State of contamination of agricultural soils after floods in August 2002

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ABSTRACT

Sixteen soil samples from agriculturally used soils flooded in August 2002 were taken because new information about the state of soil contamination was required. The area in the Vltava river basin from Prague to Mělník and in the Labe river basin from Neratovice to Děčín was investigated. The samples were taken in September 2002 and analysed for the contents of potentially risky elements and persistent organic pollutants, including persistent dibenzodioxins and dibenzofurans. The results were compared with the data from the project *Labe 1992*. The findings show a low soil load of potentially risky elements and a slight reduction of their contents in soil in comparison with the state in 1992 (except for vanadium). The same situation was observed in the case of persistent organic pollutants. Only the content of DDT was increased in the soils of most localities after floods in August 2002. This finding needs further observations on a larger collection of samples. The dreads resulting from expected soil contamination by dibenzodioxins from Spolana Neratovice factory were not confirmed and their contents in the soils of observed localities meet the requirements for plant production without any reduction.

Keywords: floods; potentially risky elements; persistent organic pollutants; dibenzodioxins and dibenzofurans

This project was actually included in a research program of the Research Institute of Soil and Water Conservation in Prague *The Contamination of the Soil and Other Ecological Media through the Soil by Risky Substances in Interaction with the Other Degradation Processes* after floods in the basins of the Vltava and Labe rivers in August 2002. The need of the solution to the problem resulted from the hazard of potential soil contamination on flooded areas by many risky substances. Increased loads of risky elements and persistent organic pollutants in Fluvisols were reported in the same areas in 1992 (Podlešáková et al. 1994). The situation after floods could change in many ways. Increased attention was paid especially to the chemical factory Spolana Neratovice, where the old load of extremely increased content of 2,3,7,8 tetrachlorodibenzodioxin (2,3,7,8 TCDD) in some not sufficiently protected facilities is known very well. The risk of leakage of high concentrations of 2,3,7,8 TCDD into the water of the Labe river could not be prevented. The aim of the project was to examine the state of soil contamination in observed areas and possibly to recommend the reduction of plant production at contaminated sites.

MATERIAL AND METHODS

Soil samples from Ap horizons (5–15 cm) of selected localities of the flooded area were taken. The observed area covered the basin of Vltava river from north of Prague to Mělník and the basin of Labe river from Neratovice (Mlékojedy locality) to Děčín (Boletice nad Labem locality). The amount of 16 samples from 15 localities was analysed. One sample of soil and one sample of top layer sediment (thickness 5 mm) were taken in Kelské Vinice locality. The map of the observed area is presented in Figure 1.

A methodological approach was developed for the compatibility with the information resulting from the project *Labe 1992*. The choice of the localities mostly followed this aim. The contents of risky elements and persistent organic pollutants (POPs) were analysed in the samples. The list of analyses is presented in Table 1. Total contents (extract of mixture of the acids, Hg by AMA method) of 12 risky elements (As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V and Zn) in the samples were analysed in central laboratories of the Research Institute of Soil and Water Conservation in Prague. The concentrations of POPs (monoaromatic, polyaromatic and chlorinated hydrocarbons, residues of pesticides and petroleum hydrocarbons) were analysed in the laboratory of AQUATEST Praha by the methods reported in the papers of Němeček et al. (1994) and Podlešáková et al. (1998). The analyses of the content of persistent dibenzo-p-dioxins and dibenzofurans (PCDD/F) in the samples were carried out in the laboratory of AXYS VARILAB in Vrané nad Vltavou by the methods reported in the paper of Jech et al. (1999) and summarised in the paper of Podlešáková et al. (2000).

The evaluation of the results was made in relation to the terrain characteristics by the use of summary statistic. The concentrations of the pollutants in the samples were compared with their concentrations in the soils 10 years ago. The content of polyaromatic hydrocarbons (PAHs) was evaluated by the use of TEF (toxic equivalent factor) that formulates a carcinogenic risk. TEF value is derived from the toxic equivalents of individual compounds (Table 2) and their concentrations.

