Long-term risks of inadequate management practices on the sustainability of agricultural soils

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ABSTRACT

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This report describes the major result of a research project funded by the INCO-Copernicus programma of European Commission under Contract number ERB-IC15-CT98-0133. The study focused on the long-term environmental risk of soil acidification on: (i) mobilisation and leaching and (ii) plant uptake of potentially toxic heavy metals (i.e. lead, cadmium, zinc and copper) from well-drained agricultural soils in Slovakia and Hungary. The research was mainly carried out in the period 1998-2001, but there was a strong delay in the final reporting of the results as summarised in this report. This report includes the major papers resulting from this study. The major result obtained from the various studies is that transfer functions and soil-to-plant transfer relationships, allowing the calculation of dissolved metal concentrations and plant meta contents from soil metal contents accounting for differences in soil properties, such as pH and organic matter content, in the solid phase, are practical and reasonably reliable approaches for use in regional risk assessments, as carried out for Hungary and Slovakia.

Keywords: acidification, food quality, heavy metals, mobilisation, risk assessment, sorption processes

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Contents

Preface 9

Summary 13

Introduction 21

Theme 1 Soil contamination problems in Slovakia and Hungary 27
1.1 Diffuse soil contamination problems in Slovak republik 27
  1.1.1 Introduction 27
  1.1.2 Inventory of contaminated soils 28
  1.1.3 Diffuse soil contamination in the Slovak Republic 29
  1.1.4 Specific problems in Slovakia 31
  1.1.5 Conclusion 32
1.2 Quality and contamination of agricultural soils in Hungary as indicated by environmental monitoring and risk assessment 35
  1.2.1 Introduction 35
  1.2.2 Approaches for Environmental Risk Assessment 36
  1.2.3 Risks of heavy metal pollution in Hungary 37
  1.2.4 Evaluation 38

Theme 2 Transfer functions relating different pools of heavy metals 41
2.1 Transfer functions between adsorption constants and soil characteristics: theory 41
  2.1.1 Introduction 41
  2.1.2 Theory of the sorption process and derivation of the transfer Function 42
2.2 Risks of metal contamination in view of soil properties 45
  2.2.1 Introduction 45
  2.2.2 Materials and methods 46
  2.2.3 Results and discussion 46
  2.2.4 Conclusions 47
2.3 Soils and sediments testing for contamination by heavy metals - new concepts and approaches 49
  2.3.1 Introduction 49
  2.3.2 Methodology 50
  2.3.3 Plant available concentrations of metals in soils by single extraction methods 53
  2.3.4 Metal fractionations based on selective sequential extraction procedures 57
  2.3.5 Metal concentrations in the soil solution 61
  2.3.6 Conclusions 66
2.4 Assessment of relationships between total and reactive concentrations of cadmium, copper, lead and zinc in Hungarian and Slovakian soils 69
  2.4.1 Introduction 70
  2.4.2 Material and Methods 71

- 2.4.3 Results 75
- 2.4.4 Discussion and conclusions 85

2.5 Copper sorption and speciation in acid sandy forest soils 89
- 2.5.1 Introduction 89
- 2.5.2 Materials and methods 91
- 2.5.3 Results and discussion 94
- 2.5.4 Conclusions 98

2.6 Assessment of soil - solution transfer functions for cadmium and copper 101
- 2.6.1 Introduction 101
- 2.6.2 Methods 103
- 2.6.3 The soil- solution transfer function of cadmium for different soils 108
- 2.6.4 The soil - solution transfer function of copper for different soils 115
- 2.6.5 Discussion and conclusions 118

Theme 3 Models describing metal uptake by plants 127

3.1 Development of a dynamic process-oriented model, CdModel, describing cadmium in the soil-crop system 127
- 3.1.1 Introduction 128
- 3.1.2 Theory 129
- 3.1.3 A dynamic Cadmium model (CdModel) 131
- 3.1.4 Simulations 137
- 3.1.5 Discussion and conclusions 141

3.2 Derivation of soil-specific quality standards for cadmium and zinc 147
- 3.2.1 Introduction 147
- 3.2.2 Materials and methods 148
- 3.2.3 Theory 149
- 3.2.4 Results and discussion 152
- 3.2.5 Conclusions 159

Theme 4 Regional impacts of acidification on leaching and plant uptake 163

4.1 Long term impacts of different fertiliser scenarios on metal leaching and metal uptake in Slovakian and Hungarian agricultural soils 163
- 4.1.1 Introduction 164
- 4.1.2 Model 165
- 4.1.3 Study sites and input data 170
- 4.1.4 Results 178
- 4.1.5 Discussion and conclusions 183

Evaluation of the results obtained 187

Annexes

1 Geographical position and soil properties of the A horizon of selected soil samples from 306 agricultural soils 189

2 Cation exchange capacity (cmol.kg^{-1}) of the A horizon of selected soil samples from 306 agricultural soils 195

3 Total content heavy metals (mg.kg^{-1}) of the A horizon of selected soil samples from 306 agricultural soils 201

4 Protocol for the determination of in-situ partition coefficients of heavy

metals and their relationship with soil properties 207
5 Protocol for the calculation of free ion activities 211
6 Protocol for the assessment of adsorption constants in relation to soil properties and the use of the copper ion selective electrode 219
7 Protocol for the determination of protonation and complexation constants for Dissolved Organic Carbon (DOC) 225

Preface

This report describes the major result of a research project funded by the INCO-Copernicus programme of European Commission under Contract number ERB-IC15-CT98-0133. The study focused on the long-term environmental risk of soil acidification on: (i) mobilisation and leaching and (ii) plant uptake of potentially toxic heavy metals (i.e. lead, cadmium, zinc and copper) from well-drained agricultural soils in Slovakia and Hungary. The research was mainly carried out in the period 1998-2001, but there was a strong delay in the final reporting of the results as summarised in this report. This report includes the major papers resulting from this study.

The project on “long-term risks of inadequate management practices on the sustainability of agricultural soils” was based on an interdisciplinary approach in which most of the laboratory and field research was carried out in Hungary (RISSAC) and Slovakia (SSCRI) and partly in the UK (UR), with advise from the Dutch partner Alterra, whereas the modelling research took place by a collaborative effort in Sweden (UL) and the Netherlands (Alterra). More specifically the authors included in this report worked at:

- W. de Vries, J.E. Groenenberg, P.F.A.M Römkens, G. J. Reinds and J. Bril: Alterra Green World research
- Murányi: Research Institute for Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences (RISSAC) or Magyar Tudományos Akadémia Talajtani és Agrokémiai Kutató Intézete MTA TAKI in Budpest, Hungary.
- J. Curlík and P. Šefcík, Soil Science and Soil Conservation Research Institute, Bratislava, Slovak Republic.
- K. Modin and H.U Sverdrup, Chemical Engineering Lund University, P.O. Box 124, Lund, Sweden Lund University
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The study is based on the hypotheses that heavy metals, which accumulated in agricultural soils as a result of manure application, fertiliser treatment, atmospheric deposition and the amendment of sewage sludge, may cause problems in situations with improper management practices, such as insufficient liming. This may cause a decrease in soil pH and thereby an increase in heavy metal bio-availability leading to risks of elevated leaching to ground water and production of agricultural crops with unacceptable levels of heavy metals and even reduced crop production.

The papers described under the first theme (Soil contamination problems in Hungary and Slovakia) are also based on research or data evaluation that was part of this project as it includes some insight in soil pollution problems in the region considered. These papers are:

1.1 Curlík, J. - Šefcík, P., 1999: Diffuse soil contamination problems in Slovak republik. Vedecké práce, Proceedings No. 22, VÚPOP, Bratislava, pp. 33 - 46
1.2 Murányi, A. 2000. Quality and contamination of agricultural soils in Hungary as indicated by environmental monitoring and risk assessment. In: Wilson, M. J. & Maliszewska – Kordybach, B. (eds.) Soil Quality, Sustainable Agriculture and Environmental Security in Central and Eastern Europe. NATO Science Series 2. Environmental Security Vol. 69. 61- 77. Kluwer Academic Publisher.

The papers published on the other themes are related to three major objectives of the project:

1 Determination of the impact of changes in pH due to soil acidification on the sorption of heavy metals by soil and complexation of heavy metals with dissolved organic carbon on the basis of literature reviews, laboratory experiments and field studies: theme 2.
2 Assessment of the impact of mobilisation of potentially toxic heavy metals on plant uptake. This includes the determination of the relation between heavy metal concentrations in the soil and in plants and the development /calibration of a plant uptake model for major crops in agricultural soils in Slovakia and Hungary: theme 3.
3 Modelling long-term environmental impacts of acidification on leaching and plant uptake in Hungarian and Slovakian agricultural soils for various liming and fertiliser application scenarios using integrated models on soil acidification and heavy metal behaviour: theme 4.

These papers are (to be) published as described below

Theme 2 related to objective 1:
Transfer functions relating total, reactive and bioavailable pools of heavy metals

2.1 J. Bril and P.F.A.M. Römkens, 1999. *Transfer functions between adsorption constants and soil characteristics: theory.* Alterra Green World Research, internal document.
2.2 Groenenberg J.E., J. Bril and W. de Vries, 1999. *Risks of metal contamination in view of soil properties.* Proceedings 5th international conference on the Biogeochemistry of trace elements. Vienna July 11-15 1999. W.W. Wenzel, D.C. Adriano, B. Alloway, H.E. Doner, C. Keller, N.W. Lepp, R. Mench, R. Naidu and G.M. Pierzynski (Eds.) p. 834-837
2.3 Curlík, J. and P. Šefcík, 2002. *Soils and sediments testing for contamination by heavy metals - new concepts and approaches*. In Slovak geological magazine 2002.
2.4 De Vries, W., J. Curlík, A. Murányi, B.J Alloway and J.E. Groenenberg, 2003. *Assessment of relationships between total and reactive concentrations of cadmium, copper, lead and zinc in Hungarian and Slovakian soils.* Submitted to European Journal of Soil Science.
2.5 Groenenberg, J.E., T.V. Pampura, H.J.M. Wieggers[1] and J. Bril, 2003. *Copper sorption and speciation in acid sandy forest soils.* Submitted to Journal of Environmental Quality.
2.6 Murányi A., J. Bril, J. E. Groenenberg and W. de Vries *Assessment of soil - solution transfer functions for cadmium and copper.* Submitted to European journal of Soil Science

Theme 3 related to objective 2:
Development and application of models describing metal uptake by plants

3.1 Modin, A.K., H.U. Sverdrup and S. Belyazid, 2001. *Development of a dynamic process-oriented model, CdModel, describing cadmium in the soil-crop system.* Proceedings of the ICOBTE 2001 6th International Conference on the Biogeochemistry of Trace Elements, July 29-August 2, 2001, University of Guelph, Guelph, Ontario, Canada: 524.

3.2 Römkens, P.F.A.M. and W. de Vries, 2003. *Derivation of soil-specific quality standards for Cd and Zn.* Accepted by Journal of Environmental Quality.

Theme 4 related to objective 3:
Long-term environmental impacts of acidification on leaching and plant uptake

4.1 Groenenberg, J.E, W. de Vries, G. J. Reinds, A. Muranyi, J. Curlík and P. Šefcík. *Long term impacts of different fertiliser scenarios on metal leaching and metal uptake in Slovakian and Hungarian agricultural soils.* Submitted to Water, Air and Soil pollution

Furthermore 7 annexes are included, related to: (i) the assessment of soil properties and heavy metal contents in Slovakia (Annex 1-3; theme 1) and (ii) the derivation of transfer functions related to metal adsorption and complexation (Annex 4-7; theme 2).

The major result obtained from the various studies is that transfer functions and soil-to-plant transfer relationships, allowing the calculation of dissolved metal concentrations and plant meta contents from soil metal contents accounting for differences in soil properties, such as pH and organic matter content, in the solid phase, are practical and reasonably reliable approaches for use in regional risk assessments, as carried out for Hungary and Slovakia.

Summary

Soil contamination problems in Hungary and Slovakia

National inventories indicate that several ten thousands of hectares in Slovakia and in Hungary are polluted with heavy metals and are a potential risk when soils acidify. In Slovakia, the ecologically endangered areas (hot spots) are distributed around mining and industrial centres. To them belong: Middle Spiš region (Krompachy, Rudnany), Žiar nad Hronom region, Jelšava - Lubenik, Hacava - Hnúšta, and Lower Orava regions. Three other very specific regions (Hacava - Hnúšta, Jelšava – Lubeník and Košice) are polluted by alkaline dust from magnezite works, together with some heavy metals. Finally, atmospheric input of heavy metals evidently resulted in accumulation in surface layers of forest soils. The available data suggest that in about 28 % of the Slovakian soils diffuse soil contamination occurs, with the content of one, or more heavy metals being higher than the target (A)-values (see paper 1.1 in this report).

Data on heavy metal contents derived from the Soil Information and Monitoring System of Hungary, including 1236 representative sampling sites on agricultural land (865), forests (183) and environmental 'hot spot' regions (189) indicate that metal pollution is not a large environmental problem in Hungary. On average, the soil cover of Hungary is not polluted. However, the average concentration of the studied 1196 samples hides the high concentrations of polluted soils. For instance. the maximum Cd, Pb and Zn content is 13.4 $mg.kg^{-1}$, 2372 $mg.kg^{-1}$ and 618 $mg.kg^{-1}$, respectively, being indicative for highly polluted soils. Quantification of the risk by comparing the Predicted Environmental Concentration (PEC) with the Predicted No Effect Concentration (PNEC), using the Dutch concept of target values in the latter case, shows that the Risk Quotients of the average soil are less than 1, but values are very high in case of contaminated soil samples. The present evaluation seems to indicate that metal pollution is not a large environmental problem in Hungary. One should, however be aware that the PNEC value used is not based on an ecotoxicological approach but on background data for metals in relatively unpolluted areas. Furthermore, the influence of soil pH, influencing metal mobility and thereby impacts on food quality and on soil life are not included (see paper 1.2 in this report).

Available monitoring data in Hungary and especially in Slovakia show that during the last decade a large area of agricultural soils acidified as a result of insufficient liming. Furthermore, liming may be discontinued by land use changes. This implies a total stop of agricultural activities such as fertilisation, ploughing, harvesting and liming. When liming is inadequate, this may cause mobilisation of heavy metals which may lead to metal concentrations in soil solution and crops exceeding threshold limits for toxicity effects on soil biota, plants, and - by entering the food chain - animals and human beings.

Approach of the study

The majority of soil quality standards for heavy metals are currently based on the total metal content of the soil as determined by a pseudo-total Aqua Regia destruction. The drawback of using a critical total metal content in the solid phase is that the toxic effects of heavy metals depend strongly on the bioavailability of metals. Dissolved metal concentrations and plant metal concentrations are much more closely linked to exotoxicological and human toxicological effects. In this context, transfer functions and soil-plant relationships, predicting those concentrations from soil metal contents and soil properties, such as pH and organic matter content, are a powerful tool. By combining information on: (i) transfer functions for heavy metals describing relationships between total and reactive heavy metal contents in the soil solid phase and dissolved metal concentrations and (ii) soil-plant relations relating total heavy metal contents in crops and in soil, while accounting for the impact of organic matter and clay content and soil pH, it is possible to (iii) predict long-term impacts of stopping with liming on soil acidification and related metal mobilisation and metal uptake in agricultural soils of Slovakia and Hungary. Results obtained in this project for these three items are described below.

Theoretical derivation and practical application of transfer functions

The theory of the sorption process of heavy metals in soil is described as a basis for the derivation of a transfer function. It is shown that from a thermodynamic point of view, combined with the principle of electroneutrality, we expect that metal sorption onto soils follows a Freundlich type of behaviour, where the Freundlich exponent is a measure of the heterogeneity of the available sites, and the Freundlich constant is a function of the average binding strength, the co-adsorbing anions, the competing cations and the number of sites available. The transfer function can be used to estimate the heavy metal sorption behaviour of any soil, with a specified error of estimate, when the major macro-chemical characteristics of the soil are known (see paper 2.1 in this report).

Transfer functions allow the prediction of dissolved metal concentrations or free metal ion activities, which are considered most relevant with respect to environmental risks. Those activities can be calculated from soil solution concentrations using a chemical speciation model that accounts for metal complexation with DOC. This requires however labour intensive measurements to determine soil solution concentrations of the metals of interest, together with the measurement of the macro chemical composition of the soil solution. Activities in soil solution calculated from ‘reactive’ metal contents and soil properties, such as organic matter content and pH, with the use of transfer functions using transfer functions do, however, lead to comparable results. Such functions do avoid those labour intensive measurements. The calculated metal activities can furthermore be compared with critical limits in soil solution that can be derived from available ecotoxicological data for aquatic organisms or by reinterpretation of ecotoxicological experiments for soils for which critical concentrations in soil solution can be estimated from critical total contents using the transfer functions mentioned above. This general applicability of transfer functions is illustrated for different sites in the Netherlands, which differ in degree of contamination (see paper 2.2 in this report)

Field transfer functions between total and reactive metal contents

To account for the difference between the total metal pool and the biologically available pool, a wide range of mild extracts have been proposed to estimate plant uptake. Despite numerous sequential extraction schemes, specific information on the availability of those pools in view of its relation with dissolved concentrations, readily available for plant uptake or leaching to groundwater is lacking. This stresses the need for a single extraction that is able to evaluate the reactive (potential available) metal content in different soils, that can be related to the dissolved metal concentration. In this study a single, dilute acid extraction by 0.43 mol.l^{-1} HNO3 was applied on 72 soil samples that are representative for Hungary (33 plots) and Slovakia (39 plots). Sampling was limited to the plough layer where most effects on solute uptake (and ecology) are to be expected, i.e. within 0-20 cm. The soil samples were also extracted with 0.05 mol.l^{-1} EDTA to compare the results obtained with the mild HNO3 extraction. Furthermore, the 'so-called total' metal content was measured by using an aqua regia extraction. The samples included a large range in soil properties and degree of contamination, the latter by including 12 plots from a long-term field experiment with heavy metals in Hungary. The main purpose of this study was to investigate the possibility to derive reactive metal contents from 'so-called total' metal contents, the latter being readily available for a large number of plots in many countries.

In a first paper, based on data for Slovakia, results of the single extraction approach are summarised in comparison to sequential extraction schemes and the various concepts and procedures used for assessing metal contamination are discussed. The results presented in this paper show that contaminated topsoils may lead to elevated metal contents in plants, whereas contaminated subsoils may cause enhanced leaching towards groundwater. The mobile fractions of contaminated Slovakian soils obtained by a single extractant are high for Cd, As, Cu and Zn. In general the mobile or reactive contents are not so clearly related to soil properties but more closely to the total content, especially for Cd. Results of the sequential extraction analyses showed that Cd, Cu and Zn are present in the most mobile fractions in contaminated alluvial soils. Results based on soil solution extractions showed that exceeded current groundwater quality standards for As, Cd, Cu, and partly Zn and Hg and critical soil solution limits for Cd and Hg (see paper 2.3 in this report).

In a second paper, based on data for both Hungary and Slovakia, a systematic comparison is presented of reactive metal contents and total metal concentrations. Results showed a considerable agreement between reactive metal concentrations measured with a mild (0.43 mol.l^{-1}) HNO3 extraction and with an EDTA extraction. Furthermore, a considerable part of the metals are present in a rather unavailable form in soils. On average, Zn has the lowest reactive to total metal ratio (0.17), followed by Pb (0.30), Cu (0.38) and Cd (0.56). For each metal considered there is a large range in ratios of reactive to total metal content. On average, a reasonable prediction can be made of reactive metal contents from total metal contents and the organic matter and clay content using regression relations. However, large errors can be made for individual samples specifically in the low concentration range. The derived relations are further completely empirical and can only to be used for the types of soil for which they were derived. The use of similar relations derived with Dutch soil samples showed reasonable agreement for Cd, but reactive metal contents were generally overestimated for Cu, Pb and Zn. This underlines the need to determine the reactive metal pool with a suitable extractant because the reliability of estimates from the total pool and soil properties is limited for specific sites (see paper 2.4 in this report).

Laboratory transfer functions between soil metal contents and dissolved metal concentrations

In the literature, various transfer functions have been derived up to now, varying from simple linear relationships relating total concentrations of the metal ions in solution to total metal contents, to non-linear relationships relating free metal ion activities (include the solution speciation) to total or reactive soil metal contents. The last approach is considered most adequate but only limited information on those relations is available up to now. Problems with the derivation of transfer functions based on activities are first of all the very few sorption studies in which metal activities are measured. An exception is the trace metal copper (Cu) because: (i) the Cu activity can be measured directly with a cupric ion selective electrode and (ii) Cu forms strong complexes with DOC in solution which will have a pronounced effect on the activity of the trace metal in soil solution. Environmentally Cu is of interest in the case of land use change of former agricultural land which received high loads of pig slurry. Pig slurry can contain high concentrations of copper which was given to pigs to improve their growth performance and feed conversion rate. Although several studies thus do exist on Cu sorption including measurements of Cu activities, there are almost no measurements for the lower pH range (below pH 4.5) at which the influence of Al might become important. Partition of trace metals in the acidic range is particularly important for acidified forest soils. Furthermore all studies are limited to topsoils whereas in the case of metal leaching subsoils are very important. In general one can say that the impact of pH and Ca on the soil-solution transfer function has not been studied systematically for most metals up to a low pH level.

To overcome the limitations described above, a laboratory study was carried out aimed at the extension of data for the derivation of transfer functions for Cu activities in the lower pH ranges. Batch adsorption studies were carried out with samples from acid forest soils at different depths. In the equilibrium solution the Cu activity was directly measured with a cupric ion selective electrode. Measurements showed that Cu activities with an ion selective electrode is possible for acid sandy soils. For low total dissolved concentrations of Cu (below 20 $\mu g.l^{-1}$) measurements are unreliable. Activities calculated with a simple diprotic acid model for the complexation of Cu with DOC gave good results compared with measured Cu activities. The dependence of Cu sorption on pH and Ca activity could be described well for different soils. It was not necessary to include a parameter for Al to describe the partitioning of Cu in acid soils. The validated transfer function worked equally well for topsoils and subsoils despite possible differences in carbon quality at different depths (see paper 2.5 in this report).

In order to derive reliable soil-solution transfer functions for soils of Hungary, the sorption behaviour of two major metals, cadmium and copper, was studied up to low pH ranges. Twelve representative soil samples of Hungary were collected and experiments were performed to analyse 252 chemical equilibria of Cd and Cu sorption. In this way soil-solution transfer functions, while accounting for differences in major soil properties (pH, organic matter and clay content) were determined and interpreted for Cd and Cu. Results showed that free metal ion activities can be derived well by measuring dissolved metal concentrations and major ions in the soil solutions, including pH, Ca and DOC. In case of Cu, the calculated Cu ion activities compared well with the measured activities, giving confidence in the used speciation model. More important, however, the results showed that the use of a transfer function, allowing to derive the free metal ion activity from the solid phase content while accounting for the effect of pH, clay content and organic matter content, gives almost equally good results. The fact that two independent concepts (transfer function approach and speciation calculations) compared well with activity measurements for Cu confirms the applicability of the transfer function approach.

Using these transfer functions the chemical risk of cadmium or copper ion mobilisation was assessed. Specifically, the risk of ground water contamination with cadmium was illustrated for soils even with a relatively low Cd content, but also a low pH and Ca concentration (e.g. forest soils). It directly shows how contamination can be limited by influencing those properties by e.g. liming. Soil-solution transfer functions can thus be used in models and decision support systems predicting impacts of e.g. land use changes and management practices, including those aimed at solving environmental problems and contributing to the protection of our environment (see paper 2.6 in this report).

Process based plant uptake modelling

There is increasing concern for the accumulation of cadmium in cereal crops, as cadmium even at low and non-phytotoxic concentrations poses a threat to consumer health. The objective of the study described in the first paper related to plant uptake was to explore the possibility of modelling the transfer of cadmium from agricultural soils to crops with a dynamic, process-oriented, multi layer model, CdModel, based on easily accessible information regarding meal inputs, soil and crop characteristics. CdModel was applied to an experimental site called Kungsängen, in which a long-term fertility experiment started in 1964. Cadmium input on the Kungsängen soil was reconstructed, using data and estimations of historical atmospheric deposition and concentrations in fertilisers and manure. Results show a large increase in cadmium input after the 2nd World War until the eighties when adverse effects started to be discussed and policies to reduce the cadmium content in fertilisers were implemented. Simulated cadmium concentrations in wheat grain, using the Kungsängen site as input for the modelling, showed reasonable values compared to field data on wheat cadmium concentrations estimated from a survey dealing with wheat Cd concentrations in specified wheat cultivars in the period 1918-1980. The substantial yearly variation in grain cadmium concentration was, however, not captured by the model. The approach of dynamically modelling cadmium uptake is also compared to empirically derived soil-plant relationships, relating soil content of cadmium to crop contents. The comparison was limited but this might be due to the fact that the soil-plant relationship was not based on the specific wheat cultivar use in Sweden. General conclusion is that the simulation of the yearly variation in crop cadmium concentration with a dynamic process-oriented biogeochemical model is difficult since much of the dynamics is probably mainly governed by plant specific processes and not so much by soil chemistry. In addition, there are few sites with long time-series of cadmium concentrations in soil and crops needed for calibration and validation of the model. Nevertheless, CdModel has shown promising reference behaviour patterns and is capable of describing trends in the average grain cadmium concentrations with reasonable accuracy (see paper 3.1 in this report).

Empirical soil-plant relationships

To derive an applicable system that enables the user to calculate soil specific target values for Cd and Zn in arable soils, data from nation-wide field inventories on heavy metals in soils and crops were used. Soil-to-plant transfer relationships for Cd and Zn based on soil pH, organic matter content, texture and the soil metal content were derived by multiple linear regression. The use of a simple Freundlich-type equation explained between 40 and 80% of the measured variation of Cd and Zn in crops such as potato, wheat, maize, sugar beet, lettuce and endive, whereas the total metal content only accounted for up to 10%. The approach described here can be used to estimate the soil-specific Cd and Zn content in various crops but also to calculate the site-specific target soil metal content at which the food quality criteria will be exceeded. The impact of pH on the soil-plant relationship illustrates that soil acidification poses a potential risk due to the transfer of metals from soil to food crops by increased metal availability and the subsequent intake of crops by human beings or animals. It also illustrated that current soil quality standards, which usually are based on the total soil metal content only, even though impacts including metal uptake are controlled largely by metal availability, are not appropriate. Considering the impacts on plants, instead of using a total soil metal content, it is better to calculate a site specific value based on food quality criteria and soil plant relationships as described in this study. Furthermore the use of soil plant relationships can give insight in changes in human toxicological risks due to changes in soil properties which is of interest in the case of management changes (e.g. acidification due to stopping with liming). The soil plant relationships derived in this study can be and have been used in models allowing such predictions (see paper 3.2 in this report).

Regional application

The last paper evaluates the possible long term (50 years) impact of the acidification of agricultural soils, due to stopping with liming, on dissolved cadmium (Cd) and zinc (Zn) concentrations and crop contents in wheat and maize for representative Slovakian and Hungarian agricultural soils for different fertiliser scenarios. The predictions were made with the soil acidification model SMART, adapted for agricultural soils, combined with previously described (i) transfer functions for heavy metals predicting reactive heavy metal contents from total soil metal contents and dissolved metal concentrations from reactive soil metal contents and (ii) soil plant relationships, predicting heavy metal contents in crops from heavy metal contents in soil, while accounting for the impact of organic matter and clay content and soil pH.

The investigated locations originally included 306 plots for Slovakia and 250 plots with data on soil properties (pH, clay content and organic matter content) and metal contents in soil and partly also in the wheat and maize (in Hungary). We however investigated the impact of stopping with liming on the non-calcareous plots only, since this measure is not relevant on the calcareous soils, being 280 of the 306 plots in Slovakia and only 25 of the 250 plots in Hungary. Initial pH values in the Slovakian and Hungarian non-calcareous soils varied mostly between 4.5 and 5.5. Simulated changes in soil pH are dependent on the soil type and time period but in general a pH drop of 0.5-1.0 is predicted in a 50-year period, the largest changes taking place in the first 20 years.

Adverse affects on soil life are most likely due to elevated dissolved Zn concentrations. In Slovakia, the predicted percentage of plots exceeding a critical Zn concentration of 250 $mg.m^{-3}$ increases from less than 10% at the start of the simulation to 40% after 50 years. The percentage of plots with a dissolved Cd concentration above a critical level of 2 $mg.m^{-3}$ increases from approximately 10 to 20% in 50 years. Adverse affects on crops are due to elevated Cd contents in wheat, whereas Zn is not a problem. Results show that the predicted percentage of plots exceeding a critical Cd content of 0.1 $mg.kg^{-1}$ is about 90% at the beginning in Slovakia and this percentage will slightly increase as a result of acidification. When one takes a higher criterion, such as 0.15 $mg.kg^{-1}$, used in the Netherlands, the percentage increases from approximately 50% at the start of the simulation to 85% after 50 years. In Hungary, Cd contents are already near 0.3 $mg.kg^{-1}$ at the start of the simulation These high Cd contents are most likely due to the low organic matter contents of the soils. The effects of an alternative fertiliser scenario on the pH and Cd contents in soil appeared to be limited (see paper 4.1 in this report).

Conclusions

Overall conclusions that can be derived from the studies carried out in this project are that:

- On average, a reasonable prediction can be made of reactive metal contents from total metal contents and the organic matter and clay content using regression but the reliability of those estimates is limited for specific sites
- Reliable transfer function can be derived allowing the calculation of total or free metal concentrations in soil solution from measured reactive or total contents in the solid phase, specifically for Cd and Cu.
- Transfer functions allowing the calculation of total or free metal concentrations in soil solution from measured contents in the solid phase is a practical method to be used for risk assessment. It avoids labour intensive measurements to determine soil solution concentrations of the metals of interest together with the measurement of the macro chemical composition of the soil solution.
- Simulation of the crop metal contents with a dynamic process-oriented model, especially the yearly variation in is difficult since much of the dynamics is probably mainly governed by plant specific processes and not so much by soil chemistry.
- Soil-to-plant transfer relationships based on soil pH, organic matter content, texture and the soil metal content as derived by multiple linear regression are reasonable for regional scale applications in the case of Cd and Zn. The use of a

simple Freundlich-type equation explained between 40 and 80% of the measured variation of Cd and Zn in crops such as potato, wheat, maize, sugar beet, lettuce and endive

- The use of transfer functions and soil plant relationships in combination with critical limits for the soil solution and crops (food quality criteria) can give insight in changes in ecotoxicological risks due to changes in soil properties which is of interest in the case of management changes, such as stopping with liming application of the transfer functions soil plant relationships derived in this study show a substantial increase in the area exceeding ecotoxicological critical limits for the soil solution and human toxicological critical limits for food crops (food quality criteria).

Introduction

This report focuses on the long-term environmental risk of soil acidification due to inadequate liming practices on mobilisation/leaching and plant uptake of potentially toxic heavy metals (i.e. lead, cadmium, zinc and copper) from agricultural soils in Slovakia and Hungary with different crops (wheat and maize) and land use practices. This included: (i) laboratory research on sorption and complexation of heavy metals, (ii) field research on effects of heavy metal mobilisation on plant uptake and (iii) modelling research including model refinement/extension, model validation and simulation of effects of various fertilisation/liming scenarios on soil acidification, heavy metal mobilisation and plant uptake.

Below, we first present some background information on: (i) metal pollution and acidification problems in Slovakia and Hungary and (ii) the processes of soil acidification, metal mobility and metal uptake before describing (iii) the specific aims objectives of the study described in this report and the contents of the report.

Metal pollution and acidification problems in Slovakia and Hungary

During the last century, the metal content (specifically cadmium, copper, lead and zinc) in most soils has increased considerable as a result of manure application, fertiliser treatment, atmospheric deposition and the amendment of sewage sludge. Risks that are associated with the presence of excess amounts of metal in soil include leaching to the groundwater, uptake by plants and effects on soil micro-organisms and, eventually the entire food chain as a results of metal transfer from micro-organisms to higher organisms. Concern about the input of heavy metals in forests, is related to the impact on soil organisms and the occurrence of bioaccumulation in the organic layer. With respect to copper and zinc, the possible occurrence of deficiencies in view of forest growth is another relevant aspect. An excess input of heavy metals in agriculture may cause agricultural products with unacceptable levels of heavy metals and even reduced crop production. To protect both soil organisms and human beings from adverse effects, soil quality standards have been developed in most countries. The levels of protection are usually based on the protection of the food-chain (risks associated with food intake by higher animals and human beings), protection of soil organisms (based on ecotoxicological data) or direct uptake by children (based on toxicological data). The majority of these standards is currently based on the total metal content of the soil as determined by a pseudo-total Aqua Regia destruction.

The ecotoxicological risks of this accumulation may, however, be very limited as long as the bioavailability and mobility of heavy metals is limited. In general, dissolved metal concentrations (or even free metal ion activities) strongly determine the effects on microbiota/soil fauna. This is also true for effects on vascular plants through metal uptake, on ground water through leaching and on terrestrial fauna through accumulation in the food chain. In some cases (e.g. for arthropods), effects are partly due to consumption of soil solid material. However, in most cases, toxic effects on micro-organisms and soil fauna are mainly due to elevated bioavailable concentrations in soil water.

Important environmental conditions which determine the bioavailability of heavy metals in soils are the pH and the macro chemistry of the soil solution (e.g. concentrations of dissolved organic carbon (DOC), calcium and aluminium). A decrease in pH increases soil solution concentrations of heavy metals. Improper management practices of agricultural land (insufficient liming, too high fertiliser applications) cause a decrease in soil pH and thus an increase in heavy metal bioavailability. The ‘chemical time bomb’-effect (mobilisation of previously fixed soil pollutants) may lead to an increase in dissolved metal concentrations to such an extent, that their concentration will become toxic for soil biota, for plants, and - by entering the food-chain - for animals and human beings. Consequently soil fertility may decrease, agricultural products may yield with unacceptable levels of heavy metals, even crop production may be reduced and ultimately human health may be affected. The prevention of these environmental hazards is thus of vital importance.

The occurrence of such a chemical time bomb is not imaginative, in several eastern European countries, including Slovakia and Hungary, since metal pollution does occur and liming is not always adequate. National inventories indicate that several ten thousands of hectares in Slovakia and in Hungary are polluted with heavy metals and are a potential risk when soils acidify. In the annex to the final report an overview on these problems in Slovakia has been given that briefly summarise the regional problems. In this country, the ecologically endangered areas (hot spots) are distributed around mining and industrial centres. To them belong: Middle Spiš region (Krompachy, Rudnany), Žiar nad Hronom region, Jelšava - Lubenik, Hacava - Hnúšta, and Lower Orava regions. Three other very specific regions (Hacava - Hnúšta, Jelšava – Lubeník and Košice) are polluted by alkaline dust from magnezite works, together with some heavy metals. Finally, atmospheric input of heavy metals evidently resulted in accumulation in surface layers of forest soils. The available data suggest that in about 28 % of the Slovakian soils diffuse soil contamination occurs, with the content of one, or more heavy metals being higher than the target (A)-values.

Available monitoring data in Hungary and especially in Slovakia also show that during the last decade a large area of agricultural soils acidified as a result of insufficient liming. Furthermore, liming may be discontinued by land use changes. This implies a total stop of agricultural activities such as fertilisation, ploughing, harvesting and liming. In Hungary, a Government decision was made to increase the forestland with about 300 000 hectares.

Available knowledge on soil acidification, metal mobility and metal uptake

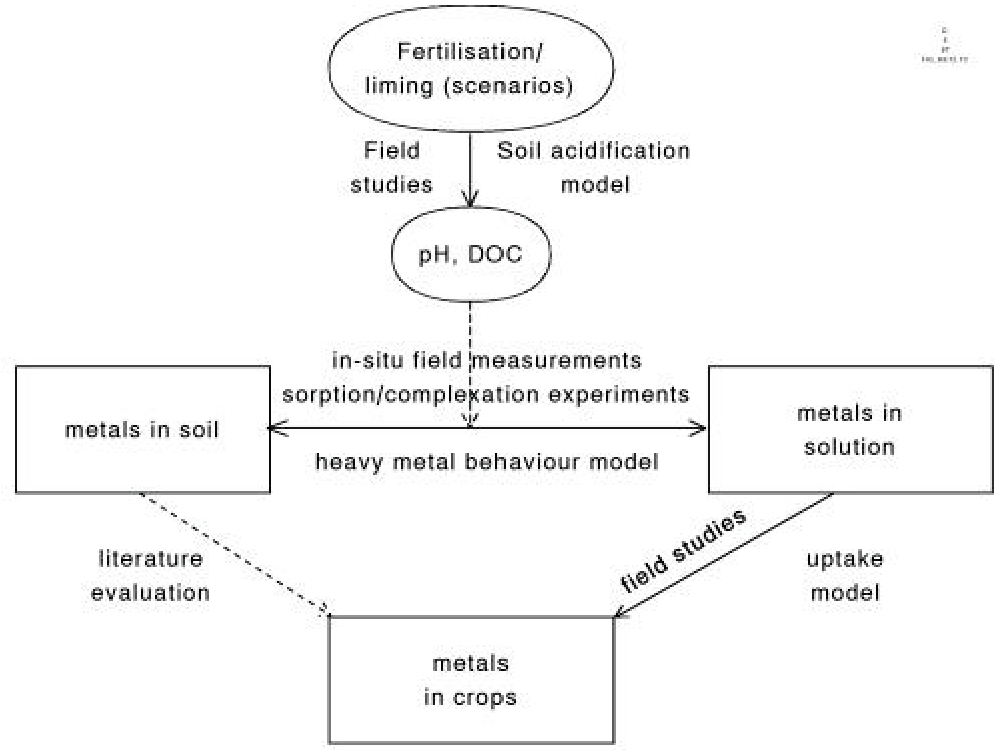
Research on acidification of forest soils has given a lot of insight in the processes that regulate soil acidification. From this process knowledge, state-of-the-art acidification models have been developed, amongst others in the Netherlands for the application at different scales. An example is the model SMART. This model can be used (with modifications to be applied for agricultural land) to predict pH changes as a result of different management practices such as fertiliser application and liming.

The impact of pH changes on metal bioavailability has also been studied for quite some time. Several studies show that bio-availability and plant uptake of heavy metals is better related with concentrations or activities of the free (uncomplexed) metal ions in the soil solution than with total or extractable concentrations in the soil solid phase. Most applicable and practical models predicting dissolved metal concentrations from metal contents in the soil are so-called transfer functions (adsorption relationships). Such functions relate soil solution concentrations or activities of heavy metals to solid phase concentrations, while accounting for the impact of soil properties, such as organic carbon content, clay content and CEC, and soil solution properties, such as pH and calcium concentration. Application allows the prediction of dissolved metal concentrations and metal leaching as a function of pH changes. At the start of this project such functions were derived amongst others in the Netherlands but for a limited pH range and based on limited data.

Finally for the quantification of heavy metal uptake by plants, a model is needed. Plant uptake of heavy metals is best correlated with concentrations or activities of metals in the soil solution. A process based metal uptake model can thus best be based on a description of the uptake from soil solution. Such models do exist by e.g. coupling metal concentrations to the water flow from soil to plants, driven by transpiration, including crop specific preference factors for heavy metals. An integrated process-based model including both soil acidification and plant uptake for local scale applications is, however, missing. Similarly, integrated more empirical models for regional scale applications, including e.g. simple direct soil-plant relationships predicting metal concentrations in plants from those in soil, accounting for the impact of soil properties are missing.

Objectives of the study

The primary research goal of the proposal was to assess the long-term environmental risk of soil acidification on mobilisation and plant uptake of potentially toxic heavy metals (i.e. lead, cadmium, zinc and copper) from agricultural soils in Slovakia and Hungary with different crops (wheat and maize) and land use practices. The assessment of inadequate liming practices and the fate and effects of heavy metals were investigated as outlined in the figure below.



According to this figure and concurrent to the project objectives, four major activities were distinguished, as described below i.e.: (i) research on sorption and complexation of heavy metals, (ii) research on effects of heavy metal mobilisation on plant uptake, (iii) modelling, which includes model refinement and extension and model validation and (iv) the simulation of effects of various fertilisation/liming/atmospheric deposition scenarios on soil acidification, heavy metal mobilisation and plant uptake. The specific research objectives, which focussed on top soils (i.e. soil depths from 0-20 cm or 0-30 cm) of well-drained agricultural soils in Slovakia and Hungary, were fourfold:

1. Determination of the impact of changes in pH due to soil acidification on the sorption of heavy metals by soil and complexation of heavy metals with dissolved organic carbon on the basis of literature reviews, laboratory experiments and field studies.
2. Assessment of the impact of mobilisation of potentially toxic heavy metals on plant uptake. This includes the determination of the relation between soluble heavy metal concentrations and the development /calibration of plant uptake models for major crops in agricultural soils in Slovakia and Hungary.
3. Elaboration of available models on soil acidification and heavy metal behaviour and calibration on field measurements.
4. Modelling the long-term environmental impacts of acidification on plant uptake for various land use management (liming and fertiliser application) scenarios.

Contents of the report

This report first describes soil contamination problems in the study area (Theme 1), divided in a chapter focusing on Slovakia (1.1) and Hungary (1.2).

Then six chapters are included, which focus on transfer functions relating different pools of heavy metals in soil and soil solution (Theme 2). This theme is related to the determination of the impact soil acidification (pH changes) on the sorption of heavy metals by soil and complexation of heavy metals with dissolved organic carbon on the basis of literature reviews, laboratory experiments and field studies. It includes two chapters in the theoretical derivation (2.1) and practical application of transfer functions (2.2), followed by two chapters on field transfer functions between total and reactive metal contents (2.3 and 2.4), finally followed by two chapters on laboratory transfer functions between soil metal contents and dissolved metal concentrations (2.5 and 2.6).

The assessment of the impact of mobilisation of potentially toxic heavy metals on plant uptake with models describing metal uptake by plants is the topic of Theme 3. This includes the development and calibration of a plant uptake model (3.1) and the determination of the relation between heavy metal concentrations in the soil and in plants (3.2). More specifically chapter 3.1 focuses on process based plant uptake modelling at an experimental site in Sweden, in which a long-term fertility experiment started in 1964, to compare simulated and measured cadmium concentrations in wheat grain. Chapter 3.2 focuses on empirical soil-plant relationships for Cd and Zn in arable soils based on nation-wide field inventories on heavy metals in soils and crops in the Netherlands.

Finally, Theme 4 which focuses on impacts of acidification on leaching and plant uptake on a regional scale, includes one article on modelling of the long-term environmental impacts of acidification on leaching and plant uptake in Hungarian and Slovakian agricultural soils (4.1). This integrating chapter describes the impact of various liming and fertiliser application scenarios, using integrated models on soil acidification and heavy metal behaviour:

Theme 1 Soil contamination problems in Slovakia and Hungary

1.1 Diffuse soil contamination problems in Slovak republik

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In Curlík, J. - Šefcík, P., 1999: Diffuse soil contamination problems in Slovak republik. Vedecké práce, Proceedings No. 22, VÚPOP, Bratislava, pp. 33 - 46

Key words: soil - geochemical mapping, diffuse contamination, ecologically endangered areas (hot spots), alkaline dust contamination, risk elements, transboundary air pollution.

Summary

Various regions in Slovakia are polluted with heavy metals and are a potential risk, e.g. when soils acidify. This paper briefly summarise the regions in Slovakia where such problems can occur. The ecologically endangered areas (hot spots) are distributed around mining and industrial centres. To them belong: Middle Spiš region (Krompachy, Rudnany), Žiar nad Hronom region, Jelšava - Lubenik, Hacava - Hnúšta, and Lower Orava regions. Three other very specific regions (Hacava - Hnúšta, Jelšava – Lubeník and Košice) are polluted by alkaline dust from magnezite works, together with some heavy metals. Finally, atmospheric input of heavy metals evidently resulted in accumulation in surface layers of forest soils. The available data suggest that in about 28 % of the Slovakian soils diffuse soil contamination occurs, with the content of one, or more heavy metals being higher than the target (A)-values.

1.1.1 Introduction

Soil under natural conditions may contain some heavy metals at phytotoxic levels. Such elevated concentrations in Slovakian soils correspond to geochemically anomalous zones which represent special type of parent rocks (mafic rocks), but more often secondary dispersion halos around mineralised zones of hydrotermally altered rocks. On the other hand, however, there is predominant contamination around the historical mining, smelting and ore processing sites, industrial and some urban centres. Although, heavy metals have been accumulated in the soils around some mining areas for centuries, but their substantial increasing occurred with rising industrialisation (the development of heavy industry after second world war and implementation of non-proper technology). The composition, concentration and speciation of the risk substances in such zones vary widely and may influence their behaviour and adverse effect to the soils. (Curlík, J. and Matušková, L., 1994; Curlík, J. and Mejeed, S.Y., 1994; Curlík, J. and Šefcík, P., 1998, 1999a).

Some elevated concentration in soils higher than the background level are caused by transboundary- air transport of the substances or by long-term application of chemicals to the soil (pesticides, fertilisers). Geochemical soil mapping and monitoring, which has been done in all territory of Slovak republic gave us an opportunity to get better insight into the problem of soil (land) contamination related to the different contamination sources (Curlík, J. and Šefcík. P.,1997; Linkeš, V. et al. 1996). By integrating geochemical mapping with geological and soil investigation the pattern of soil contamination could be better understood. Our results points to the fact that in many instances possible sources are overlapped (multisources contamination). Moreover, slope and fluvial processes caused the redistribution of contaminants downstream as mechanical particles and dissolved species, too, and led to the alluvial soil contamination. Due to the complex of contributing factors a diffuse soil contamination is observed. Under this term we understand areal soil contamination of natural (geochemical) and antropogene origin, in which the level of one or more contaminants has crossed the current background values of soils. It displays an uneven distribution pattern with the local concentration that may reach the intervention values.

The aim of this contribution is to give an overview on these problems in Slovakia and briefly summarise the regional problems which might be of general interest in reaction to solution for contaminated land and consequently for the risk to plants, water and human health.

1.1.2 Inventory of contaminated soils

It must be stressed that the ways in which soils are contaminated/degraded in Slovakia are numerous and have a different extension. They include a considerable number of co-operating factors either natural, or anthropogenic origin (Curlík J. 1999).

Soil contamination as an environmental issue has emerged in Slovakia at he end of seventieth when first limits for some heavy metals (Pb, Zn, Cu, Hg), as soil quality criteria, has been accepted. The concern on soil pollution has grown gradually and so, at present, results of several projects devoted to soil pollution are available:

- Geochemical mapping of soil in Slovak Republic started in 1991. Within this project agricultural and forest soils are sampled over all territory from the A and C horizons. Total content of the assemblage of 36 chemical elements has been analysed. This project is finished and results is published this year. These data will form a good basis for detailed studies and can contribute to a general awareness on soil degradation and its adverse effect to all environmental constituents. This mapping in Slovakia is conducting in the frame of a big national programme ‘Geochemical atlas of Slovakia’ in which the different sampling media were sampled (rocks, stream sediments, soils, water and biota) and analysed. Within the subproject ‘Soils’ the sampling programme was performed in a grid - 1 sample per 10 km^2 (in which soil samples were taken at random), from the forest and agricultural soils. Total content of 36 chemical elements namely: Al, As, B, Ba, Be, Bi, Ca, Ce, Co, Cd, Cr, Cs, Cu, F, Fe, Ga, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, Sr, V, W, Y, Zn have been measured (Curlík, J. and Šefcík, P., 1994, 1997; Vrana, K. et al. 1997).

- Regional geochemical mapping of the soils conducted by the authors showing the surface distribution of chemical elements in some industrial regions were done in addition (Curlík, J. et al. 1997a, 1997b, 1997c, 1997d, 1999a, 1999b).
- Soil monitoring has started some years ago. In the frame of this project the pollution problem has been tackled. The content of some chemical elements, PAU and mineral oil pollution has been detected. Soil monitoring system is based on 650 soil profiles from which 312 belong to agricultural and rest to the forest soils (Linkeš, V. et al.1997).
- Agrochemical soil testing which is already done in several cycles for agricultural soils and was oriented on ascertaining the ‘available’ nutrients (N, P, K), pH, and carbonate status. Later was extended for some ‘extractable’ forms of heavy metals (Cr, Cd, Hg, Pb).
- Long-term risks of inadequate management practices on the sustainability of agricultural soils, in which additional data on soil properties related to the availability of metals was derived.

By this way a first understanding on the chemical elements distribution in Slovakian soils could be established.

1.1.3 Diffuse soil contamination in the Slovak Republic

To deal with the problem of contaminated soils one have to include contaminated levels and the effect to plants (food chain) and to the other environmental constituents (integrated approach). It is necessary to deal with soil as a multi-functional ecological component that is critical to sustaining the current and future environmental quality. Soil quality must possess no harm to human, plants or animals, not adversely affect natural cycles or functions and not contaminate other environmental constituents.

Over the past decade, soil contamination has emerged in the Slovak Republic as a key environmental issue. The sources of soil contamination are very diverse. Diffuse soil contamination is both historical and nowadays and it is connected with mining and smelting operations, with fossil fuel (coal) combustion, industrial activities, transboundary air pollution, traffic and agricultural activities. Other possible sources, such as contamination along roads, are far less important and till now not very well addressed.

Historically contaminated areas

Historically most contaminated areas are represented by four regions with a very old mining history, namely: Spišsko-gemerské rudohorie Mts., Kremnické and Štiavnické vrchy Mts., Low Tatras and Little Carpathians, with many kinds of mining operations (smelters, ore processing and transport) with mined wastes and heaps disposals. The ecologically endangered areas (hot spots) are distributed around mining and industrial centres. To them belong: Middle Spiš region (Krompachy, Rudnany), Žiar nad

Hronom region, Jelšava - Lubenik, Hacava - Hnúšta, and Lower Orava regions. Upper Nitra, Ružomberok, Košice, Strážske - Humenné - Vranov regions are far less polluted.

Middle Spiš is a common name for the immision areas of metal works of Krompachy town and the mine districts in Spišsko-gemerské rudohorie Mts. Both immision areas do overlap. Heavy metals (Cu, Hg, Ni, Cd, Pb, Zn, As) are the main soil contaminants. The metal works at Krompachy has produced, according to some data in 1986, 19 838 t of SO_2, 1383 t of dust and 92 t of As. The acreage of the contaminated agricultural soils in this area is about 11 000 ha (Hronec, J. – Tóth, J. – Holobradý, K., 1992). This situation has radically changed after the substantial technological improvement and decreased by about 50%. At Rudnany mining district the most dangerous problem was the mercury production. Mercury was spread in the surroundings from the smelters and is present in the soils, stream sediments and in the water. The acreage of polluted soils is not accurately known but it may be several thousands of ha (Hronec, J. – Tóth, J. and Holobradý, K., 1992).

Alumina works at *Žiar nad Hronom* produce specific pollutant fluorine (together with Hg, As). The estimation of the water soluble F showed that about 3 700 ha have concentrations above the limit (10 $mg.kg^{-1}$ of water soluble F). The substantial improvement was reported after 1995, when the new technology was applied (MŽP SR,1997).

Dolná Orava region known by ferro-alloys factories (Istebné) in which about 13 different alloys were produced. At present the new technology is applied but in the past Cr and Mn polluted about 13 000 ha of soil (Curlík, J. and Matušková, L., 1994).

In the region of *Horná Nitra* (Upper Nitra) As and Hg are the main pollutants around the chemical factories and electric- power station. In the Galanta region an elevated concentration of nickel has been mapped around the former nickel works (Curlík, J. et al. 1997d).

At *Košice* (magnezite works, iron works) some heavy metals and dust, at Vojany (electric-power station) As. In all mentioned regions SO_2 is another important pollutant (Curlík, J.-Ivanco, P. and Šefcík, P.,1997a). At *Ružomberok* SO_2 is the main problem, but the soils are only slightly polluted by heavy metals (Curlík, J. et al. 1997c).

In addition to the polluted areas around the mining sites and smelters, also the soils of alluvial plains which drain these areas show the different stage of contamination (alluvial plains of Štiavnický potok, Pezinský potok, Hron, Hornád, Slaná and other rivers) (Curlík, J. et al. 1997a, 1999a; Curlík, J. and Šefcík, P. 1999b; Rapant, S. - Vrana, K. and Bodiš, D., 1997). The vineyards areas and vegetable growing regions are portrayed in the geochemical maps by increasing concentration (diffuse contamination) of Cu (fungicides) and Zn (the fances).

Contamination by alkaline dust
Three another very specific regions (Hacava - Hnúšta, Jelšava – Lubeník and Košice) are polluted by Mg- dust from magnezite works, together with some heavy metals. Enormous amount of alkaline dusts containing MgO, $MgCO_3$ and calcinated magnesia has sedimented within the magnezite works immision areas. The pH values of the dust are above 10. Gradually the crusts of secondary Mg minerals were formed at the surface and in topsoils, but even all soil profiles became alkaline (close to the sources). In the Hacava - Hnúšta about 3 000 ha and at Jelšava - Lubeník about 18 000 ha of soils are to different levels contaminated - alkalised (Curlík, J. - Matisová, E. and Šefcík, P. 1999b). At Košice mostly urban soils were affected but these works were fortunately closed several years ago (Curlík, J. et al. 1997a).

Transboundary air-pollution and soil contamination
Atmospheric input of heavy metals (wet and dry depositions) evidently resulted in accumulation in surface layers of forest soils. The results of geochemical mapping show that there is at least clear evidence for airborne sources for Cd, As, Hg even in high mountainous regions - High and Low Tatras (Curlík, J. and Šefcík, P. 1998, 1999a). Elevated – above background concentrations, in the acid soils developed on granitic rocks are visible. This diffuse contamination has to draw attention in relation to the inputs of other acidifying compounds (SO_x. NO_x, HN_x) to the soils (Curlík J., 1998a, b) which are already naturally acid (podzolic and cambic soils).

1.1.4 Specific problems in Slovakia

At present the responsibilities and competencies for developing and implementing soil quality policies are only fragmentary defined. Taking into account the complexity of the subject addressed, establishing a ‘task force’ aimed at initiating and co-ordinating a traject for policy- development seems a necessary condition because of:

- The lack of perception in major segments of society of the long term importance of structural attention to soil pollution problems.
- The lack of operational triggers which would put soil quality on the agenda in decision making processes, permit procedures, location development and/or property transactions.
- Present priorities for economic development, infrastructure and public services with consequences for political incentives, governmental inputs and financing inventories, investigations. These are the main reasons why the development of policies and regulations, including the remediation actions related to soil quality are unsatisfactory.
- Undefined and/or fragmented responsibilities with respect to initiating, co-ordinating and implementing soil quality related policies and regulations.
- Financial inputs to soil investigation and remediation relates to ad-hoc programmes and sometime to non professional companies.

It is clear that new data are needed to ascertain the different classes of polluted soils (hot spots) and eventually take proper measures for improvement. No special differentiation is done on the basis of soil use. Further research has to be concentrated on the modelling of behaviour and leaching of metals (inert-active pools transfer) in the soils with regard to uptake by plants and to the groundwater contamination. In this context effect-based soil quality criteria for the soils, sediment and groundwater should be established by the implanting of multifunctional principle.

1.1.5 Conclusion

Diffuse soil contamination in Slovak Republic is connected with both historical and nowadays mining, industrial and agricultural activities. In addition to these, some evidence point to air-borne contamination by transboundary air-pollution. Some of the polluted soils are due to geochemical anomalies, but mostly they are overlapped by anthropogenic ones. The less important sources of diffuse contamination (along roads, heating installations, disposal sites) are not yet addressed (or not known).

Diffuse soil contamination is not included as an environmental issue in Soil Protection Act No. 207/1992 and no special soil contamination act exists. However, guide values (A-B-C- values) were adopted (Resolution of MP SR 531/1994-540). The available data suggest that about 70% of the Slovakian soils are non-contaminated, in about 28 % soils diffuse soil contamination occurs, with the content of one, or more risk elements higher than target (A)-values, but lower than B- values. Soils in which the content of risk element crosses the B-values is about 1.4% and these in which it is above intervention (C)-values is about 0,4%. (Linkeš et al. 1997). Among other pollutants heavy metals are the most spread in Slovakian soils and so, critical concentrations of heavy metals in soils (in relation to micro-organisms, plants, surface and groundwater protection) should be derived in view of their impacts.

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1.2 Quality and contamination of agricultural soils in Hungary as indicated by environmental monitoring and risk assessment

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Summary

Data on heavy metal contents derived from the Soil Information and Monitoring System of Hungary, including 1236 representative sampling sites on agricultural land (865), forests (183) and environmental ‘hot spot’ regions (189) were used for an Environmental Risk Assessment of heavy metal content in soils of Hungary as described below. The average heavy metal contents exhibit a close relationship with the soil texture. On average, the soil cover of Hungary is not polluted. However, the average concentration of the studied 1196 samples hides the high concentrations of polluted soils. For instance the maximum Cd, Pb and Zn content is 13.4 mg.kg^{-1}, 2372 mg.kg^{-1} and 618 mg.kg^{-1}, respectively, being indicative for highly polluted soils. Quantification of the risk by comparing the Predicted Environmental Concentration (PEC) with the Predicted No Effect Concentration (PNEC), using the Dutch concept of target values in the latter case, shows that the Risk Quotients of the average soil are less than 1, but values are very high in case of contaminated soil samples. The present evaluation seems to indicate that metal pollution is not a large environmental problem in Hungary. One should, however be aware that the PNEC value used is not based on an ecotoxicological approach. Dutch target values are based on background data for metals in relatively unpolluted areas. Further research is thus needed to adequately derive target values for soil based on food quality criteria and impacts on soil life.

1.2.1 Introduction

The Hungarian Soil Information and Monitoring System

The Soil Information and Monitoring System was developed in Hungary for the sake of sustainable land use and rational soil management. 1236 representative sampling sites were selected by regional experts: 865 points on agricultural land, 183 points in forests and 189 points in environmental ‘hot spot’ regions. These sites are characterised in great detail. Not only the basic soil properties (pH, $CaCO_3$ content/acidity, humus content, CEC, exchangeable cations) and nutrient status (N forms, available plant nutrients) but also potentially toxic elements (total content, mobile content), soil physical characteristics (particle size distribution, pF curve, hydraulic conductivity) and biological activity (cellulose test, dehydrogenase activity, CO_2 production) are determined. So the chemical, physical, biological status and pollutant- and nutrient content of the soils are characterised at the same time. Some soil parameters are measured every year, some others every 3 years or every 6 years - depending on their stability as a function of time. The first sampling was in 1992. The basic database of the Soil Information and Monitoring System (with the data of the first sampling in 1992) was used for an Environmental Risk Assessment of heavy metal content in soils of Hungary as described below. More details are given in Murányi (2000).

Heavy Metal Contents in Soils of Hungary

The soil database of the Soil Information and Monitoring System can be analysed and interpreted in many ways. For instance the average heavy metal content of Hungarian soils are shown in Table 1. The data were sorted according to the soil texture and soil type.

Table 1 Average heavy metal content of soils in Hungary (mg.kg^{-1})

	As	Cd	Co	Cr	Cu	Hg	Mo	Pb	Zn
Soil types									
Skeletal soils	4	0.3	5	8	13	0.02	0.7	11	27
Lithosols	8	0.7	8	19	17	0.06	1.3	24	49
Brown forest soils	6	0.4	9	19	17	0.04	0.7	17	43
Chernozem soils	6	0.5	10	21	21	0.03	1.5	16	51
Salt-affected soils	5	0.4	11	20	20	0.04	1.9	26	54
Meadow soils	7	0.5	10	23	24	0.05	1.7	23	62
Bog soils	6	0.5	5	15	19	0.05	1.3	15	32
Alluvial & sedimentary soils	5	0.5	9	21	25	0.05	1.1	23	69
average (n=1196)	6	0.5	9	18	20	0.05	1.1	21	51
Soil texture									
Sandy soils	3	0.3	3	6	10	0.02	0.6	9	19
Loamy soils	7	0.5	8	17	18	0.03	0.9	16	44
Clayey soils	6	0.6	12	26	26	0.05	1.6	26	71

The average heavy metal contents exhibit a close relationship with the soil texture. According to the genetic soil types, the average concentrations are the highest in the case of Zn (51 mg.kg^{-1}), while Cr, Cu and Pb are in the same range (18 - 21 mg.kg^{-1}). The heavy metal contents in Table 1 clearly demonstrate that on average, the soil cover of Hungary is not polluted. However, the average concentration of the studied 1196 samples hides the high concentrations of polluted soils. For instance the Cd content is higher than 1.0 mg.kg^{-1} in 39 soil samples (the maximum is 13.4 mg.kg^{-1}), the Pb concentration is higher than 42 mg.kg^{-1} in 100 soils (the maximum is 2372 mg.kg^{-1}) and the Zn content is higher than 102 mg.kg^{-1} in 67 samples (the maximum is 618 mg.kg^{-1}). That means that 3 %, 8 % and 6 % of the samples had twice as big Cd, Pb and Zn contents as the average, respectively. The minority of the soil samples measured for heavy metal content can be considered as representing polluted sites.

1.2.2 Approaches for Environmental Risk Assessment

The main reason for risk assessment is the protection of our environment. In essence, the procedure for the Environmental Risk Assessment of a substance consists of comparing the concentration in the environmental compartments with the concentration at which no effects on organisms or ecological systems are expected to occur. In principle, human beings as well as ecosystems (aquatic, terrestrial or air) are to be protected.

The Environmental Risk Assessment focuses the attention on the quantification of the risk by comparing the Predicted Environmental Concentration (PEC) with the Predicted No Effect Concentration (PNEC). The environmental risk can be characterised quantitatively by the Risk Quotient. The Risk Quotient equals to the PEC/PNEC ratio, what indicates whether a substance (inorganic or organic) presents a risk to organisms in the environment or not, as well as it helps to elaborate appropriate decisions for sustainable soil/water/air management. An alternative approach is to use the concept of the Polluting Concentration (PC) defined as:

$PC = PEC - PNEC$

The PEC can be derived from available monitoring data (unidentified pollution source), exposure assessment (using contaminant loads), model calculations, etc. The Predicted No Effect Concentration (PNEC) is determined on the basis of the biological effects, usually taking into account the results from monospecies laboratory tests (ecotoxicological tests, bioassays) or in a few cases established concentrations from model ecosystem tests. Adequate safety factors are also taken into account. The PNEC is regarded as a level below which the probability suggests that an unacceptable effect will not occur.

The Polluting Concentration characterises the excess or deficit of a pollutant over the PNEC, over or below the acceptable level. If the Polluting Concentration is positive, harmful effects can arise. The Polluting Concentration reflects the actual extent of pollution and determines the excess of the contaminant over the acceptable level. The concept of Polluting Concentration can be applied for soils, sediments, surface waters and groundwater. The Polluting Concentration can be used for monitoring the process of accumulation or remediation, for developing remediation plans, etc.

1.2.3 Risks of heavy metal pollution in Hungary

The quantification of the Environmental Risk Assessment for soils in Hungary can be demonstrated with the examples of heavy metals (Table 2). Predicted Environmental Concentrations can be evaluated by using the data of the Soil Information and Monitoring System. Average heavy metal contents of 1196 soil samples represent the total soil cover of Hungary while the maximum heavy metal contents characterise the most contaminated sites of the monitoring system.

Table 2 The Environmental Risk Assessment of heavy metal contents in soils

	Cd	Pb	Zn
Average heavy metal content (n=1196)			
PEC average	0.5	21	51
PNEC average	0.6	77	126
Risk Quotient	0.8	0.3	0.4
Maximum heavy metal content			
PEC maximum	13.4	2372	618
PNEC maximum	0.6	77	167
Risk Quotient	22	32	4
Polluting Concentration	12.8	2295	451

Target values can be used to characterise Predicted No Effect Concentrations. The reason for this is that target values are considered as the environmental quality levels and concentrations at which the risks of adverse effects (risks to ecosystems, functional properties of the environmental compartments, etc.) are negligible. The target values can be accepted as safe environmental concentrations of predicted no effect. The comprehensive Dutch concept was applied to calculate the target values for soils. In the Netherlands the background levels in soils of relatively uncontaminated areas were used as a basis to derive target values for contaminants in case of a so-called standard soil with 10 % organic matter content and 25 % clay content. This approach is unique because the organic matter and clay content can be taken into consideration when target values of non-standard soils are determined. As a consequence of this the target values of Hungarian soils were also calculated by taking into account their measured humus content and clay contents. The average or the site specific organic matter and clay contents were used in case of the average or the maximum heavy metal contents, respectively.

It can be seen in Table 2 that the Risk Quotients of the average soil are less than 1, so the soil cover of Hungary is not contaminated with Cd, Pb and Zn. However, the Risk Quotients are very high in case of the three contaminated soil samples. The Polluting Concentration of Cd, Pb and Zn at those three contaminated soils is 12.8 mg.kg^{-1}, 2298 mg.kg^{-1} and 451 mg.kg^{-1}, respectively (Table 2).

1.2.4 Evaluation

The present evaluation seems to indicate that metal pollution is not a large environmental problem in Hungary. One should, however be aware that the PNEC value used is not based on an ecotoxicological approach. Dutch target values are based on background data for metals in relatively unpolluted areas.

This was done because those concentrations appeared to be larger than maximum permissible concentrations (MPC) derived in the laboratory. The reason for this difference may, however partly be due to differences in metal availability. MPC values are based on laboratory experiments where a certain amount of metal is added to the soil (bioavailable contents), whereas the background values are based on a total analyses including immobile metals.

Actually, the risk of metals is mainly determined by the dissolved (bioavailable) fraction, which in turn is strongly influenced by soil properties, notably pH. Consequently, strong pH changes due to soil acidification(inadequate liming) may cause metal mobilisation, that may be followed by adverse impacts on crops and soil life. This so-called 'Chemical Time Bomb' effect has been defined by Stigliani as ‘an unforeseen chain of events resulting in the delayed and sudden occurrence of harmful effects due to the mobilisation or chemical transformation of chemicals stored in soils and sediments in response to saturation or alteration in certain environmental conditions’.

Further research is thus needed to adequately derive target values for soil based on food quality criteria and impacts on soil life. The INCO research projects aims to perform more detailed studies and a site specific Environmental Risk Assessment focusing on plant impacts (food quality).

Theme 2 Transfer functions relating different pools of heavy metals

2.1 Transfer functions between adsorption constants and soil characteristics: theory

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Summary
This internal note describes the theory of the sorption process of heavy metals in soil as a basis for the derivation of a transfer function. It is shown that from a thermodynamic point of view, combined with the principle of electroneutrality, we expect that metal sorption onto soils follows a Freundlich type of behaviour, where the Freundlich exponent is a measure of the heterogeneity of the available sites, and the Freundlich constant is a function of the average binding strength, the co-adsorbing anions, the competing cations and the number of sites available. The transfer function can be used to estimate the heavy metal sorption behaviour of any soil, with specified error of estimate, when the major macro-chemical characteristics of the soil are known. It thus allows the prediction of dissolved metal concentrations from total metal contents while accounting for the impact of macro-chemical soil characteristics.

2.1.1 Introduction

A large number of sorption experiments with heavy metals (Ni, Cu, Zn, Cd, Pb) and soils have been performed, and reported in literature. From these experiments a large number of models for the sorption onto soils and/or soil materials have been derived. However, many models do not include the major variables of the soil (pore water and solids), which together determine the sorption behaviour of the metals. Furthermore, many models published are only valid for, or calibrated against data of one or very few soils, thus making a broad applicability questionable.

The aim of this work is to develop relations that fulfil the following three requirements:

1. The relations are based on a *deterministic* model of the sorption process.
2. The relations can be calibrated on data that can be determined easily.
3. The relations can be used to *estimate* the heavy metal sorption behaviour of *any* soil, with specified error of estimate, when the major macro-chemical characteristics of the soil are known (% clay, % organic carbon, cation exchange capacity, pH and pCa) and without the need for specific measurements or extra determinations of soil parameters. This makes the relations especially suited to model regional behaviour of the metals.

The relations derived in this study can only be applied when the sorption reactions described by the relations are the activity and/or concentration determining process. This is usually valid under oxic conditions, however in reduced environments (sulphate reducing and/or methanogene), sulphide mineral solubility mostly determines the solubility of these elements, and therefore (ad/de)sorption based equations cannot be used.

