Research Articles

Soil Extraction of Readily Soluble Heavy Metals and As with 1 M NH$_4$NO$_3$-Solution
Evaluation of DIN 19730

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Abstract

Background, Aims and Scope. The German DIN 19730 (1997) describes a method for the extraction of readily available trace elements from soil by shaking the soil with 1 M NH$_4$NO$_3$-solution. Based on this method trigger and action values for the transfer of heavy metals and arsenic from soils to plants have been published in the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV 1999). The chemical mechanisms involved in this soil extraction procedure were evaluated in some detail to create requirements to improve environmental risk assessment for soil contaminations.

Methods. The chemical mechanisms involved when soil is extracted with 1 M NH$_4$NO$_3$-solution were evaluated. This was followed by a laboratory experiment to quantify the formation of soluble metal ammine complexes during the extraction.
Cd, Zn, Ni, Cu, Co and Hg were extracted from 16 soils by 1 M NH$_4$NO$_3$, 1 M KNO$_3$ and water. pH was adjusted in 5 steps between 5.0 to 7.5. The potassium cation (K$^+$) and the ammonium cation (NH$_4^+$) behave similarly when cations from soil surfaces are desorbed, because they have almost identical ion radii (e.g. 0.133 and 0.143 nm). K$^+$ does not form ammine complexes with other ions, whereas, due to the increasing formation of NH$_3$ from NH$_4$ by dissociation with rising pH, metal ammine complex formation is an important process in soil extraction when using ammonium salt solutions. A difference in the extraction efficiency of 1 M NH$_4$NO$_3$- and 1 M KNO$_3$-solution for a given soil can therefore be attributed to the formation of soluble metal ammine complexes.

Conclusion. Our experiments resulted in considerably higher extraction rates of Cu, Cd and Hg by 1 M NH$_4$NO$_3$-solution as compared to 1 M KNO$_3$-solution. This effect, caused by the formation of soluble metal ammine complexes, was only evident in soils with higher readily soluble heavy metal contents and a soil pH above 6–6.5 for Cu and 7–7.5 for Cd. Further chemical mechanisms involved when soils are extracted with 1 M NH$_4$NO$_3$ are a moderate decrease in pH and an increase in ionic strength. Most of the colloids and parts of soluble metal-organic complexes are precipitated due to the high ionic strength. High ionic strength also decreases the activity of metal-OH$^+$ species and the electrostatic potential of the particle surfaces, which in turn, increases the desorption of heavy metal cations from negatively charged soil surfaces. In contrast, the adsorption of anions like arsenate is favoured by the decreasing electrostatic potential.

The prediction of heavy metal uptake by plants from the results of the 1 M NH$_4$NO$_3$-solution extraction fits well for elements, which are mainly bound by low strength electrostatic forces to the soils. Such conditions are found in acidic soils for Cd and Tl, which have a low tendency for hydrolysis compared to other heavy metals. The correlation between 1 M NH$_4$NO$_3$ soil extraction and plant uptake is less significant for Ni and Zn. Only low positive correlation coefficients have been found for Pb, As, Hg and for the Cu-uptake by wheat. Imprecise prediction of plant uptake of heavy metals by the extraction with 1 M NH$_4$NO$_3$-solution is mainly caused by conditions leading to an overestimation of plant availability such as elements are strongly bound to soils, or low soluble trace element contents in soils. Neutral to alkaline soil pH can also lead to imprecise prediction due to increasing formation of soluble metal-organic (Cu, Pb, Hg) and metal ammine (Hg, Cu, Cd) complexes and less importantly due to the formation of colloids. Therefore, at low 1 M NH$_4$NO$_3$-extractable soil contents usually no high plant contents are to be expected.

Recommendation and Outlook. Extraction of soil with 1 M NH$_4$NO$_3$-solution is a suitable method for the determination of readily soluble and plant available trace element contents. The chemical soil extraction process may cause misleading predictions of the transfer of trace elements to plants for some soil properties. This knowledge should be used to improve risk assessment of soil contaminations. It has to be considered, that the processes involved in plant uptake of trace elements are too complex to expect that just one soil extraction method can always guarantee a correct prognosis of toxicological significant element contents in plants. Soil analyses may be used for the preliminary examination of suspicious areas and the demarcation of contaminated areas. The results of soil analyses should be checked additionally by plant analyses especially under conditions with a high probability for misleading results by the 1 M NH$_4$NO$_3$-extraction. Alternatively, extraction with 1 M KNO$_3$-solution can be performed to exclude the effect of metal ammine complex formation.

