The Fluvisol and sediment trace element contamination level as related to their geogenic and anthropogenic source

R. Vácha¹, M. Sáňka², O. Sáňka², J. Skála¹, J. Čechmánková¹

¹Research Institute for Soil and Water Conservation, Prague, Czech Republic

ABSTRACT

The upper values of the extractability of trace elements (As, Be, Cd, Co, Cr, Cu, Ni, Pb and Zn) in 2 mol/L HNO $_3$ and 0.025 mol/L ethylenediaminetetraacetic acid (EDTA) (compared with their pseudototal content in *aqua regia*) for determination of prevailing anthropogenic and geogenic soil load were proposed and compared with the results of the other 30 Fluvisol samples collected from the Labe fluvial zone. The increased geogenic load of Fluvisols was confirmed in the case of Be and As in some localities where low extractability with increased pseudototal contents were detected as opposed to the other elements when their increased pseudototal contents were followed by their increased extractability. The maps of probability of increased geogenic soil load in the area of the Czech Republic based on the comparison of geological substrates and trace element load were constructed. The combination of proposed elements extractability values for geogenic load together with developed maps is a suitable tool for the definition of prevailing Fluvisol or sediment load on some localities in the whole area of the Czech Republic. The results can be also a useful tool in the decision making processes regarding dredged sediment application on agricultural soil (support tool for legislative norms, Direction No. 257/2009 Sb.).

Keywords: soil; dredged sediments; soil contamination; geological substrates

The soil load with trace elements is caused by natural (geogenic) and anthropogenic sources of contamination. The frequent aim of chemical methods is the evaluation of critical trace element contents in soils reducing their transfer into food chains, and respectively the other matrices of the environment (Hellmann 2002). Anthropogenically induced contents of trace elements in soil support an increase of their mobility and bioavailability, generally (Němeček et al. 1996, Száková et al. 2005). Although the geogenic load is connected with low element mobility, in some cases of extreme geogenic loads an increased trace element mobility was observed (Filipinsky and Kuntze 1990, Němeček et al. 2002). These findings show the importance of contamination source determination for the prediction of trace element mobility and their subsequent transfer into plant production when different methods for prevailing contamination source; like geoaccumulation index, enrichment factor or pollution index, were described (Rafiei et al. 2010).

Generally, the load of sediments and Fluvisols is predominantly connected with anthropogenic factors in the Czech Republic (Podlešáková et al. 1994, Vaněk et al. 2005). Similar results were presented by Netzband et al. (2002) and Zerling et al. (2006) in Germany. Some authors, however, pay attention to more detailed principles of Fluvisols and sediments contamination by respecting the geogenic sources of trace elements load (Schwartz et al. 2006, Anawar et al. 2010, Deng et al. 2010). The Fluvisol contamination can markedly limit the agricultural use of these soils with high fertility potential.

Similarly, the increased trace element load of river sediments was described (Heise et al. 2005). These results restrict the use of dredged sediments in ag-

Supported by the Ministry of the Interior of the Czech Republic, Project No. VG 20102014026, and by the Ministry of Agriculture of the Czech Republic, Project No. MZE 0002704902.

²Masaryk University Brno, Brno, Czech Republic

riculture when trace element contents in dredged sediments exceed valid limits (Directive No. 257/2009 Sb.) in many cases in the Czech Republic (Vácha et al. 2011). This legislative norm allows the use of sediment with increased trace element contents of geogenic origin in agriculture (direct application on the soils) but unfortunately does not provide a suitable tool for geogenic load determination (especially mobile trace element contents criteria in sediments and soils are missing).

We utilized the results of studies focused on sensitivity of the extract of 2 mol/L HNO3 and 0.025 mol/L EDTA for the assessment of anthropogenic and geogenic load with trace elements in the soils (Borůvka et al. 1996, Vácha et al. 2002) and we verified this data on a set of 30 Fluvisol samples. These extracts seem to be promising for Fluvisols and sediments contrary to weaker extracts of 1 mol/L NH₄NO₃ or 0.01 mol/L CaCl₂ for mobile trace elements contents determination because of their low contents in Fluvisols and sediments thanks to continual leaching by water in an aquatic environment (Vácha et al. 2011). The connection of proposed upper limit values of trace elements extractability for geogenic load in combination with constructed maps to determine the areas with increased geogenic load potential and the areas of Fluvial zones (polygons of the river basin of 4th order) in the area of the Czech Republic was developed as a suitable support tool for current legislation to assess the prevailing soil and sediment load (geogenic, anthropogenic) appointed to the local authorities responsible for the decision making process for example.