2.1.2 Theory of the sorption process and derivation of the transfer Function

The model developed assumes chemical equilibrium between solid and liquid phase(s) in the soil. This means that the laws of thermodynamic equilibria can be applied. Kinetic studies show that the rate of adsorption of the metals onto soil materials is fast, with first-order half-times shorter than 10 minutes (e.g. Soldatini et al., 1976). Since the timescale we are interested in is >> 1 hour, this is a reasonable assumption.

Secondly the sorption model has to obey the law of electroneutrality: When a metal ion is sorbed from the water phase, either the same amount of negative charge has to be adsorbed also (equivalent to precipitation), or the same amount of positive charge has to be expelled from the adsorption phase (equivalent to cation exchange). The real sorption relation will probably be somewhere in between these extremes. This second requirement for the sorption model is essential, since otherwise charged phases will occur. Since phases can be separated by mechanical means (by definition see Weast (ed.) (1980, F-109), e.g. centrifugation, filtration, sedimentation), charged water and charged solids are produced when this law is not kept. This is *not* in accordance with reality. Therefore a relation like

$\text{S-OH} + \text{Me}^{2+} \Leftrightarrow \text{S-OMe}^{+} + \text{H}^{+}$

can only be considered as a **half-reaction**, which is **not** independent of the charge-compensating reaction (probably anion-adsorption or cation exchange with a macrochemical cation) which ***must*** occur simultaneously. Models based only on a half-reaction such as the one shown above, are therefore by definition only valid for the system on which they were calibrated (in terms of background electrolyte composition and ionic strength), since all information on the second half-reaction is lost. The effect is that necessarily electrostatic terms have to be introduced. These however are only valid if the only competing cations are the proton (H^{+}) or the 'background electrolyte' cation of the experiment, and all anions have the same (indifferent???) binding strength.

The equilibrium reaction equation which is proposed in this study for the sorption of metal ion Me with charge 2+ is therefore:

$$\text{Surf-Ex} + \text{Me}^{2+} + \text{n L}^{a-} <=> \text{Surf-Me-L}_{n} + (2-n*a)/b\ \text{Ex}^{b+} \qquad (1)$$

where
Ex = any (combination of) cation(s) exchanged with average charge b+ (**including** H^+ !!)
L = co-adsorbing ligand with charge a-
n = stoichiometric constant of ligand L in the adsorption reaction

Assuming that the stoichiometry of the sorption reaction is constant (*assumption 1*), we can define (2-n*a)/b = q, and applying the law of mass action to this equation gives relation (2):

$$K_{eq} = (Ex)^q * \{Surf\text{-}Me\text{-}L_n\} \;/\; [(Me) * (L)^n * \{Surf\text{-}Ex\}] \tag{2}$$

where round brackets indicate *activities* in the water phase, and accolades indicate *activities* in the sorption phase. Ideally, these activities are *equal to molefractions in the respective phases*. Since real-world systems are (in this case at least) not ideal, we have to apply an activity correction to the molefractions. In the case of the activity in the water phase this is accomplished by introducing an activity correction such as the Davies equation:

$$\log \gamma_i = -a_0 \cdot Z_i^{\,2} \cdot (\sqrt{I} / [1 + \sqrt{I}] - 0.3 \cdot I) \qquad \text{(Stumm\&Morgan, 1982)}$$

When the surface sites are heterogeneous, as is true for soils, the adsorption intensity will change with the amount Me adsorbed. We can correct for this deviation from ideality by introducing an activity correction for the sorbed species. When we define for the surface phase:

SX = molefraction X adsorbed and
F_{SX} = some activity coefficient for the surface complex of X

Then equation (2) becomes:

$$K_{eq} = \gamma_{Ex}^{\,q} \cdot C_{Ex}^{\,q} \cdot F_{SMe} \cdot SMe / [\gamma_{Me} \cdot C_{Me} \cdot \gamma_L^{\,n} \cdot C_L^{\,n} \cdot F_{SEx} \cdot SEx] \tag{3}$$

where C denotes the concentration in the water phase.
When it is assumed that the activity correction for the sorbed species can be approximated with a power function of the molefraction of the adsorbed species (Langmuir, 1981), which describes the decrease of the Gibbs Free Energy (GFE) of binding of a metal when the amount of metal sorbed is increasing,

$F_{SMe} = SMe^{\alpha}$ ($\alpha = 0$ means a homogeneous surface) and
$F_{SEx} = SEx^{\beta}$

then the equation becomes

$$K_{eq} = \gamma_{Ex}^{\,q} \cdot C_{Ex}^{\,q} \cdot SMe^{(1+\alpha)} / [\gamma_{Me} \cdot C_{Me} \cdot \gamma_L^{\,n} \cdot C_L^{\,n} \cdot SEx^{(1+\beta)}] \tag{4}$$

The power α is a measure of the width of the distribution of GFE of binding (large α means a broad distribution, small α a narrow distribution of sorption energies).
Considering the fact that the metal is a micro-chemical, and a change of the amount of metal sorbed will not influence the value of the molefraction of sorbed Ex, the value of $SEx^{(1+\beta)}$ can be set to unity.
Introducing the notation: $aX = \gamma_X * C_X$ and linearising equation (4) by taking the logarithm of both sides, and rearranging gives:

$$\log(SMe) = (1+a)^{-1} \cdot [\log(K_{eq}) + \log(aMe) + n \cdot \log(aL) - z \cdot \log(aEx)] \qquad (5)$$

We can change from molefraction to amount sorbed by introducing the total number of sites, Ns ($mol.kg^{-1}$ soil). When we define

$$SMe = M_{Me} / Ns$$

and define $(1+\alpha)^{-1} = n_f$,
then the equation can be written as:

$$\log(M_{Me}) = \log(Ns) + n_f \cdot [\log(K_{eq}) + n \cdot \log(aL) - z \cdot \log(aEx)] + n_f \cdot \log(aMe) \qquad (6)$$

Here
M_{Me} = the metal concentration in the adsorbent (the solids) in $mol.kg^{-1}$
Ns = the number of adsorption sites in $mol.kg^{-1}$
K_{eq} = $\exp(-\Delta G^0/RT)$
aEx = the activity of competing cations in $mol.l^{-1}$
aL = the activity of the co-adsorbing anions in $mol.l^{-1}$
aMe = the activity of the adsorbing metal ion in $mol.l^{-1}$
n,z = stoichiometric constants

This relation is a Freundlich equation, with Freundlich exponent $n_{f,}$ dependent on the activity of the metal in solution, and with the Freundlich constant which is the combination of all other terms in this equation:

$$\log(M_{Me}) = \log(K_F) + n_f \cdot \log(aMe)$$

The assumptions underlying this model are:
1) *constant stoichiometry* of the sorption reaction,
2) the introduction of the *power function* to describe the surface heterogeneity,
3) *neglecting* the effect of adsorption of Me on the molefraction of the sorbed macroelements.

We can conclude at this point that from thermodynamic equilibrium, combined with the principle of electroneutrality, and the power function, we expect the sorption of the metal onto soils to follow Freundlich type of behaviour, where the Freundlich exponent is a measure of the heterogeneity of the available sites, and the Freundlich constant a function of the Freundlich exponent n_f and the average binding strength, the co-adsorbing anions, the competing cations and the number of sites available. It further shows that all relations in this system have to be taken as log-log rather than linear (or curvi-linear as the Langmuir isotherm assumes).

Equation (6) can be re-arranged to give a general form:

$$\log(M_{Me}) = C_0 + \log(Ns) + C_2 \cdot \log(aEx) + C_3 \cdot \log(aL) + C_4 \cdot \log(aMe) \tag{7}$$

Here $C_0 - C_4$ are constants, which can be fitted against measured sorption data. When we assume that

$$\log(Ns) = C_{11} \cdot \log S_1 + C_{12} \cdot \log S_2 \cdots + C_{1m} \cdot \log S_m \tag{8}$$

Where S_1 .. S_m are the individually distinguishable potential sorption sites, and

$$\log(aEx) = (1/C_2) \cdot (C_{12} \cdot \log(CA_1) + C_{22} \cdot \log(CA_2) \cdots + C_{2m} \cdot \log(CA_m)) \tag{9}$$

Where CA_1 .. CA_m are the individually distinguishable potentially competing cations, then equation (7) can be fitted to sorption data and should give good relations for different metals.

2.2 Risks of metal contamination in view of soil properties

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Key words: heavy metals, ecotoxicological risks, free metal ion activity, transfer functions

2.2.1 Introduction

Elevated total contents of heavy metals (Cd, Cu, Zn, Pb) can be found in soils as a result of anthropogenic inputs. This does however, not provide good information on ecotoxicological risks since effects are in general poorly correlated with total metal contents in soil. Critical contents for metals in soils as set in various countries in general lack an ecotoxicological basis (De Vries and Bakker, 1998). Interpretation of laboratory tests for ecotoxicity are hampered because of differences in (bio) availability of the metal under laboratory and field conditions. The free ion concentration or activity in soil solution gives in many cases much better relationships with effects than total metal contents in the soil solid phase. The free metal ion activity or concentration not only depends upon the degree of metal contamination of the soil but also on soil properties. Soil properties such as organic matter content, CEC, pH and the concentration of Ca in soil solution influence metal mobility and bio-availability.

2.2.2 Materials and methods

From different sites in the Netherlands, which differ in degree of contamination, soils were sampled for soil and soil solution measurements. Soils were analysed for total contents and ‘reactive contents’ of metals in soil and organic matter content. In soil solution, concentrations of the metals and major cat- and anions including DOC were measured. According to the method described in an accompanying paper (Bril and Groenenberg, 1999) activities in soil solution were calculated from ‘reactive’ metal contents and soil properties with the use of transfer functions (Bril, 1995). Activities were also calculated from soil solution concentrations using a simple chemical speciation model that accounts for metal complexation with DOC. From available ecotox data critical limits in soil solution were derived using data for aquatic organisms and by reinterpretation of ecotox experiments for soils for which concentrations in soil solution were estimated from total contents using the transfer functions mentioned above.

2.2.3 Results and discussion

Table 1 shows ‘total’ metal contents as extracted with aqua regia. The two forested sites have the lowest contents of heavy metals. The plots of agricultural land show somewhat higher contents and the plots of the former wastewater infiltration fields Zandleij are clearly the most contaminated plots. Table 3 also shows that higher metal contents not necessarily result in (proportional) higher concentrations in soil solution due to differences in soil properties It is thus not possible to assess the ecotoxicological risk from total contents only.

Table 1 Total metal contents, soil properties and metal concentrations in soil solution

Plot	Pb mg.kg^{-1}	Cd	Cu	Zn	OM (%)	pH -	Ca mg.l^{-1}	DOC mg.l^{-1}	Pb µg.l^{-1}	Cd	Cu	Zn
young forest	12	0.19	12.5	13.1	7.7	5.5	41	111	4.3	0.43	34	383
old forest	20	0.20	0.9	5.8	9.6	3.4	25	121	12.8	2.4	322	690
agric. land 1	11	0.24	14.7	31.1	2.9	6.8	37	363	8.6	4.0	370	350
agric. land 2	20	0.27	20.3	29.4	3.6	4.9	9.2	59	2.9	0.6	154	266
Zandleij 1	169	2.86	101	529	16	5.5	66	75	46	27	367	2416
Zandleij 2	180	3.01	115	610	12	5.7	70	57	41	14	201	1720

Free ionic concentrations were calculated from both ‘reactive’ metal contents and soil solution data according to Bril and Groenenberg (1999) and gave comparable results. Calculated free ionic concentrations and measured concentrations were compared with critical limits for the soil solution. Figure 1 shows a concentration gradient for free metal ion concentrations of Zn in a wastewater infiltration field (Zandleij). These concentrations were compared with a critical limit for Zn based on free metal ion concentrations for Zn (Environment Canada, 1998) (critical limit 1) and a critical limit based on data for aquatic organisms (critical limit 2). Critical limits however include uncertainty due to assumptions on the transferability of ecotox data for aquatic organisms to soil organisms and uncertainty in the calculated free ionic activity that may be relatively large for low contents.

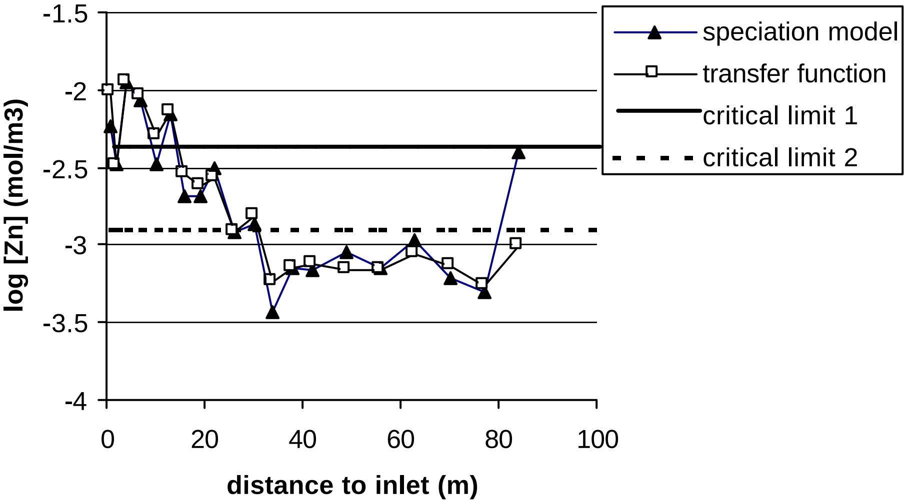

Figure 1 Comparison free metal ion concentrations Zn with critical limits.

2.2.4 Conclusions

The method to calculate free metal concentrations in soil solution from measured contents in the solid phase is a practical method to be used for risk assessment. Labour intensive measurements to determine soil solution concentrations of the metals of interest together with the measurement of the macro chemical composition of the soil solution can be left out. Furthermore the use of transfer functions in combination with critical limits for the soil solution can give insight in changes in ecotoxicological risks due to changes in soil properties which is of interest in the case of land use changes (i.e. acidification due to afforestation) or in case of active soil protection when measures are to be taken to decrease harmful effects, such as liming of acidified soils.

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2.3 Soils and sediments testing for contamination by heavy metals - new concepts and approaches

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Summary

The determination of various chemical forms of metals in soils and sediments is important in evaluating their mobility and bioavailability. It improves the assessment of risk associated with heavy metals in soils. Especially the determination of an ‘available’ fraction of metals, based on a single or sequential extraction and soil (pore) solution analyses is now gaining widespread acceptance, as a means to characterise hazards from contaminated soil. The main objective of this contribution is to summarise current testing methodologies, namely *single extraction* with a mild extractant, *sequential extraction* with multi-solution extraction and *soil solution extraction*, illustrated with analytical results obtained from some case studies in Slovakia. It examines new concepts and procedures used for assessing the hazard from metal contamination, including some limitations (analytical, soil) weakening the relationship between the content of metals in soil and actual environmental and human health hazards.

Key words: soil/sediment testing, metal speciation, single extraction, sequential extraction, soil solution, plant available metal fraction, soil contamination

2.3.1 Introduction

The accumulation of heavy metals and metalloids in soils and sediments possess many risks to human and ecosystem health. Risks may be expressed either through the food chain or through the groundwater contamination. The evaluation of soils, stream and sediments contamination is aimed at improving the assessment of environmental and human health hazards associated with the content of potentially toxic elements in plants and water. Risks due to soils and sediments pollution by metals are well recognised and major texts have been published by several authors (Alloway, 1990; Kabata - Pendias and Pendias, 1992; Salomons et al., 1995).

Many researches have tried to develop relation between concentration of potentially toxic elements in soil/plants system and effect on organisms (plants and humans) based on total element content or extractable forms of elements (Fergusson, 1990). This effect-based approach aimed at elaboration of critical limits based on adverse effect on ecosystems. The implicit assumption is that (ecotoxicological) effects are due to the metal accumulation. However, in most cases, toxic effects are mainly due to elevated bioavailable (mobile) concentration (de Vries and Bakker, 1998).

A big amount of work has been done in attempting to quantify metals held in different soil/sediment fractions, particularly those thought to be mobile and bioavailable, since these fraction can potentially adversely effect on the ecosystem. The most widely used approach is to choose a chemical extractant (single extraction) or series of extractants (sequential extraction) to remove particular chemical phases (species) of metals from soil and sediments (Tessier et al., 1979; Shuman and Hargrove, 1985; Keefer et al.1984; Miller et al., 1985).

However, in most cases, toxic effect on micro-organisms and soil fauna are mostly due to elevated bioavailable concentration in soil solution (Van Straalen and Bergema,1995). But physico - chemical properties of solids control activities and concentrations of metals in the solution, therefore, directly effect their availability to plants. In spite of the fact that modern instrumental technique has made possible to analyse of most elements in small concentration in soil solution, there are still many limitations that hampers wider use of the results of soil solution analysis. Those are theoretical, analytical and methodological (Gregor et al., 1997, 1999; de Vries and Bakker, 1998).

The aim of this paper is to illustrate on concrete results, obtained from contaminated soils studies in Slovakia, mostly within INCO-COPERNICUS project ‘Long term risk of inadequate management practices on the sustainability of agricultural soils’ (co-ordinated by W. de Vries) the possibility of using soil (and sediments) testing and summarise soil testing methodologies and concepts. The evaluation of different tests and results, towards the hazards involved, is out of the scope of this paper. However, some theoretical and methodological problems are also tackled, to point to some new trends and concepts which might be useful to apply in geochemical and environmental studies of soils, sediments and sewage sludges.

2.3.2 Methodology

Sampling and analyses

For this study the analytical results (single extraction and soil solution) of twenty contaminated soils were chosen. Their soil characteristics are presented in Table 1. Sequential analyses were performed on another set of contaminated soil samples from river Hron basin. The basic characteristics of these soils are presented in Table 4.

Table 1 Selected soil characteristics

Sample	Site	Soil unit FAO (1970)	pH/CaCl$_2$ (1 : 5)	Carbonates (%)	Humus (%)	Clay (%)	CEC (cmol.kg^{-1})
ICSK-1	Slovenská Lupca	Fluvisol	6.63	0.4	5.46	14.22	20.45
ICSK-2	Gemerská Poloma	Gleyic Fluvisol	6.92	1.6	4.17	3.84	17.39
ICSK-3	Družstevná pri Hornáde	Fluvisol	6.74	0.3	3.08	17.89	20.20
ICSK-4	Velká Lodina	Fluvisol	7.14	6.4	2.99	4.61	14.49
ICSK-5	Kluknava	Cambisol	5.51	0	3.33	13.01	15.40
ICSK-6	Markušovce	Fluvisol	6.35	0.12	4.08	7.54	16.45
ICSK-7	Gelnica	Fluvisol	5.70	0	7.08	2.74	14.05
ICSK-8	Fiacice - Lubela	Fluvisol	6.87	0.5	3.99	7.78	17.40
ICSK-9	Kozárovce	Fluvisol	7.05	7.3	3.17	14.64	20.29
ICSK-10	Starý Tekov	Fluvisol	5.82	0	3.12	21.89	22.90
ICSK-11	Hontianske Tesáre	Fluvisol	5.54	0	1.65	17.51	15.85
ICSK-12	Domaníky	Fluvisol	6.13	0	2.17	11.35	17.95
ICSK-13	Ilija	Pseudogley	5.46	0	6.67	17.50	35.65
ICSK-14	Stará Kremnicka	Fluvisol	6.70	0.52	2.17	9.69	13.75
ICSK-15	Bzenica	Fluvisol	6.03	0	5.99	11.34	20.50
ICSK-16	Tekovská Breznica	Fluvisol	7.00	4.2	2.32	7.17	14.49
ICSK-17	Kalná nad Hronom	Fluvisol	6.66	0.1	3.74	19.37	25.35
ICSK-18	Pezinok	Phaeozem	6.75	0.4	5.67	12.32	23.90
ICSK-19	Limbach	Cambisol	7.08	4.5	6.17	6.07	14.49
ICSK-20	Slovenský Grob	Fluvisol	7.06	0.3	4.64	17.47	20.80

Sampling. Sampling was done by an auger that enabled us take samples at fixed depths of the plough layer. The spatial variability of soil required that at one point 25 subsamples were taken to prepare composite sample from a plot area of 25 x 25 m.

Soil properties analyses. Fraction < 2 mm was arbitrary used for soil properties analyses by routine methods. Soil reaction was measured potentiometrically in suspensions. For determination of potential soil reaction 1M KCl solution and 20 g sample was used, for determination active soil reaction redistilled water and 20 g of soil was used. Carbonates were determined in the lime - meter by Janko, in 10 % solution HCl and from 20 g of soil sample. The classical pipette method for soil texture was used (fraction < 2 mm, after the sample dispergation by sodium hexametaphosphate).

Chemical analyses. Soil extraction methods were used followed handbook Houba et al.1996 and hence, only principals are mentioned here:

Soil extraction with 0,01 M CaCl$_2$. Soil samples dried at 40°C is were extracted at 20°C with 0.01 M CaCl$_2$. The suspension was stirred for 2 h and centrifuged. Supernatant was taken for analysis.

Soil extraction with aqua regia. Soil samples were dried at 40°C and extracted with aqua regia at room temperature for 16 h, followed by boiling under the reflux for 2 h. Extract was than filtered. The extracted solution was fulfilled to the standard volume by the adding of nitric acid.

Soil extraction with 0,05 M EDTA. Soil samples were dried at 40°C and extracted with 0,05 M EDTA solution by the stirring the suspension for 1 h at room temperature (20°C).Extract is filtrated into polyethylene bottle.

Soil extraction with 0,05 M ammonium oxalate and oxalate acid mixture. Soil samples dried at 40°C were extracted with ammonium acetate and acetic acid mixture (pH =3,0 ± 0,1). The suspension was stirred for 2 h in a dark room at 20 ± 1 °C. Extract was filtered into polyethylene bottle.

Methods for soil solution analysis. 25 g air dried sample extracted with 50 ml 0,002 M $CaCl_2$.

Sequential extraction scheme used in this work is based on Community Bureau of Reference method (1987) tested in 18 EU laboratories (Mackových et al., 1999). The following metal fractions are distinguished:

- exchangeable and carbonate fraction (0,11M acetic acid),
- reducible fraction (Fe and Mn oxides bound) fraction (0,1M hydroxylamine hydrochloric),
- organically (sulphidic) bound fraction (8,8 M peroxide + 1M ammonium acetate),
- residual fraction (total decomposition with inorganic acids mixture -HNO_3, HF, $HClO_4$).

Metal speciation and metal fractions in soils/sediments

Metals, both naturally occurring and inputted to soils and sediments are present in an extremely large range of forms. They may be distributed among many components of soils or sediments and may be associated with them in many different ways. The nature of this association is often referred to as *speciation.* Soil scientists, geochemists and biologists have attempted to extract and quantify these fractions to be held in the different soil/sediment fractions, particularly these which thought to be mobile (chemical *species* or *forms*), since they can potentially pollute the groundwater or can pass through food chain from plant uptake. In soils and sediments this generally means to identify metals held in any of following fractions:

- soluble
- extractable (adsorbed)
- organically bound
- Mn oxides occluded
- amorphous and crystalline Fe oxides occluded
- bound in carbonates
- residual (total)

The potential availability (mobility) of the elements in the different fractions of soil/sediments is illustrated in the Fig. 1.

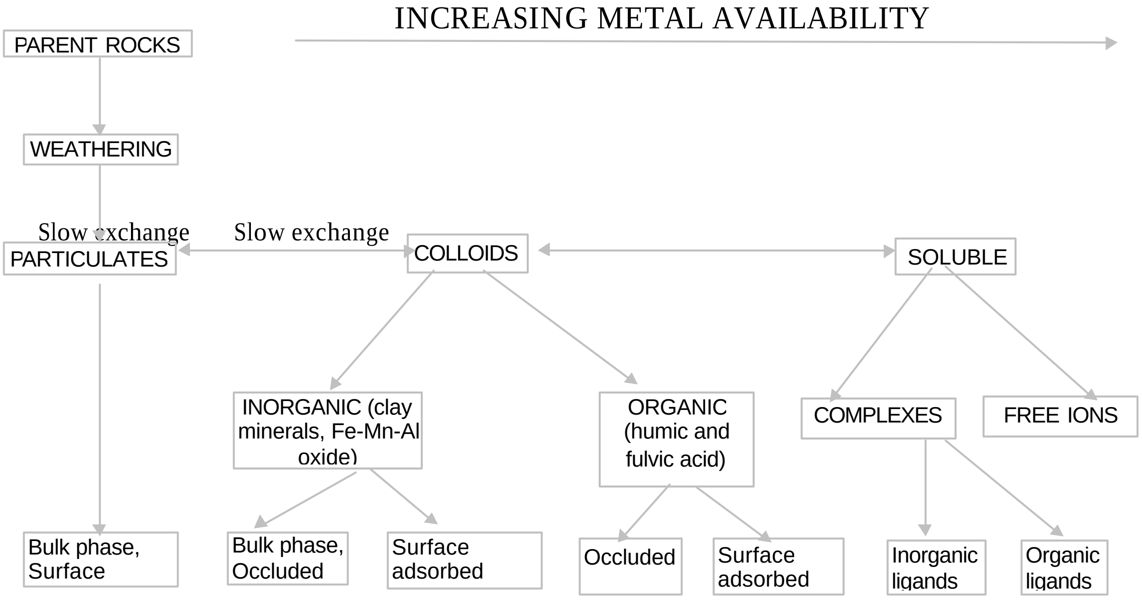

Figure 1 The potential availability of the elements in the different fractions of soil/sediments.

A big effort has been expended in attempting to quantify metals held in different fractions, particularly those fractions thought to be mobile and bioavailable. The most common and single physical separation technique is to filter solution through micropore membranes of pore size 0,45μm, thus rather crudely differentiating between ‘soluble’ and ‘particulate’ metals.

The principals and concepts behind soil testing have been reviewed by McLaughlin et al. (2000). Principally two main groups of procedures are used at present:
- single chemical extraction,
- sequential chemical extraction.

2.3.3 Plant available concentrations of metals in soils by single extraction methods

For many years chemical extractants have been tested by soil scientists and geochemists, for estimation of ‘plant available’ (‘mobile’) fractions of metals. Development of such tests were mainly in response to the needs to monitor metal uptake by plants in contaminated soils, in bottom sediments, soils loaded with sewage sludges and pesticides. Single extractions are generally used to extract the following fractions of potentially toxic metals (Berrow and Buridge, 1980):
- metals in soil solution (ionic, molecular, chelated and colloidal forms),
- exchangeable forms (readily exchangeable),
- in adsorption complexes (firmly bound),
- reducible- easily bound in sesquioxides (coprecipitated) and in hardly soluble salts,
- fixed in crystal lattices of secondary minerals (predominantly clay minerals).

In order to extract metals from the soil/sediments, the basic dissolution, chelation, desorption/ion exchange and oxidation/reduction processes are used prior to elemental determination.

Metals present in the solid phase as discrete phases (sulphides, carbonates, phosphates, oxides, or coprecipitated with sesquioxides) can be released by *dissolution processes.* Usually less soluble compounds requires more vigorous extractant (usually inorganic acids). The mechanism of *complexation* is that metal is paired with a ligand supplied by a metal ligand salt, allowing metal desorption and helping to retain the metal ion in solution in complexed form (McLaughlin et al., 2000). The weak chelating agents (EDTA, DTPA,TEA) are used most often. It seems reasonable that at least more widespread use of DTPA reagent for testing 'availability ' of Ni, Zn, Cu and Cd in contaminated soils is based on internationally standardised method.

The *desorption/ion exchange processes* for extraction metals from soil/sediments has not been used until recently, due to the very low analyte concentration resulting from the extraction based on these processes. With the improving of analytical instrumentation the detection limits have considerably fallen which allowed to detect very low concentration in the extracted solution. Mostly neutral salt solutions are used ($NaNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, NH_4NO_3, $MgCl_2$, $CaCl_2$). Generally concentration of metals extracted by Cl salts are higher, than those extracted by corresponding nitrate salts.

Metal sulphides and metals bind to organic materials can be released by *oxidation processes* (with peroxide or acid solution of HNO_3 HCl, $HClO_4$, HF or aqua regia). For heavy metals bind to (co-precipitated with) secondary sesquioxides (Fe, Mn, Al), *reducing agents* are used such as acidified hydroxilamine hydrochloride ($NH_2OH.HCl$), acidified ammonium oxalate and dithionite/citrate solution (see also sequential extraction schemes).

The heavy metal concentrations in Slovakian contaminated soils obtained by different (single) extraction methods are presented in Table 2. From presented results is clear that concentration of metals in different extractants is mainly a function of metal ability to be bound in different soil compounds. Higher concentration of several studied elements (As, Cu, Cr, Hg and Zn) in the ammonium acetate (+oxalate acid) fraction is due to selective binding of these elements to secondary Fe oxides. Especially high concentration of As present in this fraction, as compare to the total content, points to the high selectivity of As to Fe oxides. Oxido-reduction processes predominantly in alluvial soils may partly deliberate As which can be than transported to the groundwater. Similar tendencies are evident for zinc (Table 2).

$CaCl_2$ extraction has been suggested as the best predictor of phytoavailable metals in soils (Houba et al., 1996). A good correlation has been found only with the limited soil types. Soil tested in our experiments is hardly to evaluate, as different soil types has been used, and no correlation between soil and plants has been tested. Anyhow, in some cases high available concentration of Cd has been detected in soils (ICSK-11, 12).

Table 2 The heavy metal concentrations (mg.kg^{-1}*) in contaminated soils obtained by different (single) extraction methods: i - the total (pseudototal) content obtained by aqua regia extraction, ii - the mobile fraction concentration obtained by 0.05 M EDTA, iii - the mobile fraction concentration obtained by ammonium oxalate and oxalate acid, iv - the 'mobile' (available) fraction concentration obtained by 0.01 M* $CaCl_2$.

Sample	Extraction method	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
ICSK-1	i	20.95	0.5	30	57	0.080	26	62	123
	ii	0.35	0.3	< 0.1	23	< 0.005	2	25	9
	iii	5.85	0.1	1.6	32	< 0.005	4	4	18
	iv	0.05	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-2	i	54.80	0.2	35	135	0.050	44	24	123
	ii	0.10	0.2	< 0.1	40	0.019	7	8	9
	iii	19.30	0.2	1.6	56	< 0.005	9	2	18
	iv	< 0.01	< 0.05	< 0.1	< 0.5	0.005	< 0.5	< 0.5	< 0.3
ICSK-3	i	18.80	0.4	33	113	0.110	36	33	110
	ii	0.40	0.2	< 0.1	44	< 0.005	5	11	10
	iii	10.00	0.1	1.4	74	< 0.005	7	3	25
	iv	0.03	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-4	i	46.80	0.4	29	228	0.100	46	50	137
	ii	1.50	0.2	< 0.1	137	0.030	3	20	15
	iii	29.30	0.1	1.0	192	< 0.005	5	3	37
	iv	0.03	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-5	i	36.80	0.6	38	70	0.200	40	43	177
	ii	1.80	0.3	< 0.1	29	0.009	3	18	30
	iii	19.20	0.2	1.0	39	< 0.005	3	3	45
	iv	0.09	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	0.6
ICSK-6	i	20.10	0.3	28	76	0.940	26	17	70
	ii	0.50	0.2	< 0.1	35	0.061	3	7	7
	iii	9.50	0.1	1.2	49	< 0.005	4	1	14
	iv	0.02	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-7	i	87.50	0.7	17	589	0.180	25	170	243
	ii	0.60	0.3	< 0.1	260	0.048	2	58	30
	iii	50.50	0.2	1.3	372	< 0.005	3	29	61
	iv	0.05	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	0.6
ICSK-8	i	12.50	0.3	28	21	0.080	27	16	67
	ii	0.20	0.2	< 0.1	11	0.009	5	6	6
	iii	6.40	< 0.1	1.8	12	< 0.005	6	< 1	12
	iv	< 0.01	< 0.05	< 0.1	< 0.5	< 0.005	4.6	< 0.5	< 0.3
ICSK-9	i	39.20	0.7	25	117	0.120	17	62	158
	ii	1.00	0.5	< 0.1	59	0.024	3	22	35
	iii	23.70	0.1	0.8	71	< 0.005	3	3	46
	iv	0.03	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-10	i	42.70	0.6	29	130	0.140	19	72	119
	ii	0.50	0.4	< 0.1	60	0.038	3	25	12
	iii	21.50	0.1	1.3	76	< 0.005	2	9	19
	iv	0.05	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-11	i	17.50	13.7	23	201	0.030	14	1303	1704
	ii	0.10	8.4	< 0.1	81	0.019	< 1	467	400
	iii	9.20	2.2	0.4	135	< 0.005	< 2	243	595

Table 2 continued

Sample	Extraction method	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	iv	< 0.01	1.16	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	52.3
ICSK-12	i	16.90	20.5	19	236	0.030	11.0	1301	2445
	ii	0.10	16.8	< 0.1	140	< 0.005	< 1	585	853
	iii	9.70	3.7	0.4	178	< 0.005	< 2	373	994
	iv	< 0.01	1.59	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	165.6
ICSK-14	i	102.50	0.2	15	42	0.560	6	68	76
	ii	1.10	0.1	< 0.1	14	0.088	< 1	17	9
	iii	53.70	0.1	1.5	19	< 0.005	< 2	12	19
	iv	0.04	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-15	i	62.00	2.0	15	90	0.060	12	322	427
	ii	1.10	1.3	< 0.1	43	0.054	2	147	94
	iii	28.30	0.2	0.8	52	< 0.005	3	29	128
	iv	0.05	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-16	i	39.20	1.9	22	107	0.090	10	134	339
	ii	1.40	1.2	< 0.1	44	0.046	1	69	65
	iii	22.50	0.2	3.5	63	< 0.005	3	11	117
	iv	0.11	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-17	i	48.50	1.2	27	193	0.140	19	122	215
	ii	0.60	0.9	< 0.1	105	0.076	4	56	40
	iii	31.40	0.1	1.7	131	< 0.005	4	15	51
	iv	0.03	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-18	i	68.90	0.9	66	49	0.010	77	28	173
	ii	3.00	0.6	0.2	21	0.001	21	10	14
	iii	49.10	0.2	3.1	24	< 0.005	22	3	21
	iv	0.05	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-19	i	4.70	0.3	9	138	0.010	7	33	81
	ii	0.30	0.1	0.2	103	< 0.005	1	12	13
	iii	1.50	< 0.1	0.7	94	< 0.005	< 2	1	16
	iv	0.01	< 0.05	< 0.1	< 0.5	< 0.005	< 0.5	< 0.5	< 0.3
ICSK-20	i	61.80	0.3	51	26	0.020	30	21	80
	ii	0.50	0.1	< 0.1	6	< 0.005	4	4	2
	iii	39.70	< 0.1	1.1	11	< 0.005	5	2	9
	iv	0.07	< 0.05	< 0.1	< 0.5	< 0.005	0.7	< 0.5	< 0.3

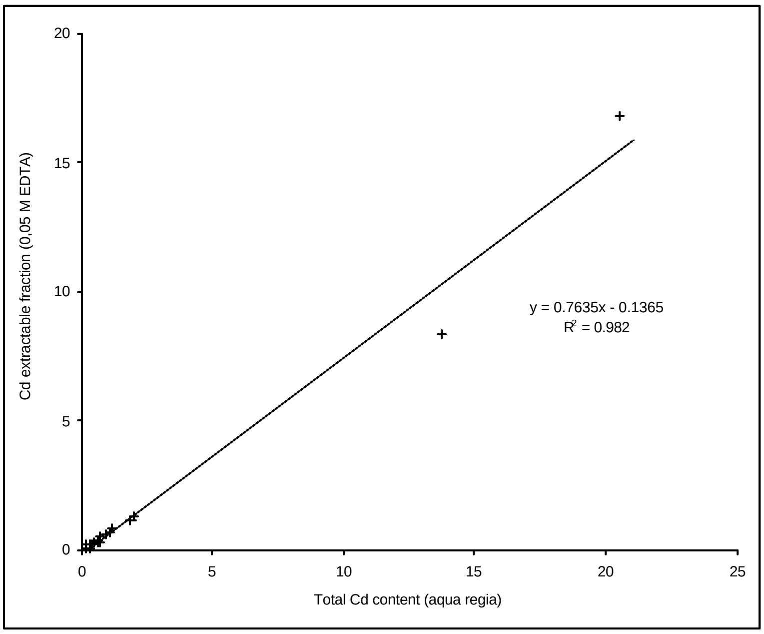

Figure 2 Relationships between total and EDTA Cd contents in soils (mg.kg-1) (n=20)

Many authors have reported good correlation between extractable metal content and metals uptake by plants. However, the comparison among the positive and negative results of the tests revealed in some cases insignificant correlation between extracted metals and metal content in tested plants. Some extractants are useful to extract metals and predict metal availability in neutral and calcareous soils (DTPA) but not in acid soils. Davies (1992) found a good correlation between plant uptake and amount of potentially toxic metals in contaminated soil with strong extractant such as EDTA.

An overview of different results (positive or negative) brought by Ross (1994) has shown that it is extremely difficult to summarise these finding since so many test solutions, different bioassay test plants, different soils and different extraction techniques were used. Our results point that the prediction of plant metal content based on single extraction is very questionable. Single extractants can not give also useful information on metal speciation in soil/sediment.

2.3.4 Metal fractionations based on selective sequential extraction procedures

Metal fractionations using sequential extraction techniques have been used to extract heavy metals from contaminated river sediments (Tessier et al., 1979) and metals applied in waste sludges. Such extraction usually starting with the weakest, least aggressive and ending with strongest and most aggressive extractant. Sequential extractants are generally used to characterise five or six of above stated fractions (see part: Metal speciation). The weakest extractants in the system are most specific, the later, stronger extractants, the least specific, but because they come late in a sequence, they may remain only one or two groups of compounds that they can dissolve (Becket, 1989; Ross, 1994). A very large number of sequential extraction schemes have been used. The principal schemes of sequential chemical extractions are presented in Table 3.

It is clear from the table, that there are some differences of opinions concerning appropriate use of extractants. Only there is some agreement about the *kinds* of extractants needed for each fraction. For example soluble and easily exchangeable fraction are commonly extracted using dilute salt solutions of replacing cations, organically bound are released using oxidising agents. Reducing agents are used to release metals bound in Fe and Mn oxides. Strong acids are used to assess residual or occluded metals in soils.

Till now a range of problems and limitations has been associated with sequential extraction. The major problem is that extractants are not so selective as it is stated. Another problem is connecting with a large number of different extracting techniques which make difficult to compare results from different studies. Apart of this Salomons and Forstner (1984) pointed to three another serious problems that must be considered when using selective sequential extraction procedures:

- labile metal phases could be transformed during sample preparation,

- re-adsorption or precipitation processes could occur during extraction,
- time of duration of the extraction and soil/solution ratios play important roles as far as quantity of extracted metals.

Metal fractionation using sequential extraction techniques (Community Bureau of Reference, 1987) has been used in our study to identify the metals fate in contaminated alluvial soils of Hron river basins. The results are presented in Table 4, especially reporting on the possibility to predict the groundwater contamination through the soils (Curlík et al., 2000). In cited work soil characteristics are described in more details. Based on this study, here only simple postulates are made.

Soil organic matter and secondary Fe and Mn oxides are mainly responsible for soil metal retention. These soil components are unevenly distributed down the soil profiles depending on soil processes. But metal affinities to the different soil fraction may play an important role for the proportion of metals held in so called ‘mobile’ forms.

As it is stated above *arsenic* is mostly present as residual fraction. Second place belong to the fraction held in Fe and Mn oxides. Hence, the distribution of As in the soil profiles partly correspond to secondary oxides formation (cumulative) within the depth. *Cadmium* shows marked tendency to be concentrated in the most mobile (exchangeable) fraction and partly in reducible fraction (in Fe, Mn-oxides). *Cromium* is mostly present in residual fraction which points to low mobility of his element in the soil (mostly Cr^{3+}). *Copper* which can forms chemical compounds of different solubility can be present in different soil fractions. This can be observed from the sequential extraction. Highly mobile (soluble) forms of copper are usually present in small amounts in soil solution. Copper is also fixed to secondary sesquioxides. *Mercury* is strongly held in organic matter. Therefore, highest concentration of mercury in organically bound fraction, in all contaminated soils, has proved this knowledge. This is fortunately a reason of low potential mercury toxicity in soils (with the exception of methylated forms). *Nickel* can be partly mobile in the soil. Small portion of nickel in exchangeable fraction points to some possibilities being transported from the contamination sources to the groundwater or from soils to plants.

Lead is concentrated mostly in secondary sesquioxes (Fe, Mn, Al), humus and clay. It is postulated that potential of lead toxicity through the soil is low. The results point to the high portion of Pb, concentrated in secondary oxides. *Antimony* is usually dispersed element in soil. In contaminated soils of Hron river basin Sb is distributed a long distant from know contamination sources (Low Tatras, Štiavnické vrchy Mts., Kremnické vrchy Mts.). Antimony when oxidised, is a weak migrant. But its concentration in the plants, and small concentrations in the very mobile fraction (exchangeable), far from the primary contamination sources, point to possible water transport of Sb similarly to As to which is geochemically linked (Alloway, 1990; Fergusson, 1990). *Zinc* is present in soil in several fractions (Alloway, 1990): water-soluble, exchangeable, fixed to organic matter, clay and non-soluble metal oxides. From the sequential extraction is clear that higher proportion of Zn is bind to secondary oxides (Fe and Al oxides).

Table 3 Five principal sequential extraction schemes for assessing metal fraction in soils/sediments. Numbers, refer to order of each stage in the extraction scheme

Fraction	Tessier et al. (1979)	Miller et al. (1986)	Sposito et al. (1982)	McLaren and Crawford (1973)	* BCR (1987)
Soluble		1 H_2O			
Exchangeable	1 1 M $MgCl_2$	2 0,5 M $Ca(NO_3)_2$	1 0,5 M KNO_3	1 0,05 M $CaCl_2$	1 0,11 M Acetate acid
Acid Soluble		4 HOAc 0,1 M $Ca(NO_3)_2$			
Adsorbed		3 $Pb(NO_3)_2$	2 H_2O	2 2,5% HOAc	
Organic	4 0,02 M HNO_3 30% H_2O_2 3,2 M NH_4OAc	5 0,1M $K_4P_2O_7$	3 0,5 M NaOH	3 1M $K_4P_2O_7$	3 8,8 M H_2O_2 1 M NH_4OAc
Fe Mn-Oxide	3 0,04 M $NH_2OH.HCl$ in 25% HOAc				2 0,1 M Hydroxylamine + hydrochloric
Mn Oxide		6 0,01 M $NH_2OH.HCl$ + 0,1 M HNO_3			2 0,1 M Hydroxylamine + hydrochloric
Fe Oxide		7 Ammonium Oxalate Acid in UV light		4 Ammonium Oxalate Acid	2 0,1 M Hydroxylamine + hydrochloric
Carbonate	2 1 M NaOAc		4 0,05 M Na_2 - EDTA		1 0,11 M Acetate acid
Residual	5 2 x 70% HNO_3 40% HF/72% $HClO_4$	8 HNO_3 + HF	5 4 M HNO_3	5 Conc. HF	4 HNO_3+HF+$HClO_4$

* BCR - Community Bureau of Reference (1987)

Table 4 The results of heavy metals concentration (mg.kg^{-1}) in different soil fraction obtained by sequential extraction analyses: i-exchangeable (carbonate) fraction (0,11 M Acetic acid), ii-fraction held in Fe-Mn oxide (0,1 M Hydroxylamine + hydrochloric), iii-organically (sulphidic) bound fraction (8,8 M H_2O_2 + 1 M NH_4Oac), iv-residual fraction (soil samples decomposition with inorganic acid mixture HNO_3+HF+$HClO_4$).

Elements	Extraction method	Samples					
		LV-1		LV-2		LV-3	
		A hor.	C hor.	A hor.	C hor.	A hor.	C hor.
As	i	0,2	< 0,1	0,1	< 0,1	0,1	< 0,1
	ii	17,1	8,3	5,8	2,2	11,9	3,6
	iii	1,2	1,0	1,1	0,7	1,7	1,1
	iv	32,3	20,1	11,8	11,4	30,9	22,1
Cd	i	1,28	0,18	0,38	0,14	0,42	0,15
	ii	0,36	0,18	0,22	0,13	0,22	0,16
	iii	0,06	< 0,01	0,03	0,02	0,04	0,02
	iv	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Cr	i	< 1	< 1	< 1	< 1	< 1	< 1
	ii	2	4	4	2	2	2
	iii	3	2	4	3	4	3
	iv	55	60	49	57	61	44
Cu	i	14	3	3	< 1	12	1
	ii	54	18	19	7	57	13
	iii	34	5	10	2	32	5
	iv	37	14	33	18	52	26
Hg	i	< 0,001	0,002	0,003	0,001	< 0,001	0,001
	ii	0,001	< 0,001	< 0,001	0,001	0,002	< 0,001
	iii	0,933	0,174	0,357	0,007	0,877	0,120
	iv	0,486	0,144	0,260	0,131	0,281	0,129
Ni	i	3	2	2	2	2	1
	ii	3	6	2	4	4	5
	iii	2	< 1	1	< 1	2	1
	iv	9	9	10	9	11	8
Pb	i	< 2	< 2	< 2	< 2	< 2	< 2
	ii	58	58	47	10	55	13
	iii	7	7	8	4	10	4
	iv	14	14	13	11	15	9
Sb	i	0,4	< 0,1	0,1	0,3	0,2	< 0,1
	ii	1,0	0,3	0,2	0,1	0,6	0,2
	iii	0,6	0,1	0,2	0,1	0,3	0,2
	iv	34,2	11,5	11,2	4,3	25,8	8,4
Zn	i	82	9	16	3	13	4
	ii	121	23	28	12	27	17
	iii	31	10	14	17	17	10
	iv	63	47	61	46	78	49
As	i	0,3	< 0,1	0,4	0,1	0,2	0,1
	ii	13,1	12,9	14,1	8,5	0,9	1,6
	iii	1,0	1,2	1,0	0,6	1,0	0,4
	iv	22,7	28,2	13,6	9,7	20,2	22,6
Cd	i	1,62	1,69	0,15	0,12	0,09	0,08
	ii	0,73	1,35	0,26	0,11	0,17	0,06
	iii	0,05	0,08	0,03	0,03	0,03	0,01
	iv	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Cr	i	< 1	< 1	< 1	< 1	< 1	< 1
	ii	2	4	2	2	1	1
	iii	3	2	5	3	3	1
	iv	40	38	48	49	46	37

Table 4: continued

Elements	Extraction method	Samples					
		LV-1		LV-2		LV-3	
		A hor.	C hor.	A hor.	C hor.	A hor.	C hor.
Cu	i	7	10	< 1	< 1	< 1	< 1
	ii	35	55	10	7	2	2
	iii	18	16	5	2	2	2
	iv	23	23	19	15	19	8
Hg	i	< 0,001	0,006	0,003	< 0,001	0,002	< 0,001
	ii	0,002	0,003	< 0,001	0,001	0,001	< 0,001
	iii	0,592	0,617	0,035	0,009	0,104	0,021
	iv	0,146	0,174	0,092	0,130	0,093	0,079
Ni	i	2	1	1	1	1	< 1
	ii	4	5	7	5	6	4
	iii	3	< 1	3	2	< 1	< 1
	iv	9	10	10	10	11	7
Pb	i	2	< 2	< 2	< 2	< 2	< 2
	ii	75	102	23	11	14	6
	iii	7	7	4	3	5	4
	iv	16	17	10	8	11	8
Sb	i	0,5	0,3	0,1	0,2	0,1	0,5
	ii	0,5	0,7	0,2	0,1	< 0,1	0,1
	iii	0,2	0,1	< 0,1	< 0,1	0,1	< 0,1
	iv	18,1	20,0	10,5	5,8	4,5	4,7
Zn	i	71	63	3	3	2	< 1
	ii	130	152	23	15	12	7
	iii	27	32	10	9	6	7
	iv	66	73	58	49	51	39

LV-1 - Kozárovce (Gleyic Fluvisol, pH/KCl - 6,72), LV-2 - Hronský Benadik (Fluvisol, pH/KCl - 6,41), LV-3 - Starý Tekov (Fluvisol, pH/KCl - 5,4), LV-5 - Tekovský Hrádok (Fluvisol, pH/KCl - 7,31), LV-6 - Mýtne Ludany (Phaeozem, pH/KCl - 6,93), LV-8 - Hronské Klacany (Phaeozem, pH/KCl - 7,04).

Various sequential extraction schemes have been developed including this of European Commision (formerly BCR) which is used in our presentation. This scheme can be improved only in this way to be predictable for plant uptake of metals or adverse effect on human health or eco-toxicity, but such results are missing (McLaughlin et al., 2000).

2.3.5 Metal concentrations in the soil solution

Apart from the occurrence of the elements in the solid phase of soil/sediment little is known about their concentration and speciation in the soil solution. Knowledge of soil solution concentration and solubility of the elements is of a great importance in studying their biogeochemical cycles and availability to plants. Plants essentially take up heavy metals from soil via solution. On the other hand heavy metals from the solution may be transferred (leached) to the groundwater and cause its contamination.

The soil solution is the most important constituent influencing chemical and biological activities in the soils/sediments. Soil organisms without water die or become dormant. Mineral transformation become slow and chemical weathering is limited. In spite of overall acceptance of these general statements there is no meaningful definition of soil solution. From the viewpoint of soil chemistry the soil solution is defined as *'the aqueous liquid phase in whose composition is influenced by flows of matter and energy between it and it surroundings and by the gravitational field of the Earth* (Sposito, 1989).

By this definition soil solution is an open system that exchange matter and energy with the other subsystems (air, water, biota). Also, defining it as a phase implies that soil solution has uniform properties and can be isolated from the soils (sediments). These requirements of uniformity (stable composition, temperature) can be met only on small time- space area because of variable nature of these bodies. Soil solution is not distinct entity but rather continuum of phases, from that bound in colloids, through the immobile water in micropores, to free water percolating through macropores.

Because soil solution is highly variable their composition can be discussed only in general term. Concentration of inorganic constituents in the soil solution are controlled by pH, Eh and solid phase composition. Commonly found inorganic components in soil solution are given in Table 5. Trends in composition are similar but natural and anthropogenic factors can have big influences on this composition. The composition of soluble organic components in the soil solution reflects the composition of organic matter in the solid phase. Major organic components found in soil solution are present in Table 6. All studies of metals in soil solution suffer from two major problems:

- finding suitable techniques for detecting extremely low concentrations,
- differentiating between free metal ions in solution and soluble organo/metalic complexes.

Table 5 Major inorganic components in soil solution (Sumner, 2000).

Category	Major component (10^{-4} to 10^{-2} mol.l^{-1})	Minor components (10^{-6} to 10^{-4} mol.l^{-1})	Others
Cations	Ca^{2+}, Mg^{2+}, Na^+, K^+	Fe^{2+}, Mn^{2+}, Zn^{2+},Cu^{2+}, NH_4^+, Al^{3+}	Cr^{3+}, Ni^{2+}, Cd^{2+}, Pb^{2+}
Anions	HCO_3^-, Cl^-, SO_4^{2-}	$H_2PO_4^-$, F^-, HS^-	CrO_4^{2-}, $HMoO_4^+$
Neutral	$Si(OH)_4^0$	$B(OH)_3^0$	

Table 6 Major organic components found in soil solution (Sumner, 2000).

Source	Major components (10^{-5} to 10^{-3} mol.l^{-1})	Minor components ($<10^{-5}$ mol.l^{-1})
Natural	carboxylic acids, amino acids, simple sugars	carbohydrates, phenols, proteins, alcohols, sulfhydryls
Antropogenic		herbicides, fungicides, insecticides, PCBs, PAHs, petroleum, hydrocarbons, surfactants, solvents

Other problems are associated with obtaining unaltered solution. The moisture of field soils and fresh sediments can range from air dried to saturated, over short period of time. Most techniques for obtaining samples of solution function poorly when water content is below the saturation.

The methods for obtaining the soil solution can be broadly categorised in three groups: *aqueous extracts, column displacements and pressure extraction.* An alternative method is to use saturated soil paste (USDA, 1954). To obtain *aqueous extract* include adding water to the samples, to the point of saturation or beyond, equilibrating and removing solution. *Column displacement* consist of forcing a fraction of soil solution to move from the soil (sediment) by leaching with an aqueous solution or with non-soluble organic solvent. This procedure can be modified to include pressure from the top or vacuum applied to the bottom of the column. Neither variation in total electrolyte concentration nor the activity ratios of specific ion components of the soil solution can be adequately resolved when water to sample ratios vary from field moisture contents to ratio >1. This is the main limitation to the use of water extracts as models for soil solution (Sumner, 2000).
*Pressure extr*action is the use positive pressure or vacuum eventually centrifugation to remove soil solution.

Field methods include several types of lysimetric studies. From above stated is obvious that at least:

- the definition of soil solution is idealised and more functional definition is needed before the concentration/activities of free metal ions in soil solution will be used for the assessment of critical limits;
- the adjustment in design, execution and interpretation of methods in studying soil solution is strongly recommended;
- the derivation of total dissolved metal concentration from total soil concentration should be based on clear understanding of soil solution. The partition of metals concentration over solid phase and solution should clearly relate to the transfer functions.

The solubility of heavy metals under field conditions is linked strongly to soil parameters such as pH, SOM and DOC (Römkens and Salomons, 1998).

The soils under study have acidic to neutral character (pH 5,51- 7,14) with CEC ranging from 13,75- 35,65 cmol.kg^{-1} (Table 1). As it is stated in methodological part of this paper, soil solution in this study was extracted by 0,002 M $CaCl_2$. When one compare the obtained results (Table 7) it should be noted that concentrations of Ca^{2+} and Cl^- are very high. It is clear that the results are influenced by the background solution. To this conclusion points also relatively low HCO_3^- concentration which should relate to Ca^{2+} content in these soils.

The content of SO_4^{2-} is relatively high and points to the fact that some elements in solution were leached due to acid sulphate weathering of sulphides (and hence, sulphatic complexation of the metals may play some role in metals transfer). The nutrient elements concentration in soil solution (K, Mg, Na) shows some relation to the parent rocks resp. to the fertilisers application (agricultural soils). The Al and Fe concentration in soil solution does not give clear evidence to soil properties. Higher Fe concentration is appearing in the soils with some gleyic features.

The potential toxic elements (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) show relatively high concentration in soil solution. The limit value for As in the groundwater (5 µg.l^{-1}) is crossed in more than half of the samples. Arsenic which is occurring as oxoanions in the soils may show an increase of concentration in soil solution with rising pH. This might be the case of soils with gleyic carbonatic processes.

The total content of Cd in studied soil range from 0,3 to 20,5 mg.kg^{-1}. Cd solution concentration range from below 2 (detection limit) to 138 µg.l^{-1} which is extremely high. The critical limit proposed for Cd concentration in soil solution (precautionary principle) is 10 µg.l^{-1} (Curlík et al. 2000) is crossed in several soils contaminated by Zn-Pb (ICSK 11-16). As it is stated by Römkens and Salomons (1998) there appeared to be no single relation between the total Cd content and the solution concentration. In the forest soils frequently higher Cd content in soil solutions is due to lower pH values and higher soluble organic fraction content.

The concentration of Cr in soil solution relatively low and point to known aspects of low solubility/mobility Cr^{3+} compounds. The Cu solution concentration range from 31 to 269 µg.l^{-1}. These concentrations are high and may have and adverse effect to plants (de Vries and Römkens, 2000; In Curlík et al. 2000). Higher Cu concentrations in soil solution may be controlled by DOC (dissolved organic carbon) to which pointed Römkens and Salomons (1998), and in alkaline soils Fotovat and Naidu (1998). Cu solution concentration in studied contaminated soil is above the limit for groundwater (20 µg.$l^{-1)}$). Suggested critical limit for mercury concentration in soil solution is 0,1 µg.l^{-1} (Curlík et al., 2000). In spite of the fact that studied soil are not Hg contaminated (see Table 2- total content) its solution concentration is mostly above the limit.

The solution concentration for nickel in several soils are above the current groundwater quality standards (20 µg.l^{-1}). This may lead to leaching of Ni to groundwater. The proposed critical limit for lead in soil solution is 50 to 80 µg.l^{-1} (Curlík et al., 2000). The results show that lead is a bad migrant and its concentrations in soil solution are not high. Current Dutch groundwater quality standards for Zn are 65 µg.l^{-1} (Römkens and Salomons, 1998). The solution concentration of Zn are much above the standards.

The solubility of the potentially toxic elements under field condition is thought to be linked to soil parameters (Römkens and Salomons, 1998). To obtain more reliable estimates there are still needed more results related to metal solubility and leaching.

Table 7 The soil solution concentration (soil solution extraction by 0,002 M $CaCl_2$)

Sample	pH	EC mS/m	Cl^- mg/l	$(SO_4)^{2-}$ mg/l	$(HCO_3)^-$ mg/l	N-NO_2 mg/l	N-NO_3 mg/l	N-NH_4 mg/l	N-tot. mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Al mg/l	Fe mg/l	As mg/l	Cd mg/l	Cr mg/l	Cu mg/l	Hg mg/l	Ni mg/l	Pb mg/l	Zn mg/l
ICSK-1	6,7	21,95	13570	5200	183	378	< 90	3885	13945	90,374	19480	2700	20040	37	62	20	2	< 2	48	0,1	14	< 10	93
ICSK-2	7,3	21,47	14810	9400	153	566	4179	2139	13583	121,45	8530	2090	3010	< 20	20	2,7	5	3	74	0,1	152	< 10	720
ICSK-3	6,8	18,63	12340	3400	122	2750	2146	1926	18576	63,735	31410	3480	13340	< 20	20	6,7	3	< 2	77	0,1	44	13	210
ICSK-4	7,4	16,74	9880	3800	122	798	2733	1148	10342	86,229	17010	610	9550	< 20	10	12,6	< 2	2	62	< 0,1	35	12	110
ICSK-5	6,0	21,47	17280	11200	37	1684	6438	1829	15441	84,610	10090	3430	37290	35	40	18,1	2	< 2	129	< 0,1	52	< 10	300
ICSK-6	6,8	16,74	9880	4600	122	1236	2485	1193	8618	109,19	12690	1340	1790	< 20	30	2,4	< 2	< 2	31	0,1	16	< 10	80
ICSK-7	6,4	14,38	9880	13400	37	1833	9849	4053	16354	81,736	7910	1630	5240	32	60	10,4	2	2	269	0,3	44	< 10	270
ICSK-8	7,1	16,74	14810	4000	153	1784	3840	1779	18243	95,655	26880	870	3419	< 20	40	1,4	< 2	2	26	< 0,1	21	< 10	110
ICSK-9	7,2	21,5	11110	6600	183	1964	1694	2252	6715	107,21	18510	4070	7680	46	10	40,8	2	3	73	< 0,1	13	< 10	68
ICSK-10	6,3	12,91	20980	6800	37	1145	474	1548	7924	74,775	15570	9450	4550	95	20	10,5	< 2	< 2	66	0,3	17	< 10	58
ICSK-11	6,5	11,56	23450	5400	18	37	< 90	676	7356	81,204	9520	5860	15770	47	16	1,5	7	< 2	50	0,3	10	< 10	466
ICSK-12	6,1	8,84	20980	11200	37	37	1649	1070	5795	63,177	1383	4960	14420	27	22	1,1	32	2	86	0,9	19	< 10	2790
ICSK-13	6,7	34,28	13570	8600	183	< 6	< 90	5348	9458	118,78	15480	1350	31860	125	67	11,1	26	< 2	40	1,3	35	26	209
ICSK-14	6,8	12,97	11110	5000	37	79	836	1070	14257	65,199	22550	2660	20940	< 20	283	2,9	138	8	56	1,2	36	< 10	189
ICSK-15	7,2	28,51	13570	6400	214	1322	565	1661	10444	96,263	22160	2280	29670	53	41	11,9	19	3	68	1,0	< 10	< 10	75
ICSK-16	6,9	17,85	16040	2400	122	1023	3569	1126	15851	93,912	15940	5980	6780	< 20	20	26,7	5	< 2	46	1,3	< 10	< 10	106
ICSK-17	6,8	39,61	18510	87500	183	1065	9510	760	22341	126,98	24750	7930	4920	< 20	42	6,5	7	2	77	0,7	< 10	< 10	101
ICSK-18	6,9	31,62	25920	19200	183	1309	2259	1126	17248	112,89	21400	16810	2480	176	99	13,3	8	< 2	46	0,9	17	< 10	137
ICSK-19	7,0	20,07	6170	2000	122	956	2711	2167	8114	101,12	5290	985	40960	224	103	7,0	3	4	97	0,4	< 10	12	57
ICSK-20	6,8	21,85	25920	3800	122	518	271	1281	5799	97,471	14770	9000	3180	56	43	6,7	5	4	33	0,6	16	< 10	46

2.3.6 Conclusions

Soils and sediments testing for potentially toxic elements advanced recently due to improvement of analytical methods, especially low concentration detection but also due to better understanding the behaviour of metals in soils relating to their properties. Recent developments of the testing methods goes in three directions: *single extraction* with a mild extractant, *sequential extraction* with multi-solution extraction and *soil solution testing* which is thought to be best predictor of plant available metals. For all mentioned methods which are widely used, no meaningful measures exist for metal bioavailability, till now. To improve these methods, first of all the information level on mobility (toxicity) of extracted species of elements has to be increased.

The results which are presented in this work show that contaminated soil may possess some danger for the plants in the topsoils and for the enhanced leaching towards to the groundwater in subsoils. Mobile fraction concentration of different contaminated Slovakian soils obtained by single extractant are high for heavy metals (Cd, As, Cu, Zn) but no calibration data exist as far as real toxicity to plants. The mobile Cd fraction concentration is not clearly related to soil properties (pH) but more closely to the total Cd content, resp. to the form of Cd occurrence in soil (anthropogenic).

The results of sequential extraction analyses of contaminated alluvial soils of river Hron basin show that some potentially toxic elements (Cd, Cu, Zn and possibly As, Sb) are present in the most mobile fractions. These elements are brought from different remote sources (mining drainage basin). This gives some evidence of possible adverse effect for plants and groundwater (groundwater - soil interaction).

Soil solution testing results based on soil solution extraction method show that As, Cd, Cu, and partly Zn and Hg exceeded current groundwater quality standard or critical limits (for Cd, Hg) proposed during Bratislava meeting (Curlík et al., 2000). High concentration of potentially toxic elements in soil solution can be harmful for plants and groundwater. The acidification of diffusely contaminated soils may speeds the mobility (leaching) of these elements and their transfer to plants (groundwater).

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2.4 Assessment of relationships between total and reactive concentrations of cadmium, copper, lead and zinc in Hungarian and Slovakian soils

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Summary

To account for the difference between the total metal pool and the biologically available pool, a wide range of mild extracts have been proposed to estimate plant uptake. Despite numerous sequential extraction schemes, specific information on the availability of those pools in view of its relation with dissolved concentrations, readily available for plant uptake or leaching to groundwater is lacking. This stresses the need for a single extraction that is able to evaluate the reactive (potential available) metal content in different soils, that can be related to the dissolved metal concentration. In this study a single, dilute acid extraction by 0.43 $mol.l^{-1}$ HNO_3 was applied on 72 soil samples that are representative for Hungary (33 plots) and Slovakia (39 plots). Sampling was limited to the plough layer where most effects on solute uptake (and ecology) are to be expected, i.e. within 0-20 cm. The soil samples were also extracted with EDTA to compare the results obtained with the mild HNO_3 extraction. Furthermore, the 'so-called total' metal content was measured by using an aqua regia extraction. The samples included a large range in soil properties and degree of contamination, the latter by including 12 plots from a long-term field experiment with heavy metals in Hungary. The main purpose of this study was to investigate the possibility to derive reactive metal contents from 'so-called total' metal contents, the latter being readily available for a large number of plots in many countries.

Results showed a considerable agreement between reactive metal concentrations measured with a mild (0.43 $mol.l^{-1}$) HNO_3 extraction and with an EDTA extraction. Furthermore, a considerable part of the metals are present in a rather unavailable form in soils. On average, Zn has the lowest reactive to total metal ratio (0.17), followed by Pb (0.30), Cu (0.38) and Cd (0.56). For each metal considered there is a large range in ratios of reactive to total metal content. On average, a reasonable prediction can be made of reactive metal contents from total metal contents and the organic matter and clay content using regression relations. However, large errors can be made for individual samples specifically in the low concentration range. The derived relations are further completely empirical and can only to be used for the types of soil for which they were derived. The use of similar relations derived with Dutch soil samples showed reasonable agreement for Cd, but reactive metal contents were generally overestimated for Cu, Pb and Zn. This underlines the need to determine the reactive metal pool with a suitable extractant because the reliability of estimates from the total pool and soil properties is limited for specific sites.

2.4.1 Introduction

During the last century, the metal content in most soils has increased considerable as a result of atmospheric deposition and application of sludge, manure, fertilisers and other soil amendments. Especially in the vicinity of non-ferrous industries levels of heavy metal have reached toxic levels. Risks that are associated with the presence of excess amounts of metal in soil include leaching to the groundwater, uptake by plants and effects on soil micro-organisms and, eventually the entire food chain as a result of metal transfer from micro-organisms to higher organisms. To protect both soil organisms and human beings from adverse effects, soil quality standards have been developed in most countries. The levels of protection are usually based on the protection of the food-chain (risks associated with food intake by higher animals and human beings), protection of soil organisms (based on ecotoxicological data) or direct uptake by children (based on toxicological data).

The majority of these standards is currently based on the total metal content of the soil as determined by a total (HF destruction), or pseudo-total Aqua Regia (AR) destruction (hot concentrated HCl and HNO_3). However, during the last two decades it has become clear that metals included in the crystal structure of clay minerals or oxides are not chemically available and therefore not related to the various risks mentioned earlier. Under conditions that prevail in aerated soils (pH 3 - 8, organic matter 2 - 60%, clay 2 - 60%), the availability of metals in these compounds is virtually zero. It is therefore not realistic to calculate metal uptake or metal leaching with empirical relations or process models using the total fraction of metals in soils, including the unavailable or inert fraction. To account for this problem several chemical extractants are proposed to extract a '(biological) available pool. These extractions range from so called readily exchangeable fractions as extracted with 0.01 $mol.l^{-1}$ $CaCl_2$ or 1 $mol.l^{-1}$ NH_4NO_3 to stronger complexing extractions with DTPA and NH_4Ac. All these extractants are however too weak to extract the total chemical reactive pool, being the total amount of metals available for exchange with the soil solution. Sequential extractions are developed rather to distinguish the amounts bound to the different soil constituents (organic matter, oxides etc.) than to quantify the total chemical reactive fraction of metals in soils. Furthermore they are laborious and results are often hard to interpret for environmental purposes.

This stresses the need for a single extraction that is able to evaluate the total potential metal availability in different soils, i.e. with a range in soil properties and degree of contamination. Here we propose to achieve this with a single, dilute acid extraction such as 0.43 $mol.l^{-1}$ HNO_3. The use of a 0.43 $mol.l^{-1}$ HNO_3 as an estimate of the total available pool has been proposed earlier and is already being used as the standard extraction method for Cu in agricultural advisory regulations in the Netherlands. The strength of the acid (pH 1 - 1.5) implies that all metals that can potentially - not only now but also in the future - participate in equilibrium reactions are dissolved, without dissolving those that will not contribute to the chemical and biological equilibrium reactions. In the literature, transfer functions are available relating the 0.43 $mol.l^{-1}$ HNO_3 extractable content to the dissolved metal concentration, needed in plant uptake and metal leaching studies (Römkens et al., 2003). The results of the HNO_3

extraction are compared to a 0.05 mol.l^{-1} EDTA extraction, another single extraction widely used extraction to determine the reactive metal fraction in soils.

