Polychlorinated dibenzo-*p*-dioxines and dibenzofurans in agricultural soils of the Czech Republic

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ABSTRACT

The set of 102 samples of agricultural soils was taken for the study of the load of agricultural soils with polychlorinated dibenzo-*p*-dioxins and dibenzofuranes (PCDDs/Fs). The background value of PCDDs/Fs in agricultural soils of the Czech Republic was determined. The soils with different sources of the load of PCDDs/Fs were compared. It was concluded that fluvisols in fluvial zones and soils with long-term sludge application are soils with the highest contents of PCDDs/Fs. The soils affected by imission outputs show a lower intensity of the load with PCDDs/Fs that is characterised by higher content of toxic congeners.

Keywords: polychlorinated dibenzo-*p*-dioxins and dibenzofurans; persistent organic pollutants; agricultural soil; contamination

The paper brings the information about the load of agricultural soils with polychlorinated dibenzo-*p*-dioxines and dibenzofurans (PCDDs/Fs) in the Czech Republic. The research is the continuation of the work started in 1999 (Podlešáková et al. 2000).

PCDDs/Fs are three aromatic nucleus compounds with 1–8 substituted chlorine atoms. The substances are also mono-octa substituted and the substances with 4–8 chlorine atomic are called polysubstituted. 75 substances of dibenzo-*p*-dioxines and 135 substances of dibenzofurans could be originated generally (Holoubek et al. 2002). Only seventeen most toxic substances are used for the evaluation of the load of the environment with PCDDs/Fs. The concentrations of individual substances are multiplied by their toxicity factors (TEF 0.01–1) derived from the human-toxicological studies and reflect the risk of cancerogenity. Resultant sum of these values determines the load with PCDDs/Fs and is used as an international toxicity equivalent quotient (I-TEQ PCDDs/Fs) or World Health Organisation toxicity equivalent quotient (WHO PCDDs/Fs). The differences could be found between toxicity factors of 1, 2, 3, 7, 8 PeCDD and OCDD (octachlordibenzodioxin) congeners for human/mammals risk. The differences between I-TEQ and WHO TEQ PCDD/F values only rarely overcome the range of analytical deviation of the assessment (Dyke and Stratford 2002). The I-TEQ PCDDs/Fs has been used in this work since 1999 (Podlešáková et al. 2000).

The risk derived from increased exposition with PCDDs/Fs related with bioaccumulative tendency based on high solubility of PCDDs/Fs in fats. PCDDs/Fs are persistent substances and the period of their persistence in fat tissues of living organisms could outreach 15 years. The persistence in soils is determined from 3 to 18 years. The 2, 3, 7, 8 tetra-chorine-dibenzo-dioxine (2, 3, 7, 8 TeCDD) is designated as the most toxic congener because of its high metabolism transformation resistance in the body. All the substituents with 2, 3, 7, 8 position are characterised by increased toxicity. Only 2, 3, 7, 8 TeCDD is supposed to cause the human cancerogenity. Many serious defects such as teratogenity, imunotoxicity, skin damage (chlorine-acne) could be caused by increased load of the organism with PCDDs/Fs (Holoubek et al. 2002). These substances are included on the list of persistent organic pollutants (POPs) of Stockholm convention that observed the most important POPs in the environment on the world scale. The load of many components of the environment with PCDDs/Fs including the soil was incorporated in the national stocktaking of POPs in the Czech Republic (Holoubek et al. 2003).

PCDDs/Fs enter into the environment mostly by burning processes. They can also originate from the chemical production as its by-products. They can be concieved as practically omnipresent (Holoubek et al. 1999). PCDDs/Fs have no economic importance and are not produced purposely. PCDDs/Fs enter into the soil by imission outputs (Jech et al.

