Possibilities of some methods for risk assessment of arsenic load in soils

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ABSTRACT

The paper deals with the possibilities of arsenic analysis in the soil. The aim is the selection and verification of the methods for analysis of As in the soil, which seem to be suitable for risk evaluation based on the increased As soil load. Economical and analytical availability of the methods is an important criterion. A sample set of 6 heavily contaminated soils was used to compare application potential of prevalent as well as less common procedures for determination of arsenic forms in soils. The results showed that substitution of analytically more demanding As total content analysis and sequential analysis for simple extraction using one-off agents seemed to be promising in many cases. The comparison and evaluation of statistical correlation of used methods of As analysis in the soil was realised. The results suggested that using the combination of simple 1M $\rm NH_4NO_3$ extraction and determination procedure for amorphous Fe forms in the soil (the Tamm method) was suitable for the risk assessment stemming from the As contamination without necessity of the application of more complicated sequential extraction procedures.

Keywords: arsenic; soil; arsenic fractionation; extraction agents

Arsenic belongs to the group of trace elements; it means that As content exceeding the trace concentration level in the environment may lead to a toxic effect. An increased level of As concentration in human organism can cause carcinogenic and teratogenic symptoms. Weis and Weis (1991), Abedin et al. (2002), Urminská et al. (2002), Yerebakan et al. (2002) or Saha (2003) document and discuss it in a more detailed way.

Arsenic is usually found in soil in inorganic forms – arsenite [As (III)] and arsenate [As (V)]; it generally occurs in the pentavalent state because the As (III) form oxidizes to the As (V) form. The pentavalent form of As was found less toxic (Weis and Weis 1991). Although As human and zoo toxicity is usually reported, many authors deal with As influence on plant growth and plant physiology (Pavlíková et al. 2007, Das et al. 2008).

In the case of As, an interference between geogenic and anthropogenic origin of increased As content in Czech soils can be found.

Primarily atmospheric deposition, floods and load spreading round the mine dumps lead to the anthropogenic As contamination of the soil (Vácha

et al. 2002, Garrido et al. 2003). Studying the soil contamination in the Northern and Northwestern Bohemian region, the highest values of As contents were registered in the immission-impacted zone with the highest scale of the atmosphere pollution matter – Most, Teplice, Ústí nad Labem. The highest As total content (1526 mg/kg) was recorded in the Teplice region sample (Podlešáková et al. 1999).

In the soils of the immission – free regions, particularly As of geogenic origin prevails. According to the As present in rocks two categories of the geogenic load can be distinguished – lithogenic and chalcogenic. Both types of As geogenic load were recognised in the Czech Republic.

In the soils (especially in the Cambisols) of acid igneous and metamorphic rocks affected by metallogenic zones deposits of valued metals (Au, Cu) accompanied with increased As amounts sometimes occur. The As occurrence in ore veins is associated with the whole range of minerals depending on the type of mineralization. The increased As amount in gold bearing quartz veins of acid rocks or as part of hydrothermal mineral

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association were discussed (Bernard et al. 1981, Vácha et al. 2002, Filippi et al. 2004).

Solving the question of the ratio of geogenic and anthropogenic loads rests on the assessment of spatial distribution of the soil substrates indicating geogenic soil load (Němeček et al. 1996).

The geochemical properties of As are very complicated because various chemical modifications of As naturally occur in the environment, resulting from the amphoteric nature of As ions. Insoluble As sulphides are oxidised through the As-bearing rock weathering and thus arsenites and arsenates are produced. As is present mainly in the form of arsenates in the aerated soil, nevertheless under redox conditions another oxidative states (arsenites) may also occur, whereas a gradual methylation of As and the following production of toxic alkyl compounds arrive under anaerobic conditions. Sodium arsenite, arsenite oxide and methylated arsenic compounds are recognised to be the most toxic As compounds (Urminská et al. 2002). The As bonds in the soil resemble phosphorus soil bonds and they are based especially on compounds with Fe, Al and Cd. A certain As amount can be bound into organic compounds (Nriagu 1994).

Different As bonds significantly influence the arsenic plant uptake. Numbers of sequential extraction procedures (SEPs) have been developed to assess limit values of element contents in plants. A very detailed compendium of extract agents in use and their application potential was published in Beckett (1987). The weakly bound and phytoavailable portions of soil elements are released by the application of deionized water or neutral salts (Beckett 1987). Comparing the extractability of As, Cd, Zn in 35 soil samples with different physiochemical properties, Száková et al. (2001) found that As and Zn contents after the extraction in low strength agents did not exceed 0.5% of their total contents in the soils. Among used extraction agents the 0.01M CaCl₂ solution seemed as the most suitable for extraction of the elements (Száková et al. 2001).