MATERIAL AND METHODS

The set of 30 soil samples from fluvial zones of the Labe river was collected. The Fluvisol samples (soils developed on alluvial sediments) were taken from Ap horizons of agriculturally used soils (meadows, arable soils) in widths of up to 50 m from river channels. This area is periodically flooded (in the spring usually). The length of the study area was up to 100 km (Figure 1). The coordinates of sampled localities and soil characteristics (pH $_{\rm H_2O}$, $\rm C_{\rm ox}$, depth of humic horizon) were specified. The contents of trace elements (As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, V and Zn) were analysed in soil samples in the following extracts.

Aqua regia extraction (CSN EN 13346) – pseudototal content. The extract is quantified in Czech legislation giving limit values to trace elements in agricultural soils (Direction No. 13/1994 Sb.) and limit values in sediments for agricultural use (Direction No. 257/2009 Sb.).

The procedure is provided in the laboratory temperature 2 mol/L HNO₃ extraction (20°C, reciprocating shaker, 200 cycles per minute, 6 h, Zbíral et al. 2004). The extract is quantified in Czech as 0.025 mol/L EDTA extraction – potentially mobile contents of trace elements in soils and sediments (Zbíral et al. 2004).

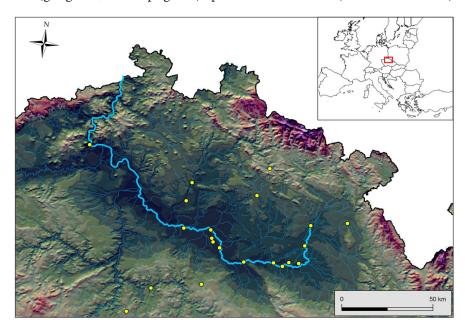


Figure 1. The Labe water basin and sample points

The soil samples for analysis were prepared from soil particles < 2 mm following the methodology CSN ISO 11464. Contents of trace elements in the extract were analysed by the Atomic Absorption Spectrometry (AAS) method using the following equipment: VARIAN AA 240Z – ETA (Palo Alto, USA; electrother-mic atomization) for Cd and Be analysis, VARIAN AA 240 – FAAS (Palo Alto, USA; flame technique) for Co, Cr, Cu, Ni, Pb and Zn analysis and VARIAN AA 240 – VGA (Palo Alto, USA; hydride technique) for As analysis.

The analyses were done in the accredited laboratory of the Research Institute for Soil and Water Conservation in Prague. The quality assurance of analytical data is guaranteed by the control process using matrix certificated materials (soils and sediments, CRM 7001–7004, Prague, Czech Republic) and certified methods of the analyses. The laboratory test protocol of every analysis is available.

The approach using geographical information system (GIS) was applied for the demarked areas (river basin) where geogenic load could be expected.

The maps of geogenic load with trace elements potentially influencing fluvial zones were generated using following sources:

Vector layer of the river basin of 4th order in the scale of 1:1 000 000 loaded in ESRI shapefile format, source Digital Base of water economic data (DIBAVOD, Prague, Czech Republic).

Geological map of the Czech Republic in the scale 1:500 000, coordinate system JTSK and S42, source atlas of maps of the Czech Republic GEOCR500, Czech Geological Institute.

The register of contaminated sites was processed by the Central Institute for Supervising and Testing in Agriculture in the Czech Republic (Kubík 2009). The database is an output of the soil agronomical testing process following the Czech legislation, Act No. 156/1998 Sb.

Based on the register of the contaminated sites database, the localities exceeding the limit values for sediment use in agriculture (Direction No. 257/2009 Sb.) were selected (at least one element exceeded the limit value on such locality). The geological map of the Czech Republic including 20 substrate units was divided into three categories based on the probability of geogenic load. On the basis of localisation of the contaminated points from the register of contaminated sites, water basins of the 4th order were delimited using an intersect function and were depicted on a layer of geological map selected on the basis of geogenic load potential.