Figure 1. Map of the observed area

Table 1. List of the analyses

Analyses	Laboratory	Samples
pH, C_{ox}	RISWC Praha	16
As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn – total contents	RISWC Praha	16
Monoaromatic hydrocarbons		
benzene, toluene, xylene, ethylbenzene	Aquatest Praha, a.s.	16
Polyaromatic hydrocarbons		
naphthalene, anthracene, pyrene, fluoranthene, fenanthrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)anthracene, benzo(a)pyrene, indeno(c,d)pyrene, benzo(ghi)perylene		
Chlorinated hydrocarbons		
PCB, HCB, α-HCH, β-HCH, γ-HCH		
Pesticides		
DDT, DDD, DDE		
Petroleum hydrocarbons		
PCDF		
2,3,7,8 TeCDF, 1,2,3,7,8 PeCDF, 2,3,4,7,8 PeCDF, 1,2,3,4,7,8 H_xCDF, 1,2,3,6,7,8 H_xCDF, 1,2,3,7,8,9 H_xCDF, 2,3,4,6,7,8 H_xCDF, 1,2,3,4,6,7,8 H_pCDF, 1,2,3,4,7,8,9 H_pCDF, OCDF PCB 189, PCB 170, PCB 180	Axys Varilab, s.r.o.	16
PCDD		
2,3,7,8 TeCDD, 1,2,3,7,8 PeCDD, 1,2,3,4,7,8 H_xCDD, 1,2,3,6,7,8 H_xCDD, 1,2,3,7,8,9 H_xCDD, 1,2,3,4,6,7,8 H_pCDD, OCDD		
PCB		
PCB 77, PCB 126, PCB 169, PCB 105, PCB 114, PCB 118 + 123, PCB 156, PCB 157, PCB 167		

C_{ox} = organic carbon

The evaluation of the PCDD/F in samples was made by the use of I-TEQ factors, the principle is reported by Podlešáková et al. (2000). Only three samples from the period before the floods were available for the comparison of PCDD/F concentrations in soils.

RESULTS AND DISCUSSION

RISKY ELEMENTS

The soil load of potentially risky elements after floods is presented in Table 3. The number of exceeded values over prevention limit (limit A) and indication limit (limit B) is reported in the table. The used limit values were proposed for the amendment of Czech Regulation No. 13/1994 to Soil Protection Act (Sáňka et al. 2002). Prevention limit was derived from background values of risky elements in the soil. Indication limit gives the information about the risk of exceeding of safety concentrations of risky elements

Table 2. Toxic equivalents of PAHs

US EPA	Equivalent
Compound	
Benzo(a)pyrene	1
Benzo(a)anthracene	0.1
Benzo(b)fluoranthene	0.1
Benzo(k)fluoranthene	0.01
Indeno(1,2,3-cd)pyrene	0.1
Fluoranthene	0.01

Table 3. The numbers of values exceeding the proposed limit values of risky elements in soil

Element	Sediment		Soil		Soil 92	
	A	B	A	B	A	B
As	1	0	3	0	3	0
Be	1	–	1	–	7	–
Cd	1	1	8	0	8	2
Co	0	0	0	0	0	0
Cr	0	0	3	0	3	0
Cu	0	0	0	0	2	0
Hg	1	0	2	0	8	1
Mn	0	–	0	–	1	–
Ni	0	0	0	0	1	0
Pb	1	0	0	0	4	0
V	0	–	1	–	0	–
Zn	1	0	4	0	7	1