In many cases, information is only available on the total concentration of metals, mostly derived by an aqua regia extraction. To overcome this obvious limitation we studied the relationship between the Aqua Regia extractable pool, as a measure for the total metal pool, and the 0.43 mol.l^{-1} HNO_3 extractable pool taking into account soil properties such as clay and organic matter content. This was done to test whether these soil properties influence the reactive metal fraction in soil, for example by inclusion of metals in the mineral structure. The data that are presented on the 0.43 mol.l^{-1} HNO_3 and Aqua Regia extractable metal content in this paper cover a wide range of soils in Slovakia and Hungary, from acid forest soils to calcareous agricultural soils, and a wide range in state of pollution, from background levels (most plots in Slovakia and Hungary) to highly polluted experimental plots (in Hungary). We also included EDTA as an extraction method, since this extractant is used in many countries including Slovakia and Hungary, to study the relationship between EDTA and 0.43 mol.l^{-1} HNO_3. The functional relationships that are presented to estimate the 0.43 mol.l^{-1} HNO_3 fraction in soils from the Aqua Regia extractable metal content in combination with the soil clay- and organic matter content, based on the presented data are used in overall study focusing on the impact of soil acidification (by stopping liming) on dissolved metal concentrations and plant metal contents in both countries (Groenenberg et al., 2003)

2.4.2 Material and Methods

Locations

In order to derive functional relationships between the reactive and total metal content, it was essential to select representative soil samples with a wide range in soil properties that may influence the heavy metal distribution in soils. A geographic overview of the selected sites is given in Fig. 1. In Slovakia 39 sites were selected from the database of the geochemical map of Slovakia (Curlík and Šefcik, 1997). From this database 20 contaminated agricultural soils were selected. Additionally 19 soils were selected especially to extend the pH range of the soils with acid soils.

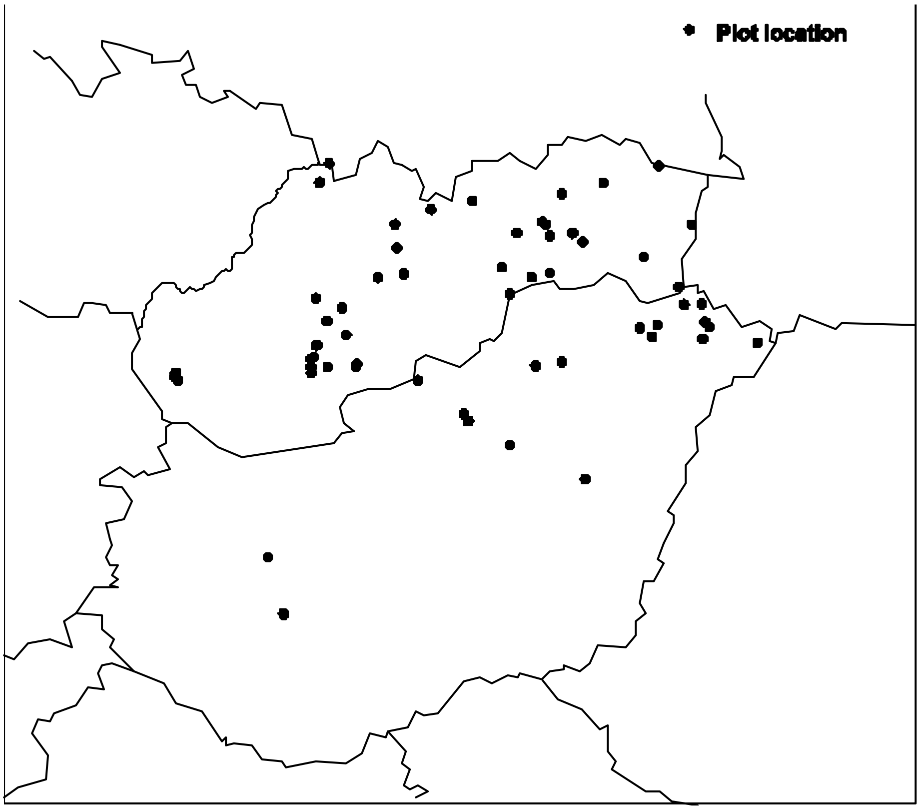

Figure 1 Location of the selected sites

In Hungary 33 sites were sampled with a large range in soil properties (pH, organic matter content and clay content) and a large range in metal (Cd, Cu, Pb or Zn) concentrations. Use was made of the Soil Information and Monitoring System of Hungary (SIMS, Murányi, 2000), which has been developed for the sake of sustainable land use and rational soil management. The SIMS contains 1236 representative sampling sites, including polluted soils. From this system 10 contaminated sites were selected. Furthermore, sites were selected where a long-term field experiment with heavy metals has been set up (in Gyöngyös). In this experiment different heavy metal doses were mixed into the ploughed layer (0 - 20 cm) in 1994 and the fate of heavy metals has been followed as a function of time including a control with no treatment (Gyöngyös 0). Furthermore a long-term fertilisation experiment at Karcag was also selected (B17). This experiment started in 1967 to study the effect of fertiliser doses (N, P, K) on the crop yields (wheat and maize). The sample was taken from the plot of the highest NPK dose (B1732 II/20). All other sites were randomly selected sites with average metal contents in non-polluted areas.

Sampling and analyses

Sampling

The samples were collected using a soil auger. In agricultural soils, the sampling was limited to the plough layer of 20 cm where most effects on solute uptake (and ecology) are to be expected. In forest soils the upper A horizon was sampled, varying in depth between 5 and 30 cm. The spatial variability in soil and soil solution chemistry requires that at least 25 samples should be taken to derive either one pooled sample. The samples were thus collected in a fixed grid of 5 x 5 sampling points that are situated at regular intervals from each other, such that the plot area is homogeneous in soil type and crop. Use was mostly made of intervals of 5 meters or 10 meters apart leading to a plot area of 25 x 25 m or 50 x 50 m. From each layer or diagnostic horizon, soil material was sampled to obtain at least 1 kg of soil material from each site and horizon. After transport to the laboratory, the soil material was dried at 40 degrees for 40 tot 72 hours depending on texture and organic matter content. Finally all soil samples were sieved on a contaminant-free 2 mm sieve.

Analyses of soil properties

In the dried and sieved soil samples the following general soil parameters were determined: pH-$CaCl_2$, carbonate content, total carbon content by loss on ignition and clay content (gravimetric methods). The pH-$CaCl_2$ was determined by extracting soil samples at 20°C with 0.01 M $CaCl_2$. The suspension was stirred for 2 h and centrifuged. The supernatant was taken for the analysis. The $CaCO_3$-equivalent of soil was determined by the method of Trierweiler and Lindsay (1969). The organic carbon was determined by a modification of Alten et al. (1935) method (Tares and Sippola, 1978). An amount of soil containing 30-100 mg of humus, 25 ml 0.25 M $K_2Cr_2O_7$ and 40 ml conc. H_2SO4 were put into a 400 ml flask. The mixture was kept for 1.5 h in a hot water bath, allowed to cool for 30 min and 175 ml of water added. After standing overnight, the solution was measured colorimetrically against standards (red filter, 620-645 nm). The particle size distribution was determined by dry and wet sieving and for the finer fractions by a pipette method (Elonen, 1971). Four fractions (< 0.002, 0.002-0.06, 0.06-2.0 and > 2.0 mm) were determined.

Several extractions were performed to obtain both the 'total' and 'reactive' heavy metal content of the soil samples. The total pseudo - total heavy metal content was determined by extraction with *aqua regia* ($HCl:HNO_3$ = 3:1) at room temperature for 16 h, followed by boiling under the reflux for 2 h. The extract was than filtrated and brought to the standard volume by the adding of nitric acid. The reactive heavy metal content was determined by extraction with 0.43 $mol.l^{-1}$ HNO_3 extraction (option 1). In this case, 5 g of moist soil was shaken with 50 ml of a 0.43 $mol.l^{-1}$ HNO_3 solution for 1 hour on an end over end shaker. The supernatant of the solution was filtered through a Whatman no. 541 filter paper. This solution was made up to 100 ml with ultra pure water. This solution was analysed for heavy metals with ICP-AES. Also a measurement of the water content was made to calculate the metal content expressed as $mg.kg^{-1}$ dried soil. An 0.05 $mol.l^{-1}$ EDTA extraction was also used to determine the reactive heavy metal content (option 2). To 10 g. of dried soil (40 °C), 40 ml of a 0.05 $mol.l^{-1}$ EDTA solution was added and shaken for 24 hours. Thereafter it was centrifuged for 10 minutes and filtered through a 0.45µ filter. The metal contents in the extract were measured using ICP-AES.

Derivation of relationships between different extractions

Relations between reactive metal extracted with EDTA and 0.43 mol.l^{-1} HNO_3

To relate the amounts of metal extracted with EDTA with the amounts extracted with 0.43 mol.l^{-1} HNO_3 both linear and logarithmic regression relations were used. Linear regression relations are derived according to Eq. 1. The regression line is forced to go through the origin to avoid negative predictions of the reactive metal content. Regressions were done both for the whole concentration range as for a limited concentration range for low concentrations to test whether this gives better relationships for the lower range.

$$M_{re,HNO3} = \alpha \cdot M_{re,EDTA} \tag{1}$$

Besides a linear relation also a logarithmic function was used to relate the two extractions to each other according to:

$$\log M_{re,HNO3} = \log \alpha + \log M_{re,EDTA} \tag{2}$$

The logarithmic function always gives positive estimates.

Relations between reactive metal and total metal concentrations

The reactive metal concentration, approximated by mild 0.43 mol.l^{-1} HNO_3 or EDTA extraction, was related to the total concentration (aqua regia digestion) and soil properties using a logarithmic relation according to:

$$\log M_{re} = \beta_0 + \beta_1 \cdot \log M_{soil} + \beta_2 \cdot \log(\%OM) + \beta_3 \cdot \log(\%clay) \tag{3}$$

where:

M_{re} = reactive concentration of heavy metal M in soil (mg.kg^{-1})
M_{tot} = total concentration of heavy metal M in soil (mg.kg^{-1})

The idea behind the relation is that the reactive metal content increases with an increase in organic matter content, considering that metals that are complexed with organic matter are readily available (positive sign) and decreases with an increase in clay content, considering that metals that are included in the lattice structure of clay minerals are not readily available (negative sign).

2.4.3 Results

Soil properties and metal concentrations

Soil properties

Data on soil properties (pH, $CaCO_3$, humus content, carbon content, clay content and soil type) are presented in Table 1. The set of collected soils include a large range of different soils according to the FAO classification. These soils span a large range of soil properties. Figure 2 shows the cumulative distribution frequency of the organic matter, carbon and clay content together with several measures of the pH. Clay contents range from 2-50%, thus going from sandy soils with almost no clay to heavy clay soils.

The set also includes soils with almost no organic matter to soils with 30% of organic matter. Peat soils are, however, not included. The pH range of the soils is between pH 4.3 to 8. Most of the soils (80%) have a pH > 6, this because most of the selected soils are used for agriculture. Even a large part of the soils (50%) has a pH higher than 7, being calcareous soils.

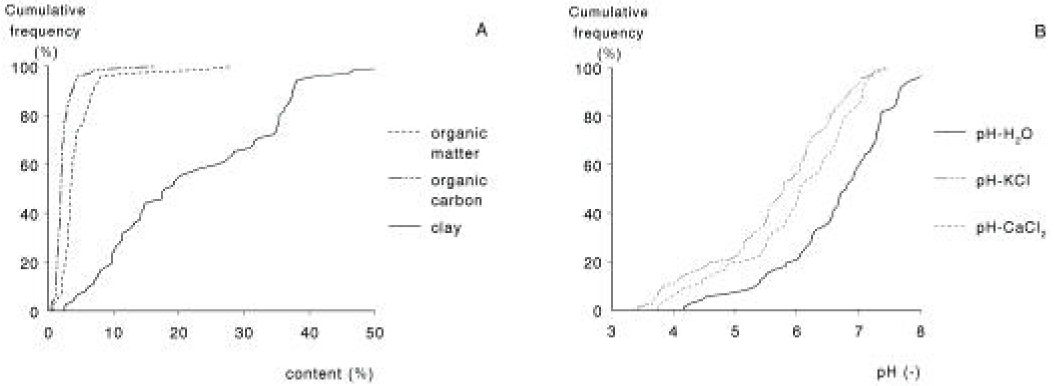

Figure 2 Cumulative frequency distribution of the organic matter content, organic carbon content and clay content (A) and of the pH (B)

Metal concentrations

Total metal concentrations and the reactive metal concentrations for Cd, Cu, Pb and Zn as determined with both 0.05 $mol.l^{-1}$ EDTA and 0.43 $mol.l^{-1}$ HNO_3 are presented in Table 2. Figure 3 shows the cumulative distribution frequency of the metals for the three different extractions used. Median total concentrations of Cd (0.41 $mg.kg^{-1}$), Cu (55 $mg.kg^{-1}$), Pb (29 $mg.kg^{-1}$) and Zn (98 $mg.kg^{-1}$) are within the normal range of metal concentrations in unpolluted and not geochemical enriched soils in Europe. The highest concentrations in the studied soils, Cd (45 $mg.kg^{-1}$), Cu (589 $mg.kg^{-1}$), Pb (1303 $mg.kg^{-1}$) and Zn (2445 $mg.kg^{-1}$) are, however, severely polluted soils. These extremely high concentrations do occur in Slovakia (ICSK 11 and 12).

Table 1 Basic characteristics (Longitude, Latitude, land use, soil type and soil depth) and soil properties (pH, CaCO3, humus, carbon and clay content) of the selected sampling locations

Sample name	Longitude	Latitude	land use	FAO soil type	depth	pH H_2O	pH KCl	pH $CaCl_2$	$CaCO_3$ %	Content %		
										humus	carbon	clay
Hungary												
E7405	48.0667	20.8833	Forest	Eutric Fluvisols	0-20	6.4	5.5	5.9	0	7.4	4.3	46
E9105	48.0667	20.6333	Forest	Haplic Arenosols	0-20	6.1	5.1	5.4	0	6.4	3.7	35
I1710	47.6	20.2833	Agriculture	Haplic Vertisols	0-20	6.7	5.5	6.0	0	3.3	1.9	41
I1810	47.6	20.2833	Agriculture	Luvisols	0-20	7.3	6.6	6.7	0	1.3	0.77	8.8
I5005	48.2	21.6667	Agriculture	Eutric Fluvisols	0-20	7.3	6.1	6.7	0	2.5	1.3	26
S3612	48.0833	19.5167	Agriculture	Luvisols	0-20	7.6	6.9	7.1	0	2.1	1.2	28
S4810	47.8333	19.9	Agriculture	Eutric Fluvisols	0-20	7.0	5.9	6.4	0	2.8	1.6	35
I0215	48.3	22.1167	Agriculture	Haplic Vertisols	0-20	6.3	5.2	5.9	0	3.4	2.0	56
I0615	48.2833	22.2833	Agriculture	Mollic Fluvisols	0-20	6.2	4.9	5.5	0	4.2	2.4	47
I1115	48.1333	21.7667	Agriculture	Calcic Chernozems	0-20	6.1	5.1	5.3	0	2.5	1.5	15
I1415	47.9833	22.7333	Agriculture	Mollic Fluvisols	0-20	5.8	4.4	4.9	0	2.6	1.5	32
I1715	48.1333	22.3167	Agriculture	Umbric Fluvisols	0-20	7.7	7.0	7.1	0	2.2	1.3	9.9
I2015	48.1667	22.2833	Agriculture	Haplic Arenosols	0-20	8.0	7.4	7.5	0	0.84	0.48	11
I2715	48.0667	22.2333	Agriculture	Haplic Arenosols	0-20	4.5	3.7	3.8	0	0.72	0.42	4.2
Gyöngyös 0	47.7833	19.9333	Agriculture	Luvisols	0-20	7.2	6.0	6.6	0	2.8	1.7	37
Cu 1	47.7833	19.9333	Agriculture	Luvisols	0-20	6.8	5.8	6.2	0	3.0	1.7	38
Cu 2	47.7833	19.9333	Agriculture	Luvisols	0-20	6.7	5.7	6.0	0	3.7	2.2	38
Cu 3	47.7833	19.9333	Agriculture	Luvisols	0-20	6.7	5.6	6.0	0	3.8	2.2	35
Cd 1	47.7833	19.9333	Agriculture	Luvisols	0-20	6.9	6.0	6.3	0	3.5	2.0	37
Cd 2	47.7833	19.9333	Agriculture	Luvisols	0-20	7.3	6.4	6.7	0	3.6	2.1	35
Cd 3	47.7833	19.9333	Agriculture	Luvisols	0-20	7.1	6.1	6.5	0	3.6	2.1	37
Pb 1	47.7833	19.9333	Agriculture	Luvisols	0-20	7.5	6.7	7.0	0	3.4	2.0	35
Pb 2	47.7833	19.9333	Agriculture	Luvisols	0-20	7.2	6.2	6.6	0	3.3	1.9	36
Pb 3	47.7833	19.9333	Agriculture	Luvisols	0-20	7.1	6.1	6.4	0	3.3	1.9	38
Zn 1	47.7833	19.9333	Agriculture	Luvisols	0-20	6.7	5.7	6.0	0	3.4	2.0	35
Zn 2	47.7833	19.9333	Agriculture	Luvisols	0-20	6.6	5.6	5.9	0	4.2	2.4	35
Zn 3	47.7833	19.9333	Agriculture	Luvisols	0-20	7.0	6.1	6.4	0	3.8	2.2	36
B1732 II.1	47.3167	20.9333	Agriculture	Phaeozem	0-20	6.6	5.3	5.6	0	2.8	1.7	37
B1732 II.20	47.3167	20.9333	Agriculture	Phaeozem	0-20	5.4	4.6	4.9	0	3.1	1.8	38
S4920	46.7333	18	Agriculture	Histosols	0-20	7.0	6.5	6.8	0	28	16	13
I2802	48.2	21.8333	Agriculture	Phaeozem	0-20	6.5	5.8	6.0	0	3.5	2.0	32
S5319	47.1	17.9167	Agriculture	Haplic Arenosols	0-20	6.8	6.2	6.1	0	2.2	1.3	9.7
E5107	*	*	Forest	Haplic Chernozems	0-20	6.3	5.5	5.6	0	3.4	2.0	15
Slovakia												
ICSK-1	48.75737	19.27247	Agriculture	Fluvisol	0-20	7.2	6.5	6.6	0.4	5.5	2.6	14
ICSK-2	48.71186	20.45553	Agriculture	Gleyic Fluvisol	0-20	7.4	6.8	6.9	1.6	4.2	1.9	3.8

Sample name	Longitude	Latitude	land use	FAO soil type	depth	pH H_2O	pH KCl	pH $CaCl_2$	$CaCO_3$	Content %		
									%	humus	carbon	clay
ICSK-3	48.79231	21.25931	Agriculture	Fluvisol	0-20	7.4	6.5	6.7	0.3	3.1	1.9	18
ICSK-4	48.85554	21.17554	Agriculture	Fluvisol	0-20	7.7	7.1	7.1	6.4	3.0	1.3	4.6
ICSK-5	48.93552	20.93585	Agriculture	Cambisol	0-20	6.1	5.3	5.5	0	3.3	2.0	13
ICSK-6	48.91031	20.64999	Agriculture	Fluvisol	0-20	6.9	6.2	6.4	0.12	4.1	2.3	7.5
ICSK-7	48.86074	20.95761	Agriculture	Fluvisol	0-20	6.2	5.6	5.7	0	7.1	2.8	2.7
ICSK-8	49.07495	19.50104	Agriculture	Fluvisol	0-20	7.4	6.5	6.9	0.5	4.0	2.1	7.8
ICSK-9	48.30514	18.53716	Agriculture	Fluvisol	0-20	7.7	6.7	7.1	7.3	3.2	1.9	15
ICSK-10	48.25473	18.53094	Agriculture	Fluvisol	0-20	6.6	5.4	5.8	0	3.1	1.8	22
ICSK-11	48.21842	18.95219	Agriculture	Fluvisol	0-20	6.3	5.2	5.5	0	1.7	1.3	18
ICSK-12	48.2381	18.96544	Agriculture	Fluvisol	0-20	6.9	5.8	6.1	0	2.2	1.4	11
ICSK-13	48.42817	18.90035	Agriculture	Pseudogley	0-20	6.0	5.1	5.5	0	6.7	3.5	18
ICSK-14	48.59669	18.89644	Agriculture	Fluvisol	0-20	7.3	6.5	6.7	0.52	2.2	1.2	9.7
ICSK-15	48.52731	18.73545	Agriculture	Fluvisol	0-20	6.7	5.8	6.0	0	6.0	2.3	11
ICSK-16	48.38367	18.60815	Agriculture	Fluvisol	0-20	7.7	6.8	7.0	4.2	2.3	1.2	7.2
ICSK-17	48.21772	18.52431	Agriculture	Fluvisol	0-20	7.3	6.2	6.7	0.1	3.7	2.1	19
ICSK-18	48.31793	17.24906	Agriculture	Phaeozem	0-20	7.3	6.3	6.8	0.4	5.7	2.9	12
ICSK-19	48.29244	17.24256	Agriculture	Cambisol	0-20	7.8	7.3	7.1	4.5	6.2	1.4	6.1
ICSK-20	48.26556	17.2646	Agriculture	Fluvisol	0-20	7.6	6.6	7.1	0.3	4.6	1.7	17
GAL-BB-037	48.92499	19.48962	Forest	Ferro-humic podzol	0-5	4.5	3.8	3.9	0	23	7.1	9.8
GAL-KE-504	48.63171	20.90394	Forest	Rendzina	5-9	8.1	7.3	7.3	0	13	6.4	7.0
GAL-LM-062	49.13509	19.86682	Forest	Cambic Arenosol	0-10	4.2	3.8	4.0	0	4.2	2.6	14
GAL-PD-035	48.67971	18.6554	Forest	Ando-humic Cambisol	0-5	5.5	3.9	4.3	0	2.3	1.3	8.1
GAL-SN-051	48.95482	20.90981	Forest	Ferro-orthic podzol	0--5	4.3	3.4	3.8	0	5.5	2.4	11
GALE-LV-001	48.3138	18.56974	Forest	Ando-humic Cambisol	0-21	4.9	3.7	4.1	0.32	6.4	4.1	20
GALE-PP-006	49.1526	20.27136	Forest	Eutric Cambisol	5-20	5.3	4.2	4.5	0.4	8.0	3.1	14
GAN-MI-003	48.78343	22.32111	Forest	Eutric Cambisol	0-10	5.4	4.0	4.5	0	5.4	3.3	2.5
GAP-BB-072	48.75754	19.52065	Agriculture	Calcaric Cambisol	5-12	5.5	4.1	4.6	2.5	4.5	2.4	20
GAP-CA-011	49.50974	18.95266	Agriculture	Stagno-gleyic Cambisol	5-13	5.6	4.3	4.7	0	6.0	2.9	10
GAP-CA-039	49.40112	18.83348	Agriculture	Eutric Fluvisol	5-15	5.8	4.5	4.9	0	3.3	1.2	10
GAP-HN-098	49.18267	22.10475	Agriculture	Eutric Cambisol	0-18	5.2	3.7	4.1	0	3.1	1.6	5.9
GAP-MI-003	48.63655	21.81294	Agriculture	Fluvi-eutric Gleysol	15-25	8.0	6.9	7.2	0	4.2	3.2	28
GAP-PO-067	49.10754	21.13532	Agriculture	Calcaric Cambisol	5-15	8.1	7.0	7.2	0	3.6	1.5	27
GAP-RV-038	48.53659	20.49623	Agriculture	Calcaric Lithosol	3-10	6.2	5.0	5.4	0	7.1	4.0	31
GAP-RV-133	48.62115	20.72152	Agriculture	Rendzina	5-15	6.6	5.5	5.8	0	8.0	4.2	23
GAP-SK-085	49.13678	21.54656	Agriculture	Stagno-gleyic Cambisol	0-5	6.9	5.5	5.9	0	3.1	1.5	28
GAP-TV-047	48.41222	22.09106	Agriculture	Fluvi-eutric Gleysol	10-20	7.6	6.1	6.6	0	3.4	1.9	32
GAPE-LV-002	48.24176	18.68437	Agriculture	Stagno-gleyic Luvisol	0-30	7.4	6.1	6.4	0.2	2.1	1.2	19

Table 2 Total metal concentrations (aqua regia) and reactive metal concentrations for Cd, Cu, Pb and Zn(0.05 mol.l^{-1} EDTA and 0.43 mol.l^{-1} HNO_3 extraction) of the selected sampling locations

Sample name	Total metal content (Aqua regia) in mg.kg^{-1}				Reactive metal content (EDTA) in mg.kg^{-1}				Reactive metal content (0.43 mol.l^{-1} HNO_3) in mg.kg^{-1}			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Hungary												
E7405	0.41	28	22	109	0.50	36	18	22	0.22	22	7.6	19
E9105	2.6	62	31	142	0.51	5.8	9.9	3.5	0.32	5.8	7.0	5.0
I1710	0.26	105	25	109	0.25	65	15	15	0.14	48	4.2	16
I1810	0.09	110	12	33	0.05	69	4.3	5.0	0.07	81	4.6	7.9
I5005	0.98	36	57	183	0.61	16	16	18	0.62	17	19	38
S3612	0.09	14	61	70	0.11	5.3	7.1	17	0.07	4.5	4.2	20
S4810	3.2	91	144	645	2.3	51	64	256	2.1	49	51	384
I0215	1.1	45	77	230	0.79	20	26	15	0.58	13	18	29
I0615	0.78	36	57	198	0.48	14	21	12	0.47	13	25	29
I1115	0.19	21	17	71	0.17	12	6.5	8.3	0.09	8.2	4.5	12
I1415	0.11	13	21	57	0.07	4.4	6.1	4.6	0.01	4.0	5.9	4.2
I1715	1.0	25	42	177	0.70	13	19	41	0.68	13	21	69
I2015	0.13	12	13	43	0.04	2.7	2.5	1.4	0.01	3.0	3.2	2.6
I2715	0.02	7.2	17	26	0.02	1.8	2.5	0.9	0.01	2.2	3.4	2.1
'Gyöngyös 0'	0.22	24	86	76	0.16	10	9.0	4.2	0.10	6.5	3.4	5.8
'Cu 1'	0.36	33	23	100	0.21	15	8.7	11	0.14	9.7	4.0	12
'Cu 2'	0.32	38	23	91	0.27	23	12	9.6	0.12	15	3.8	9.1
'Cu 3'	0.34	73	24	89	0.35	56	10	9.0	0.23	33	4.2	11
'Cd 1'	6.2	30	23	96	5.25	15	10	11	3.9	9.8	4.0	13
'Cd 2'	17	32	27	86	16	17	9.4	7.8	14	11	4.1	9.4
'Cd 3'	45	30	22	85	38	14	8.2	6.7	33	11	5.1	9.6
'Pb 1'	0.54	29	30	84	0.75	15	54	9.3	0.41	10	7.8	10
'Pb 2'	4.0	30	41	87	3.74	16	24	7.3	2.0	11	14	9.4
'Pb 3'	0.35	29	58	88	0.39	15	42	13	0.25	10	20	11
'Zn 1'	0.33	28	23	99	0.24	14	13	14	0.12	8.7	4.0	17
'Zn 2'	0.57	29	24	112	0.28	14	11	25	0.33	7.4	3.0	25
'Zn 3'	0.52	28	23	131	0.20	8.2	6.7	24	0.29	7.8	3.6	38
'B1732 II.1'	0.23	26	23	83	0.27	10	16	14	0.17	8.7	15	20
'B1732 II.20'	0.21	26	23	84	0.14	7.8	7.1	2.1	0.12	4.6	3.2	4.5
S4920	0.48	29	29	58	0.23	14	12	5.2	0.16	7.9	7.6	7.6
I2802	0.21	24	21	71	0.33	135	24	23	0.07	6.8	3.8	6.4
S5319	0.14	152	14	51	0.11	151	5.6	21	0.03	141	3.9	19
E5107	0.11	9.7	15	36	0.06	4.0	4.9	2.8	0.05	3.1	3.1	3.8
Slovakia												
ICSK-1	0.50	57	62	123	0.21	33	17	8.0	0.24	29	15	9.9
ICSK-2	0.20	135	24	71	0.28	43	14	11	0.18	43	10	8.7

Sample name	Total metal content (Aqua regia) in mg.kg^{-1}				Reactive metal content (EDTA) in mg.kg^{-1}				Reactive metal content (0.43 mol.l^{-1} HNO$_3$) in mg.kg^{-1}			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
ICSK-3	0.40	113	33	110	0.20	56	13	16	0.19	49	9.9	20
ICSK-4	0.40	288	50	137	0.34	134	24	23	0.43	141	23	30
ICSK-5	0.60	70	43	177	0.30	31	19	33	0.37	32	20	45
ICSK-6	0.30	76	17	70	0.15	37	8.0	11	0.15	39	7.1	13
ICSK-7	0.70	589	170	243	0.43	305	77	47	0.40	287	82	50
ICSK-8	0.30	21	16	67	0.26	8.7	4.9	3.3	0.07	9.0	6.3	9.0
ICSK-9	0.70	117	62	158	0.56	59	26	42	0.40	61	25	59
ICSK-10	0.60	130	72	119	0.34	59	24	12	0.23	63	24	23
ICSK-11	14	201	1303	1704	11	100	633	547	9.7	97	432	630
ICSK-12	21	236	1301	2445	14	113	448	772	15	120	412	1044
ICSK-13	1.1	39	220	178	0.34	32	21	39	0.52	9.3	88	32
ICSK-14	0.20	42	68	76	0.15	13	18	9.9	0.20	16	22	13
ICSK-15	2.0	90	322	427	1.5	46	168	107	1.3	47	157	145
ICSK-16	1.9	107	134	339	1.5	53	79	86	1.3	54	74	128
ICSK-17	1.2	193	122	215	1.0	108	63	46	0.78	109	55	65
ICSK-18	0.90	49	28	173	0.64	26	12	35	0.63	24	12	64
ICSK-19	0.30	138	33	81	0.09	81	8.1	10	0.09	61	7.1	9.6
ICSK-20	0.30	26	21	80	0.15	8.1	5.9	2.4	0.18	8.8	6.3	9.2
GAL-BB-037	0.90	32	105	260	0.16	1.4	21	5.2	0.16	2.1	25	7.1
GAL-KE-504	1.8	32	88	166	1.47	4.3	39	7.3	1.7	2.3	14	12
GAL-LM-062	3.7	23	76	177	< 0.1	0.53	4.6	0.85	< 0.2	< 1	7.1	1.4
GAL-PD-035	0.40	32	26	68	0.12	< 0.5	4.8	0.93	< 0.2	< 1	6.0	1.6
GAL-SN-051	8.5	905	810	1865	0.47	35	30	70	0.47	36	31	80
GALE-LV-001	0.20	10	20	44	0.21	2.7	12	8.2	0.15	2.5	10	13
GALE-PP-006	0.20	4.0	23	64	0.14	1.4	15	4.9	< 0.2	2.0	16	7.6
GAN-MI-003	0.30	11	32	63	0.18	1.0	6.9	2.3	0.17	1.5	8.7	4.6
GAP-BB-072	0.70	24	54	137	0.17	1.7	7.3	2.9	< 0.2	2.4	9.8	5.1
GAP-CA-011	0.70	24	37	108	0.50	4.5	12	6.6	0.51	5.4	14	11
GAP-CA-039	0.60	26	25	79	0.21	5.0	4.4	4.1	0.19	6.3	5.9	9.5
GAP-HN-098	0.40	35	38	115	0.16	5.0	7.8	3.7	0.18	6.9	7.3	6.6
GAP-MI-003	0.20	31	18	104	0.23	16	7.2	4.8	0.22	15	7.3	12
GAP-PO-067	0.20	34	19	71	0.16	7.6	8.7	4.6	0.17	7.6	11	8.4
GAP-RV-038	0.90	28	29	98	0.41	7.8	10	5.9	0.36	6.0	4.6	5.9
GAP-RV-133	0.50	45	68	214	0.30	12	20	9.9	0.31	11	18	15
GAP-SK-085	0.20	18	15	59	0.11	20	4.2	10	< 0.2	18	4.6	14
GAP-TV-047	0.20	25	25	111	0.13	13	5.3	4.0	< 0.2	12	5.1	12
GAPE-LV-002	0.20	13	15	44	0.10	4.3	4.3	5.5	-0.20	4.5	5.0	4.8

The cumulative distribution functions of the reactive metal contents as determined with 0.43 mol.l^{-1} HNO_3 and EDTA are quite similar and have the same order of magnitude. Figure 3 shows that a considerable part of the metals present in the studied soils are in a rather unavailable or inert form (total metal –reactive metal). Especially Zn with an average ratio of the reactive to the total metal content ($M_{re, HNO3/EDTA}/M_{tot}$) of 0.17 is largely in a chemically unavailable form. This is a rather surprising result since Zn is thought to be one of the more mobile elements (together with Cd) in soils.

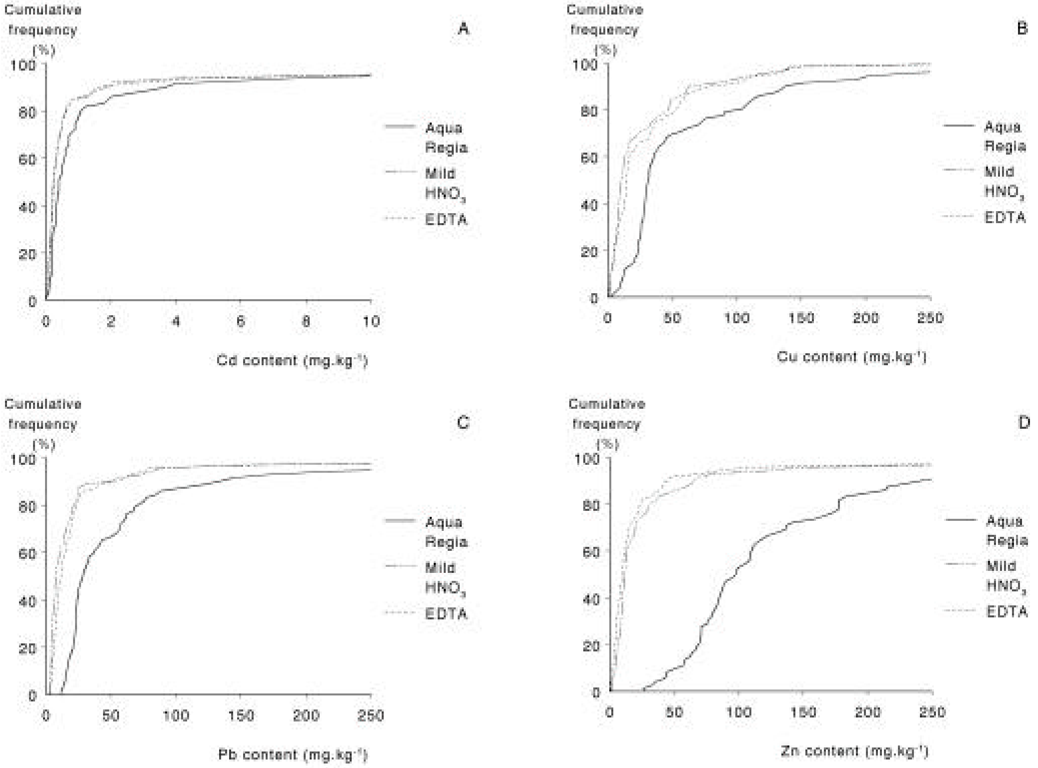

Figure 3 Cumulative distribution fractions of the different metal extracts for Cd (A), Cu (B), Pb (C) and Zn (D)

The order of metals according to their average reactive to total fraction is Cd (0.56) > Cu (0.38) > Pb (0.30) >Zn (0.17). This only reflects the average reactive to total fraction. For each metal a wide range of this ratio is found going from 0.05-1.0 for Cd, 0.01-0.9 for Cu, 0.04-0.7 for Pb and 0.01-0.6 for Zn. Figure 4 shows that there is some relationship between this ratio and the total metal content of the soil. At low concentrations both low and high ratio's are present. For high total concentrations the ratio's are generally confined to the higher reactive to total ratio's (in case of Cu, Pb and Zn, there is always one exception) which might indicate that anthropogenic raised metal levels are in a more available form.

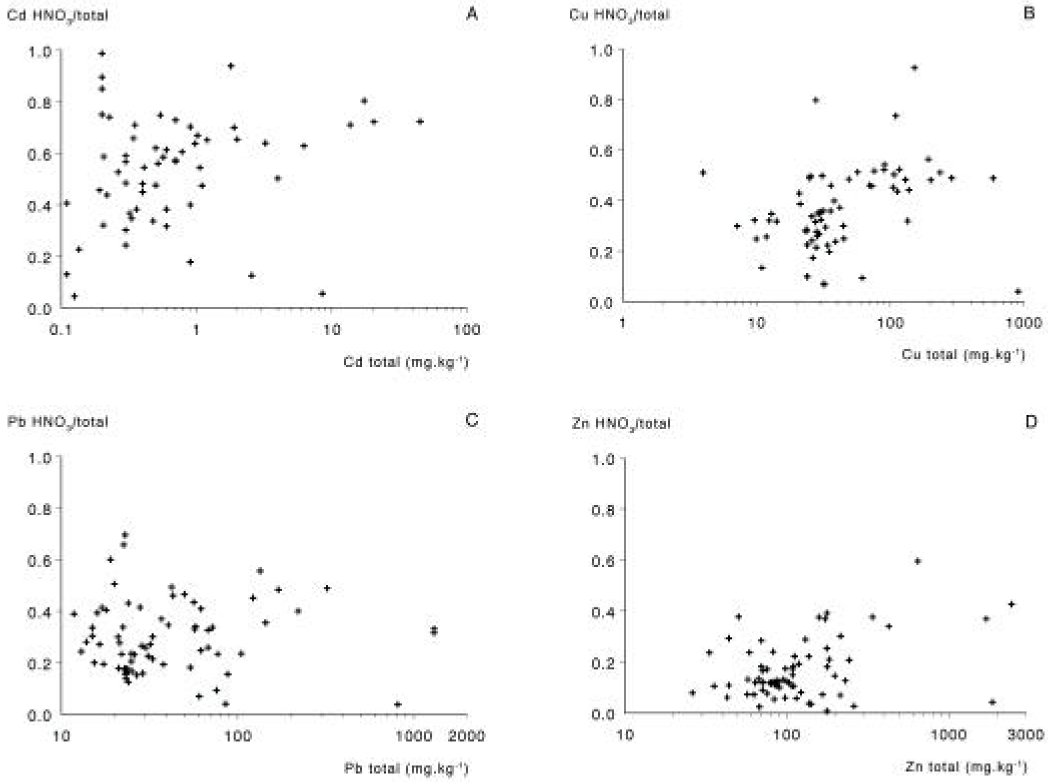

Figure 4 Relationships between the reactive to total metal content ratio and the total metal content of the soil for Cd (A), Cu (B), Pb (C) and Zn (D)

Relationships between reactive concentrations measured with a mild HNO_3 extraction and with EDTA

There was a considerable agreement between reactive metal concentrations measured with a mild (0.43 $mol.l^{-1}$) HNO_3 extraction and with an EDTA extraction as shown in figure 5. For Cd, Cu and Pb the EDTA extraction is somewhat stronger, whereas for Zn more is extracted with 0.43 $mol.l^{-1}$ HNO_3. Tipping et al. (2002) found also a close relation between 0.43 $mol.l^{-1}$ HNO_3 and EDTA extracts for organic rich soils in the UK although they found in general a larger amount extracted with HNO_3.

Table 3 gives the results for both the linear and logarithmic regression relations according to Eq. 1 and 2, respectively. The use of a limited concentration range in the case of a linear relation gives less strong relationships (with R^2 as measure) but lowers the error of the estimated value (se y-est) for Cd, Pb and Zn, which improves the predictions in the low concentration range. Considering the value of R^2 logarithmic relations give better results than linear relations. However a comparison of predicted and measured values shows that linear equations ultimately give better estimates than the logarithmic equation. In general the relationships derived do allow a reasonable estimate of the reactive metal content based on a mild HNO_3 extraction on the basis of available EDTA extraction data.

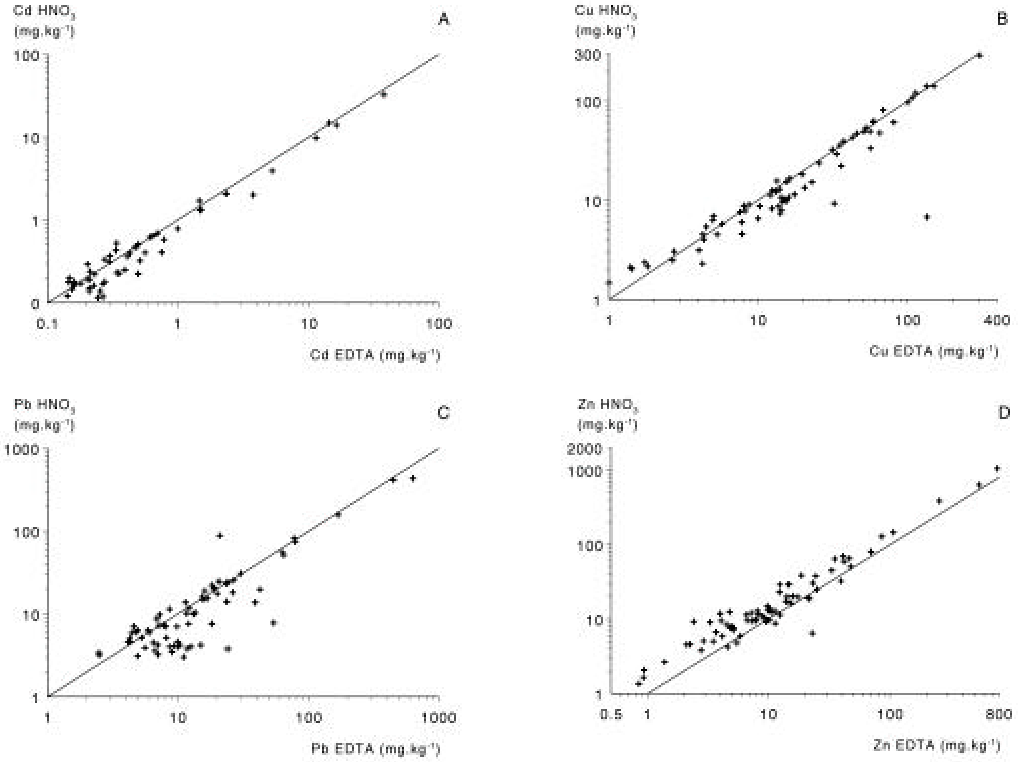

Figure 5 Comparison of measured reactive concentrations of Cd, Cu, Pb and Zn with a mild (0.43 mol.l^{-1}*)* HNO_3 *extraction and an EDTA extraction for Cd (A), Cu (B),Pb (C) and Zn(D).*

Table 3 Values for the regression coefficients in the linear and logarithmic relationship between reactive concentrations of Cd, Cu, Pb and Zn extracted by 0.43 mol.l^{-1} HNO_3 *and by EDTA (see Eq. 1 and Eq. 2).*

Metal	Linear relationships: whole concentration range			Linear relationships limited concentration range			Logarithmic basis: whole concentration range			
	Reg.coeff	R^2	se y-est	Reg.coeff	R^2	se y-est	Intercept	Reg.coeff	R^2	se y-est
Cd	0.873	99	0.360	0.820	73	0.0897	-0.094	1.065	91	0.203
Cu	0.879	89	15.3	0.840	79	15.1	0.0557	0.8938	87	0.187
Pb	0.774	95	15.4	0.839	60	11.1	-0.0294	0.9268	75	0.238
Zn	1.301	99	14.1	1.336	93	6.79	0.2442	0.9050	92	0.152

Relationships between reactive and total metal concentrations

To test the possibility to relate the reactive metal content to the total metal content and soil properties regression relations according to Eq. 3 were derived. Values for the various coefficients relating reactive and total soil concentrations of Cd, Cu, Pb and Zn (Eq. 3) derived for the 72 soils investigated in Slovakia and Hungary are shown in Table 4 and 5, while distinguishing between HNO_3 and EDTA, respectively. The explained variance for the metals Cd, Cu and Pb are reasonable, whereas the explained variance for Zn is distinctly lower. The relations between the reactive metal content as determined with EDTA give poorer predictions than those for HNO_3. The coefficient ß1 (for the total metal content) being close to 1 indicates almost linear relations for the metals Cd, Cu and Pb. For Zn this coefficient is larger than 1 which indicates an increasing ratio of the reactive to total metal content with an increase in the total metal content.

Table 4 Values for the coefficients ß0-ß3 in the relationship relating reactive (0.43 mol.l^{-1} HNO_3) and total soil concentrations of Cd, Cu, Pb and Zn, according to Eq. (3) derived for 72 soils in Slovakia and Hungary.

Metal	ß0	ß1	ß2	ß3	R^2	se y-est
Cd	-0.302	1.037			85.1	0.264
Cu	-0.382	1.0742	-0.377		80.2	0.232
Pb	-0.245	0.939		-0.192	75.4	0.238
Zn	-1.122	1.212	-0.339		65.0	0.315

Table 5 Values for the coefficients ß0-ß3 in the relationship relating reactive (0.05 M EDTA) and total soil concentrations of Cd, Cu, Pb and Zn, according to Eq. (3) derived for 72 soils in Slovakia and Hungary.

EDTA	ß0	ß1	ß2	ß3	R^2	se y-est
Cd	-0.440	0.926		0.176	86.1	0.224
Cu	-0.870	1.1256	-0.303	0.336	67.1	0.326
Pb	-0.237	0.856			67.0	0.259
Zn	-1.400	1.182			56.2	0.373

For the extraction of Cd with HNO_3, there is no relation with soil properties and the regression predicts a constant ratio between the reactive and total metal content. For Pb the regression relation predicts a decreasing reactive to total ratio with increasing clay content as follows from the negative value for coefficient ß3. This can be the result of Pb present in the lattice structure of oxides in the clay fraction of the soil. In case of an EDTA extraction, the signs are, however, opposite for both Cd and Cu and there is no relationship at all with soil properties for Pb and Zn. Similarly, the negative influence of organic matter (coefficient ß2) on the reactive to total ratio of Cu and Zn, in case of HNO_3, and of Cu only, in case of EDTA, is opposite to the expectation and not understood.

A comparison of the reactive metal concentrations thus estimated and the measured metal concentrations do also give an indication of the reliability of the estimates. Results thus obtained for the metals considered are presented in Figure 6. The figure shows that reasonable estimates of the reactive metal contents can be made for Cd, Cu, Pb, and Zn.

To evaluate how well the derived functions describe the reactive to total ratio, the ratio’s calculated from the regression functions were plotted against the ratio’s of the measured reactive to total concentrations. Figure 7 shows that the regression relations give a poor prediction of the reactive to total metal ratio. From this it can be concluded that the reasonable estimates as shown in figure 6 are largely the result of the correlation of the reactive metal content with the total metal content. This is in line with the results of the regressions showing that the reactive metal content can mainly be predicted as a function of the total metal content, whereas the differences in the immobile fraction are not simply captured by the range in soil properties.

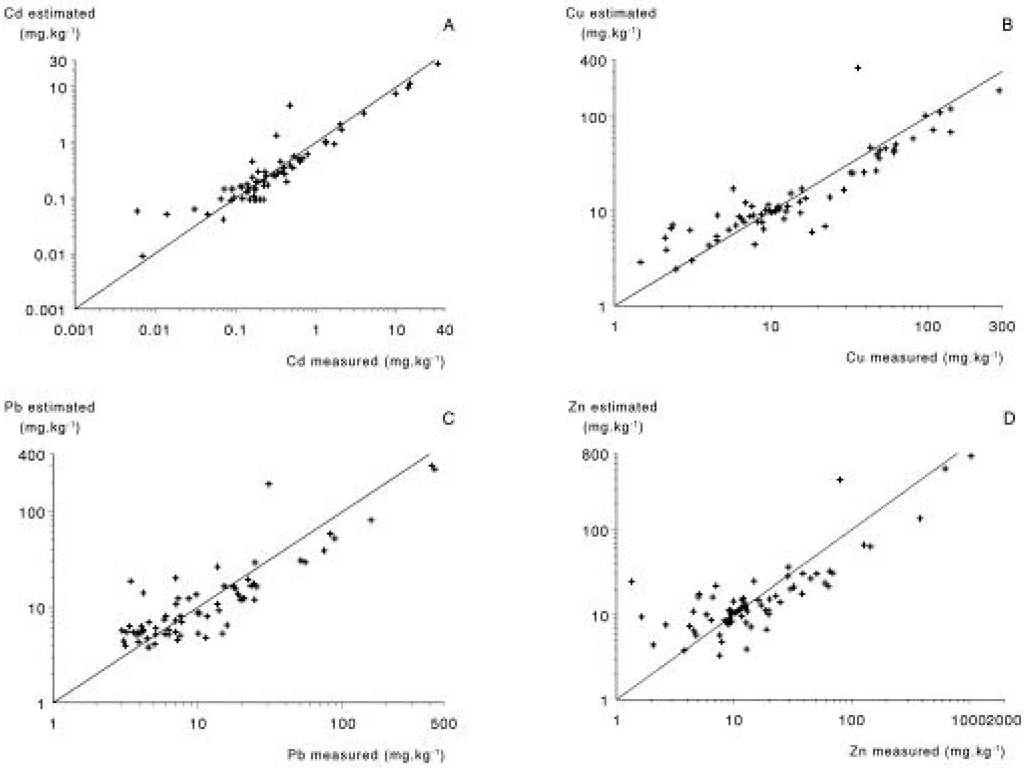

Figure 6 Comparison of measured reactive concentrations of Cd, Cu, Pb and Zn and estimated concentrations, using the logarithmic relationship between reactive and total metal concentrations (Eq.3) and the model parameters derived in this study (Table 2)

In case of Cd, soil properties did not influence at all the regression result (see Table 4) and this is reflected in the nearly constant predicted reactive to total Cd ratio, while the real ratio varies strongly.

Validation of relationships derived with a Dutch data set

Values for the various coefficients relating reactive (as determine with 0.43 mol.l^{-1} HNO$_3$) and total soil concentrations of Cd, Cu, Pb and Zn (Eq. 3) were also derived for a very large set of Dutch soils (Römkens et al., 2003). The results thus obtained are presented in Table 6.

Table 6 Values for the coefficients ß0-ß3 in the relationship relating reactive (0.43 mol.l^{-1} HNO$_3$) and total soil concentrations of Cd, Cu, Pb and Zn, according to Eq. (1) derived for 300 soils in the Netherlands (Römkens et al., 2003.)

Metal	ß0	ß1	ß2	ß3	R^2	se y-est
Cd	-0.089	1.075	0.022	-0.062	0.96	0.11
Cu	-0.331	1.152	0.023	-0.171	0.93	0.13
Pb	-0.263	1.089	0.031	-0.112	0.92	0.16
Zn	-0.703	1.235	0.183	-0.298	0.96	0.16

The Dutch relations also predict an almost linear relation for Cd not influenced by the clay and organic matter content. For Cu, Pb and Zn an expected negative correlation of the reactive metal content is found with clay. As expected, there is a positive influence of the organic matter content on the reactive metal content, although the effect is small except for Zn.

Comparison of the relations from this study with the results from the Netherlands gives insight in the general applicability of the derived regression relations.

A comparison of the reactive metal concentrations thus estimated and the measured metal concentrations is presented in Figure 8. The figure shows a similar good estimate for Cd by the Dutch relation. For the metals Cu, Pb and Zn the Dutch relationship generally overestimates the reactive metal content, specifically in the low concentration ranges, i.e. Cu, Pb and Zn contents below 50-100 mg.kg^{-1}. This implies that the availability of metals in Hungarian and Slovakian soils is generally less than in Dutch soils, even when correcting for differences in clay and organic matter content. Preferably, the relationships should thus not be applied outside the area where they were obtained.

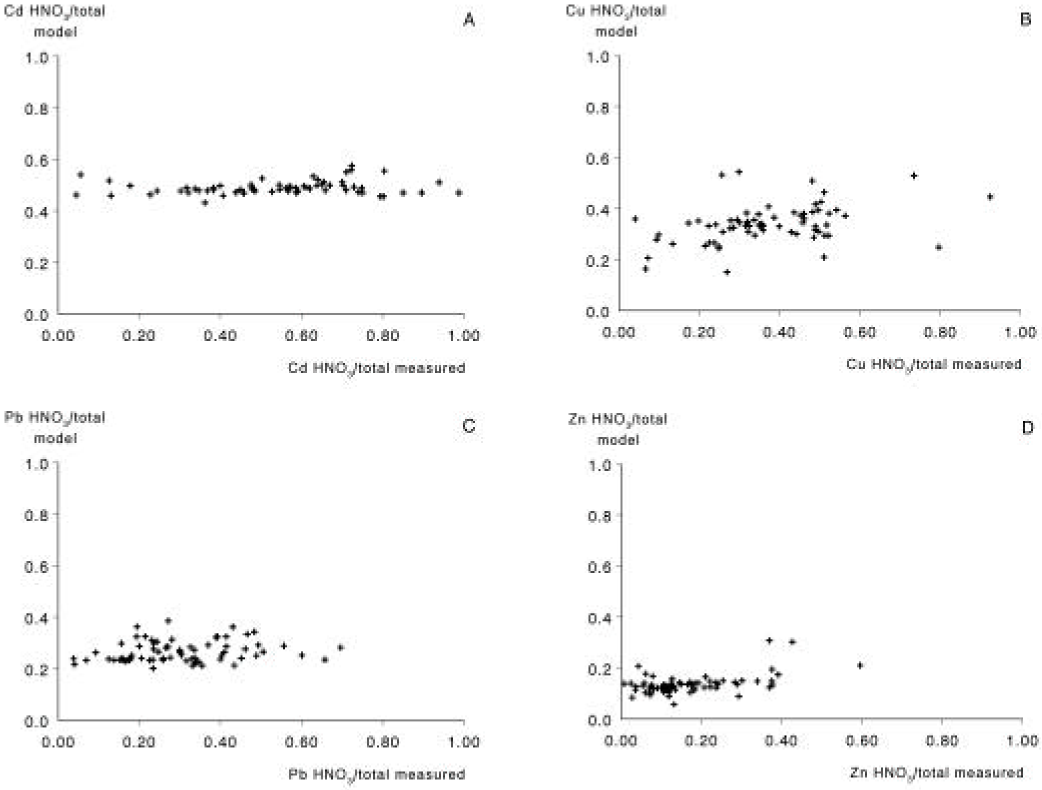

Figure 7 Comparison of estimated and measured ratios of the reactive to total concentrations of Cd (A), Cu (B), Pb (C) and Zn (D), using the logarithmic relationship between reactive and total metal concentrations (Eq.3) and the model parameters derived in this study (Table 4)

2.4.4 Discussion and conclusions

This study shows that a considerable part of the metals are present in a rather unavailable form in soils. This implies the possibility of large errors when predicting leaching and (plant) uptake using the total metal concentration in soils. From the metals studied, Zn has on average the lowest reactive to total metal ratio, followed by Pb, Cu and Cd the highest reactive to total metal ratio. The extractants EDTA and 0.43 mol.l^{-1} HNO_3 extract about the same amount of (chemically reactive) metal and do correlate well.

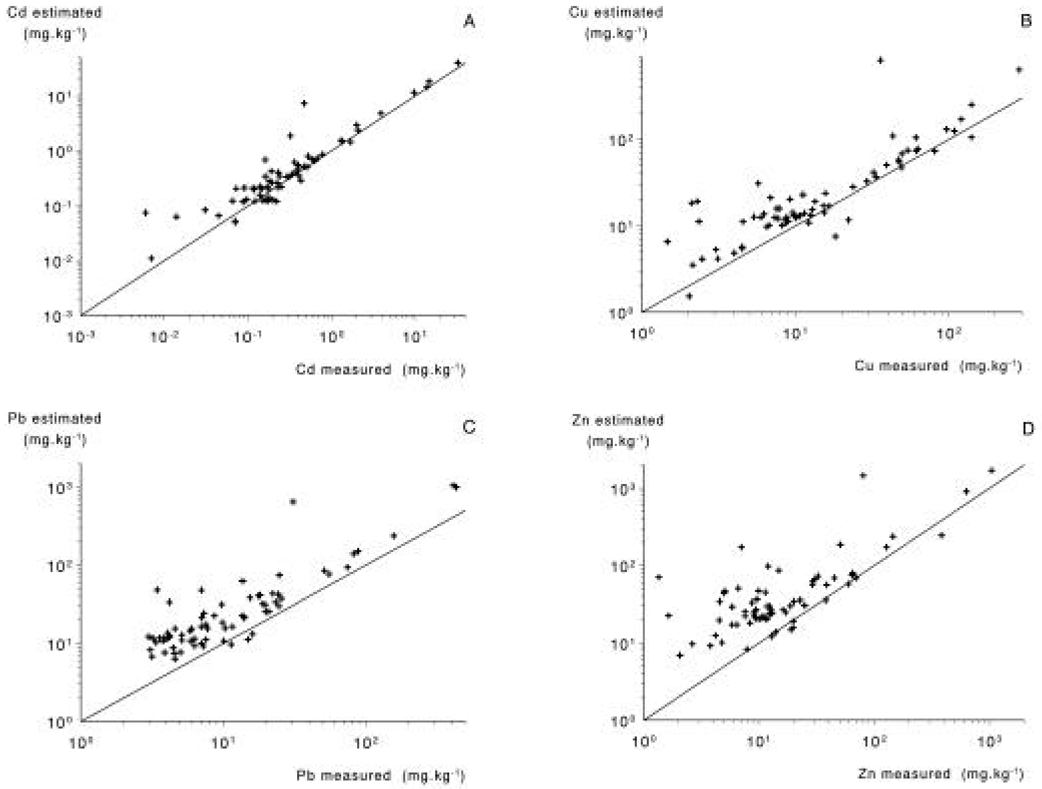

Figure 8 Comparison of estimated reactive concentrations of Cd (A), Cu (B), Pb (C) and Zn (D) and measured concentrations, using the logarithmic relationship between reactive and total metal concentrations (Eq.3) and the model parameters derived by Römkens et al. (2003) (Table 16)

For each metal considered there is a large range in ratios of reactive to total metal content. On average, a reasonable prediction can be made of reactive metal contents from total metal contents and the soil properties organic matter and clay content. using the regression relations described in this study. However comparison of the predicted with the measured reactive to total metal ratio shows a large variation. Using these relations large errors can be made for individual samples. This is specifically true in the low concentration range. The derived relations are completely empirical and can only to be used for the types of soil for which they were derived. The use of similar relations derived for other soils (Dutch dataset) show clear deviations, in this case an overestimation of the reactive pool.

The results of this study underlines the need to determine the reactive metal pool with a suitable extractant because the reliability of reactive metal pool estimates from the total pool and easily available soil properties, such as the clay and organic matter content, is limited for specific sites.

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2.5 Copper sorption and speciation in acid sandy forest soils

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Summary

Problems with the derivation of transfer functions based on activities are the few sorption studies in which metal activities are measured. Most studies focus on Cu sorption, but there are almost no measurements for the lower pH range at which the influence of Al might become important. Partition of trace metals in the acidic range is particularly important for acidified forest soils. Furthermore all studies are limited to topsoils whereas in the case of metal leaching subsoils are very important. To overcome those limitations, a laboratory study was carried out aimed at the extension of data for the derivation of transfer functions for Cu activities in the lower pH ranges. Batch adsorption studies were carried out with samples from acid forest soils at different depths.

In the equilibrium solution the Cu activity was directly measured with a cupric ion selective electrode. Environmentally Cu is of interest in the case of land use change of former agricultural land which received high loads of pig slurry. Measurements showed that Cu activities with an ion selective electrode is possible for acid sandy soils. For low total dissolved concentrations of Cu (below 20 $\mu g.l^{-1}$) measurements are unreliable. Activities calculated with a simple diprotic acid model for the complexation of Cu with DOC gave good results compared with measured Cu activities. The dependence of Cu sorption on pH and Ca activity could be described well for different soils. It was not necessary to include a parameter for Al to describe the partitioning of Cu in acid soils. The validated transfer function worked equally well for topsoils and subsoils despite possible differences in carbon quality at different depths.

2.5.1 Introduction

The partitioning of trace metals between the solid phase and the solution phase of the soil, by sorption processes together with complexation in the soil solution, is the most important process which regulates the concentrations of metals in soils under aerobic conditions (Mc Bride, 1989). Trace metal partitioning of a certain metal depends both on soil properties such as the organic matter content and soil solution properties such as pH, ionic strength and concentrations of complexing ligands.

Insight in and quantitative relationships which describe the influence of both soil and soil solution properties on trace metal partitioning are crucial to quantify the effects of soil pollution with trace metals such as leaching to groundwater and surface water, uptake by agricultural crops and exposure to biota. Furthermore quantitative relations which take into account soil and soil solution properties can be used to predict the effects of land use changes which may increase trace metal mobility (Römkens and Salomons, 1998) and the calculation of critical loads for trace elements on soil. Insight in and the ability to predict the effects of land user changes is actual because of the conversion of agricultural land into (semi) natural areas such as forests, heathlands and wetlands in several countries of the European Community. In Europe there is increasing interest in the use of the critical load approach in the abatement of atmospheric deposition of trace metals. One of the most important relationships in models to calculate critical loads for heavy metals is the description of partitioning as a function of soil and solution properties.

Several studies showed that sorption of trace metals can be described with the Freundlich equation according to.

$$Q_{Me} = K_f \cdot (Me)^n \qquad [1]$$

With Q_{me} the sorbed amount of metal Me (mol.kg^{-1}); K_f the Freundlich constant (mol^{n-1}.l.kg^{-1}); (Me) the concentration or activity of Me in solution (mol.l^{-1}) and n the Freundlich coefficient (-).

To account for soil and soil solution properties such as organic matter and pH, Freundlich equations were introduced with pH and organic matter dependent Freundlich constants (Boekhold et al., 1993). However these isotherms were limited to the use of a certain soil type. Bril (1995) and Elzinga et al. (1999) introduced pedotransfer functions based on the Freundlich isotherm for several metals which were derived and should be applicable for a variety of soils. These transfer functions are multiple linear regression functions and include soil properties as the organic matter and clay content, CEC, contents of oxalate extractable Al end Fe and solution properties as pH and concentrations of competing cations according to:

$$\log K_f = \beta_0 + \sum_{i=1}^{n} \beta_i \log x_i \qquad [2]$$

With x_i is a soil or soil solution property (e.g. % org. matter, H$^+$ activity), $ß_i$ is the regression coefficient related to soil or solution property x_i and $ß_0$ is the regression constant (intercept).
Most of the published transfer functions relate the sorbed metal to the concentration of metal in solution. Based on thermodynamic principles Bril (1995) derived transfer functions which relate the reactive metal content (adsorbed metal) to the activity of the metal ion in solution. The importance of transfer functions in terms of activity rather then in terms of total concentrations is underlined by the results of Pampura and Ustinin (1996), who showed that the adsorption isotherms of Cu in the presence and in the absence of organic acids differ when expressed in terms of concentrations but coincide when expressed in terms of activities.

Problems with the derivation of transfer functions based on activities are the few sorption studies in which metal activities are measured. Lexmond (1980) estimated the activity of Cu in solution with a resin method, Sanders (1982) measured the activity of Cu in equilibrium solutions of Cu batch adsorption experiments direct with the use of a cupric ion selective electrode. Despite the fact that both the studies of Lexmond (1980) and Sanders (1982) describe the effect of pH on Cu sorption there are almost no measurements for the lower pH range (below pH 4.5) at which the influence of Al might become important. Partition of trace metals in the acidic range is particularly important for acidified forest soils. Furthermore all studies are limited to topsoils whereas in the case of metal leaching subsoils are very important. Therefore with this study we want to extend the amount of data for the derivation of transfer functions based on activities and to extend these data to lower pH ranges. Furthermore we want to include soils from various depths. Batch adsorption studies where done for Cu in acid forest soils from different depths. In the equilibrium solution the Cu activity is directly measured with the use of a cupric ion selective electrode. The trace metal Cu was chosen because for copper we can measure the activity directly using a cupric ion selective electrode and because Cu forms strong complexes with DOC in solution which will have a pronounced effect on the activity of the trace metal in soil solution. Environmentally Cu is of interest in the case of land use change of former agricultural land which received high loads of pig slurry. Pig slurry can contain high concentrations of copper which was given to pigs to improve their growth performance and feed conversion rate.

Existing transfer functions based on activities as derived by Bril(1995) and Elzinga et al. (1999) will be evaluated on the data from the present study.

2.5.2 Materials and methods

Soils and site description

Soil samples were taken from forests of different stand age planted on former agricultural land around Sellingen in the north of the Netherlands (Römkens et al., in prep). All soils were classified as Gleyic Podzols (FAO) and planted with Oak (Quercus Robur). Soils were sampled from different depths (i.e. 0-10, 10-30, 30-60 and 60-100 cm below the mineral soil surface). Soils were analysed for organic matter content (loss on ignition), clay content, actual CEC ($BaCl_2$ non buffered pH) and exchangeable cations, potential CEC ($BaCl_2$, pH buffered at 8.2) and oxalate extractable iron and aluminium. All methods are described in Houba et al. (1995)

Table 1 Characteristics of the soils used

Sample	depth	pH	clay	organic matter	CEC ($mmol_c.kg^{-1}$)		exchangeable cations ($mmol.kg^{-1}$)			oxalate extractable ($mol.kg^{-1}$)	
	(cm)		(%)	(%)	actual	pH 8.2	Ca	Mg	Al	Al	Fe
F1	0-10	4.7	2	9.4	79.93	189.18	39.24	4.83	25.34	49.61	14.23
F2	10-30	5.45	1	6.7	114.31	198.29	49.2	3.63	15.68	57.62	12.16
F3	30-60	5.39	3	4.4	58.35	143.32	26.47	2.8	34.69	82.54	2.99
K1	0-10	3.26	1	9.6	53.41	155.04	6.16	1.94	16.41	16.84	23.25

The native contents of copper in these soils were determined with aqua regia as a measure for the total amount in the soil and with 0.43 $mol.l^{-1}$ HNO_3 and with EDTA to estimate the reactive metal content in the soil. All extraction methods are described in Houba et al. (1995).

Table 2 Aqua regia, 0.43 mol.l^{-1} and EDTA extractable Cu contents of the soils.

Sample	depth (m)	extracted metal (mg.kg^{-1}) aqua regia	0.43 mol.l^{-1} HNO_3	EDTA
F1	0-0.1	15.0	10.4	8.29
F2	0.1-0.3	15.0	9.3	7.29
F3	0.3-0.6	15.0	2.3	0.95
K1	0-0.1	15.0	1.1	0.53

Batch adsorption experiments

For each soil batch experiments were carried out at 3 pH levels and two electrolyte levels of respectively 0.01 and 0.001M $CaNO_3$ and 6 levels of added Cu ranging from 0-100 mg Cu per kg dry soil. For each soil 7 grams of soil were suspended in 80 ml of 0.01 or 0.001M electrolyte solutions with different concentrations of Cu. The soil suspensions were shaken 24 hours at slow speed. Then the samples were centrifuged and the pH and pCu was measured in the supernatant in the tubes, thereafter and the supernatant solution was passed through a 0.45 µm filter. The supernatant was split into two volumes, one for measurement of Cu, other metals and major elements with ICP-AES (or if necessary Cu on graphite-furnace AAS) and one for the measurement of DOC on a Shimadzu Carbon analyser.

Activity measurements

The activity of the cupric ion was measured using a cupric ion selective electrode. The electrode was calibrated according to a method developed by Avdeev et al. (1983). This method enables the calibration of the electrode for very low Cu-activities in solution (down to pCu of 19) from calculated activities using complexation with Ethylene diamine hydro chloride (En_2HCl)for which stability constants are known. The strong complexation of Cu with En_2HCl makes it possible to measure low activities at relatively high Cu concentrations. In soil solutions the concentration in solution is buffered by the complexation of Cu by DOC. The electrode was tested with a titration of $CuNO_{3,}$, En_2HCl.

Before every measurements series the electrode was calibrated with the measurement of the pH and electrode potentials of the Cu-ISE in a solution of 0.001 M $Cu(NO_3)_2$ with 0.015 M En_2HCl (Ethylene diamine hydro chloride) and 0.1 M $NaNO_3$ with 0, 2, 4, 5 and 7 ml 0.085 M NaOH. Figure 1 gives an example of such an electrode calibration. The electrode potential of the ISE was measured with a potentiometer in mV. The pH in the calibration solutions was measured with a combined glass electrode. Activities for the calibration points were calculated from the measured pH and concentrations of Cu, $NaNO_3$ and Etthylene diamine with the chemical speciation program (EPIDIM, Groenendijk, 1995) with the use of the complexation constants for Cu-En complexes from table 3. The electrode always showed Nernstian behaviour and the linear regression was always very good (r^2>0.995).