The data was processed by the use of elementary statistical methods (Microsoft Excel, Redmont, USA) and geographic information systems (ESRI ArcGIS 9.2, Redlands, USA).

RESULTS AND DISCUSSION

The selection of extracts and trace elements extractability assessment in Fluvisol samples were calculated and evaluated with the use of previous works (Němeček et al. 1996, Vácha et al. 2002) when the extractability for individual trace elements from geogenic and anthropogenic sources

Table 1. Extractability of risk elements (%) in soils with different source of load derived from the data of Němeček et al. (1996) and Vácha et al. (2002)

Element		2 mol/L HNO_3	0.025 mol/L EDTA				
	geogenic	air deposition	fluvial	geogenic	air deposition	fluvial	
As	13	40	42	3.5	9.3	25.5	
Be	15*	20-50	30-90	_	_	_	
Cd	70*	87	95	51	40-72	95	
Cr	< 10	< 10	48-67	0.5	> 1	> 1	
Cu	30	44	72	18	28	40	
Mn	33	55	78	17	28	57	
Ni	_	_	_	25	40	60	
Pb	32	57	83	50	> 60	> 60	
Zn	20	50	70	25	> 40	> 40	

Be* – derived for soils developed on parent materials from acid rocks; Cd* – derived for soils developed on parent materials from weathering limestone products

Table 2. Extractability of risk elements in 2 mol/L HNO₃ (%) in set of Fluvisols (medians)

	As	Be	Cd	Cr	Cu	Ni	Pb	Zn
A	28	29	92	10	52	30	68	35
В	48	18	95	67	77	no	90	55

A – load under background values in Czech agricultural soils; B – load over background values in Czech agricultural soils. no – no relevant data analysed

was derived (Table 1). The solubility was calculated for the extracts of 2 mol/L HNO $_3$ and 0.025 mol/L EDTA. In our case, the *aqua regia* soluble element content was used for the calculation of the 2 mol/L HNO $_3$ and 0.025 mol/L EDTA soluble element portion instead of the pseudototal content (*aqua regia* extract). The borderline extractability for the load from geogenic sources was derived. The relevance of calculated extractability values was verified on the set of 30 Fluvisol samples.

The values of trace elements extractability in 2 mol/L HNO₃ (extract in 2 mol/L HNO₃/extract in aqua regia \times 100) derived from the set of 30 Fluvisol samples and calculated as median values are presented in Table 2. The extractability for fluvial load under and over background values were calculated separately. It is documented that an increased load of Fluvisols by trace elements is followed by its increased extractability. Sharp differences were found in cases of elements with generally low mobility. Cr, As and Pb caused the enrichment of anthropogenic load increases the extractability of elements markedly. For the most mobile Cd gives rise to a low difference between the extractability of background and increased load prospective regardless of the differences in the case of Zn are surprisingly much more evident.

Be shows an opposite trend where increased Fluvisol load is followed by lower extractability in an observed set of Fluvisol samples. General Be extractability values in 2 mol/L HNO $_3$ did not reach the extractability values for fluvial load in Table 1 but overcome the value of geogenic load and are still typical for anthropogenic load. The extractability value for Ni was calculated only for low Fluvisol load because no increased Fluvisol Ni load was observed. On the basis of this fact and previous works (Němeček et al. 1996, Vácha et al. 2002) it could be concluded that 2 mol/L HNO $_3$ is not a suitable agent for Ni geogenic load evaluation.

