Risks Following from Husbandry on Agricultural Soils in Loaded Areas of the Czech Republic

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Abstract: In the Czech Republic, industrial areas, mining areas and military zones can be found. These areas represent potential risks for the agricultural production from the viewpoint of hygienic standards. The industrial areas and mining areas are the topic of the present study. The industrial areas are combined with present or past mining activities in the Czech Republic in most cases. The widest industrial areas located in North-Bohemian and North-Moravian regions were based on the mining of brown and black coal. North-Bohemian region was affected by the combustion of brown coal in the power stations during many years and the region was a part of the Middle-European area called black triangle. The problems with increased contents of risky elements (mainly As from brown coal combustion) and persistent organic pollutants in the soil are documented. North-Moravian region with the mining of black coal is typical with its industrial metallurgical activities. Increased contents of Cd and persistent organic pollutants-POPs (mainly polycyclic aromatic hydrocarbons-PAHs and dibenzo-p-dioxines and dibenzofurans-PCDD/F) in the soils of the region are a topical problem. In addition to this fact, mainly native soil owners use the soil for husbandry (gardens, crofts). The contents of risky elements and POPs (including PCDD/F) in selected soil samples from the area are documented. Next area of a similar kind is represented by the Příbram district where the mining and treatment of the ores has been under way since Middle Ages. The serious contamination of the agricultural soils by Pb, Cd, and Zn was and still is being solved by research projects. The contamination of the soil by As in the Kutná Hora district represents a typical past mining load caused by the spread of mining wastes on the soils in the vicinity of the medieval mining town Kutná Hora. The last type of the increased soil load presented is connected with fluvial zones of some rivers. The floods by contaminated water were the source of the soil contamination.

Keywords: potentially risky elements; persistent organic pollutants; dibenzo-*p*-dioxins and dibenzofuranes; husbandry on agricultural soils; mining activities and old soil load; contamination of fluvisoils

The article deals with the problems of the load of agriculturally utilised soils in the industrial and mining areas. Both kinds of load can be found in the Czech Republic and the areas can be differentiated as:
– the areas with the load resulting from the mining of metal ores,
– the areas with the load resulting from the mining of uranium ores,
– the areas with the load resulting from the mining of brown and black coal and their energy used,
– the areas of industrial towns with increased emission out-puts,
– the mountainous areas with the load resulting from increased imission out-puts,
– the areas of fluvial zones with the load resulting from floods by contaminated water.

The aim of this article is not a detailed analysis of the areas presented. The problems will be interpreted on the basis of the description of the soil contamination in particular localities from

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the areas mentioned. The areas with the load resulting from the mining of uranium ores will not be included because of the lack of data. The description of the areas will be classified in the dependence on the importance of the dimensions of the contaminated areas. Attention will be first focused on the areas with the mining of brown and black coal. The surface load of the soils with risky substances is caused due to the combustion of coal and the existence of metallurgy. Two widespread areas are affected in this way in the Czech Republic. They are called Northwest Bohemian imission region (NW of the Czech Republic) and North Moravian imission region (NE of the Czech Republic). The industrial towns where the load of the soils with risky substances in their vicinity has been detected are situated in these areas.

The mountainous areas in the Northwest and the North of the republic were affected by increased imission fall-outs in the second half of 20th century. Massive damage to the forests and the soil contamination were the consequences of that.

The load of the soils resulting from the mining of metal ores will be documented in the description of the two most important cases detected in the districts Příbram and Kutná Hora.

The last type of load is the contamination of fluvisoils in the fluvial areas of the most important Czech rivers where the loads of all the other sources join in.

MATERIALS AND METHODS

The data and results were obtained in the framework of the project "The monitoring of risky substances in soils and plants" that was funded by the Ministry of Agriculture of the Czech Republic. The project started in 1990 and was focused on the monitoring of the soil load by potentially risky elements. Since 1993, the load of soils and plants by persistent organic pollutants, has been also observed. In 1999, the observation was started of the polychlorinated dibenzo-*p*-dioxins and dibenzofuranes in agricultural soils. The project is still underway and more than 50% of the area of the Czech Republic have been evaluated by this monitoring by the present time. Some other data regarding the contents of risky substances in the soil profiles or in fluvisoils were obtained during the realisation of other research projects.