The extraction in 2M HNO $_3$ is used for determination of potentially risk elements in soil. The limit values of risk element contents in agricultural soils, determined by the HNO $_3$ extraction technique, are included in the directive from the Ministry of Environment of the Czech Republic (Directive No. 13/1994 Coll.). The extractions in 1M NH $_4$ NO $_3$ and 0.025M EDTA (ethylenedinitrilotetraacetic acid) are used for rating of the portion of mobile or potentially mobilizable contents of risk elements in a soil (Podlešáková et al. 2001).

Arsenic belongs to the trace elements with low but established positively pH-dependent mobility. The enhanced As transfer from soils to plants also occurs in geochemically anomalous soils if the total arsenic content is extremely high. The critical levels of As amounts in plants (2–5 mg/kg) were exceeded by the total As amount above 2000 mg/kg in the soil even by low portion of the mobile fraction (< 10%, the 2M HNO₃ extraction) and by very low soil pH (3.9-4.8) (Němeček et al. 2002). Provided that effects of the geochemical anomaly and anthropogenic contamination coincide as in the case of the Kutná Hora locality, the mobility of soil As can rapidly increase. The As mobility in the Kutná Hora soil sample reached the level of the As mobility comparable to the samples from the immission impacted areas. Higher As mobility was then documented in soils with the fluvial load (Vácha et al. 2002). Makovníková et al. (2007) presents possibilities for the primary assessment of As contents in agricultural soils of Slovakia. Generally, low As mobility in the soil complicates the removal of As from contaminated soils by the use of gentle techniques including phytoremediation (Tlustoš et al. 2006).

The methods of sequential analysis can be used for detailed studies of different As forms in soil. An array of extraction methods for the cationic form of elements of the soil media are available e.g. the commonly used Tessier procedure (Tessier et al. 1979). Zeien and Brümer (1989) SEP is used for potentially risk elements assessment in the Research Institute for Soil and Water Conservation (RISWC). The application of this method for the soil As with anionic nature can be disputatious. Therefore specific schemes and sequential analysis for the assessment of soil As were developed (McLaren et al. 1998, Wenzel et al. 2001). The extraction scheme devised by Wenzel et al. (2001) stemmed from the chemical resemblance of arsenic to phosphorus or selenium.

Because of growing number of analytical methods their comparability turned problematic and a European recommending standard for SEP for some risk elements (BCR EUR 19775 EN) was developed (Rauret et al. 2001). This procedure was tested for our soil conditions in the study carried out by Száková et al. (1999) – a sample set of 35 Czech soils was analysed there. It was found out that the residual immobile As fraction bound to silicates (75%) occurs largely in monitored soil samples. The results of this SEP were compared with the results of two other analytical schemes and it was ascertained that the total As ratio was

different and hardly comparable if using individual methods. Nevertheless, a statistical significant correlation of analytical data suggested that trends in the As distribution into main soil fractions reflected the applied extraction scheme (Száková et al. 2003).

Similarly conceived studies in geological branches were published (Mihaljevič et al. 2003) where the suitability of SEP for the assessment of As bound into a mineral soil phase is discussed. Filippi et al. (2004) supplemented simple As extraction with the determination of As in the mineral soil phase. The As-bearing minerals were determined using the X-ray diffraction and electron microscopy scanning.

MATERIAL AND METHODS

Six soil samples with increased As contents were used. Soil properties, locality characterisation and supposed dominant type of the As load are depicted in Table 1.

Soil samples were taken with a non-metallic tool from a divot horizon in the depth of 5–15 cm in the localities of the permanent grassland land use. GPS localisation, the site description and pedologic characterisation were done using the Taxonomic Soil Classification System of the Czech Republic (Němeček et al. 2002).

Following soil properties were determined in the central laboratory of the Research Institute for Soil and Water Conservation:

- (a) a grain size distribution (ISO 11277);
- (b) soil pH using the 1M KCl solution (ISO 10390);
- (c) qualitative and quantitative humus indicators including the content of organic carbon C_{org} (ISO 14235) and the humic- and fulvo acid ratio in sodium pyrophosphate;
- (d) the indicators of the cation exchange capac-

- ity (ISO 13536) the T value (mmol⁺/100 g), exchangeable H⁺ determined by titration in the same extract;
- (e) the arsenic content the total content extracted with the acid mixture and the content extracted with 2M HNO₃ under cold conditions;
- (f) besides the total Fe content Fe species were determined in soil samples to elucidate an interaction between the As and Fe. The Fe content extracted with pyrophosphate, ammonium oxalate and dithionate were measured (Buurman et al. 1996);
- (g) the crystalline Fe form and the ratio between Fe bound into amorphous and crystalline oxides and the complexly bound Fe with the organic matter (the chelate bond) were calculated from the difference of the Fe content in ammonium oxalate and dithionate extract.