Introduction

Extraction of soil with 1 M NH_4NO_3-solution is used to determine readily soluble trace element contents. In Germany this method has been published as an official standard (DIN 19730 1997) and is used to estimate the transfer of heavy metals and arsenic from soils to plants in the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV 1999).

Our intention was to evaluate this soil extraction method in order to identify soil properties, which influence the extraction process and may cause misleading predictions of the transfer of trace elements from soil to plants. This should help to improve risk assessment of soil contamination.

1 Methods

A literature review was followed by laboratory experiments in order to quantify the influence of ammine complex formation in the NH_4NO_3-extraction solution on the extraction of various heavy metals from soils.

The extraction with a KNO_3-solution was compared to NH_4NO_3-solution in order to quantify the influence of metal ammine complex formation on soil extraction. In contrast to NH_3 which is increasingly formed by dissoziation of NH_4^+ with rising pH, K^+ does not form complexes with metal ions. The cations K^+ and NH_4^+ desorbe comparable amounts of metals from soils because they have nearly identical ionic radii (i.e. 0.133 and 0.143 nm), respectively.

16 soils with different soil properties and different sources of contaminations with heavy metals were each extracted with 1 M NH_4NO_3-solution, 1 M KNO_3-solution and water. The extraction was carried out as described in DIN 19730 (1997). 50 ml of the particular extract solution was added to 20 g soil and was shaken for 2 hours. Each soil was extracted at 5 different pH-values from 5.0 to 7.5. The pH was adjusted with 0.2 M HNO_3 or 0.1 M KOH during soil extraction. To avoid changes of the adjusted pH due to long filtration times we performed the soil extraction without membrane filtration, which is normally prescribed in DIN 19730. Instead we did a normal filtration (ash free paper filters) and subsequent centrifugation with 2000 rpm lasting 5 minutes. In spite of the

reduced filtration efficiency, the 1 M NH_4NO_3 and 1 M KNO_3-soil extracts were mostly clear. Only 2 of the 16 soil extracts have shown slightly visible traces of precipitating colloids at neutral to alkaline pH in 1 M NH_4NO_3- and 1 M KNO_3-solution. Such a low formation of colloids has no influence on the difference of heavy metal contents of 1 M NH_4NO_3- and 1 M KNO_3-solution, because similar colloid contents are to be expected in cause of same ionic strength in both soil extracts. The resulting solutions were analysed for Cd (1.3 µg/kg), Zn (62.5 µg/kg), Ni (1.3 µg/kg), Cu (1.3 µg/kg), Co (1.3 µg/kg) by inductive coupled plasma mass spectrometry (ICP-MS) and for Hg (3.75 µg/kg) by cold vapour atomic absorption spectrometry (CV-AAS) (detection limits in parentheses).

Carbon content (C) of the soils was read with a commercial C/N-Analyser. The cation exchange capacity (CEC) was determined with 1 M sodium acetate at pH 7, the sodium-exchange with 1 M ammonium acetate. Total trace element contents were analysed by extracting the soil with aqua regia in a closed micro wave digestion system. The elements were measured by ICP-MS, Hg by CV-AAS.

2 Results and Discussion

2.1 Correlation between soil extraction with 1 M NH_4NO_3 and plant uptake

Soil extraction methods like 1 M NH_4NO_3 and other salt solutions, which operate at approximately the original pH of the soil generally achieve relatively close correlations to trace element contents in plants, when compared to other soil extraction procedures (Prüeß 1992, Birke et al. 1991). Poor correlation coefficients have been found at low soluble trace element contents in soil (Merkel 1996, Prüeß 1992).

High positive correlation coefficients between soil extraction with 1 M NH_4NO_3-solution and plant contents are found for Cd and Tl. The correlation is less close for Ni and Zn. Only small positive correlations have been found for As and Pb. Variable results have been found for Cu, showing a weak positive correlation between soil extraction with wheat uptake and a high positive correlation coefficient with lettuce uptake. However only few samples of lettuce have been analysed (n = 26) (**Table 1**). There are few results for Hg.