The soil samples were taken out from the humic horizons (except the soil profile samples) of arable land and grassland from the depth 5–20 cm. The soil and plant samples for risky elements analyses were taken out using non-metal equipment and were transported in plastic bags. The soil samples for the analyses of persistent organic pollutants were transported in glass containers and stored at –18°C.

The soil types and subtypess, the parent material of the soil, the description of the locality, and the assessment of co-ordinates by GPS were done determined in all localities. The following groups of risky substances were analysed.

Potentially risky elements (RE)

The contents of the following elements were determined: As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, V, and Zn.

The total contents in the extract obtained with an acid mixture (HNO_3, HF, $HClO_3$) and the contents in the extract obtained with 2M HNO_3 (cold method) were measured. The contents of RE in the extracts obtained with 1M NH_4NO_3 or EDTA were determined in selected soil samples. The sequential analysis using the method by Zeien and Brümmer (1989) was used in some cases. The laboratory analysis was realised in the laboratories of the Research Institute for Soil and Water Conservation, Prague.

Persistent organic pollutants (POPs)

The "Dutch list" was used for the selection of the substances in 1993. The substances from the groups of monocyclic aromatic, polycyclic aromatic, chlorinated and petroleum hydrocarbons were included into the Czech legislative norms (the Direction of Ministry of Environment No. 13/1994) for the soil protection. The list of substances is presented in Table 1. The laboratory analysis was done by order in a commercial accredited laboratory. The laboratory methods used were published by Němeček *et al.* (1994).

Polychlorinated dibenzo-*p*-dioxins and dibenzofuranes (PCDD/F)

The contents of 16 congeners were assessed and the sum and international toxic quotient (I-TEQ) PCDD/F were evaluated. The laboratory analysis was done by order in a commercial accredited laboratory. The laboratory methods used were published by Podlešáková *et al.* (2000).

Table 1. The summary of POPs

POPs
Monocyclic aromatic hydrocarbons
benzene, toluene, xylene, ethylbenzene
Polycyclic aromatic hydrocarbons
naphtalene, anthracene, pyrene, phluoranthene, phenanthrene, chrysen, benzo(b)phluoranthene, benzo(k)phluoranthene, 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
Others
styrene, 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
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

The evaluation of the results

The data were processed using the elementary statistical methods. The contents of the risky substances were compared with those in the proposal for renovation in the Directive of the Ministry of Environment No. 13/1994 Sb. (Sáňka *et al.* 2002). The proposal is constructed as a system of hierarchical limits. The preventive limit (limit A) was derived from the background values of RE and POPs in Czech agricultural soils. The indicative limit (limit B) was derived from the study of the mobility of RE in soil and their transfer from the soil into the plants. This limit indicates an increased risk of surpassing the critical plant loads by RE.

RESULTS AND DISCUSSION

The brown and black coal mining areas

The activities are concentrated in the two named regions of the Czech Republic. The load of the air reached maximum in the eighties years of 20^{th} century and the regions were categorised as imission areas due to the intensity of the load. The year averages of the day average concentrations reached the maximum value of 130 micrograms per cubic meter in the case of SO_4 and 140 micrograms per cubic meter in the case of solid fall-outs.

Northwest Bohemian imission region is located on the border of the Czech Republic with Germany and covers the area of eight districts (Děčín, Ústí nad Labem, Teplice, Most, Chomutov, Karlovy Vary, Sokolov and Cheb). Under the base of the mountains of Krušné hory is stretched a coal pelvis where the brown coal activities are still continued. Power stations are operated in the regions and they use mined brown coal with increased contents of As. The emissions from the power stations were one of the most important reasons for the high imission load of the region. In the nine tieths, the modernisation of the combustion technology focused on the installation of the chimney filters was realised. The load of the air by risky substances in the recent past affected the soil load in the vicinity of the industrial towns in the coal pelvis and the mountain area of Krušné hory as well.

