

Soil Contamination in a Flooded Area of Morava River Basin after the Flooding in 1997

EVA KVĚTOŇOVÁ¹, PAVEL MÜLLER¹ and JAROMÍR HANÁK²

¹Czech Geological Institute, Leitnerova 22, 658 69 Brno, Czech Republic

²ENVI 2000, s.r.o., Vaculíkova 1a, 638 00 Brno, Czech Republic

Abstract. During the flood of 1997 of parts of the Moravia River much sediment was redistributed as a sediment sheet several centimeters thick over an extensive area. Along with this redistribution of sediment there was also a redistribution of organic pollutants, trace elements and radioactive material.

Although at first the contamination level was feared to be high, it later turned out in most areas to be less critical. There were several local exceptions, however, where Ministry of Environment critical levels were exceeded. On the whole, however, it appears that pollutants were scattered rather than concentrated. In this study 111 near surface soil samples and 30 core samples of flood deposits were taken. Lab tests were run on 15 of trace elements, 34 of organic toxins and 4 of radioactive elements. The analytical results were treated statistically by correlations and evaluation of the spatial distribution trends.

Background concentrations were exceeded for following substances: TPH, PAHs, PCBs, chlorinated pesticides (DDT, DDE), trace elements (Cd, Co, Cr, Ni, Pb, Zn, Sb, Hg, Ba) and radioactive elements (Cs¹³⁷, U(Ra)).

Keywords. Environmental geochemistry, regional geology, floods in 1997 on the Morava River, organic contamination of sediments, contents of trace and radioactive elements in alluvial sediments.

Introduction

There was an extensive mass redistribution due to erosion in upper and middle part of Morava River basin during the flood in 1997. Eroded matter was deposited along the original riverbeds and river channels during flooding of alluvial areas. Huge areas were covered by an extensive sheet of sediments only several centimetres thick. The sediments in the flood plain area were composed dominantly of silt to sand size of particles, and sediments in and near riverbeds by sand to gravel size of particles. After the retreat of the flood waters the affected area became part of a gradually drying lagoon flooded by very fine-grained and loamy deposits (Ottesen et al., 1989). The new alluvial sediments were separated from the riverbed by a natural levee or from dams with nearby natural depressions.

Along with minerals and soils from the source areas anthropogenic matter originating from technological facilities and landfills were also moved into the flooded area.

Many of the substances originating from this matter could have an immediate toxic effect. Others threaten organisms by their slow but gradually increasing concentration in tissues that could have a gradual toxic effect on humans. In the case of floods of long or short duration there is a real threat of contamination by flood sediments and soils having the trace elements (Hg, Pb, Cd, As), cyanides, oil substances composing in significant part of total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and also polychlorinated biphenyls (PCBs).

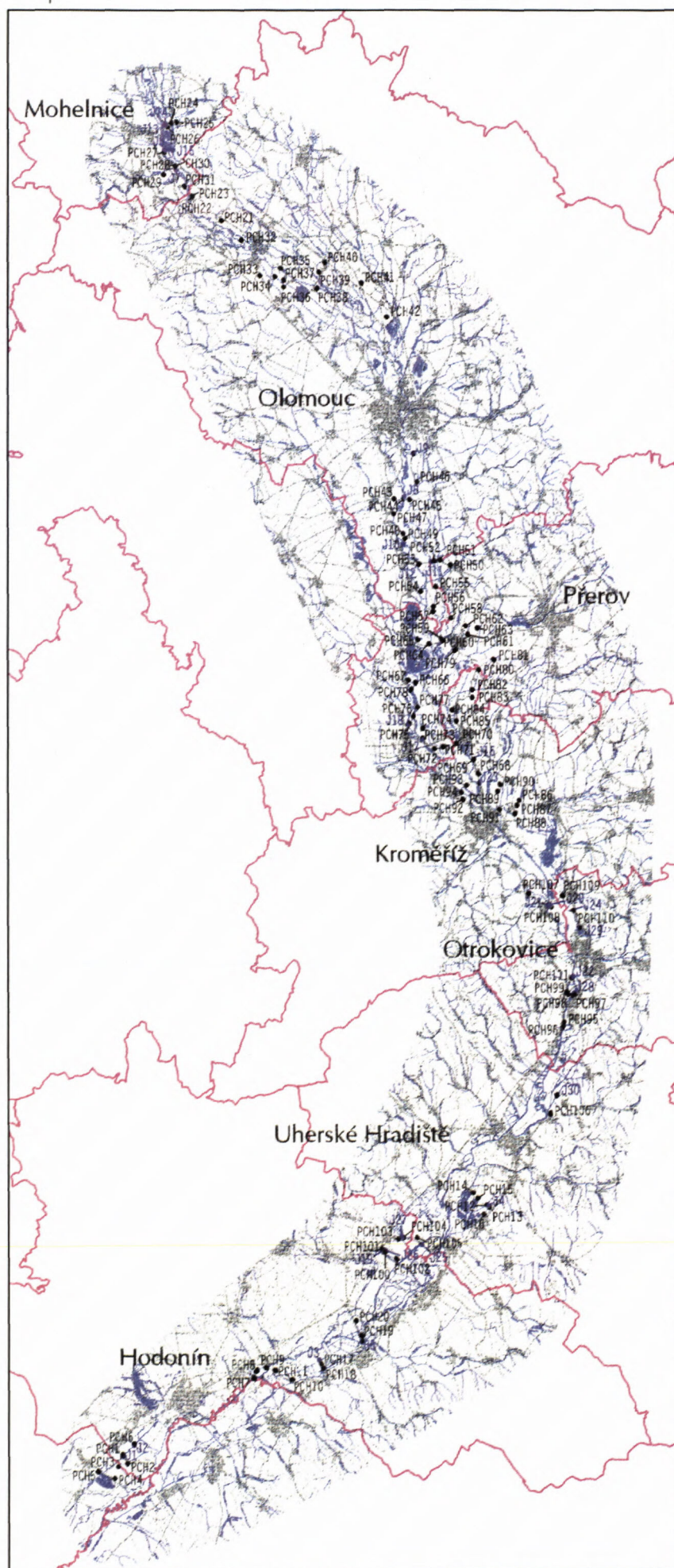
Further, there was erosion of radioactive elements derived from rock minerals coming from source areas and there also was a redistribution of radioactive fallout, material that was aftermath of the Chernobyl accident (Cs¹³⁷). This fallout material was "leached", together with other inorganic and organic substances originating from the upper part of soils of the entire Morava River basin. Because of the extensive migration of matter and toxicity of some of the substances to man and the environment, we have decided to map the distribution of selected pollutants in the present soil environment.