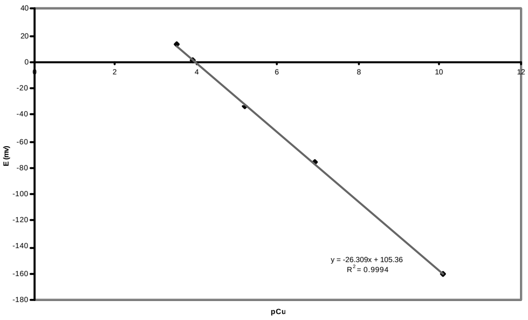

Figure 1 Electrode calibration

Table 3 Cu-En stability constants

Component	Ionic strength mol.l^{-1}	log K^0
ENH^+	0.092-0.286	10.008
ENH_2^{2+}	0.092-0.286	16.912
$EnCu^+$	0.113-0.295	10.562
$Cu(En)_2^{2+}$	0.113-0.295	19.646

Activities of Cu^{2+} and pH were measured directly in the supernatant after centrifugation. This was decided after measurements before filtration and after filtration gave very similar results and the earlier these measurements are done the less disturbance can be expected.

Calculation of activity

Beside the measurement the activity of copper and all other ions was also calculated from the measured composition of the soil solution, including all major cations and DOC with the chemical speciation EPIDIM (Groenendijk, 1995). Besides the complexation of cations with inorganic ligands the complexation of cations with DOC was calculated. Complexation of cations with DOC is modelled using a diprotic acid analogue for DOC (for details see Bril, 1995). Protonation of and complexation of cations with DOC is described with two reactions and corresponding equilibrium constants according to:

$$Cat^{n+} + HHUM^{-} \leftrightarrow Cat\mathrm{HHUM}^{(n-1)+} \quad pK_1 \qquad [3]$$

$$Cat^{n+} + HUM^{2-} \leftrightarrow CatHUM^{(n-2)+} \quad pK_2 \qquad [4]$$

Where *Cat* stands for cations (protons, base cations and trace metals). An overview of relevant pK_i values used in the model is given in Table 4. For DOC we assumed a site density of 10 $mol_c.kg^{-1}$ according to Römkens and Bril (1999). Formation constants for inorganic complexes were taken from the dataset by Ball et al. (1980).

Table 4 List of model parameters used to calculate the speciation of the soil solution

Element	pK_1	pK_2	Element	PK_1	pK_2
Al^{1*}	11.4	29.4	H^+	4.4	9.4
Ca^{2+}	3.6	6.1	Pb^{2+}	5.5	10.0
Cd^{2+}	4.0	7.9	Zn^{2+}	4.0	8.2
Cu^{2+}	6.5	11.4	$Fe(III)^{1*}$	15.2	34.5

[1]: also mixed Fe-Al-DOC complexes are taken into account

*: for both Al and Fe(III) the complexes used here are $MeHUM^+$ for pK_1 and $MeHUM(OH)_2^-$ for pK_2 respectively.

2.5.3 Results and discussion

Heterogeneity of used soil material

Contents of organic matter and heavy metals were determined (aqua regia) in several subsamples from the bucket with the sampled material, to determine the heterogeneity of the used material. The heterogeneity for organic matter was very small with a relative standard deviation of 0.8-2.9% and a moderate heterogeneity for the contents of heavy metals of 4.8-8.7% for Cd, 4-8% for Pb and somewhat higher 4-20% for Cu and Zn 5-20%.

Determination of copper activity

Comparison of the copper activities measured with the ISE with concentrations in solution shows a large variation (see figure 2a). The ratio between the activity and concentration in solution ranges between approximately (just below) 1 and 10,000. The difference between activity and concentration is almost solely the result of complexation of Cu with DOC in solution.

Measurements of the activity with the ISE no always gave reliable results. Within each series of copper additions (single isotherm) for a certain soil at constant pH, DOC and Ca concentration an increase in the ratio between activity and concentration is expected. This was however not always the case. To obtain a set of reliable data on measured activities dataseries without this expected trend were excluded. It appeared that part of the measured activities at the lowest concentrations in solution (first points (without copper addition) in isotherms) were not in agreement with the expected trend. Problems with measurements at low Cu concentrations were also reported by Sanders (1982) and Avdeev et al. (1983). Most problems were found for the subsoil because this soil has the lowest Cu content in combination with the lowest DOC concentrations. Furthermore problems there were problems with activity measurements for samples for which base was added to raise the pH. This problem is possibly due to the dissolution of organic matter.

Figure 2b shows the comparison between calculated and measured activities. Calculated activities compare well with measured activities. At the higher end of the range the calculated activity is somewhat underestimated, possibly due to a decreasing affinity with increasing copper concentration, whereas at the lower end of the activity range calculated activities are somewhat overestimated.

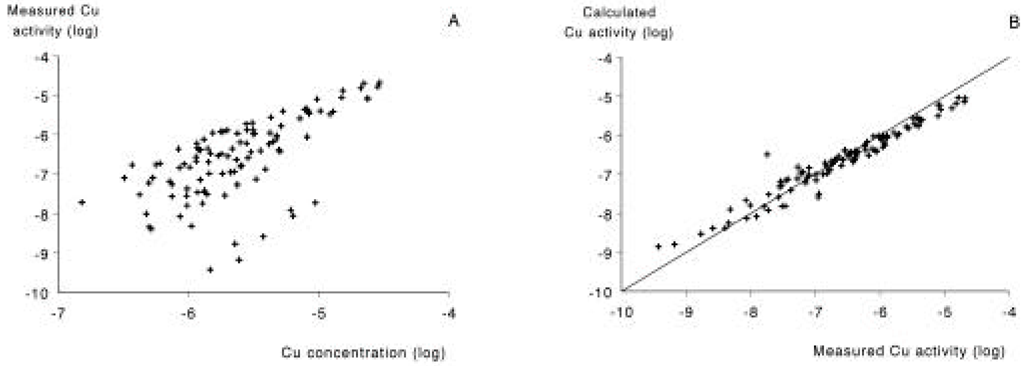

Figure 2 Measured Cu activities versus concentrations in solution (A) and calculated activities versus measured activities (B) for all adsorption experiments.

Adsorption

Adsorption is calculated from the difference in added amount of copper in solution minus the amount in solution calculated from the measured concentration plus the native copper content as measured by extraction with $0.43 \mathrm{mol.l}^{-1}$ HNO_3. Figure 3 shows for two soils the adsorption isotherms as a function of the concentration Cu in solution for different levels in pH and $CaNO_3$ concentration. The figure clearly shows the effect of pH and electrolyte concentration on the sorption of Cu by the soil.

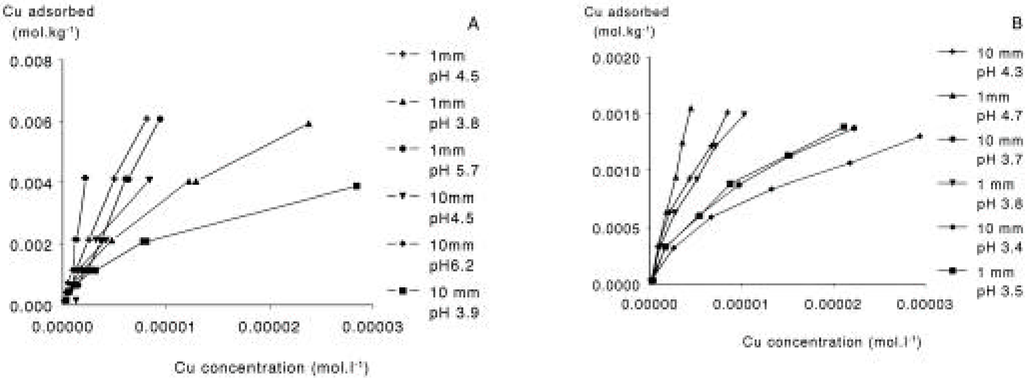

Figure 3 Adsorption isotherms for sample F1 (0-10cm depth; A) and sample F3 (30-60 cm depth; B)

Logarithmisation of the Freundlich equation results in a linear function according to:

$$\log Q_{Me} = \log K_F + n_F \cdot \log(Me) \qquad [3]$$

Plotting of the log of the adsorbed concentration Q_{Me} against the log of the metal activity in the soil gives, in case the adsorption can be described with a Freundlich equation, a linear line with intercept K_F and slope n_F.

Figure 4 shows for both samples F1 and F3 linear relations between the log of Q_{Cu} and the copper activity.

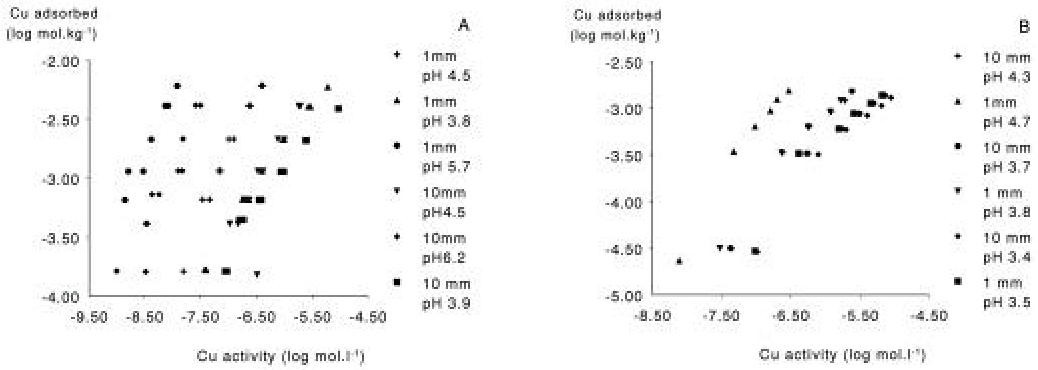

Figure 4 Linearised adsorption isotherms for sample F1 (0-10cm depth; A) and sample F3 (30-60 cm depth; B)

The different linearised adsorption isotherms are (almost) parallel to each other and thus have the same slopes. The different intercepts are caused by the differences in the Freundlich constant which depends on pH and electrolyte concentration. Coefficients for pH and Ca-activity in the transfer function according to equation 2 can be determined by regression analysis relating log Q_{Me} (explained variable) to the log activity of Ca, the log activity of Cu and the pH according to:

$$\log Q_{Me} = A + b \cdot pH + c \cdot \log(Ca) + n_F \cdot \log(Me) \qquad [4]$$

or by linear regression relating log Me (explained variable) to log Q_{Me} and pH and calcium activity according to:

$$\log(Me) = D + q \cdot pH + r \cdot \log(Ca) + s \cdot \log Q_{Me} \qquad [5]$$

Equation [5] can be rewritten in the form of equation [4] with $n_F=1/s$, $b=-q/s$, $c= -r/s$ and $A=-D/s$. Ideally the results of both regressions are identical to each other. However because these relations will never explain 100% of the variance it makes a difference whether the relationship is optimised to reduce the sum of squares in log Q_{me} (equation [4]) or the relationship is optimised to the lowest sum of squares for log (Cu). Table 5 lists the optimised parameters for both methods expressed as parameters for equation 4 so they are directly comparable.

Table 5 Optimised parameters regression functions

	eqn. 4			eqn. 5		
sample	b	c	nF	b	c	nF
F1	0.67	-0.57	0.79	0.78	-0.61	0.91
F2	0.62	-0.34	0.78	0.68	-0.36	0.83
F3	0.62	-0.44	0.85	0.66	-0.47	0.91
all				0.78	-0.56	0.92

The parameters from the regression analysis were all highly significant. The optimised parameters for the different regression methods compare well with each other. Regression on field data for which the variation in adsorbed metal contents are small for comparable soils and for which metal contents correlate well with soil properties as the organic matter content large differences between the two methods can be found. Because in these experiments both the adsorbed amount as the solution concentration were manipulated both methods give significant results. The Freundlich coefficient and the coefficient for the pH dependence for the three soils are quite similar. The coefficient for Ca activity however differs for the different soils. Regression analysis for the data on all three soils (last row in table 5) gives good results with an explained variance of 95%.

In acid soils concentrations of Al and the occupation of the exchange complex by Al are much higher than in (near) neutral soils. It was therefore expected that Al may have influence on Cu-adsorption in acid soils. Regression analysis in which the activity of Al was introduced as an explaining variable however did not improve the regression analysis. This does not mean that Al does not influence Cu adsorption, however the strong correlation between pH and Al activity possibly hides the effect of Al. From the good results of the regression even for low pH values it can be concluded that the dependence of adsorption on acidification can be described with dependence on pH.

Validation of transfer function

The transfer function by Bril (1995) is tested by comparison of the activities calculated with the use of the transfer function from solid phase data with the activities calculated with the speciation model. This procedure is represented schematically in Fig. 5. This procedure can also be used in the case that no measured activities are available. In this case we choose for this method because the validation of the speciation model showed good agreement between measured and calculated activities and with the use of calculated activities all adsorption data can be used also for those measurements for which reliable activity measurements failed.

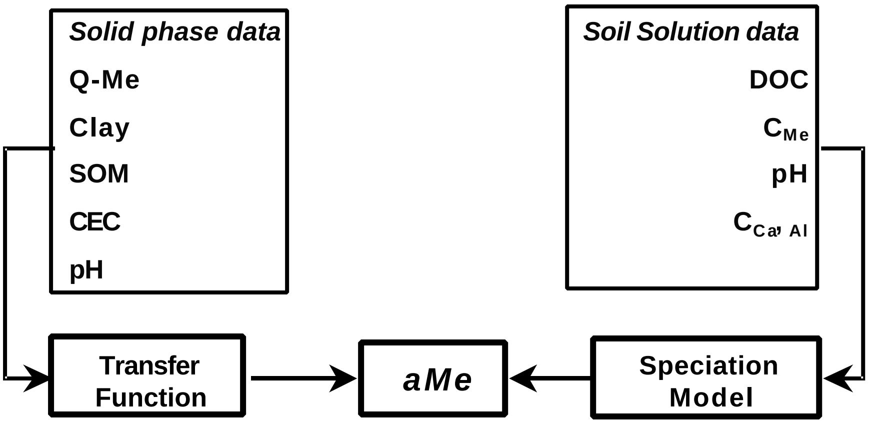

Figure 5 Schematic diagram of comparison of activities calculated with a transfer function and with a speciation model.

Figure 6 shows the comparison between the activities calculated with the use of the transfer function and those calculated with the speciation model. The figures shows good agreement for the soils F1, F2 and F3 within the activity range between $-9<\log a_{Cu}<-4$. This is a common range of activities found in these soils. The calculated activities for soil K1 however are overestimated by the transfer functions.

The transfer function estimates equally well activities for the samples F1, F2 and F3. The model is able to account for differences in soil properties of these samples (mainly CEC and organic matter content) and works equally well for top soils (F1, F2) and subsoils (F3).

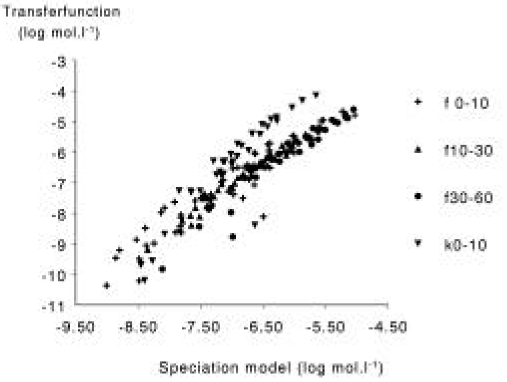

Figure 6 Comparison of Cu activities calculated with the transfer function with activities calculated with the speciation model

2.5.4 Conclusions

Measurements of Cu activities with an ion selective electrode is possible for acid sandy soils. For low concentrations of Cu (below 20 µg.$^{-1}$.measurements are unreliable. Activities calculated with a simple diprotic acid model for the complexation of Cu with DOC give good results compared with measured Cu activities.

The dependence of Cu sorption on pH and Ca activity can be described well for different soils. It is not necessary to include a parameter for Al to describe the partitioning of Cu in acid soils. The validated transfer function works equally well for topsoils and subsoils despite possible differences in carbon quality at different depths.

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2.6 Assessment of soil - solution transfer functions for cadmium and copper

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Summary

The goal of the research presented in this paper is to study the sorption behaviour of two major metals, cadmium and copper, up to low pH ranges and to derive reliable soil- solution transfer functions for soils of Hungary. Twelve representative soil samples of Hungary were collected and experiments were performed to analyse 252 chemical equilibria of Cd and Cu sorption. The Freundlich constants were calculated and harmonised with soil characteristics, by optimising the Freundlich exponent. In this way soil-solution transfer functions, while accounting for differences in major soil properties (pH, organic matter and clay content) were determined and interpreted for Cd and Cu. Results showed that free metal ion activities can be derived well by measuring dissolved metal concentrations and major ions in the soil solutions, including pH, Ca and DOC. In case of Cu, the calculated Cu ion activities compared well with the measured activities, giving confidence to the used speciation model. More important, however, the results showed that the use of a transfer function, allowing to derive the free metal ion activity from the solid phase content while accounting for the effect of pH, clay content and organic matter content, gives almost equally good results. The fact that two independent concepts (transfer function approach and speciation calculations) compared well with activity measurements for Cu confirms the applicability of the transfer function approach. Using these transfer functions the chemical risk of cadmium or copper ion mobilisation was assessed. Specifically, the risk of ground water contamination with cadmium was illustrated for soils even with a relatively low Cd content, but also a low pH and Ca concentration (e.g. forest soils). It directly shows how contamination can be limited by influencing those properties by e.g. liming. Soil-solution transfer functions can thus be used in models and decision support systems predicting impacts of e.g. land use changes and management practices, including those aimed at solving environmental problems and contributing to the protection of our environment.

2.6.1 Introduction

During the last century, the metal content (specifically cadmium, copper, lead and zinc) in most soils has increased considerable as a result of atmospheric deposition and application of sludge, manure, fertilisers and other soil amendments (e.g. Moolenaar and Lexmond, 1998). Risks that are associated with the presence of excess amounts of metal in soil include leaching to the groundwater, uptake by plants and effects on soil micro-organisms and, eventually the entire food chain as a results of metal transfer from micro-organisms to higher organisms. Concern about the input of heavy metals in forests, is related to the impact on soil organisms and the occurrence of bioaccumulation in the organic layer (Bringmark and Bringmark, 1995; Bringmark et al., 1998; Palmborg et al., 1998). With respect to copper and zinc, the possible occurrence of deficiencies in view of forest growth is another relevant aspect. An excess input of heavy metals in agriculture may cause agricultural products with unacceptable levels of heavy metals and even reduced crop production (Alloway, 1990). To protect both soil organisms and human beings from adverse effects, soil quality standards have been developed in most countries. The levels of protection are usually based on the protection of the food-chain (risks associated with food intake by higher animals and human beings), protection of soil organisms (based on ecotoxicological data) or direct uptake by children (based on toxicological data). The majority of these standards is currently based on the total metal content of the soil as determined by a pseudo-total Aqua Regia destruction (hot concentrated HCl and HNO_3).

The drawback of using a critical total metal content in the solid phase is that the toxic effects of heavy metals depend strongly on the bioavailability of metals. In general, dissolved metal concentrations (or even free metal ion activities) strongly determine the effects on microbiota/soil fauna. This is also true for effects on vascular plants through metal uptake, on ground water through leaching and on terrestrial fauna through accumulation in the food chain. In some cases (e.g. for arthropods), effects are partly due to consumption of soil solid material. However, in most cases, toxic effects on micro-organisms and soil fauna are mainly due to elevated bioavailable concentrations in soil water (Belfroid, 1994; Van Straalen and Bergema, 1995). In order to derive critical dissolved metal concentrations, transfer functions relating metal contents in the soil to dissolved metal concentrations as a function of soil properties, such as pH and organic matter content, are a powerful tool.

The sorption of heavy metals onto soils and soil components has been intensively studied. Mc Grath (2000) evaluated the environmental risk of heavy metal excess and concluded that copper can be toxic to soil organisms, phytotoxic and zootoxic, while cadmium can be dangerous for human health. Alloway (1999) studied the inputs of heavy metals in England and Wales, in the period 1995 – 1997. Most of the total annual input for copper derived from animal manure (39%) and from atmospheric deposition (33%). The total annual input of cadmium was related to the atmospheric deposition (50%) and fertilisers and lime (34%). These figures demonstrate that cadmium and copper have maybe the highest environmental risks. As a consequence of this cadmium and copper are studied in the present paper.

In the literature, various transfer functions have been derived up to now. The most simple ones, are linear relationships relating total concentrations of the metal ions in solution (cMe) to total metal contents (e.g. Janssen et al., 1996), whereas other include the solution speciation by relating free metal ion activities (aMe) to the total soil metal content in a non-linear way (e.g. Sauve et al. 1998, Sauve et al. (2000). Complexation of metal ions with DOC is of importance, especially for Cu and Pb. Up to now, however, the impact of pH and Ca on the soil-solution transfer has not been studied systematically up to a low pH level. The goal of the present paper is to study the sorption behaviour of cadmium and copper, and to derive reliable soil / solution transfer functions for soils of Hungary. The basis for the evaluation of the sorption experiments is a general equation of heavy metal sorption is the Freundlich equation according to:

$$Q_{Me} = K_F \cdot (a_{Me})^{nF} \tag{1a}$$

or

$$\log(Q_{Me}) + n_F \cdot \log(a_{Me}) = \log(K_F) \tag{1b}$$

Where (Bril, 1995):

$$\begin{aligned}\log(K_F) = {} & \beta_1 \cdot pH + \beta_2 \cdot \log(\text{clay},\%) + \beta_3 \cdot \log(\text{humus},\%) + \beta_4 \cdot \log(\text{Al},\%) \\ & + \beta_5 \cdot \log(\text{Fe},\%) + \beta_6 \cdot \log(\text{DOC}, \text{mg}/\text{l}) - \beta_7 \cdot \log(\text{Ca}^{2+}, \text{mol}/\text{l})\end{aligned} \tag{2}$$

Equation (1) characterises the heavy metal distribution between the solid and solution phase of the soil as a Freundlich function, while Equation (2) takes into consideration the soil characteristics, which may have an influence on the Freundlich constant (K_F), The combination of Equation (1) and (2) can be regarded as a general soil / solution transfer function., with independent soil and solution properties as predictor variables. In this paper, we derive a general soil / solution transfer function for Cd and Cu on the basis of well-established experimental results.

2.6.2 Methods

Selected soil samples, metal contents and soil properties

On the basis of the previous considerations, it was essential to select representative soil samples, which characterise a wide range of those soil properties that may influence the heavy metal distribution in soils. Well-selected soil samples and well-established experiments are needed to get reliable soil / solution transfer functions for Cd and Cu, which are valid in soils of Hungary. From 33 representative soil samples of Hungary – which had been taken to determine the *in situ* soil/solution partition coefficient of heavy metals in field moist soils – 12 soil samples were selected for the sorption experiments.

The 33 sites - contaminated with Cd, Cu, Pb or Zn - were sampled at the very beginning of spring. The sampling time was based on three key factors. At this time, the moisture content of soils was high and sufficient in-situ solution could be extracted for analyses. The soil surface and the solution phase were supposed to be in chemical equilibrium after the long wintertime. The soil solution composition was considered to be characteristic and stable, not yet influenced by soil microbial life and by the plant root activity.

Among the 12 representative soil samples 10 contaminated samples were taken from the Soil Information and Monitoring System of Hungary (SIMS), which had been developed for the sake of sustainable land use and rational soil management. The SIMS contains 1236 representative sampling sites, including polluted soils. A long-term field experiment with heavy metals set up in Gyöngyös was also selected. In this experiment different heavy metal doses were mixed into the ploughed layer (0 - 20 cm) in 1994 and the fate of heavy metals has been followed as a function of time. The control treatment was sampled (Gyöngyös 0). The B17 long-term fertilisation experiment at Karcag was also selected. This experiment started in 1967 to study the effect of fertiliser doses (N, P, K) on the crop yields (wheat and maize). The sample was taken from the plot of the highest NPK dose (B1732 II/20).

The ‘plant available’ soil solution fraction (pF < 4.2) was extracted from the field moist soils, taken from the 0-20 cm top-layer. The *in situ* soil solution was analysed in details (pH_{CaCl2}, DOC-, Cd-, Cu-, Al-, Fe-concentration, etc.). The soil properties, related to the chemical equilibria of heavy metals in soils were also determined (humus content, clay content, total Cd-, Cu-, Al-, Fe- content, etc.). The total heavy metal content was determined by microwave digestion. The reactive heavy metal content was determined according to the Lakanen - Erviö method (Lakanen & Erviö, 1971).

The European Research Network on Trace Elements also used this method as a reference method for a number of microelements (Sillanpaa & Jansson, 1992). The heavy metal content in the extract was measured with ICP - AES. The properties of the selected 12 soil samples are shown in Table 1. The relevant soil parameters covered a wide range in order to ensure the reliability of the soil / solution transfer functions for Hungarian soils.

Table 1 The properties of the selected soil samples used for the experiments.

sample no.	sample name	FAO soil type	humus content %	clay fraction %	Al content total %	Fe content total %	pH $CaCl_2$	DOC soil solution mg.l^{-1}	Cd soil total mg.kg^{-1}	Cu soil total mg.kg^{-1}
30	S4920	Histosols	28.20	13.28	2.81	2.31	6.81	223	0.48	29
1	E7405	Fluvisols	7.44	45.99	1.18	1.25	5.93	136	0.41	28
2	E9105	Arenosols	6.44	35.36	3.37	2.69	5.42	100	2.55	62
9	I0615	Fluvisols	4.16	46.80	3.51	3.20	5.51	91	0.78	36
8	I0215	Vertisols	3.41	55.93	3.69	3.10	5.85	127	1.06	45
29	B1732 II/20	Phaeozem	3.13	37.87	3.16	2.92	4.86	39	0.21	26
15	Gyöngyös0	Luvisols	2.83	37.31	3.17	2.54	6.57	73	0.22	24
7	S4810	Fluvisols	2.76	35.01	3.23	2.74	6.38	55	3.23	91
11	I1415	Fluvisols	2.60	31.57	2.32	2.13	4.94	72	0.11	13
32	S5319	Arenosols	2.20	9.72	1.04	1.47	6.08	109	0.14	152
4	I1810	Luvisols	1.32	8.79	0.89	1.26	6.66	92	0.09	110
14	I2715	Arenosols	0.72	4.19	0.64	1.09	3.75	35	0.02	7
	minimum		0.72	4.19	0.64	1.09	3.75	35	0.02	7
	maximum		28.20	55.93	3.69	3.20	6.81	223	3.23	152
	max./min.		39	13	6	3	2	6	162	21

The sorption experiments

The sorption experiments were carried out in order to determine the soil / solution transfer functions for cadmium and copper. Therefore all significant factors were taken into account when the experiments were planned.

The experimental conditions

In all 12 soils, electrolyte concentrations of 0.002 M, 0.01 M and 0.05 M were used. Two samples – containing the highest and the lowest humus content – were analysed with lower electrolyte concentrations too (0.001 M, 0.005 M and 0.025 M). The concentration ratio of 25 (0.05/0.002 or 0.025/0.001) gave the possibility to quantify the effect of the electrolyte concentration. $Ca(NO_3)^2$ was chosen as background electrolyte, since nitrate-ions cannot be considered to be typical complex forming ligands. Using calcium ions – what is usually the major cation in soils – large dispersion of humic acids cannot be expected to occur, thus the separation of liquid and solid phase after equilibration is not difficult.

The pH of the soil suspension was modified with a strong acid. The 0.1 M HNO_3 concentration assured that small acid quantities were sufficient to be used: 2.5 ml, 1.0 ml and 0.0 ml 0.1 M HNO_3 were added to the soil samples. The concentrations of the metal stock solution were 100 mg Cd.l^{-1} and 400 mg Cu.l^{-1} (both as nitrate) in 0.01 M HNO_3 (to prevent precipitation of metal oxides). 2 ml and 0 ml stock solution were given to the soil samples. In each experimental series 3 Ca levels, 3 pH levels and 2 Cd and Cu levels, that is 18 soil / solution equilibria were studied. During the sorption experiments 14 experimental series were carried out and 252 equilibria were established.

The experimental procedure

At each electrolyte level: 10.0 g soil and 90 ml background electrolyte were put in 6 centrifuge tubes and were equilibrated on a slow shaker overnight (about 16 hours). The soils were pre-adjusted to the background electrolyte, since re-wetting of air-dry soil samples took time. The overnight equilibration was supposed to be enough for soil conditioning. Then the 6 tubes were split into 2 groups of 3 tubes. 0 ml or 2 ml stock metal solution were given to group I or group II, respectively. The heavy metal treatment corresponded to 20 mg Cd and 80 mg Cu addition per kg soil.

Within each group, 2.5 ml, 1.0 ml and 0.0 ml 0.1 M HNO_3 were added to the first, to the second and to the third tube, respectively. Finally, all volumes were adjusted to 100 ml with the appropriate background electrolyte. The 2 * 3 design assured a reasonable pH and metal concentration range in the final solutions. Shaking was carried out for about 16 hours at room temperature to reach a stable equilibration.

The set up of the experiments is demonstrated in Table 2, what shows the effect of pH and electrolyte concentration on DOC. The soil solution concentration at field capacity is about 0.01 M in ‘normal’ soils of the temperate region and this concentration may increase to about 0.05 M around the wilting point (Bolt & Bruggenwert, 1978). So our experiment covers the potential range of solution concentrations under field condition. Our experimental results proved that the DOC content in the equilibrium soil solution was greatly influenced by the pH value and by the EC value of the solution phase.

Table 2 The effect of the experimental conditions on the DOC of the equilibrium soil solutions.

calcium-nitrate M	added HNO_3 ml	Soil No.	EC mS.cm^{-1}	pH	DOC mg.l^{-1}	Soil No.	EC mS.cm^{-1}	pH	DOC mg.l^{-1}	Soil No.	EC mS.cm^{-1}	pH	DOC mg.l^{-1}
0.002	0.0	30	0.57	7.07	149	1	0.50	6.52	119	2	0.48	6.31	40
0.002	1.0	30	0.66	6.98	146	1	0.58	6.23	86	2	0.58	5.92	35
0.002	2.5	30	0.78	6.78	143	1	0.75	5.79	53	2	0.74	5.75	34
0.010	0.0	30	2.10	6.92	110	1	2.10	6.20	53	2	2.13	5.90	30
0.010	1.0	30	2.16	6.81	111	1	2.16	5.90	50	2	2.20	5.64	28
0.010	2.5	30	2.25	6.64	114	1	2.28	5.47	37	2	2.25	5.38	24
0.050	0.0	30	7.60	6.64	88	1	7.70	5.89	45	2	8.00	5.66	26
0.050	1.0	30	7.60	6.50	85	1	7.70	5.57	36	2	7.80	5.42	24
0.050	2.5	30	7.60	6.35	83	1	7.80	5.08	28	2	7.70	5.11	20
0.002	0.0	9	0.44	6.20	45	8	0.48	5.90	39	29	0.62	5.15	11
0.002	1.0	9	0.56	5.71	33	8	0.58	5.37	32	29	0.74	4.81	12
0.002	2.5	9	0.75	5.17	25	8	0.75	5.37	21	29	0.93	4.46	6
0.010	0.0	9	2.15	5.70	32	8	2.10	5.90	28	29	2.38	4.84	5
0.010	1.0	9	2.22	5.30	25	8	2.15	5.54	24	29	2.46	4.58	9
0.010	2.5	9	2.38	4.86	19	8	2.30	5.12	19	29	2.60	4.22	10
0.050	0.0	9	8.20	5.26	22	8	7.80	5.58	28	29	8.90	4.61	2
0.050	1.0	9	8.30	4.91	18	8	7.80	5.23	23	29	9.00	4.32	1
0.050	2.5	9	8.20	4.47	17	8	7.80	4.85	22	29	9.00	4.02	4
0.002	0.0	15	0.58	6.56	26	7	0.54	6.48	15	11	0.53	5.26	13
0.002	1.0	15	0.67	6.11	21	7	0.66	6.04	10	11	0.65	4.72	8
0.002	2.5	15	0.84	5.68	9	7	0.84	5.61	5	11	0.84	4.21	10
0.010	0.0	15	2.30	6.38	22	7	2.26	6.20	6	11	2.33	4.85	7
0.010	1.0	15	2.38	5.96	14	7	2.33	5.72	1	11	2.41	4.41	8
0.010	2.5	15	2.46	5.56	7	7	2.46	5.36	0	11	2.52	3.94	9
0.050	0.0	15	8.30	6.10	17	7	8.70	6.21	3	11	8.80	4.57	5
0.050	1.0	15	8.30	5.68	7	7	8.70	5.60	0	11	9.00	4.15	6
0.050	2.5	15	8.30	5.37	6	7	8.80	5.22	0	11	9.00	3.74	9
0.002	0.0	32	0.55	6.48	21	4	0.53	6.82	26	14	0.52	4.13	8
0.002	1.0	32	0.66	5.81	12	4	0.63	5.98	10	14	0.70	3.43	10
0.002	2.5	32	0.84	5.20	11	4	0.81	5.26	6	14	1.07	2.96	13
0.010	0.0	32	2.27	6.04	9	4	2.20	6.35	13	14	2.12	3.92	10
0.010	1.0	32	2.35	5.40	5	4	2.29	5.65	5	14	2.32	3.39	12
0.010	2.5	32	2.46	5.00	7	4	2.40	4.99	4	14	2.62	2.94	13
0.050	0.0	32	8.60	5.75	10	4	8.40	6.23	9	14	7.90	3.90	12
0.050	1.0	32	8.70	5.29	5	4	8.50	5.50	3	14	8.20	3.37	13
0.050	2.5	32	8.70	4.77	8	4	8.60	4.83	4	14	8.60	2.96	15

The chemical analyses

The equilibrium pH and equilibrium EC (electric conductivity) were measured in the settled suspension. The suspension was centrifuged for 30 min at 5000 rpm (corresponding to 4900 g), in a Beckmann J-21 centrifuge. The supernatant solution was filtered through a membrane filter of 0.2 µm and was split into 3 parts. 25 ml soil solution was used to determine the metal and total dissolved carbon contents with ICP - AES. 20 ml was used to determine the HCO_3^- ion concentration (inorganic carbon) by titration and to determine the anion concentrations by Ion Chromatograph. 20 ml was used to measure the copper ion activity by Ion Selective Electrode (ISE).

Dissolved Organic Carbon (DOC) determination

DOC plays an important role in the fate of heavy metals in soils and soil solutions. The total dissolved carbon was measured by ICP - AES instrument (Oweczkin et al., 1996) at two different carbon lines (197.09 nm and 247.856 nm). The carbon content was calculated at both carbon line and their average value was accepted as the total dissolved carbon concentration. The dissolved inorganic carbon was determined by titration to pH 4.00, using Radiometer Titralab32 titrator. The DOC concentration of the equilibrium soil solution was calculated by subtracting the dissolved inorganic carbon content from the total dissolved carbon. The elaborated method was checked and proved to be reliable.

Copper ion activity measurement

Metrohm Ion Selective Electrode measured the copper ion activity of the equilibrium soil solutions. The copper-ion buffer contained: $Cu(NO_3)_2$ ($5*10^{-5}$ mol.l^{-1}), ethylene-diamine ($2*10^{-4}$ mol.l^{-1}) and $NaNO_3$ (0.03 mol.l^{-1}). The method used ethylene-diamine for complexation and not EDTA, because EDTA might corrode the electrode surface introducing unstable response. The calibration of copper ISE (Avdeev et al., 1983, Benedetti et al., 1995) was carried out by the acidification of the copper-ion buffer. 0.00 - 0.05 - 0.10 - 0.15 - 0.20 - 0.25 - 0.30 ml HNO_3 (0.03 mol.l^{-1}, ionic strength is constant) was added to the copper-ion buffer. In the acidified copper-ion buffer the pH value was measured by a pH electrode as well as the electrode potential (mV) – corresponding to the copper-ion activity – was measured by the copper ISE. From each measured pH value (if $5 < pH < 9$) the pCu value was calculated according to the following formula: $pCu = –21.7 + 4.72 * pH + (0.9 * pH)/(pH-4.0) – 0.012335 * pH^3$. The calibration curve was determined by plotting the calculated pCu values against the electrode potentials (in mV). The linear calibration curve was used to calculate the copper-ion activity in the equilibrium soil solutions. The copper-ion activity measurement is not reliable when the total dissolved copper concentration is lower than 15 µg.l^{-1}. Therefore it is useful to determine the total dissolved copper concentration in the soil solution before the copper-ion activity measurement.

Derivation of Freundlich constants as a function of soil characteristics

The experiments were established to give the necessary information to determine the soil / solution transfer function for Cd and Cu, as described in Equation (1) and (2). the values of Q_{Me} and a_{Me} were determined in the experiments. The sorbed heavy metal concentration (Q_{Me}) was calculated by using a mass balance: the total / reactive heavy metal content of the untreated soil + the quantity of the added heavy metal – the heavy metal concentration of the equilibrium solution. A speciation program (de Rooij & Kroot, 1991) – taking into account the solution composition – was used to calculate the cadmium ion activity (a_{Cd}) in the solution phase. The copper ion activity (pCu) was measured by copper ion selective electrode. The capacity controlling soil properties (log clay %, log humus %, log Al %, log Fe %, pH) and the major solution properties (log Ca^{2+} mol.l^{-1}, DOC mg.l^{-1}) included in Equation (2) were determined for the 252 chemical equilibria. Only the value of n_F in Equation (8) is unknown. In order to get a representative equation, which is applicable for different soils, the value of n_F was optimised. For the sake of this, the left-hand side of Equation (1b) was considered to be the dependent variable (Y), while Equation (2) represented the dependent variables (x_1, x_2, x_3, x_4, x_5, x_6, x_7). The value of n_F was set to 1.0, the left-hand side of the 252 equations were calculated and the linear regression between the dependent and independent variables were carried out using all the 252 equations. Then the n_F was systematically decreased and the linear regressions were repeated. The optimal n_F value was accepted when the fit of the linear regression was the highest.

The individual effect of the independent variables was also evaluated by the calculated t-value and the corresponding P-value. When the P-value belonging to a given independent soil property was higher than 5% (the t-value had a low value) the independent variable had little and uncertain contribution to the overall linear function and its role could be neglected. This independent variable was omitted, then the n_F optimisation was repeated without this parameter.

Calculation of chemical speciation

The activity of copper and cadmium was calculated from the measured composition of the soil solution, including all major cations and DOC with the chemical speciation program CHARON Besides the complexation of cations with inorganic ligands the complexation of cations with DOC was calculated. Complexation of cations with DOC is modelled using a diprotic acid analogue for DOC (for details see Bril, 1995; Römkens, 1998) Protonation and complexation of cations with DOC is described with two reactions and corresponding equilibrium constants according to:

$$Cat^{n+} \quad + \quad \mathrm{HHUM}^{-} \quad \leftrightarrow \quad Cat\mathrm{HHUM}^{(n-1)+} \qquad \mathrm{p}K_1 \tag{3}$$

$$Cat^{n+} \quad + \quad \mathrm{HUM}^{2-} \quad \leftrightarrow \quad Cat\mathrm{HUM}^{(n-2)+} \qquad \mathrm{p}K_2 \tag{4}$$

Where *Cat* stands for cations (protons, base cations and trace metals). An overview of relevant pK_i values used in the model is given in Table 3. For DOC we assumed a site density of 10 $mol_c.kg^{-1}$ according to Römkens and Bril (1999).

Table 3 List of model parameters used to calculate the speciation of the soil solution

Element	pK_1	pK_2	Element	pK_1	pK_2
Al^{1*}	11.4	29.4	H^+	4.4	9.4
Ca^{2+}	3.6	6.1	Pb^{2+}	5.5	10.0
Cd^{2+}	4.0	7.9	Zn^{2+}	4.0	8.2
Cu^{2+}	6.5	11.4	$Fe(III)^{1*}$	15.2	34.5

[1]: also mixed Fe-Al-DOC complexes are taken into account

*: for both Al and Fe(III) the complexes used here are $MeHUM^+$ for pK_1 and $MeHUM(OH)_2^-$ for pK_2 respectively.

2.6.3 The soil- solution transfer function of cadmium for different soils

The derived soil-solution transfer function

The soil-solution transfer function of cadmium was determined as described before. In case of cadmium 234 chemical equilibria – belonging to 12 representative soils samples – could be taken into account during the calculations. The following soil / solution transfer function was accepted for cadmium:

$$\log(Q_{Cd-total}) - 0.8846 \cdot \log(a_{Cd}) = \log(K_F) = -3.3677 + 0.6688 \cdot pH + 0.6273 \cdot \log(humus,\%) + \\ + 0.4497 \cdot \log(clay,\%) - 0.2475 \cdot \log(c_{Ca}, mol/l) \qquad (5)$$

Equation (3) represents the best fit between the left-hand side and the right-hand side of the equation. The coefficient of determination (R^2) is 0.9063, the standard error of the predicted y value is 0.3031. The n_F value was optimised for $Q_{Cd\text{-}total}$ contents, resulting in 0.8846.Studying the left-hand side of Equation (3), it can be seen that the soil / solution transfer function of cadmium was determined for the total cadmium content. The transfer function was also calculated for the reactive cadmium content. The slightly acid extraction using a complexing agent is supposed to characterise the plant available fraction of heavy metals in soils. However, the n_F value could not be optimised, because $n_F > 1$. The positive sign of the pH value, humus % and clay % implies that higher values for the pH, the humus %, the clay % leads to more cadmium ions be sorbed on the soil surface. The lower the pH, the humus %, the clay % the less cadmium ions can be sorbed on the soil surface. The calcium ion concentration has negative sign. Increasing the calcium concentration decreases the cadmium sorption strength. The right-hand side of Equation (3) is different from the general soil / solution transfer function. The log(Al, %), log(Fe, %) and log(DOC, mg.l^{-1}) are not included into the equation (see Equation 1), since they either had a negative contribution (coefficient) to the equation (which s physically impossible) or a high uncertainty compared to the coefficient itself (high P-value).

The effect of the different soil properties on the cadmium ion distribution can be compared by the extent of the coefficients. The sequence of the soil characteristics in Equation (3) corresponds to the significance of their individual contribution to the linear regression. That means that the pH value has the highest and the calcium concentration has the lowest individual contribution, according to the t-statistics and P-values. The direct relationship between the representative Freundlich constant and the soil characteristics gives the opportunity to distinguish the individual contributions of different soil properties on the representative K_F value. Table 4 demonstrates the individual contributions (experimental average * Cd transfer coefficient) and the sum of the individual contributions. The individual contributions can be compared by relative contribution percentages (individual contribution / sum of contributions). The results indicate that among soil properties the influence of pH is dominating (71%). The effect of humus content, clay content and calcium ion concentration is roughly the same (7 – 12%). According to Table 4 the Capacity Controlling Parameters (pH, humus content and clay content) determined 90% of the overall contribution of soil properties.

Table 4 The representative Freundlich constants, built up by the influencing soil and solution properties of Equation 3 and 4.

Cadmium transfer function	nF	intercept	pH	log(OM) %	log(Ca) mol.l^{-1}	log(clay) %	KF-repr.
experimental average (n=234)			5.4364	0.6041	-2.0691	1.3555	
Cd transfer function coeff.	0.8846	-3.3677	0.6688	0.6273	-0.2475	0.4497	
individual attribution			3.6360	0.3789	0.5121	0.6096	
sum of attributions			3.6360	4.0149	4.5270	5.1366	1.7689
relative attribution %			71	7	10	12	
Copper transfer function	nF	intercept	pH	log(OM) %	log(Ca) mol.l^{-1}	log(clay) %	KF-repr.
experimental average (n=252)			5.2940	0.5506	-2.0738	1.3031	
Cu transfer function coeff.	0.5202	-2.9067	0.6532	0.5394	-0.1272	0.0992	
individual attribution			3.4579	0.2970	0.2637	0.1293	
sum of attributions			3.4579	3.7549	4.0186	4.1479	1.2411
relative attribution %			83	7	6	3	

The overall soil / solution transfer function can be used to study the relation between the adsorbed Cd content (Q_{Me}) and the free cadmium ion activity (a_{Me}) as a function of the different soil properties.. For examples in case of 608 non-calcareous soils of Hungary the following averages values can be used according to the Soil Information Monitoring System (SIMS): humus content = 2.25%, clay fraction = 26.13%, pH_{H2O} = 6.07. For calcium concentration $10^{-2.5}$ mol.l^{-1} (Lindsay, 1979) can be applied. In this case the right-hand side is +2.1690. In this representative, 'average' non-calcareous soil the Freundlich – type cadmium ion distribution is 148, indicating that most of the cadmium ions is adsorbed on the soil surface.

Impacts of soil type, pH and calcium concentration on the Freundlich constant and cadmium ion activity

Soil type: Figure 1 demonstrates the close linear relationship between the value of Kf derived with the transfer function (right hand side of Equation 5) and the value calculated from the measured adsorbed amounts and the calculated Cd ion activity with a speciation model (left hand side of Equation 3;R^2 = 0.8989, the standard error = 0.2972). Three major soil types were distinguished namely clayey soils (10 soil samples), an organic peat soil with an extremely high humus content (soil no. 30) and a very poor sandy soil with extremely low clay and humus content (soil no. 14). In the organic peat soil the cadmium ions were strongly adsorbed on the soil surfaces what is reflected by the high K_F values. It can be estimated that $Q_{Cd\text{-}total}$ is about 1000 times higher than $a_{Cd}^{\ 0.8846}$. In the sandy soil, however, the Freundlich constants were very low. Most of the $\log(K_F)$ values were below 1.0, what indicated that most of the cadmium ions remained in the solution phase and the adsorption of cadmium ions was low. In this sandy soil cadmium ions could not be bound to the soil surfaces due to the low clay and organic matter content.

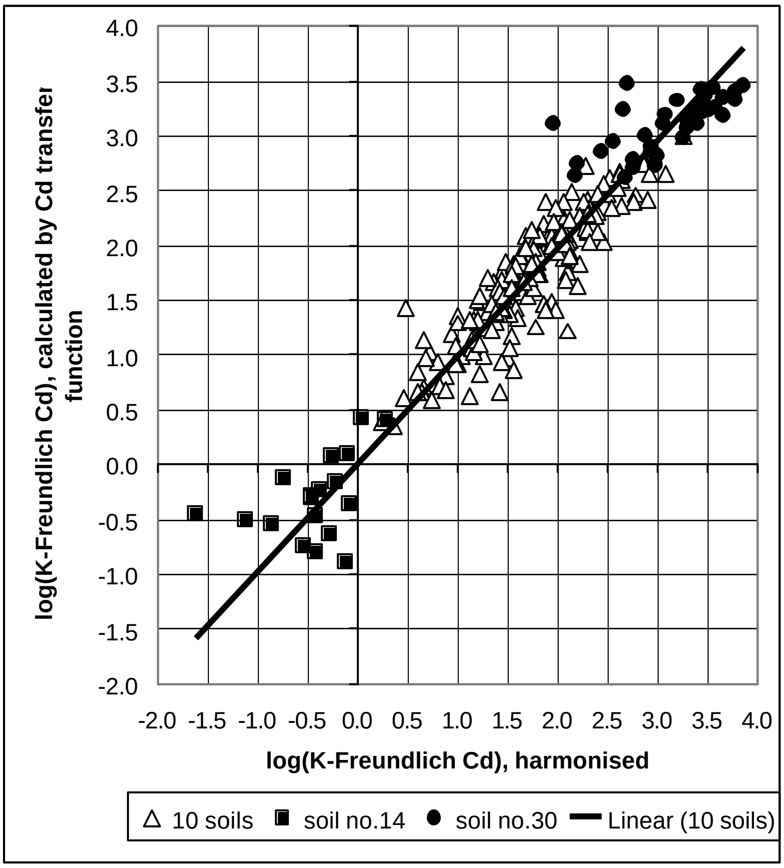

Figure 1 The comparison of the Freundlich constants for cadmium. The x-axis represents the K_F values calculated by the left-hand side of Equation 5. The y-axis represents the K_F values calculated by the right-hand side of Equation 5.

pH: The individual effect of the solution properties on the cadmium ion activity calculated by transfer function is also demonstrated. Figure 2 shows the effect of pH. The points are rather scattering. The higher range characterises the effect of the cadmium treatment. For instance, the organic peat soil (soil no. 30) has two linear and parallel curves, demonstrating the effect of 20 mg cadmium addition per kg soil. In the peat soil the cadmium ions were very strongly bound to the organic compounds, since cadmium ion activities of the solution phase were very low. Although 20 mg Cd was added to 1 kg soil the cadmium ion activities remained below 10^{-7} mol.l^{-1}. In the sandy soil (soil no. 14) only a single point could be measured without cadmium addition. Nevertheless very high cadmium activities could be found in this sandy soil after cadmium addition. In fact these values do not fit well into the general tendency. The cadmium ion activities calculated by transfer function cover a wide vertical range in a narrow pH range below 3.5.

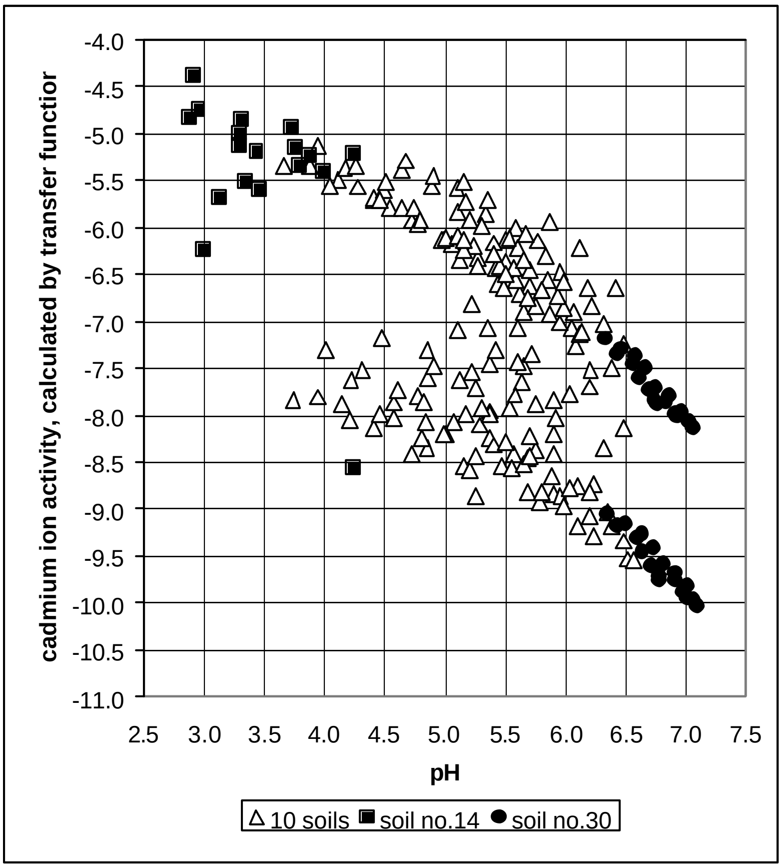

Figure 2 The effect of pH on the cadmium ion activities of the soil solutions. The a_{Cd} values were calculated by the soil / solution transfer function for cadmium (Equation 5).

The deviating behaviour of the sandy soil no. 14 is because the soil surface lost its ability to control the pH of the soil solution since more acid was added to the soil than the sum of the exchangeable basic cations. That is the sum of the exchangeable and soluble Ca, Mg, K, Na content of the soil suspension increased after shaking for 24 hours, indicating the dissolution of soil minerals. This could be measured in sandy soils (Murányi, 1988). Soil no. 14 is also a very poor sandy soil, its exchangeable cation content is low. When 1 mmol or 2.5 mmol H^+ were added to 100 g soil the pH values decreased below 4.0 as well as the sum of dissolved aluminium and iron content increased in the soil solution phase. The dissolution of aluminium/iron oxides/hydroxides started to work and the H^+ ion consumption of dissolution regulated the pH value.

The chemistry of aluminium is especially important in this respect (Lindsay, 1979). As a consequence of all these, the points of soil no. 14 do not fit perfectly to the general tendency (Unclear explanation, say that Al cam in solution?).

Calcium: The effect of calcium concentration is shown on Figure 3.

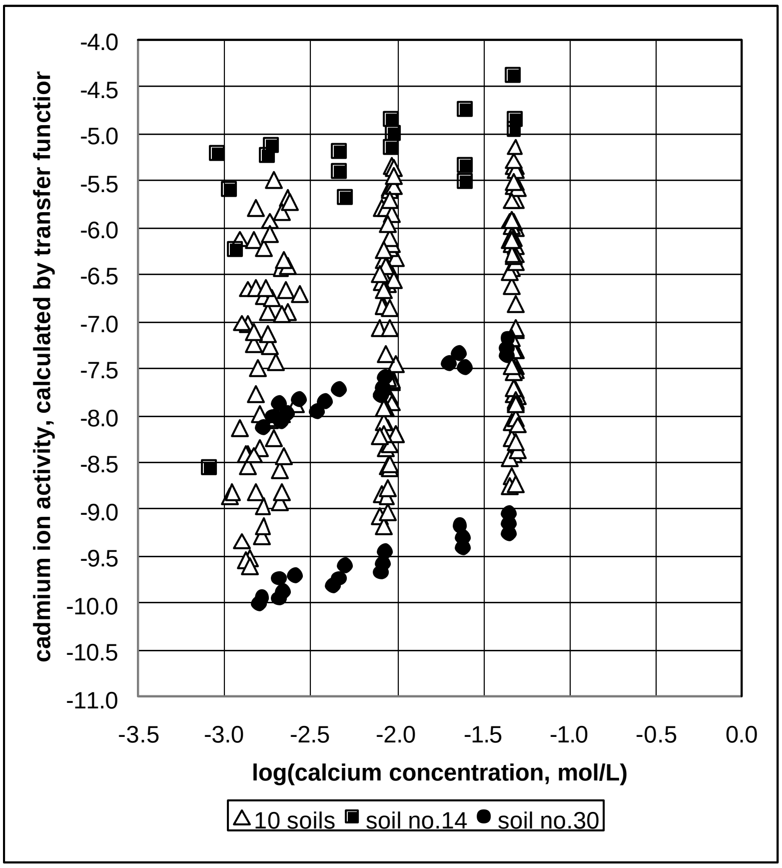

Figure 3 The effect of calcium concentration on the cadmium ion activities of the soil solutions. The a_{Cd} *values were calculated by the soil -solution transfer function for cadmium (Equation 5).*

The cadmium addition can also be seen here, but the vertical trends are more interesting. When low calcium concentration were applied the points are scattering due to the original soluble calcium content. When the calcium concentrations are higher then the vertical trends become more perfect. Quite a lot of points are situated above 10^{-7} mol.l^{-1}, in the range where the groundwater is contaminated. In Hungary the groundwater is contaminated when its cadmium concentration exceeds 5 µg.l^{-1} (logc_{Cd} > –7.3518 mol.l^{-1}). The individual effect of pH and c_{Ca} on a_{Cd} - transfer function gave additional information about the cadmium mobilisation, about the chemical risks.

The assessment of chemical risk of cadmium mobilisation

In Equation (5) the pH and calcium concentration can change as a function of time. This change modifies the cadmium ion distribution in soils and the chemical risk of cadmium mobilisation, that can be assessed by the soil / solution transfer function. For this reason the soil characteristics of a representative soil was used. The 'average' non-calcareous soil contained 2.25% humus and 26 % clay (608 samples). These values were applied to characterise the chemical risk of cadmium mobilisation as a function of pH and calcium concentration. The pH range of 3 – 7 was studied. Two calcium concentration levels 0.001 M and 0.01 M were selected. The cadmium content was taken 1 mg.kg^{-1}, 2 mg.kg^{-1} and 10 mg.kg^{-1}. In Hungary 1 mg Cd/kg soil is considered to be the limit value of contamination. 2 mg Cd/kg soil and 10 mg Cd/kg soil represent a contaminated and a highly contaminated soil, respectively. The characterisation of chemical risk of cadmium mobilisation is demonstrated in Figure 4. The horizontal line represents the limit concentration of groundwater pollution in Hungary (5 µg.l^{-1}; logc$_{Cd}$ = -7.3518).

Figure 4 exhibits the effect of pH and c$_{Ca}$ on the cadmium ion activity of soil solutions. Below the horizontal part the cadmium content is safe and above the line soil solutions are contaminated. The effect of pH on cadmium mobilisation is very high. The decrease of pH from 7 to 3 increases the cadmium activity of the representative soil solution by 3 order of magnitude (0.6688 * 4 / 0.8846 = 3.0242). The effect of c$_{Ca}$ on cadmium ion activity is lower. Increasing the calcium concentration from 0.001 M to 0.01 M pushes the lines upward by about 0.3 unit (0.2475 * 1 / 0.8846 = 0.2798). The increase of calcium concentration has an unfavourable effect on cadmium ion activity of the soil solution. It can be concluded that the chemical risk of cadmium mobilisation is determined mainly by the soil pH, but the role of calcium concentration cannot be neglected either.

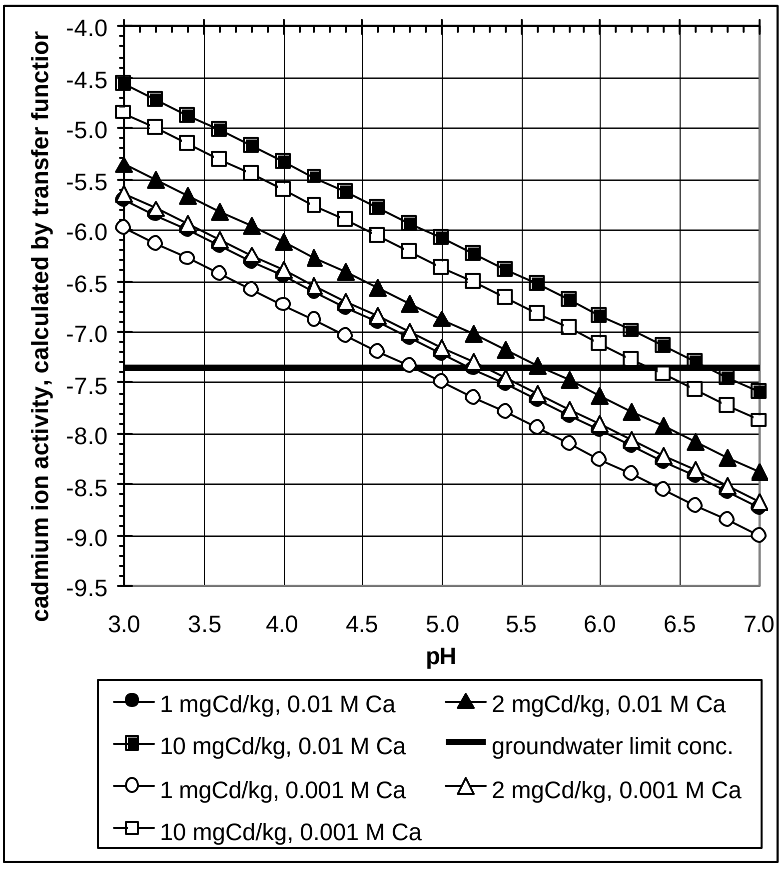

Figure 4 The chemical risk of cadmium mobilisation, assessed by the soil / solution transfer function for cadmium

2.6.4 The soil - solution transfer function of copper for different soils

The derived soil-solution transfer function

In case of copper each of the 252 chemical equilibria – representing the behaviour of 12 representative soils – were taken into consideration. The soil / solution transfer function of copper was determined for the total copper content, similarly to cadmium. The following soil / solution transfer function was accepted for copper:

$$\begin{aligned}&\log(Q_{Cu-total}) - 0.5202\cdot(-pCu) = \log(K_F) = -2.9067 + 0.6532\cdot pH + \\ &+ 0.5394\cdot\log(humus,\%) - 0.1272\cdot\log(c_{Ca}, mol/l) + 0.0992\cdot\log(clay,\%)\end{aligned} \qquad (6)$$

The coefficient of determination (R^2) is 0.9210, the standard error of the predicted y-value is 0.2744. The optimised n_F value was found to be 0.5202, what is surprisingly close to 0.5. In case of copper the transfer function could be calculated for the reactive copper content too. It is evident that $Q_{Cu\text{-}reactive}$ is always smaller than $Q_{Cu\text{-}total}$, because only a part of the total copper content can be reactive. In the 12 representative soils the $Q_{Cu\text{-}reactive}$ / $Q_{Cu\text{-}total}$ ratio were calculated and the average, the minimum and the maximum ratio were 0.36, 0.10 and 0.88, respectively. Very large differences could be found between the total and the reactive copper content of the 12 soils. These deviations depend on the soil development processes, on the genesis of soils. The n_F value was optimised for the reactive copper content and it was found to be 0.88.

As with Cd, the pH, humus content and clay content coefficients have a positive sign and calcium coefficient is negative, whereas the aluminium, iron and DOC contents is not included (Compare Equation 2 and 6) for reasons mentioned before for Cd. The sequence of the soil characteristics in Equation (6) corresponds to the significance of their individual contribution to the linear regression. This is illustrated in Table 24, which summarises the individual contributions and the sum of the individual contributions. The results indicate that among soil properties the influence of pH is dominating (83%). The contribution of the humus content, clay content and calcium concentration is 7%, 3% and 6%, respectively. The effect of clay % on copper adsorption is rather low (3%), indicating that mainly the humus content and the pH value influence the copper adsorption in soils. (In case of reactive copper content the effect of clay % was uncertain, thus clay % had to be left out from the equation.). Altogether the Capacity Controlling Parameters (pH, humus content and clay content) determined 94% of the overall contribution of soil properties.

The validation of the soil / solution transfer function by measured copper ion activities

The soil / solution transfer function of copper can be used to assess the copper ion activity of the solution phase on the basis of the soil properties (humus %, clay %) and the experimental results (pH, c_{Ca}). The measured copper ion activities can be used to validate the copper ion activities calculated either by transfer function (Eq. 6) or by speciation. Figure 5 demonstrates the close linear relationships. Applying the transfer function a close linear relationship was found between copper ion activities: $a_{Cu\ transfer\ function} = 0.9967 * a_{Cu\ measured}$ (R^2 = 0.9005; the standard error = 0.5225).

Applying the speciation method the relationship is also very close: $a_{\mathrm{Cu\ speciation}} = 0.9711 * a_{\mathrm{Cu\ measured}}$ ($R^2 = 0.8951$; the standard error = 0.5266). The transfer function took into consideration the major soil characteristics, which controlled the copper sorption. The speciation method calculated the copper ion activities by taking into account only the composition of the soil solution phase.

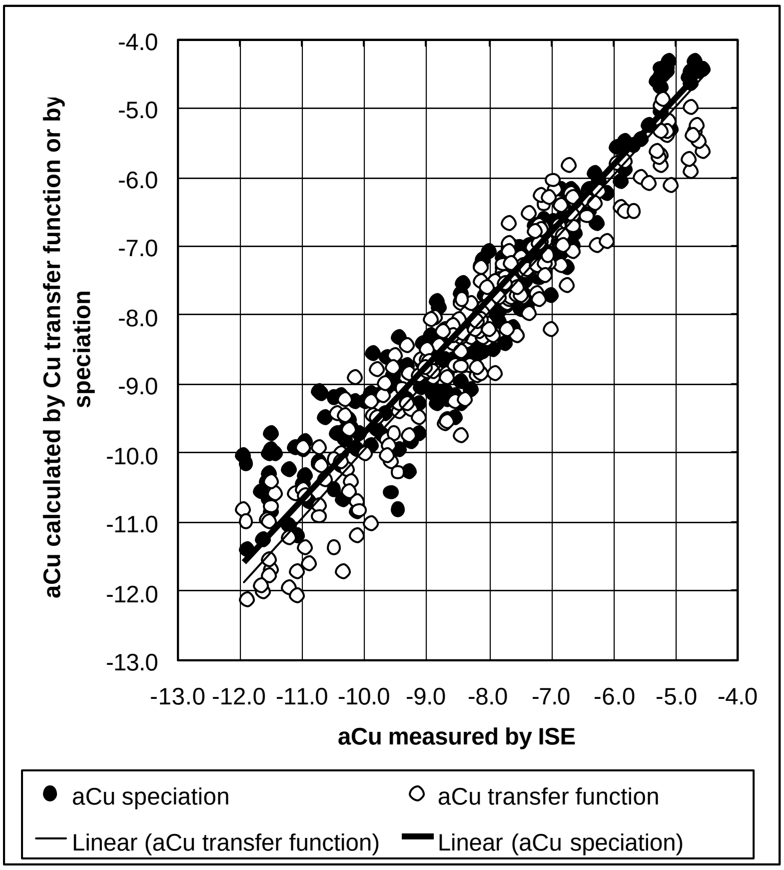

Figure 5 The validation of the calculated copper ion activities by the measured copper ion activities. The $a_{\mathrm{Cu\ transfer\ function}}$ was calculated by using Equation 6. The $a_{\mathrm{Cu\ speciation}}$ was calculated by using the CHARON speciation program.

In spite of the fact that the two methods are based on entirely different soil properties, the transfer function gave almost the same results as the speciation method. These findings also proved the reliability and applicability of our soil / solution transfer function.

Impacts of soil type, pH and calcium on the Freundlich constant and cadmium ion activity

Soil type: Figure 6 demonstrates the close linear relationship between the value of Kf derived with the transfer function (right hand side of Eq. 4) and the value calculated from the measured adsorbed Cu amounts and the calculated Cu ion activity with a speciation model (left hand side of Eq. 4)

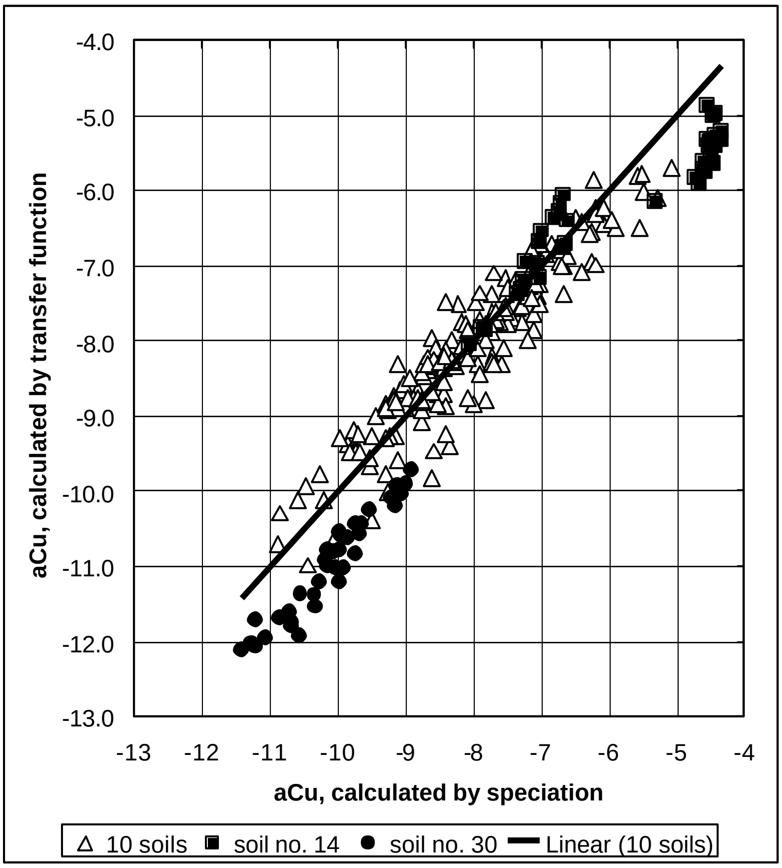

Figure 6 The comparison of copper ion activities calculated by two different concepts. The x-axis represents the a_{Cu} *values calculated by a speciation model. The y-axis represents the* a_{Cu} *values calculated by the soil / solution transfer function for copper (Equation 6).*

The linear regression was calculated for the 10 clay soils, resulting in the following equation: $a_{Cu\ transfer\ function} = 1.0023 * a_{Cu\ speciation}$ ($R^2 = 0.8515$, the standard error = 0.4223). The behaviour of the sandy soil (no. 14) is different from the 10 'clay' soils. High copper ion activities could be measured in this sandy soil. In case of control treatments (+0 mg Cu/kg soil) the a_{Cu} calculated by transfer function and the pCu measured by ISE fit the linear line. In case of copper treatments (80 mg Cu/kg soil) the measured pCu values and the corresponding a_{Cu} values calculated by transfer function did not fit well. When $a_{Cu\ speciation}$ is between –5 and –4, the $a_{Cu\ transfer\ function}$ points exhibit a vertical tendency. These 17 points belong to the copper treated samples, having a pH value below 4.0. In these soils the dissolution of aluminium/iron oxides/hydroxides could be detected, which regulated the pH value. Thus the soil surface lost its pH controlling ability, as it was discussed before. When the dissolution of minerals does occur, then the role of soil surfaces – as well as the validity of the soil /solution transfer function – becomes limited. The soil / solution transfer function can be applied as long as the chemical equilibria are determined by the soil surfaces. When the charge carrying soil surfaces are not able to determine the chemical equilibria between the solid phase and the solution phase, then the soil / solution transfer function cannot be valid any more either. This is the reason why these 17 points are out of the general tendency.

