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

Radim Vacha[A], Hana Macurova[A], Jarmila Cechmankova[A], Hana Javurkova[A] and Jan Skala[A]

[A]Research Institute for Soil and Water Conservation, Zabovreska 250, Prague 5, 156 27, Czech Republic, Email vacha@vumop.cz

Abstract

The contribution deals with the methods of arsenic analysis for soil. The selection and verification of the methods for As analysis which seem to be suitable for risk evaluation following from increased As soil load is presented. Economical and analytical availability of the methods is an important criterion. A sample set of 6 heavily contaminated soils was used to compare testing methods. The results showed that substitution of analytically more demanding As total content analysis and sequential analyse using simple extraction with one-off agents is promising in many cases. The comparison and evaluation of statistical correlation of used methods of As analyse in the soil was realised. The results confirmed that the use of the combination of simple 1M NH_4NO_3 extraction and determination procedure for amorphous Fe forms in the soil (the Tamm method) was suitable for the definition of main risks, following from As contamination without necessity of application of more complicated sequential extraction procedures.

Key Words

Arsenic, agricultural soils, soil contamination, chemical methods, load evaluation, methodical approach.

Introduction

Arsenic belongs to the group of trace elements and an increase in soil load of As may lead to many environmental risks, including As toxicity for living organisms. An increased As concentration in human organism can cause carcinogenic and teratogenic symptoms. Abedin *et al.* (2002), Yerebakan *et al.* (2002) document and discuss it more detailed. Arsenic can be usually found in inorganic forms – arsenite [As(III)] and arsenate [As(V)] in the soil. As generally occurs in the pentavalent state in the soil because the As (III) form oxidizes to the As (V) form. The pentavalent form of As is less toxic. Although As human and zootoxicity is reported, many authors deal with how As influences plant growth and plant physiology (Das *et al.* 2008). Increased soil As can be caused by geogenic and anthropogenic sources. Primarily atmospheric deposition, floods and load spreading round mine dumps leads to the anthropogenic As contamination of the soil (Vácha *et al.* 2002). In the soils of the emission– free regions there particularly prevails As content of geogenic origin. According to the As present in rocks there can be distinguished two categories of geogenic load - lithogenic and chalcogenic. Both types of As geogenic load occur in the Czech republic. Solving the question of the ratio of geogenic and anthropogenic loads rests on the assessment of the spatial distribution of the soil substrates indicating geogenic soil load (Němeček *et al.* 1996; Vácha *et al.* 2002). Different As bonds significantly influence plant uptake of As.

Sequential extraction procedures (SEPs) have been developed to assess limits of element contents in plants. 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 extracted in low strength reagents have not exceeded 0.5% of their total contents in soils. Among used extraction agents the 0.01M $CaCl_2$ solution seems to be the most appropriate for the extraction of elements (Száková *et al.* 2001). Extractions in 1M NH_4NO_3 and 0.025M EDTA (ethylenedinitrilotetraacetic acid) are used predicting mobile or potentially mobilizable contents of risky elements in the soil (Podlešáková *et al.* 2001). The methods of sequential analysis can be used for detailed studies of different As forms in the soil. The Zeien and Brűmer (1989) SEP procedure is used for potentially risky element assessment in the Research Institute for Soil and Water Conservation (RISWC).

The application of this method for soil As with its the anionic nature can be disputed. Therefore specific schemes and sequential analyses for the assessment of soil As have been developed (Wenzel *et al.* 2001). Because of the growing number of analytical methods their comparability is problematic and a European recommended standard for SEP for some risky elements (BCR EUR 19775 EN) has been developed. This procedure was tested for our soil conditions in the study carried out by Száková *et al.* (1999) –set on a of 35 Czech soils. It was found that there is a large proportion of residual immobile As fraction bound to silicates (75%) in monitored soil samples. The results of this SEP were compared with the results of two another analytical schemes and was ascertained that the extractable As ratio was different and hardly comparable for different methods. Nevertheless a statistically significant correlation of analytical data suggested that trends in the As distribution into main soil fractions was reflected by the applied extraction scheme.

Material and methods

Six soil samples were used with increased As contents with different sources of As (emission out-puts, fluvial load, geogenic load). Only humic horizons of agricultural soils were used for the sampling. Soil properties were analysed in the Research Institute for Soil and Water Conservation in Prague. The grain size distribution (5 categories) used burette method. Soil pH in the extract of 1M KCl and the value of cation exchange capacity (mmol+/100g) were measured for soil samples. Soil organic matter (C_{ox}) water-soluble carbon (C_{ws}), hot water-soluble carbon (C_{hws}) and organic carbon (C_{ox}) were measured. The quantity of humus (the carbon content of humic and fulvo acids measured in a solution of sodium pyrophosphate) and quality of humus (the ration of the carbon in humic and fulvo acids) was analysed. The total content of As was extracted with the acid mixture (HNO_3 + $HClO_4$ + HF) and was also the content extracted with 2M HNO_3 under cold conditions was analysed by AAS (Varian 240). Besides the total Fe content there were determined Fe species in soil samples to elucidate an interaction between the As and Fe content. The Fe content extracted with pyrophosphate, ammonium oxalate and dithionate were measured (Burman *et al.* 1996). The crystalline Fe form and the ratio between Fe bound into amorphous and crystalline oxides and the Fe compared with organic matter (the chelate bond) were calculated from the difference of Fe content in ammonium oxalate and dithionate extracts.