Sampling

All together 111 near-surface soil samples (up to 3 cm from the surface) and 30 core samples were taken to map the contamination of the Šumperk, Olomouc, Přerov, Kroměříž, Uherské Hradiště, Hodonín and Břeclav Districts with radioactive elements. The distribution of sample sites is shown on the figure 1. Core samples were taken from the alluvial deposits by sampling probe to a 70 cm depth. Each 15 cm of the core samples was then sampled in a lab and each sample was individually analysed. An average value was then calculated for each core. The samples were also characterised visually and petrographically.

Analytical Methods

A wide variety of substances were analysed in the samples: organic compounds - (total organic carbon, TPH, PAHs, PCBs, OCPs), cyanides, trace elements (Ba,



Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn, V, As, Sb, Hg, Sr) and radionuclides, (Th, U (Ra), K, Cs¹³⁷). The following analytical methods were used:

Total organic carbon (TOC). For analysis of carbon was used analyzer ELTRA METALYT CS 1000S (Germany). Total carbon was determined by the heating of 400 to 500 mg samples in an oxygen atmosphere at 1250°C. Generated carbon dioxide was measured by infrared detectors. The content of inorganic carbon was determined after reaction of a sample with phosphoric acid. The content of TOC was detected by subtraction of inorganic carbon from total carbon.

The total extractable compounds (TEC) and nonpolar extractable compounds (or total petroleum hydrocarbons - TPH). Dried and homogenized samples were extracted with 1,1,2-trifluoroethane. To determine TPH, the co-extractive polar and semi-polar compounds was removed from the extract with silica gel absorbent. The concentrations of TEC and TPH in extracts were measured by infrared (IR) absorption photometry (Perkin-Elmer 783).

Persistent organic pollutants (PAHs, PCBs, OCPs). The substances were extracted by a device Soxtec HT2 (Tecator, Sweden) with dichloromethane. To detect polycyclic aromatic hydrocarbons (PAHs), a portion of dichloromethane extract was fractionated (after the addition of internal standards and after partial drying) by column chromatography on silica gel by a gradual elution of n-pentane and dichloromethane and analysed by capillary gas chromatography with flame-ionization detector (GC/FID, Hewlett-Packard HP6890). In the case of PCBs and chlorinated pesticides a portion of the dichloromethane extract was re-extracted with n-hexane after the addition of internal standards and drying (active copper was added in order to remove elemental sulphur). The detection was done by gas chromatograph with an electron-capture detector (GC/ECD, Hewlett-Packard HP6890).

Fig. 1 Localization of sampling sites

Total and toxic cyanides. Total cyanides include free cyanides and bonded cyanides bounded in complexes, including organic substrates containing the cyanide group that creates HCN under conditions of analytical process. During the analysis the HCN was separated from the sample by distillation, with the help of diluted sulphuric acid and in the presence of magnesium salt and following the absorption of HCN in a solution of sodium hydroxide. Cyanide ions are then determined by photometry.

Toxic cyanides include free and also unstably bonded cyanides, which are released in a neutral pH, under temperature of 40°C in air bubbles. The freed cyanide is captured and determined by photometry.

Trace elements. Elements Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn, V, As and Sb were determined by AAS method, Ba and Sr by ICP method and Hg by cold vapor AAS method.

Radionuclides. Each sample core was divided into smaller samples 8 to 10 cm long (to provide sufficient sample with respect to sample composition). The divided sample cores and the A soil horizons were dried at temperatures to 105°C, homogenised, and then inserted into a measuring case, where they remained for two weeks in order to set the radioactive balance between Ra^{226} and $DP\ Rn^{222}$. A scintillation spectrometer PCAP (Nucleus USA) with detector NaI(Tl) 4 x 4" with a resolution 7.9% was used for measurements. A lead box with 9 cm walls was used to shield background radiation. The observed 512-channel spectrums were compared with observed spectrums of IAEA (The International Atomic Energy Agency) etalons (RG set: Th, U(Ra) a K). The observed values lower than above-mentioned detection limit is also entered onto the documentation charts, because they still have certain informative value. Under favourable conditions (if the large case is filled), the U content independent of Ra can be also determined, and thus the radioactive balance between U and Ra^{226} can be evaluated. However, the determination of U on the base of low-energy gamma radiation Th^{234} and the radiation of isotope U^{235} is effected by several times higher error than the determination of Ra^{226} , thus the real accuracy of direct determination of U is about 1.5 ppm.

Criteria of Environmental Risks Assessment

Concerning the hazard for the environment, the weight of observed concentrations of individual substances (organic matter and trace elements) were assessed according to the methods set by the Ministry of Environment of the Czech Republic (ME CR, 1996):

Criteria A - are about the same as natural concentrations of analysed substances or the background. Anything in excess is taken as a contamination of examined area of environment, excluding areas with naturally increased concentrations. However, if the criteria B are not exceeded, the contamination is not considered critical enough to justify the starting of research or to start monitoring it.

Criteria B - are artificially set up criteria that are approximately equal to the arithmetical averages of criteria

A and C. Excesses of the criteria B requires a preliminary analyses of the risk resulting from the observed contamination to identify the sources and reasons of contamination. According to the results decisions about any following research and monitoring are made.

Criteria C - was defined with respect to the physical, chemical, toxic, ecological and another properties of the substances. Different criteria are defined for different types of planned land use. (residential, recreational, industrial and general). Exceeding the criteria C means contamination that can be a real threat to human health and components of the living environment.

Because the criteria C are set up with respect to standard soil (25% of clay particles and 10% of organic matter), the adjustment for individual samples (only for organic matter) was made according to the following equation, given in the methodical directions:

$$I_c = I_{st} (\% \text{ organic matter} / 10),$$

Where I_{st} is the criterion of the C category for a standard soil type, and I_c is the calculated critical limit of the C category for a concrete portion of organic matter, which can be considered about the double of the C_{org} content value.

The Results of Analyses of Organic Geochemistry and Cyanides

The contents of organic and inorganic carbons and cyanides. The TOC (Fig. 2, localities are arranged from N to S in the flow direction of the Morava River) are in the range from 0.26% to 7.08%. Although the contents of organic matter can be, and certainly they are, the function of many factors (content, size and type of floating particles, particle size distribution, speed of the flow and its changes, and many others), the most probable general trend of organic matter (C_{org}), the concentrations seem to increase in the direction of the river flow (fining of the sedimentation, usually increased portions of organic matter in clays and claystones compared to silt (and siltstones) and sands (and sandstones)). With respect to the lack of relationship with other parameters of organic contamination analyses, which works with fractions extracted from rocks by organic solvents, a dominantly humic character of organic substances can be assumed (remains of higher plant parts, roots and fragments of herbs and farming crops, etc.) Some of these phytoclasts were visually observed during the sampling in the field.