1999), by the sludge application (Jones and Sewart 1995, Podlešáková et al. 2000, Schaecke and Pöplan 2000), and by floods (Holoubek et al. 2002, Petruš et al. 2003, Vácha et al. 2003). PCDDs/Fs are characteristic for their low mobility in the soil profile, they are not transported into ground water table intensively and their transfer from soil into plants via roots of the plants is minimal (Simonich and Hites 1995). The most important ways of plant contamination with PCDDs/Fs are the contact of polluted water, soil, sludge or elevated imission outputs. The input of PCDDs/Fs into human body via food chain is a decisive way of the exposition (Holoubek and Kaláčková 1992).

The load of the environment including agricultural soils with PCDDs/Fs has been observed since the second half of the nineties in the Czech Republic (Kalač 1995, Vácha et al. 2001). The information about PCDDs/Fs in agricultural soils of the Czech Republic obtained in Central Institute for Supervising and Testing in Agriculture, Agency of Nature and Landscape Protection or some universities is available at present (Holoubek et al. 2003, Petruš et al. 2003).

Compared to the world scale the average and critical values of PCDDs/Fs in soils were determined rather sporadically. The Methodological Approach of the Ministry of Environment of the Czech Republic (MŽP 1996) determines contents for A limit 1 ng/kg (background value of I-TEQ PCDDs/Fs in soils), B limit 100 ng/kg (average of A and C limits), and C limit (decontamination limit) 500 ng/kg for residential areas, 1000 ng/kg for recreational areas, and 10 000 ng/kg for industrial areas. Legislative norm in Netherlands determines the limit value of I-TEQ PCDDs/Fs 10 ng/kg in agriculture soils. German proposal supposes use of the soil for agriculture without any limitation for the values up to 5 ng/kg I-TEQ PCDDs/Fs, the use of the soil for agriculture and horticulture with the controls for the values 5–40 ng/kg I-TEQ PCDDs/Fs, and limited use for agriculture with minimal transfer of PCDDs/Fs for the values 40–400 ng/kg I-TEQ PCDDs/Fs. The value 20 ng/kg I-TEQ PCDDs/Fs was determined as an indicative limit for agricultural use of the soils in Switzerland. The proposal of the amendment of the Czech Regulation No. 13/1994 to Soil Protection Act (Sáňka et al. 2002) includes the value 1 ng/kg I-TEQ PCDDs/Fs as a prevention limit (background value) for agricultural soils.

MATERIAL AND METHODS

The set of 102 soil samples was taken out on the territory of the Czech Republic. The way of the load of the soils with PCDDs/Fs and terrain characteristics selected the localities to subsets. The first division includes the subsets with industrial load (the vicinity of industrial sites), fluvial load (the areas under periodical floods), and load from the sludge application on agricultural soil. The second division concerns the subsets of highland localities, agricultural localities and localities in the vicinity of rural settlements.

The soil samples were taken out from humic horizons of agricultural soils. The depth of the soil layer for sampling was between 5 and 15 cm. The samples were stored and transported in jars and frozen to the temperature –18°C after the transport. The determined soil characteristics include soil type, soil subtype, sort of soil (soil texture), pH value and the content of C_{org}. The content of potentially dangerous elements (As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, V and Zn, total content and content in the extract of 2M HNO_3) and POPs substances (polycyclic and monocyclic aromatic hydrocarbons, chlorinated hydrocarbons, pesticides residua and petroleum hydrocarbons) were analysed in soil samples.

The content of PCDDs/Fs was analysed in soil extracts with the use of high-differentiated weight spectrometer (Ultima 2). The precision of the results is indicated with the deviation 20% of resulted sum including detection limit. A detailed analytical approach is described in the paper by Jech et al. (1999). The laboratory analysis was done in the laboratory with an international certificate.

