation of dioxins in a soil-water environment.

Tabela. Zawartość kongenerów PCDDs i PCDFs w próbkach gleb leśnych pobranych na terenie Nadleśnictwa Antonin (gleba A) i Nadleśnictwa Gniezno (gleba B)

Table. Contents of PCDDs and PCDFs congeners in forest soils sampled from area of Antonin Forest District (soil A) and Gniezno Forest District (soil B)

No − Lp.	PCDDs/PCDFs	TEF_i	m_i ng · kg^{-1}		$TEQ_i = m_i\ TEF_i$ ng-TEQ · kg^{-1}	
			Gleba − Soil A	Gleba − Soil B	Gleba − Soil A	Gleba − Soil B
1	2,3,7,8-TCDD	1	0.271	0.093918	0.27052	0.0939183
2	1,2,3,7,8-P_5CDD	1	0.355	0.072054	0.35521	0.0720543
3	1,2,3,4,7,8-H_6CDD	0.1	0.397	0.104652	0.03967	0.0104652
4	1,2,3,6,7,8,-H_6CDD	0.1	0.611	0.287264	0.06112	0.0287264
5	1,2,3,7,8,9-H_6CDD	0.1	0.472	0.216147	0.04722	0.0216147
6	1,2,3,4,6,7,8-H_7CDD	0.01	10.05	2.316089	0.10045	0.0231609
7	OCDD	0.0001	105.3	9.298244	0.01053	0.0009298
8	2,3,7,8-TCDF	0.1	6.338	0.322935	0.63382	0.0322935
9	1,2,3,7,8-P_5CDF	0.05	3.332	0.073752	0.16659	0.0036876
10	2,3,4,7,8-P_5CDF	0.5	4.534	0.048131	2.26702	0.0240655
11	1,2,3,4,7,8-H_6CDF	0.1	2.193	0.628994	0.21934	0.0628994
12	1,2,3,6,7,8-H_6CDF	0.1	1.958	0.445847	0.19576	0.0445847
13	1,2,3,7,8,9-H_6CDF	0.1	2.326	0.329482	0.23262	0.0329482
14	2,3,4,6,7,8-H_6CDF	0.1	0.091	0.050083	0.00907	0.0050083
15	1,2,3,4,6,7,8-H_7CDF	0.01	8.714	2.500407	0.08714	0.0250041
16	1,2,3,4,7,8,9-H_7CDF	0.01	0.768	0.143651	0.00768	0.0014365
17	OCDF	0.0001	25.14	4.135243	0.00251	0.0004135
Result of determination Wynik oznaczenia		$TEQ = \sum TEQ_i$ (i = 1, …, 17)			4.7063	0.4832

PCDDs − polychlorinated dibenzodioxins − dibenzodioksyny polichlorowane
PCDFs − polychlorinated dibenzofurans − dibenzofurany polichlorowane
TEF_i − Toxicity Equivalency Factor of individual congener − współczynnik równoważności toksycznej danego kongenera
m_i − determined mass of individual congener − oznaczona masa danego kongenera
TEQ_i − partial Toxic Equivalent − cząstkowy równoważnik toksyczny TCDD

CONCLUSION

The level of dioxins in the soil from the Orchówek Forest Range, expressed as TEQ, was 0.48 ng·kg^{-1}, and that in the soil from the Czarnylas Forest Range reached 4.70 ng · kg^{-1}. Even the higher value fell within the range characteristic of the natural background (1.0−5.0 ng · kg^{-1} soil). This indicates that the compounds in question have not accumulated in the forest soils under study, hence they do not represent any threat to the biocenosis.

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IDENTYFIKACJA DIOKSYN W GLEBIE LEŚNEJ

Streszczenie. Celem pracy było określenie stopnia zanieczyszczenia dioksynami próbek gleb pobranych z dwóch nadleśnictw nie sąsiadujących bezpośrednio z potencjalnymi źródłami zanieczyszczeń przemysłowych. Uzyskane wyniki porównano z danymi dotyczącymi gleb z terenów położonych w okolicy Warszawy oraz z terenów ekologicznie czystych (tło naturalne). Analizy chemiczne wykazały, że zawartość dioksyn w badanych glebach leśnych wynosi odpowiednio 0,48 i 4,70 ng · kg^{-1} gleby i odpowiada wartościom charakterystycznym dla tła naturalnego (1−5 ng · kg^{-1} gleby). Stwierdzono, że dioksyny nie kumulowały się w glebie i nie stanowią zagrożenia dla organizmów żywych.

Słowa kluczowe: dioksyny, TEQ, gleba leśna, zanieczyszczenie

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