Table 1: Correlation coefficients between concentrations of various elements extracted with 1 M NH_4NO_3 from soils and plant contents (Knoche et al. 1997[a], Liebe et al. 1997[b], Prüeß 1992[c])

Element	Kale	Wheat		Potato	Carrot	Spinach	Celery root	Beet leaf	Lettuce
As (r^2)	0.67[b]	0.02[a]	0.50[b]	0.20[a]	0.32[a]	0.39[a]			0.18[a]
n	17	208	88	43	68	51			56
Cd (r^2)		0.66[a]		0.21[a]	0.54[a]	0.76[a]	0.39[a]		0.67[a]
n		401		33	159	155	102		72
Cu (r^2)		0.19[b]							0.80[a]
n		56							26
Ni (r^2)		0.46[b]				0.46[a]			
n		56				88			
Pb (r^2)		0.12[a]		0.39[a]	0.26[a]	0.40[a]			0.23[a]
n		302		27	142	118			57
Tl (r^2)	0.72[a]				0.78[a]	0.77[a]			0.65[a]
n	17				63	29			23
Zn (r^2)	0.59[b]	0.53[b]						0.61[a]	0.49[c]
n	15	18						51	28
	r^2 >0.40	r^2 >0.60							

Some are from a contaminated mining area in the North Palatinate mountainous region, which show at most only small positive insignificant correlation coefficients to soil extraction with 1 M NH$_4$NO$_3$-solution for most plant species (Steubing et al. 1996).

2.2 Chemical processes involved when extracting soils with 1 M NH$_4$NO$_3$-solution

The chemical processes involved, when soil is extracted with 1 M NH$_4$NO$_3$-solution are a moderate drop in pH, the effects of high ionic strength on desorption of trace elements and on precipitation of colloids and soluble metal organic complexes and the formation of soluble metal ammine complexes.

2.2.1 pH

pH is the most important factor influencing the sorption of heavy metals in soils. The adsorption of divalent heavy metal cations is mainly related to metal ion hydrolysis. Thus, the adsorption of heavy metals increases with increasing pH and with decreasing pK value of the metal ion hydrolysis reaction in the sequence Cd (10.1) < Ni (9.9) < Co (9.7) < Zn (9.0) << Cu (7.7) < Pb (7.7) << Hg (3.4) (Brümmer et al. 1986).

The pH-values in 1 M NH$_4$NO$_3$ soil extracts are about 0.5–1 units lower than in water soil extracts. In acid soils the pH-values in 1 M KNO$_3$-solution and 1 M NH$_4$NO$_3$-solution are identical. Due to the dissociation of ammonium at neutral to alkaline conditions, pH in 1 M NH$_4$NO$_3$-soil extract is lower than in 1 M KNO$_3$-soil extract (**Fig. 1**).

2.2.2 Formation of soluble metal ammine complexes

Under acid conditions comparable amounts of Cd (**Fig. 2**), Cu (**Fig. 3**), Zn and Ni (Gryschko et al. (2000) are extracted by KNO$_3$- and NH$_4$NO$_3$-solutions. With the exception of
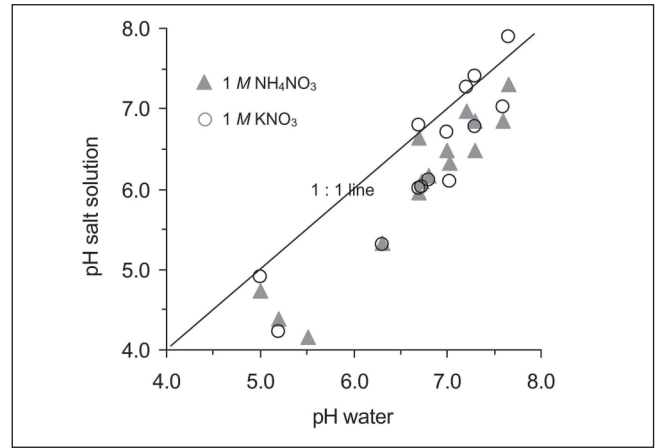