The number of samples exceeding background values of 1 of trace elements in Czech soils is shown in Table 3 together with the samples with low trace elements extractability that is typical for geogenic load (exceeding 2). The samples with trace elements contents over their background values and low trace elements extractability (geogenic load) are presented as exceeding 3. The data shows that the most problematic are Be, Zn and Cd. The low extractability typical for geogenic load was observed in Fluvisols in the case of Cr >> Cd > Be > As and Zn. Cu and Pb show increased extractability in all samples and their prevailing anthropogenic inputs into Fluvisols could result. Opposed to this, low extractability typical for Cr could be connected with geogenic load especially in the Fluvisols with low Cr load. Increased Cr contents (3 samples)

Table 3. Number of samples exceeding background values of risk elements and number of samples with risk elements extractability value under value typical for geogenic load

	As	Ве	Cd	Cr	Cu	Ni	Pb	Zn
Background	20	2	0.5	90	60	50	60	120
Exceeding 1	5 n	10 n	8 n	3 n	4 n	0 n	4 n	7 n
Exceeding 2	1 n	4 n	5 n	14 n	0 n	_	0 n	1 n
Exceeding 3	1 n	3 <i>n</i>	0 n	0 n	0 n	_	0 n	0 n

Background – risk elements background values in Czech agricultural soils; exceeding 1 – exceeding number of risk elements background values in a set of Fluvisol samples; exceeding 2 – samples number of extractability values under value of geogenic load in a set of Fluvisol samples; exceeding 3 – samples number of extractability values under value of geogenic load in a set of Fluvisol samples and with increased load over background values simultaneously

are connected with increased Cr extractability. Similarly, increased Cd contents in the Fluvisols reflect anthropogenic load. Nevertheless, Be (3 samples) and As (1 sample) show that increased trace element contents in the Fluvisols could be related to geogenic load in some cases.

The extractability of 0.025 mol/L EDTA shows comparable values with 2 mol/L HNO3 when sharper differences were observed in the case of Cr (20 times lower) and were problematic in the case of Be. The values of Be extractability in EDTA differed in the set of samples with different loads and no statistically relevant data could be derived. The same situation occurs at evaluation of Ni extractability results in 2 mol/L HNO₃ and the combination of both extracts can be recommended to avoid the described problems. On the basis of selected data the values of trace elements extractability for both extracts (2 mol/L HNO2 and 0.025 mol/L EDTA) defined as upper limits for geogenic load in Fluvisols and sediments were proposed (Table 4). The samples with trace elements extractability equal to and lower than the defined limit values could be designated as the samples with prevailing geogenic load.

The observed load of Fluvisol of the Labe River is in good agreement with the results of Netzband et al. (2002). These authors document an increased load with As, Cd and Zn. The extractability of trace elements indicates their increased anthropogenic inputs into Fluvisols in most cases. The load with Cd and Zn could be connected especially with anthropogenic inputs as it was also confirmed e.g. by Zerling et al. (2006) in the European context. The load of Fluvisols with trace element contents under background values is proven by geogenic sources and is more evident (lower extractability) than in Fluvisols with trace elements contents exceeding background values (higher extractability). The data confirms that geogenic sources of trace elements play an important role in uncontaminated Fluvisols (Deng et al. 2010), but increased contents are usually related to anthropogenic load (Podlešáková et al. 1994). This trend could be presented using the example of Cr especially. Nevertheless, in the case of As and Be it was documented that a strong influence of geogenic load resulting in an increased load of alluvial sediments could not be excluded. In these cases quantitative load with As and Be from geogenic sources leads to exceeding their background values in the soils. The low extractability in 2 mol/L HNO₃ confirms prevailing geogenic sources. The observed data confirmed a predominance of anthropogenic load in loaded Fluvisols but the existence of prevailing geogenic load over anthropogenic load was confirmed also (As, Be) in the Fluvisols with their increased contents. The construction of maps presenting the probability of increased geogenic load in the area of the Czech Republic was realized. The probability of geogenic contamination of agricultural soils was derived as the correlation of geological substrate categories with GIS layer showing the samples which exceed limit values on the area of the Czech Republic (Kubík 2009) and with GIS layer showing the polygons of river basin of the 4th order. The combination of these three individual GIS layers into one complex GIS layer gives the information on which localities or just river basin of the Czech Republic area with increased trace element contents it can be detected and highlights if these cases could be related to geogenic load.

This approach was done in two main steps. In the first step only two GIS layers were combined and the resultant map (Figure 2) shows the areas of river basins of the 4th order and shows sampling sites with increased contents of trace elements in the area of the Czech Republic. In the final map (Figure 3), the third GIS layer showing areas of probability of geogenic contamination was added.