The contents of inorganic carbons are usually very low which suggest a low content of carbonates in the mineral matrix after flooding of fine-grained sediments. The highest and highly extreme value 1.5% C_{inorg} (PCH17 - Hodonín district) corresponds to a maximum content 3.75% $CaCO_3$. The upper quarter of the values of C_{min} shows portions smaller than 0.48% $CaCO_3$ for more than 1/3 of the samples.

The contents of all cyanides, mainly toxic cyanides are very low in all near surface samples. In the case of toxic cyanides, the highest observed value is 0.3 ppm for the sample from the Hodonín district, which is five times

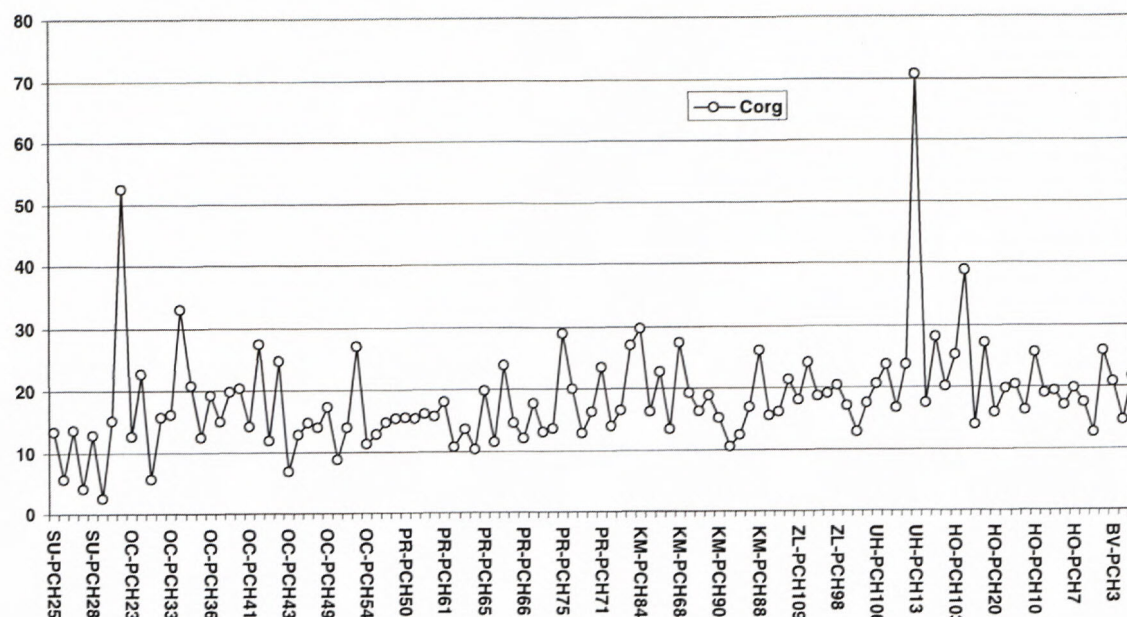


Fig. 2 The Content of total organic carbon in the samples (g/kg)

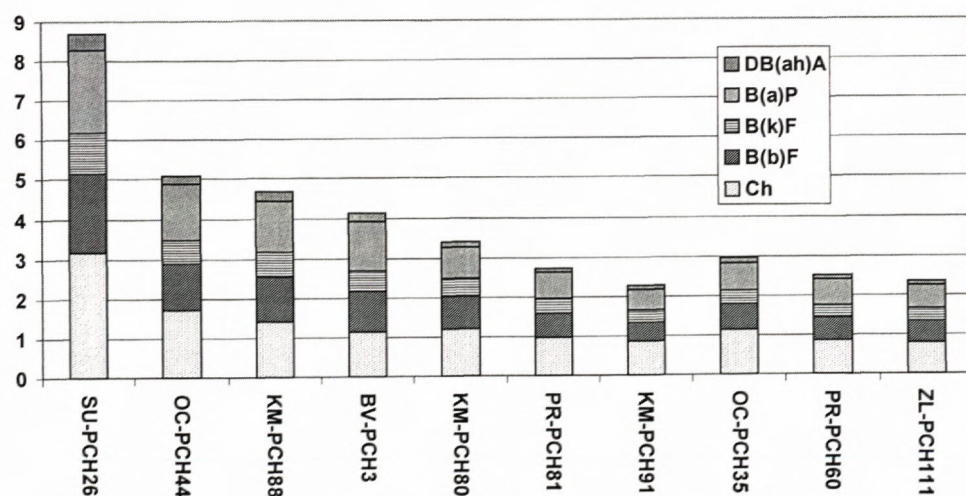


Fig. 3 Shares of some toxic and carcinogenic PAHs (ppm) for samples with highest total contents

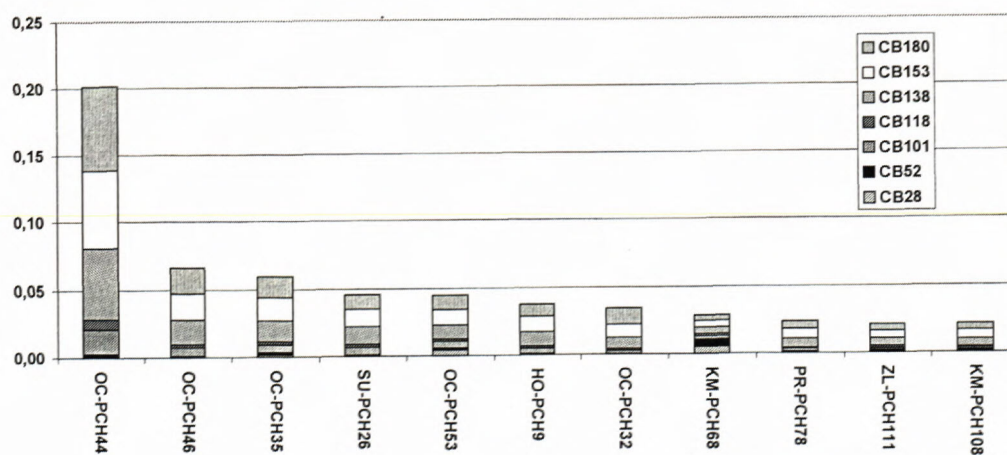


Fig. 4 Shares of individual congeners on total content of PCBs for 11 samples with concentrations of PCBs greater than 0.02 ppp (criterion A)

lower than the maximum acceptable critical value of the category A (1.5 ppm).

Contents of TEC and TPH. There is a close relationship between the total extracted portion (TEC) and non-polar substances (TPH) with a correlation coefficient of 0.97. The prevailing majority of the extracted portions are composed of nonpolar substances (hydrocarbons).

The critical limit of category B for TPH (400 ppm) was not exceeded, which would otherwise call for additional detailed research. Even the highest observed concentration (150 ppm) is more than two-times smaller.