In the peat soil very low copper ion activities were measured (a_{Cu} < -9.5). The points of soil no. 30 are parallel with the linear trend. On one hand this indicates that the concept of soil / solution transfer function can be applied in organic soils too. On the other hand these results suggest that in case of an area what is covered by organic soils it would be better to determine a soil / solution transfer function valid for organic soils. The behaviour of the other 10 clay soils follow the same linear trend. In Hungary the groundwater is contaminated when the copper ion concentration is higher than 200 $\mu g.l^{-1}$ (a_{Cu} > -5.50). Only the copper treated soil solutions of soil no. 14 were contaminated. In the soil solutions of copper contaminated soils the a_{Cu} values did not exceed the limit value for the groundwater. This reflects that copper ions are very strongly bound to soil components.

pH and calcium concentration: The effect of pH is shown on Figure 7. The points seem to be situated along two parallel lines. The points below the lower line represent the copper treated soil samples. The lowest points belong to the originally contaminated soil samples (no. 32, 4, and 7). The organic peat soil (soil no. 30), the very poor sandy soil (soil no. 14) and the copper contaminated soils (soil no. 32, no. 4, no. 7) are shown separately on Figure 7. In Hungary the soil is contaminated if its copper content is higher than 75 mg/kg soil. The effect of calcium concentration is demonstrated by the vertical trends on Figure 25. It is seen that altogether 6 calcium concentrations were applied. At the lowest concentrations (0.001 M and 0.002 M) the points are rather scattering due to the original salt content of soils. When more calcium ions were applied the role of the original salt content was reduced and the vertical trends become more perfect.

2.6.5 Discussion and conclusions

Comparison of cadmium and copper sorption

The sorption experiments were planned to characterise both the cadmium and the copper adsorption on different soils. The dual adsorption of two heavy metals can be compared in such a way. The sorption characteristics – the adsorbed heavy metals and the dissolved heavy metals – are demonstrated (Figure 9) as a function of pH, what is the dominating Capacity Controlling Parameter. The sorption characteristics of heavy metal treated soil samples are shown.

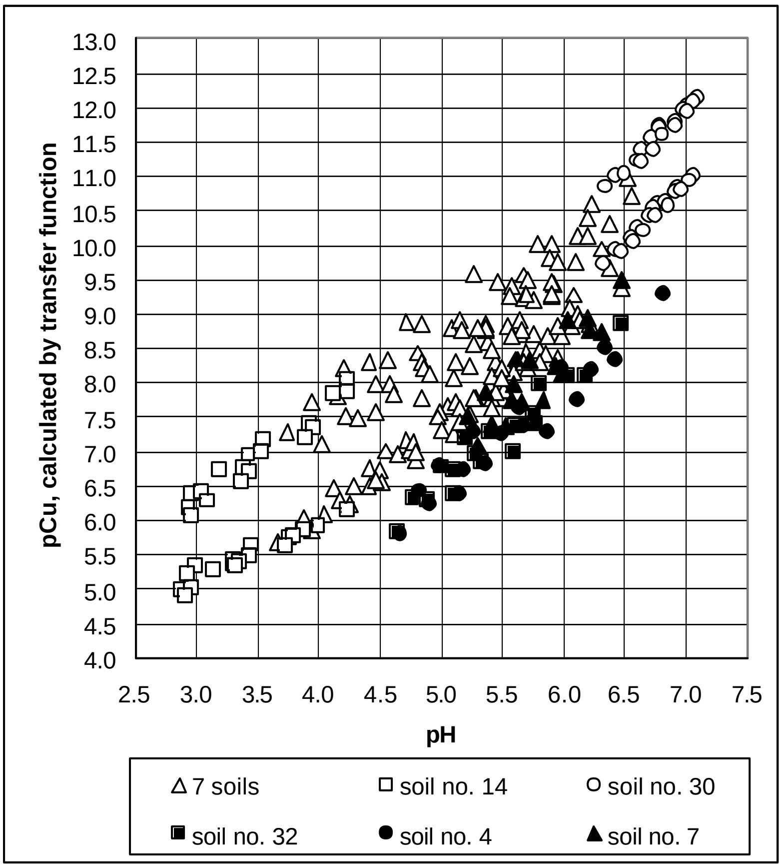

Figure 7 The effect of pH on the copper ion activities of the soil solutions. The a_{Cu} values were calculated by the soil / solution transfer function for copper (Equation 6).

In the experiments 20 mg cadmium and 80 mg copper were added to 1 kg soil, corresponding to log(Q_{Me}, mol.kg^{-1}) -3.75 for cadmium and -2.90 for copper. Figure 9 clearly shows these values in the pH range above 5.0. Below pH 5.0 the horizontal lines start to bend downward, especially in case of cadmium. Most of these points belong to soil no. 14. That reflects that the quantity of adsorbed heavy metal ions significantly decreases when the dissolution of minerals starts to work, as it was discussed before.

Comparing the adsorbed heavy metal concentrations it is clearly seen that the concentration of the adsorbed copper ions are always higher than that of cadmium ions. On the contrary, the activities of dissolved cadmium ions are usually higher than that of copper ions. In order to indicate the tendencies the linear regression lines of dissolved heavy metal ions are plotted. The high environmental risk of cadmium ions in soils can also be evaluated by the equilibrium constant of the heavy metal sorption (Equation 2). In the soil / solution transfer function of cadmium (Equation 5) and copper (Equation 6) the K_{eq} values are included in the intercept, what corresponds to the product of n_F * log(K_{eq}).

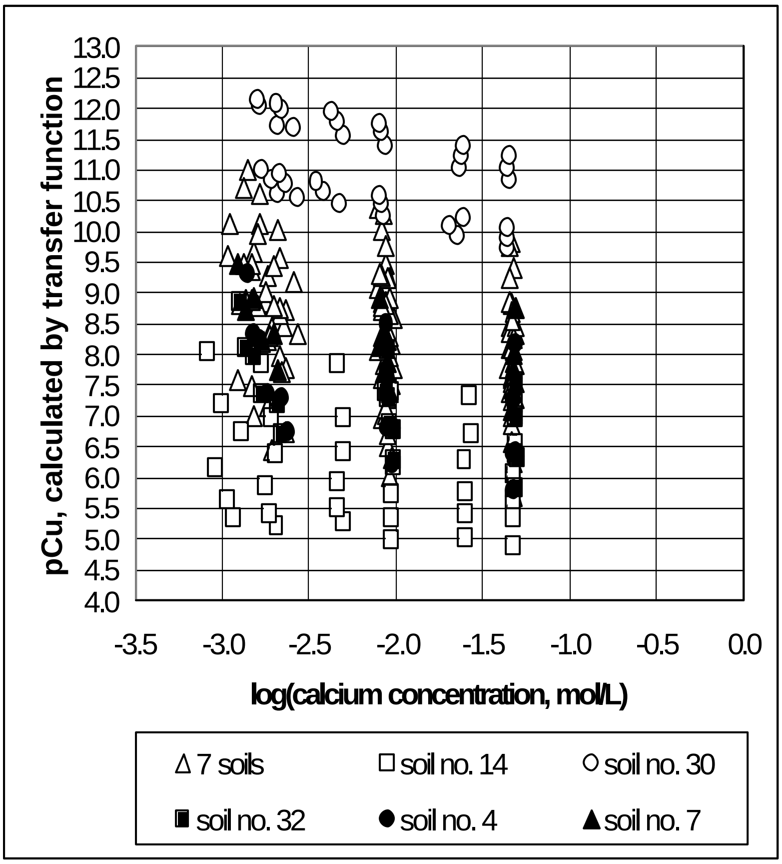

Figure 8 The effect of calcium concentration on the copper ion activities of the soil solutions. The a_{Cu} values were calculated by the soil / solution transfer function for copper (Equation 6).

Thus the equilibrium constants, valid for the total heavy metal contents, can be determined. The equilibrium constant for cadmium is log($K_{eq,Cd}$) = –3.8070, and for copper it is log($K_{eq,Cu}$) = –5.5877. The higher equilibrium constant of cadmium adsorption reflects the higher risk of cadmium mobilisation. Figure 9 clearly demonstrates that the distribution of the cadmium and copper ions between the solid and solution phase are distinct. In case of dual adsorption, however, the soil samples and the experimental conditions are the same. As a consequence of this, the Freundlich - type distribution (K_F) of cadmium and of copper ions can be compared.

Figure 10 indicates the experimental results of both heavy metal ions. The y - axis shows the log(K_F) values, which were calculated by the transfer function of cadmium and of copper, by using the right-hand side of Equation 3 and 4, respectively. The x - axis corresponds to the log(K_F) values, which were calculated by using the left-hand side of Equation 5 and 6, respectively. In case of the x-axis, the Cd ion activities were calculated by speciation method and the Cu ion activities were measured by ISE. Surprisingly the two heavy metals, the joint 486 points, exhibit a close linear relationship: $K_{F\ \mathrm{transfer\ function}} = 0.9749 * K_{F\ \mathrm{harmonised}}$ (n = 486, R^2 = 0.9149; the standard error = 0.2823).

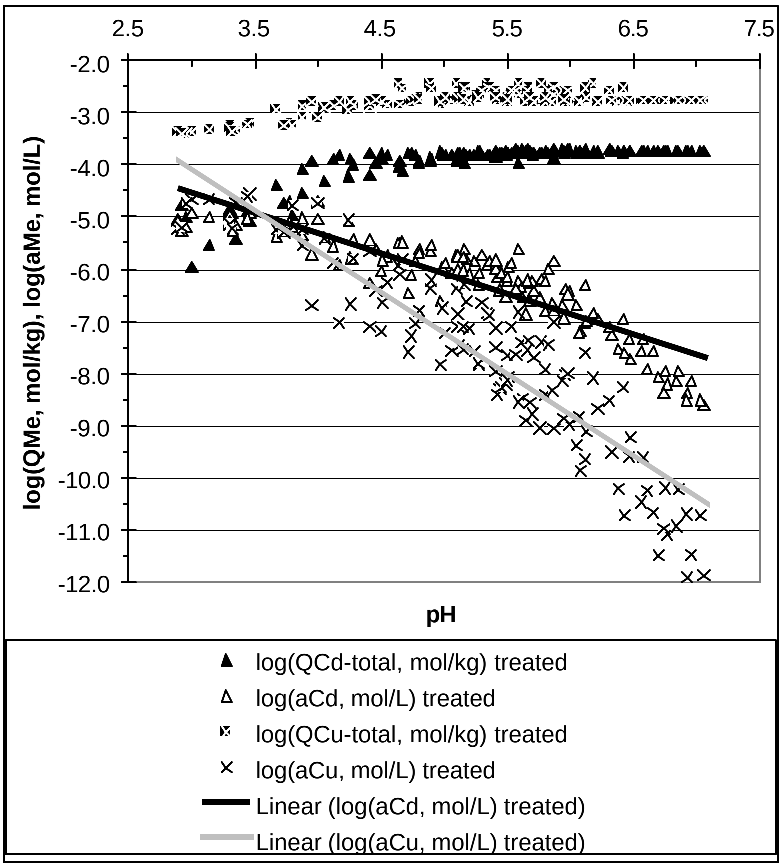

Figure 9 The distribution of cadmium and copper ions in treated soil samples as a function of pH.

This close relationship proves that:

- In the solution phase the activity of the heavy metal ions was independent on the activity determination: either the calculation by speciation method or the measurement by ion selective electrodes could be applied.
- The transfer function of cadmium ions and the transfer function of copper ions fitted the same line, confirming that the surfaces properties [surface sites (N_S) and a through n_F] were reasonably characterised by the Capacity Controlling Parameters.
- The general soil / solution transfer function – derived from the general equation of heavy metal sorption – could properly describe the heavy metal sorption in different soils, characterised by a wide range of soil properties.

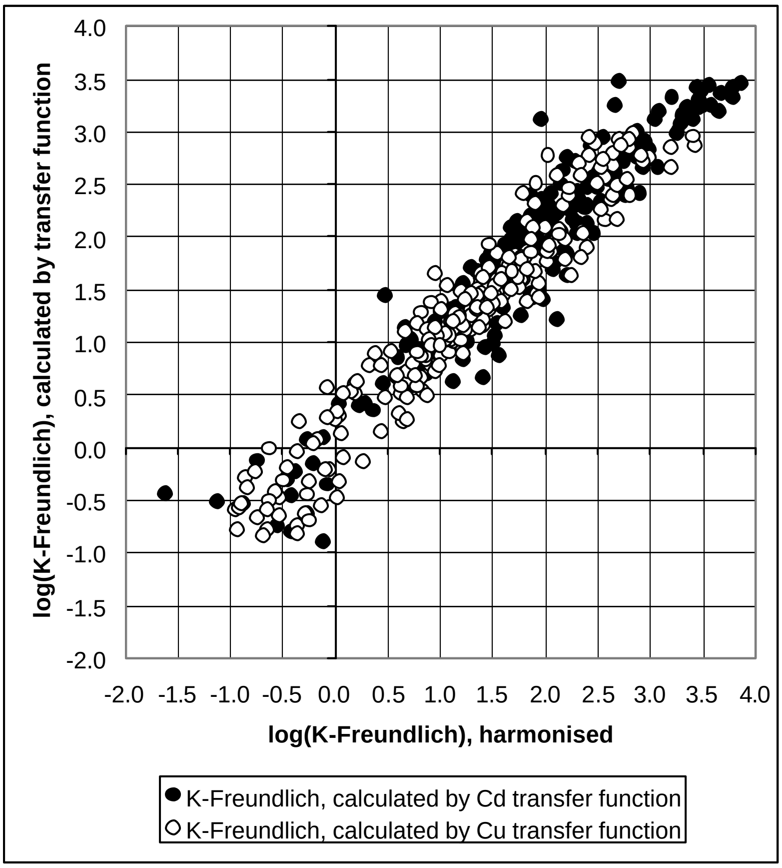

Figure 10 The comparison of the Freundlich constants for cadmium and for copper. The x-axis represents the K_F values calculated by the left-hand side of Equation 5 and 6. The y-axis represents the K_F values calculated by the right-hand side of Equation 5 and 6.

Conclusions

This study showed that free metal ion activities can be derived reasonably well by measuring dissolved metal concentrations and major ions in the soil solutions, including pH, Ca and DOC. In case of Cu, the calculated Cu ion activities compared well with the measured activities, giving confidence to the used speciation model. More important, however, the results showed that the use of a transfer function, allowing to derive the free metal ion activity from the solid phase content while accounting for the effect of pH, clay content and organic matter content gives almost equally good results. The chemical behaviour of cadmium and of copper was efficiently distinguished by their different transfer function characteristics [Freundlich exponents (n_F), and transfer function coefficients of controlling properties] in Equation 3 and 4, respectively. Using these transfer functions the chemical risk of cadmium or copper ion mobilisation can be assessed. By applying the soil / solution transfer function for cadmium as an example, the risk of ground water contamination could be illustrated, even for soils with a relatively low Cd content, but also a low pH and Ca concentration. It directly shows how contamination can be limited by influencing those properties by e.g. liming. Soil-solution transfer functions can thus be used in models and decision support systems predicting impacts of e.g. land use changes and management practices, including those aimed at solving environmental problems and contributing to the protection of our environment.

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Theme 3 Models describing metal uptake by plants

3.1 Development of a dynamic process-oriented model, CdModel, describing cadmium in the soil-crop system

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Summary

There is increasing concern for the accumulation of cadmium in cereal crops, as cadmium even at low and non-phytotoxic concentrations poses a threat to consumer health. The objective of this study is to explore the possibility of modelling the transfer of cadmium from agricultural soils to crops with a dynamic, process-oriented, multi layer model, CdModel, based on easily accessible information regarding meal inputs, soil and crop characteristics. CdModel was applied to a long-term fertility experimental site called Kungsängen, being a clay soil with a pH of 6.9 at the soil surface and decreasing with depth. A 5-year crop rotation with three years of grass-clover, one year of wheat and one year of spring cereals was practised in the period 1907-1963 and in 1964 the fertility experiment started. Since data on cadmium concentrations in soil or grain from the Kungsängen site were lacking, those data were estimated from a survey dealing with wheat Cd concentrations in specified wheat cultivars in the period 1918-1980.

Cadmium input on the Kungsängen soil was reconstructed, using data and estimations of historical atmospheric deposition and concentrations in fertilisers and manure. Results show a large increase in cadmium input after the 2nd World War until the eighties when adverse effects started to be discussed and policies to reduce the cadmium content in fertilisers were implemented. Simulated cadmium concentrations in wheat grain, using the Kungsängen site as input for the modelling, show reasonable values compared to field data on wheat cadmium concentrations during the period 1918-1980, but the substantial yearly variation in grain cadmium concentration was not captured by the model. The approach of dynamically modelling cadmium uptake is also compared to empirically derived soil-plant relationships, relating soil content of cadmium to crop contents. The comparison was limited but this might be because the soil-plant relationship was not based on the specific wheat cultivar use in Sweden.

General conclusion is that the simulation of cadmium in the agricultural soil-plant system with a dynamic process-oriented biogeochemical model is a challenging task since many of the processes influencing the plant uptake of this heavy metal are not

yet fully understood and hence not parameterised. It was therefore difficult to construct a computer model able to simulate the yearly variation in crop cadmium concentration since much of the dynamics is probably to a great extent mainly governed by plant specific processes and not so much steered by soil chemistry. In addition, there are few sites with long time-series of cadmium concentrations in soil and crops needed for calibration and validation of the model. Nevertheless, CdModel has shown promising reference behaviour patterns and is capable of describing the grain cadmium concentrations with reasonable accuracy. The structure of the model enables the user to improve parameterisation of the processes when new data is available that sheds new light on the mechanisms governing the uptake process and the internal allocation of cadmium in the plants.

3.1.1 Introduction

Problems with cadmium accumulation in crops

There is increasing concern for the accumulation of cadmium in cereal crops, as cadmium even at low and non-phytotoxic concentrations poses a threat to consumer health (McLaughlin et al., 1999). Exposure to cadmium can lead to kidney dysfunction (Buchet et al., 1990). The diet is the main source of cadmium exposure in the general non-smoking population of Sweden (Vahter et al., 1991). Increasing consumer awareness of the negative health effects of heavy metals and governmental concern for public health have put focus on the necessity to reduce cadmium content in staple foods. The *Codex Alimentarius* Commission, a subsidiary of the United Nation's Food and Agricultural Organisation and the World Health Organisation, has recommended a maximum tolerable intake for an adult of 60-70 µg cadmium per day and a limit of 0.1 mg Cd per kg crop dry weight has been set as a maximum limit for grain destined for export (FAO/WHO, 1993). Grain concentrations of cadmium show a positive correlation with soil cadmium concentration (Eriksson et al., 2000). Trying to capture the dynamics of the metal in the soil is therefore a crucial step in modelling the mechanisms influencing crop uptake of cadmium. Tools to predict the cadmium content in different crops are valuable for farmers, the food manufacturing industry, and for authorities involved in public health and environmental issues. Predicting the concentration of cadmium in products from certain regions and/or farming systems will enable these actors to take precautionary measures.

Objective

The objective of this study is to explore methods of modelling the transfer of cadmium from agricultural soils to crops. A dynamic, process-oriented, multi layer model, CdModel, is proposed as a means to do this. In order to calculate the cadmium concentration in grain we must establish the links in the chain deposition-soil solution-plant. The goal is to construct a simplistic process-oriented dynamic uptake model that is capable of predicting the cadmium concentration in crops, based on easily accessible information regarding deposition patterns, soil and crop characteristics, as well as based on generic data. The approach of dynamically modelling the cadmium content in crops is compared to empirically derived transfer functions, relating soil content of cadmium to crop concentrations.

The accumulation of cadmium in crops is governed by a number of complex biogeochemical processes in the soil-plant system. One of the most influential parameters to include in the analysis is the soil solution pH, as it strongly affects the bio availability of this heavy metal. The present report explores the possibility of coupling cadmium mass balance calculations to the dynamic multi-layer soil chemistry model SAFE, simulating soil solution concentrations of nutrients and pH over time. Field data from a site called Kungsängen, situated close to the city of Uppsala, Sweden, was used as input regarding soil characteristics, historic crop rotation and management in the simulations.

3.1.2 Theory

Basic principles

Due to the complexity of the agricultural soil-plant system, involving non-linear as well as dynamic interrelations, the approach of system analysis and subsequent mathematical modelling is particularly suitable. Results from controlled experiments are used to parameterise the model. Subsequent calibration and validation of the model is done using field data. Biogeochemical modelling facilitates analysing the dynamics of the system in different time perspectives, and is hence a useful tool for sustainability discussions regarding agricultural management practices. A causal loop diagram, schematically defining the system components and their basic interrelations, is presented below (fig. 1). The causality is symbolised with arrows, the signs indicating the causality and co-variation, positive or negative.

In CdModel, cadmium in soil solution is dealt with as concentrations and not as activities. Generally, the accumulation of cadmium in higher plants are best correlated to the activity of the free, uncomplexed ion in solution (Cd^{2+}) (Grant et al., 1998); (Parker and Pedler, 1997); (Sposito et al., 1982); (Wagner, 1993). However, over the limited range in ionic strength relevant to terrestrial plants, the quantities activity and concentration of this ion can be used interchangeably without loss of accuracy (Parker and Pedler, 1997).

The free divalent ion (Cd^{2+}) is the most common cadmium species in soil solution (Stumm and Morgan, 1981). In addition, it has also been shown that Cd^{2+} is the only cadmium species adsorbing to soil to any greater extent (Boekhold et al., 1993). Cadmium may however be present as a complex ion in solution in association with inorganic ligands such as Cl^-, SO_4^{2-} or HCO_3^- (McLaughlin et al., 1996). In contrast to other trace elements it seems like organic ligands do not have great significance in the overall speciation of Cd in soil solutions (McLaughlin et al., 1999). The complexation of Cd^{2+} with any type of ligand is so far ignored for simplicity in CdModel.

The Cd^{2+} concentration is influenced by changes in the total metal concentration in the soil and by soil properties governing adsorption. The soil solution cadmium concentration is increased by deposition and reduced by plant uptake and leaching from the soil. The amount of adsorbed Cd^{2+} will increase with the cation exchange capacity (CEC) of the soil. The adsorbed amount of cadmium is reduced by high concentrations of divalent base cations (Bc^{2+}) and hydrogen ions (H^+) due to competition for exchange sites in the adsorption process. A similar process governs plant uptake of cadmium, as root surfaces are assumed to act as organic ion exchange surfaces in the soil and Bc^{2+} and H^+ will act to reduce the amount of Cd^{2+} adsorbed to the roots. Cadmium is supplied to the root system by root interception, mass flow and diffusion, with diffusion being reported as the rate limiting process for cadmium uptake (Cutler and Rains, 1974); (Grant et al., 1998). However, in modelling plant cadmium uptake in CdModel, mass flow is regarded as the main transport mechanism influencing the transfer of this heavy metal from soil solution to plant root surfaces.

Precipitation will increase soil water content, which in turn will increase the degree of wetness of root surfaces and hence the exposure of these surfaces to soil solution concentrations of ions.

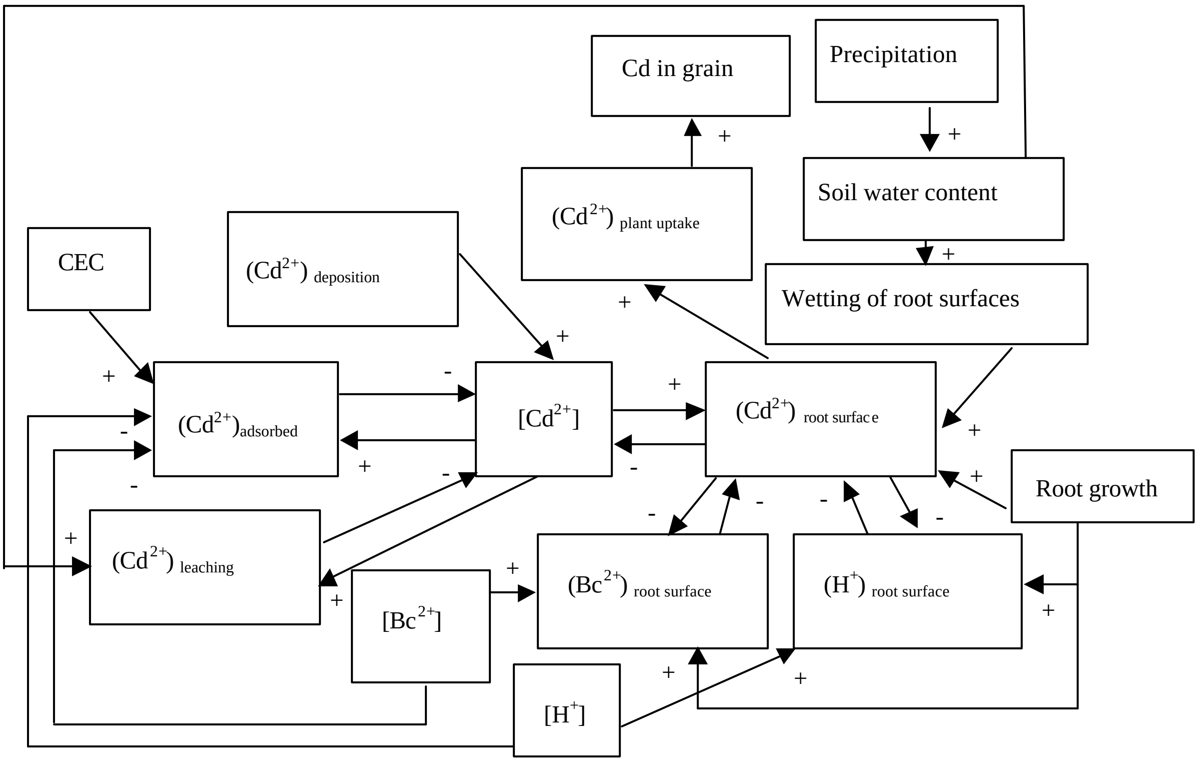

Figure 1 Causal loop diagram, showing the components of the soil-crop system and their interrelations with reference to the concentration of cadmium in the system.

Defining the model

A dynamic process-oriented multi-layer soil model (CdModel), simulating cadmium dynamics in soil, has been coupled to the dynamic soil model SAFE (fig. 2). The SAFE model includes process-oriented descriptions of cation exchange reactions, chemical weathering of minerals, solution equilibrium reactions involving carbon dioxide, organic acids and aluminium species, and finally leaching and accumulation of dissolved chemical components. For an elaborate discussion on the SAFE model, see (Alveteg, 1998). Output from the SAFE model calculations is used as input in the

CdModel model calculations. SAFE provides the concentration of divalent base cations and pH in the soil solution.

3.1.3 A dynamic Cadmium model (CdModel)

General approach

Critical processes to target in modelling cadmium in the agricultural soil-plant system are deposition, ion exchange, leaching, plant uptake and to a lower extent weathering of cadmium containing minerals. In the soil, cadmium is considered to be in either of two forms; adsorbed $(\mathrm{Cd}^{2+})_{\mathrm{ads}}$ or free uncomplexed in soil solution $[\mathrm{Cd}^{2+}]$. These two fractions are distributed according to equilibrium, defined in equation 3 below. For each soil layer the total cadmium content $(\mathrm{Cd})_{\mathrm{Total}}$ is calculated as the sum of these two (Eq. 1).

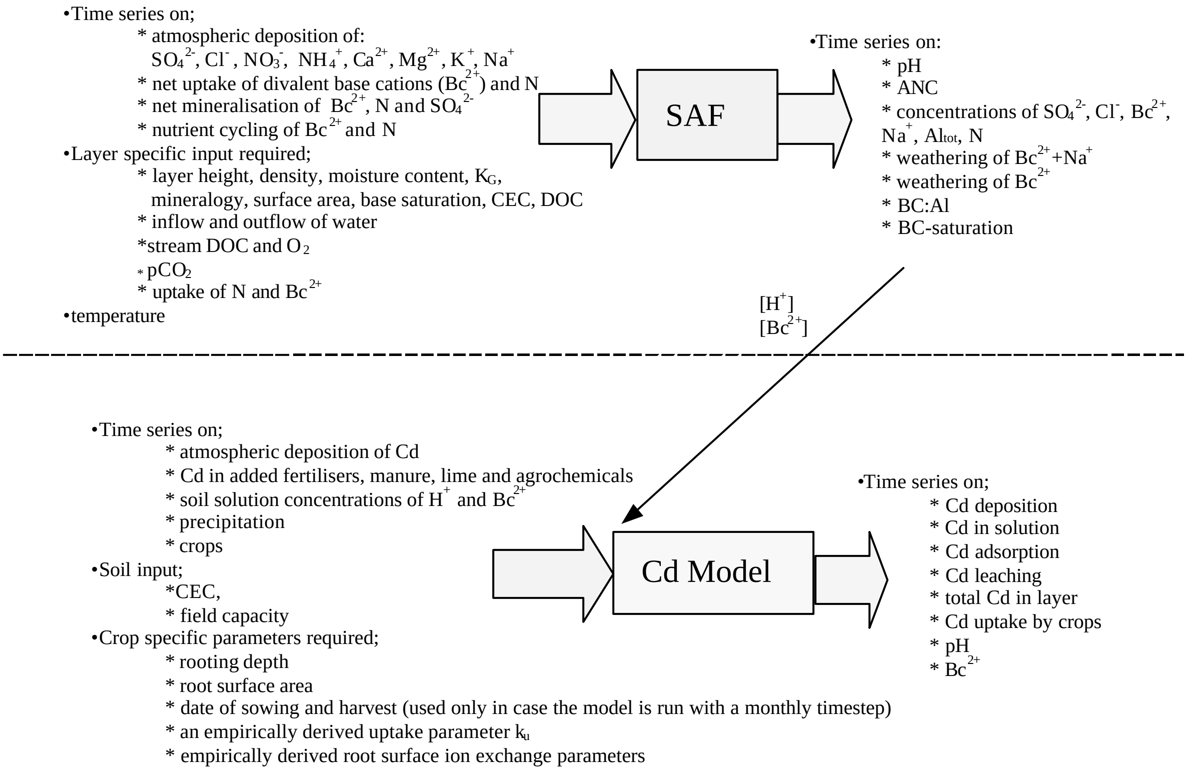

Figure 2 The SAFE model is used as a core model for simulating cadmium in the soil-plant system. Output from SAFE used in the CdModel is soil solution concentrations of divalent base cations and pH.

$$(\mathrm{Cd})_{\mathrm{Total}} = (\mathrm{Cd}^{2+})_{\mathrm{ads}} + [\mathrm{Cd}^{2+}] \qquad (1)$$

The total cadmium in the soil is schematised as a pool. Input to the pool is deposition and in specific cases weathering. Adsorption processes, described in equation 3 below, are shown in fig 3 as $r_{Cd,X}$. Leaching and uptake are the processes decreasing the cadmium concentration in the soil. The change in cadmium content of the soil over a time period, dt, is given by equation 2.

$$d[Cd^{2+}]/dt = r_{Cd,In} + r_{Cd,W} - r_{Cd,U} - r_{Cd,Out} \qquad (2)$$

$r_{Cd,In}$ is the rate at which cadmium ions are added to the soil through atmospheric deposition, fertilisers, manure and other agrochemicals. This parameter is discussed in further detail below.
$r_{Cd,W}$ is the weathering rate of minerals containing cadmium as described below.
$r_{Cd,U}$ is the rate by which cadmium is taken up by crops and as discussed in further detail below.
$r_{Cd,Out}$ is the leaching rate of cadmium from each layer as described below.

The equilibrium is recalculated for each time step, after modifying the [Cd^{2+}], according to the following equation (eq.3), discussed in further detail in section 4.1 below.

$$\log(Cd^{2+})_{ads} = k^{*}_{Cd} + (m \cdot \log[H^{+}] + (n \cdot \log[Cd^{2+}]) + (o \cdot \log[Bc^{2+}]) + (p \cdot \log(CEC)) \qquad (3)$$

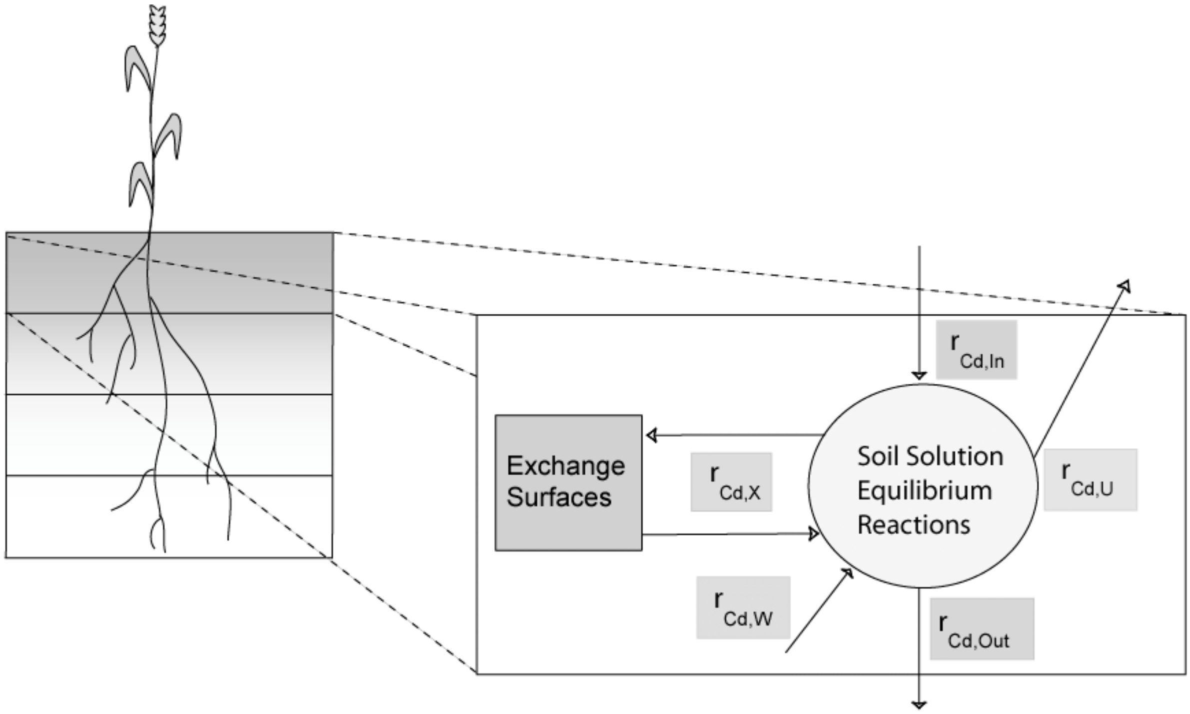

Figure 3 The soil column is divided into layers. The cadmium concentration in each layer is calculated as a mass-balance with inputs and outputs.

In addition, the model calculates the total cadmium in the soil at each time step following the equation:

$$Cd_{total} = [Cd^{2+}] * V + Cd_{ads} + \frac{d([Cd^{2+}])}{dt} \qquad (4)$$

Cd_{total} is the total cadmium in the soil at time $t+dt$
dt is the time step
Cd_{ads} is the adsorbed cadmium at time t
$[Cd^{2+}]$ is the concentration of the cadmium in the soil
V is the unit volume of soil solution
The model solves equation 3 and 4 for the two unknown quantities $[Cd^{2+}]$ and Cd_{ads}. The resulting equation for the unknown $[Cd^{2+}]$ has the form:

$$[Cd^{2+}] + 10^{k_{Cd}} + 10^{m} * [H^{+}] + 10^{n} * [Cd^{2+}] + 10^{o} * [BC^{2+}] + 10^{p} * CEC + \frac{d([Cd^{2+}])}{dt} - Cd_{total} = 0$$

However, the above equation has no analytical solution for the unknown $[Cd^{2+}]$. For this purpose, a numerical routine is adopted. The routine guesses a value of $[Cd^{2+}]$ between 0 and the maximum value of $[Cd^{2+}]$ possible in the soil. This value is substituted in the equation and if the result is higher than 0, a smaller value is put into trial, while in the other case a larger value of $[Cd^{2+}]$ is tried. The routine iterates in this way until a sufficiently small value is returned from the equation.

The ion exchange process

The distribution of cadmium between soil solution and ion exchange surfaces in soils has proven to be successfully described by a Freundlich adsorption isotherm equation (Christensen, 1989); (Elzinga et al., 1999); (Escrig and Morell, 1998); (Wilkins et al., 1998). In CdModel a general adsorption equation is used (Eq. 3). The parameters used (table 1) have been found in an extensive survey of literature data on adsorption of cadmium (Elzinga et al., 1999). The CdModel is structured in such a manner that these parameters can easily be changed if better data material regarding specific adsorption characteristics of a certain soil is available. This is an important aspect of CdModel since calibration of the sorption equations to the soil conditions is beneficial for model performance.

Table 1 Parameters used in equation 3, an extended Freundlich equation, describing the distribution between adsorbed cadmium and cadmium in solution. Values taken from (Elzinga et al., 1999).

k^*_{Cd}	m	n	o	p
–3.22	–0.445	0.870	–0.47	0.659

The rate of input

Cadmium is added to agricultural soils from atmospheric deposition, fertilisers, manure, sludge, lime and other agrochemicals. Atmospheric deposition is a significant contribution to the total cadmium load of agricultural soils. In Sweden, there is a trend with decreasing cadmium deposition northwards in the country, with 0.52 g/ha in the very south and 0.30 g/ha in the north (Jordbruksverket, 1999). Atmospheric cadmium is derived from mining and smelting of nonferrous metals, the production of iron and steel, combustion of fossil fuels and waste incineration (McLaughlin et al., 1999). The significant contribution from atmospheric deposition to the soil content seems to have been high during the past century. It has been estimated that the average concentration of cadmium in Swedish agricultural topsoil have increased by 33% during the 1900's (Andersson, 1992). This value seems to be in accordance with findings from the Rothamsted experimental station in the U.K. where an increase in the soil cadmium concentrations by 27-55% was observed for the period 1850-1980 (Jones and Johnston, 1989). It was concluded that this increase was solely due to atmospheric deposition. In addition to the diffuse contamination of soils from atmospheric fallout there is also deposition from cadmium containing fertilisers. Apatite, containing varying concentrations of cadmium naturally, is used as a source of phosphorous in agriculture. The weathering rate of apatite is quantified in the SAFE model and can be used together with the stochiometric content of cadmium in the mineral to calculate the release rate of cadmium from fertilisers based on this mineral.

The weathering rate

The rate by which cadmium is added to the soil solution from weathering of cadmium containing minerals, $\mathbf{r_{Cd,\ w}}$, can be quantified in the same manner as weathering of other minerals is calculated in the SAFE model. In most situations $r_{Cd,\ W}$ is set to zero, as the content of cadmium containing minerals in agricultural soils generally is low and the contribution to the total cadmium load from weathering hence is of minor importance. However, an inclusion of the contribution from weathering could be useful when simulating cadmium in soils with a high background concentration of cadmium. Geology has proven to be of significant influence regarding background concentrations of cadmium (McLaughlin et al., 1999). This is also the case when studying cadmium concentrations in Swedish grain, which have been found to correlate with surface and subsurface soil cadmium concentrations (Eriksson et al., 2000). The geographical pattern in Sweden indicated that the highest concentrations were found in areas with Cambrian sedimentary bedrock, such as alum shale and sandstones with cadmium containing zinc sulphide impregnations (Kornfält et al., 1996); (Söderström and Eriksson, 1996). Hence, the mineralogical composition of the soil is of interest in calculating the risks of elevated concentrations of cadmium in the crops grown in certain regions.

Rate of plant uptake

Earlier attempts at describing cadmium in the soil-plant system have primarily focused on the behaviour of the metal in soil and not so much on the actual bioaccumulation processes. Plant accumulation of cadmium has been described as a passive uptake, coupled to the water flow from soil to plants driven by transpiration (Palm, 1996). Other modelling approaches includes additional factors to the volume rate of plant water uptake, such as a crop specific preference factor for cadmium as well as an allocation factor to account for the transfer of cadmium to different plant parts (Tiktak et al., 1998). In CdModel, an attempt at describing the plant uptake of cadmium focusing on the dynamics at the root surface is presented.

From a mechanistic point of view, cadmium can be taken up when it is available at the plant root surface. Hence, the root surface concentration of cadmium and the root area will govern the uptake of cadmium into the plant. In the CdModel, plant roots are considered to act as ion exchange surfaces, much the same way as any other organic material in the soil. The amount of desorbable root surface cadmium is considered to be relatively small compared to the total pool of adsorbed cadmium, at least when the soil solution concentration is low (Grant et al., 1998). Michaelis-Menten kinetics can be used to describe plant uptake of ions present in low concentrations in soil (Marschner, 1995). Studies of cadmium uptake in barley and wheat have indicated that membrane transport of cadmium is a passive process at high concentrations of cadmium in the soil solution but that it is an active, energy requiring process at low concentrations, i.e. the kind of concentrations normally found in agricultural soils (Hart et al., 1998). It is assumed that the plants can take up a large proportion of the amount of cadmium adsorbed on the root surfaces. The adsorption sites at the root surface are able to attract many types of ions and therefore the adsorption of cadmium will be influenced by the concentration of other ions in the soil solution. The amounts of ions available at the surface will be controlled by selective ion exchange between H^+ and divalent base cations (Bc^{2+}). These ions will force Cd^{2+}. The selectivity of the reaction is such that K^+ and Na^+ do not interfere significantly with the reaction (Christensen, 1989); (Ziper et al., 1988). In addition, the influence from H^+ includes pH dependent influence from Al^{3+}. Results from pot experiments (Eriksson, 1990) point toward an empirical expression describing plant uptake (Eq. 5).

$$r_{Cd,U} = k_{Cd} \cdot m_{Cd} \cdot [H^+]^m \cdot [BC^{2+}]^n \tag{5}$$

The uptake rate coefficient, k_{Cd}, is plant specific and follows the uptake of chemically similar ions from the soil solution, such as calcium. The amount of cadmium at the root surface, m_{Cd}, is governed by the soil solution concentration, which in turn is dependent on the ion exchange equilibrium. The coefficients accounting for the influence on the cadmium uptake from pH and the concentration of divalent base cations were found to be m=-0.5 and n= -1 (Eriksson, 1990).

It has been shown that relative cadmium uptake is roughly proportional to root surface area, root biomass, root volume and the number of root tips (Noordwijk et al., 1995) (Berkelaar and Hale, 2000); (Piñeros et al., 1998). In CdModel, the plant cadmium uptake is proportional to the root surface area in each layer and the wetting of these root surfaces with soil solution. Root distribution is described as a decrease of biomass with depth (Gerwitz and Page, 1974). It is approximated that 85 per cent of the wheat plant roots are found in the uppermost 50 cm of the soil whereas 15 per cent is found in the 50-100 cm depth interval. These assumptions are in accordance with approximations made in other models regarding root growth of crops (Porter et al., 1986). It is however important to note that root biomass and nutrient uptake from different soil horizons are not always correlated, due to differences in the morphology and function of different plant roots (Haak, 1994). This complexity is however ignored in the CdModel.

The empirically derived uptake function (Eq. 5) is geared by two components involving the roots, describing root-growth and wetting of root surfaces (Eq. 6). The root-growth depends on the length of the growing season and the maximal rooting depth of the crop. Root growth is assumed to increase linearly from the date of planting to harvest, from 0 to max growth of the specific crop simulated. However, the dates of sowing and harvest are only needed when running the model on a monthly time step, since that dynamics is lost when using a yearly time step. The CdModel has a structure that enables the user to modify the root parameters for different crops easily. The root wetting is calculated from the water content of the soil according to the following formula (Walse et al., 1998), assuming that the relation between root wetting and water supply follows a Langmuir adsorption isotherm for physical adsorption of water to root surfaces:

$$f(\theta) = (k_w \cdot (\theta / \theta_{max})^{nw}) / (1 + (k_w \cdot (\theta / \theta_{max})^{nw})) \qquad (6)$$

$?$ is soil solution content in the soil (m^3/m^3)
$?_{max}$ is the soil water content at field capacity (m^3/m^3)
k_w is an empirical coefficient
nw is an empirical exponent

The root-wetting value thus calculated is used in the following equation (Eq. 7) to conclude the cadmium uptake in the plants:

$$\text{uptake} = f(\theta) * \text{root\_growth} * k_u * \left[Cd^{2+}\right] * \left[H^{+}\right]^{m} * \left[BC^{2+}\right]^{n} \qquad (7)$$

There is a plant specific uptake parameter, k_u, which has been derived empirically from uptake experiments with wheat, where the amount cadmium adsorbed per unit root surface area has been determined (Berkelaar and Hale, 2000). This parameter is easy to change in the CdModel to make it applicable to different crops and varieties.

Several studies have found that most of the cadmium that is taken up by plants is accumulated in plant roots (Cieslinski et al., 1996); (Florijin and VanBeusichem, 1993); (Jalil et al., 1994). Consequently, the movement of cadmium inside the plants seems to be restricted somewhat. It has been proposed that an increased uptake of Cd^{2+} by the roots could stimulate plants to form organic ligands, which can limit the translocation of cadmium from roots to other parts of the plants (Cataldo et al., 1983); (Cieslinski et al., 1996). Varieties with a high proportion of cadmium in the roots had less in the grain and vice versa. Similar patterns of restricted root to shoot translocation of cadmium were also found in maize (Florijin and VanBeusichem, 1993). Translocation of cadmium from root to shoot is likely to take place via the xylem and to be driven by transpiration (Hart et al., 1998). However, this mechanism seems to be plant specific and findings from uptake experiments on maize did not show any correlation between cadmium uptake and transpiration (Florijin and VanBeusichem, 1993). In CdModel there is at present no link between transpiration and allocation of cadmium within the plant.

The uptake of cadmium from the soil into cultivars of wheat seems to be influenced by the calcium concentration in the soil solution (Wenzel et al., 1996). Indications of a competition between calcium and cadmium regarding the translocation process within bean and corn have also been reported (Tyler and McBride, 1982). One possible explanation is that cadmium is translocated within the plants via the normal calcium pathway. Cadmium and calcium compete for cation exchange sites in the cell wall (Tyler and McBride, 1982). In a situation where the concentration of Ca^{2+} is low there is a proportionally higher concentration of Cd^{2+} on the exchange sites and hence the mobility of Cd^{2+} in the plant is reduced (Cieslinski et al., 1996). Similar theories have been put forward regarding the influence from zinc on the reallocation of cadmium in durum wheat seedlings (Cakmak et al., 2000). Cakmak et al. (2000) found an inverse relationship between the amount of zinc in the growth media and the mobility of cadmium within the plants and concluded that the mechanism explaining these findings is a competition for binding sites in the cell walls, thus mainly influencing the reallocation of cadmium within the plants rather than the actual uptake at the root surface. Other authors have found antagonistic effects of zinc on the cadmium accumulation in crops both for wheat (Oliver et al., 1994), and durum wheat (Choudhary et al., 1994). In the CdModel, the competition between cadmium and calcium regarding plant uptake is only quantified at the root surface and zinc is not included at all at present. It proved to be very difficult to parameterise the process of internal allocation of cadmium within the plant, as many of the processes are not fully understood yet.

Rate of leaching

The vertical distribution of cadmium in soils generally exhibits a decreasing concentration with depth due to the deposition on the soil surface and the high adsorptive capacity in the plough layer due to a high organic material content (Tiktak et al., 1998). Such patterns of distribution are particularly suitable to analyse in a multi-layer model such as CdModel (fig 3). The transport of cadmium in the soil is described as a mass-flow, following the downward percolation of water in the soil profile. Leaching is calculated using the model hydrology and the cadmium concentration in the soil solution. The leached amount of cadmium is equal to the cadmium concentration times the amount of water flowing out of the soil.

Hydrology is described in a simplistic manner in the model and will be modified later for more detailed analysis regarding the movement of cadmium in the soil profile.

3.1.4 Simulations

A long-term fertility experimental site called Kungsängen was used for soil- and crop data in the simulations. The site is situated close to the city of Uppsala (59°50' N. 17°40E', altitude 4 m). Kungsängen soil is an acid sulphate clay soil with a pH of 6.9 at the soil surface and decreasing with depth. A 5-year crop rotation with three years of grass-clover, one year of wheat and one year of spring cereals was practised 1907-1963. Prior to that the land was used for grazing during the 19th century. In 1964 the fertility experiment started. The soil characteristics, crop rotation and fertiliser treatment have been described in detail in (Kirschman, 1991). Unfortunately, there was no data on cadmium concentrations in soil or grain from the Kungsängen site. Instead, data on wheat accumulation of cadmium was taken from a survey dealing with wheat Cd concentrations in specified wheat cultivars from the period 1918-1980 (Andersson and Bingefors, 1985). The concentrations reported in this survey were used to check if the model gave reasonable simulated values regarding grain concentrations.

Cadmium input and pH

Cadmium deposition on Kungsängen soil was reconstructed, using data and estimations of historical atmospheric deposition and concentrations in fertilisers and manure (fig. 4). The increase of cadmium deposition started after the 2nd World War and continued to increase until the adverse effects started to be discussed and policies to reduce the cadmium content in fertilisers were implemented.

The bioavailable fraction of the total cadmium content of agricultural soil is the most important aspect to discuss when investigating grain concentrations. Soil pH is the most influential factor when it comes to mobility and bioavailability of cadmium in these soils (Andersson and Siman, 1991); (Christensen, 1989); (Eriksson, 1990); (Gray et al., 1999); (Kabata-Pendias and Pendias, 1992); (Salam and Helmke, 1998); (Öborn et al., 1995). The activity of Cd^{2+} in solution is negatively correlated with soil pH (Salam and Helmke, 1998) (Temminghoff et al., 1995). The reason for the decrease in activity with increasing soil pH is that the adsorption capacity of the soils, in particular of those with colloids dominated by pH-dependent charges, increases due to the deprotonation of the surface-bound H^+ on the soil exchange sites (Kabata-Pendias and Pendias, 1992). The model is capable of describing the dynamics of crop cadmium uptake with reference to pH (fig. 5.). The cadmium concentration in grain was increased by about 0.2 $nmol.g^{-1}$ grain (dry weight) when pH is lowered with one unit. This is in accordance with findings from Swedish field experiments on cadmium uptake and pH in wheat grain where the increase in wheat grain was about 0.3 $nmol.g^{-1}$ per lowering of pH-unit (Jansson and Öborn 2001, unpublished data). A competitive effect of Ca^{2+} on the Cd adsorption has been reported by several authors (Christensen, 1989); (Temminghoff et al., 1995); (Escrig and Morell, 1998); (Boekhold et al., 1993). Raising the pH of the soil through liming, as a means of reducing the cadmium concentrations in crops, has shown ambiguous results in field trials (Andersson and Siman, 1991); (Oliver et al., 1996). The complexity of the ion exchange processes makes it difficult to predict the resulting effect of adding calcium carbonate to the system, taking both the pH effect and the effect of competition between Ca^{2+} and Cd^{2+} for adsorption sites in the soil as well as on root surfaces into consideration (Boekhold et al., 1993).

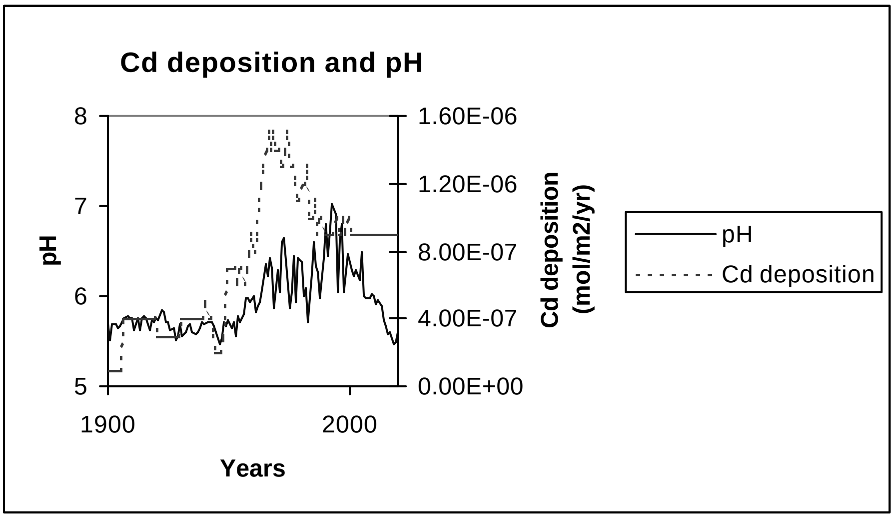

Figure 4 Deposition (input) of cadmium on to agricultural soils has been reconstructed and shows an increasing time trend, as fertiliser use increased in Sweden after the end of the 2nd World War. This trend has however turned since measures to reduce cadmium in fertilisers were implemented. After year 2000 the deposition was set to a constant value whereas the pH level was dropped to check model behaviour with reference to pH, see fig. 32 below.

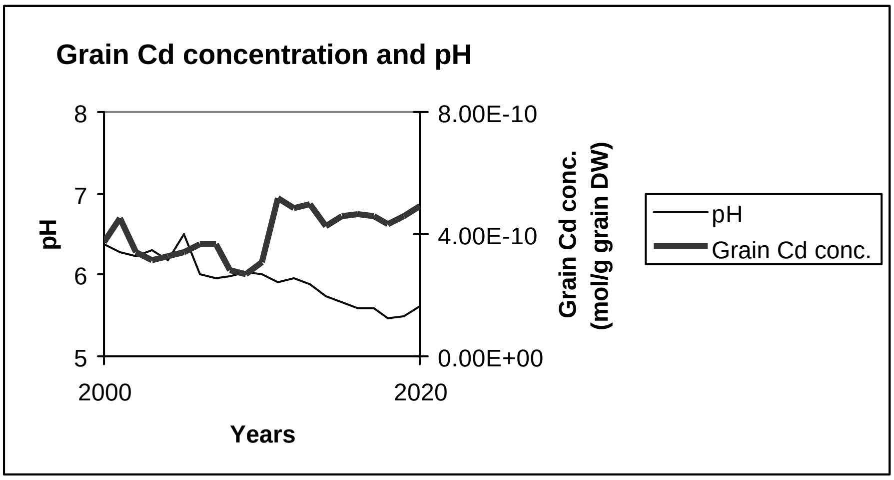

Figure 5 Grain cadmium concentration is influenced by soil solution pH, showing a negative correlation with high uptake at low pH-values and vice versa.

Simulated cadmium concentrations in wheat grain, using the Kungsängen site as input for the modelling of soil chemistry using SAFE, show reasonable values compared to field data on wheat cadmium concentrations during the period 1918-1980 (Andersson and Bingefors, 1985), fig. 6. There is however a substantial yearly variation in grain cadmium concentration which is not captured by the model.

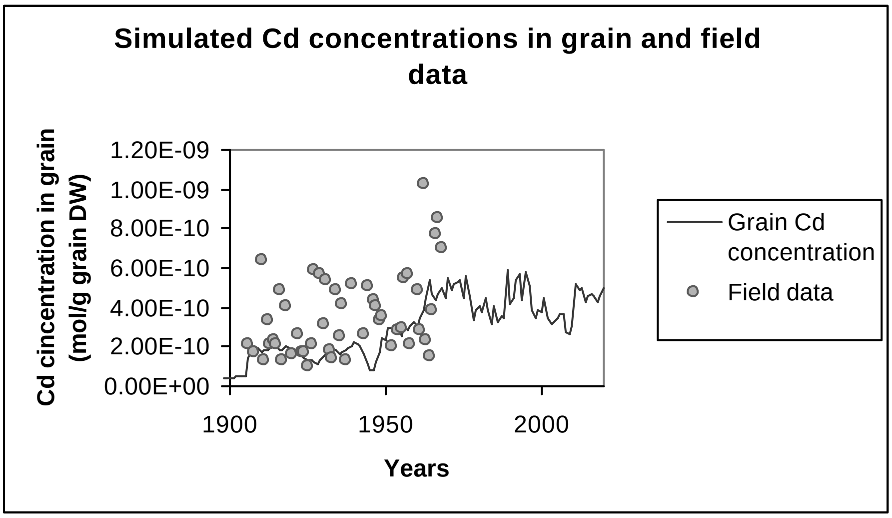

Figure 6 . Simulated grain cadmium concentrations, compared to field data, show that the CdModel is capable of predicting the grain content within the right magnitude. It is however not possible to mimic the large annual variations with the model yet.

Empirically derived transfer functions

Empirically derived soil-plant transfer functions deal with the direct relation between soil properties and crop metal concentrations, without explicitly trying to capture the dynamics in the soil solution. One such transfer function (Eq. 8), presented by (Römkens, P.F.A.M. de Vries, W. et al., pers. communication), has been applied to the data material used in simulations with the CdModel.

$$\log(\mathrm{Me})_{\mathrm{plant}} = 0.43 - 0.44 \cdot \log(\%\mathrm{OM}) - 0.17 \cdot \mathrm{pH}_{\mathrm{KCl}} + 0.36 \cdot \log(\mathrm{Me})_{\mathrm{soil}} \qquad (\mathrm{Eq.}\ 8)$$

$(\mathrm{Me})_{\mathrm{plant}}$ = plant content of cadmium (mol kg^{-1})
$(\mathrm{Me})_{\mathrm{soil}}$ = total metal content in the soil (mol kg^{-1})

Due to the fact that there are no measurements of cadmium from the Kungsängen site, simulated values for the soil cadmium concentration $(\mathrm{Me})_{\mathrm{soil}}$ and simulated pH values from the SAFE model were used in the transfer function calculations. The two approaches, a dynamic model relating the crop uptake to soil solution concentrations of cadmium and a transfer function describing a direct relationship between soil parameters and crop content, were compared to field data on crop cadmium concentrations, fig. 7. The comparison appeared to be relatively weak.

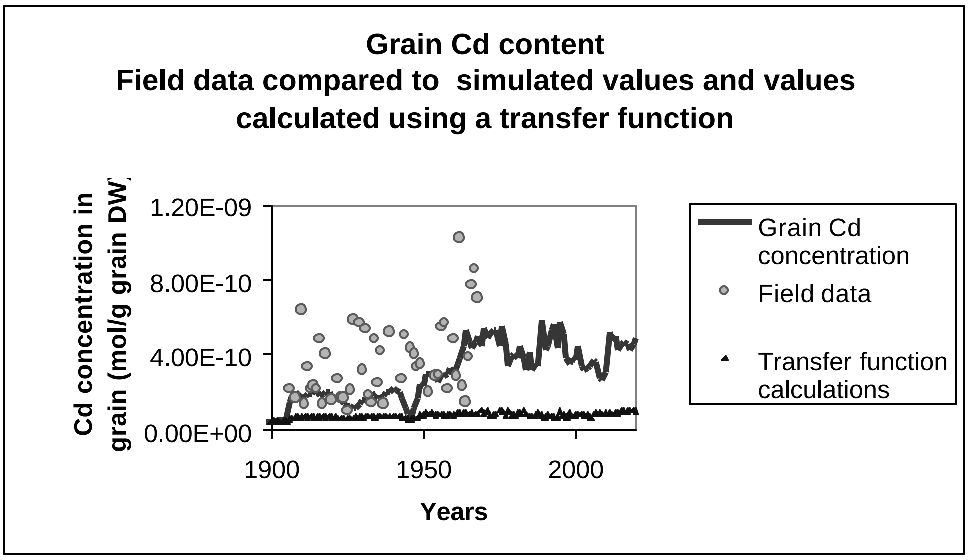

Figure 7 . Field data on grain cadmium concentrations are compared to the simulated values from using the CdModel and to the values from calculations using a transfer function.

3.1.5 Discussion and conclusions

Simulating cadmium in the agricultural soil-plant system with a dynamic process-oriented biogeochemical model proved to be a challenging task. Many of the processes influencing the plant uptake of this heavy metal are not yet fully understood and hence not parameterised. It was therefore difficult to construct a computer model able to mimic the dynamics in detail and the yearly variation in crop cadmium concentration in particular. It has become evident during the course of the project that much of the dynamics involved in crop uptake of cadmium is very complex and probably to a great extent mainly governed by plant specific processes and not so much steered by soil chemistry.

In addition, it has been somewhat difficult to find field data for calibration and validation of the model. Using long time-series of historical data to check if the model is capable of predicting the current situation accurately is a way to validate model performance. However, there are few sites with long time-series of cadmium concentrations in soil and crops.

However, the CdModel has shown promising reference behaviour patterns and is capable of describing the grain cadmium concentrations with reasonable accuracy. The structure of the model enables the user to improve parameterisation of the processes when new data is available that sheds new light on the mechanisms governing the uptake process and the internal allocation of cadmium in the plants.

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3.2 Derivation of soil-specific quality standards for cadmium and zinc

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Summary

The presence of heavy metals in soils poses potential risks due to the transfer of metals from soil to food crops and the subsequent intake of crops by human beings or animals. However, current soil quality standards usually do not consider uptake to be soil specific and standards are based on the total soil metal content only, although uptake is controlled largely by metal availability (e.g. solubility or speciation) instead of the total soil metal content. To derive an applicable system that enables the user to calculate soil specific target values for Cd and Zn in arable soils, data from nation-wide field inventories on heavy metals in soils and crops were used. Soil-to-plant transfer relationships for Cd and Zn based on soil pH, organic matter content, texture and the soil metal content were derived by multiple linear regression. The use of a simple Freundlich-type equation explained between 40 and 80% of the measured variation of Cd and Zn in crops such as potato, wheat, maize, sugar beet, lettuce and endive, whereas the total metal content only accounted for up to 10%. The approach described here can not only be used to estimate the soil-specific Cd and Zn content in various crops but also to calculate the site-specific target soil metal content at which the food quality criteria will be exceeded.

3.2.1 Introduction

The average heavy metal content in soils has increased during the last few decades due to atmospheric deposition, application of fertilisers and other soil amendments (e.g. sludge or manure). Especially in the vicinity of industrial areas, elevated metal contents are common which can lead to enhanced uptake of metals by arable food crops and increased dietary loads of metals by human beings (McLaughlin et al., 1999). To prevent excessive intake of metals via food, crop quality standards have been imposed above which the crop cannot be sold on the market. In the Netherlands, additional soil quality criteria exist that are developed to protect the quality of food crops (LAC, 1991). These and many other soil quality standards currently in use are based on the total acid extractable metal content only. Metal uptake by crops and other adverse effects of metals in soils such as toxicity for soil organisms and leaching to groundwater, however, are not related to the soil metal content alone, but controlled merely by the actual availability and/or speciation in the soil solution (Hani, 1996; Hayes and Traina. 1998). Plant roots do not take up metals directly from the solid phase, but through soil solution. Recent research results suggest that the free metal ion is one of the main chemical species that can be taken up by plants (Bell et al., 1991, Sauvé et al., 1996), although there is evidence that small organic compounds and inorganic ligands such as chloride can enhance uptake as well (Parker and Pedler, 1997). It is obvious, though, that those parameters that control the solubility and speciation of metals in the soil solution have a large impact on plant uptake and should be considered when evaluating the potential risk of metal accumulation by crops in a specific soil. Especially soil pH, organic matter content and clay content are crucial with respect to metal solubility (Rieuwerts et al., 1998). Although chemical models are available to calculate metal speciation in the soil solution (e.g. Plette et al., 1999), the capacity of mechanistic models to accurately estimate the plant metal content under field conditions is still limited due to spatial and temporal variability of input parameters. Furthermore, most models require extensive calibration which requires a large number of parameters that are usually unavailable or highly variable in time and space such as the dissolved organic carbon concentration (DOC) or the dissolved calcium concentration in the soil solution. A more practical approach that should be used in a wide range of soils and crops should, therefore, comply to the limitations mentioned above. The choice of parameters has to be limited to generally available soil properties such as pH, organic matter and clay content in combination with the metal content of the soil. These properties are usually available through soil maps on the farm-, regional- and national level and are less variable than DOC or the dissolved Calcium concentration. On the other hand, soil properties that control metal availability have to be included to obtain reasonable estimates of the plant metal content. Here, we will evaluate various approaches that are used to estimate the plant metal content in an attempt to derive functional relationships between the parameters mentioned above and the Cd and Zn content in a range of common food crops such as lettuce, endive, potato and cereals. The approaches evaluated here include the commonly used BioConcentrationFactor (BCF) approach (USEPA, 1993), an extended version of the BCF approach where the BCF is related to soil properties (Huinink, 1999) and a Soil-to-Plant transfer approach where the metal content in the plant is related directly to various soil properties including the soil metal content (Wenzel et al., 1996). The data used in this study are from field studies only since well controlled pot experiments are likely to result in different uptake patterns compared to actual field data from non-treated plots. The aim of this study is, however, not only to derive functional relationships between soil properties and the metal content in plants under field conditions, but also to develop a conceptual framework for site-specific risk assessment of heavy metals in arable soils that can be used to evaluate whether or not a soil can be used safely for arable crop production.

3.2.2 Materials and methods

Data used in the Analysis

The data used in this study originate from two large field studies. The first one serves as a reference database for background levels of metals in arable soils and crops in the Netherlands (Wiersma et al., 1986). This data set – from here on referred to as the national database - mainly contains non-polluted sites and represents the major soil types present in the Netherlands (mostly sedimentary clay, sand, loess and peat soils). In total, this database contains more than 1000 plant – soil combinations including crops like lettuce, endive, maize, sugar beets, potato, wheat and pasture.

The second data set, referred to as the floodplain database, was collected to investigate the metal content in soils and arable crops in floodplains soils along three rivers in the southern parts of the Netherlands (river Meuse, Geul and Roer; van Driel et al., 1988). As a result of deposition of contaminated sediments, some of the sites in this database are highly contaminated with Cd and Zn. The floodplain database contains the same crops as described previously for the national database. All the sites in both databases are still used for arable crop production.

Soil and Plant Sampling and Chemical Analysis

Soils Soil material was collected while the crop was still on the field just before harvest. Between 10 and 20 samples from the topsoil (0 to 30 cm) from each site were collected and mixed to obtain a representative sample (approx. 2 kg of soil material). After drying at 40 ºC for 3 days, the soil material was crushed using a platinum crusher with a diameter of 0.2 cm (clay and peat soils only) and sieved on a contaminant-free 2 mm sieve. The total metal content in the soil was determined in a hot acid destruction (Aqua Regia, Sparks et al., 1996). Soil organic matter was determined by loss on ignition at 850 ºC for 4 hours (Vierveyzer et al., 1979). pH KCl was measured in a 1 to 5 (m:m) soil - 1N KCl suspension after 4 hours of equilibration. The clay content was determined by gravimetric methods (Vierveyzer et al., 1979).

Crops. Ten to twenty samples of crop material from each sampling point was collected prior to harvest to obtain at least 1 kg of plant material. After washing with demineralised water, the plant material was dried at 70 ºC for 3 days and subsequently ground in a platinum grinder to obtain homogeneous material. Cd and Zn was determined in a hot digestion using 1 gram of dried crop material, which was dissolved in a mixture of concentrated HNO_3 (65%), H_2SO_4 (96%) and $HClO_4$ (70%). Here, the results from 6 different crops will be used because they were analysed in both data sets: lettuce, potato and wheat (food crops); grass, maize and sugar beet (food crops for cattle).

3.2.3 Theory

Various approaches are tested to derive functional relationships between soil properties and the Cd and Zn content in plants. In figure 1, these approaches are shown together.