The resultant set of experimental data was processed in the Excel programme and the statistical dependency of selected indicators on risk elements contents in individual soil fractions according to the selected sequential analysis was tested with the correlation analysis.

The As contents in the characterised soil fractions were analysed after using three SEPs. The first one is the method by Wenzel et al. (2001) that was developed especially for soil As by the modification of the Zeien and Brümmer (1989) SEP. The second technique used was the fractionation in accordance to the BCR 701 EUR 19775 EN (2001) norm relevant for number of risk elements in various types of matrix (sewage sludge, soil). The third method was then the original scheme according to Zeien and Brümmer (1989).

Our survey attempted not only to test individual methods but also to look for the possibilities of using more simple, economically and analytically less demanding methods while maintaining comparable predicative ability to sequential schemes. When using the SEPs, 20% measurement

Table 1. Basic	characterisation	of samplii	ng localities
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Locality	District	Elevation (m above sea level)	Soil type	Substrate	Supposed As load
Mikulov	Teplice	600	KAd	gneiss	immission and geogenic
Klinovcik	Teplice	815	KAd	gneiss	immission and geogenic
Mokrsko	Pribram	420	KAd	acid intrusive rocks	geogenic
Litavka	Pribram	440	FLm	alluvial sediments	fluvial
Kank	Kutna Hora	275	HNm	loess	anthropo-geogenic
Zaskali	Liberec	550	KAd	mica schist and flysh	immission and geogenic

Table 2. Operating procedure of Tamm method

	Extraction	Extraction	Extraction technique		
Tamm method	agent pH	agent chemist	sample/reagent (w/v)	extraction duration	
metnod	3.0	ammonium oxalate oxalic acid	1 g + 50 ml	4 h (horizontal shaker)	

uncertainty is commonly counted for the As assessment in individual extracts. If the uncertainty value reaches 20% in the first step of the Zeien and Brümmer SEP, then it increases up to 53% in the seventh step. It can result in a consideration in term of the replacement of the SEP for the simultaneous extraction using several one-off extraction agents.

Considering the chemical similarity of P and As and the assumption that both elements are particularly associated with hydrated Al, Fe oxides, one-off extraction agents can be then divided into 2 categories.

The first class includes soft agents that are used for the assessment of mobile and potentially mobilizable portions of risk elements (Száková et al. 2001). In regard of gathered experiences we prefer using of 1M NH $_4$ NO $_3$ (for mobile contents) and 0.025M Na $_2$ EDTA for potentially mobilizable contents. Especially the first scheme is crucial, if only for the reason that it is employed as the international standard for the soil quality evaluation (ISO/DIS 19730).

The established As association with soil Fe oxides provides an opportunity for proofing the procedure for the assessment of Fe and Al active forms significant for the P fixation in the soil. The

Fe-associated As content is then compared with the contents of other soil As forms of interest. For those purposes the extraction procedure originated from Tamm (1922) was used, intended for determination of amorphous Fe forms and based on the extraction using ammonium oxalate and oxalic acid. This scheme was successively modified owing to an instrumental technique progression (Buurman et al. 1996). Although the modified method was used in our laboratory it carries the name after its original author ("the Tamm method") to make the following text more lucid (Table 2).

All measurements were carried out twice in three repetitions. The summary results of measurements were proceeded by elementary statistics. The correlation analysis using the ANOVA method and the Pearson correlation coefficient calculation were accomplished.