Polycyclic aromatic hydrocarbons. The following PAHs compounds were determined: acenaphthylene, acenaphthene, fluorene, benzo(j)fluoranthene, dibenz (a,h) anthracene, anthracene, phenanthrene, fluoranthene, pyrene, benzo(a)pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)anthracene, indene(1,2,3 cd)pyrene, benzo(ghi)perylene. The sum of PAHs, according to methodical directions, includes only benzo (a)anthracene, benzo(a)pyrene, benzo(ghi)perylene, benzo(k)fluoranthene, fluoranthene, phenanthrene, chrysene, indene(1,2,3 cd)pyrene and pyrene.

The contents of PAHs are statistically closely related to the contents of TEC, which suggests (with a significance level of 0.001 for a given amount of analyses) that the extracted portion is composed mostly of nonpolar hydrocarbons, of which the dominant group is PAHs. The PAHs concentration also has a significant correlation with the PCBs (coefficient 0.47).

The values of the observed PAHs concentrations are summarised in Table 1. The most contaminated samples are from the Šumperk district, where the criterion C_{popul} for benzo(a)pyrene was exceeded in one sample. Practically in all samples in which the increased concentrations of acenaphthene were detected, the increased concentrations of fluorene and phenanthrene are also observed. In three samples the values of total PAHs concentrations approximate the adjusted values of C criteria for general land use. The values concern the contents of organic matter. In the cases of samples from the Šumperk district, this adjusted value is significantly exceeded. The contents of the most common PAHs in the ten most contaminated samples are given in Figure 3.

Polychlorinated biphenyls. The increased contents of PCBs usually parallels the increased contents of PAHs, which supports an inference of a close structural, chemical and perhaps also in some cases genetical relationship of these substances, expressed by the coefficient 0.47, with a significance level of 0.001 for a given amount of observations (samples). In the samples where an increased amount of extractable matter was observed, there also commonly were increased concentrations of PCBs. A correlation coefficient also proves the relationship between the contents of PCBs and contents of TEC (coeff. 0.51) and TPH (coeff. 0.46).

The critical concentration of PCBs 0.02 ppm for category A was exceeded in 11 cases. In the samples with the highest contents of PCBs, the highest portions of PCBs compounds are equally shared by hexachlorobiphenyls

CB138, CB153 and heptachlorobiphenyl CB180, which contain the highest amount of Cl and therefore are the most persistent against degradation. Usually they compose about 75% of the total PCBs content. The portions of individual substances of the most contaminated samples are given on Figure 4.

Organochlorine pesticides. These substances include DDT and its decay products - DDE and DDD which are also persistent in the environment. Hexachlorocyclohexane, lindane and heptachlor were also determined. However, their concentrations were very low, or under the detection limit. The critical limits for total chlorinated pesticides for soil for agricultural use (0.1 ppm) were exceeded in nine cases in the Hodonín, Kroměříž, Zlín and Přerov districts.

Results of Analyses of Trace Elements

The analyses concern not only the concentrations of individual elements but also their mutual relationship with respect to their space distribution (Table 2). A statistically significant relationship was determined especially between Pb and As, As and Sb, and also among the elements Cu, Ni, Zn and V. Concentrations of Be in samples were low, their values were in range of 1.5 - 4.4 ppm, which means that there were no values greater than the critical limit of the category A (5 ppm).

All 71 samples with a content of Cd greater than the detection limit (0.8 ppm), are considered to be contaminated soils in the category A, having a critical limit of 5 ppm. (according to existing Methodical Directions of ME CR, 1996). This result indicates a significant contamination of the study area in category A or, what is more probable, the critical value for the category A was set too low.

The Co concentration in the study samples have values of 6 - 50 ppm. The only observed maximum value of 50 ppm (a sample from Olomouc district) twice the critical limit (25 ppm) given for the category A. In the case of Cr the critical limit of category A (130 ppm) was exceeded in only one sample, (246 ppm) from the Zlín district.

In the cases of Cu, V, and As no samples exceeded the critical limit of category A (Cu - 70 ppm, V - 180 ppm, As - 30 ppm). The concentration of Mo in all but one case below was the detection limit (5 ppm). The concentration of the one case was at the detection limit.

The critical limit (60 ppm) accepted in A category for the concentration of Ni was exceeded in six samples. The content of Pb in many samples were approaching critical limit 80 ppm in A category. In one case, from the Hodonín district, the observed concentration of Pb was 4380 ppm what exceeded many times the critical limit of C category set up for general land use (300 ppm).

The concentration of Zn exceeded the critical limit (150 ppm) for contamination in the category A in seven cases. They are mainly from the Olomouc district (4 samples). In the case of Sb, only one sample from the Hodonín district, having a concentration of 39.08 ppm exceeded the 25 ppm the critical limit set for the category B. Another three