The described approach based on the comparison of trace elements extractability in 2 mol/L HNO $_3$ and 0.025 mol/L EDTA (with the existence of the proposed upper values for geogenic load) and the comparison of observed data with the map overview showing the presence of the areas with increased geogenic sources is a suitable tool for the differentiation of anthropogenic and geogenic load of Fluvisols and sediments and can serve as

Table 4. Upper limits of risk elements extractability (%) in 2 mol/L HNO $_3$ and 0.025 mol/L EDTA for geogenic load in Fluvisols and sediments

Extract	As	Cd	Ве	Со	Cr	Cu	Ni	Pb	Zn
HNO ₃	15	70	15	30	10	30	_	30	20
EDTA	5	50	_	25	0.5	25	25	50	25

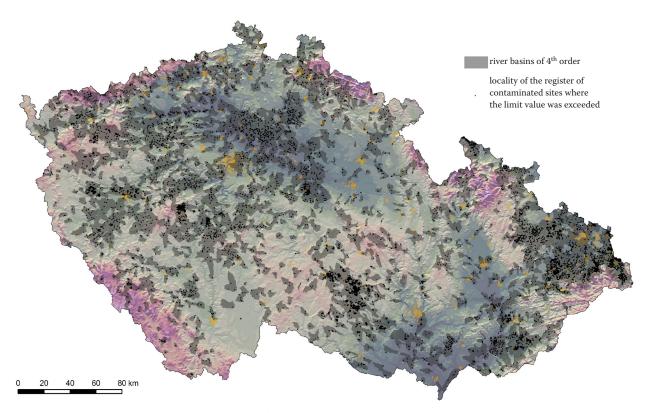


Figure 2. Localisation of the river basins of $4^{\rm th}$ order with sampling sites (Kubík 2009), where the limit value for risk element content was exceeded

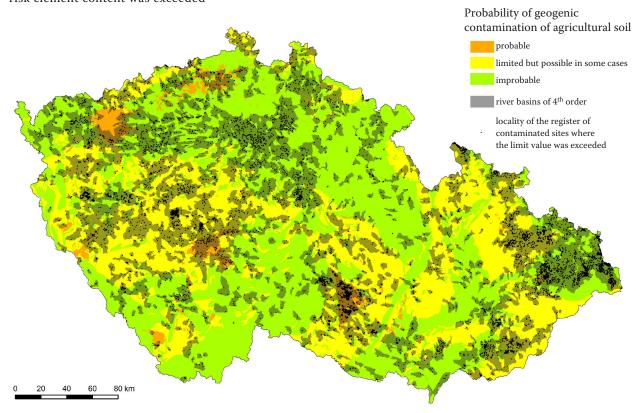


Figure 3. Probability of geogenic contamination of agricultural soils – correlation of geological substrate categories with sampling sites (Kubík 2009), where the limit value for risk element content was exceeded and polygons of river basin of $4^{\rm th}$ order

an informative source in any decision-making process concerning the application of sediments on agricultural land (Direction No. 257/2009 Sb.).

Acknowledgements

The authors thank Mr Lee Anthony Buck for his kind language correction.