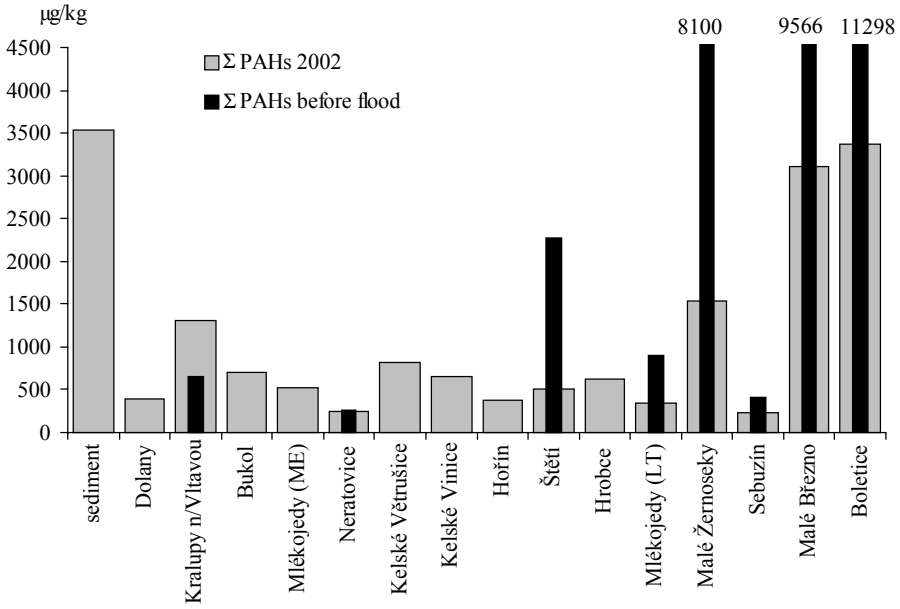

Figure 2. The sum of PAHs in soil after flood and in the past

in the plants. The concentrations of risky elements in the soil from 1992 are reported for comparison (soil 92). The values for the top layer sediment are reported individually.

Increased concentrations of As, Be, Cd, Hg, Pb and Zn were detected in the top layer sediment from Kelské Vinice locality. The values higher than the prevention limit were detected in all cases. The value of indication limit was exceeded in the case of Cd only. The concentrations of all elements except As, Cr and V reached the maximum in the top layer sediment. In the soils of all localities the value of indication limit was not achieved. The risk of the contamination of crops planted at the observed sites by risky elements is not imminent.

An increase in V concentrations was detected only in the soil in comparison with the state before the floods. The concentrations of most elements in the soils are increased after floods (in comparison with the state before the floods) in the localities of the river basin from Prague to Kelské Vinice. Decreased concentrations of these elements in the soils (in comparison with the state before the floods) were detected on most localities of the river basin from Štětí to Boletice nad Labem where the industrial towns of Lovosice and Ústí nad Labem are situated. The contamination of Fluvisols by many risky elements (Cd > Hg, Zn > Cu > Pb and Cr) was found in the past mostly in the vicinity of these towns (Podlešáková et al. 1994).