Fig. 1: pH of soil water extracts in relation to pH in 1 M NH$_4$NO$_3$- and 1 M KNO$_3$-soil extracts

Cu, the amounts extracted decrease with increasing soil pH. Above pH 6, the amounts of Cu extracted by 1 M KNO$_3$-solution increase in top soil samples which contain higher amounts of organic matter (soils no. 1, 8, 13). In soil samples with low organic matter content (no. 10), the amount of Cu extracted does not increase at elevated pH. The increased solubility of Cu in humic soils is probably caused by the dissolution of alkaline soluble organic Cu complexes.

NH$_4$NO$_3$-solution extracted considerably higher amounts of Cd and Cu than KNO$_3$ at neutral to alkaline pH and highly soluble heavy metal contents in the soils (see Fig. 2 and 3). The results in both salt solutions were comparable for Ni and Zn with the exception of soil no. 10 (see soil properties in Fig. 3), which has a very low buffering capacity for heavy metals and shows considerably higher Zn- and Ni-contents in 1 M NH$_4$NO$_3$-solution at neutral to alkaline pH-values (Gryschko et al. 2000). High Cu extraction dif-
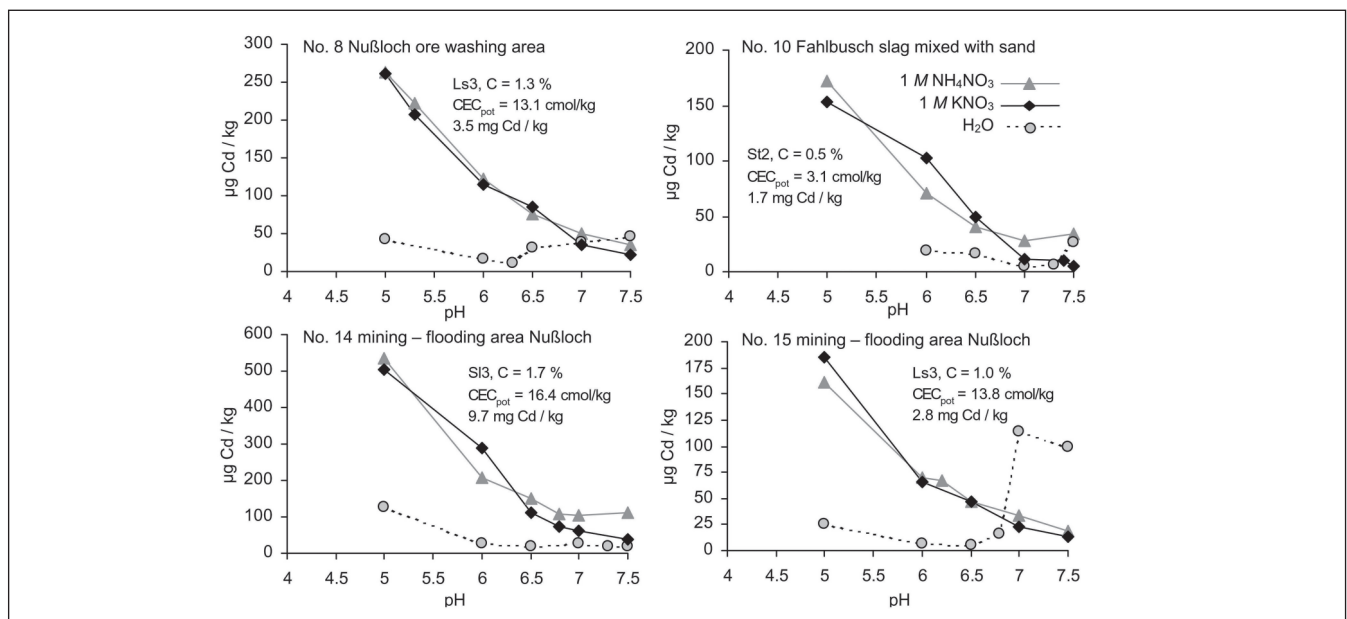