The overground mining leads to the damage to the face of landscape. The mined areas were reclaimed predominantly, the mining activities are continued in two overground mines. One of them reached the base of the Krušné hory mountains. The problems with the stability of the slopes were observed because of the damage to the slope bases. In spite of the realisation of the technologies focused on the increase of the stability of the most endangered slopes, the problems are still existing.

The load enriched with As, Be and Cd was observed predominantly in the district with the highest values of the imission fall-outs. The characteristics of the load by individual elements are different. Cd is an element input into the soil mainly by human activities. The maps of the load with risky elements developed in our institute show increased loads of the soils with Cd, predominantly in the vicinity of the district industrial towns. The sporadically increased contents of Cd in agricultural soils were detected also in the area of the Krušné hory mountains.

The evaluation of the load of soils with Be and As is more difficult. In the case of As, particularly where the load shows the surface character, a mixture of anthropogenic and geogenic (ore zones in acid metamorphic rocks, As-CoNi formation) loads was observed. The load in the vicinity of the industrial towns shows anthropogenic character. The definition of the prevailing type of load in mountainous areas is more complicated.

The intensity of the load with risky elements (total contents) is the highest in the case of As (surpassing the indication limit). Total contents of Cd and Be exceeded indication limits only sporadically. On the base of the observation of the contents of elements in plants, it was concluded that the exceeding of the critical values of elements in plants occurred only exceptionally. In the case of As, only one case was observed in one area out of the whole region (Table 2).

The contents of POPs in the soils confirm increased loads of the soils in the vicinity of the district industrial towns in the region. Predominantly, the group of polycyclic aromatic hydrocarbons (PAHs) indicates increased loads due to the combustion processes on the base of the proportions of the individual substances (increased proportion of fluoranthene). The maximal content of fluoranthene in the soil reached 500% of the prevention limit (300 μg/kg). The load of the Krušné Hory mountains area is significantly lower.

The observation of PCDD/F contents in the soils was realised in 12 soil samples from the region. The exceeding of the proposed prevention limit (1 ng/kg I-TEQ PCDD/F) was detected in eight soil samples. The maximum content (600% of the prevention limit) was observed in the vicinity of the district town Chomutov. The increased values of PCDD/F in the soil were detected in the vicinity of the industrial towns practically in all cases. Only one from eight samples with increased PCDD/F was taken in the mountainous area of Krušné hory.

Table 2. Cases of exceeding risky elements critical values in plants

District	*n*	As	Cu	Pb	Co	Cr	Ni	Mn	Cd	Hg	*Zn*
Český Krumlov	10	0	0	0	0	0	0	0	0	0	0
Prachatice	6	0	0	1	0	0	0	0	0	0	0
Pelhřimov	39	0	0	0	0	0	1	0	0	0	0
Chomutov	21	0	0	0	0	0	1	3	0	0	0
Most	22	0	0	1	0	1	2	7	2	0	0
Teplice	32	0	3	2	0	0	1	3	0	0	0
Ústí n. L.	31	0	0	2	1	2	3	1	1	2	0
Litoměřice	8	0	0	0	0	0	0	0	0	0	0
Děčín	13	0	0	0	0	0	2	2	0	0	0
Cheb	39	0	0	0	0	3	0	5	0	2	0
Sokolov	48	1	0	1	1	3	2	7	0	2	0
Karlovy Vary	47	0	0	0	0	1	0	11	0	1	1
Critical values		4*	50+	40*	2+	3**	5**	100+	1*	0.1*	250+

*Direction of Ministry of Agriculture CR No. 264/1993; **Direction of Ministry of Agriculture CR No. 194/1996; +Direction of Ministry of Agriculture ČSSR No. 117/1987

North Moravian imission region situated in Northeast part of the Czech Republic on the border with Poland covers the area of three districts (Ostrava, Frýdek-Místek and Karviná). In the region Black coal underground mines are situated. The mining activities are realised in one of them all in at the present time. The load of the region is caused predominantly by the metallurgy industry that is located in the vicinity of the towns Ostrava and Třinec. The reduction of the mining activities increased unemployment and caused many social problems in the region.