The content of PCDDs/Fs and the value of I-TEQ PCDDs/Fs were obtained. The list of observed congeners is presented in Table 1. The basic statistic (programme Unistat 5.1) was used for the evaluation of the load of soil subsets with PCDDs/Fs. The congener analysis was performed for the comparison of qualitative differences of the load with PCDDs/Fs between the subsets. The contents

Table 1. Observed congeners of PCDDs/Fs

PCDD	PCDF
2, 3, 7, 8 TeCDD	2, 3, 7, 8 TeCDF
1, 2, 3, 7, 8 PeCDD	1, 2, 3, 7, 8 PeCDF
1, 2, 3, 4, 7, 8 HxCDD	2, 3, 4, 7, 8 PeCDF
1, 2, 3, 6, 7, 8 HxCDD	1, 2, 3, 4, 7, 8 HxCDF
1, 2, 3, 7, 8, 9 HxCDD	1, 2, 3, 6, 7, 8 HxCDF
1, 2, 3, 4, 6, 7, 8 HpCDD	1, 2, 3, 7, 8, 9 HxCDF
	2, 3, 4, 6, 7, 8 HxCDF
OCDD	1, 2, 3, 4, 6, 7, 8 HpCDF
	1, 2, 3, 4, 7, 8, 9 HpCDF
OCDF	PCB 189, PCB 170, PCB 180

and I-TEQ PCDDs/Fs were compared with the contents of the other POPs substances (PCBs and polycyclic aromatic hydrocarbons-PAHs) and the reciprocal dependencies of their presence in soils were searched.

RESULTS AND DISCUSSION

The background value of I-TEQ PCDDs/Fs 1 ng/kg was processed on the basis of the evaluation of the set of 102 samples of agricultural soils. The value shows an agreement with the Methodological Approach of the Ministry of Environment (MŽP 1996).

With respect to I-TEQ PCDDs/Fs values the set of samples was separated to three levels:

0.1–0.4 ng/kg the group of soils from clean areas with sporadic presence of the industry

0.5–1.5 ng/kg the group of soils with mixed load and soils from highland areas

1.6–14 ng/kg the group of soils with fluvial load, marked industrial load and soils with long-term sludge application

The comparison of soils with different types of load showed that the fluvisols in many river basins belong to the most polluted soils in the Czech Republic. At the same time the increased load of fluvisols by potentially dangerous elements and POPs was documented (Vácha et al. 2003). The increase of the load of fluvisols by dangerous substances was usually detected near the settlements down the stream. Not only industrial settlements caused an increasing load of the fluvisols in their vicinity. The elevated load of fluvisols with PCDDs/Fs was observed in the vicinity of the settlements of medium size (district towns) very probably due to the production of municipal wastewater in spite of an increasing number of sewage disposal plants. The median values of the contents of PCDDs/Fs in soils of individual subsets are presented in Figure 1.

The similar characteristics of the contents of PCDDs/Fs in comparison with the fluvisols show the soils with long-term application of the sludge. More than 10-year period of sludge application was determined.

The contents of PCDDs/Fs in the soils from highland areas move under upper limit of their background value in the agricultural soils. The increased values of PCDDs/Fs were observed not only in the soils of highland areas with increased imission fallouts in the north of the Czech Republic (Orlické hory, Krkonoše, Krušné hory) but in the soils of relatively clean Šumava mountains as well. Long distance transfer of the imission fallouts caused higher load of the soils of highland areas with PCDDs/Fs in comparison with the soils of industrial areas (Figure 1).

Low contents of PCDDs/Fs in soils were detected in soils from open agricultural landscape. Soils in the vicinity of rural settlements show only a slight increase of I-TEQ PCDDs/Fs value.