The As contents in the characterised soil fractions were analysed using of three sequential extract procedures (SEPs). The first one is the method by Wenzel *et al.* (2001) that was developed for soil As especially by the modification of the Zeien and Brümmer (1989) SEP. The second technique in use was the fractionation in accordance to the BCR 701 EUR 19 775 EN (2001) norm relevant for number of risky elements in diverse materials (sewage sludge, soil). The third method was the 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 simpler, economically and analytically less demanding methods while maintaining comparable predicative ability to sequential schemes. By the use of SEPs there is commonly 20% measurement uncertainty for the As assessment in individual extracts. If the uncertainty value reaches 20 % in the first step of the Zeien, Brümmer SEP, then it increases up to c. 53% in the seventh step. The SEP for the simultaneous extraction could thus be replaced 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 risky elements (Száková *et al.* 2001). In regard of gathered experiences we prefer using 1M NH_4NO_3 (for mobile contents) and 0.025M Na_2EDTA 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/DIS19730).

The established As association with the soil Fe oxides provides an opportunity for evaluating the procedure for the assessment of Fe and Al active forms significant for 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 we used the extraction procedure originated by Tamm (1922) intended for the determination of amorphous Fe forms and based on extraction using ammonium oxalate and oxalic acid. This scheme was successively modified with respect to instrumental technique progression (Buurman 1996). All measurements have been carried out twice in three repetitions. The summary results of measurements have been processed by elementary statistics. Correlation analysis using ANOVA method and the Pearson correlation coefficient calculation have been accomplished.

Results

There were basic differences in the quantification of As content in defined soil fractions during the SEP testing for the assessment of As in the set of samples with the different type and level of contamination. The Wenzel procedure and the Zeinen and Brűmer technique proved the dominant As association with amorphous and crystalline Fe and Al oxides in the soils. The proportion of amorphous to crystalline oxides is mainly given by the soil matrix and by the load type. There was a characteristic a balanced ratio with a moderate dominance of the As association with crystalline Fe oxides (due to the primary As incorporation into the crystal lattice of the minerals) 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 (emission fallout, flood). Using the BCR technique there was detected a major ratio of As 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 selective to As detection. The detection of Mn, Fe associated arsenic is during the determination of the residual As fraction using the aqua-regia extraction. There may be a dominant arsenic portion in the residual fraction using the method by Száková *et al.* (1999) as well. With the BCR technique the organically associated As fraction amounted to low level values and did not exceed the Wenzel proportion values of the organically bound As to other soil fractions (2 – 7%). There was achieved a preferable correlation between the 2M HNO_3 extraction and easily exchangeable soil As using the Wenzel and the Zeinen and Brűmmer procedures. The BCR method was less sensitive to the exchangeable soil As 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 0.908) was reached through using of the Wenzel and Zeien and Brűmmer SEP.

This ratio was quantitatively higher by 10% using the Wenzel technique. We are not generally inclined to the opinion that the content of As in individual fractions resulting from the application of the procedure are not utilisable. The Wenzel procedure can be preferred for more precise quantification owing to the probability of the lower analytical error alone. Within the testing of simple extraction procedures using soft extraction agents there is an assessment of the mobile As fraction in the 1M NH_4NO_3 extract used in the first extraction step of the Zeien and Brümmer SEP compared to the NH_4NO_3 extraction according to the international standard ISO/DIS 19730. The schemes differ in extraction duration as well as in the proportion of the extraction agent to the sample. Hence different absolute values of the As content (mg/kg) in both extracts can be expected. There can be assumed an ideal equilibrium 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 there was found very tight correlation (the Pearson correlation coefficient = 0.999) among results of As assessment in the 1M NH_4NO_3 extract using the procedures of interest.

The application of the simpler scheme by ISO/DIS 19730 can be considered in terms of simplicity and economy. Using 1M NH_4NO_3 refers to the assessment of the soil As mobile forms that are determining in terms of risks under consideration. A completely new approach to the As assessment is using 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. There results a statistically significant correlation among tracked parameters from the mentioned results. It is presumed that the Tamm method is suitable for the quick assessment the portion of As associated with amorphous Fe, 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 will not be valid for organic soils with a minor mineral fraction (Wenzel *et al.* 2001). Obtaining required information on potential risk resulting from As load of the soil can be obtained by using of combination of simple 1M NH_4NO_3 extraction and the Tamm method (without the necessity of the application of more complicated SEPs).

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