The North Moravian imission region can be characterised by minimal geogenic load in comparison with North Bohemian region. The landscape has a flat character in most areas of the region. Only the flysh zone of the mountains Moravské Beskydy is spread in the Southeast part of the region.

An increased surface load in the soil was observed in the case of Cd only. The source of Cd are in most cases the emission out-puts from the metallurgy industry. The maximal contents of Cd in the soils were detected in the vicinity of the industrial town Třinec (the exceeding of the indication limit) and in the mountainous zone of Moravské Beskydy. The contents near the indication limit were found in the vicinity of the industrial town Ostrava. Only three cases of increased As content in the soil (exceeding the indication limit) near the Třinec town were detected in the whole area of the North Moravian region.

The load of the soil by human activities can also be confirmed by increased contents of POPs. The exceeding of the prevention limit of POPs in the soil were detected predominantly in the vicinity of the Ostrava town. The lower intensity of the load was observed in the vicinity of Trinec town and in the area of the Moravské Beskydy mountains.

The contents of PCDD/F were analysed in eleven soil samples. The value of I-TEQ PCDD/F exceeded the proposed prevention limit (1 ng/kg I-TEQ PCDD/F) in all samples. The maximum amount was located near the Ostrava town; I-TEQ PCDDF reached almost 800% of the proposed prevention limit. The results of PCDD/F analyses in the soils of both regions are presented in Figure 1.

The metal ore mining areas

The problematic cases of the load of soil with risky elements related with past mining activities of ore minerals mining can be found in the vicinity of the towns Příbram and Kutná Hora. The mining activities focused on ore minerals were realised in the district of the towns Příbram and Kutná Hora since the Middle Ages. The character of the load is different in these localities.

The anthropogenic load was caused through the treatment of gallenit (the production of lead) in the Příbram district. The emission out-puts from the smelter were the main reason for the contamination of the soils with Cd, Pb, and Zn. The increased contents of As in the soils of the district can be connected with geogenic load in most cases. The treatment of gallenit was terminated in the past and the activities of the smelter are focused on the recycling of vehicular accumulators at the present time.

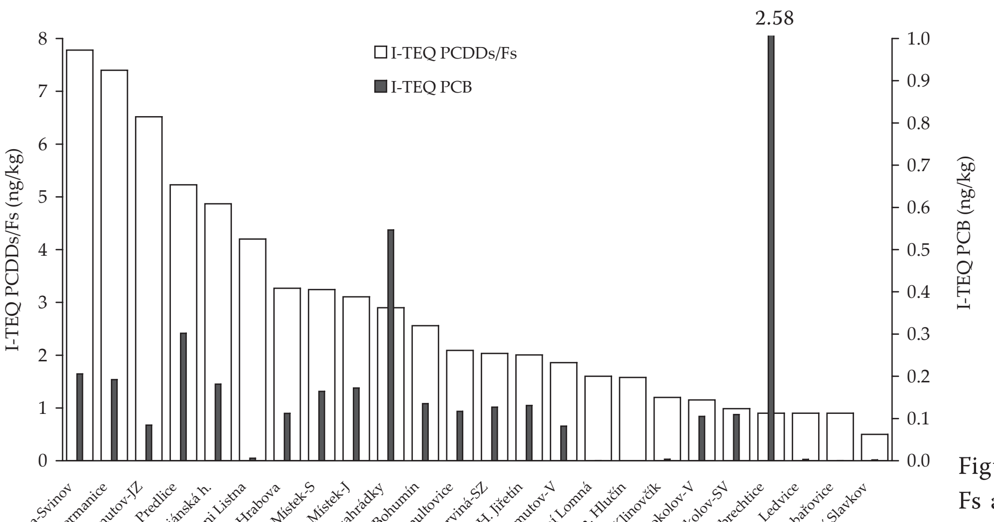

Figure 1. I-TEQ PCDDs/Fs and I-TEQ PCB in the soil samples from invidual localities