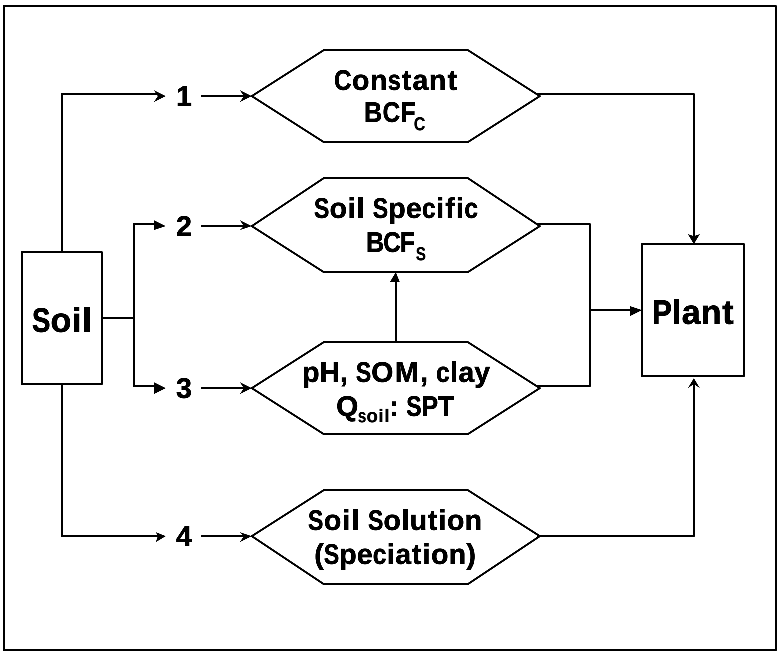

Figure 1 Various approaches to derive functional relationships between soil properties and the Cd and Zn content in plants

From 1 to 4, the approaches become both more reliable but also more complex. The first approach (1) is the constant BioConcentrationFactor (BCF$_C$) approach. It is assumed that the ratio between the metal content in the plant and the soil is constant for a given crop:

$$\mathrm{BCF_C} = [\mathrm{Metal_{plant}}]/[\mathrm{Metal_{soil}}] \tag{1}$$

with:
[Metal$_{plant}$] = Metal content of the crop in mg.kg^{-1} (on dry weight)
[Metal$_{soil}$] = Soil metal content in mg.kg^{-1} (dry soil)

Using Eq. [1], the plant metal content can be estimated once the BCF$_C$ is known for a specific crop:

$$[\mathrm{Metal_{plant}}] = \mathrm{BCF_C} \cdot [\mathrm{Metal_{soil}}] \tag{2}$$

This approach is currently used in various risk estimation models (e.g. USEPA, 1993). In most cases, however, the BioConcentrationFactor is not constant but depends on soil properties such as pH, organic matter (OM) and clay content. To account for this, a Freundlich type equation is used to related the BCF to soil properties (second approach shown in figure 1) to obtain the so-called soil-specific BioConcentrationFactor (BCF$_S$, Huinink, 1999):

$$\log[\mathrm{BCF_S}] = \alpha + \beta \cdot \log[\mathrm{OM}] + \gamma \cdot \log[\mathrm{clay}] + \delta \cdot \mathrm{pH_{KCl}} \tag{3}$$

with:

$\alpha, \beta, \gamma, \delta$ = crop specific regression coefficients

pH_{KCl} = pH of the soil measured in 1N KCl

OM = soil organic matter content in %

clay = soil clay content in %

from which after rearrangement of equation (3), the plant metal content can be calculated:

$$[\mathrm{Metal_{plant}}] = [\mathrm{Metal_{soil}}] \cdot 10^{(\alpha+\beta\cdot\log[\mathrm{OM}]+\gamma\cdot\log[\mathrm{clay}]+\delta\cdot\mathrm{pH_{KCl}})} \tag{4}$$

The values of α through δ can be obtained by multiple linear regression.

The third approach, which we call the Soil-to-Plant Transfer relationship (SPT), relates the plant metal content directly to the soil properties used in the BCF_S approach but in combination with the soil metal content (Wenzel et al., 1996):

$$\log[\mathrm{Metal_{plant}}] = \alpha + \beta\cdot\log[\mathrm{OM}] + \gamma\cdot\log[\mathrm{clay}] + \delta\cdot\mathrm{pH_{KCl}} + \varepsilon\cdot\log[\mathrm{Metal_{soil}}] \tag{5}$$

Eq. (5) now resembles the Freundlich adsorption isotherm that is often used to describe the solubility of heavy metals in soils (Elzinga et al., 1999; Gray et al., 1999). Although this approach looks quite similar to the previous one, the differences between both methods - apart from methodological ones - when applied to field data can be considerable (see Results and Discussion). Equation 5 can be used to derive soil specific soil quality standards (SSQS). To obtain values for SSQS for arable crops (human food crops), the maximum tolerable metal content in crops (e.g. the food quality criteria, called [$\mathrm{Metal_{plant\text{-}critical}}$], is used as input value for [$\mathrm{Metal_{plant}}$]. Taking into account soil pH, organic matter- and clay content, the soil-specific SSQS can be calculated from this:

$$\mathrm{SSQS} = 10^{(\varepsilon\cdot\log[\mathrm{Metal_{plant-critical}}]-(\alpha+\beta\cdot\log[\mathrm{OM}]+\gamma\cdot\log[\mathrm{clay}]+\delta\cdot\mathrm{pH_{KCl}}\ )/\,\varepsilon)} \tag{6}$$

with:

$\mathrm{Metal_{plant\text{-}critical}}$ = Food quality criteria in $mg.kg^{-1}$ (dry weight)

If the SSQS calculated for a given site is lower than the actual metal content, the crop grown on that site is likely to exceed food quality criteria and cannot be sold or otherwise used. For animal food crops (grass, sugar beet, corn), also maximum tolerable metal concentrations exist which enable a similar approach as outlined for human food crops. In this paper we will not consider method number 4, which relates soil solution speciation to metal uptake (e.g. Sauvé et al., 1996), not only because application on a large scale is probably not feasible yet but also because there is still considerable debate as to whether the free ionic activity is the sole predictor of plant uptake in soils as well (Lorenz et al., 1997).

3.2.4 Results and discussion

Metal content in soils and crops

In table 1, data on soils and plants are shown. As can be seen from the range in soil properties, soil types included ranged from sandy soils with a low clay- and organic matter content, to clay soils with more than 40% clay. In general, soil pH was near neutral due to natural abundance of lime (data not shown here) but non-calcareous soils were included as well with pH value as low as 3.8. Apart for being used as pasture, peat soils were rare and were only included for lettuce (2 sampling points) and wheat (1 sampling point). Cd and Zn contents in the soils ranged from less than 0.1 mg.kg^{-1} for Cd and 18 mg.kg^{-1} for Zn to more than 35 mg.kg^{-1} for Cd and 1500 mg.kg^{-1} for Zn in one of the floodplain soils. According to the current Dutch legislation, these soils exceed the so called 'intervention value' (12 mg.kg^{-1} for Cd and 720 mg.kg^{-1} for Zn respectively) and are considered polluted (Ministry of VROM, 2000). However, the Cd and Zn content in the majority (> 95%) of the soils included here, does not exceed current soil quality limits and these soils are considered to be safe for agricultural crop production based on the total metal content.

In contrast to the low number of soil samples that exceed Dutch soil quality standards, quite a significant number of crop samples exceed either human or cattle food quality standards as is shown in Table 2. Especially Cd uptake by wheat, sugar beet and, to a lesser extent, endive resulted in a surprisingly large number of samples with Cd concentrations exceeding current quality standards (0.1 mg.kg^{-1} for wheat and 0.2 mg.kg^{-1} for endive based on fresh weight and 0.57 mg.kg^{-1} for sugar beet based on dry weight). For Zn, the situation is different; no samples exceeded the quality standards for animal food except sugar beet where 6% of the samples had a Zn content higher than 250 mg.kg^{-1} (based on fry weight). These examples illustrate that food quality criteria are in fact exceeded in soils where soil quality standards are below current safety guideline levels. This stresses the need for guidelines that do incorporate those soil properties that control metal uptake from soil and enable the user - e.g. farmers or policy makers- to evaluate whether soils in specific regions can be used safely for various crops.

Table 1 Selected properties in soils from the national inventory and the floodplain soils.

		Soil Properties				Crop	BCF[a]		n
		SOM %	clay %	pH-KCl	metal[b] mg.kg^{-1}	metal[b] mg.kg^{-1}	value	ratio[c]	
Wheat									
Cd	min	1.4	2.0	4.2	0.10	0.02	0.02	57	106
	max	42.1	32.0	7.7	10.61	0.58	1.03		
	avg	4.3	15.1	6.9	1.30	0.16	0.20		
Zn	min	1.4	11.1	5.9	85.0	33.0	0.05	8	18
	max	9.9	29.5	7.3	1138.0	94.0	0.43		
	avg	4.3	16.4	6.7	371.2	53.6	0.19		
Lettuce									
Cd	min	1.2	1.5	4.7	0.08	0.25	0.19	55	152
	max	35.5	30.7	7.7	12.60	8.86	10.28		
	avg	6.8	12.1	6.4	1.68	1.55	1.99		
Zn	min	1.2	4.4	4.7	42.0	40.0	0.07	42	77
	max	12.0	30.7	7.7	1474.0	203.0	2.88		
	avg	4.7	14.3	6.3	375.1	96.9	0.55		
Potato									
Cd	min	1.2	1.5	4.7	0.10	0.01	0.01	112	118
	max	15.0	33.7	7.6	10.90	0.42	1.60		
	avg	2.9	13.5	6.9	0.70	0.13	0.33		
Zn	min	1.2	4.2	4.7	41.0	12.0	0.03	15	25
	max	7.5	25.2	7.3	538.0	25.0	0.45		
	avg	2.7	13.2	6.2	185.8	17.0	0.14		
Endive									
Cd	min	1.4	4.6	4.7	0.43	0.36	0.17	35	52
	max	12.0	23.3	7.1	12.60	8.76	6.00		
	avg	4.7	13.9	6.2	2.16	1.85	1.52		
Zn	min	1.4	4.6	4.7	64.0	51.0	0.07	41	52
	max	12.0	23.3	7.1	1474.0	353.0	2.90		
	avg	4.7	13.9	6.2	356.1	112.1	0.63		
Grass									
Cd	min	2.1	1.0	3.8	0.20	0.03	0.01	142	115
	max	69.2	41.2	7.4	37.00	0.93	1.00		
	avg	14.1	14.5	5.9	2.87	0.20	0.20		
Zn	min	2.8	6.7	3.8	71.0	38.0	0.04	29	33
	max	14.1	41.2	7.4	1686.0	176.0	1.08		
	avg	7.5	18.3	6.4	732.0	77.2	0.18		
Sugar Beet									
Cd	min	1.3	0.5	4.5	0.14	0.11	0.12	41	112
	max	13.5	30.6	7.5	11.40	3.20	4.90		
	avg	4.0	14.2	6.6	1.72	0.72	0.74		
Zn	min	1.3	2.9	4.5	49.0	30.0	0.07	45	64
	max	13.5	30.5	7.4	1140.0	343.0	3.30		
	avg	4.2	15.4	6.4	313.3	104.8	0.57		
Maize									
Cd	min	1.7	0.5	4.2	0.09	0.07	0.03	88	83
	max	22.0	37.4	7.5	11.75	6.06	2.89		
	avg	4.7	9.3	5.9	1.52	0.41	0.59		
Zn	min	1.9	2.5	4.2	18.0	28.0	0.06	29	39
	max	14.0	37.4	7.5	1520.0	174.0	1.89		
	avg	4.6	15.4	6.4	344.3	69.6	0.34		

[a]: expressed as [metal-plant]/[metal-soil]

[b]: based on dry matter

[c]: ratio = BCF_{max}/BCF_{min}

Table 2 Food quality criteria for Cd and Zn and percentage of samples that exceed the quality criteria (in mg.kg^{-1})

	Cd			*Zn*	
	standard		% above standard	standard	% above standard
Crop	human	cattle		cattle	
Potato[a]	0.1	-	0	-	-
Endive[a]	0.2	-	11	-	-
Lettuce[a]	0.2	-	2	-	-
Wheat[1]	0.15	-	**30**	-	-
Sugar beet[b]	-	0.57	**48**	250	6
Grass[b]	-	0.57	6	250	0
Maize[b]	-	0.57	9	250	0

[a] food quality standards based on fresh weight, assumed dry weight percentages are 0.25 for potato, 0.07 for Endive, 0.05 for lettuce and 0.88 for wheat (grain).

[b] quality criteria for animal food are based on dry matter for both Cd and Zn.

BioConcentrationFactors of Cd and Zn: application of the BCF$_C$ and BCF$_S$ approaches.

The large range in both the soil Cd or Zn content and the content in crops resulted in a pronounced range in BCF values, defined as the metal content in the crop divided by the metal content in the soil. In table 1, the average, minimum and maximum BCF values found for each crop are shown. BCF values range from less than 0.01 for Cd in potato to more than 10 for Cd in lettuce. The differences between crops can be explained by differences in the specific metal uptake by crops. In general crops like lettuce and endive have a higher metal uptake than crops like potato and wheat (Wiersma et al., 1986). Apart from the differences between crops, also the range in BCF values for a single crop is considerable; this is illustrated by the ratio of the highest and lowest BCF value for every crop. BCF$_{max\text{-}min}$ ratios range from 8 for Zn in wheat to 142 for Cd in grass. Except for Zn uptake by wheat and potato, which have a limited range in BCF values, the use of a BCF$_C$ approach is, therefore, not suitable for an accurate prediction of the metal content in the crops studied here. In figure 2, the metal content in lettuce is calculated using Eq. 2 (BCF$_C$ approach).

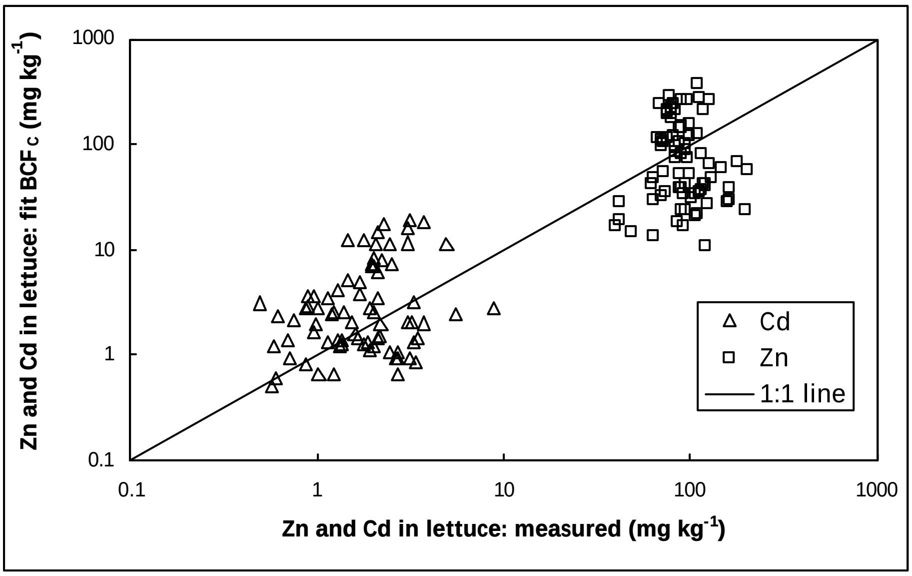

Figure 2 The metal content in lettuce, calculated using Eq. 2 (BCF$_C$ approach)

No relation whatsoever exists between the observed and predicted metal content. The range in BCF values for metals in crops like lettuce is due to the variation in soil properties. With an increase in the soil organic matter- or clay content, the availability of metals in soils usually decreases (McBride et al., 1997), which can result in a decrease in plant uptake. With a decrease in soil pH, metal availability increases which might result in higher uptake rates. To account for differences between soils, the soil specific BCF (BCF_S) approach was tested (Eq. 3). In table 3, the BCF_S relationships for Cd and Zn but also for Cu and Pb for maize are shown based on data from both data sets (data on Cu and Pb not included in table 1).

Table 3 BCF_S relationships for Cd, Cu, Pb and Zn in Maize[a].

Metal	regression coefficients				R^2_{BCF}[b]	R^2_{plant}[c]
	α (intercept)	β (OM)	γ (clay)	δ (pH)		
Cd	0.77	0.25	-0.39	-0.19	0.40	0.39
Cu	0	-0.67	-0.17	-0.04	0.73	0.15
Pb	0	-1.13	-0.19	-0.14	0.93	0.12
Zn	1.32	-0.34	-0.31	-0.21	0.82	0.44

[a]: $\log[BCF_S] = \alpha + \beta\cdot\log[OM] + \gamma\cdot\log[clay] + \delta pH_{KCl}$

[b]: R^2 of predicted vs. measured BCF_S

[c]: R^2 of plant metal content calculated from BCF_S vs. measured plant metal content

In general, the BCF_S could be predicted rather accurately (with the exception of Cd) by this approach as can be seen in Figure 3 for Cd, Cu, Pb and Zn in maize.

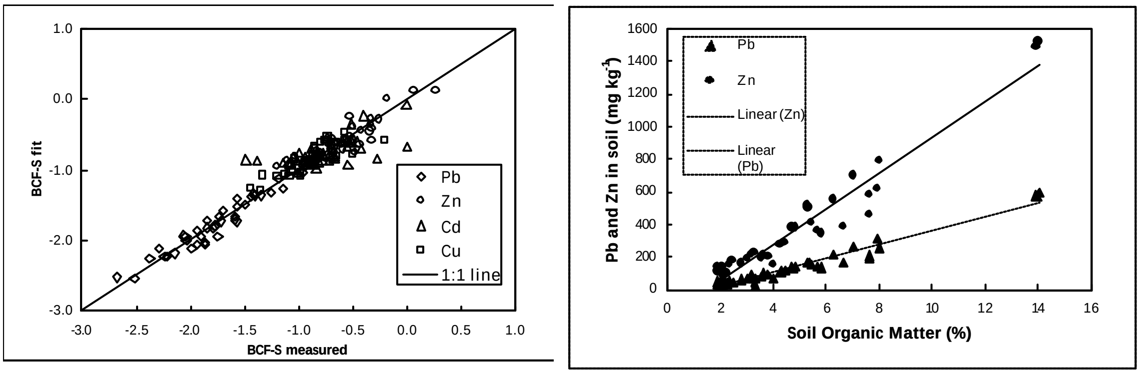

Figure 3 Calculated and measured BCF values for Cd, Cu, Pb and Zn in maize(left) and the relationship between organic matter content and Pb and Zn contents in soil (right)

However, the close correlation between soil properties and BCF_S does not necessarily result in an adequate prediction of the plant metal content if equation 4 is used to predict $[metal_{plant}]$. In table 3 also the correlation between the measured and predicted plant metal content for the 4 metals is shown that were calculated based on equation 4. For all metals the R^2 of the measured versus predicted $[metal_{plant}]$ is lower than that of the BCF_S. Especially for Pb and Cu the use of the BCF_S cannot be applied to predict the plant metal content. Various reasons can explain this discrepancy which limits the applicability of the BCF_S approach: (*i*) in many soils, the total metal content is correlated quite strongly to the soil organic matter content; figure 3.2 for example, shows the correlation between the soil organic matter content on one hand and the soil Pb content on the other. This correlation influences the degree of correlation between BCF_S and soil properties since one of the components of the BCF_S (in this case the soil metal content) is strongly correlated to one of the regression variables; (*ii*) often, the range in the soil metal content is larger than the range in the plant metal content. For example, the soil Zn content in the plots with lettuce ranges from 42 to 1474 (range ≈35) whereas the Zn content in lettuce ranges from 40 to 203 (ratio ≈ 5). In those cases where the range in the plant metal content is limited - as is the case for Cu and Pb - in combination with a high correlation between the soil metal content and the soil organic matter content, the BCF_S function is merely a regression between the soil metal content and the soil organic matter content, (*iii*) in equation 4, the coefficient of the soil metal content (ε in equation 5) is not included (it is always 1). However, metal uptake by plants is highly plant specific, and the actual metal uptake of crops varies considerably at a certain level of availability; the transfer of Cd from soil to carrots or radish in a certain soil is likely to be higher than that of Cd to potato in the same soil at the same degree of availability. It is, therefore, unlikely that the value of the power for the soil metal content is equal to 1 for all crops; (*iv*) in many cases, positive coefficients for organic matter and clay were obtained in the regression of BCF_S versus soil properties (e.g. for Cd in the example shown here and for various other crops not shown here). This suggests that metal uptake by plants increased with an increase in the soil organic matter- and clay content although the actual availability of metals in the soil usually decreases with an increase in both soil properties. It is, therefore, not consistent to obtain a positive contribution of the soil organic matter content to the BCF_S.

Application of the soil - plant transfer relationships (SPT)

In contrast to the BCF_S approach, the use of the soil - plant transfer relationships implies that the contribution of the soil metal content can be variable as is shown in equation 5. For all crops shown in table 1, SPT equations were derived (Table 4).

With the exception of Cd in potato (potato-'low' only) a reasonable to good relation was found between the metal content in the plants and the soil properties for Cd and Zn. For Cd, and to a lesser extent for Zn (in corn and potato only), no single equation could be obtained that adequately covered the entire range. It appeared that two equations were required, one in the low metal range (indicated with 'crop-low' in table 4) with a soil Cd content less than 0.85 to 1 $mg.kg^{-1}$ (250 $mg.kg^{-1}$ for Zn) and a high range with a soil metal content higher above this limit. This effect is most likely related to the chemical form in which metals are present in non-polluted soils on one hand and moderately to strongly polluted soils on the other. In the non-polluted soils, a significant fraction of the metals extracted by aqua regia can be in a chemically inert form which means that under conditions prevailing in arable soils, they are not available for plant uptake. In the moderately to heavily polluted soils, the contribution of the inert fraction is much less and a large part of the total metal content can be considered available for plant uptake (Shuman, 1991). This is reflected by the different values of the regression coefficient ε in equation 5 when comparing the 'high' and 'low' equations. One potential option to obtain a single equation for the entire range is the use of a less strong extractant (e.g. a dilute acid extraction) that is able to extract the available fraction only. No significant relationships could be obtained for Pb and only a few for Cu (not shown here). In contrast to the solubility of Cd and Zn, which is controlled largely by pH and organic matter in combination with the soil metal content, both solubility and speciation of Pb and Cu strongly depend on the solution composition and especially the dissolved organic carbon content (McBride et al., 1997). Since the approach used here does not include soil solution speciation, it cannot be expected that the properties included here cover all factors that control Cu and Pb availability in soils. Furthermore, Cu and Pb levels in plants (data not shown here) did not vary as much as Cd and Zn which indicates that plants do not take up both elements relative to the availability in the soil solution but merely maintain a fixed level.

Table 4 Soil to plant Transfer (SPT) equations[a] for the calculation of the Cd and Zn content in arable crops

Metal	Crop	data[b]	n	limit[c]	a (intercept)	ß (SOM)	? (clay)	d (pH)	e (Q_{soil})	R^2	se-y[d]
Cd	Sugar beet	M + L	112	-	1.33	-	-0.13	-0.22	0.62	0.83	0.15
	Maize-low	L	44	< 0.85	0.17	-0.21	-0.05	-0.07	0.44	0.58	0.12
	Maize-high	M	39	> 0.85	0.9	-	-0.32	-0.21	1.08	0.62	0.26
	Pasture	M + L	116	-	0	-0.24	-	-0.1	0.47	0.53	0.22
	Lettuce-low	M + L	83	< 0.85	1.33	-0.28	-	-0.16	0.31	0.41	0.19
	Lettuce-high	M + L	69	> 0.85	2.56	-0.39	-0.19	-0.33	0.85	0.71	0.16
	Endive	M	52	-	3.18	-0.46	-0.33	-0.41	0.94	0.59	0.19
	Wheat-low	M + L	84	< 1.0	0.43	-0.44	-	-0.17	0.36	0.44	0.20
	Wheat-high	M + L	22	> 1.0	1.49	-0.92	-	-0.30	1.4	0.83	0.09
	Potato-low	M	15	<0.90	0	0.16	-0.4	-0.07	0.33	0.27	0.11
	Potato-high	M	13	>0.90	0	-	-	-0.14	0.48	0.36	0.14
Zn	Sugar beet	M	64		2.69	-0.71	-0.37	-0.41	1.13	0.67	0.14
	Maize-low	M	22	< 250	0.91	-	-0.57	-0.10	0.93	0.54	0.11
	Maize-high	M	17	> 250	3.05	-	-0.61	-0.31	0.64	0.67	0.12
	Maize	M	39		1.37	-	-0.23	-0.15	0.70	0.68	0.13
	Pasture	M	11	< 500	2.06	1.09	-1.05	-0.09	0.41	0.49	0.11
	Lettuce	M	77	-	2.76	-	-0.26	-0.21	0.34	0.71	0.08
	Endive	M	52	-	3.17	-0.38	-0.23	-0.31	0.52	0.74	0.10
	Wheat	M	15	< 500	1.32	-	-0.24	-0.06	0.45	0.56	0.09
	Potato-low	M	15	< 160	1.08	-	-0.25	-0.10	0.47	0.85	0.04
	Potato-high	M	10	> 160	0.87	-0.50	-	-0.13	0.63	0.68	0.05

[a] $\log[\text{metal-plant}] = \alpha + \beta \cdot \log[\text{SOM}] + \gamma \cdot \log[\text{clay}] + \delta \cdot pH_{KCl} + \varepsilon \cdot \log[\text{metal-soil}]$

[b] M: river floodplain soils along the river Meuse, L: national database

[c] limit value, above this limit, the equation 'high' is used, if no 'high-low' equation is shown, this is the upper limit of the measured soil metal content

[d] se-y: standard error of the estimate (on a logarithmic base).

The different values obtained for ε for various crops indicate that the soil specific BioConcentration factor approach (BCF_S, with a constant value for ε, i.e. 1) described earlier cannot be used to predict the plant metal content. Although the correlation coefficient in the SPT approach for certain crops (potato, lettuce, pasture) is less than 0.5, reasonable to good predictions of the measured plant metal contents could be obtained using the equations shown in table 4 despite a large range in soil properties (illustrated in figure 4 for lettuce, endive, maize and sugar beet).

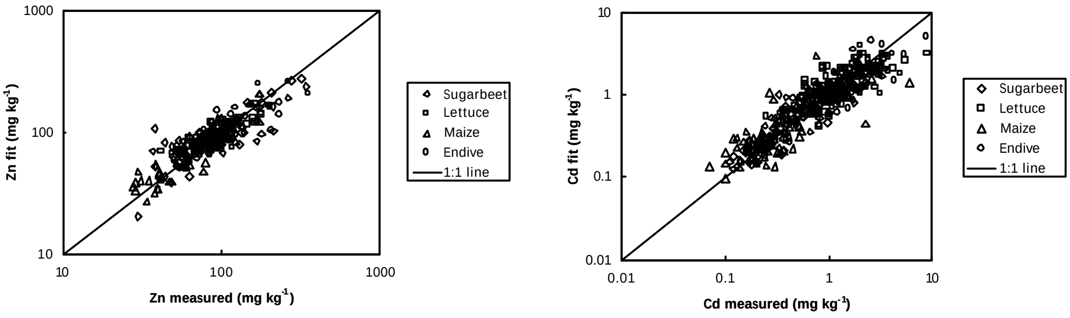

Figure 4 Relationships between calculated and measured Zn and Cd contents in crops

Derivation of soil specific quality standards (SSQS)

To obtain site-specific soil quality standard for a given site and crop, the measured organic matter content, clay content and pH were used in combination with a target plant metal concentration. Current food quality criteria for human food crops (shown in table 2) were used to calculate the maximum tolerable Cd (for endive) and Zn (for sugar beet used for animal food) content in soil with pH levels ranging from 4 to 7; organic matter content ranging from 2 to 15 % and at two texture levels (clay content of 2% and 15 % respectively). The results in shown in table 5 clearly illustrate the impact of soil properties on the uptake of metals by crops.

At pH levels higher than 6 to 6.5, both crops can be grown safely in both sandy and clayey soils. However, below pH 6, the SSQS for both Cd and Zn are well within the range of the soil metal content in non-polluted soils (see table 1). To evaluate whether current soil metal levels in the floodplain soils are exceeding calculated SSQS values, a frequency distribution of both the measured soil metal content in the floodplain soils used for endive cropping as well as the calculated SSQS values for each of these soils was constructed (figure 5).

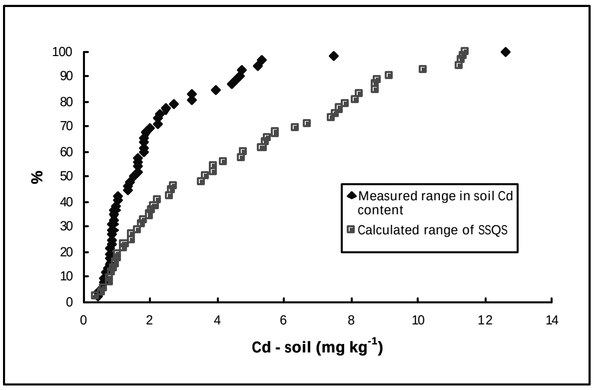

Figure 5 Frequency distribution of soil specific quality standards and measured contents of Cd in floodplain soils used for endive cropping

It shows that, although the average level of the SSQS levels exceeds that of the measured Cd content in the soil, the calculated SSQS levels are within the same range as the measured soil metal content. Comparison of the soil Cd content in each point and the corresponding SSQS level showed that in 6 (out of 52) locations, current Cd levels exceeded the SSQS level.

Table 5 Calculated SSQS values for Zn (Sugar beet) and Cd (Endive) based on the Soil to Plant Transfer relationships (SPT).

Zn – Sugar beet
(food quality standard : 250 mg.kg^{-1} dry weight)

2% clay	*Soil pH (pH$_{KCl}$)*						
OM	4	4.5	5	5.5	6	6.5	7
2	30	46	70	106	161	244	371
4	47	71	108	164	249	377	573
8	72	110	167	253	384	583	886
15	107	163	247	376	570	866	1315

15% clay	4	4.5	5	5.5	6	6.5	7
2	58	89	135	205	311	472	717
4	90	137	208	317	481	730	1109
8	140	212	322	489	743	1128	1713
15	207	315	478	726	1103	1675	2543

Cd – Endive
(food quality standard : 0.20 mg.kg^{-1} fresh weight)

2% clay	*Soil pH (pH$_{KCl}$)*						
OM	4	4.5	5	5.5	6	6.5	7
2	0.13	0.21	0.34	0.57	0.94	1.55	2.56
4	0.18	0.29	0.48	0.80	1.32	2.18	3.59
8	0.25	0.41	0.68	1.12	1.85	3.05	5.05
15	0.34	0.56	0.92	1.52	2.51	4.15	6.86

15% clay	4	4.5	5	5.5	6	6.5	7
2	0.26	0.42	0.70	1.15	1.90	3.14	5.19
4	0.36	0.59	0.98	1.62	2.67	4.41	7.29
8	0.50	0.83	1.37	2.27	3.75	6.19	10.23
15	0.68	1.13	1.87	3.09	5.10	8.43	13.92

3.2.5 Conclusions

The soil to plant transfer relationships (SPT) derived in this study for Cd and Zn can be used as an effective tool to estimate whether or not current soil metal levels will lead to unacceptable metal levels in crops. The application of the constant BioConcentrationFactor (BCF$_C$) proved to be too crude to result in a reliable estimate of the plant metal content because uptake of metals by crops strongly depends on soil properties such as organic matter, clay and pH. Although the soil specific BioConcentrationFactor (BCF$_S$) could be predicted rather well by the soil properties included here, it was shown also that this did not necessarily result in a good prediction of the plant metal content. In certain cases (e.g. for Cu and Pb), misleading relationships were obtained due to a high correlation between one of the independent variables (in this case organic matter) and the soil metal content. Also for Cd and Zn higher correlation coefficients between measured and predicted plant metal content were higher using the SPT relationship compared to the soil specific BCF relationships.

The SPT method evaluated here can be used not only to calculate the soil specific quality standards for Cd and Zn in specific points (e.g. on the farm level), but also to generate maps on a higher scale level (regional, national, Brus et al., 2000). This enables policy makers to identify regions with an elevated risk of metal transfer from soils to crops. It also can be used to evaluate the risk of increased metal uptake in case of changing soil conditions such as a change in soil pH. In certain eastern European countries, regular lime application has been reduced due to financial reasons which could lead to a significant drop in soil pH and, consequently an increase in the plant metal content. Although the approach described here works quite well for Cd and Zn, improvements still are necessary. Currently the use of a less strong extraction (0.43 N HNO_3) is tested on the same data as an alternative for the Aqua Regia extraction to serve as the soil metal content used in the soil to plant transfer relationships. Future developments include the application of a standardised dilute salt extraction (e.g. a 1:10 v:v 0.01 M $CaCl_2$ extraction; Houba et al., 1996) that can be used directly to estimate the plant metal content based on the amount of metals extracted. One of the factors not yet included here is the differences in rooting depth between crops. Crops with a moderate rooting depth such as lettuce and pasture will take up the majority of nutrients and metals from the topsoil but crops like maize or wheat will root below the topsoil. This means that the value for [Metal-soil] for crops with deep rooting systems (> 30 cm) is not equal to the one used in the equation. Also differences in atmospheric deposition between regions have not been accounted for. However, in the Netherlands regional differences in atmospheric deposition are small and it is unlikely that this could have caused significant differences in the metal content of the crops included in this study. In regions with high variations in metal deposition (e.g. around smelters), the contribution of atmospheric deposition can be significant and probably cannot be neglected. Despite these limitations and future improvements, the soil-to-plant transfer relationships can serve as an easy-to-use tool to predict not only the plant metal content based on a limited number of generally available soil properties but also to estimate the maximum tolerable metal content in soils. Currently the STP approach is already implemented on a national scale to identify regions in the Netherlands where the actual Cd content in the soil already exceeds the maximum tolerable metal content (Brus et al., 2000).

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Theme 4 Regional impacts of acidification on leaching and plant uptake

4.1 Long term impacts of different fertiliser scenarios on metal leaching and metal uptake in Slovakian and Hungarian agricultural soils

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Summary

In several eastern European countries, including Slovakia and Hungary, liming is not always adequate and this may cause mobilisation of heavy metals which may lead to metal concentrations in soil solution and crops exceeding threshold limits for toxicity effects on soil biota and plants. This paper evaluates the possible long term (50 years) impact of the acidification of agricultural soils, due to stopping with liming, on dissolved cadmium (Cd) and zinc (Zn) concentrations and crop contents in wheat and maize for representative Slovakian and Hungarian agricultural soils for different fertiliser scenarios. The predictions were made with the soil acidification model SMART, adapted for agricultural soils, combined with transfer functions for heavy metals describing relationships between: (i) total and reactive heavy metal contents in the soil solid phase, (ii) dissolved metal concentrations and reactive soil metal contents and (iii) total heavy metal contents in crops and in soil, while accounting for the impact of organic matter and clay content and soil pH.

The investigated locations include 280 non-calcareous plots for Slovakia and 25 non-calcareous plots in Hungary with data on soil properties (pH, clay content and organic matter content) and metal contents in soil and partly also in the wheat and maize (in Hungary). Input data on metals and acidity by fertilisers, animal manure and atmospheric deposition were derived Statistical Yearbooks, the FAOSTAT database and EMEP deposition model results. Precipitation data and actual evapotranspiration for the Hungarian plots were based on long-term average precipitation and evapotranspiration within the period 1950-1980 (Hungary) or 1950-1999 (Slovakia).

Initial pH values in the Slovakian and Hungarian non-calcareous soils varied mostly between 4.5 and 5.5. Simulated changes in soil pH are dependent on the soil type and time period but in general a pH drop of 0.5-1.0 is predicted in a 50-year period, the largest changes taking place in the first 20 years. Adverse affects on soil life are most likely due to elevated dissolved Zn concentrations. In Slovakia, the predicted percentage of plots exceeding a critical Zn concentration of 250 $mg.m^{-3}$ increases

from less than 10% at the start of the simulation to 40% after 50 years. The percentage of plots with a dissolved Cd concentration above a critical level of 2 mg.m^{-3} increases from approximately 10 to 20% in 50 years. Adverse affects on crops are due to elevated Cd contents in wheat, whereas Zn is not a problem. The predicted percentage of plots exceeding a critical Cd content of 0.15 mg.kg^{-1}, used in the Netherlands, increases from approximately 50% at the start of the simulation to 85% after 50 years in Slovakia. In Hungary, Cd contents are already near 0.3 mg.kg^{-1} at the start of the simulation These high Cd contents are most likely due to the low organic matter contents of the soils. The effects of an alternative fertiliser scenario on the pH and Cd contents in soil appeared to be limited.

4.1.1 Introduction

Heavy metals have accumulated in agricultural soils as a result of manure application, fertiliser treatment, atmospheric deposition and the amendment of sewage sludge. (Van Driel and Smilde, 1990; Moolenaar and Lexmond, 1998). Changes in environmental conditions may change the bioavailability and mobility of heavy metals. Important environmental conditions that determine the bioavailability of heavy metals in soils are the pH and the macro chemistry of the soil solution (e.g. concentrations of dissolved organic carbon (DOC), calcium and aluminium). A decrease in pH increases soil solution concentrations of heavy metals. Improper management practices of agricultural land (insufficient liming, too high fertiliser applications) cause a decrease in soil pH and thus an increase in heavy metal bio-availability. As a result, elevated metal concentrations in agricultural soils may lead to agricultural products with unacceptable metal levels (exceeding human food standards or standards of fodder crops) and at very high levels even reduced crop production (Alloway, 1990; Fergusson, 1990). Further elevated metal concentrations affect soil organisms, such as micro-organisms (Bååth, 1989), nematodes (Bengtsson and Tranvik, 1989) and earthworms (Ma and Van der Voet, 1993). Protection of those organisms is relevant to sustain so-called Life Support Functions, such as decomposition processes, which are essential in the nutrient cycle of elements. An increase in metal bio-availability may also cause elevated leaching to ground water and surface water, thus affecting drinking water quality and aquatic organisms, respectively (Crommentuijn et al., 1997).

A quantitative characterisation of metal mobilisation induced by soil acidification (‘chemical time bomb’-effect) and its consequences for soil fertility, crop production/crop quality and risks for groundwater pollution are urgent and challenging tasks in cases where liming is not (adequately) practised. The occurrence of such a chemical time bomb is not imaginative, in several eastern European countries, including Slovakia and Hungary, since liming is not always adequate. National inventories indicate that around 12000 hectares in Slovakia and around 75000 hectares in Hungary are polluted with heavy metals and are a potential risk when soils acidify (Várallyay, 1993). Results from the soil fertility monitoring system in Hungary show an acidification of agricultural soils since the start of the monitoring programme in 1978 (Murányi, 2000). Furthermore, liming may be discontinued by land use changes. This implies a total stop of agricultural activities such as fertilisation, ploughing, harvesting and liming. In the present EC policy it is envisaged that 30% of the agricultural soils will be abandoned to avoid overproduction. In non-EU countries abandoning or reforestation of (former) agricultural land also occurs, especially in areas that are highly polluted with heavy metals.

A relevant policy question is whether the mobilisation of previously fixed soil pollutants has vital impacts on ecosystems and the quality of life. More specifically, whether it may lead to metal concentrations in soil solution and crops exceeding threshold limits for toxicity effects on soil biota, plants, and - by entering the food chain - animals and human beings, resulting in health problems. The aim of this paper is to answer this question by evaluating the long term (50 years) impact of soil acidification, due to stopping with liming, on cadmium (Cd) and zinc (Zn) leaching and crop contents in wheat and maize for representative Slovakian and Hungarian agricultural soils for different fertiliser scenarios. Time trends in both dissolved Cd and Zn concentrations and Cd and Zn contents in crops are evaluated in view of critical limits related to impact on soil organisms and food quality criteria.

4.1.2 Model

General approach

Metal contents in crops are rather determined by the availability of metals, which is reflected by dissolved metal concentrations, than by the total content of metals in soils. Changes in dissolved concentrations are due to changes in: (i) the total metal concentrations in the soil and (ii) soil properties influencing the partitioning of metals between the solid and solution phase, such as the content of organic matter and clay and the soil pH. In this approach we assume that the pH is the dominant factor of change in the coming period due to limited or even no liming. Changes in soil metal concentrations may also occur, when the net input (input corrected for uptake) is different from metal leaching. Information of metal input on a regional scale is, however, very scarce and furthermore, the impact of those changes is likely to be much more limited on the concentration of dissolved metals than pH changes. The same is true for possible changes in the content of organic matter.

When agricultural soils are not limed they will acidify as a result of natural and land use induced acidification. An overview of sources and sinks of acidity in relation to element cycling is given by De Vries and Breeuwsma (1987). Natural acidification of soils with a $pH>5$ is caused by the dissociation of CO_2, furthermore the dissociation of organic acids may contribute to some extend. The main sources of acidification are the atmospheric deposition of nitrogen and sulphur and the addition of N with fertilisers. It is a widespread misunderstanding that the use of ammonium fertilisers as such causes acidification because of the proton production as a result of nitrification. Uptake of nitrate by the crop with the consumption of protons compensates it. However an excess of nitrogen may lead to acidification according to: H^+-production = $(NH_4{}^+{}_{in} - NH_4{}^+{}_{out}) - (NO_3{}^-{}_{in} - NO_3{}^-{}_{out})$. Another source of acidification is the net removal of cations with harvesting of crops. In predicting the possible impact of different fertiliser scenarios while stopping with liming, we thus focused on the prediction of pH changes using the regional soil acidification model SMART (De Vries et al., 1989). Impacts of those pH changes on dissolved Cd and Zn concentrations and Cd and Zn contents in wheat and maize were assessed from transfer functions with soil metal concentrations (assumed to stay constant) and soil properties influencing metal adsorption, i.e. the content of organic matter and clay (assumed to stay constant) and the soil pH (changing in time). The general approach is further illustrated in Figure 1. The model was applied for a soil layer of 0.5 m.

The acidification model

The acidification model used was SMART, first being described by (De Vries et al., 1989). Since then, the model has been extended by describing N immobilisation (formerly a model input), by including denitrification and improving the description of Al release and complexation (e.g. De Vries et al., 1994). The model consists of a set of mass balance equations, describing the soil input-output relationships, and a set of equations describing the rate-limited and equilibrium soil processes. All major ions have been included. SMART was constructed by using a process-aggregated approach, to minimise the input data requirements for applications on a regional scale. This implied the following simplifying assumptions:

i. The various ecosystem processes have been limited to a few key processes: The soil solution chemistry in SMART depends solely on the net element input from the atmosphere together with inputs from fertilisers and manure which was added particularly for this study (deposition plus fertiliser minus net uptake minus net immobilisation) and the geochemical interaction in the soil (CO_2 equilibria, weathering of carbonates, silicates and/or Al-hydroxides and cation exchange). Processes that are not taken into account, are: (i) canopy interactions, (ii) nutrient cycling processes, (iii) N fixation and NH_4 adsorption and (iv) uptake, immobilisation and reduction of SO_4.
ii. The included processes have been represented by simplified conceptualisations: Soil interactions are either described by simple rate-limited (zero-order) reactions (e.g. uptake and silicate weathering) or by equilibrium reactions (e.g. carbonate and Al-hydroxide weathering and cation exchange).

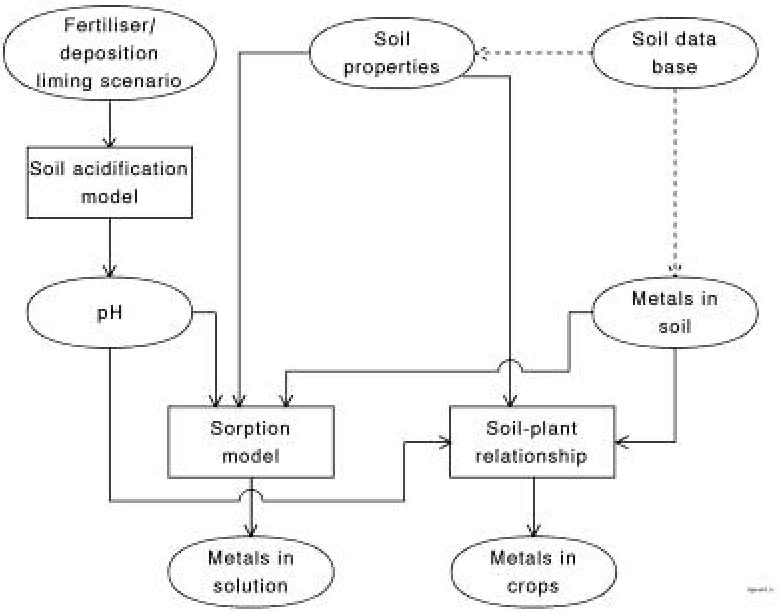

Figure 1 General approach illustrating the assessment and evaluation of the impact of different fertiliser and liming scenarios.

Influence of environmental factors such as pH on rate-limited reactions and rate-limitation of weathering and exchange reactions are ignored. Solute transport is described by assuming complete mixing of the element input within one homogeneous soil compartment with a constant density and a fixed depth (at least the rooting zone). Since SMART is a single layer soil model neglecting vertical heterogeneity, it predicts the concentration of the soil water leaving the root zone. The annual water flux percolating from this layer is taken equal to the annual precipitation excess that is assumed constant during the model runs (steady state hydrology). The time step of the model is one year, so seasonal variations are not considered. Justifications for the various assumptions and simplifications have been given by De Vries et al. (1989). Furthermore phosphorus is not included in the model because of the low P inputs, all added P is assumed to be taken up and thus not contributes to soil acidification.

The metal behaviour model

Dissolved metal concentrations/metal leaching

The annual leaching of heavy metals from the plough layer (topsoil of 0-30 cm) was calculated by multiplying a calculated annual precipitation excess with a calculated annual average dissolved metal concentration. The precipitation excess was calculated as:

$$PE = (1 - fr_{int}) \cdot P - E_s - E_t \quad (1)$$

where:
PE = precipitation excess ($mm.yr^{-1}$)
P = precipitation ($mm.yr^{-1}$)
E_s = soil evaporation ($mm.yr^{-1}$)
E_t = transpiration ($mm.yr^{-1}$)
fr_{int} = interception fraction (-)

According to Eq. (1), interception evaporation is implicitly described as a fraction of the precipitation.

There are various possible approaches to derive total dissolved metal concentrations from total soil metal concentrations as illustrated in Figure 2.

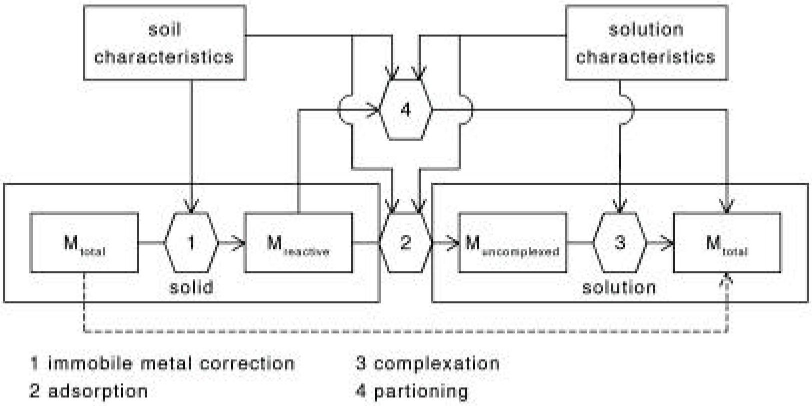

Figure 2 Diagram illustrating different possibilities to calculate total dissolved metal concentrations from total concentrations in the soil solid phase.

The simplest approach is a direct empirical approach relating both concentrations, while accounting for the impact of major soil properties influencing the sorption relationship (e.g. Jansen et al., 1996). The most fundamental approach is to relate the free metal ion activity to the reactive metal concentration (metals that can be extracted by a weak acid or a complexing agent such at EDTA), accounting for the impact of both soil properties and major ions in soil solution competing with the metals. Such an approach (e.g. Bril, 1995), however, requires additional relationships relating (i) the reactive metal concentration to the total soil metal concentration and (ii) the total dissolved metal concentration to the free metal ion activity, using a (simple) complexation model (De Vries and Bakker, 1998).

In this study, we used an intermediate approach, relating the total dissolved metal concentration to the reactive soil metal concentration. We applied a Freundlich isotherm to relate the total metal content to the solution concentration, according to (after log transformation):

$$\text{Log}[M_{re}] = \log K_F + n \cdot \log[M_{ss}] \tag{2}$$

where:
$[M]_{ss}$ = concentration of heavy metal M in the soil solution ($mol.l^{-1}$)
M_{re} = reactive concentration of heavy metal M in the soil ($mol.kg^{-1}$)
K_F = the Freundlich constant
n = the Freundlich coefficient (non-linearity term.)

To obtain an equation that can be used for a range of soils, K_F can be written as:

$$K_F = K_F + a \cdot \log[\%OM] + b \cdot \log[\%clay] + c \cdot pH \quad (3)$$

The values of K_F*, a, b, c and n can be obtained by multiple linear regression. More parameters can be included, such as DOC, but since lack of data on larger scale levels (such as the national, data sets used in this study) limits the application, we limited the soil properties to organic matter, clay and pH.

Most often the regression parameters are derived by optimisation of M_{re} as a function of M_{ss} and soil properties or either by optimisation of M_{ss} as a function of M_{re} and soil properties. Both methods give different results as in the first case the equation is optimised for a minimal error in M_{re} whereas in the second case the equation is optimised for a minimal error in M_{ss}, these relations can thus only be used in one direction. To come to an equation that can be used in both directions we choose to optimise the following equation:

$$Log[M_{re} / \{M_{ss}\}n] = logK + a' \cdot \log[\%OM] + b' \cdot \log[\%clay] + c' \cdot pH \quad (4)$$

A problem is however that the value of n is not apriori known therefore the optimal value of n was derived by maximising the F-value of the regression as a function of n (See Section 3.2.3).

The reactive metal concentration, which was approximated by mild (0.43N) HNO_3 extraction, was related to the total concentration (aqua regia digestion) according to:

$$\log M_{re} = \beta_0 + \beta_1 \cdot \log M_{soil} + \beta_2 \cdot \log(\%OM) + \beta_3 \cdot \log(\%clay) \quad (5)$$

where:
M_{soil} = total concentration of heavy metal M in soil ($mol.kg^{-1}$)

Values for the various regression coefficients in Eq. (5) and (6) are presented in Section 3.2.3. The two relationships were applied at each plot, using the measured total metal concentrations (aqua regia extraction) and soil properties (pH, organic matter and clay content).

Metal concentrations in plants

Metal concentrations in the plant were related to soil concentrations, while accounting for the impact of soil properties influencing metal availability, according to:

$$\log M_{plant} = \alpha + \beta \cdot \log(\%OM) + \gamma \cdot \log(\%clay) + \delta \cdot pH\text{-}KCl + \varepsilon \cdot \log M_{soil} \tag{6}$$

where:

M_{plant} = total concentration of heavy metal M in plants ($mg.kg^{-1}$)

Values for the various coefficients have been derived for Cd, Cu, Pb and Zn in grass, wheat and maize, being the main crops on the various farms, based on different Dutch data sets (Römkens et al., 2003b). In general, relationships were better for Cd and Zn than for Cu and Pb. The results for Cd and Zn in wheat and maize used in this study are presented in Section 3.2.3.

In Hungary, data were available on metal concentrations in both plants and soil and on the soil properties (organic matter and clay content and pH). In this situation, only the pH dependence in Eq. (7) was used to scale the changes in pH in time to changes in the metal contents in plants, under the assumption that the soil properties and the metal contents in soil do not change:

$$\log M_{plant(te)} = \log M_{plant(t0)} + \delta \cdot (pH\text{-}KCl_{te} - pH\text{-}KCl_{to}) \tag{7}$$

4.1.3 Study sites and input data

Locations

The investigated locations originally included 306 plots for Slovakia with data on soil properties (pH, clay content and organic matter content) and metal contents in soil and 250 plots for Hungary with the same data, while including metal concentrations in the crops wheat and maize. The plots include agricultural soils only. In Figure 3, the location of the plots is indicated, while distinguishing between non-calcareous soils (carbonate content of 0.0%) and calcareous soils (carbonate content more than 0.0%). In Slovakia, most soils are non-calcareous (280 of the 306 plots) but in Hungary the reverse is true (25 of the 250 plots). In this study we only investigated the impact of stopping with liming on the non-calcareous plots since this measure is not relevant on the calcareous soils. This implies that most of the results do refer to the situation in Slovakia.

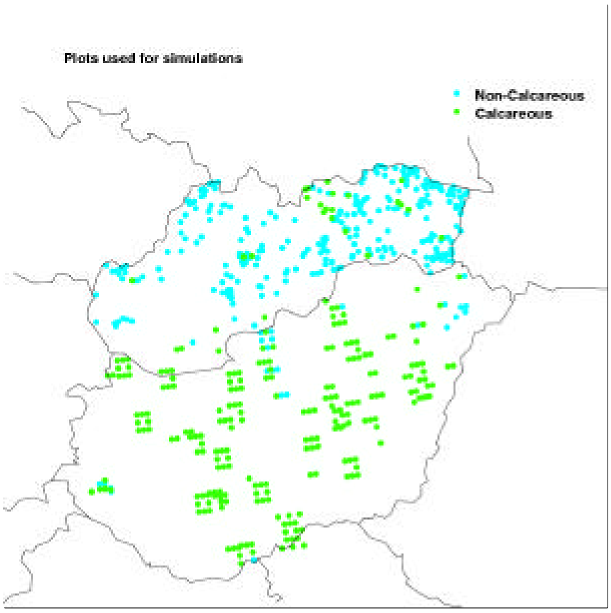

Figure 3 Geographic distribution of calcareous and non-calcareous plots in Slovakia and Hungary investigated in this study.

Soil properties

Ranges in the organic matter and clay content, which are major soil properties influencing metal behaviour are given in Figure 4. Results show a large range in both soil properties in Slovakia, indicating that most soils in this country are clayey soils (only 16% of the soils has a clay content below 18%) with a clay content ranging between approximately 20% (light clay soils) up to 75% (heavy clay soils) with an organic matter content ranging between 1 and 10%. The range in organic matter and clay content in Hungary however is small. Organic matter contents are nearly always less than 1 % (Fig 4 A) and clay contents are always lower than 30% (Fig 4 B). Ranges in soil pH at the start of the simulation are presented in the results section together with model predictions for the coming 50 years. An overview of all the data that were measured in view of this study are given in Annex 1. Information on the CEC that was needed to calculate the acidification is given in Annex 2

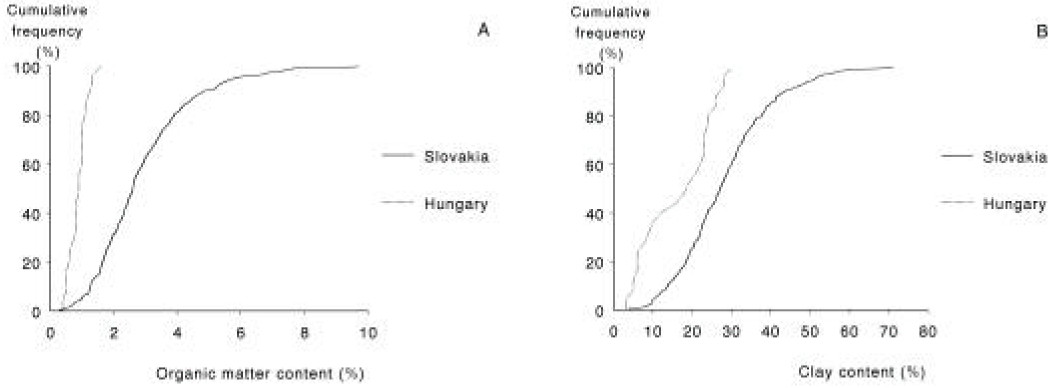

Figure 4 Cumulative frequency distributions of organic matter content (A) and clay content (B) of the 280 non-calcareous plots in Slovakia and the 25 non-calcareous plots in Hungary.

Metal concentrations

Metal concentrations in the solid phase are used to calculate metal concentrations in soil solution and metal concentrations in crops. To calculate metal concentrations in crops total metal concentrations are to be used (only for Slovakia see 2.3) whereas for metal concentrations in soil solution reactive metal contents (as determined with 0.43 mol.l^{-1} HNO_3) are needed. For the sites in Slovakia the total metal concentration is available as determined with an aqua regia extraction. Results are presented in Annex 3. For Hungary metal concentrations were determined with an AAAc-EDTA extraction. To derive the required metal data regression relations were used in which the different metal extracts are linked to each other. Ranges in the reactive Cd and Zn concentrations in the soil, as approximated by a mild HNO_3 extraction (0.43 mol.l^{-1} HNO_3), are given in Figure 5. For Slovakia, those concentrations were calculated from the measured total concentrations (with an aqua regia extraction) and the clay and organic matter content, using Eq. 6 (see also Section 3.2.3, Table 5 for the parameters that were used to perform this calculation). For Hungary, those concentrations were based on measurements of metal concentrations in an extraction with AAAc-EDTA (a mixture of 0.5 M CH_3COONH_4, 0.5 M CH_3COOH, 0.02 M Na_2EDTA, Lakanen & Erviö, 1971). To relate these AAAc-EDTA extractable contents in Hungary to mild HNO_3 extractable contents a correction was made based on results of EDTA and 0.43 mol.l^{-1} HNO_3 extractions in 72 soils in Hungary and Slovakia (see also Section 3.2.3, Table 6 for the parameters that were used to perform this calculation).

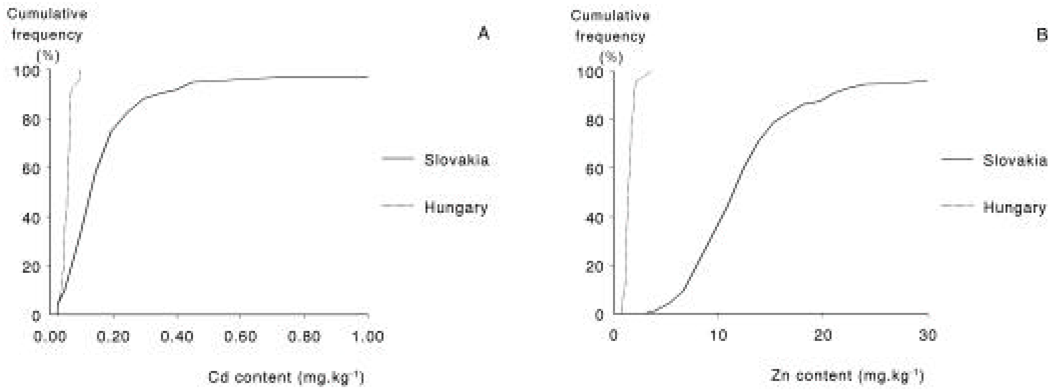

Figure 5 Cumulative frequency distributions of reactive Cd concentrations (A) and Zn concentrations (B) in the soil of the 280 non-calcareous plots in Slovakia and the 25 non-calcareous plots in Hungary

Results show that most Cd concentrations for Slovakia range between 0.1 and 0.5 mg.kg^{-1} whereas Cd concentrations for Hungary are much lower i.e. between 0.02 and 0.1 mg.kg^{-1}. Zn concentrations for Slovakia range mostly between 5 and 30 mg.kg^{-1}, the concentrations for Hungary are clearly lower between 1 and 4 mg.kg^{-1}. The concentrations in Hungary are likely underestimated. The extraction with AAAc-EDTA as used in Hungary most likely extracts lower amounts of metal than the 0.005 M EDTA extraction which was used in the relation between HNO_3 and EDTA extractable metal. Limited available literature information suggests that impacts on microbiota and soil invertebrates may occur at Cd concentrations between 0.5 and 2.0 mg.kg^{-1} and Zn concentrations between 50-200 mg.kg^{-1} (see review by De Vries and Bakker, 1998), being the common range for the investigated soils. It is likely that in the sites with extremely high metal concentrations, soil life is inhibited. In other sites, this may also be the case depending on the sensitivity of the soil organism and the soil properties influencing bioavailability.

Fertiliser and deposition scenarios

Deposition of SO_x, NO_x and NH_x was set to the EMEP data for the relevant grid cells of 150×150 km^2 in the region (EMEP, 2002). Fertiliser additions were added to deposition. For Slovakia the general average input of N fertiliser is 43 kg N.ha^{-1}.yr^{-1}, once every 4 years an additional amount of 41000 kg.ha^{-1} manure is applied (Statistical Yearbook Slovak Republic 1994, 1995, 1999). For Hungary the N gifts were available per plot. Average N fertiliser inputs were about 100 kg N.ha^{-1}.yr^{-1}. Additionally an estimated 10690 kg.ha^{-1} manure was added. Information of the specific type of fertiliser added was not available and an estimate was made with data for the period 1996-2001 from the FAOSTAT database (FAO). This database shows that ammonium nitrate and calcium ammonium nitrate together with a class ‘other complex N fertilisers’ are the most important N fertilisers used. Total N in fertilisers was divided over ammonium nitrate and calcium ammonium nitrate according to the ratio in the total use of fertilisers given in the FAO database. The ratio between calcium ammonium nitrate and ammonium nitrate was on average 0.12 for Hungary and 7.0 for Slovakia. Inputs of elements were calculated from the fertiliser amounts and element contents in the different types of fertiliser and manure (Table 2).

Table 1 Composition of fertiliser and manure used in the fertiliser and manure application in the model runs (mol.kg^{-1} N for N fertilisers, mol.kg^{-1} for manure, pers. Comm. Bril)

Fertiliser	NO_3	NH_4	Ca	Mg	K	Na	SO_4	PO_4	Cl	CO_3
Calcium ammonium nitrate	35.71	35.71	17.08	0.	0.	0.37	0.	0.	0.37	17.08
Ammonium nitrate	35.71	35.71	0.	0.	0.	0.	0.	0.	0.	0.
Cow manure	0.	0.315	0.075	0.05	0.117	0.032	0.045	0.075	0.085	0.384

The net uptake of elements (N, Ca, Mg and K) for each crop was estimated by multiplying the average uptake in the harvested part, derived for crops in the Netherlands with the ratio of the yield in respectively Slovakia and Hungary and the yield in the Netherlands. The yields in both Slovakia and Hungary are about 50% for wheat and 70% for maize of yields in the Netherlands (FAOSTAT).

Hydrological data

Precipitation data and actual evapotranspiration for the Hungarian plots were derived by an overlay of the plots with the regions for which precipitation normals for over the period 1950-1980 were available as given in Table 2.

Table 2 Thirty year average precipitation (P), evapotranspiration (E_{act}) and precipitation excess (PE) for different regions in Hungary

Meteorological station	P	Eact	PE
Gyor-Sopron	565	462	103
Vas	617	503	114
Zala	709	564	145
Somogy	746	571	175
Veszprem	624	490	134
Komarom	628	472	156
Fejer	564	417	147
Tolna	643	517	126
Baranya	639	518	121
Bacs-Kiskun	535	411	124
Pest	529	408	121
Szolnok	513	402	111
Csongrad	517	423	94
Bekes	577	440	137
Hajdu-Bihar	564	452	112
Szabolcs-Szatmar	551	428	123
Borsod-Abauj-Zemplen	603	481	122
Heves	569	446	123
Nograd	629	450	179

Precipitation data and actual evapotranspiration for the Slovakian plots were derived by interpolating long-term average precipitation and evapotranspiration values at different meteorological stations in Slovakia. The precipitation data were based on observations within the period 1956-1999 and the number of years with observations varied between 24 and 34, whereas the evapotranspiration data referred to the period 1950-1980. The original data are presented in Table 3.

The variation in the long-term precipitation, evapotranspiration and precipitation excess thus obtained for the various plots are presented in Table 4. The precipitation excess data were used to calculate leaching fluxes by multiplying these water fluxes with the calculated dissolved metal concentrations.

Table 3 Long-term average precipitation (P and actual evapotranspiration (E_{act}) data for different meteorological stations in Slovakia

Station	P
Banská Bystrica	769
Bolkovce	494
Bratislava	609
Hurbanovo	529
Liesek	776
Lucenec	584
Malacky	573
Martin	788
Milhostov	578
Mochovce	629
Nitranské Pravno	758
Oravský Podzámok	788
Pieštany	572
Poprad	579
Prešov	611
Somotor	574
Spišská Nová Ves	605
Stará Lesná	708
Starina	764
Topolníky	585
Trencín	606

Station	Eact
Bardejov	469
Bratislava, Ivanka	465
Cadca	485
Cerveny Klastor	472
Hurbanovo	451
Kamenica n./C.	518
Kosice, letisko	482
Kuchyna - Novy Dvor	507
Liptovsky Hradok	477
Moldava n./B.	491
Myjava	454
Nitra	449
Oravska Lesna	431
Piestany	474
Plavec o. Stara Lubovna	487
Poprad	456
Prievidza	487
Rimavska Sobota	456
Roznava	508
Sliac	481
Somotor	465
Strbske Pleso	397
Svermovo	467
Trebisov	451
Trenc. Biskupice	451
Trstena - Ustie n./P.	451
Viglas - Pstrusa	442
Ziharec	452

Table 24 Variation in the long-term year average precipitation (P), evapotranspiration (E_{act}) and precipitation excess (PE) for the considered 280 plots in Slovakia and 25 plots in Hungary.

Statistic	Slovakia			Hungary		
	P	E act	PE	P	E act	PE
Minimum	576	436	102	529	408	112
5 percentile	586	458	107	529	408	119
50 percentile	638	475	160	551	428	123
95 percentile	777	488	306	709	564	179
Maximum	780	497	331	709	564	179

Metal transfer coefficients

Metal transfer coefficients to derive reactive metal content from total soil content

Values for the various coefficients relating reactive concentrations of Cd and Zn (approximated by mild (0.43N) HNO_3) and total soil concentrations of Cd and Zn (aqua regia digestion), according to (Eq. 5), are shown in Table 5 (De Vries et al., 2002). The values are based on results of reactive and total soil concentrations of Cd and Zn, including organic matter and clay contents for 72 soils investigated in Slovakia and Hungary. The value of ß1 above 1 implies that at higher soil concentrations it would ultimately lead to reactive contents being higher than total contents.

Within the total concentration range considered, however, it leads to (much) lower reactive contents because of the negative intercept ßo.

Table 5 Values for the coefficients ß0-ß3 in the relationship relating reactive (0.43N HNO_3) and total soil concentrations of Cd and Zn, according to Eq. (5) derived for 72 soils in Slovakia and Hungary.

Metal	ßo	ß1	ß2	ß3	R^2	se y-est 1)
Cd	-0.302	1.037	-	-	0.85	0.264
Zn	-1.122	1.212	-0.339	-	0.65	0.315

1) The standard error of the y-estimate on a logarithmic basis

A comparison of the reactive metal concentrations thus estimated and the measured metal concentrations do also give an indication of the reliability of the estimates. Results thus obtained for the metals considered in the 72 plots are presented in Figure 6. It illustrates that results are better for Cd than for Zn.

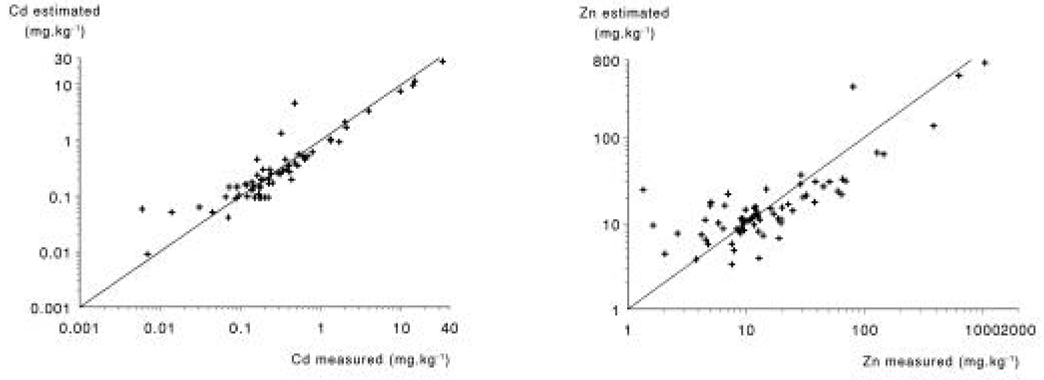

Figure 6 Comparison of measured reactive concentrations of Cd and Zn and estimated concentrations, using the logarithmic relationship between reactive and total metal concentrations (Eq. 6) and the model parameters derived in this study (Table 5).

In Hungary, the reactive metal contents were directly measured but this was done in an EDTA extract. To relate this EDTA extractable contents to mild HNO_3 extractable contents, being the extraction basis for deriving metal transfer coefficients relating reactive soil content to dissolved concentrations, a correction was made based on results of both extractions in 72 soils in Hungary and Slovakia. There was a considerable agreement between reactive metal concentrations measured with a mild (0.43N) HNO_3 extraction and with and EDTA extraction as shown in Figure 7.