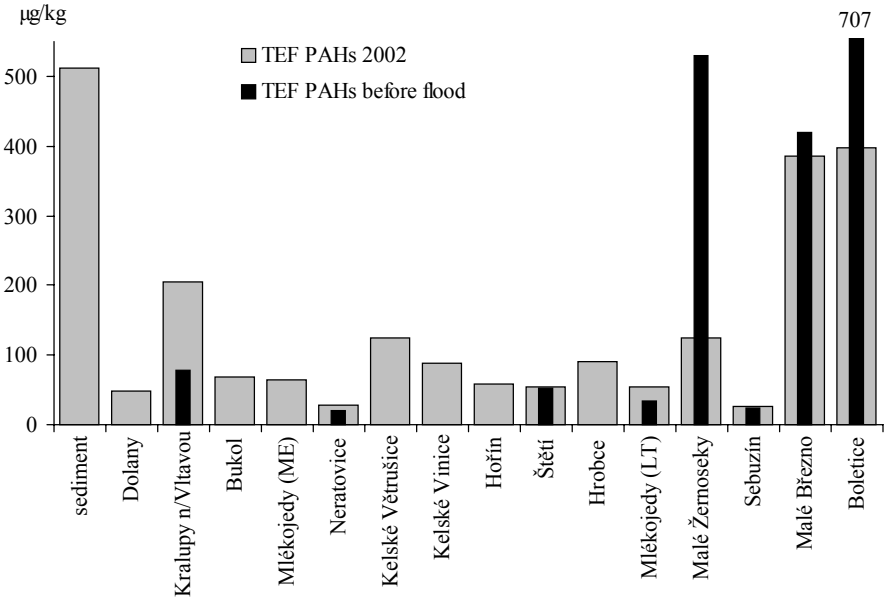

Figure 3. TEF values of PAHs in soil after flood and in the past

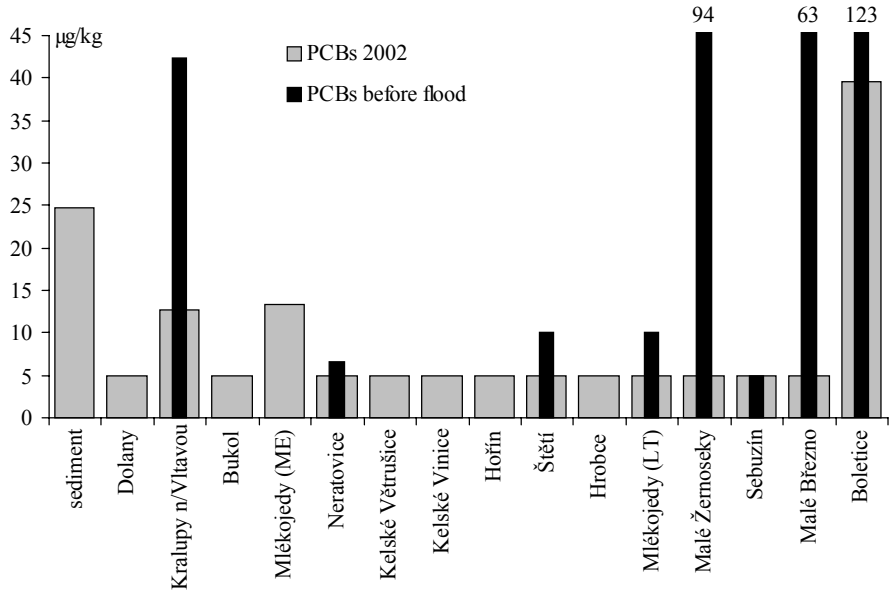

Figure 4. The sum of PCBs in soil after flood and in the past

PERSISTENT ORGANIC POLLUTANTS

Polyaromatic hydrocarbons (PAHs)

The values of the concentrations of the sum of polyaromatic hydrocarbons are presented in Figure 2. The highest load of PAHs was found in the top layer sediment from Kelské Vinice locality. We can draw a conclusion about an increased input of PAHs into the water of the Labe river from different sources. The concentration of PAHs in the top layer sediment exceeds the prevention limit of PAHs in agriculturally used soils three times. But the influence of increased concentrations of PAHs in water on their concentrations in soil is limited. In the soils of the basin of Vltava and Labe rivers from Prague to Ústí nad Labem the concentrations of PAHs are below the value of prevention limit for agricultural soils. The increase in the concentration of PAHs in the soils in the basin of Labe river from Ústí nad Labem to the north (the influence of industrial towns) is evident. Therefore all the concentrations of PAHs in Fluvisols reach lower values in comparison with the state ten years ago. The trend of decrease in high PAHs concentrations in Fluvisols in the basin of Labe river (Podlešáková et al. 1994) very probably relates with the increase in water quality in Labe during the last ten years. The risk for plant production