Tab. 1 Concentrations PCBs and PAHs in soils

	substance unit	PCB	N	Acen	Acen	Fluoren	Fen	A	F	P	B(a)A	Ch	B(b)F	B(j)F	B(k)F	B(a)P	I(123-cd)P	DB(ah)A	B(ghi)P	Suma PAU-A	Suma PAU-B
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
SU	PCH25	0,0016	<0,008	0,0101	0,0222	0,0244	0,1692	0,0272	0,7647	0,5821	0,2468	0,4044	0,2926	0,1232	0,1587	0,2860	0,2299	0,0582	0,2274	3,6271	3,0692
	PCH24	0,0019	0,0186	<0,008	0,0252	0,0203	0,1462	0,0398	0,4826	0,3703	0,1839	0,2714	0,1910	0,0801	0,1075	0,1933	0,1549	0,0478	0,1681	2,5010	2,0782
	PCH26	0,0454	0,0201	0,0707	0,3983	0,5283	2,9188	0,3318	7,2115	5,3325	2,1940	3,1663	1,9969	0,8443	1,0355	2,0725	1,4774	0,4083	1,3282	31,3354	26,7367
	PCH27	0,0016	0,0413	<0,008	0,0174	0,0203	0,0327	0,0121	0,1063	0,0874	0,0402	0,0697	0,0403	0,0177	0,0209	0,0482	0,0316	<0,008	0,0337	0,6198	0,4707
	PCH28	0,0019	0,0389	<0,008	0,0082	0,0142	0,0644	0,0153	0,2561	0,2020	0,0953	0,1428	0,1054	0,0464	0,0523	0,1179	0,0729	0,0196	0,0665	1,3182	1,0702
	PCH30	0,0030	-	<0,008	0,0190	<0,008	0,0180	0,0097	0,0521	0,0467	0,0205	0,0336	0,0275	0,0100	0,0211	0,0196	0,0177	0,0047	0,0193	0,3195	0,2486
	PCH29	0,0047	0,0092	0,0082	0,0441	0,0465	0,2799	0,0663	1,1376	0,8888	0,4376	0,6466	0,4679	0,2192	0,2303	0,5058	0,3548	0,0993	0,3208	5,7629	4,8022
PCH31	0,0043	0,0134	<0,008	0,0116	0,0130	0,0736	0,0222	0,2890	0,2398	0,1193	0,2177	0,1439	0,0631	0,0748	0,1194	0,2079	0,0432	0,0813	1,7332	1,4228	
OC	PCH23	0,0136	0,0120	<0,008	0,0181	0,0210	0,1455	0,0278	0,5215	0,4061	0,2073	0,3283	0,2500	0,1031	0,1273	0,2367	0,1967	0,0622	0,1665	2,8301	2,3359
	PCH22	0,0070	0,0116	<0,008	0,0096	0,0175	0,1190	0,0274	0,4640	0,3822	0,1972	0,3050	0,2328	0,0907	0,1236	0,2426	0,1738	0,0510	0,1514	2,5994	2,1588
	PCH21	0,0019	0,0120	<0,008	0,0094	0,0134	0,0978	0,0214	0,2665	0,2165	0,1221	0,1905	0,1248	0,0622	0,0740	0,1376	0,1106	0,0361	0,0965	1,5914	1,3121
	PCH32	0,0343	-	<0,008	<0,008	<0,008	0,0157	<0,008	0,0623	0,0469	0,0253	0,0466	0,0327	0,0151	0,0187	0,0297	0,0202	0,0079	0,0178	0,3389	0,2832
	PCH33	0,0034	-	<0,008	<0,008	0,0081	0,0288	<0,008	0,1164	0,0977	0,0542	0,0870	0,0615	0,0301	0,0363	0,0562	0,0449	0,0112	0,0323	0,6647	0,5538
	PCH35	0,0597	0,0142	0,0128	0,0460	0,0555	0,4640	0,0903	1,4070	1,1326	0,6161	1,1448	0,6467	0,3292	0,3265	0,7084	0,5036	0,1388	0,5094	8,1459	6,8124
	PCH34	0,0035	<0,008	<0,008	0,0116	0,0108	0,1146	0,0333	0,3912	0,2865	0,1783	0,2548	0,1833	0,0888	0,0939	0,1969	0,1373	0,0389	0,1275	2,1477	1,7810
	PCH37	0,0020	-	<0,008	<0,008	<0,008	0,0376	<0,008	0,1451	0,1190	0,0543	0,0913	0,0695	0,0289	0,0353	0,0691	0,0496	0,0164	0,0479	0,7640	0,6492
	PCH36	0,0035	<0,008	<0,008	<0,008	0,0114	0,0453	0,0082	0,1929	0,1581	0,0803	0,1363	0,1100	0,0535	0,0548	0,1111	0,0824	0,0211	0,0767	1,1421	0,9379
	PCH40	0,0020	-	<0,008	<0,008	<0,008	0,0143	<0,008	0,0542	0,0437	0,0204	0,0396	0,0301	0,0109	0,0162	0,0361	0,0248	<0,008	0,0253	0,3156	0,2746
	PCH39	0,0127	0,0124	0,0103	0,0369	0,0350	0,3757	0,0686	0,9656	0,7659	0,4098	0,6640	0,4203	0,2187	0,2164	0,5492	0,3159	0,0836	0,2976	5,4459	4,5601
	PCH38	0,0029	-	0,0094	<0,008	<0,008	0,0372	<0,008	0,0863	0,0688	0,0347	0,0708	0,0352	0,0157	0,0216	0,0420	0,0288	<0,008	0,0242	0,4747	0,4144
	PCH41	0,0019	-	<0,008	0,0090	0,0110	0,0613	0,0091	0,1443	0,1113	0,0587	0,0966	0,0673	0,0400	0,0282	0,0693	0,0431	0,0120	0,0436	0,8048	0,6564
	PCH42	0,0022	0,0128	<0,008	<0,008	<0,008	0,0469	0,0144	0,2401	0,1598	0,0805	0,1952	0,1054	0,0415	0,0540	0,0924	0,0751	0,0180	0,0549	1,1910	0,9989
	PCH46	0,0662	-	<0,008	<0,008	<0,008	0,0237	<0,008	0,0508	0,0434	0,0196	0,0415	0,0259	0,0144	0,0125	0,0235	0,0176	<0,008	0,0203	0,2932	0,2529
	PCH44	0,2019	0,0192	0,0162	0,0634	0,0811	1,0547	0,1977	3,0835	2,3584	1,1487	1,7289	1,1663	0,5520	0,5877	1,3832	0,7764	0,2160	0,7076	15,4140	12,8291
	PCH43	0,0026	-	<0,008	<0,008	<0,008	0,0606	0,0188	0,1694	0,1346	0,0699	0,1182	0,0828	0,0408	0,0427	0,0756	0,0576	0,0139	0,0475	0,9324	0,7761
	PCH45	0,0023	-	<0,008	<0,008	<0,008	0,0374	<0,008	0,1223	0,0930	0,0414	0,0753	0,0621	0,0262	0,0338	0,0531	0,0450	0,0127	0,0400	0,6423	0,5413
	PCH47	0,0062	0,0132	<0,008	<0,008	<0,008	0,0442	<0,008	0,1393	0,1104	0,0590	0,0925	0,0640	0,0314	0,0315	0,0640	0,0419	0,0128	0,0422	0,7464	0,6250
	PCH48	0,0024	0,0161	<0,008	0,0230	0,0201	0,0951	0,0209	0,3717	0,2707	0,1158	0,1716	0,1168	0,0571	0,0613	0,1169	0,0783	0,0301	0,0738	1,6393	1,3552
	PCH49	0,0025	0,0244	<0,008	0,0163	0,0179	0,2209	0,0443	0,8396	0,6180	0,2991	0,4951	0,3084	0,1373	0,1723	0,3004	0,1993	0,0628	0,1704	3,9265	3,3151
	PCH51	0,0018	<0,008	<0,008	<0,008	0,0094	0,0548	0,0117	0,1915	0,1539	0,0844	0,1398	0,0912	0,0465	0,0498	0,0919	0,0652	0,0162	0,0508	1,0571	0,8821
PCH52	0,0033	0,0084	<0,008	<0,008	0,0085	0,0873	0,0177	0,4905	0,3795	0,2034	0,3264	0,2408	0,0955	0,1317	0,2556	0,1517	0,0423	0,1423	2,5816	2,1684	
PCH53	0,0450	0,0110	0,0132	0,0527	0,0676	0,5002	0,1301	1,3378	1,0420	0,5179	0,8677	0,5747	0,2459	0,3407	0,5363	0,4224	0,1185	0,3612	7,1399	5,9262	
PCH54	0,0019	0,0160	<0,008	0,0574	0,0778	0,2727	0,0533	1,0269	0,7960	0,3517	0,4689	0,2861	0,1424	0,1542	0,3417	0,1979	0,0571	0,2003	4,5004	3,8103	
PCH55	0,0016	<0,008	<0,008	<0,008	<0,008	0,0498	0,0105	0,3529	0,2533	0,1566	0,2359	0,1446	0,0674	0,0757	0,1199	0,0837	0,0212	0,0688	1,6403	1,3966	
PCH56	0,0029	0,0145	<0,008	<0,008	<0,008	0,0320	<0,008	0,1265	0,0962	0,0376	0,0681	0,0469	0,0224	0,0260	0,0527	0,0334	<0,008	0,0342	0,5905	0,5067	
PCH57	0,0020	-	<0,008	<0,008	<0,008	0,0151	<0,008	0,0704	0,0549	0,0351	0,0626	0,0298	0,0156	0,0148	0,0312	0,0183	<0,008	0,0154	0,3632	0,3178	
PR	PCH50	0,0044	0,0077	<0,008	<0,008	0,0098	0,0716	0,0175	0,1767	0,1371	0,0834	0,1335	0,0880	0,0398	0,0407	0,0806	0,0546	0,0170	0,0484	1,0064	0,8266
	PCH58	0,0029	0,0216	<0,008	<0,008	0,0111	0,0695	0,0097	0,2513	0,1982	0,0924	0,1578	0,0996	0,0468	0,0605	0,0994	0,0678	0,0178	0,0654	1,2689	1,0623
	PCH62	0,0058	0,0100	<0,008	<0,008	<0,008	0,0323	<0,008	0,1221	0,1058	0,0490	0,0836	0,0657	0,0288	0,0304	0,0540	0,0426	0,0077	0,0419	0,6739	0,5617
	PCH63	0,0075	0,0101	<0,008	0,0156	0,0234	0,1438	0,0389	0,4733	0,3824	0,2001	0,3035	0,2079	0,1068	0,0967	0,2105	0,1337	0,0351	0,1259	2,5077	2,0699
	PCH61	0,0115	0,0108	<0,008	0,0172	0,0160	0,1249	0,0217	0,5228	0,4343	0,2077	0,3540	0,2727	0,1109	0,1621	0,2523	0,1921	0,0517	0,1838	2,9350	2,4340
	PCH59	0,0021	-	<0,008	<0,008	<0,008	0,0169	<0,008	0,0561	0,0531	0,0202	0,0418	0,0328	0,0162	0,0154	0,0246	0,0165	0,0040	0,0169	0,3145	0,2615
	PCH60	0,0124	0,0110	0,0138	0,0650	0,0560	0,5337	0,1181													