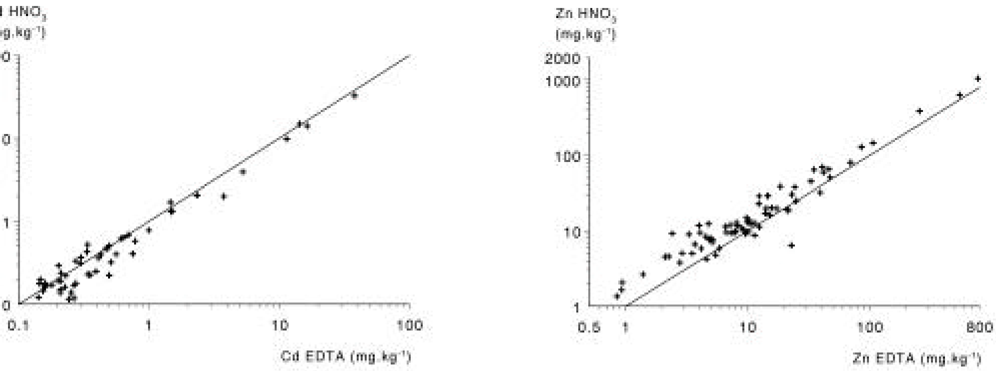

Figure 7 Comparison of measured reactive concentrations of Cd and Zn with a mild (0.43 N) HNO_3 extraction and an EDTA extraction.

A regression of 0.43N HNO_3 extractable values against EDTA extractable values, using the original and the log-transformed data, is given in Table 6. Results are based on the relationship

$$\text{Log}[M_{re,\ HNO3}] = a + b \cdot \log[M_{re,\ EDTA}] \qquad (8)$$

In general the Cd contents compared very well, but the reactive metal contents in an mild acid extract for Zn are generally higher than in an EDTA extract, especially in the lower range. We used this approach to derive the 0.43N HNO_3 extractable data from the measured EDTA extractable values.

Table 6 Values for the regression coefficients in the logarithmic relationship between reactive concentrations of Cd and Zn extracted by 0.43N HNO_3 and by EDTA (Eq. 6).

Metal	Intercept a	Coefficient b	R^2
Cd	-0.094	1.065	0.91
Zn	0.2442	0.9050	0.92

Metal transfer coefficients from soil to soil solution

Values for the various regression coefficients relating dissolved concentrations and reactive soil concentrations of Cd and Zn (Eq. 5) are given in Table 7. Data were derived from two data-sets of 114 soil samples and 1466 complete records of both solid phase and solution from Dutch locations (Römkens et al., 2003a). In the data set pH equals pH solution, M_{re} is the amount extractable by 0.43 N HNO_3 in mol.kg^{-1} and M_{ss} is the measured concentration in the extracts in mmol.l^{-1}. In deriving results, n was varied between 0 and 1 and the optimal value (i.e. the value for n at which F was highest) was chosen as the best model. For all elements it was observed that the shape of the n vs. F curve was parabolic with only one maximum in the range between 0 and 1. Using the data of n and the values of F, the optimal value of n was derived by calculation of the maximum of the parabolic curve. More information is given in Römkens et al. (2003a).

Table 7 Values for the coefficients K, a, b, c and n in the relationship relating dissolved concentrations and reactive soil concentrations of Cd and Zn, according to Eq. (5).

Metal	logK	a' (%OM)	b' (%clay)	c' (pH)	n-opt.	R^2	se-yest 1)
Cd	-4.85	0.58	0.28	0.27	0.54	0.80	0.33
Zn	-4.51	0.39	0.35	0.45	0.74	0.82	0.40

1) The standard error of the y-estimate on a logarithmic basis

Metal transfer coefficients from soil to plants

Values for the various coefficients relating total concentration of Cd and Zn in maize and wheat with soil metal concentrations are presented in Table 8. Data were based on a regression analyses for different Dutch data sets (Römkens et al., 2003b). In general, relationships were quite good for Cd and Zn. In some cases, different relationships were found for polluted and unpolluted soils. The parameters in Table 8 refer to the results for Cd and Zn in unpolluted soils

Table 8 Values for the coefficients a-e in the relationship relating total concentration of Cd and Zn in maize and wheat with soil metal concentrations according to Eq. (7).

Metal	Crop	a	ß	?	d	e	R^2	se-yest 1)
Cd	Maize	0.17	-0.05	-0.21	-0.07	0.44	0.58	0.12
	Wheat	0.43	-0.44	-	-0.17	0.36	0.44	0.20
Zn	Maize	0.91	-	-0.57	-0.10	0.93	0.54	0.11
	Wheat	1.32	-	-0.24	-0.06	0.45	0.56	0.09

1) The standard error of the y-estimate on a logarithmic basis

4.1.4 Results

Results of the various fertilisation scenarios focus on the predicted impacts on soil pH (acidification) and the related predicted trends in Cd and Zn concentrations in soil solution and in wheat and maize. In We limit our results to dissolved Cd concentrations below wheat and dissolved Zn concentrations below maize. The same is the case for metal contents in crops. The reason is that for wheat quality criteria are available for Cd, whereas this is not the case for maize. Furthermore, for Zn concentrations there are no food quality criteria, but only literature indications of adverse phytotoxicological affects of too high plant Zn contents on crops. The results for Zn in and below maize presented here are comparable for wheat. Results focus on both temporal changes and geographic variation in dissolved metal concentrations and plant metal contents.

Soil acidification

Initial pH values in the Slovakian non-calcareous soils varied mostly between 4.5 and 5.5. Simulated changes in soil pH are dependent on the soil type and time period but in general a pH drop of 0.5-0.75 is predicted in a 50-year period, the largest changes taking place in the first 20 years for both maize and wheat (Figure 8). Initial pH values in the Hungarian non-calcareous soils varied mostly between 4.2 and 5.8. Simulated changes in soil pH are dependent on the initial pH and time period but in general a pH drop between 0.5 and 1.0 is predicted in a 50-year period (Figure 9).

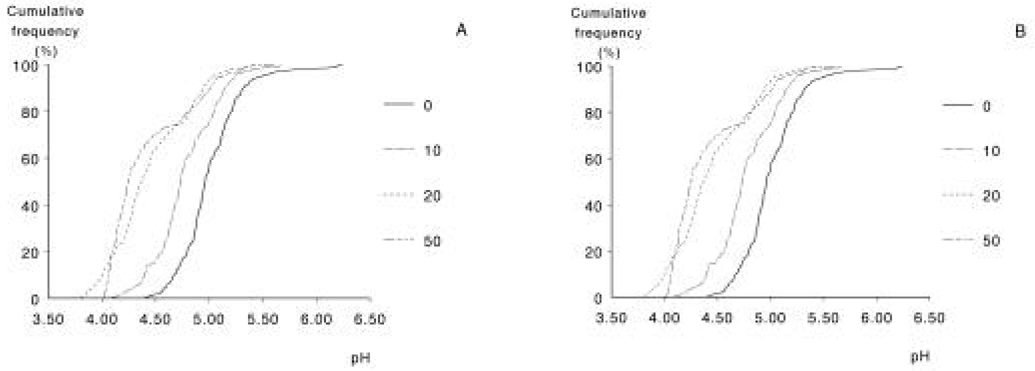

Figure 8 Frequency distributions of simulated pH at start and after 10, 20 and 50 years for wheat (A) and maize (B) in the soil of the 280 non-calcareous plots in Slovakia for the standard scenario.

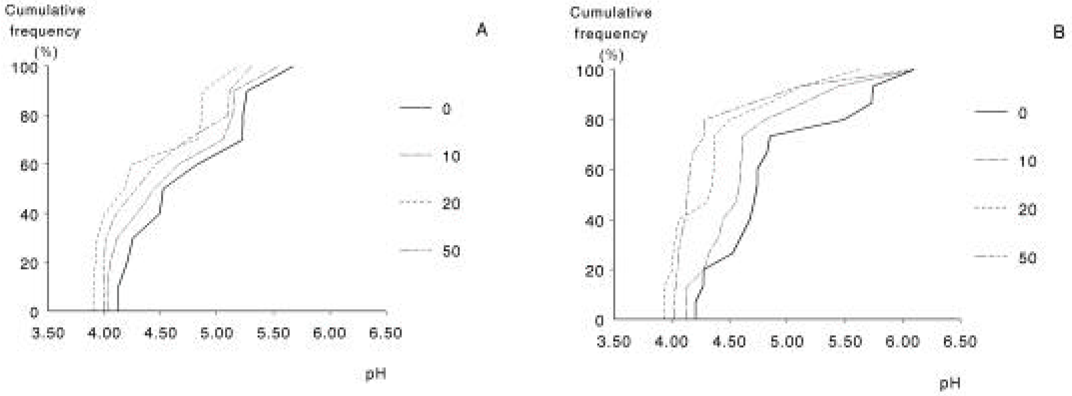

Figure 9 Frequency distributions of simulated pH at start and after 10, 20 and 50 years for wheat (A) and maize (B) in the soil of the 25 non-calcareous plots in Hungary for the standard scenario.

Trends in dissolved cadmium and zinc concentrations and leaching fluxes in time

At the start of the simulation period, dissolved Cd concentrations in the Slovakian non-calcareous soils below wheat mostly ranged between 0 and 2 mg.m^{-3} with extremes up to 10 mg.m^{-3} (Figure 10A). Dissolved Zn concentrations below maize mostly ranged between 20 and 250 mg.m^{-3} with extremes up to 1000 mg.m^{-3} (Figure 10B Simulated concentrations of both Cd and Zn are significantly lower for the Hungarian soils with most concentrations below 0.6 mg.m^{-3} for Cd (Figure 11A) and below 60 mg.m^{-3} fore Zn (Figure 11B). The much lower concentrations in soil solution are due to the much lower concentrations in the solid phase due to the use of a weaker extractant (AAAc-EDTA see 3.1.3). Consequently, the predicted concentrations for Hungary are likely an underestimate

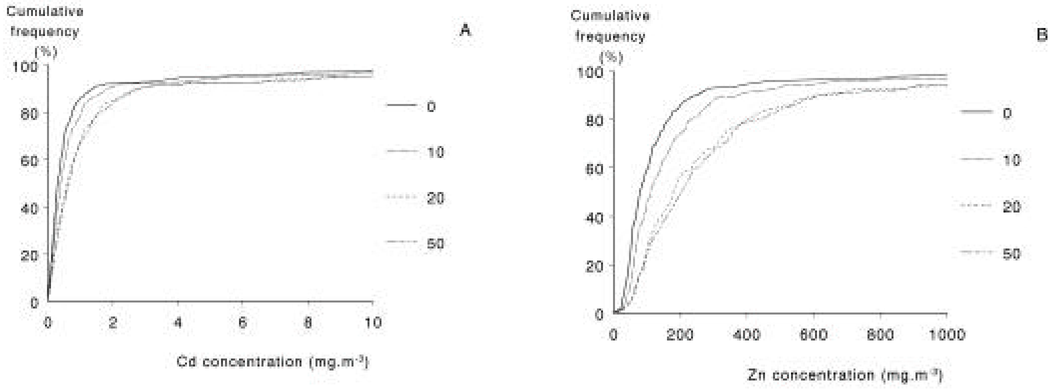

Figure 10 Frequency distributions of simulated dissolved Cd concentrations below wheat (A) and dissolved Zn concentrations below maize (B) in the 280 non-calcareous plots in Slovakia at the start and after 10, 20 and 50 years for the standard scenario.

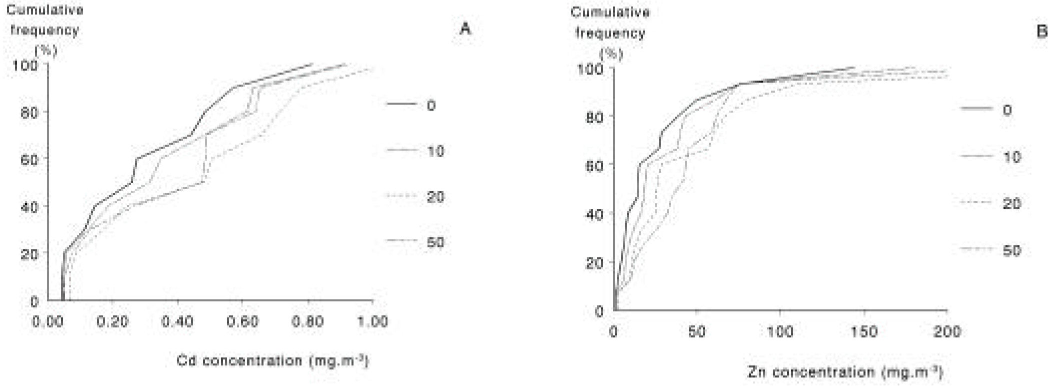

Figure 11 Frequency distributions of simulated dissolved Cd concentrations below wheat (A) and dissolved Zn concentrations below maize (B) in the 25 non-calcareous plots in Hungary at the start and after 10, 20 and 50 years for the standard scenario.

There are indications that Cd concentrations above 2 mg.m^{-3} and Zn concentrations above 250 mg.m^{-3}, as predicted in Slovakia, do have adverse affects on microbiota and plants (Tyler, 1992; De Vries and Bakker, 1998). For Slovakia the percentage of plots with a dissolved Cd concentration above 2 mg.m^{-3} increases from approximately 10 to 20% in 50 years. The percentage of plots with a dissolved Zn concentration above 250 mg.m^{-3} increases from approximately 10 to 40% in this period. This result shows that ongoing acidification due to stopping of liming will have an affect on the soil ecosystem, due to adverse metal effects. The simulated dissolved Cd and Zn concentrations in Hungary stay well below these critical metal concentrations, but this conclusion is affected by the most likely underestimation of the reactive metal concentrations and thereby dissolved metal concentrations because of a too weak extractant.

Simulated average leaching rates (at 0.5 m depth) for Cd below maize in Slovakia increase from around 0.4 g.ha.yr^{-1} at the start of the simulation to about 0.9 g.ha.yr^{-1} after 50 years. For Zn leaching rates increase from about 33 to 97 g.ha.yr^{-1} (Table 9). The variation in leaching rates is, however, extremely large as shown by the large standard deviation in the same table. The leaching rates for the Hungarian sites are low due to the low simulated metal concentrations for these sites, for reasons mentioned above. The increase in leaching rate is due to the decrease in pH, which results in an increase of metal concentrations. Leaching rates of Cd and Zn as calculated for Slovakia are in the lower range as those estimated for arable soils in the Netherlands (De Vries et al., 2002). The relatively low leaching rates are partly due to the lower metal contents in the soil in Slovakia as compared to the Netherlands.

Table 9 Average values and standard deviations of leaching rates of Cd under all wheat plots and of Zn under all maize plots.

Country	Year	Cd leaching flux (g.ha^{-1}.yr^{-1})		Zn leaching flux (g.ha^{-1}.yr^{-1})	
		average	sd	average	sd
Slovakia	Start	0.39	2.84	33	104
	10	0.51	3.80	51	163
	20	0.77	5.80	87	284
	50	0.87	7.19	97	355
Hungary	Start	0.04	0.03	3.9	5.2
	10	0.05	0.03	4.8	6.3
	20	0.06	0.03	7.3	10.6
	50	0.05	0.03	6.4	7.4

Trends and geographic distribution of cadmium and zinc concentrations in crops

At the start of the simulation period, simulated contents of Cd in wheat mostly ranged between 0.1 and 0.2 mg.kg^{-1} with extremes up to 0.5 mg.kg^{-1}, while simulated contents of Zn in maize mostly ranged between 2 and 50 mg.kg^{-1} in the Slovakian plots with extremes up to 70 mg.kg^{-1} (Figure 12). The food quality criteria in Slovakia for Cd in wheat and Zn in maize are 0.1 and 80 mg.kg^{-1}, respectively. Results show that, unlike the soil solution, Cd seems to be problem for wheat (also for maize, which is not presented here), whereas Zn is not and will neither become a problem as well. Results show that the predicted percentage of plots exceeding a Cd content of 0.1 mg.kg^{-1} is about 90% at the beginning, and that this percentage will slightly increase. When one takes a higher criterion, such as 0.15 mg.kg^{-1}, used in the Netherlands, the percentage increases from approximately 50% at the start of the simulation to 85% after 50 years (Figure 12).

The simulated contents of Cd in wheat are high compared to measured concentrations in wheat in the Netherlands (De Vries et al., 2002), whereas concentrations in soil and soil solution were higher in the Netherlands. The higher concentrations are caused by the lower pH and much lower organic matter contents for the Slovakian soils compared to the Dutch agricultural soils. Clay contents are higher in the Slovakian soils, but the clay content does not significantly affect Cd concentrations in wheat (see Table 8).

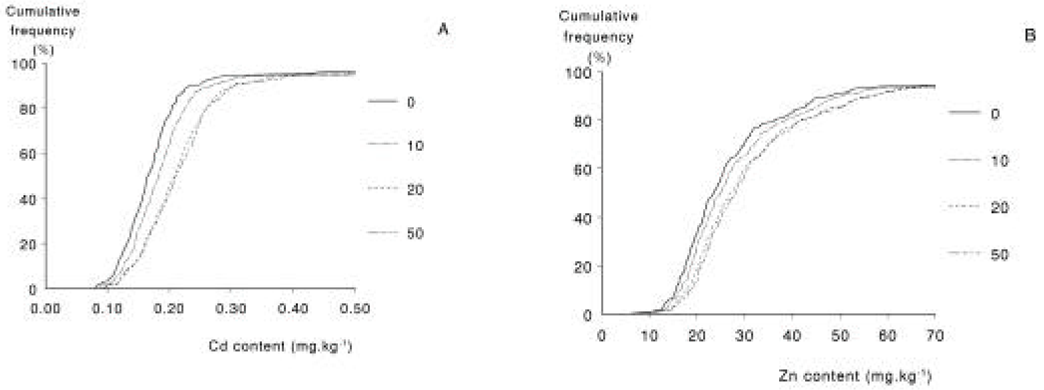

Figure 12 Frequency distributions of simulated Cd contents in wheat (A) and Zn contents in maize (B) in the 280 non-calcareous plots in Slovakia at the start and after 10, 20 and 50 years for the standard scenario.

Contents of Cd in wheat for the Hungarian soils are high (Figure 13). Minimum contents at the start are just below 0.3 mg.kg^{-1}. As a result of the acidification the contents after 50 years are even a little higher. Metal contents for Hungary at the start are based on measured contents in crops. The high Cd contents in wheat are probably the result of the very low organic matter contents in the Hungarian soils. Zn concentrations in maize are comparable to those in Slovakia.

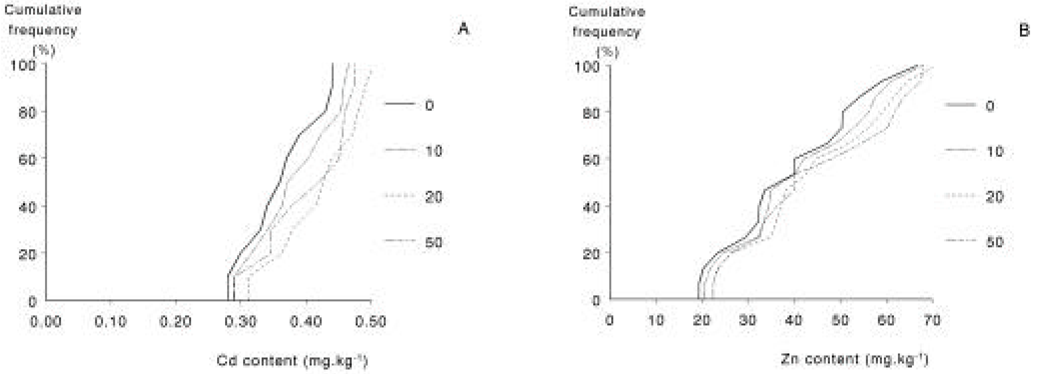

Figure 13 Frequency distributions of simulated Cd contents in wheat (A) and Zn contents in maize (B) in the 25 non-calcareous plots in Hungary at the start and after 10, 20 and 50 years for the standard scenario.

Results of the geographic distribution of the Cd contents in wheat at the start and end of the simulation period shows that large changes take place in Slovakia throughout the whole country (Figure 53). Changes are most severe for plots with low clay and organic matter contents, where the capacity to buffer the incoming acidity is relatively low. Similar geographic changes are predicted for Zn (Figure 55). In Hungary however, the changes are small. Values are already high at the beginning and only increase in a limited way over time (see also Fig. 13).

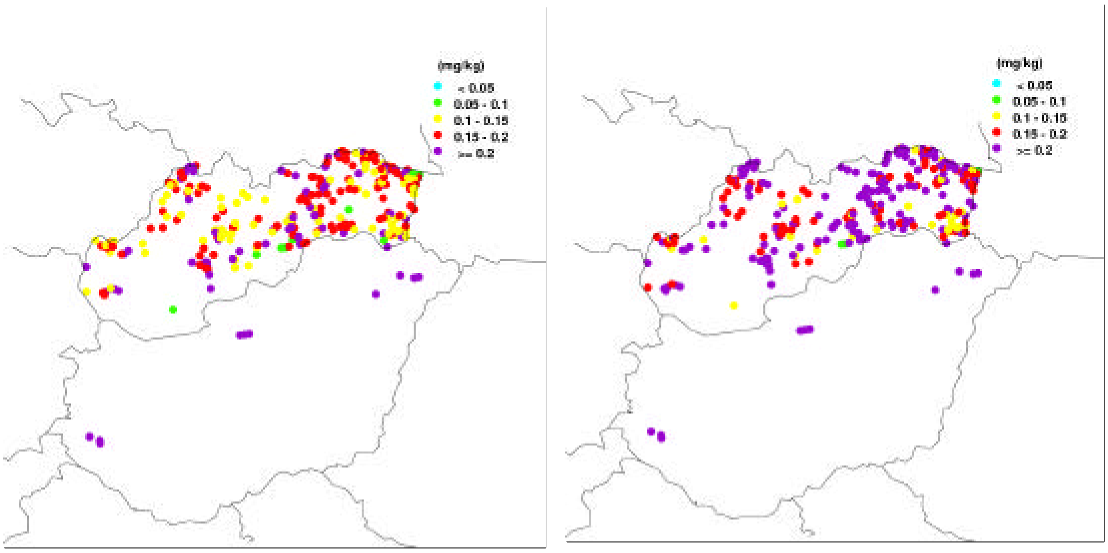

Figure 14 Geographic distribution of Cd contents (mg.kg-1) in wheat at the start (A) and end (B) of the simulation period in the 280 non-calcareous plots in Slovakia and the 25 non-calcareous plots in Hungary.

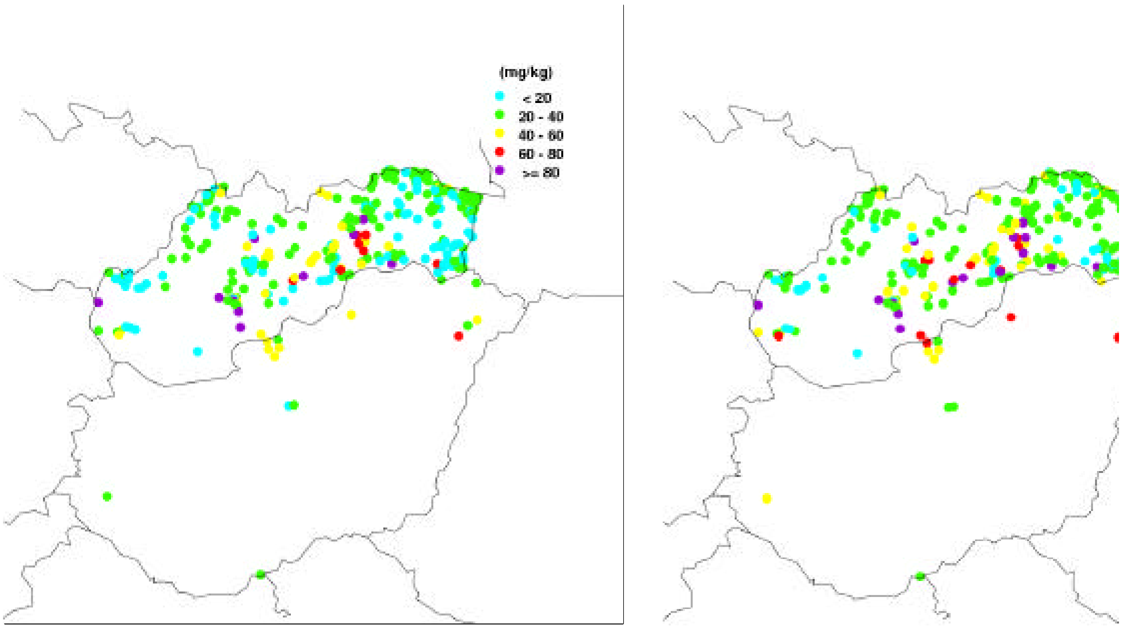

Figure 15 Geographic distribution of Zn contents (mg.kg-1) in wheat at the start (A) and end (B) of the simulation period in the 280 non-calcareous plots in Slovakia and the 25 non-calcareous plots in Hungary.

4.1.5 Discussion and conclusions

In figure 16 the effects of an alternative fertiliser scenario on the pH and Cd contents in soil are shown. In the alternative scenario all N-fertiliser is applied as calcium ammonium nitrate whereas at present part of the N-fertiliser is given as ammonium nitrate. The use of calcium ammonium nitrate shows a slight improvement, however the use of this type of fertiliser can not stop acidification without the additional use of lime (Figure 16). It is questionable, however, that liming will not be applied by farmers since crop growth is seriously limited below a pH of 4.5-5.0. In other words, one may also assume liming such that the minimum pH will not drop below 4.5. The results of the alternative scenario are comparable for the crop contents.

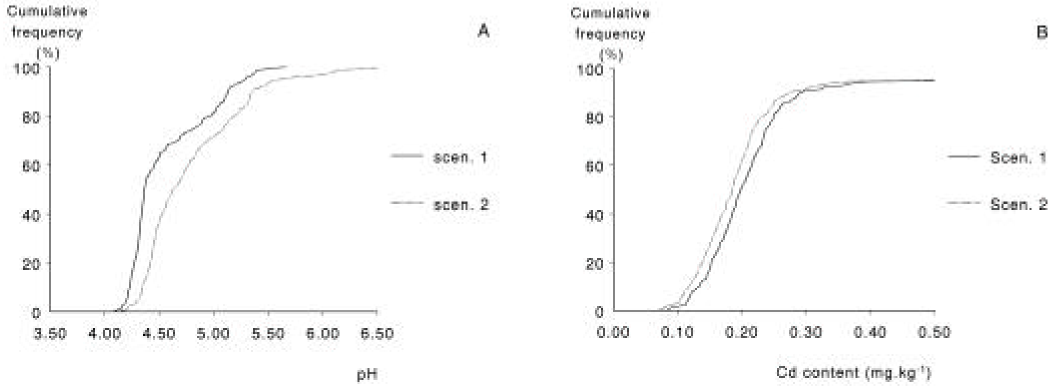

Figure 16 Frequency distributions of pH below wheat (A) and Cd content in wheat (A) of the 180 non-calcareous plots in Slovakia after 50 years for both fertiliser scenarios

In summary, the results show that adverse affects on soil life are most likely due to elevated dissolved Zn concentrations. The predicted percentage of plots exceeding a critical Zn concentration of 250 mg.m^{-3} increases from less than 10% at the start of the simulation to 50% after 50 years. Adverse affects on crops are due to elevated Cd contents in crops (wheat and also for maize, which is not presented here), whereas Zn is not a problem. Results show that the predicted percentage of plots exceeding a critical Cd content of 0.1 mg.kg^{-1} is about 90% at the beginning in Slovakia and always above this content in Hungary, and that this percentage will slightly increase as a result of acidification. The high Cd contents in wheat for Slovakia and especially for Hungary are most likely due to the low organic matter contents of the soils.

Acknowledgements

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Evaluation of the results obtained

The results of the study show that by combining information on: (i) transfer functions for heavy metals describing relationships between total and reactive heavy metal contents in the soil solid phase and dissolved metal concentrations and (ii) soil-plant relations relating total heavy metal contents in crops and in soil, while accounting for the impact of organic matter and clay content and soil pH, it is possible to (iii) predict long-term impacts of stopping with liming on soil acidification and related metal mobilisation and metal uptake in agricultural soils of Slovakia and Hungary. Results obtained in this project for these three items are described below.

Overall conclusions that can be derived from the studies carried out in this project are that:

- On average, a reasonable prediction can be made of reactive metal contents from total metal contents and the organic matter and clay content using regression but the reliability of those estimates is limited for specific sites
- Reliable transfer function can be derived allowing the calculation of total or free metal concentrations in soil solution from measured reactive or total contents in the solid phase, specifically for Cd and Cu.
- Transfer functions allowing the calculation of total or free metal concentrations in soil solution from measured contents in the solid phase is a practical method to be used for risk assessment. It avoids labour intensive measurements to determine soil solution concentrations of the metals of interest together with the measurement of the macro chemical composition of the soil solution.
- Simulation of the crop metal contents with a dynamic process-oriented model, especially the yearly variation in is difficult since much of the dynamics is probably mainly governed by plant specific processes and not so much by soil chemistry.
- Soil-to-plant transfer relationships based on soil pH, organic matter content, texture and the soil metal content as derived by multiple linear regression are reasonable for regional scale applications in the case of Cd and Zn. The use of a simple Freundlich-type equation explained between 40 and 80% of the measured variation of Cd and Zn in crops such as potato, wheat, maize, sugar beet, lettuce and endive
- -The use of transfer functions and soil plant relationships in combination with critical limits for the soil solution and crops (food quality criteria) can give insight in changes in ecotoxicological risks due to changes in soil properties which is of interest in the case of management changes, such as stopping with liming application of the transfer functions soil plant relationships derived in this study show a substantial increase in the area exceeding ecotoxicological critical limits for the soil solution and human toxicological critical limits for food crops (food quality criteria).

Annex 1 Geographical position and soil properties of the A horizon of selected soil samples from 306 agricultural soils

No	Sample	Longitude	Latitude	Soil unit FAO (1970)	Hor.	pH / H_2O	pH / KCl	Carbonate	Clay (%)	Humus (%)
1	GAP-BB-014	19.45737	48.80704	Eutric Fluvisol	A	5.85	5.08	0.00	11.45	12.48
2	GAP-BB-015	19.40696	48.80666	Eutric Fluvisol	A	5.30	4.58	0.00	8.19	9.09
3	GAP-BB-017	19.29963	48.77095	Eutric Cambisol	A	6.09	5.30	3.20	14.46	3.58
4	GAP-BB-018	19.27061	48.75584	Eutric Fluvisol	A	6.94	6.44	0.00	10.86	8.31
5	GAP-BB-034	19.15113	48.79856	Eutric Cambisol	A	4.89	3.70	0.00	11.43	9.09
6	GAP-BB-046	19.14673	48.72747	Albo-gleyic Luvisol	A	5.70	4.62	0.00	13.90	7.72
7	GAP-BB-058	19.33925	48.67934	Eutric Cambisol	A	5.18	4.33	0.00	8.18	8.07
8	GAP-BB-062	19.37543	48.74373	Eutric Fluvisol	A	6.41	5.38	0.00	6.97	7.50
9	GAP-BB-063	19.45929	48.85286	Eutric Cambisol	A	6.20	4.86	0.00	7.95	4.56
10	GAP-BB-082	19.84039	48.86124	Albo-gleyic Luvisol	A	5.13	4.05	0.00	4.95	3.81
11	GAP-BB-093	19.74823	48.80696	Eutric Cambisol	A	5.66	3.80	0.00	7.38	1.78
12	GAP-BB-103	19.12568	48.80630	Eutric Cambisol	A	4.86	3.65	0.00	7.38	9.30
13	GAP-BB-113	19.12088	48.78134	Eutric Cambisol	A	5.87	4.83	0.00	14.21	2.88
14	GAP-BB-120	19.15743	48.69574	Stagno-gleyic Cambisol	A	5.82	4.92	0.00	6.53	3.40
15	GAP-BB-125	19.23349	48.79983	Dystric Cambisol	A	3.63	3.37	0.00	10.76	7.55
16	GAP-BB-126	19.17659	48.77218	Fluvi-eutric Gleysol	A	7.56	7.14	8.00	8.16	6.36
17	GAP-BB-127	19.21316	48.75540	Eutric Cambisol	A	6.51	5.73	0.00	8.38	6.03
18	GAP-BB-128	19.19585	48.71466	Calcaric Cambisol	A	7.40	6.58	0.00	25.66	5.22
19	GAP-BH-027	17.47218	48.29795	Haplic Chernozem	A	6.80	5.94	0.00	15.55	2.85
20	GAP-BH-038	17.40122	48.32071	Orthic Luvisol	A	5.75	4.73	0.00	21.24	1.86
21	GAP-BH-055	17.27186	48.30437	Stagno-gleyic Cambisol	A	6.77	5.80	0.00	7.47	5.38
22	GAP-BH-056	17.21881	48.29428	Dystric Regosol	A	5.67	4.88	0.00	6.11	6.02
23	GAP-BH-058	17.23711	48.26802	Ranker	A	6.08	5.15	0.00	5.73	4.48
24	GAP-BH-073	16.95830	48.32443	Fluvi-mollic Gleysol	A	5.74	5.02	0.00	6.34	8.98
25	GAP-BH-113	17.34543	48.33394	Eutric Fluvisol	A	4.48	3.44	0.00	24.18	4.41
26	GAP-BJ-011	21.25410	49.40021	Stagno-gleyic Cambisol	A	4.55	3.90	0.00	6.92	5.34
27	GAP-BJ-012	21.27493	49.37579	Ranker	A	4.84	3.78	0.00	8.70	4.24
28	GAP-BJ-015	21.31350	49.44160	Stagno-gleyic Cambisol	A	5.10	3.80	0.00	28.82	7.29
29	GAP-BJ-017	21.26641	49.42456	Ranker	A	4.63	3.83	0.00	6.84	5.93
30	GAP-BJ-019	21.36709	49.13188	Calcaric Cambisol	A	5.85	4.46	0.00	28.02	3.72
31	GAP-BJ-035	21.09623	49.39750	Stagno-gleyic Cambisol	A	6.28	5.35	0.00	10.19	2.28
32	GAP-BJ-039	21.37584	49.33988	Stagno-gleyic Cambisol	A	5.20	4.20	0.00	10.13	3.72
33	GAP-BJ-044	21.34727	49.43685	Eutric Cambisol	A	5.90	4.70	0.00	10.22	6.78
34	GAP-BJ-046	21.39899	49.40886	Eutric Cambisol	A	5.60	4.40	0.00	11.00	5.76
35	GAP-BJ-051	21.46857	49.26750	Stagno-gleyic Cambisol	A	5.37	4.28	0.00	22.22	4.48
36	GAP-BJ-056	21.02495	49.30365	Stagno-gleyic Cambisol	A	4.66	3.63	0.00	8.55	3.55
37	GAP-BJ-060	21.06755	49.34668	Stagno-gleyic Cambisol	A	5.02	4.08	0.00	10.64	4.24
38	GAP-CA-001	18.47769	49.36756	Eutric Cambisol	A	4.74	3.62	0.00	11.63	4.14
39	GAP-CA-008	18.80539	49.29909	Stagno-gleyic Cambisol	A	6.61	5.74	0.00	20.61	3.67
40	GAP-CA-011	18.95266	49.50974	Stagno-gleyic Cambisol	A	5.93	5.12	0.00	10.23	6.78
41	GAP-CA-013	18.89488	49.48786	Eutric Cambisol	A	4.56	3.53	0.00	7.96	5.34
42	GAP-CA-014	18.89390	49.50291	Stagno-gleyic Cambisol	A	5.39	4.23	0.00	7.80	4.74
43	GAP-CA-015	18.84021	49.49343	Eutric Cambisol	A	4.39	3.62	0.00	5.43	5.00
44	GAP-CA-016	18.84501	49.50546	Eutric Fluvisol	A	4.81	3.80	0.00	8.80	3.90
45	GAP-CA-018	18.81808	49.49924	Stagno-gleyic Cambisol	A	5.15	4.56	0.00	6.46	3.90
46	GAP-CA-022	18.72321	49.45942	Stagno-gleyic Cambisol	A	5.00	3.83	0.00	12.65	5.09
47	GAP-CA-023	18.75280	49.44460	Fluvi-eutric Gleysol	A	5.33	4.45	0.00	10.20	2.71
48	GAP-CA-024	18.89597	49.45264	Eutric Cambisol	A	4.95	3.75	0.00	4.00	5.48
49	GAP-CA-034	18.68360	49.39380	Stagno-gleyic Cambisol	A	4.86	3.86	0.00	12.78	5.24
50	GAP-CA-035	18.72106	49.40071	Eutric Cambisol	A	5.00	3.87	0.00	18.90	4.22
51	GAP-CA-051	18.69064	49.45367	Stagno-gleyic Cambisol	A	5.27	4.22	0.00	15.33	3.98
52	GAP-HN-001	21.84405	49.05103	Ranker	A	5.80	4.50	0.00	14.77	3.40
53	GAP-HN-008	22.31659	48.92212	Calcaric Cambisol	A	5.87	4.82	0.00	14.68	3.90
54	GAP-HN-013	22.24509	48.99208	Stagno-gleyic Cambisol	A	5.48	4.29	0.00	8.08	1.69
55	GAP-HN-016	22.24594	49.05884	Stagno-gleyic Cambisol	A	5.96	4.16	0.00	11.95	1.28
56	GAP-HN-029	22.33623	49.12653	Eutric Cambisol	A	5.00	3.88	0.00	9.70	4.57
57	GAP-HN-030	22.33130	49.10196	Eutric Cambisol	A	5.19	4.07	0.00	12.42	3.22
58	GAP-HN-031	22.28528	49.09810	Eutric Cambisol	A	5.56	4.44	0.00	13.11	0.93
59	GAP-HN-033	22.51007	49.05455	Eutric Cambisol	A	4.98	3.73	0.00	11.04	7.26
60	GAP-HN-035	22.47929	49.03064	Eutric Cambisol	A	5.30	4.04	0.00	11.84	4.29
61	GAP-HN-044	22.41190	49.07657	Eutric Cambisol	A	6.19	4.84	0.00	7.86	4.07
62	GAP-HN-048	22.40603	49.01303	Eutric Fluvisol	A	5.05	4.18	0.00	8.66	6.59

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63	GAP-HN-050	22.42816	48.95828	Eutric Fluvisol	A	5.90	4.96	0.00	10.14	3.03
64	GAP-HN-054	21.79792	49.01266	Dystric Planosol	A	6.46	4.99	0.00	23.62	2.28
65	GAP-HN-055	21.83356	48.99806	Stagno-gleyic Cambisol	A	6.31	4.99	0.00	20.17	1.47
66	GAP-HN-059	21.81191	48.99186	Stagno-gleyic Cambisol	A	6.98	5.60	0.00	31.40	2.77
67	GAP-HN-063	22.32759	48.94781	Dystric Planosol	A	6.46	5.59	0.00	12.82	2.60
68	GAP-HN-064	22.36477	48.93690	Calcaric Cambisol	A	6.90	5.75	0.00	30.07	3.67
69	GAP-HN-065	22.37654	48.91829	Eutric Cambisol	A	7.28	6.26	0.00	12.65	2.27
70	GAP-HN-070	22.38958	48.92281	Stagno-gleyic Cambisol	A	5.73	4.42	0.00	15.20	7.17
71	GAP-HN-072	22.31669	49.04377	Eutric Cambisol	A	6.73	5.64	0.00	11.75	7.66
72	GAP-HN-078	21.81200	49.36077	Eutric Cambisol	A	5.43	4.49	0.00	6.21	9.79
73	GAP-HN-079	21.83356	49.35105	Eutric Cambisol	A	5.94	4.37	0.00	15.65	6.59
74	GAP-HN-080	21.85537	49.33364	Eutric Cambisol	A	5.64	4.17	0.00	9.74	4.81
75	GAP-HN-085	21.95975	49.23407	Stagno-gleyic Cambisol	A	6.99	5.64	0.00	9.34	6.51
76	GAP-HN-086	21.98422	49.21021	Eutric Cambisol	A	5.43	3.98	0.00	9.57	4.97
77	GAP-HN-087	22.04728	49.20035	Eutric Cambisol	A	6.46	4.94	0.00	12.73	7.82
78	GAP-HN-088	22.02270	49.20358	Eutric Cambisol	A	6.51	5.34	0.00	6.01	4.56
79	GAP-HN-089	22.02025	49.18342	Stagno-gleyic Cambisol	A	6.13	4.88	0.00	11.16	7.01
80	GAP-HN-096	22.02957	49.16194	Eutric Cambisol	A	5.60	4.20	0.00	9.30	4.29
81	GAP-HN-097	22.05077	49.16487	Stagno-gleyic Cambisol	A	5.43	4.02	0.00	16.29	3.03
82	GAP-HN-098	22.10475	49.18267	Eutric Cambisol	A	5.62	3.87	0.00	5.87	6.83
83	GAP-HN-099	22.09777	49.15887	Eutric Cambisol	A	5.48	4.19	0.00	9.58	4.38
84	GAP-HN-102	22.14988	49.14348	Eutric Cambisol	A	5.32	4.05	0.00	8.13	3.48
85	GAP-HN-103	22.15995	49.10739	Eutric Cambisol	A	6.24	5.16	0.00	14.45	5.31
86	GAP-HN-107	22.14231	49.12391	Stagno-gleyic Cambisol	A	6.05	5.35	0.00	13.64	4.24
87	GAP-HN-136	21.95174	49.01184	Eutric Fluvisol	A	5.59	4.72	0.00	16.75	2.83
88	GAP-HN-138	21.89406	49.04484	Stagno-gleyic Cambisol	A	5.53	5.14	0.00	10.04	7.78
89	GAP-HN-141	21.93999	49.09272	Stagno-gleyic Cambisol	A	5.45	4.76	0.00	15.83	4.59
90	GAP-HN-144	21.94045	49.15937	Calcaric Regosol	A	6.06	5.54	0.00	10.92	11.74
91	GAP-HN-145	21.91185	49.18543	Dystric Planosol	A	5.24	4.13	0.00	18.80	2.17
92	GAP-KE-022	20.97202	48.67353	Stagno-gleyic Cambisol	A	5.20	4.08	0.00	27.74	2.19
93	GAP-KE-032	21.13831	48.74569	Ranker	A	5.40	4.20	0.00	7.47	4.65
94	GAP-KE-046	21.29902	48.65215	Eutric Fluvisol	A	6.15	5.35	0.00	19.94	5.05
95	GAP-KE-065	21.14759	48.58002	Fluvi-eutric Gleysol	A	5.85	5.06	0.00	13.40	4.10
96	GAP-KE-071	21.19953	48.66858	Eutric Cambisol	A	5.80	4.75	0.00	14.23	3.05
97	GAP-KE-085	21.10796	48.65251	Eutric Gleysol	A	5.78	5.00	0.00	15.41	3.74
98	GAP-KE-099	20.98817	48.62420	Dystric Planosol	A	5.88	4.90	0.00	18.96	3.52
99	GAP-KE-109	20.82149	48.66554	Rendzina	A	6.07	5.21	0.00	13.21	13.12
100	GAP-KE-110	21.32396	48.59856	Fluvi-eutric Gleysol	A	5.87	4.91	0.00	29.68	3.36
101	GAP-KE-115	20.94828	48.61660	Rendzina	A	7.65	6.88	3.00	17.28	12.38
102	GAP-KE-131	21.20751	48.63594	Dystric Planosol	A	6.38	5.84	0.00	18.35	6.11
103	GAP-LC-005	19.72986	48.48954	Eutric Cambisol	A	6.23	4.70	0.00	26.23	3.26
104	GAP-LC-036	19.57715	48.38498	Ranker	A	5.63	4.99	0.00	18.55	4.50
105	GAP-LC-054	19.74737	48.56306	Eutric Cambisol	A	5.14	4.47	0.00	2.06	11.62
106	GAP-LC-055	19.77022	48.58722	Cambic Arenosol	A	5.24	4.30	0.00	4.37	2.71
107	GAP-LM-001	19.28333	49.13594	Calcaric Cambisol	A	7.65	6.94	0.00	17.30	7.33
108	GAP-LM-004	19.17250	48.93224	Dystric Cambisol	A	5.13	4.22	0.00	7.19	6.14
109	GAP-LM-008	19.29039	48.99556	Eutric Cambisol	A	6.94	6.22	0.00	7.19	11.24
110	GAP-LM-009	19.27210	49.03416	Eutric Cambisol	A	5.73	5.15	0.00	30.66	9.90
111	GAP-LM-021	19.52937	49.05945	Stagno-gleyic Cambisol	A	5.70	4.68	0.00	19.28	4.91
112	GAP-LM-033	19.98823	49.05123	Eutric Cambisol	A	5.83	4.74	0.00	13.40	5.57
113	GAP-LM-050	19.64779	49.15260	Eutric Cambisol	A	5.74	4.84	0.00	14.78	8.34
114	GAP-LM-058	19.71600	49.10481	Stagno-gleyic Cambisol	A	5.56	4.88	0.00	17.96	6.55
115	GAP-MI-033	21.93845	48.57800	Fluvi-eutric Gleysol	A	5.88	3.87	0.00	36.34	5.60
116	GAP-MI-044	22.17301	48.61588	Fluvi-eutric Gleysol	A	4.95	4.12	0.00	13.49	1.78
117	GAP-MI-047	22.13229	48.66095	Eutric Gleysol	A	4.75	3.95	0.00	25.93	8.17
118	GAP-MI-050	22.28188	48.74984	Eutric Cambisol	A	4.73	4.12	0.00	18.88	1.34
119	GAP-MI-053	22.32736	48.70149	Eutric Cambisol	A	5.31	4.52	0.00	14.79	2.34
120	GAP-MI-064	22.37078	48.86290	Stagno-gleyic Cambisol	A	5.29	4.28	0.00	15.08	3.03
121	GAP-MI-087	21.86996	48.87370	Ranker	A	5.87	4.37	0.00	25.85	2.31
122	GAP-MI-094	21.87727	48.67975	Fluvi-eutric Gleysol	A	5.70	5.28	0.00	14.69	4.55
123	GAP-MI-113	21.91370	48.71898	Fluvi-eutric Gleysol	A	5.78	4.62	0.00	17.98	2.19
124	GAP-MI-114	21.94015	48.69918	Eutric Fluvisol	A	5.33	4.12	0.00	18.92	1.84
125	GAP-MI-115	21.88339	48.65492	Eutric Gleysol	A	6.81	6.00	0.00	29.40	6.11
126	GAP-MI-116	21.81999	48.66742	Fluvi-eutric Gleysol	A	4.04	3.47	0.00	34.51	4.72
127	GAP-MI-120	22.02330	48.63851	Fluvi-eutric Gleysol	A	5.81	4.54	0.00	23.75	4.48
128	GAP-MI-121	22.03724	48.66814	Eutric Gleysol	A	5.30	3.93	0.10	57.37	5.05

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129	GAP-MI-122	22.07878	48.66253	Eutric Gleysol	A	5.32	4.42	0.00	33.00	5.05
130	GAP-NZ-052	18.29706	48.03183	Luvi-haplic Chernozem	A	4.81	4.14	0.00	23.55	4.15
131	GAP-NZ-059	18.13244	47.98597	Haplic Chernozem	A	6.45	5.98	0.90	7.59	7.82
132	GAP-PO-004	21.05377	48.93202	Stagno-gleyic Cambisol	A	5.40	4.60	0.00	13.10	2.41
133	GAP-PO-010	21.28924	48.81555	Stagno-gleyic Cambisol	A	5.72	4.75	0.00	47.82	5.45
134	GAP-PO-015	21.39284	49.10056	Ranker	A	5.56	4.54	0.00	25.33	6.26
135	GAP-PO-033	21.34910	49.03083	Dystric Planosol	A	5.81	4.94	0.00	20.20	2.64
136	GAP-PO-040	20.89303	49.11225	Ranker	A	5.92	4.61	0.00	12.85	3.38
137	GAP-PO-047	20.91160	49.18995	Ranker	A	5.81	4.75	0.00	6.98	7.93
138	GAP-PO-049	20.91138	49.14402	Stagno-gleyic Cambisol	A	5.75	4.82	0.00	22.23	3.97
139	GAP-PO-050	20.93868	49.11803	Stagno-gleyic Cambisol	A	5.65	4.62	0.00	12.71	4.21
140	GAP-PO-055	20.98070	49.11686	Ranker	A	5.94	4.55	0.00	19.96	3.47
141	GAP-PO-057	21.02496	49.14351	Stagno-gleyic Cambisol	A	5.84	4.74	0.00	16.83	2.97
142	GAP-PO-060	21.06809	49.15624	Stagno-gleyic Cambisol	A	5.58	4.73	0.00	17.65	5.12
143	GAP-PO-100	20.77765	49.21897	Ranker	A	4.92	3.65	0.00	13.78	5.78
144	GAP-PO-101	20.81028	49.21570	Stagno-gleyic Cambisol	A	4.50	3.62	0.00	12.14	5.12
145	GAP-PO-104	20.94213	49.03623	Ranker	A	5.90	4.64	0.00	19.83	1.72
146	GAP-PO-105	20.93803	49.06466	Eutric Cambisol	A	5.61	4.59	0.00	21.48	3.12
147	GAP-PO-110	20.98515	49.01207	Dystric Regosol	A	5.46	4.14	0.00	12.16	2.72
148	GAP-PO-117	20.96236	49.09615	Ranker	A	5.28	4.14	0.00	13.37	2.14
149	GAP-PO-121	21.20633	49.01989	Eutric Cambisol	A	5.76	4.60	0.00	15.01	2.97
150	GAP-PP-005	20.40029	49.29343	Ranker	A	4.70	3.70	0.00	6.83	7.59
151	GAP-PP-006	20.30570	49.33423	Ranker	A	5.15	4.10	0.00	9.09	4.78
152	GAP-PX-012	18.33373	49.17580	Fluvi-gleyic Phaeozem	A	6.85	6.11	0.00	29.07	6.19
153	GAP-PX-019	18.41694	49.23652	Fluvi-gleyic Phaeozem	A	5.88	5.04	0.00	25.27	3.83
154	GAP-PX-026	18.32222	49.07342	Fluvi-gleyic Phaeozem	A	6.96	6.49	0.00	16.05	3.34
155	GAP-PX-038	18.37266	49.01299	Stagno-gleyic Cambisol	A	4.94	4.20	0.00	13.14	5.28
156	GAP-RS-008	20.19247	48.52011	Rendzina	A	5.63	4.48	0.00	37.91	4.03
157	GAP-RS-062	20.24970	48.52505	Eutric Fluvisol	A	6.94	5.92	0.00	10.62	4.31
158	GAP-RS-090	20.12487	48.52340	Albo-gleyic Luvisol	A	6.08	4.89	0.00	29.58	3.42
159	GAP-RS-101	19.89993	48.58889	Ranker	A	4.88	3.93	0.00	4.05	4.52
160	GAP-RV-001	20.32553	48.59244	Fluvi-mollic Gleysol	A	4.40	3.40	0.00	17.82	5.81
161	GAP-RV-025	20.28232	48.70812	Stagno-gleyic Cambisol	A	6.55	5.42	0.00	13.09	2.93
162	GAP-RV-026	20.34702	48.78894	Eutric Fluvisol	A	5.48	4.90	0.00	3.65	4.59
163	GAP-RV-028	20.27091	48.79226	Eutric Cambisol	A	5.75	4.84	0.00	5.64	6.55
164	GAP-RV-037	20.42925	48.53243	Eutric Cambisol	A	6.57	5.28	0.00	40.70	4.06
165	GAP-RV-038	20.49623	48.53659	Calcaric Lithosol	A	6.50	5.40	0.00	30.95	6.33
166	GAP-RV-040	20.53996	48.54184	Calcaric Lithosol	A	6.42	5.54	0.00	18.22	9.17
167	GAP-RV-045	20.05043	48.72620	Eutric Cambisol	A	5.42	4.10	0.00	10.32	2.83
168	GAP-RV-047	20.11159	48.75835	Eutric Cambisol	A	5.29	3.81	0.00	4.61	5.97
169	GAP-RV-051	20.02626	48.70312	Eutric Cambisol	A	5.55	4.15	0.00	6.85	6.47
170	GAP-RV-058	20.33275	48.75196	Ranker	A	6.93	6.17	0.00	7.71	9.25
171	GAP-RV-062	20.38070	48.71241	Ranker	A	6.62	5.89	0.00	5.24	3.73
172	GAP-RV-075	20.38535	48.84576	Eutric Cambisol	A	5.10	3.86	0.00	6.79	8.71
173	GAP-RV-076	20.34343	48.83699	Eutric Cambisol	A	5.84	4.35	0.00	7.16	3.38
174	GAP-RV-077	20.35785	48.81856	Dystric Lithosol	A	4.82	4.07	0.00	6.25	16.21
175	GAP-RV-078	20.38453	48.82436	Eutric Cambisol	A	6.52	5.30	0.00	2.92	2.27
176	GAP-RV-086	20.72968	48.63661	Rendzina	A	5.92	5.29	0.00	12.20	8.31
177	GAP-RV-104	20.34061	48.64058	Ranker	A	6.74	6.19	0.00	10.60	2.27
178	GAP-RV-122	20.42621	48.61394	Dystric Lithosol	A	5.88	5.29	0.00	9.21	16.77
179	GAP-RV-123	20.41950	48.59793	Dystric Lithosol	A	5.18	4.52	0.00	6.25	12.69
180	GAP-RV-132	20.32854	48.72456	Ranker	A	5.22	4.13	0.00	8.18	2.74
181	GAP-RV-133	20.72152	48.62115	Rendzina	A	5.53	4.83	0.00	23.24	9.60
182	GAP-SE-001	17.26837	48.78433	Orthic Luvisol	A	6.04	5.09	0.00	29.28	2.27
183	GAP-SE-010	17.18776	48.84657	Fluvi-eutric Gleysol	A	5.35	4.24	0.00	18.53	5.83
184	GAP-SE-028	17.39992	48.70458	Orthic Luvisol	A	5.65	4.37	0.00	28.80	2.10
185	GAP-SE-036	17.35806	48.75665	Eutric Cambisol	A	6.75	5.90	0.00	37.91	4.06
186	GAP-SE-060	16.99629	48.57916	Eutric Fluvisol	A	6.42	5.72	0.00	3.05	0.81
187	GAP-SE-066	17.34402	48.78546	Stagno-gleyic Cambisol	A	5.26	4.38	0.00	29.08	4.09
188	GAP-SE-068	17.41306	48.81028	Fluvi-gleyic Phaeozem	A	6.95	6.28	0.00	14.59	10.55
189	GAP-SE-069	17.44830	48.81637	Stagno-gleyic Cambisol	A	5.58	4.52	0.00	18.97	3.86
190	GAP-SE-071	17.47708	48.82089	Eutric Cambisol	A	5.75	4.82	0.00	20.66	6.21
191	GAP-SE-081	17.53670	48.67748	Fluvi-gleyic Phaeozem	A	7.78	7.04	10.30	15.90	2.60
192	GAP-SE-094	17.61913	48.67184	Eutric Cambisol	A	7.02	6.19	0.00	12.81	0.48
193	GAP-SE-095	17.57739	48.67336	Stagno-gleyic Cambisol	A	6.74	5.80	0.00	16.23	2.92
194	GAP-SE-120	17.45068	48.76341	Stagno-gleyic Cambisol	A	5.58	5.30	0.00	23.47	4.91

No	Sample	Longitude	Latitude	Soil unit FAO (1970)	Hor.	pH / H_2O	pH / KCl	Carbonate	Clay (%)	Humus (%)
195	GAP-SK-001	21.66312	49.21495	Stagno-gleyic Cambisol	A	5.47	4.21	0.00	16.71	2.21
196	GAP-SK-006	21.64776	49.35369	Stagno-gleyic Cambisol	A	5.48	4.33	0.00	13.98	4.83
197	GAP-SK-027	21.67967	49.38977	Stagno-gleyic Cambisol	A	4.37	3.68	0.00	14.31	4.67
198	GAP-SK-031	21.54702	49.39290	Stagno-gleyic Cambisol	A	5.49	4.88	0.00	16.93	9.19
199	GAP-SK-039	21.60829	49.26842	Eutric Cambisol	A	8.20	7.30	0.30	17.00	2.92
200	GAP-SK-054	21.54102	49.17516	Luvic Cambisol	A	6.37	5.33	0.00	22.55	4.22
201	GAP-SK-056	21.66288	49.31738	Stagno-gleyic Cambisol	A	5.12	4.21	0.00	10.88	4.83
202	GAP-SK-057	21.66908	49.27888	Stagno-gleyic Cambisol	A	5.66	4.54	0.00	10.75	4.09
203	GAP-SK-058	21.74389	49.36409	Stagno-gleyic Cambisol	A	5.00	3.75	0.00	29.10	5.90
204	GAP-SK-060	21.74278	49.32251	Stagno-gleyic Cambisol	A	5.60	4.75	0.00	21.20	9.59
205	GAP-SK-065	21.79133	49.32487	Luvic Cambisol	A	5.30	4.48	0.00	10.89	5.65
206	GAP-SK-067	21.84550	49.27862	Luvic Cambisol	A	5.65	4.48	0.00	10.72	7.29
207	GAP-SK-081	21.68387	49.29807	Stagno-gleyic Cambisol	A	5.25	4.45	0.00	13.46	2.38
208	GAP-SK-082	21.67685	49.25703	Stagno-gleyic Cambisol	A	5.08	4.18	0.00	18.70	3.05
209	GAP-SL-004	20.52603	49.25705	Stagno-gleyic Cambisol	A	5.59	4.41	0.00	12.29	2.98
210	GAP-SN-001	20.82850	48.82138	Stagno-gleyic Cambisol	A	6.60	5.50	0.00	3.05	4.54
211	GAP-SN-002	20.78097	48.74129	Ranker	A	5.00	3.80	0.00	2.35	6.81
212	GAP-SN-008	20.84931	48.88066	Ranker	A	5.50	4.30	0.00	3.95	5.17
213	GAP-SN-012	20.72607	48.88834	Dystric Regosol	A	5.40	4.40	0.00	3.76	6.98
214	GAP-SN-014	20.56999	49.01419	Eutric Cambisol	A	5.92	5.24	0.00	13.97	3.17
215	GAP-SN-015	20.59255	48.99545	Eutric Cambisol	A	5.55	4.52	0.00	14.96	2.17
216	GAP-SN-017	20.64039	49.04811	Dystric Lithosol	A	5.42	4.68	0.00	6.70	4.65
217	GAP-SN-019	20.65570	49.07223	Eutric Cambisol	A	5.82	5.14	0.00	5.39	3.62
218	GAP-SN-022	20.67940	48.90289	Ranker	A	7.06	6.12	0.00	2.35	3.73
219	GAP-SN-044	20.68167	48.87256	Ranker	A	4.46	3.62	0.15	4.29	13.41
220	GAP-SN-045	20.64841	48.96444	Calcaric Cambisol	A	5.80	5.02	0.00	11.52	3.33
221	GAP-SN-046	20.53301	48.99521	Eutric Cambisol	A	6.71	6.14	0.00	7.98	2.92
222	GAP-SN-048	20.51491	49.01793	Ranker	A	5.31	4.36	0.05	7.35	2.41
223	GAP-SN-050	20.73097	48.81174	Eutric Cambisol	A	6.08	3.77	0.00	3.53	3.98
224	GAP-SN-051	20.84699	49.02433	Ranker	A	5.65	4.44	0.00	6.17	3.17
225	GAP-SN-055	20.73942	49.02909	Ranker	A	5.56	4.78	0.00	5.78	4.33
226	GAP-TN-001	18.09368	48.90854	Eutric Fluvisol	A	5.03	3.86	0.00	13.26	6.00
227	GAP-TN-004	18.29050	48.90015	Rendzina	A	7.40	6.37	0.00	21.69	4.64
228	GAP-TN-010	17.95763	48.65769	Rendzina	A	5.83	5.24	0.00	15.82	3.98
229	GAP-TN-015	17.93685	48.75877	Orthic Luvisol	A	6.00	5.00	0.00	22.06	2.50
230	GAP-TN-067	17.69576	48.70166	Eutric Cambisol	A	5.46	4.16	0.00	23.05	2.24
231	GAP-TV-012	22.13096	48.49812	Fluvi-eutric Gleysol	A	2.75	2.17	0.00	24.27	5.26
232	GAP-TV-017	22.07243	48.50592	Eutric Gleysol	A	4.73	3.42	0.00	27.50	6.78
233	GAP-TV-020	21.79856	48.35944	Dystric Regosol	A	6.41	5.94	0.00	5.57	1.07
234	GAP-TV-027	21.86157	48.47169	Fluvi-eutric Gleysol	A	5.42	4.08	0.00	29.71	3.74
235	GAP-TV-028	21.97954	48.46504	Fluvi-eutric Gleysol	A	3.57	2.71	0.00	35.97	1.24
236	GAP-TV-029	21.97528	48.49758	Eutric Gleysol	A	6.19	5.30	0.00	57.20	1.57
237	GAP-TV-032	21.89569	48.48512	Fluvi-eutric Gleysol	A	3.01	2.44	0.00	21.31	2.83
238	GAP-TV-039	22.04723	48.49209	Eutric Gleysol	A	5.53	4.08	0.00	37.55	4.50
239	GAP-TV-043	22.06033	48.44153	Fluvi-eutric Gleysol	A	5.93	4.58	0.00	16.10	1.24
240	GAP-TV-055	21.94046	48.53046	Eutric Gleysol	A	5.58	4.33	0.00	34.01	7.93
241	GAP-TV-064	21.77823	48.50811	Dystric Regosol	A	6.46	5.63	0.00	7.04	0.75
242	GAP-TV-086	21.76637	48.43201	Ranker	A	3.45	3.15	0.00	11.40	3.09
243	GAP-TV-113	22.14832	48.50451	Eutric Gleysol	A	5.94	4.73	0.00	39.44	4.60
244	GAP-TV-115	22.15206	48.54481	Fluvi-eutric Gleysol	A	5.60	4.91	0.00	23.49	3.00
245	GAP-TV-116	22.12988	48.43459	Fluvi-eutric Gleysol	A	6.15	4.76	0.00	22.13	5.06
246	GAP-TV-122	22.01339	48.49926	Eutric Gleysol	A	5.82	4.71	0.00	41.39	7.76
247	GAP-TV-123	22.02005	48.50930	Eutric Gleysol	A	4.61	3.78	0.00	29.81	10.28
248	GAP-TV-130	21.76135	48.66134	Eutric Gleysol	A	6.67	5.47	0.00	46.30	4.72
249	GAP-TV-133	21.86092	48.49625	Eutric Gleysol	A	5.60	4.38	0.00	30.98	11.77
250	GAP-TV-141	21.61967	48.57838	Albo-gleyic Luvisol	A	5.75	4.81	0.00	31.84	2.50
251	GAP-VK-180	19.36006	48.38336	Eutric Cambisol	A	5.56	4.65	0.00	6.34	9.67
252	GAP-VV-021	21.49952	49.07096	Ranker	A	8.28	7.24	3.00	22.50	1.72
253	GAP-VV-026	21.54457	49.04054	Rendzina	A	8.11	7.18	2.75	36.47	3.73
254	GAP-VV-029	21.48496	49.01575	Ranker	A	7.88	7.44	0.00	25.55	2.73
255	GAP-VV-032	21.60663	48.94817	Ranker	A	5.90	4.24	0.00	21.47	2.07
256	GAP-VV-042	21.79918	49.16158	Stagno-gleyic Cambisol	A	5.33	4.07	0.00	7.11	10.34
257	GAP-VV-056	21.43647	49.01374	Eutric Cambisol	A	5.35	4.45	0.00	8.31	6.00
258	GAP-ZA-006	18.92779	49.21774	Stagno-gleyic Cambisol	A	5.14	3.78	0.00	21.10	6.36
259	GAP-ZA-009	18.97264	49.28369	Stagno-gleyic Cambisol	A	5.82	4.68	0.00	12.16	5.86
260	GAP-ZA-011	19.00961	49.28408	Stagno-gleyic Cambisol	A	5.44	4.10	0.00	11.97	5.19

No	Sample	Longitude	Latitude	Soil unit FAO (1970)	Hor.	pH / H_2O	pH / KCl	Carbonate	Clay (%)	Humus (%)
261	GAP-ZA-015	19.08165	49.26049	Stagno-gleyic Cambisol	A	5.42	3.92	0.00	14.57	4.52
262	GAP-ZA-019	18.75877	49.23896	Stagno-gleyic Cambisol	A	5.15	4.36	0.00	18.35	2.76
263	GAP-ZA-023	18.52970	48.96255	Stagno-gleyic Cambisol	A	7.31	6.58	0.00	30.73	5.63
264	GAP-ZA-024	18.60960	49.01113	Calcaric Cambisol	A	7.87	7.05	0.00	19.24	6.70
265	GAP-ZA-025	18.77238	49.25497	Stagno-gleyic Cambisol	A	5.40	4.64	0.00	13.77	2.84
266	GAP-ZA-029	18.57823	49.28723	Stagno-gleyic Cambisol	A	5.69	4.50	0.00	17.57	5.10
267	GAP-ZA-030	18.57082	49.35231	Dystric Cambisol	A	5.02	3.85	0.00	25.03	4.84
268	GAP-ZA-031	18.52861	49.34391	Dystric Cambisol	A	5.29	4.34	0.00	9.13	6.26
269	GAP-ZA-034	18.49842	49.33717	Stagno-gleyic Cambisol	A	5.44	3.87	0.00	35.53	4.43
270	GAP-ZA-054	18.76234	49.16278	Dystric Planosol	A	6.56	5.41	0.00	22.80	3.15
271	GAP-ZH-003A	18.96123	48.60089	Luvic Cambisol	A	5.35	4.37	0.00	10.36	5.72
272	GAP-ZH-010	18.90146	48.62852	Fluvi-eutric Gleysol	A	6.41	5.70	0.00	7.54	1.33
273	GAP-ZH-023	18.82506	48.55904	Fluvi-eutric Gleysol	A	5.43	4.84	0.00	21.03	5.86
274	GAP-ZH-043	18.90715	48.71296	Eutric Cambisol	A	4.64	3.81	0.00	9.73	12.64
275	GAP-ZH-055	18.92743	48.47824	Eutric Cambisol	A	4.97	4.51	0.00	10.25	3.67
276	GAP-ZH-056	18.91158	48.46427	Eutric Cambisol	A	4.73	3.68	0.00	11.29	7.10
277	GAP-ZH-057	18.92397	48.44751	Eutric Cambisol	A	6.97	6.18	0.00	9.65	2.90
278	GAP-ZH-058	18.92227	48.43418	Eutric Cambisol	A	6.04	4.78	0.00	10.65	2.90
279	GAP-ZH-060	18.92601	48.40143	Stagno-gleyic Cambisol	A	5.04	3.97	0.00	14.83	6.60
280	GAP-ZH-062	18.93446	48.34737	Fluvi-eutric Gleysol	A	4.25	3.71	0.00	7.40	13.22
281	GAP-ZH-063	18.89795	48.48131	Eutric Cambisol	A	5.63	4.90	0.00	8.94	5.52
282	GAP-ZH-064	18.88446	48.47181	Eutric Cambisol	A	4.61	3.92	0.00	7.64	4.26
283	GAP-ZH-065	18.87443	48.44958	Stagno-gleyic Cambisol	A	5.57	4.54	0.00	17.55	8.95
284	GAP-ZH-067	18.89269	48.42031	Eutric Cambisol	A	4.91	3.71	0.00	10.65	4.59
285	GAP-ZH-077	18.80614	48.45968	Eutric Cambisol	A	4.98	3.80	0.00	11.84	6.60
286	GAP-ZH-083	18.68797	48.49716	Eutric Cambisol	A	5.24	4.23	0.00	15.49	7.10
287	GAP-ZV-001	18.92896	48.20346	Eutric Fluvisol	A	6.89	6.39	0.00	13.73	2.24
288	GAP-ZV-012	19.04678	48.54841	Stagno-gleyic Cambisol	A	5.34	4.77	0.00	15.53	3.34
289	GAP-ZV-059	19.37027	48.46886	Eutric Cambisol	A	6.48	5.70	0.00	37.43	7.13
290	GAP-ZV-060	19.33827	48.47655	Eutric Cambisol	A	5.48	4.39	0.00	5.43	5.59
291	GAP-ZV-076	19.46597	48.54837	Fluvi-eutric Gleysol	A	6.65	5.78	0.00	5.88	3.31
292	GAPE-LV-125	18.64730	48.12407	Haplic Chernozem	A	6.40	5.10	0.08	32.78	3.23
293	GAPE-NZ-041	18.65077	47.91864	Eutric Fluvisol	A	6.80	5.60	0.08	23.13	2.24
294	GAPE-NZ-053	18.05943	47.98128	Fluvi-mollic Gleysol	A	6.60	5.40	0.24	28.74	5.72
295	GAPE-PO-001	20.80548	49.20657	Gleyic Planosol	A	5.90	5.20	0.08	10.86	5.17
296	GAPE-PP-020	20.38348	49.15984	Eutric Cambisol	A	5.70	4.80	0.08	12.75	3.09
297	GAPE-PP-027	20.45173	49.11094	Eutric Cambisol	A	5.90	5.30	0.08	13.76	3.64
298	GAPE-PP-028	20.41164	49.08300	Eutric Cambisol	A	6.50	5.90	0.12	22.21	5.14
299	GAPE-PP-033	20.54016	49.09503	Ranker	A	6.00	5.10	0.08	6.20	6.69
300	GAPE-PP-040	20.19817	49.32511	Ranker	A	4.50	3.90	0.12	13.99	5.98
301	GAPE-PP-042	20.23750	49.33047	Ranker	A	4.70	3.80	0.08	9.10	6.86
302	GAPE-PP-050	20.20906	49.24375	Rendzina	A	4.30	3.20	0.20	3.80	12.96
303	GAPE-SL-002	20.58456	49.24889	Ranker	A	5.20	4.40	0.04	12.92	4.34
304	GAPE-SL-008	20.53436	49.36610	Ranker	A	5.40	4.00	0.04	15.69	5.19
305	GAPE-VK-029	19.36246	48.18135	Stagno-gleyic Cambisol	A	5.50	4.10	0.24	30.93	3.60
306	GAPE-VV-006	21.63497	48.98359	Dystric Planosol	A	6.60	5.20	0.12	29.79	1.74