As the most important can be considered increased contents of Cd and Pb in the agricultural soils. The contamination of the soils with either element shows very similar spatial variability. The maximums are concentrated close to the smelter and the contents exceeding the indicative limits of Cd and Pb in the soil can be detected in the area up to 15 km distant from the smelter. The maximal total content of Cd reaches the value of 10 mg/kg and that of Pb the value of 2000 mg/kg, respectively.

The exceeding of the critical load, mainly by mobile Cd in the plants, is not sporadic because of the presence of acid Cambisols. The husbandry of agricultural subjects on the soils meets a real problem of the soil contamination. The research activities of some institutes in co-operation with the soil owners help to solve the situation. The research deals with the mobility of trace elements in the soil and their transfer from the soil into different plant species. The recommendations are presently focused on the soil acidity control and the application of organic matter.

The specific problem is the contamination of fluvisols with risky elements in fluvial zone of the river Litavka caused by floods. Cd, Pb, and Zn contaminated the water of the river because of the rapture of wastewater reservoir in recent past. The contamination of fluvisols with Cd, Pb, and Zn was confirmed in a detailed research (Borůvka *et al.* 1996). The contamination of the soil with water and imission out-puts as well as geogenic load were observed. The soil in fluvial zone of the river Litavka is not agriculturally used.

The increased load of the soil with Cd and mainly with As was detected in the district Kutná Hora. Cd is input into soils predominantly by imission fall-outs, and the increased load of the soils with As is related to the old mining activities. The rubbish with a high content of arsenopyrite from the mining has been spread on the agriculturally used soils since the Middle Ages. The contents of As in soils exceeding the proposed indication limit for As in the soil are presently observed.

Regardless of the primary geogenic source of As (arsenopyrite), the increase of As mobility in the topsoil can be caused due to the treatment of the ore and the weathering of the rubbish. The comparison of the solubility of As in the soil of the Kutná Hora district (locality Kank) and the soils of the others localities is presented in Table 3. The prevailing source of the load is indicated (anthropogenic, geogenic).

A detailed study of the risk of As transfer from the soil into different plant species and groundwater was realised by the Central Institute of Supervising and Testing. The results did not confirm the necessity of the reduction of plant the production or the threat to the groundwater quality.

Fluvial zones loaded by the flood

Because the load of soils with risky substances in fluvial zones can relate with the problems presented (river Litavka, the rivers in imission regions), the theme of fluvisols is shortly dealt with.

The most important source of the risky substances in fluvisols is predominantly municipal and industrial wastewater. The contamination of the most important Czech river the Labe culminated in eighties years of 20th century. The water quality