RESULTS AND DISCUSSION

The variance in the soil grain size structure of tested soils reflected the soil types. The highest portion of clay elements comprises the haplic Luvisol developed on the loess on the Kank locality. The increased content of the 0.05–0.25 mm size fraction

Table 3. Characteristics of used soils

Locality	pH exchange- able -	C_{org}	T value (CEC)	H ⁺ exchange- able	Grain size < 0.001 mm		HA:FA	As (total)	As (HNO ₃)	As (EDTA)
	able -	(%)	(mmo	l/100 g)	(%	%)			(mg/kg)	
Mikulov	5.06	3.1	24.3	11.5	6.7	21.4	1:1.15	364.2	124.2	7.65
Klinovcik	3.63	4.82	34.8	38.0	7.7	23.8	1:2.15	227.8	29.1	1.17
Mokrsko	5.09	0.92	39.5	3.5	7.7	17.6	1:2.45	424.3	77.9	4.66
Litavka	5.59	1.25	7.8	4.0	5.7	12.1	1:2.46	227.7	183.7	11.5
Kank	6.54	1.57	20.3	0.5	21.6	35.7	1:1.9	170.3	72.9	30.8
Zaskali	5.53	0.89	13.8	7.0	6.1	30.9	1:2.5	44.6	10.8	0.98

HA:FA - the ratio of carbon content in humic and fulvic acids

(characterising the sandy fraction) was detected in the Fluvisol from the Litavka site. Similar grain size distribution was observed among the locality couples of Cambisols (between the Mikulov and Mokrsko couple, and Klinovcik and Zaskali couple). The crucial soil properties are figured in Table 3.

The exchangeable soil pH values within the set of samples ranged between 3.63 and 6.54. The lowest soil pH-value as well as the highest portion of exchangeable H+ were detected in the Klinovcik soil sample. On the contrary, the highest pH-value were predictably measured in the soil from the Kank locality. The exchangeable soil pH values of other localities were in acid pH-range and the soil from Zaskali had the highest pH value among Cambisols (pH 5.53). 5.59 pH value was measured in the sandy Fluvisol originated from the Litavka river alluvium.

The values indicating sorption properties of studied soils show that the Fluvisol of the Litavka river alluvium had the lowest cation exchange capacity (CEC) (7.8 mmol⁺/100 g).

The highest CEC values were found in soils from Mokrsko (39.5 mmol⁺/100 g) and Klinovcik (34.8 mmol⁺/100 g). The 2M HNO₃ extract/total extract ratio indicates a significant contribution of the geogenic load in the soil from Klinovcik (12.8%) and Mokrsko (18.4%). The ascertained values of the solubility correspond to preceding findings (Vácha et al. 2002). Hence, presumed enhanced As amount from the immission load on the Mikulov locality (34.1%) and the solubility value of the Zaskali sample (24%) is characteristic rather for prevailing geogenic load. The highest solubility value were measured in the Fluvisol from the Litavka river alluvium (80.7%) and the increased solubility in the Kank soil (42.8%) markedly exceeded the values commonly measured in geogenic loaded soils. The enhanced portion of the potentially mobilizable fraction (the EDTA extraction) was also registered in the Kank locality, suggesting the anthropogenic origin of the As contamination stemming from the ore mining slash deposition (Vácha et al. 2002).

The highest Fe amount was measured out in the soil from Klinovcik, where Fe occurs in the prevailing form of complexes with humic matter, confirmed by the high C_{org} content as well. The narrowest ratio was also observed between Fe bound into crystalline and amorphous oxides. The second highest Fe content was assessed in the Cambisol from Zaskali, there was surprisingly a high amount of organically bound Fe in spite of the fact that C_{org} content was the lowest among all soil samples. The lowest Fe content was recorded in the Kank Luvisol, not surprisingly considering the soil type. In this sample there was a relatively high proportion of Fe bound into crystalline oxides. We suppose that it relates to the ore mining gangue application into the upper soil horizon.

Markedly different content of Fe forms was found in the Fluvisol from the Litavka river alluvium, where Fe bound into amorphous oxides dominates As in just one case and where the proportion of Fe associated with humic matter is the lowest from the set of soil samples (Table 4).

Basic differences were found in the quantification of the As content in defined soil fractions during the SEPs testing for the assessment of As in the set of samples with different type and level of contamination.

The Wenzel procedure and the Zeien and Brümmer technique proved dominant As association with amorphous and crystalline Fe and Al oxides in soils. The proportion of amorphous to crystalline oxides is mainly given by the soil matrix and by the load type. There was a balanced ratio of presented bonds with a moderate dominance of the As association with crystalline Fe oxides (due to the primary As incorporation into the crystal

Table 4. Fe contents in the soil samples

Locality	Fe (total)	Fe (oxal)	Fe (dithio)	Fe (pyro)	Amorphous:crystalline
Locality		(g,	/kg)		organically bound:
Mikulov	29.6	7.1	23.0	3.5	1:2.24:0.49
Klinovcik	69.1	15.1	32.4	32.4	1:1.15:0.90
Mokrsko	44.2	2.5	13.8	13.8	1:4.52:0.50
Litavka	36.3	12.3	20.0	20.0	1:0.63:0.23
Kank	27.2	3.0	13.6	13.6	1:3.53:0.31
Zaskali	48.8	5.5	14.6	14.6	1:1.66:0.71