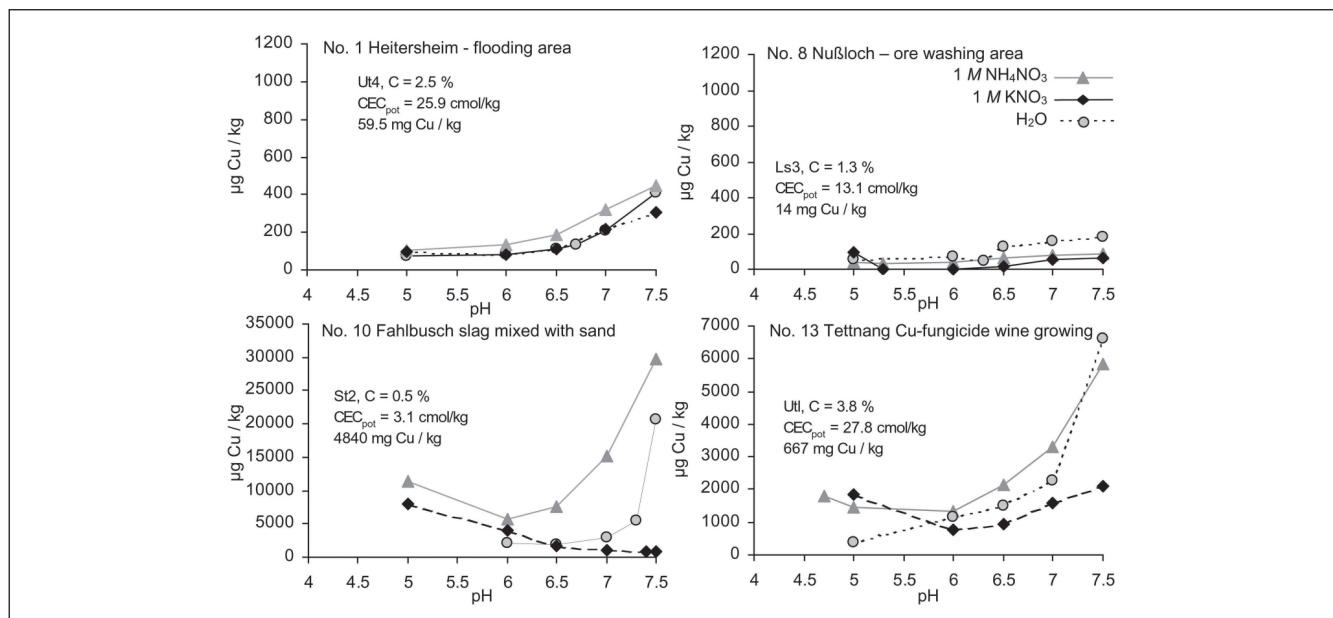**Fig. 2:** Cd-contents in 1 M NH$_4$NO$_3$-, 1 M KNO$_3$- and in water soil extracts in relation to pH

Fig. 3: Cu-contents in 1 M NH$_4$NO$_3$-, 1 M KNO$_3$- and in water soil extracts in relation to pH

ference has been found between 1 M NH$_4$NO$_3$- and 1 M KNO$_3$-solutions above pH 6.0 in soils no. 10 and 13 which have high soluble Cu-contents. The high readily soluble Cu-contents in these soils are caused by high total Cu-contents (4840 mg/kg in soil no. 10 and 667 mg/kg in no. 13) and very low binding capacity for heavy metals (soil no. 10). There is only a moderate (soil no. 1) or insignificant increase (soil no. 8) of Cu-content in 1 M NH$_4$NO$_3$-solutions compared to KNO$_3$-solutions in soils no. 1 and 8 which have low extractable Cu-contents.

A high difference between extraction of Cd by 1 M NH$_4$NO$_3$ and 1 M KNO$_3$ has been found above pH 7.0 in the sandy soils No. 10 and 14, which are characterised by a very low buffering capacity for heavy metals (no. 10) or very high total Cd-contents (9.7 mg/kg in soil no. 14). In the loamy soils no. 14 and 15, in spite of high Cd-contents (2.8–3.5 mg/kg), only moderately higher amounts of Cd are extracted by NH$_4$NO$_3$ as compared to KNO$_3$. A high extraction difference was also found for Hg in soil no. 7 (**Fig. 4**). This was the only soil having detectable Hg-contents in our study and must therefore be considered as a single result.