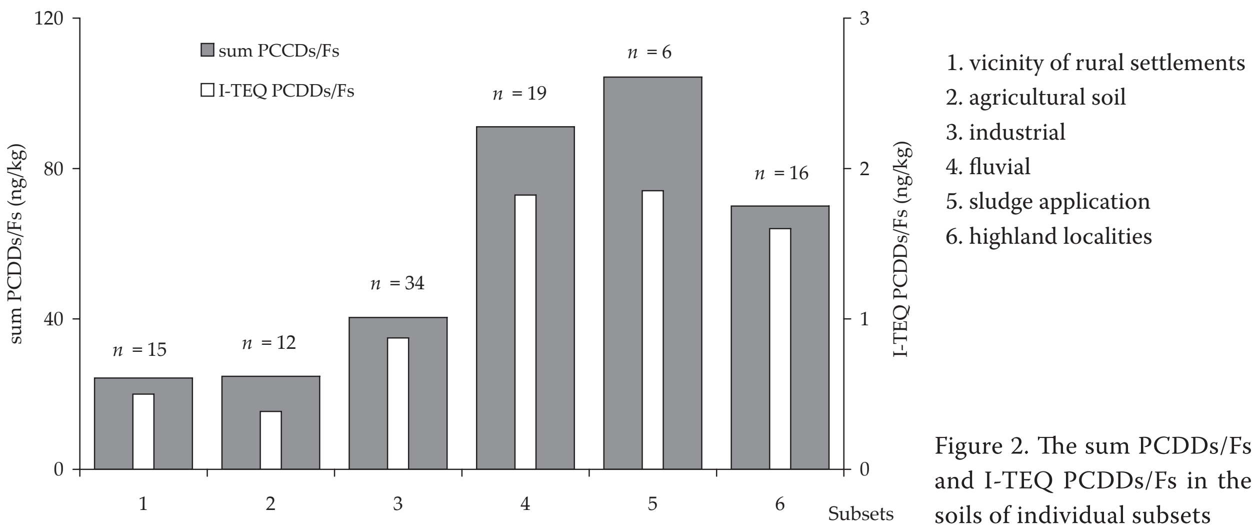

Figure 2. The sum PCDDs/Fs and I-TEQ PCDDs/Fs in the soils of individual subsets

Table 3. Increased contents of As in the soils (* solubility %)

No.	Locality	Horizon	Soil type	Parent material	Load		pH	C_{org} (%)	As_{tot} (mg/kg)	HNO_3	$NH_4NO_3 \times 100$* (total)	EDTA
					A	G						
1927	Mokrsko	A	KAm	Granodiorite (amphibol. biotit.)		+	4.45	0.85	477.50	20.8	0.0	1.5
		B					4.35	0.20	224.10	6.3	0.0	0.3
		C					4.55	0.08	1045.00	48.1	0.0	3.6
2286	Klinovčík	A	KAd	Gneiss (muscovitic)		+	3.47	3.60	49.02	65.9	0.6	71.2
		B					3.28	1.70	85.80	36.4	0.1	28.6
		C					3.88	0.85	100.40	54.6	0.0	39.8
2283	Ředice	Ah	KAm	Granite (amphibol. biot.)		+	6.21	1.25	31.88	9.	0.1	3.6
		B					6.13	0.32	30.84	5.9	0.0	2.2
		C					5.82	0.04	32.24	9.3	0.0	2.7
2284	Horní Hanychov	A	KAd	Phyllite		+	3.71	2.95	55.60	13.5	0.0	4.5
		B					3.87	1.05	38.40	5.3	0.0	1.0
		C					4.19	0.28	59.48	10.2	0.0	0.7
1926	Příbram	A	KAm	Slates, Greywackes	+		4.45	1.94	75.64	45.9	0.0	10.5
		B					4.35	0.44	27.00	22.7	0.1	7.1
		C					4.15	0.08	23.18	7.7	0.0	1.8
1933	Moldava	A	KAd	Gneiss (biotit.)	+		4.80	4.36	44.22	44.3	0.0	1.5
		B					4.90	3.39	21.70	23.7	0.0	0.8
		C					4.35	0.20	12.47	10.5	0.0	1.0
2237	Starý Kolín	A	KAr	Terrace gravels	+		3.98	3.23	25.52	32.2	0.1	18.3
		B1					3.99	0.36	12.29	45.9	0.1	12.2
		B2					4.24	0.08	6.02	34.9	0.2	14.1
1931	Kank	A	HMm	Loesses		+	6.70	1.54	191.14	43.1	0.4	52.9
		B					7.05	0.61	245.90	26.8	0.3	38.8
		C					7.20	0.40	1115.00	70.8	0.1	16.6
1932	Piešťany	A	FLm	Non-carb. alluvial deposits	+		6.60	5.47	37.03	53.0	0.1	34.6
		B					6.60	2.93	46.13	64.2	0.0	25.5
		C					6.65	1.05	18.40	33.3	0.0	21.7

A – anthropogenic; G – geogenic

improved rapidly after the installation of municipal and industrial wastewater treatment plants at the end of 20th century. But the contamination of fluvisols with risky substances is still current and the contents of the risky substances decrease slowly. The following risky elements mostly contaminating the fluvisols are Cd > Hg, Zn > Cu > Pb, and Cr. The exceeding of the proposed indicative limit has been observed in many cases. The situation is complicated by the increased solubility of the risky elements in fluvisols and also by the increased risk of their transfer into plants.