Table 5. Content of As (mg/kg) in individual fractions (1-7) determined by Zeien and Brümmer extraction procedure

Step of extraction	Soil origin					
As (mg/kg)	Mikulov	Klinovcik	Mokrsko	Litavka	Kank	Zaskali
1	0.75	0.27	1.24	0.58	5.20	0.10
2	1.57	0.36	2.61	0.91	11.03	0.29
3	4.26	0.69	5.86	5.18	9.87	0.45
4	13.95	1.57	8.33	21.14	13.73	0.96
5	140.97	108.46	131.56	149.47	87.67	25.90
6	109.59	89.06	135.20	15.25	39.75	19.86
7	44.31	40.46	45.00	9.34	14.12	11.85
Sum	315.38	240.86	329.78	201.86	181.36	59.39
Total	359.25	248.05	427.65	236.85	172.15	43.96
Recovery factor (%)	87.8	97.1	77.1	85.2	105.3	135.1

1 – mobile; 2 – easily available; 3 – Mn-oxides bound; 4 – organically associated; 5 – amorphous Fe/Al oxides bound; 6 – crystalline Fe/Al oxides bound; 7 – residual fraction

lattice of the minerals) characteristic for soil samples with the geogenic load. The ratio was most likely dependent upon the stage of the soil matrix weathering and upon the process of anthropogenic input of As into the soil (immission fallout, flood). Using the BCR technique the major ratio of As was detected in the residual fraction most likely caused by the analytical scheme in the second extraction step (targeted on the As bound into Mn, Fe oxides). This extraction step is not sufficiently productive and selective for the As detection. The detection of Mn, Fe associated arsenic was arrived as late as during the determination of the residual As fraction using the *Aqua regia* extrac-

tion. A dominant arsenic portion in the residual fraction was present while using this method by Száková et al. (1999) as well.

After the BCR technique the organically associated As fraction amounted to low level values and did not exceed the Wenzel's proportion values of the organically bound As to other soil fractions (2-7%).

A preferable correlation between the 2M $\rm HNO_3$ extraction and easily exchangeable soil As was achieved using the Wenzel and the Zeien and Brümmer procedures. The BCR method was found less sensitive to the exchangeable soil As fraction.

Table 6. Content of As (mg/kg) in individual fractions (1-4) determined by BCR extraction procedure

Step of extraction	Soil origin						
As (mg/kg)	Mikulov	Klinovcik	Mokrsko	Litavka	Kank	Zaskali	
1	2.98	0.13	6.75	0.19	18.85	0.22	
2	71.45	5.88	31.15	133.65	39.28	3.8	
3	18.75	6.71	4.14	2.16	9.89	2.12	
4	319.5	283.5	406.5	246.0	114.0	42.5	
Sum	412.68	296.22	448.84	381.99	182.02	48.64	
Total	359.25	248.05	427.65	236.85	172.15	43.96	
Recovery factor (%)	114.86	120.13	104.88	152.81	105.77	110.64	

1 - exchangeable; 2 - associated with Fe/Al oxides; 3 - organically bound; 4 - residual fraction

Table 7. Content of As (mg/kg) in individual fractions (1-5) determined by Wenzel extraction procedure

Step of extraction			Soil origin				
As (mg/kg)	Mikulov	Klinovcik	Mokrsko	Litavka	Kank	Zaskali	
1	4.67	0.60	8.10	1.29	12.44	0.75	
2	13.15	6.21	17.57	21.48	27.78	2.46	
3	250.10	121.65	206.00	360.65	140.60	16.87	
4	183.95	134.00	230.45	36.45	25.05	26.65	
5	29.62	29.17	20.79	6.75	7.39	5.60	
Sum	481.48	291.63	482.90	426.62	213.26	52.33	
Total	359.25	248.05	427.65	236.85	172.15	43.96	
Recovery factor (%)	134.04	118.62	112.93	180.61	123.89	119.10	

1 – non-specifically bound, easily exchangeable; 2 – specifically bound (bound to mineral surface); 3 – associated with amorphous Fe/Al oxides; 4 – As associated with crystalline Fe/Al oxides; 5 – residual fraction

The BCR technique is not to be recommended for the assessment of As soil fractions.