HO	PCH104	0,0036	0,0271	<0,008	<0,008	<0,008	0,0445	0,0085	0,1400	0,1203	0,0533	0,0900	0,0712	0,0356	0,0401	0,0655	0,0569	0,0107	0,0516	0,8153	0,6622
	PCH103	0,0036	0,0143	<0,008	0,0076	0,0099	0,0495	0,0094	0,1558	0,1205	0,0593	0,1029	0,0771	0,0274	0,0463	0,0656	0,0524	0,0196	0,0458	0,8634	0,6981
	PCH102	0,0034	0,0262	<0,008	<0,008	<0,008	0,0297	<0,008	0,0670	0,0597	0,0264	0,0541	0,0381	0,0145	0,0204	0,0339	0,0521	<0,008	0,0180	0,4401	0,3613
	PCH101	0,0044	0,0149	<0,008	<0,008	<0,008	0,0263	<0,008	0,0856	0,0673	0,0423	0,0597	0,0468	0,0188	0,0290	0,0518	0,0236	<0,008	0,0320	0,4981	0,4176
	PCH100	0,0049	0,0313	<0,008	<0,008	<0,008	0,0244	<0,008	0,0271	0,0239	0,0147	0,0163	0,0254	0,0090	<0,008	0,0246	0,0397	0,0148	0,0323	0,2835	0,2030
	PCH20	0,0032	0,0248	<0,008	0,0086	<0,008	0,0638	<0,008	0,2372	0,1838	0,0764	0,1477	0,1004	0,0432	0,0576	0,0896	0,0735	0,0137	0,0615	1,1818	0,9911
	PCH19	0,0027	0,0290	<0,008	0,0124	0,0198	0,1725	0,0152	0,6969	0,5362	0,2293	0,4478	0,3368	0,1449	0,1860	0,3042	0,2610	0,0581	0,2243	3,6744	3,0582
	PCH18	0,0058	0,0249	<0,008	0,0121	0,0153	0,1028	0,0236	0,3735	0,3141	0,1699	0,2845	0,2181	0,0996	0,1121	0,1960	0,1556	0,0502	0,1519	2,3042	1,8604
	PCH17	0,0048	0,0297	<0,008	0,0135	0,0185	0,1045	0,0197	0,3014	0,2464	0,1250	0,2036	0,1513	0,0701	0,0800	0,1430	0,1147	0,0333	0,1037	1,7584	1,4223
	PCH10	0,0047	-	<0,008	<0,008	0,0228	0,0391	0,0167	0,0575	0,0479	0,0217	0,0440	0,0320	0,0147	0,0151	0,0291	0,0201	<0,008	0,0185	0,3792	0,2930
	PCH11	0,0043	0,0661	<0,008	<0,008	<0,008	0,0428	<0,008	0,0885	0,0626	0,0413	0,0499	0,0379	0,0163	0,0154	0,0402	0,0332	<0,008	0,0325	0,5267	0,4064
	PCH9	0,0371	0,0328	0,0106	0,0211	0,0209	0,1602	0,1644	0,5528	0,4674	0,2561	0,4354	0,3521	0,1507	0,1822	0,3155	0,2682	0,0775	0,2668	3,7347	2,9046
	PCH8	0,0034	0,8536	<0,008	<0,008	0,0209	0,0310	0,0106	0,0469	0,0353	0,0140	0,0290	0,0222	0,0114	0,0105	0,0195	0,0196	<0,008	0,0221	1,1466	0,2279
	PCH7	0,0095	0,0455	<0,008	<0,008	0,0141	0,0746	0,0389	0,2480	0,2074	0,1107	0,1875	0,1255	0,0609	0,0639	0,1316	0,0940	0,0431	0,0652	1,5109	1,1829
	PCH6	0,0058	0,0260	<0,008	0,0096	<0,008	0,0518	0,0289	0,1579	0,1341	0,0719	0,1361	0,0927	0,0401	0,0491	0,0719	0,0672	0,0246	0,0538	1,0157	0,7938
	PCH1	0,0026	-	<0,008	<0,008	<0,008	0,0397	<0,008	0,0921	0,0816	0,0393	0,0789	0,0488	0,0205	0,0298	0,0374	0,0262	<0,008	0,0318	0,5261	0,4568
	PCH2	0,0045	0,0242	<0,008	<0,008	0,0093	0,0373	<0,008	0,0573	0,0531	0,0264	0,0476	0,0399	0,0159	0,0194	0,0393	0,0309	<0,008	0,0226	0,4232	0,3339
BV	PCH3	0,0033	0,0148	0,0165	0,0280	0,0308	0,3690	0,0924	1,0119	0,9113	0,7661	1,1506	1,0156	0,5215	0,5094	1,2350	0,8884	0,2194	0,8901	9,6708	7,7318
	PCH4	0,0038	0,0285	<0,008	<0,008	<0,008	0,0448	<0,008	0,0668	0,0557	0,0246	0,0513	0,0333	0,0141	0,0207	0,0332	0,0344	0,0103	0,0256	0,4433	0,3571
	PCH5	0,0044	-	<0,008	<0,008	<0,008	0,0400	<0,008	0,1119	0,0819	0,0334	0,0687	0,0531	0,0270	0,0313	0,0414	0,0287	<0,008	0,0277	0,5451	0,4650
Values of criteries	A	0,02	0,05				0,15	0,1	0,3	0,2	0,1	0,05	0,1		0,05	0,1	0,1		0,05	1	
MD ME	B	2,5	40				30	40	40	40	4	25	4		10	1,5	4		20	190	
C-gener.	I																				40