REFERENCES

- Anawar H.M., Mihaljevič M., Garcia-Sanchez A., Akai J., Moyano A. (2010): Investigation of sequential chemical extraction of arsenic from sediments: Variations in sample treatment and extractant. Soil and Sediment Contamination, 19: 133–141.
- Borůvka L., Huan-Wei Ch., Kozák J., Krištoufková S. (1996): Heavy contamination of soil by cadmium, lead and zinc in the alluvium of the Litavka river. Rostlinná výroba, 42: 543–550.
- ČSN ISO 11464 (2011): Soil quality Pretreatment of samples for physico-chemical analysis. Czech Technical Norm, ICS 13.080.05.
- ČSN EN 13346 (2001): Characterization of sludges Determination of trace elements and phosphorus *Aqua regia* extraction methods. Czech Normalisation Institute, ICS 13.030.20.
- Deng J., Wang Q.F., Yang L.Q., Wang Y.R., Gong Q.J., Liu H. (2010): Delineation and explanation of geochemical anomalies using fractal models in the Heqing area, Yunnan Province, China. Journal of Geochemical Exploration, 105: 95–105.
- Filipinski M., Kuntze H. (1990): Plant uptake and solubility of lithogenous, pedogenous and anthropogenous cadmium of an Ap-horizon from orthic luvisol. Zeitschrift fuer Pflanzenernährung und Bodenkunde, *153*: 403–408.
- Heise S., Claus E., Heininger P., Krämmer Th., Krüger F., Schwarz R., Förstner U. (2005): Studie zur Schadstoffbelastung der Sedimente im Elbeeinzugsgebiet – Ursachen und Trends. Im Auftrag von Hamburg Port Authority. Abschlussbericht Dezember, 169.
- Hellmann H. (2002): Definitions of background-concentrations An overview. Acta Hydrochimica et Hydrobiologica, 29: 391–398.
- Kubík L. (2009): Register of contaminated sites 1990–2008. Final report UKZUZ. Available at http://www.ukzuz.cz/Folders/Articles/46660-2-Registr+kontaminovanych+ploch.aspx
- Ministry of Agriculture and Ministry of Environment of Czech Republic (2009): Direction No. 257/2009 Sb. for sediment use on agricultural soils.

- Ministry of Environment of Czech Republic (1994): Direction No. 13/1994 Sb. regulating some details of agricultural soil fund protection.
- Němeček J., Podlešáková E., Vácha R. (1996): Geogenic and anthropogenic soil loads. Rostlinná výroba, 42: 535–541.
- Němeček J., Podlešáková E., Vácha R. (2002): Transfer of trace elements with low soil mobility into plants. Rostlinná výroba, 48: 45–50.
- Netzband A., Reincke A., Bergemann M. (2002): The river Elbe
 A case study for the ecological and economical chain of sediments. Journal of Soils and Sediments, 2: 112–116.
- Podlešáková E., Němeček J., Hálová G. (1994): The load of Fluvisols of the Labe river by risk substances. Rostlinná výroba, 40: 69–80.
- Rafiei B., Khodaei A.S., Khodabakhsh S., Hashemi M., Nejad M.B. (2010): Contamination assessment of lead, zinc, copper, cadmium, arsenic and antimony in Ahangaran mine soils, Malayer, west of Iran. Soil and Sediment Contamination, 19: 573–586.
- Schwartz R., Gerth J., Neumann-Hensel H., Förstner U. (2006):
 Assessment of highly polluted Fluvisol in the Spittelwasser floodplain Based on national guideline values and MNA-criteria. Journal of Soils and Sediments, 6: 145–155.
- Száková J., Sysalová J., Tlustoš P. (2005): Particular aspects of environmental impact of potentially risk elements from airborne particulate matter. Plant, Soil and Environment, *51*: 376–383.
- Vácha R., Němeček J., Podlešáková E. (2002): Geochemical and anthropogenic soil loads by potentially risky elements. Rostlinná výroba, 48: 441–447.
- Vácha R., Čechmánková J., Skála J., Hofman J., Čermák P., Sáňka M., Váchová T. (2011): Use of dredged sediments on agricultural soils from viewpoint of potentially toxic substances. Plant, Soil and Environment, 57: 388–395.
- Vaněk A., Borůvka L., Drábek O., Mihaljevič M., Komárek M. (2005): Mobility of lead, zinc and cadmium in alluvial soils heavily polluted by smelting industry. Plant, Soil and Environment, 51: 316–321.
- Zerling L., Hanisch C., Junge F.W. (2006): Heavy metal inflow into the floodplains at the mouth of the river Weisse Elster (Central Germany). Acta Hydrochimica et Hydrobiologica, *34*: 234–244.
- Zbíral J., Honsa I., Malý S., Čižmár D. (2004): Soil Analysis III. Central Institute for Supervising and Testing in Agriculture, Brno, 199. (In Czech)

Received on October 30, 2012 Accepted on December 7, 2012

Corresponding author:

Doc. Ing. Radim Vácha, Ph.D., Výzkumný ústav meliorací a ochrany půdy, v.v.i., Žabovřeská 250, 156 27 Praha 5-Zbraslav, Česká republika

phone: + 420 257 027 281, fax: + 420 257 921 246, e-mail: vacha.radim@vumop.cz