The percentage of metals forming metal ammine complexes in 1 M NH$_4$NO$_3$-solution was calculated by complex for-
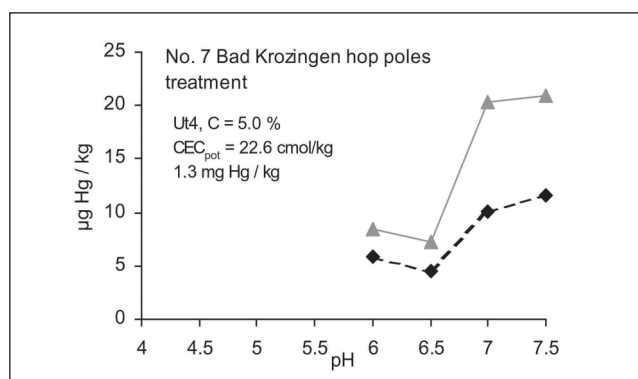

Fig. 4: Hg-contents in 1 M KNO$_3$- and 1 M NH$_4$NO$_3$-soil extracts in relation to pH

mation constants according to Fluck & Becke-Goehring (1980). The proportion of metal ammine complexes increases with increasing pH due to increasing dissociation of NH$_4^+$. Hg and Cu have the highest affinity to form metal ammine complexes of all the heavy metals tested. The formation of Cu and Hg ammine complexes in 1 M NH$_4$NO$_3$-solution becomes significant at pH values as low as 6.0, whereas ammine complex formation of Cd, Co, Ni and Zn starts to become significant at pH 6.5–7.0 (**Table 2**).

Table 2: Metal ammine complex formation constants and calculated effect on metal ammine complex formation in 1 M NH$_4$NO$_3$-solution

Element	k_1	Complexed metal / Total dissolved metal [%]				
		pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0
Cd	400	18.4	41.6	69.2	87.7	95.7
Hg	$6.3*10^8$	100.0	100.0	100.0	100.0	100.0
Ni	630	26.2	52.8	78.0	91.8	97.3
Zn	190	9.7	25.3	51.7	77.2	91.4
Cu	13,000	88.0	95.9	98.7	99.6	99.9
Co^{2+}	130	6.8	18.8	42.2	69.8	88.0

Our experiments indicate increased Cd solubility in soil extracts due to metal ammine complex formation. Although Co, Ni and Zn have metal ammine complex formation constants, which are comparable to the one for Cd, the solubility of these elements was increased in only one soil sample. It is conceivable that this results from the lower binding strength of Cd to soil as compared to Co, Ni and Zn. The formation of soluble metal ammine complexes is significant if the energetic gain of the metal complex formation is higher than the binding strength of the metals to the soil. These conditions are most likely for Cd, when compared to Co, Ni and Zn and are only found at higher soluble heavy metal contents, when heavy metal ions are also bound to binding sites with low binding strength. The energetic gain of ammine complex formation with Cu and probably Hg is sufficiently high due to the high complex formation constants, in spite of the high binding strength of these elements to soils.

2.2.3 Ionic strength

The dispersion of small soil particles is favoured in negatively charged soils by high pH and low ionic strength (Kretzschmar et al. 1999). The content of heavy metals (see Fig. 2 and 3) which are most likely bound to small soil colloids in the water extracts, which have low ionic strength increase therefore with increasing pH. This can be seen by the turbid water extracts in contrast to the salt solutions (1 M NH$_4$NO$_3$ and 1 M KNO$_3$) which are mostly clear. Only 2 of the 16 soil extracts have shown slightly visible traces of precipitating colloids at neutral to alkaline pH in the 1 M NH$_4$NO$_3$-solution.