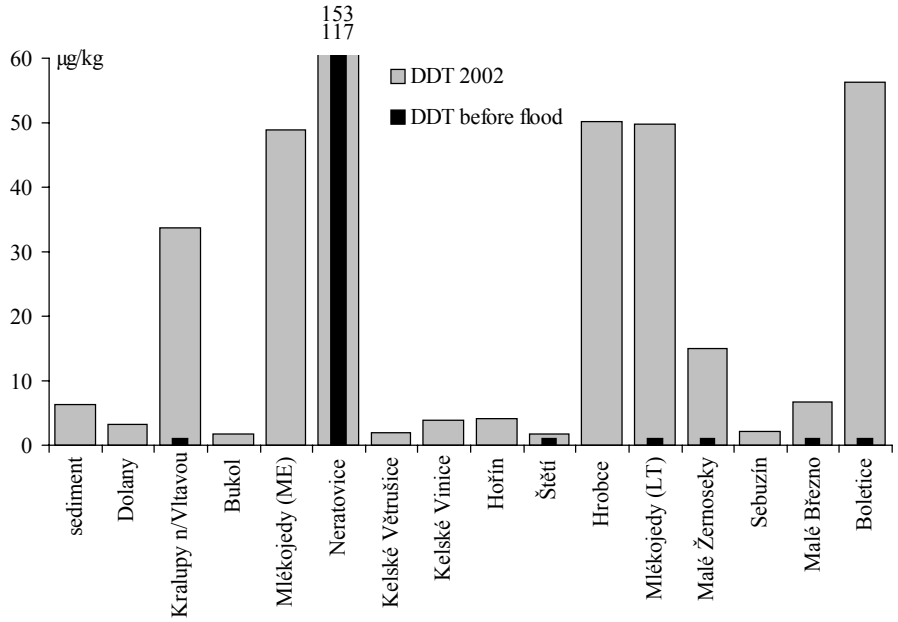

Figure 5. DDT in soil after flood and in the past

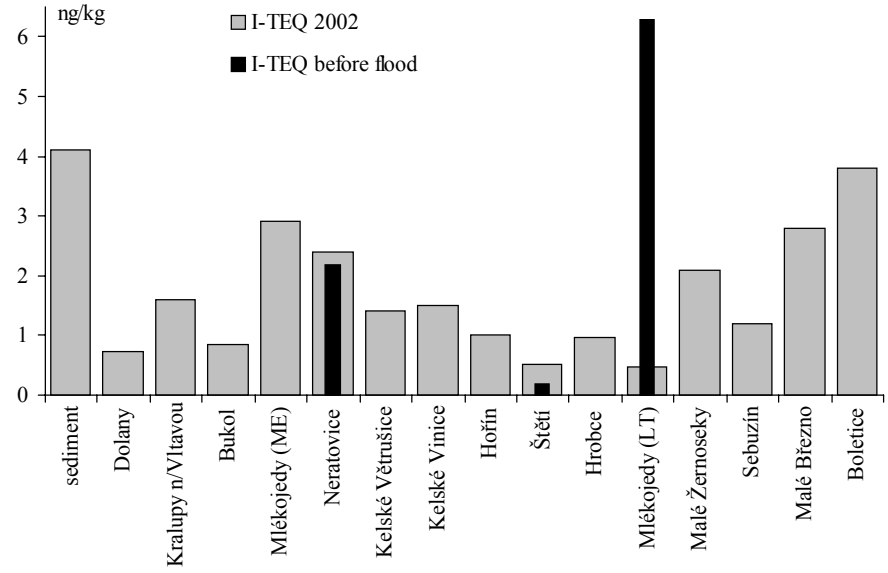

Figure 6. I-TEQ PCDD/F values in soil after flood and in the past

resulting from the concentrations of PAHs in the soil is lower after floods than ten years ago.

A similar result follows from a comparison of the values of toxic equivalent factors (TEF) of carcinogenic compounds from the group of PAHs (Figure 3). Increased persistence of these compounds in the soil results from the comparison of recent and older values (1992). The differences between these values are not so opposed as the differences between the values of the sum of PAHs.

Chlorinated hydrocarbons (ClHs)

The concentrations of the sum of six PCB compounds are presented in Figure 4. The concentration in the top layer sediment exceeds the proposed prevention limit for agricultural soils only slightly. PCB concentrations in the soils do not reach (except for Boletice nad Labem locality) the value of the proposed prevention limit for agricultural soils. A decrease in PAH concentration in Fluvisols of Labe in comparison with the situation in the past could be observed. The load of PCBs in the soils of the observed localities was not significant after floods.

DDT shows converse trends of occurrence in the Fluvisols of the Labe river contrary to other POPs (Figure 5). While the low concentrations of DDT were established in Fluvisols in recent past, the values exceeding the proposed prevention limit of DDT in agricultural soils of five localities were recorded after floods. DDT concentrations mostly exceed the prevention limit twice (three times in Boletice nad Labem locality). The leakage of a higher amount of DDT in floodwater from old loads or wrongly liquidated reserves could be assumed.