A high level correlation of differences in the As distribution to particular fractions (especially for As bound into Al, Fe amorphous oxides where Pearson correlation coefficient attained the value of 0.908) was reached using the Wenzel and Zeien and Brümmer SEP. This ratio was quantitatively higher by 10% while using the Wenzel technique. We do not generally incline to the opinion that the contents of As in individual fractions resulting from the application of the procedure are not utilisable. But the Wenzel procedure can be preferred for more precise quantification owing to the probability of the lower analytical error effect alone. The results of the SEPs of the trial soil samples are figured in Tables 5–7.

Within the testing of simple extraction procedure using soft extraction agents the assessment of the mobile As fraction in the 1M $\rm NH_4NO_3$ extract used in the first extraction step of the Zeien and Brümmer SEP was compared to the $\rm NH_4NO_3$ extraction according to the international standard ISO/DIS 19730. Both schemes differ in the extraction duration as well as in the proportion

of the extraction agent to sample. Hence different absolute values of the As content (mg/kg) in both extracts can be expected. Measurement values are given in Table 8.

The presented values are arithmetic means of 3 independent measurements with 2 duplicates, where the repeatability value (duplicates) as well as the intermediate repeatability came out more favourable in the case of the Zeien and Brümmer scheme. As presumptive cause the fact is considered that it is the first extraction step, that is not weighed with the error of the following extraction steps and there is more favourable proportion of the sample to the extraction agent reducing the matrix effect. An ideal equilibrium can be assumed stabilising between the sample and the extraction agent owing to the 24 h extraction interval, the final concentration is then c. 20 times the value resulting from the standard method ISO/DIS 19730.

Nevertheless, a very tight correlation (the Pearson correlation coefficient = 0.999) was found among the results of the As assessment in the 1M $\rm NH_4NO_3$ extract using the procedures of interest. The application of the more simple scheme by ISO/DIS

Table 8. Comparison of the assessment of the mobile As fraction in the 1M $\rm NH_4NO_3$ extract used in the first extraction step of the Zeien a Brümmer SEP and in the international standard method ISO/DIS 19730

Method	Extraction duration	Sample/ extract (w/v)	Mikulov	Klinovcik	Mokrsko	Litavka	Kank	Zaskali
Zeien and Brümmer	24 h	1:25	0.75	0.26	1.24	0.28	5.2	0.1
ISO/DIS 19730	2 h	1:2.5	0.033	0.01	0.076	0.018	0.336	0.005

Table 9. Comparison of the As contents (mg/kg) in the extracts assigned for the determination of the active Fe forms

Locality	Wenzel 3	Brümmer 5	Tamm
Mikulov	250.10	140.97	277.50
Klinovcik	121.65	108.46	147.38
Mokrsko	206.00	131.56	225.84
Litavka	360.65	149.47	328.4
Kank	140.60	87.67	146.25
Zaskali	16.87	25.90	32.54

Table 10. Pearson correlation coefficient for the As content determined by various methods

Tamm/	Tamm/	Brümmer 5/
Brümmer 5	Wenzel 3	Wenzel 3
0.955	0.986	0.908

19730 can be considered in terms of operativeness and economy. Using 1M $\rm NH_4NO_3$ refers to the assessment of the soil As mobile forms that are determined in terms of risks under consideration.

Completely new approach to the As assessment is use of the determination procedure for amorphous Fe in the soil (the Tamm method). The As content resulting from the Tamm method significantly correlates with the content of As associated with Fe and Al amorphous oxides analysed by SEPs (Zeien and Brümmer – 5^{th} fraction, Wenzel et al. – 3^{rd} fraction) (Table 9). The values of the Pearson correlation coefficient are shown in Table 10.

It results in statistically significant correlation among tracked parameters from the mentioned results. It is presumable that the Tamm method is suitable for quick and orientational assessment and for the portion approximation of As associated with amorphous Fe and Al oxides in the soil. This assessment approximates the total As content in the soil owing to the predominant proportional representation of soil As binding to mentioned fractions. This assumption is not valid only for organic soils with a marginal portion of the mineral fraction (Wenzel et al. 2001); obtaining required information on potential risk resulting from As load of the soil by using the combination of simple 1M NH₄NO₃ extraction and the Tamm

method (without necessity of the application of more complicated SEPs) is presumed.

We are going to focus on verification of the acquired results by using of an enlarged set of samples, on potential use of complex-forming agents in the assessment of organically associated As in horizons of the forest soils or possibly of selected histosols.

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