The increased contents of POPs, including PCDD/F, were detected. The load of fluvisols with PCDD/F was the highest out of the whole set of 102 soil samples. The load of the soil groups separated by different sources of PCDD/F is presented in Figure 2.

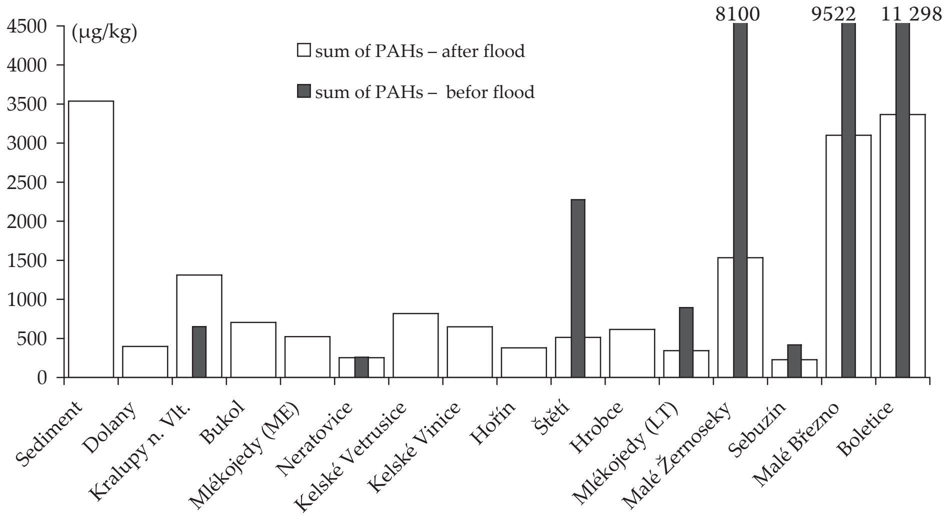

Figure 3. Comparison of PAHs before and after the flood in 2002

The monitoring of soils in the fluvial zone of the Labe was realised after the flood in 2002 by our institute (Vácha *et al*. 2003). The contents of the risky substances were compared with the state of the load ten years ago. The results of the study confirmed a decreasing tendency of the risky substances contents in fluvisols (Figure 3). In spite of this finding, the theme of fluvisols contamination is still topical because of its high potential in the crop production.

CONCLUSIONS

On the base of the results presented, it can be concluded that increased contents of risky substances in agricultural soils were detected in all areas observed. Form the viewpoint of the extent of contamination, the imission regions can be considered the most important. The intensity of contamination is lower in these areas. The increased contents of Cd, PAHs, and PCDD/F in North Moravian imission region and the increased content of As in Northwest Bohemian imission region seem to be the most important consequences of the soil load with risky substances. The reduction of the plant production or the application of the soil remediation techniques can not be generally considered in these regions.

The areas loaded due to the past mining of metals are characteristic by lower extents of contamination but the intensity of contamination is higher in comparison with the imission regions. The contents of Cd, Pb, and Zn in the soils, plants, eventually also groundwater in the Příbram district must be under periodic control. The application of gentle remediation methods is needed and the reduction of the production of some plant species will be very probably recommended. The increased content of As in the soils of the Kutná Hora district is not risky for the plant production and groundwater according to the studies realised but the problem will be observed.

The use of fluvisols in the fluvial zones for the plant production must follow the legislative norms (Directive of Ministry of Environment 13/1994) designated for the protection of the food chain. The monitoring of the risky substances on individual locations used for the plant production is highly recommended.

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