The congener analysis presents the proportion of individual PCDDs/Fs congeners on general load of soils of subsets (Figure 2). OCDD is the most frequent group of the congeners in all soil subsets. The highest proportion of OCDD was observed in soils with sludge application. The widest rate between the sum and I-TEQ PCDDs/Fs in the soil with sludge application could be explained by low

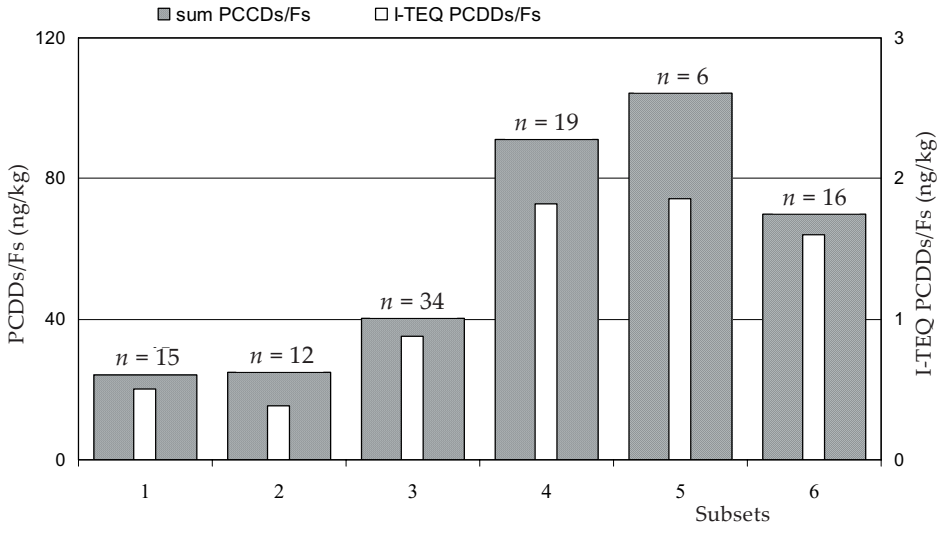

Figure 1. The sum PCDDs/Fs and I-TEQ PCDDs/Fs in soils of individual subsets (1. vicinity of rural settlements, 2. agricultural soil, 3. industrial, 4. fluvial, 5. sludge application, 6. highland localities)