N	naphthalene	Ch	chrysene
Ac1en	acenaphthylene	B(b)F	benzo(b)fluoranthene
Ac2en	acenaphthene	B(j)F	benzo(j)fluoranthene
Fluoren	fluorene	B(k)F	benzo(k)fluoranthene
Fen	phenanthrene	B(a)P	benzo(a)pyrene
A	anthracene	I(123-cd)P	indene(1,2,3cd)pyrene
F	fluoranthene	DB(ah)A	dibenz(ah)anthracene
P	pyrene	B(ghi)Pe	benzo(ghi)perylene
B(a)A	benzo(a)anthracene		

Sum PAHs-A	sum of all listed PAHs
Sum PAHs-B	sum of PAHs responding to Methodical Direction of ME CR 1996
MD ME	Methodical Direction of Ministry of Environment of Czech Republic
	substances for which there are no criteria in MD ME

Tab. 2 Correlation coefficients of elements

	Cd	Co	Cr	Cu	Ni	Zn	V	As	Sb	Hg	Sr	Ba
Be	0,39	0,28	0,63	0,69	0,68	0,59	0,69	0,35	0,10	0,09	-0,17	0,08
	Cd	0,18	0,41	0,32	0,35	0,44	0,33	0,13	-0,10	-0,02	-0,35	-0,06
		Co	0,28	0,34	0,47	0,22	0,29	0,22	-0,01	-0,03	0,01	0,08
			Cr	0,61	0,61	0,50	0,65	0,37	0,03	0,06	-0,13	0,03
				Cu	0,77	0,78	0,72	0,27	0,03	0,21	-0,03	0,03
					Ni	0,57	0,74	0,21	0,06	0,06	-0,24	-0,01
						-0,01	-0,01	0,72	0,99	-0,03	-0,04	-0,03
						Zn	0,55	0,32	0,00	0,20	-0,08	0,04
							V	0,24	0,00	0,07	-0,07	0,05
								As	0,73	0,07	-0,01	0,03
									Sb	0,06	0,02	0,01
										Hg	0,55	0,40
											Sr	0,35

Note: At the significance level 0.001 and number of observations 111 the critical value of correlation coefficient is $R=0.320$.

The correlation of Cd with the other elements is preliminary only, about 1/3 of given Cd contents were under detection limit.

samples slightly exceeded the critical limit for A category (1 ppm). In the case of Hg, the critical limit A (0.4 ppm) was exceeded in two samples (0.96 and 2.15 ppm) from the Břeclav district. The level of contamination caused by Sr was not possible to judge, because no critical limits for individual categories were available either from the Methodical Directions of Ministry of Environment of the Czech Republic or in other guiding documents. The concentrations of Sr 78 - 265 ppm. The distribution of concentrations of Ba in samples of the analysed series was strange. Ten highest values exceeded the critical limit 625 ppm set for the category C for general land use. The critical limit C does not differ significantly from the critical limit A (600 ppm), below which the Ba concentrations were for the remaining samples. Inasmuch as no analytical value fell between 600 and 625, we assumed that the Ba concentration of most of the samples is the natural concentration or the background value.

Results of Measurement of Radionuclides

In the case of radionuclides, the studied parameters were the distribution of Th, U(Ra), K and Cs¹³⁷, and

combinations of these elements with C_{org} and with some selected trace elements.

The Th content was 4 - 17 ppm and their distribution showed a slight increase southward. The U concentration decreased southward, although exceptions occurred. However no geographical variation was observed for U(Ra). The oscillating character of the U distribution curve was given mostly by higher error of analyses, mainly due to a higher weight of activities of Ra²²⁶ and Th²³². The value of U(Ra) was given mainly by activity of Ra²²⁶ that was more or less solid matter. The higher values of U again U(Ra) could be excepted mainly in places where, in areducing environment, the U⁺⁶ (for example UO₂²⁺) in solution was reduced to U⁺⁴ in the solid phase - the change of redox potential in basal sediments with organic impurities. There is no mutual correlation of weight activities or concentrations of U and U(Ra). The ratio of both values expresses the radioactive balance between U²³⁸ and Ra²²⁶. The decreasing trend of U from N to S indicates transport of this element from upper parts of the river basin and also the gradual establishing of radioactive balance between U²³⁸ and Ra²²⁶.

The K concentration increases slightly southward. The adsorption of K by clay minerals must be considered as it

was for Th. If we overlay the curve of Cs^{137} with the exponential curve, then it indicates a southward decrease. Both analysed elements do not indicate any mutual relationship. It is important to mention here, that both compared elements have significant positive linear correlation with a probability of 95% at least, which confirms the facts known about the relationship of Cs^{137} with organic matter.

On the base of correlation analyses between radioactive and metal elements some significant relationship were observed between Th and some metal elements (Ba, Sr, Cu, Zn, Cr, Ni a V). Ba has a significant positive correlation with Th (correlation coefficient 0.3138 with a significance 0.05). Sr, which has a significant positive correlation with Ba, but does not have any relationship with Th. There are notable correlations between Th/Cu (coeff. 0.3091) and Th/Zn (coeff. 0.4262, with a significance of 0.01). The reasons for the associations may be that they had a in common source or they had a similar geochemical behaviour.

The correlation coefficients for the association of Th with Cr and Ni are significantly positive with a probability of 98% at least. All these elements increase southward. Below the mouth of the tributary Dřevnice there is a notable increase in the contents of Cr and Ni of anthropogenic origin after the flooding of Zlín, Otrokovice and Napajedla. The correlation coefficient of Th/V = 0.279.