Petroleum hydrocarbons (PHs)

The leakage of petroleum hydrocarbons into floodwater documents their increased content in the top layer sediment where the concentration is 180 multiple of the proposed prevention limit for agricultural soils. The influence of this leakage of PHs on their concentration in the soils is limited. An increase in PH concentrations was detected in the Fluvisol of the Vltava river basin in Kralupy nad Vltavou locality only. In the Fluvisols of the Labe river basin the PH concentrations reached the same or markedly lower level (from Štětí locality to the north) in comparison with the state in recent past. The deterioration of the hygienic state of soils caused by the leakage of PHs into floodwater was not found.

Persistent dibenzo-p-dioxins and dibenzofurans (PCDD/F)

PCDD/F are a group of compounds that attract attention after the floods, first of all thanks to the Spolana Neratovice factory (2,3,7,8 TeCDD was produced in the factory as a by-product in the past). It could be concluded from Figure 6 that the maximum of the I-TEQ PCDD/F value was reached after floods in the top layer horizon in Kelské Vinice locality. This maximum value (4.1 ng/kg) of I-TEQ PCDD/F does not exceed for example the German limit for unlimited agriculture. The maximum value of I-TEQ PCDD/F in the soil (3.8 ng/kg) was detected in Boletice nad Labem locality. The value of I-TEQ PCDD/F did not exceed the background value (1.0 ng/kg) proposed for agriculturally used soils in the Czech Republic (Vácha et al. 2001) in seven localities (out of their total number fifteen). It is very presumptive that the massive leakage of

PCDD/F from the Spolana Neratovice factory into floodwater could not lead to so low values of I-TEQ PCDD/F in the soil. The obvious leakage of PCDD/F from the Spolana Neratovice factory into floodwater was not established by the comparison of individual PCDD isomers in Fluvisols, either. The prevailing content of OCDD and OCDF isomers and very low content of 2,3,7,8 TeCDD confirm other sources of PCDD/F in soils than the Spolana factory. Besides, a markedly higher value of I-TEQ PCDD/F was detected in Mlékojedy locality before the flood. The concentrations of PCDD/F in the soils of the observed localities do not pose any risk for plant production on flooded soils.

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Received on February 20, 2003

ABSTRAKT

Stav kontaminace zemědělských půd po povodních v srpnu 2002

Bylo analyzováno šestnáct vzorků zemědělských půd z ploch postižených povodněmi v srpnu 2002 s cílem získat první údaje o hygienickém stavu půd. Sledovaná oblast zahrnovala povodí Vltavy v úseku od Prahy k Mělníku a povodí Labe v úseku od Neratovic k Děčínu. Vzorky půd byly odebrány v září 2002 a byl v nich stanoven obsah potenciálně rizikových prvků a obsah perzistentních organických polutantů, včetně perzistentních dibenzodioxinů a dibenzofuranů. Výsledky rozborů byly porovnány s výsledky získanými v rámci projektu *Labe 1992*. Závěry potvrdily nízkou úroveň zátěže půd sledovaných lokalit rizikovými prvky a mírný pokles jejich obsahů při srovnání se stavem v roce 1992 (kromě vanadu). Podobná situace byly zjištěna v případě perzistentních organických polutantů. Pouze obsahy DDT dosahovaly po povodních v srpnu 2002 ve srovnání se stavem v nedávné minulosti zvýšených hodnot v půdách z většiny lokalit. Toto zjištění vyžaduje podrobnější šetření na rozšířeném souboru vzorků. Obavy vyplývající z kontaminace půd dibenzodioxiny ze Spolany Neratovice nebyly potvrzeny a jejich obsah v půdách sledovaných lokalit vyhovuje požadavkům na pěstování zemědělských plodin bez omezení.

Klíčová slova: povodně; potenciálně rizikové prvky; perzistentní organické polutanty; dibenzodioxiny a dibenzofurany

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