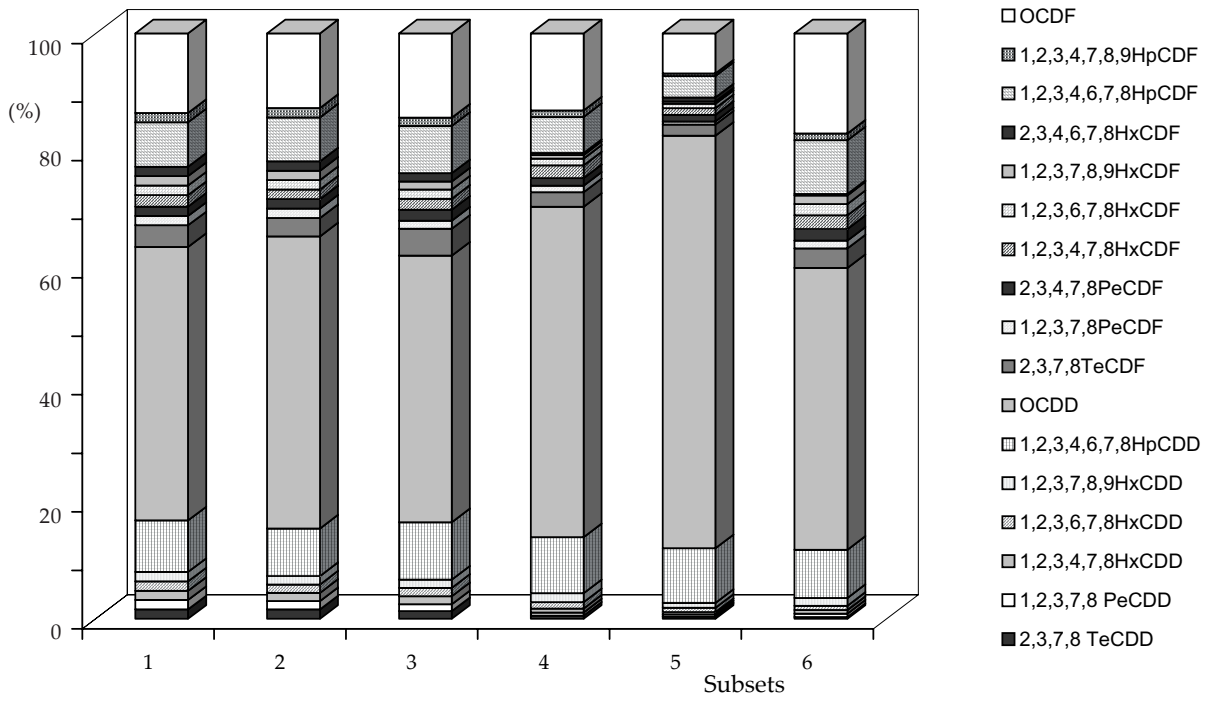

Figure 2. The congener analysis of soil load with PCDDs/Fs of individual subsets (1. vicinity of rural settlements, 2. agricultural soil, 3. industrial, 4. fluvial, 5. sludge application, 6. highland localities)

toxicity of OCDD congeners. The similar characteristics could be seen in the case of fluvisols. On the contrary, the soils in the vicinity of rural settlements show the lowest proportion of OCDD congeners and are characteristic for a higher proportion of the other congeners. It causes the increase of the toxicity and a thin rate between the sum and I-TEQ of PCDDs/Fs can be observed in soils from highland and industrial areas (Figure 1). The comparison between soils from open agricultural areas and soils from the vicinity of rural settlements shows a similar trend. The imission load of soils from the vicinity of rural settlements probably leads to the increase of the toxicity of this load. It could result from the presented findings that imission load is characteristic for a higher risk of toxicity in comparison with the fluvial load and sludge application load.

The comparison of the load of the soils with PCDDs/Fs and with PCB_6 and PAHs was performed. There was an idea to use less expensive analyses as the indicators of soil load by PCDDs/Fs.

Nevertheless, a low dependency was observed not only between I-TEQ PCDDs/Fs and the sum of PAHs but also between I-TEQ PCDDs/Fs and PCB_6. Closer dependencies were determined between the values of I-TEQ PCDDs/Fs and I-TEQ PCB but the presence of marked deviations was nor exceptional. Besides, the value of I-TEQ PCB was processed on the base of analysis of 14 toxic PCBs congeners, where the financial requirement is not too different from PCDDs/Fs analysis.

The results that could be deduced from the analysis of the set of 102 soil samples reflect the load of soil of individual subsets with PCDDs/Fs. From the assessment of background value of I-TEQ PCDDs/Fs (1 ng/kg) was concluded that the general load of agricultural soils of the Czech Republic does not overcome average values of other countries of Europe.

Fluvisols and soils with long-term application of sludge could be marked as soils with the highest load with PCDDs/Fs in the set of samples. The highest relative toxicity from the observed subsets was found in soils with imission load in the vicinity of rural settlements where an increased proportion of toxic PCDDs/Fs congeners was present. But the intensity of imission load is usually lower in comparison with fluvial and sludge application load.

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ABSTRAKT

Polychlorované dibenzo-*p*-dioxiny a dibenzofurany v zemědělských půdách ČR

Na souboru 102 vzorků zemědělských půd, odebraných na území ČR, byla studována zátěž polychlorovanými dibenzo-*p*-dioxiny a dibenzofurany (PCDD/F). Byla stanovena pozaďová koncentrace uvedených látek v zemědělských půdách a byly porovnány půdy s rozdílným zdrojem zátěže PCDD/F. Bylo zjištěno, že k nejvíce zatíženým půdám se řadí fluvizemě nivních oblastí a půdy s dlouhodobou a opakovanou aplikací kalů ČOV. Půdy s imisní zátěží PCDD/F vykazují menší celkovou intenzitu zátěže, která je však charakteristická vyšším podílem toxických kongenerů.

Klíčová slova: polychlorované dibenzo-*p*-dioxiny a dibenzofurany; perzistentní organické polutanty; zemědělská půda; kontaminace

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