Due to the high ionic strength of 1 M NH$_4$NO$_3$-solutions the activity of metal-OH$^+$-species in solution is decreased, which favours the desorption of divalent heavy metal cations. The electrostatic potential of the particle surfaces decreases, which increases desorption of cations (heavy metals) and adsorption of anions like arsenate on commonly negatively charged mineral surfaces in temperate soils. In highly weathered tropical Ferralsols with prevailing positive surface charge the desorption of anions and adsorption of cations is favoured with increasing electrolyte concentration (Barrow 1987). This has been proven in many extraction experiments with salt solutions, such as NH$_4$NO$_3$, while extracting at pH-values, which are close to those in the soil solution. Increasing salt concentrations mainly increased the desorption of relatively mobile elements like Cd, Co, Ni, Zn from negatively charged soils or clay minerals (e.g., Garcia-Miragaya et al. 1976, Sparks et al. 1995). On positively charged soils Cd adsorption was favoured (Naidu et al. 1994). Experimental results for less mobile elements like Cu, Pb and Hg, which normally show low ionic contents in soil extracts and have a high affinity for forming metal organic complexes, are less obvious. This is due to an increasing presence of colloids and a higher solubility of metal organic complexes at low electrolyte concentrations (e.g., Mc Bride 1997, Hoffmann et al. 1997).

3 Conclusion

Soil extraction with 1 M NH$_4$NO$_3$ is performed at a pH-value comparable to the soil solution. The extraction of metals is mainly caused by desorption of cations, while the formation of colloids and soluble metal-organic complexes, which are hardly taken up by plants, is strongly suppressed due to the high ionic strength of the 1 M NH$_4$NO$_3$-solution. These are factors, which assists in a precise prediction of trace element uptake by plants from contaminated soils.

The formation of colloids, soluble metal-organic complexes and metal ammine complexes hinders the precise prediction of plant uptake from soil extraction with 1 M NH$_4$NO$_3$-solution, especially under near neutral to alkaline soil pH. The dissociation of NH$_4^+$ and subsequent formation of soluble ammine complexes results in an overestimation of readily soluble Cd above pH 7–7.5 and readily soluble Cu and Hg above pH 6.0. For Ni, Zn and Co significant effects of the formation of soluble metal ammine complexes can only be found in soils having very low buffering capacity for heavy metals. The desorption of oxyanions like arsenate is reduced in 1 M NH$_4$NO$_3$-solution in comparison to the soil solution in commonly negatively charged soils. This favors the predominance of oxyanions which are bound in larger dissolved organic and colloidal particles and which are less likely to be responsible for plant uptake than ionic species.

Heavy metal contents in plants can be predicted easily for elements, which are bounded with low binding strength to the soil. These conditions are found in acid soils for Cd and Tl, which have a low tendency for hydrolysis compared to other heavy metals.

Low correlations between trace elements in soil extract and plant contents are found when the concentration of ionic species in soil solution or 1 M NH$_4$NO$_3$-extract is low compared to the amounts of these elements in dissolved organic complexes and colloidal particles. These conditions are prevelant if the ionic concentration in solution is low compared to the total element content in a soil. This is often the case for the elements Hg, Pb and Cu, which are strongly bound to soils and have a high affinity for the formation of soluble metal-organic complexes. It also occured at low trace element contents in soil and at neutral to alkaline soil pH, if most of the binding sites have a high binding strength. Soil extraction with 1 M NH$_4$NO$_3$ is also less suitable for oxyanions like As, because the ionic concentration of oxyanions will be reduced in NH$_4$NO$_3$ compared to the soil solution.

4 Recommendation and Outlook

Extraction of soil with 1 M NH$_4$NO$_3$-solution is generally a suitable method for the prediction of readily soluble and plant available trace element contents. However it should be considered, that the method is not equally suitable for all elements. The chemical soil extraction process may also cause misleading predictions of the transfer of trace elements to plants for some soil properties. This knowledge can be used to improve risk assessment of soil contaminations.

It is important to consider that the factors which effect the uptake of trace elements to plants are very complex. Therefore it probably will not be possible to find a soil extraction method, which guarantees a precise prediction of toxicological significant trace element contents in plants in all circumstances. Soil analyses may be used for the preliminary examination of suspicious areas and the demarcation of contaminated areas. The results of soil analyses should be further verified through plant analyses, especially under conditions were the extraction by 1 M NH_4NO_3-solution may result in an overestimation of the plant availability of trace elements. As an alternative an extraction with 1 M KNO_3-solution can be performed, which will avoid the effect of metal ammine complex formation on the trace element extraction.

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