The dependence of a connection of Cs^{137} to the content of organic matter in sediments was also observed in the sample cores. In one third of the samples there was observed an imbalance between U and U(Ra) in the upper part of the profile (in flood water-laid deposits), which indicates a risk of a mobilisation of uranium by water. We have established certain critical limits for the judging of possible risks that results from the geochemical character of the studied elements, their migration abilities, and mainly from a proven long lasting negative influence on organisms. In the case of U(Ra) we consider as a critical value values equal or greater than 5 ppm, and at the same time values equal or greater than 3 in a ratio U/U(Ra). In the case of Cs^{137} we consider values equal or greater than 30 Bq/kg as critical values. We set up these limits considering radioactive background of the studied area, which we had obtained from geophysical data, and also considering known values of clark values of their content in rocks. From this point of view our critical limits are almost 2 times greater. Throughout the world, Cs^{137} is being monitored from the limit 30 Bq/kg. In the studied area this limit was exceeded in ten samples, mostly in the top part of core profiles. The limit of 5 ppm for U(Ra) was exceeded in two samples, also in top parts of the profile.

The distribution of radioactive elements in alluvial deposits, soils and soils of flooded areas of the Hornomoravský and Dolnomoravský Úval Depression could be effected by several factors. The depression area was provided with sediments, including Cs^{137} , from source areas with different geological environment. Also, there could have been erosion of material from chemical storage facilities, with some possibility thereby of enriching the radioactive elements.

The mountain catchment area is formed mainly by the crystalline areas of the Jenseníky and Rychlebské Hory Mts., in which underground mining was intensive in the past. In the case of the catastrophic flooding in July 1997, the radioactive elements, and also other minerals, could be moved from the mining area in the ion form (fixed to clay minerals, for example). They could be also fixed to eroded clastic particles, especially to heavy minerals of certain rock types. The rocks of the Orlicko-kladské crystalline complex should be considered as another natural rock sources. Mainly the west wing of the Sněžnická group represents a natural donation area, with increased contents of uranium. The transportation and accumulation of matter from flysch areas, mainly from Zlín, Vsetín and Kromněž areas, and its geochemical character, are conditioned by the erosion of individual flysch sequences. It was proved by a geophysical study that some flysch sequences have increased natural contents of radioactive elements (for example belowvážské sequences of magurka flysch and menilit sequences of inner flysch have increased the U content by tens ppm).

An important element, whose presence cannot be underestimated during cultivation of new farming soils, is Cs^{137} . As was mentioned above, the level of radioactivity in rocks is controlled by the contents of Th, U, K, and also Cs^{137} has some share. Each of these elements is controlled by the character of its migration.

Thorium (Th) belongs to elements having a low mobility; thus, during weathering processes, it passes into water solution in only a limited amount. In clastic particles Th is fixed to some heavy minerals (zircon for example), and it is also adsorbed by clay particles.

Uranium (U) occurs in rocks in two forms: with four charges (U^{4+}) and with six charges (U^{6+}). On the other hand U^{6+} is very mobile and the mobility of U^{4+} is also relatively small. During a reduction of U^{6+} to U^{4+} (for example in organic components) The U solidifies in a form of complexes and thus it can create secondary accumulations.

Potassium (K) does not show anomalies, however, its concentration is characteristic for many lithotypes. It is fixed mainly to silicates with layer structures of tetrahedrons (micas and hydromicas); it is also adsorbed by kaolinite and montmorillonite and its carrier could also be K-feldspar of clastic origin.

Most of the caesium (Cs^{137}) is a residue of the Chernobyl accident. Cs^{137} is strongly tied in soil horizons, thanks to its large ion diameter. Plants (mainly mushrooms) accumulate and bring the radioactive caesium into the food chain. In the case of flooded areas, it is important to take in to consideration a great run off of Cs^{137} from forest plant cover and its accumulation in sedimentation areas, together with organic matter and another mechanical fractions.

Conclusion

In the Czech Republic this is the first attempt to evaluate the contamination of soil or rock environment by flood sediments on a regional scale. This attempt includes the application of methods of organic geochemistry, deter-

mination of metal elements and also radionuclides in lithologically and genetically relatively related matter (near surface sampling of mostly fine-grained flood sediments).

It seems that the research of radioactive matter distribution can notably contribute not only in an evaluation of contamination of rock environment, but also in a search for source matter from source areas and in understanding the processes of redistribution in general.

The results show that the anthropogenic Cs^{137} that was deposited in our country after the Chernobyl accident will still contaminate the soil horizons on a regional scale, probably for a long time. The high content of this radionuclide (for example, in forest soils and also in plants, mainly in mushrooms, and subsequently in forest animals) were not, and still are not, evaluated with such support as they were in the developed countries. During the dynamic and long gradual processes of matter redistribution the radionuclides not only get into the soils and rock environment of flooded areas but also into alluvial and reservoir sediments. In the preserved samples from some reservoirs the layer enriched with Cs^{137} can be used for dating deposits as "before and after Chernobyl".

With regards to the vague evaluation of Cd and Ba contamination, it seems unavoidable to specify the critical limits for concentrations of trace elements,

group organic substances and individual organic pollutants, and to set up new concentrations for the evaluation of radioactive risks.

References

- MP 1992: Postup vyhodnocování závazků podniku z hlediska ochrany životního prostředí při zpracování privatizačního projektu. Metodický pokyn ministerstva pro správu národního majetku a jeho privatizaci ČR a MŽP ČR z roku 1992 k zabezpečení zákona č. 92/1992.
- MP 1996: Metodické pokyny MŽP ER k zajištění procesu nápravy starých ekologických zátěží. Příloha Zpravodaje MŽP ČR, 8, 1996, Praha.
- Ondra P. & Hanák J., 1989: Některé zákonitosti distribuce radioaktivních prvků v klastikách sekvencí karpatského flyše. *Mineralia Slovaca* (Košice), 21, 131-139.
- Ottesen et al., 1989: Overbank sediment: a representative sampling medium for regional geochemical mapping. *Journal of Geochemical Exploration*, 32, 257-277.
- Schwarzenbach R. P., Gschwend P. M. & Imboden, D. M., 1993: *Environmental Organic Chemistry*. New York, Vyd. John Wiley & Sons, Inc.
- Strnad M. et al., 1996: Výzkum kontaminace půd brněnské aglomerace PAH a PCB. Brno. MS, ČGÚ Praha.
- Tomlin C., editor, 1994: *The Pesticide Manual*, Tenth Edition. Crop Protection Publications. Farnham, UK.
- Vyhláška MŽP ER, Sb. zákonů č. 13/1994, kterou se upravují některé podrobnosti ochrany zemědělského půdního fondu.