Annex 2 Cation exchange capacity (cmol.kg^{-1}) of the A horizon of selected soil samples from 306 agricultural soils

No.	Sample	Soil unit FAO (1970)	Hor	pH/NH4OAc	CEC	Caex	Mgex	Kex	Naex	SBC
1	GAP-BB-014	Eutric Fluvisol	A	7.0	24.57	12.18	1.56	0.44	0.04	14.22
2	GAP-BB-015	Eutric Fluvisol	A	7.0	23.12	10.38	1.15	0.74	0.03	12.30
3	GAP-BB-017	Eutric Cambisol	A	7.0	20.22	14.37	6.09	0.48	0.09	21.04
4	GAP-BB-018	Eutric Fluvisol	A	7.0	23.12	14.47	3.45	1.05	0.02	18.99
5	GAP-BB-034	Eutric Cambisol	A	7.0	30.36	9.38	2.30	0.38	0.04	12.11
6	GAP-BB-046	Albo-gleyic Luvisol	A	7.0	27.46	14.37	2.30	0.33	0.03	17.03
7	GAP-BB-058	Eutric Cambisol	A	7.0	28.91	12.08	3.46	1.10	0.03	16.67
8	GAP-BB-062	Eutric Fluvisol	A	7.0	20.22	10.48	3.46	0.59	0.03	14.56
9	GAP-BB-063	Eutric Cambisol	A	7.0	20.22	8.38	2.30	0.13	0.08	10.89
10	GAP-BB-082	Albo-gleyic Luvisol	A	7.0	11.52	2.20	1.15	0.33	0.02	3.70
11	GAP-BB-093	Eutric Cambisol	A	7.0	17.32	6.88	2.80	0.13	0.03	9.84
12	GAP-BB-103	Eutric Cambisol	A	7.0	14.42	2.89	1.15	0.13	0.03	4.20
13	GAP-BB-113	Eutric Cambisol	A	7.0	17.32	3.79	0.99	0.79	0.02	5.59
14	GAP-BB-120	Stagno-gleyic Cambisol	A	7.0	11.52	3.49	1.15	0.64	0.03	5.31
15	GAP-BB-125	Dystric Cambisol	A	7.0	21.67	16.37	3.78	0.18	0.02	20.35
16	GAP-BB-126	Fluvi-eutric Gleysol	A	8.2	26.81	21.96	1.56	0.36	0.05	23.93
17	GAP-BB-127	Eutric Cambisol	A	8.2	13.77	5.49	1.32	1.07	0.04	7.92
18	GAP-BB-128	Calcaric Cambisol	A	8.2	24.64	13.97	7.74	0.49	0.02	22.22
19	GAP-BH-027	Haplic Chernozem	A	8.2	22.46	11.58	3.46	0.51	0.07	15.62
20	GAP-BH-038	Orthic Luvisol	A	7.0	14.49	7.09	2.47	0.59	0.03	10.18
21	GAP-BH-055	Stagno-gleyic Cambisol	A	8.2	22.46	11.58	4.11	0.21	0.20	16.10
22	GAP-BH-056	Dystric Regosol	A	7.0	11.59	4.89	0.82	0.23	0.06	6.00
23	GAP-BH-058	Ranker	A	7.0	8.70	4.14	0.82	0.38	0.06	5.40
24	GAP-BH-073	Fluvi-mollic Gleysol	A	7.0	22.46	14.57	2.47	0.33	0.06	17.43
25	GAP-BH-113	Eutric Fluvisol	A	7.0	15.94	4.99	0.99	0.92	0.04	6.94
26	GAP-BJ-011	Stagno-gleyic Cambisol	A	7.0	17.39	7.68	2.14	0.28	0.06	10.16
27	GAP-BJ-012	Ranker	A	7.0	11.59	2.29	0.90	0.49	0.02	3.69
28	GAP-BJ-015	Stagno-gleyic Cambisol	A	7.0	23.91	11.48	3.46	0.59	< 0.01	15.53
29	GAP-BJ-017	Ranker	A	7.0	15.94	3.39	0.99	0.23	0.02	4.63
30	GAP-BJ-019	Calcaric Cambisol	A	7.0	18.84	10.18	2.47	0.43	0.27	13.35
31	GAP-BJ-035	Stagno-gleyic Cambisol	A	7.0	14.49	2.99	2.06	0.13	0.05	5.23
32	GAP-BJ-039	Stagno-gleyic Cambisol	A	7.0	14.49	5.69	1.81	0.33	0.03	7.86
33	GAP-BJ-044	Eutric Cambisol	A	7.0	15.94	6.19	1.65	0.51	0.06	8.41
34	GAP-BJ-046	Eutric Cambisol	A	7.0	17.39	7.19	3.46	0.54	0.09	11.28
35	GAP-BJ-051	Stagno-gleyic Cambisol	A	7.0	17.39	8.38	2.47	0.33	0.16	11.35
36	GAP-BJ-056	Stagno-gleyic Cambisol	A	7.0	13.04	3.39	0.99	0.13	0.03	4.53
37	GAP-BJ-060	Stagno-gleyic Cambisol	A	7.0	14.49	5.39	1.97	0.23	0.03	7.62
38	GAP-CA-001	Eutric Cambisol	A	7.0	17.39	4.09	0.82	0.18	0.05	5.14
39	GAP-CA-008	Stagno-gleyic Cambisol	A	8.2	23.91	12.98	2.47	0.61	0.04	16.10
40	GAP-CA-011	Stagno-gleyic Cambisol	A	7.0	20.29	10.18	3.29	0.31	0.03	13.80
41	GAP-CA-013	Eutric Cambisol	A	7.0	17.39	3.39	0.66	0.36	< 0.01	4.41
42	GAP-CA-014	Stagno-gleyic Cambisol	A	7.0	17.39	6.69	1.65	0.23	0.04	8.61
43	GAP-CA-015	Eutric Cambisol	A	7.0	11.59	2.39	0.82	0.13	0.05	3.39
44	GAP-CA-016	Eutric Fluvisol	A	7.0	12.32	2.99	0.99	0.13	< 0.01	4.11
45	GAP-CA-018	Stagno-gleyic Cambisol	A	7.0	12.32	4.29	1.15	1.30	0.10	6.84
46	GAP-CA-022	Stagno-gleyic Cambisol	A	7.0	19.42	6.79	1.48	0.21	0.05	8.53
47	GAP-CA-023	Fluvi-eutric Gleysol	A	7.0	13.62	6.79	1.48	0.15	< 0.01	8.42
48	GAP-CA-024	Eutric Cambisol	A	7.0	21.59	6.69	1.65	0.36	0.02	8.72
49	GAP-CA-034	Stagno-gleyic Cambisol	A	7.0	20.87	8.58	1.97	0.21	< 0.01	10.76
50	GAP-CA-035	Eutric Cambisol	A	7.0	16.52	6.19	1.40	0.10	< 0.01	7.69
51	GAP-CA-051	Stagno-gleyic Cambisol	A	7.0	15.07	5.69	1.15	0.21	< 0.01	7.05
52	GAP-HN-001	Ranker	A	7.0	16.52	8.28	2.63	0.15	0.04	11.10
53	GAP-HN-008	Calcaric Cambisol	A	7.0	15.80	8.58	1.97	0.31	< 0.01	10.86
54	GAP-HN-013	Stagno-gleyic Cambisol	A	7.0	9.27	3.79	0.82	0.15	0.01	4.77
55	GAP-HN-016	Stagno-gleyic Cambisol	A	7.0	9.27	4.39	0.99	0.10	< 0.01	5.48
56	GAP-HN-029	Eutric Cambisol	A	7.0	15.07	3.19	0.66	0.26	0.04	4.15
57	GAP-HN-030	Eutric Cambisol	A	7.0	20.87	7.38	1.48	0.41	0.02	9.29
58	GAP-HN-031	Eutric Cambisol	A	7.0	16.52	7.58	1.32	0.21	0.04	9.15
59	GAP-HN-033	Eutric Cambisol	A	7.0	20.14	2.99	0.99	0.36	0.03	4.37
60	GAP-HN-035	Eutric Cambisol	A	7.0	16.52	6.29	1.81	0.31	0.01	8.42

No.	Sample	Soil unit FAO (1970)	Hor	pH/NH4OAc	CEC	Caex	Mgex	Kex	Naex	SBC
61	GAP-HN-044	Eutric Cambisol	A	7.0	17.97	9.48	1.15	0.10	0.07	10.80
62	GAP-HN-048	Eutric Fluvisol	A	7.0	20.87	13.47	2.30	0.36	0.06	16.19
63	GAP-HN-050	Eutric Fluvisol	A	7.0	12.17	7.19	1.65	0.21	0.06	9.11
64	GAP-HN-054	Dystric Planosol	A	7.0	19.42	10.98	2.47	0.67	0.05	14.17
65	GAP-HN-055	Stagno-gleyic Cambisol	A	7.0	13.62	9.58	1.48	0.41	0.02	11.49
66	GAP-HN-059	Stagno-gleyic Cambisol	A	8.2	26.81	14.97	2.47	0.77	0.03	18.24
67	GAP-HN-063	Dystric Planosol	A	7.0	22.32	9.98	3.13	0.21	0.04	13.36
68	GAP-HN-064	Calcaric Cambisol	A	8.2	23.91	13.97	1.65	0.67	0.02	16.31
69	GAP-HN-065	Eutric Cambisol	A	8.2	16.67	7.59	0.66	0.92	0.03	9.20
70	GAP-HN-070	Stagno-gleyic Cambisol	A	7.0	19.42	9.98	1.81	0.51	< 0.01	12.30
71	GAP-HN-072	Eutric Cambisol	A	8.2	25.36	13.97	1.48	0.46	0.01	15.92
72	GAP-HN-078	Eutric Cambisol	A	7.0	19.42	9.98	1.48	0.21	0.09	11.76
73	GAP-HN-079	Eutric Cambisol	A	7.0	23.77	12.97	1.65	0.10	0.12	14.84
74	GAP-HN-080	Eutric Cambisol	A	7.0	16.52	8.38	1.81	0.15	0.04	10.38
75	GAP-HN-085	Stagno-gleyic Cambisol	A	8.2	35.51	18.96	3.78	0.31	0.03	23.08
76	GAP-HN-086	Eutric Cambisol	A	7.0	19.42	7.48	1.48	0.41	0.06	9.43
77	GAP-HN-087	Eutric Cambisol	A	7.0	28.12	15.97	2.14	0.15	0.10	18.36
78	GAP-HN-088	Eutric Cambisol	A	8.2	21.01	8.18	0.99	1.18	< 0.01	10.35
79	GAP-HN-089	Stagno-gleyic Cambisol	A	7.0	20.87	10.98	1.81	0.31	0.09	13.19
80	GAP-HN-096	Eutric Cambisol	A	7.0	19.42	9.58	1.97	0.18	0.08	11.81
81	GAP-HN-097	Stagno-gleyic Cambisol	A	7.0	16.52	7.88	1.15	0.26	0.05	9.34
82	GAP-HN-098	Eutric Cambisol	A	7.0	20.87	7.28	2.80	0.21	0.04	10.33
83	GAP-HN-099	Eutric Cambisol	A	7.0	17.97	9.68	1.97	0.10	0.11	11.86
84	GAP-HN-102	Eutric Cambisol	A	7.0	15.07	6.89	1.15	0.10	0.03	8.17
85	GAP-HN-103	Eutric Cambisol	A	7.0	16.52	9.98	0.66	0.15	0.04	10.83
86	GAP-HN-107	Stagno-gleyic Cambisol	A	7.0	17.97	10.98	2.80	0.20	0.05	14.03
87	GAP-HN-136	Eutric Fluvisol	A	7.0	15.07	9.28	1.65	0.41	0.09	11.43
88	GAP-HN-138	Stagno-gleyic Cambisol	A	7.0	16.52	9.98	2.80	0.15	0.09	13.02
89	GAP-HN-141	Stagno-gleyic Cambisol	A	7.0	17.97	10.98	2.63	0.26	0.10	13.97
90	GAP-HN-144	Calcaric Regosol	A	7.0	31.74	21.96	2.80	0.41	0.10	25.27
91	GAP-HN-145	Dystric Planosol	A	7.0	16.52	9.38	2.14	0.36	0.05	11.93
92	GAP-KE-022	Stagno-gleyic Cambisol	A	7.0	15.94	8.98	2.14	0.51	0.06	11.69
93	GAP-KE-032	Ranker	A	7.0	14.49	7.98	1.15	0.56	0.03	9.72
94	GAP-KE-046	Eutric Fluvisol	A	7.0	17.39	10.98	2.14	0.46	0.03	13.61
95	GAP-KE-065	Fluvi-eutric Gleysol	A	7.0	15.94	8.98	2.30	1.23	0.07	12.58
96	GAP-KE-071	Eutric Cambisol	A	7.0	11.59	6.99	1.65	0.61	0.01	9.26
97	GAP-KE-085	Eutric Gleysol	A	7.0	15.94	9.98	2.80	0.36	0.13	13.27
98	GAP-KE-099	Dystric Planosol	A	7.0	14.49	8.98	1.48	1.18	0.05	11.69
99	GAP-KE-109	Rendzina	A	7.0	34.78	20.96	1.81	0.20	0.06	23.03
100	GAP-KE-110	Fluvi-eutric Gleysol	A	7.0	18.84	14.97	3.79	0.41	0.15	19.32
101	GAP-KE-115	Rendzina	A	8.2	52.17	27.94	2.14	0.41	0.13	30.62
102	GAP-KE-131	Dystric Planosol	A	7.0	26.09	15.97	5.93	0.51	0.23	22.64
103	GAP-LC-005	Eutric Cambisol	A	7.0	18.84	12.97	2.96	0.77	0.03	16.73
104	GAP-LC-036	Ranker	A	7.0	13.77	8.98	1.32	0.15	0.03	10.48
105	GAP-LC-054	Eutric Cambisol	A	7.0	18.84	7.98	0.66	0.20	0.08	8.92
106	GAP-LC-055	Cambic Arenosol	A	7.0	13.04	5.99	1.48	0.72	0.03	8.22
107	GAP-LM-001	Calcaric Cambisol	A	8.2	28.26	18.96	2.80	0.67	0.03	22.46
108	GAP-LM-004	Dystric Cambisol	A	7.0	17.39	7.98	1.32	0.10	0.04	9.44
109	GAP-LM-008	Eutric Cambisol	A	8.2	24.64	9.98	3.29	0.08	0.02	13.37
110	GAP-LM-009	Eutric Cambisol	A	7.0	23.19	14.97	2.63	0.15	0.05	17.80
111	GAP-LM-021	Stagno-gleyic Cambisol	A	7.0	21.74	11.98	3.29	0.41	0.05	15.73
112	GAP-LM-033	Eutric Cambisol	A	7.0	20.29	10.98	3.13	0.41	0.03	14.55
113	GAP-LM-050	Eutric Cambisol	A	7.0	28.99	16.97	4.61	0.43	0.06	22.07
114	GAP-LM-058	Stagno-gleyic Cambisol	A	7.0	23.19	13.97	2.14	0.41	0.06	16.58
115	GAP-MI-033	Fluvi-eutric Gleysol	A	7.0	31.88	15.47	8.07	0.56	0.29	24.39
116	GAP-MI-044	Fluvi-eutric Gleysol	A	7.0	11.59	6.99	1.48	0.61	0.04	9.12
117	GAP-MI-047	Eutric Gleysol	A	7.0	30.44	12.97	5.27	0.41	0.17	18.82
118	GAP-MI-050	Eutric Cambisol	A	7.0	14.49	6.99	1.48	0.92	0.02	9.41
119	GAP-MI-053	Eutric Cambisol	A	7.0	14.49	7.98	1.48	0.92	0.03	10.41
120	GAP-MI-064	Stagno-gleyic Cambisol	A	7.0	15.94	9.98	2.47	0.46	0.03	12.94
121	GAP-MI-087	Ranker	A	7.0	17.39	10.98	2.14	0.36	0.03	13.51
122	GAP-MI-094	Fluvi-eutric Gleysol	A	7.0	23.19	15.97	3.79	1.28	0.55	21.59
123	GAP-MI-113	Fluvi-eutric Gleysol	A	7.0	15.22	9.98	1.65	0.41	0.03	12.07
124	GAP-MI-114	Eutric Fluvisol	A	7.0	14.49	9.48	1.97	0.36	0.04	11.85
125	GAP-MI-115	Eutric Gleysol	A	8.2	30.43	10.98	5.76	1.07	0.17	17.98
126	GAP-MI-116	Fluvi-eutric Gleysol	A	7.0	28.99	14.97	3.79	0.87	0.04	19.67

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127	GAP-MI-120	Fluvi-eutric Gleysol	A	7.0	21.74	12.97	4.11	0.41	0.11	17.60
128	GAP-MI-121	Eutric Gleysol	A	7.0	23.19	13.97	6.09	0.49	0.15	20.70
129	GAP-MI-122	Eutric Gleysol	A	7.0	28.99	15.97	4.94	0.51	0.11	21.53
130	GAP-NZ-052	Luvi-haplic Chernozem	A	7.0	23.19	11.98	3.95	1.79	0.10	17.82
131	GAP-NZ-059	Haplic Chernozem	A	7.0	17.39	13.97	4.61	3.17	0.10	21.85
132	GAP-PO-004	Stagno-gleyic Cambisol	A	7.0	13.77	8.98	1.97	0.46	0.03	11.44
133	GAP-PO-010	Stagno-gleyic Cambisol	A	7.0	29.71	21.96	8.23	0.77	0.05	31.01
134	GAP-PO-015	Ranker	A	7.0	17.39	12.97	1.97	0.61	0.06	15.61
135	GAP-PO-033	Dystric Planosol	A	7.0	13.04	8.98	1.65	0.66	0.05	11.34
136	GAP-PO-040	Ranker	A	7.0	18.84	12.97	2.80	0.36	0.05	16.18
137	GAP-PO-047	Ranker	A	7.0	20.29	12.97	2.96	0.51	0.03	16.47
138	GAP-PO-049	Stagno-gleyic Cambisol	A	7.0	18.84	12.97	1.65	1.07	0.05	15.74
139	GAP-PO-050	Stagno-gleyic Cambisol	A	7.0	17.39	9.98	1.65	0.54	0.02	12.19
140	GAP-PO-055	Ranker	A	7.0	18.84	10.98	2.47	0.49	0.01	13.95
141	GAP-PO-057	Stagno-gleyic Cambisol	A	7.0	14.49	7.98	2.80	0.54	0.03	11.35
142	GAP-PO-060	Stagno-gleyic Cambisol	A	7.0	18.84	12.97	2.63	0.43	0.03	16.06
143	GAP-PO-100	Ranker	A	7.0	15.94	5.99	1.32	0.33	0.04	7.68
144	GAP-PO-101	Stagno-gleyic Cambisol	A	7.0	15.94	6.99	0.99	0.49	0.03	8.50
145	GAP-PO-104	Ranker	A	7.0	14.49	10.98	2.14	0.18	0.03	13.33
146	GAP-PO-105	Eutric Cambisol	A	7.0	14.49	8.98	2.63	0.28	0.03	11.92
147	GAP-PO-110	Dystric Regosol	A	7.0	10.15	6.99	1.15	0.28	0.03	8.45
148	GAP-PO-117	Ranker	A	7.0	13.04	7.98	1.32	0.23	0.03	9.56
149	GAP-PO-121	Eutric Cambisol	A	7.0	15.94	9.98	1.98	0.54	0.07	12.57
150	GAP-PP-005	Ranker	A	7.0	18.84	6.99	1.48	0.49	0.05	9.01
151	GAP-PP-006	Ranker	A	7.0	17.39	9.98	1.98	0.26	0.07	12.29
152	GAP-PX-012	Fluvi-gleyic Phaeozem	A	8.2	29.71	17.96	1.48	0.87	0.01	20.32
153	GAP-PX-019	Fluvi-gleyic Phaeozem	A	7.0	17.39	11.98	2.30	0.41	0.07	14.76
154	GAP-PX-026	Fluvi-gleyic Phaeozem	A	8.2	17.39	4.99	2.47	1.56	0.05	9.07
155	GAP-PX-038	Stagno-gleyic Cambisol	A	7.0	23.19	11.98	1.32	0.33	0.03	13.66
156	GAP-RS-008	Rendzina	A	7.0	23.19	11.98	4.94	0.69	0.09	17.70
157	GAP-RS-062	Eutric Fluvisol	A	8.2	20.29	7.98	2.47	0.20	0.05	10.70
158	GAP-RS-090	Albo-gleyic Luvisol	A	7.0	24.64	15.97	5.10	0.69	0.06	21.82
159	GAP-RS-101	Ranker	A	7.0	13.04	3.99	0.49	0.13	< 0.01	4.61
160	GAP-RV-001	Fluvi-mollic Gleysol	A	7.0	28.99	28.94	4.94	0.33	0.12	34.33
161	GAP-RV-025	Stagno-gleyic Cambisol	A	8.2	18.84	3.99	0.99	1.23	< 0.01	6.21
162	GAP-RV-026	Eutric Fluvisol	A	7.0	13.04	6.99	0.82	0.79	0.02	8.62
163	GAP-RV-028	Eutric Cambisol	A	7.0	15.94	8.98	0.66	1.66	0.03	11.33
164	GAP-RV-037	Eutric Cambisol	A	8.2	27.54	9.48	5.27	0.87	0.08	15.70
165	GAP-RV-038	Calcaric Lithosol	A	7.0	29.71	22.95	1.32	0.49	0.04	24.80
166	GAP-RV-040	Calcaric Lithosol	A	7.0	34.78	26.95	1.48	0.59	0.05	29.07
167	GAP-RV-045	Eutric Cambisol	A	7.0	11.59	4.99	1.15	0.18	0.02	6.34
168	GAP-RV-047	Eutric Cambisol	A	7.0	20.29	5.99	1.32	0.13	0.07	7.51
169	GAP-RV-051	Eutric Cambisol	A	7.0	17.39	13.97	2.80	0.13	0.02	16.92
170	GAP-RV-058	Ranker	A	8.2	28.26	11.98	2.63	4.81	< 0.01	19.42
171	GAP-RV-062	Ranker	A	8.2	12.32	7.98	0.99	0.15	< 0.01	9.12
172	GAP-RV-075	Eutric Cambisol	A	7.0	21.74	5.99	1.65	0.54	0.03	8.21
173	GAP-RV-076	Eutric Cambisol	A	7.0	5.94	12.97	1.65	1.76	0.03	16.41
174	GAP-RV-077	Dystric Lithosol	A	7.0	17.39	7.98	3.13	0.28	0.02	11.41
175	GAP-RV-078	Eutric Cambisol	A	8.2	16.67	8.98	1.65	0.56	0.04	11.23
176	GAP-RV-086	Rendzina	A	7.0	23.19	14.97	1.32	0.43	0.02	16.74
177	GAP-RV-104	Ranker	A	8.2	10.87	6.99	0.66	0.61	< 0.01	8.26
178	GAP-RV-122	Dystric Lithosol	A	7.0	42.03	28.94	2.96	1.30	0.04	33.24
179	GAP-RV-123	Dystric Lithosol	A	7.0	36.23	19.96	2.30	0.72	0.05	23.03
180	GAP-RV-132	Ranker	A	7.0	11.59	3.99	1.48	0.20	0.03	5.70
181	GAP-RV-133	Rendzina	A	7.0	32.61	22.95	1.48	0.41	0.02	24.86
182	GAP-SE-001	Orthic Luvisol	A	7.0	21.74	13.97	2.96	0.72	0.06	17.71
183	GAP-SE-010	Fluvi-eutric Gleysol	A	7.0	17.39	10.98	2.14	0.46	0.06	13.64
184	GAP-SE-028	Orthic Luvisol	A	7.0	21.74	13.97	4.44	0.51	0.09	19.01
185	GAP-SE-036	Eutric Cambisol	A	8.2	25.36	13.97	2.80	2.30	0.21	19.28
186	GAP-SE-060	Eutric Fluvisol	A	7.0	4.35	2.00	0.49	0.41	0.02	2.92
187	GAP-SE-066	Stagno-gleyic Cambisol	A	7.0	20.29	11.98	1.65	0.82	0.03	14.48
188	GAP-SE-068	Fluvi-gleyic Phaeozem	A	8.2	41.30	21.96	4.28	1.07	0.10	27.41
189	GAP-SE-069	Stagno-gleyic Cambisol	A	7.0	17.39	8.98	1.48	0.46	0.03	10.95
190	GAP-SE-071	Eutric Cambisol	A	7.0	24.64	13.97	1.81	1.18	0.06	17.02
191	GAP-SE-081	Fluvi-gleyic Phaeozem	A	8.2	16.67	14.97	1.65	0.67	0.05	17.31
192	GAP-SE-094	Eutric Cambisol	A	8.2	15.22	8.98	2.96	0.77	< 0.01	12.71

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193	GAP-SE-095	Stagno-gleyic Cambisol	A	8.2	18.12	9.98	4.28	0.51	0.05	14.82
194	GAP-SE-120	Stagno-gleyic Cambisol	A	7.0	21.74	12.97	1.32	1.07	0.01	15.37
195	GAP-SK-001	Stagno-gleyic Cambisol	A	7.0	13.04	7.98	1.32	0.20	0.06	9.56
196	GAP-SK-006	Stagno-gleyic Cambisol	A	7.0	20.29	11.98	1.81	0.26	0.04	14.09
197	GAP-SK-027	Stagno-gleyic Cambisol	A	7.0	18.84	6.99	0.99	0.66	0.02	8.66
198	GAP-SK-031	Stagno-gleyic Cambisol	A	7.0	21.74	13.97	3.13	0.56	0.17	17.83
199	GAP-SK-039	Eutric Cambisol	A	8.2	15.22	10.98	2.47	0.92	0.04	14.41
200	GAP-SK-054	Luvic Cambisol	A	7.0	23.19	15.97	2.47	0.51	0.04	18.99
201	GAP-SK-056	Stagno-gleyic Cambisol	A	7.0	17.39	8.98	1.98	0.46	0.03	11.45
202	GAP-SK-057	Stagno-gleyic Cambisol	A	7.0	15.94	8.48	2.14	0.41	0.04	11.07
203	GAP-SK-058	Stagno-gleyic Cambisol	A	7.0	26.09	11.98	2.47	0.72	0.03	15.20
204	GAP-SK-060	Stagno-gleyic Cambisol	A	7.0	26.09	13.97	2.30	0.72	0.03	17.02
205	GAP-SK-065	Luvic Cambisol	A	7.0	20.29	9.98	1.65	0.46	0.03	12.12
206	GAP-SK-067	Luvic Cambisol	A	7.0	24.64	13.97	2.80	0.46	0.03	17.26
207	GAP-SK-081	Stagno-gleyic Cambisol	A	7.0	13.04	6.99	1.81	0.26	0.03	9.09
208	GAP-SK-082	Stagno-gleyic Cambisol	A	7.0	14.49	6.99	1.81	0.20	0.03	9.03
209	GAP-SL-004	Stagno-gleyic Cambisol	A	7.0	15.94	8.98	1.32	0.26	0.03	10.59
210	GAP-SN-001	Stagno-gleyic Cambisol	A	8.2	15.22	6.99	0.66	1.07	0.01	8.73
211	GAP-SN-002	Ranker	A	7.0	13.77	2.99	0.49	0.18	0.03	3.69
212	GAP-SN-008	Ranker	A	7.0	13.04	3.99	2.14	0.20	0.03	6.36
213	GAP-SN-012	Dystric Regosol	A	7.0	17.39	5.99	0.66	0.15	< 0.01	6.80
214	GAP-SN-014	Eutric Cambisol	A	7.0	14.49	7.98	1.15	0.66	< 0.01	9.79
215	GAP-SN-015	Eutric Cambisol	A	7.0	14.49	7.98	1.65	0.20	0.07	9.90
216	GAP-SN-017	Dystric Lithosol	A	7.0	13.04	4.99	1.15	0.36	0.03	6.53
217	GAP-SN-019	Eutric Cambisol	A	7.0	11.59	6.99	1.32	0.15	0.03	8.49
218	GAP-SN-022	Ranker	A	8.2	16.67	10.98	2.14	0.31	0.03	13.46
219	GAP-SN-044	Ranker	A	7.0	21.74	4.99	1.15	0.56	0.04	6.74
220	GAP-SN-045	Calcaric Cambisol	A	7.0	15.94	10.98	1.98	0.26	0.07	13.29
221	GAP-SN-046	Eutric Cambisol	A	8.2	10.87	6.99	1.15	0.56	0.02	8.82
222	GAP-SN-048	Ranker	A	7.0	14.49	6.99	1.48	0.20	0.03	8.70
223	GAP-SN-050	Eutric Cambisol	A	7.0	11.59	2.00	0.33	0.15	0.04	2.52
224	GAP-SN-051	Ranker	A	7.0	11.59	5.99	0.82	0.31	0.03	7.15
225	GAP-SN-055	Ranker	A	7.0	11.59	7.98	1.81	0.43	0.02	10.24
226	GAP-TN-001	Eutric Fluvisol	A	7.0	16.67	4.99	1.15	0.66	0.03	6.83
227	GAP-TN-004	Rendzina	A	8.2	22.46	13.97	0.99	0.41	0.04	15.41
228	GAP-TN-010	Rendzina	A	7.0	14.49	9.98	1.81	1.59	0.02	13.40
229	GAP-TN-015	Orthic Luvisol	A	7.0	20.29	10.98	3.46	0.41	0.07	14.92
230	GAP-TN-067	Eutric Cambisol	A	7.0	15.94	7.98	2.63	0.49	0.05	11.15
231	GAP-TV-012	Fluvi-eutric Gleysol	A	7.0	28.99	17.96	5.60	0.31	0.17	24.04
232	GAP-TV-017	Eutric Gleysol	A	7.0	27.54	12.97	4.44	0.41	0.07	17.89
233	GAP-TV-020	Dystric Regosol	A	7.0	7.25	6.99	0.99	0.61	0.02	8.61
234	GAP-TV-027	Fluvi-eutric Gleysol	A	7.0	23.19	12.97	4.77	0.56	0.13	18.43
235	GAP-TV-028	Fluvi-eutric Gleysol	A	7.0	24.64	17.96	7.90	0.31	0.53	26.70
236	GAP-TV-029	Eutric Gleysol	A	7.0	43.48	29.94	10.53	0.61	0.37	41.45
237	GAP-TV-032	Fluvi-eutric Gleysol	A	7.0	18.84	10.98	3.29	0.51	0.09	14.87
238	GAP-TV-039	Eutric Gleysol	A	7.0	33.33	16.97	7.24	0.49	0.20	24.90
239	GAP-TV-043	Fluvi-eutric Gleysol	A	7.0	11.59	7.98	2.14	0.26	0.05	10.43
240	GAP-TV-055	Eutric Gleysol	A	7.0	37.68	17.96	7.24	0.46	0.27	25.93
241	GAP-TV-064	Dystric Regosol	A	7.0	5.80	5.99	0.66	0.56	0.01	7.22
242	GAP-TV-086	Ranker	A	7.0	10.15	8.98	1.32	0.61	0.02	10.93
243	GAP-TV-113	Eutric Gleysol	A	7.0	27.54	14.97	7.24	0.46	0.15	22.82
244	GAP-TV-115	Fluvi-eutric Gleysol	A	7.0	17.39	9.98	2.47	0.97	0.01	13.43
245	GAP-TV-116	Fluvi-eutric Gleysol	A	7.0	27.54	18.96	8.40	0.56	0.40	28.32
246	GAP-TV-122	Eutric Gleysol	A	7.0	46.38	27.94	8.89	0.72	0.16	37.71
247	GAP-TV-123	Eutric Gleysol	A	7.0	36.23	17.96	7.08	0.64	0.17	25.85
248	GAP-TV-130	Eutric Gleysol	A	8.2	35.51	17.96	5.60	0.87	0.27	24.70
249	GAP-TV-133	Eutric Gleysol	A	7.0	33.33	17.96	6.26	0.61	0.21	25.04
250	GAP-TV-141	Albo-gleyic Luvisol	A	7.0	20.29	13.47	3.79	0.61	0.13	18.00
251	GAP-VK-180	Eutric Cambisol	A	7.0	18.84	9.98	2.30	0.79	0.03	13.10
252	GAP-VV-021	Ranker	A	8.2	19.57	18.96	1.48	0.41	0.03	20.88
253	GAP-VV-026	Rendzina	A	8.2	25.36	22.95	1.81	0.71	0.08	25.55
254	GAP-VV-029	Ranker	A	8.2	15.22	10.98	2.96	0.77	0.04	14.75
255	GAP-VV-032	Ranker	A	7.0	17.39	11.98	5.43	0.31	0.07	17.79
256	GAP-VV-042	Stagno-gleyic Cambisol	A	7.0	14.49	7.98	1.65	0.33	0.07	10.03
257	GAP-VV-056	Eutric Cambisol	A	7.0	14.49	7.98	1.81	0.36	0.03	10.18
258	GAP-ZA-006	Stagno-gleyic Cambisol	A	7.0	23.19	7.48	2.63	0.41	0.04	10.56

No.	Sample	Soil unit FAO (1970)	Hor	pH/NH4OAc	CEC	Caex	Mgex	Kex	Naex	SBC
259	GAP-ZA-009	Stagno-gleyic Cambisol	A	7.0	20.29	10.98	1.81	0.20	0.04	13.30
260	GAP-ZA-011	Stagno-gleyic Cambisol	A	7.0	17.39	6.99	1.48	0.31	0.02	8.80
261	GAP-ZA-015	Stagno-gleyic Cambisol	A	7.0	20.29	8.98	2.30	0.31	0.02	11.61
262	GAP-ZA-019	Stagno-gleyic Cambisol	A	7.0	15.94	9.98	1.32	0.66	0.03	11.99
263	GAP-ZA-023	Stagno-gleyic Cambisol	A	8.2	28.26	17.96	0.99	0.67	0.03	19.65
264	GAP-ZA-024	Calcaric Cambisol	A	8.2	26.81	18.96	1.40	0.49	< 0.01	20.85
265	GAP-ZA-025	Stagno-gleyic Cambisol	A	7.0	14.49	10.48	1.98	0.51	0.05	13.02
266	GAP-ZA-029	Stagno-gleyic Cambisol	A	7.0	24.64	13.97	2.14	0.74	0.02	16.87
267	GAP-ZA-030	Dystric Cambisol	A	7.0	14.49	5.99	1.15	0.46	0.03	7.63
268	GAP-ZA-031	Dystric Cambisol	A	7.0	18.84	9.48	1.81	0.46	0.04	11.79
269	GAP-ZA-034	Stagno-gleyic Cambisol	A	7.0	15.94	6.49	1.65	0.38	0.04	8.56
270	GAP-ZA-054	Dystric Planosol	A	8.2	26.81	11.98	3.29	0.97	0.07	16.31
271	GAP-ZH-003A	Luvic Cambisol	A	7.0	20.29	10.98	3.54	0.61	0.04	15.17
272	GAP-ZH-010	Fluvi-eutric Gleysol	A	7.0	13.04	7.98	3.95	0.82	0.04	12.79
273	GAP-ZH-023	Fluvi-eutric Gleysol	A	7.0	26.09	13.97	6.91	0.87	0.13	21.88
274	GAP-ZH-043	Eutric Cambisol	A	7.0	20.29	5.99	1.81	0.82	0.03	8.65
275	GAP-ZH-055	Eutric Cambisol	A	7.0	14.49	7.98	3.29	0.66	< 0.01	11.93
276	GAP-ZH-056	Eutric Cambisol	A	7.0	15.94	2.99	1.32	0.36	0.03	4.70
277	GAP-ZH-057	Eutric Cambisol	A	8.2	21.01	11.98	3.46	1.74	0.06	17.24
278	GAP-ZH-058	Eutric Cambisol	A	7.0	18.84	9.98	4.61	1.00	0.04	15.63
279	GAP-ZH-060	Stagno-gleyic Cambisol	A	7.0	24.64	10.98	3.29	1.07	0.05	15.39
280	GAP-ZH-062	Fluvi-eutric Gleysol	A	7.0	36.23	18.96	5.93	1.02	0.04	25.95
281	GAP-ZH-063	Eutric Cambisol	A	7.0	15.94	7.98	2.14	0.51	0.02	10.65
282	GAP-ZH-064	Eutric Cambisol	A	7.0	10.15	2.99	0.66	0.41	0.02	4.08
283	GAP-ZH-065	Stagno-gleyic Cambisol	A	7.0	27.54	9.98	2.96	0.66	0.01	13.61
284	GAP-ZH-067	Eutric Cambisol	A	7.0	20.29	7.98	1.56	0.61	0.17	10.32
285	GAP-ZH-077	Eutric Cambisol	A	7.0	18.84	4.99	2.14	0.41	0.04	7.58
286	GAP-ZH-083	Eutric Cambisol	A	7.0	28.99	13.97	5.43	0.46	0.33	20.19
287	GAP-ZV-001	Eutric Fluvisol	A	8.2	16.67	9.98	2.30	0.87	0.04	13.19
288	GAP-ZV-012	Stagno-gleyic Cambisol	A	7.0	17.39	7.98	1.32	1.43	0.03	10.76
289	GAP-ZV-059	Eutric Cambisol	A	7.0	21.74	13.97	2.14	0.77	0.03	16.91
290	GAP-ZV-060	Eutric Cambisol	A	7.0	26.09	12.97	4.77	0.61	0.08	18.43
291	GAP-ZV-076	Fluvi-eutric Gleysol	A	8.2	13.04	7.98	1.40	0.10	0.11	9.59
292	GAPE-LV-125	Haplic Chernozem	A	7.0	24.64	16.97	6.26	0.46	0.16	23.85
293	GAPE-NZ-041	Eutric Fluvisol	A	8.2	22.46	10.98	5.10	0.26	0.08	16.42
294	GAPE-NZ-053	Fluvi-mollic Gleysol	A	8.2	37.68	37.94	10.86	0.61	0.31	49.72
295	GAPE-PO-001	Gleyic Planosol	A	7.0	18.84	11.98	2.63	0.51	0.05	15.17
296	GAPE-PP-020	Eutric Cambisol	A	7.0	13.77	6.99	1.65	0.72	0.03	9.39
297	GAPE-PP-027	Eutric Cambisol	A	7.0	15.94	8.98	1.65	0.66	0.16	11.45
298	GAPE-PP-028	Eutric Cambisol	A	7.0	24.64	15.97	2.30	0.51	0.05	18.83
299	GAPE-PP-033	Ranker	A	7.0	14.49	8.98	1.15	0.31	0.02	10.46
300	GAPE-PP-040	Ranker	A	7.0	18.84	4.99	1.81	0.46	0.05	7.31
301	GAPE-PP-042	Ranker	A	7.0	21.01	8.98	1.56	0.36	0.03	10.93
302	GAPE-PP-050	Rendzina	A	7.0	14.49	0.50	0.49	0.41	0.02	1.42
303	GAPE-SL-002	Ranker	A	7.0	17.39	9.98	1.63	0.36	0.04	12.01
304	GAPE-SL-008	Ranker	A	7.0	17.39	8.98	1.98	0.46	0.03	11.45
305	GAPE-VK-029	Stagno-gleyic Cambisol	A	7.0	23.19	12.97	4.61	0.72	0.08	18.38
306	GAPE-VV-006	Dystric Planosol	A	8.2	28.26	13.97	4.28	0.56	0.04	18.85

Annex 3 Total content heavy metals (mg.kg^{-1}) of the A horizon of selected soil samples from 306 agricultural soils

No.	Sample	Soil unit FAO (1970)	Hor.	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1	GAP-BB-014	Eutric Fluvisol	A	435.0	0.60	57	23.0	0.270	18	69	178
2	GAP-BB-015	Eutric Fluvisol	A	33.8	0.80	77	25.0	0.120	22	54	147
3	GAP-BB-017	Eutric Cambisol	A	29.7	0.60	71	31.0	0.040	28	155	192
4	GAP-BB-018	Eutric Fluvisol	A	32.9	0.40	77	310.0	0.140	30	108	106
5	GAP-BB-034	Eutric Cambisol	A	12.4	0.50	167	39.0	0.130	107	61	145
6	GAP-BB-046	Albo-gleyic Luvisol	A	14.5	0.50	115	42.0	0.070	52	52	90
7	GAP-BB-058	Eutric Cambisol	A	4.7	0.20	93	55.0	0.050	10	26	56
8	GAP-BB-062	Eutric Fluvisol	A	19.6	0.20	43	299.0	0.030	21	92	55
9	GAP-BB-063	Eutric Cambisol	A	732.0	0.20	60	32.0	0.120	15	116	135
10	GAP-BB-082	Albo-gleyic Luvisol	A	15.0	0.20	115	24.0	0.030	42	23	60
11	GAP-BB-093	Eutric Cambisol	A	1.7	0.05	127	29.0	0.010	40	7	46
12	GAP-BB-103	Eutric Cambisol	A	22.5	0.40	48	40.0	0.140	14	48	60
13	GAP-BB-113	Eutric Cambisol	A	23.0	0.30	90	78.0	0.090	43	65	52
14	GAP-BB-120	Stagno-gleyic Cambisol	A	24.6	0.30	84	72.0	0.110	6	65	51
15	GAP-BB-125	Dystric Cambisol	A	16.0	0.50	77	39.0	0.030	55	36	71
16	GAP-BB-126	Fluvi-eutric Gleysol	A	14.0	0.40	103	96.0	0.590	50	83	71
17	GAP-BB-127	Eutric Cambisol	A	11.2	0.20	71	16.0	0.060	7	34	51
18	GAP-BB-128	Calcaric Cambisol	A	12.4	0.40	92	18.0	0.020	37	34	50
19	GAP-BH-027	Haplic Chernozem	A	6.9	0.90	89	18.0	0.040	30	25	55
20	GAP-BH-038	Orthic Luvisol	A	5.7	0.30	72	64.0	0.020	27	14	55
21	GAP-BH-055	Stagno-gleyic Cambisol	A	39.3	0.70	118	43.0	0.170	59	35	128
22	GAP-BH-056	Dystric Regosol	A	19.1	0.30	28	237.0	0.100	3	28	63
23	GAP-BH-058	Ranker	A	3.4	0.20	46	228.0	0.100	16	29	101
24	GAP-BH-073	Fluvi-mollic Gleysol	A	9.1	0.40	85	25.0	0.100	35	27	61
25	GAP-BH-113	Eutric Fluvisol	A	7.5	0.10	58	156.0	0.080	12	20	30
26	GAP-BJ-011	Stagno-gleyic Cambisol	A	4.4	0.30	187	17.0	0.220	58	22	72
27	GAP-BJ-012	Ranker	A	5.9	0.20	221	14.0	0.140	43	15	47
28	GAP-BJ-015	Stagno-gleyic Cambisol	A	5.6	0.20	187	33.0	0.080	45	18	73
29	GAP-BJ-017	Ranker	A	5.8	0.50	291	15.0	0.110	48	28	75
30	GAP-BJ-019	Calcaric Cambisol	A	9.2	0.30	176	37.0	0.080	80	15	71
31	GAP-BJ-035	Stagno-gleyic Cambisol	A	8.7	0.30	106	20.0	0.070	216	19	93
32	GAP-BJ-039	Stagno-gleyic Cambisol	A	5.8	0.30	221	33.0	0.050	41	16	63
33	GAP-BJ-044	Eutric Cambisol	A	5.3	0.50	204	13.0	0.140	40	23	62
34	GAP-BJ-046	Eutric Cambisol	A	5.7	0.50	203	23.0	0.120	58	20	75
35	GAP-BJ-051	Stagno-gleyic Cambisol	A	10.0	0.30	113	30.0	0.100	35	20	57
36	GAP-BJ-056	Stagno-gleyic Cambisol	A	10.5	0.30	109	24.0	0.100	41	18	78
37	GAP-BJ-060	Stagno-gleyic Cambisol	A	6.3	0.20	110	18.0	0.100	36	19	77
38	GAP-CA-001	Eutric Cambisol	A	5.3	0.20	141	23.0	0.100	41	17	71
39	GAP-CA-008	Stagno-gleyic Cambisol	A	6.6	0.40	90	43.0	0.060	46	23	99
40	GAP-CA-011	Stagno-gleyic Cambisol	A	8.6	0.70	167	24.0	0.080	50	37	108
41	GAP-CA-013	Eutric Cambisol	A	7.6	0.60	135	24.0	0.080	39	35	89
42	GAP-CA-014	Stagno-gleyic Cambisol	A	6.2	0.50	127	22.0	0.070	46	26	88
43	GAP-CA-015	Eutric Cambisol	A	5.0	0.90	66	14.0	0.080	20	38	89
44	GAP-CA-016	Eutric Fluvisol	A	6.4	0.60	109	24.0	0.060	41	31	96
45	GAP-CA-018	Stagno-gleyic Cambisol	A	4.5	0.90	93	11.0	0.080	21	21	49
46	GAP-CA-022	Stagno-gleyic Cambisol	A	6.7	0.40	148	29.0	0.110	63	23	86
47	GAP-CA-023	Fluvi-eutric Gleysol	A	5.3	0.40	125	22.0	0.080	49	21	75
48	GAP-CA-024	Eutric Cambisol	A	7.7	0.60	131	34.0	0.090	58	31	131
49	GAP-CA-034	Stagno-gleyic Cambisol	A	6.0	0.60	126	28.0	0.120	35	30	104
50	GAP-CA-035	Eutric Cambisol	A	6.4	0.50	106	28.0	0.080	36	31	106
51	GAP-CA-051	Stagno-gleyic Cambisol	A	6.0	0.30	118	13.0	0.070	39	19	65
52	GAP-HN-001	Ranker	A	6.0	0.20	107	21.0	0.060	38	23	82
53	GAP-HN-008	Calcaric Cambisol	A	5.1	0.30	108	32.0	0.140	43	21	101
54	GAP-HN-013	Stagno-gleyic Cambisol	A	5.8	0.05	101	27.0	0.080	55	16	57
55	GAP-HN-016	Stagno-gleyic Cambisol	A	6.2	0.10	106	24.0	0.100	40	12	54
56	GAP-HN-029	Eutric Cambisol	A	7.1	0.30	89	30.0	0.090	40	32	96
57	GAP-HN-030	Eutric Cambisol	A	7.0	0.40	98	36.0	0.130	39	28	101
58	GAP-HN-031	Eutric Cambisol	A	11.7	0.20	110	39.0	0.100	45	22	91
59	GAP-HN-033	Eutric Cambisol	A	10.2	0.05	107	33.0	0.120	38	20	89
60	GAP-HN-035	Eutric Cambisol	A	10.5	0.20	110	31.0	0.130	42	23	82
61	GAP-HN-044	Eutric Cambisol	A	4.1	0.05	108	48.0	0.070	48	16	97
62	GAP-HN-048	Eutric Fluvisol	A	8.9	0.40	95	34.0	0.080	45	30	100

No.	Sample	Soil unit FAO (1970)	Hor.	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
63	GAP-HN-050	Eutric Fluvisol	A	8.6	0.30	77	28.0	0.140	37	26	88
64	GAP-HN-054	Dystric Planosol	A	15.8	0.10	110	68.0	0.170	87	15	92
65	GAP-HN-055	Stagno-gleyic Cambisol	A	12.8	0.20	309	45.0	0.360	144	19	89
66	GAP-HN-059	Stagno-gleyic Cambisol	A	10.1	0.20	185	46.0	0.170	135	19	104
67	GAP-HN-063	Dystric Planosol	A	7.8	0.20	158	41.0	0.090	97	21	116
68	GAP-HN-064	Calcaric Cambisol	A	8.5	0.30	105	43.0	0.170	47	21	70
69	GAP-HN-065	Eutric Cambisol	A	4.0	0.10	211	35.0	0.090	125	11	86
70	GAP-HN-070	Stagno-gleyic Cambisol	A	21.0	0.40	134	64.0	0.170	90	20	106
71	GAP-HN-072	Eutric Cambisol	A	10.4	0.40	107	59.0	0.230	86	16	72
72	GAP-HN-078	Eutric Cambisol	A	4.4	0.60	199	15.0	0.150	41	31	69
73	GAP-HN-079	Eutric Cambisol	A	8.1	0.60	122	39.0	0.250	43	34	89
74	GAP-HN-080	Eutric Cambisol	A	8.1	0.40	100	25.0	0.170	36	29	77
75	GAP-HN-085	Stagno-gleyic Cambisol	A	7.4	0.20	99	38.0	0.140	58	19	97
76	GAP-HN-086	Eutric Cambisol	A	18.2	0.80	134	48.0	0.170	79	25	92
77	GAP-HN-087	Eutric Cambisol	A	9.2	0.30	113	47.0	0.200	64	22	90
78	GAP-HN-088	Eutric Cambisol	A	8.0	0.40	112	36.0	0.130	43	31	86
79	GAP-HN-089	Stagno-gleyic Cambisol	A	16.9	2.10	135	52.0	0.140	122	21	87
80	GAP-HN-096	Eutric Cambisol	A	5.9	0.40	86	27.0	0.090	36	22	87
81	GAP-HN-097	Stagno-gleyic Cambisol	A	16.0	1.10	119	36.0	0.130	59	21	75
82	GAP-HN-098	Eutric Cambisol	A	7.6	0.40	126	35.0	0.170	72	38	115
83	GAP-HN-099	Eutric Cambisol	A	6.4	0.40	106	24.0	0.090	44	26	88
84	GAP-HN-102	Eutric Cambisol	A	7.2	0.40	92	29.0	0.070	35	29	77
85	GAP-HN-103	Eutric Cambisol	A	9.1	0.50	66	42.0	0.210	44	24	72
86	GAP-HN-107	Stagno-gleyic Cambisol	A	9.0	0.40	99	36.0	0.220	39	26	72
87	GAP-HN-136	Eutric Fluvisol	A	5.8	0.20	84	23.0	0.140	35	16	59
88	GAP-HN-138	Stagno-gleyic Cambisol	A	7.2	0.20	82	25.0	0.240	37	20	72
89	GAP-HN-141	Stagno-gleyic Cambisol	A	7.2	0.40	125	20.0	0.140	42	20	62
90	GAP-HN-144	Calcaric Regosol	A	12.4	0.60	162	45.0	0.180	62	32	103
91	GAP-HN-145	Dystric Planosol	A	5.3	0.10	133	19.0	0.160	43	15	54
92	GAP-KE-022	Stagno-gleyic Cambisol	A	12.7	0.20	115	21.0	0.110	43	86	109
93	GAP-KE-032	Ranker	A	9.7	0.20	149	41.0	0.190	62	22	114
94	GAP-KE-046	Eutric Fluvisol	A	21.0	0.30	104	94.0	0.260	40	38	101
95	GAP-KE-065	Fluvi-eutric Gleysol	A	365.0	3.50	70	58.0	2.150	30	636	297
96	GAP-KE-071	Eutric Cambisol	A	11.0	0.30	102	22.0	0.020	44	13	63
97	GAP-KE-085	Eutric Gleysol	A	11.0	0.40	130	35.0	0.080	69	18	74
98	GAP-KE-099	Dystric Planosol	A	9.3	0.20	167	15.0	0.110	50	28	58
99	GAP-KE-109	Rendzina	A	30.3	2.00	94	29.0	0.490	54	125	125
100	GAP-KE-110	Fluvi-eutric Gleysol	A	18.7	0.30	93	120.0	0.550	40	26	100
101	GAP-KE-115	Rendzina	A	27.1	1.00	6096	34.0	0.120	2066	54	140
102	GAP-KE-131	Dystric Planosol	A	14.5	0.40	104	38.0	0.160	37	25	86
103	GAP-LC-005	Eutric Cambisol	A	3.5	0.05	199	75.0	0.130	82	10	82
104	GAP-LC-036	Ranker	A	17.8	0.10	117	22.0	0.080	37	17	59
105	GAP-LC-054	Eutric Cambisol	A	9.8	0.30	69	25.0	0.110	30	27	146
106	GAP-LC-055	Cambic Arenosol	A	3.8	0.20	124	28.0	0.020	46	12	98
107	GAP-LM-001	Calcaric Cambisol	A	9.7	0.40	148	35.0	0.100	124	35	157
108	GAP-LM-004	Dystric Cambisol	A	12.4	0.40	113	27.0	0.090	59	23	117
109	GAP-LM-008	Eutric Cambisol	A	15.1	0.90	75	17.0	0.130	14	86	303
110	GAP-LM-009	Eutric Cambisol	A	8.4	0.40	61	18.0	0.050	39	28	73
111	GAP-LM-021	Stagno-gleyic Cambisol	A	9.6	0.10	116	29.0	0.090	46	18	75
112	GAP-LM-033	Eutric Cambisol	A	7.1	0.30	108	23.0	0.060	37	16	70
113	GAP-LM-050	Eutric Cambisol	A	10.5	0.30	126	25.0	0.050	42	22	78
114	GAP-LM-058	Stagno-gleyic Cambisol	A	9.3	0.30	144	27.0	0.060	46	17	77
115	GAP-MI-033	Fluvi-eutric Gleysol	A	8.9	0.20	120	36.0	0.210	49	25	99
116	GAP-MI-044	Fluvi-eutric Gleysol	A	5.5	0.20	90	21.0	0.050	40	15	67
117	GAP-MI-047	Eutric Gleysol	A	6.0	0.40	113	37.0	0.140	52	25	101
118	GAP-MI-050	Eutric Cambisol	A	3.5	0.10	77	38.0	0.020	19	14	60
119	GAP-MI-053	Eutric Cambisol	A	3.1	0.20	68	39.0	0.030	16	13	60
120	GAP-MI-064	Stagno-gleyic Cambisol	A	4.1	0.10	95	19.0	0.060	36	17	61
121	GAP-MI-087	Ranker	A	10.6	0.20	114	27.0	0.080	52	19	76
122	GAP-MI-094	Fluvi-eutric Gleysol	A	7.5	0.30	107	33.0	0.060	51	19	109
123	GAP-MI-113	Fluvi-eutric Gleysol	A	8.3	0.20	104	27.0	0.005	43	19	77
124	GAP-MI-114	Eutric Fluvisol	A	8.1	0.20	100	26.0	0.040	42	18	71
125	GAP-MI-115	Eutric Gleysol	A	9.6	0.30	124	41.0	0.050	60	25	96
126	GAP-MI-116	Fluvi-eutric Gleysol	A	9.0	0.30	154	30.0	0.110	59	21	91
127	GAP-MI-120	Fluvi-eutric Gleysol	A	9.2	0.20	112	31.0	0.100	44	18	96
128	GAP-MI-121	Eutric Gleysol	A	9.0	0.20	124	27.0	0.110	49	27	99

No.	Sample	Soil unit FAO (1970)	Hor.	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
129	GAP-MI-122	Eutric Gleysol	A	8.4	0.40	104	36.0	0.140	51	27	108
130	GAP-NZ-052	Luvi-haplic Chernozem	A	8.9	0.05	115	19.0	0.040	44	16	49
131	GAP-NZ-059	Haplic Chernozem	A	4.2	0.30	79	58.0	0.110	31	20	272
132	GAP-PO-004	Stagno-gleyic Cambisol	A	15.7	0.20	144	17.0	0.190	44	23	83
133	GAP-PO-010	Stagno-gleyic Cambisol	A	4.3	0.20	106	18.0	0.070	40	18	42
134	GAP-PO-015	Ranker	A	7.4	0.30	111	25.0	0.040	39	19	72
135	GAP-PO-033	Dystric Planosol	A	8.6	0.30	119	32.0	0.120	48	21	121
136	GAP-PO-040	Ranker	A	11.4	0.30	115	29.0	0.100	38	21	78
137	GAP-PO-047	Ranker	A	13.8	0.60	141	39.0	0.230	73	20	87
138	GAP-PO-049	Stagno-gleyic Cambisol	A	10.1	0.30	121	40.0	0.160	49	20	83
139	GAP-PO-050	Stagno-gleyic Cambisol	A	11.4	0.30	112	31.0	0.180	47	23	81
140	GAP-PO-055	Ranker	A	13.8	0.20	137	32.0	0.160	46	19	86
141	GAP-PO-057	Stagno-gleyic Cambisol	A	8.9	0.40	180	23.0	0.120	65	16	63
142	GAP-PO-060	Stagno-gleyic Cambisol	A	9.9	0.30	114	31.0	0.130	54	18	76
143	GAP-PO-100	Ranker	A	11.7	0.30	124	27.0	0.180	45	20	83
144	GAP-PO-101	Stagno-gleyic Cambisol	A	10.9	0.40	128	26.0	0.150	44	22	79
145	GAP-PO-104	Ranker	A	12.6	0.30	138	25.0	0.140	46	16	72
146	GAP-PO-105	Eutric Cambisol	A	10.9	0.40	152	24.0	0.220	47	19	79
147	GAP-PO-110	Dystric Regosol	A	16.6	0.20	116	23.0	0.220	43	19	85
148	GAP-PO-117	Ranker	A	8.1	0.40	127	21.0	0.130	35	22	76
149	GAP-PO-121	Eutric Cambisol	A	7.8	0.20	111	21.0	0.110	35	22	64
150	GAP-PP-005	Ranker	A	9.8	0.70	137	17.0	0.170	49	36	155
151	GAP-PP-006	Ranker	A	11.9	0.60	146	25.0	0.090	60	29	133
152	GAP-PX-012	Fluvi-gleyic Phaeozem	A	11.4	0.40	124	40.0	0.100	65	25	109
153	GAP-PX-019	Fluvi-gleyic Phaeozem	A	6.4	0.30	187	34.0	0.090	53	23	91
154	GAP-PX-026	Fluvi-gleyic Phaeozem	A	6.9	0.30	101	44.0	0.070	30	28	91
155	GAP-PX-038	Stagno-gleyic Cambisol	A	7.7	0.20	141	27.0	0.060	66	21	93
156	GAP-RS-008	Rendzina	A	4.2	0.05	37	17.0	0.050	36	15	86
157	GAP-RS-062	Eutric Fluvisol	A	14.2	0.20	116	44.0	0.130	35	21	57
158	GAP-RS-090	Albo-gleyic Luvisol	A	9.6	0.05	116	36.0	0.160	36	17	85
159	GAP-RS-101	Ranker	A	202.0	0.30	95	57.0	0.090	33	27	110
160	GAP-RV-001	Fluvi-mollic Gleysol	A	12.9	0.30	150	36.0	0.130	93	23	63
161	GAP-RV-025	Stagno-gleyic Cambisol	A	14.6	0.20	97	36.0	0.080	33	18	118
162	GAP-RV-026	Eutric Fluvisol	A	25.9	0.30	67	216.0	0.960	19	21	69
163	GAP-RV-028	Eutric Cambisol	A	6.7	0.30	51	49.0	0.190	12	21	60
164	GAP-RV-037	Eutric Cambisol	A	12.8	0.90	72	19.0	0.100	27	114	180
165	GAP-RV-038	Calcaric Lithosol	A	12.3	0.90	82	28.0	0.030	44	29	98
166	GAP-RV-040	Calcaric Lithosol	A	14.1	0.90	69	29.0	0.050	38	37	100
167	GAP-RV-045	Eutric Cambisol	A	40.6	0.30	130	35.0	0.070	63	33	123
168	GAP-RV-047	Eutric Cambisol	A	4.3	0.30	155	27.0	0.060	56	12	83
169	GAP-RV-051	Eutric Cambisol	A	49.3	0.60	117	33.0	0.090	51	39	170
170	GAP-RV-058	Ranker	A	19.5	0.30	152	81.0	0.150	78	25	133
171	GAP-RV-062	Ranker	A	38.2	0.20	71	45.0	0.310	35	11	27
172	GAP-RV-075	Eutric Cambisol	A	20.2	0.40	134	41.0	0.630	48	26	96
173	GAP-RV-076	Eutric Cambisol	A	8.2	0.10	123	34.0	0.230	39	8	51
174	GAP-RV-077	Dystric Lithosol	A	41.9	0.40	109	54.0	0.500	65	26	87
175	GAP-RV-078	Eutric Cambisol	A	18.2	0.30	162	36.0	0.150	50	17	119
176	GAP-RV-086	Rendzina	A	17.6	0.70	114	31.0	0.250	54	39	107
177	GAP-RV-104	Ranker	A	20.6	0.10	74	74.0	0.160	29	9	39
178	GAP-RV-122	Dystric Lithosol	A	22.7	3.10	110	26.0	0.300	61	228	153
179	GAP-RV-123	Dystric Lithosol	A	16.6	1.40	98	22.0	0.200	42	107	160
180	GAP-RV-132	Ranker	A	59.5	0.30	111	36.0	0.110	34	46	91
181	GAP-RV-133	Rendzina	A	31.6	0.50	88	45.0	0.190	41	68	214
182	GAP-SE-001	Orthic Luvisol	A	7.7	0.20	91	20.0	0.050	31	18	56
183	GAP-SE-010	Fluvi-eutric Gleysol	A	7.2	0.20	106	27.0	0.080	41	20	75
184	GAP-SE-028	Orthic Luvisol	A	7.6	0.05	92	20.0	0.050	37	15	83
185	GAP-SE-036	Eutric Cambisol	A	7.4	0.30	105	43.0	0.090	44	22	91
186	GAP-SE-060	Eutric Fluvisol	A	3.4	0.40	132	17.0	0.130	200	28	94
187	GAP-SE-066	Stagno-gleyic Cambisol	A	7.5	0.20	95	47.0	0.070	39	23	69
188	GAP-SE-068	Fluvi-gleyic Phaeozem	A	7.1	0.30	147	45.0	0.060	45	23	85
189	GAP-SE-069	Stagno-gleyic Cambisol	A	5.9	0.30	87	26.0	0.090	36	23	56
190	GAP-SE-071	Eutric Cambisol	A	6.5	0.30	89	40.0	0.070	40	25	81
191	GAP-SE-081	Fluvi-gleyic Phaeozem	A	10.1	0.30	349	23.0	0.150	166	21	65
192	GAP-SE-094	Eutric Cambisol	A	6.6	0.20	676	17.0	0.090	181	15	41
193	GAP-SE-095	Stagno-gleyic Cambisol	A	10.4	0.30	347	19.0	0.130	198	18	52
194	GAP-SE-120	Stagno-gleyic Cambisol	A	10.0	0.40	99	28.0	0.110	37	30	91

No.	Sample	Soil unit FAO (1970)	Hor.	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
195	GAP-SK-001	Stagno-gleyic Cambisol	A	4.8	0.05	120	18.0	0.040	39	12	52
196	GAP-SK-006	Stagno-gleyic Cambisol	A	4.8	0.20	127	17.0	0.030	38	18	63
197	GAP-SK-027	Stagno-gleyic Cambisol	A	8.1	0.70	104	26.0	0.150	45	40	117
198	GAP-SK-031	Stagno-gleyic Cambisol	A	5.8	0.30	120	26.0	0.080	46	21	69
199	GAP-SK-039	Eutric Cambisol	A	6.0	0.30	182	28.0	0.100	85	16	73
200	GAP-SK-054	Luvic Cambisol	A	40.8	2.20	138	57.0	0.240	87	26	97
201	GAP-SK-056	Stagno-gleyic Cambisol	A	5.1	0.30	117	19.0	0.170	40	22	64
202	GAP-SK-057	Stagno-gleyic Cambisol	A	5.0	0.30	166	19.0	0.170	49	18	66
203	GAP-SK-058	Stagno-gleyic Cambisol	A	7.2	0.40	99	25.0	0.230	37	22	100
204	GAP-SK-060	Stagno-gleyic Cambisol	A	10.0	0.60	110	30.0	0.170	46	40	98
205	GAP-SK-065	Luvic Cambisol	A	10.4	0.50	104	36.0	0.180	52	33	96
206	GAP-SK-067	Luvic Cambisol	A	8.7	0.60	122	32.0	0.220	50	36	108
207	GAP-SK-081	Stagno-gleyic Cambisol	A	4.4	0.20	116	14.0	0.030	36	13	47
208	GAP-SK-082	Stagno-gleyic Cambisol	A	4.5	0.10	144	13.0	0.030	44	14	55
209	GAP-SL-004	Stagno-gleyic Cambisol	A	12.2	0.30	123	24.0	0.130	40	22	79
210	GAP-SN-001	Stagno-gleyic Cambisol	A	19.5	0.20	88	78.0	0.750	23	37	108
211	GAP-SN-002	Ranker	A	54.0	0.20	104	209.0	1.480	34	144	144
212	GAP-SN-008	Ranker	A	140.0	0.30	99	323.0	1.100	36	38	148
213	GAP-SN-012	Dystric Regosol	A	91.0	0.20	134	160.0	5.310	65	28	118
214	GAP-SN-014	Eutric Cambisol	A	14.4	0.30	110	40.0	0.410	51	31	86
215	GAP-SN-015	Eutric Cambisol	A	8.3	0.10	108	25.0	0.170	45	20	70
216	GAP-SN-017	Dystric Lithosol	A	10.3	0.30	151	24.0	0.310	40	18	73
217	GAP-SN-019	Eutric Cambisol	A	8.9	0.40	138	19.0	0.180	37	17	68
218	GAP-SN-022	Ranker	A	41.6	1.00	109	82.0	9.970	99	70	222
219	GAP-SN-044	Ranker	A	29.6	0.60	115	43.0	13.720	40	99	245
220	GAP-SN-045	Calcaric Cambisol	A	13.0	0.20	132	22.0	0.470	39	19	86
221	GAP-SN-046	Eutric Cambisol	A	12.1	0.20	132	43.0	0.200	42	22	101
222	GAP-SN-048	Ranker	A	11.4	0.20	131	27.0	0.070	48	19	66
223	GAP-SN-050	Eutric Cambisol	A	40.9	0.30	47	139.0	1.770	11	65	173
224	GAP-SN-051	Ranker	A	28.1	0.20	98	42.0	0.210	43	31	184
225	GAP-SN-055	Ranker	A	17.3	0.30	127	22.0	0.430	36	21	78
226	GAP-TN-001	Eutric Fluvisol	A	9.0	0.50	114	23.0	0.050	58	20	89
227	GAP-TN-004	Rendzina	A	11.3	0.50	141	25.0	0.050	94	28	120
228	GAP-TN-010	Rendzina	A	6.9	0.20	123	21.0	0.060	60	24	91
229	GAP-TN-015	Orthic Luvisol	A	7.7	0.05	94	15.0	0.030	36	11	56
230	GAP-TN-067	Eutric Cambisol	A	7.1	0.20	85	19.0	0.040	36	14	49
231	GAP-TV-012	Fluvi-eutric Gleysol	A	7.7	0.20	100	18.0	0.080	42	25	109
232	GAP-TV-017	Eutric Gleysol	A	6.8	0.20	110	16.0	0.070	39	22	112
233	GAP-TV-020	Dystric Regosol	A	3.9	0.20	80	157.0	0.005	24	12	53
234	GAP-TV-027	Fluvi-eutric Gleysol	A	5.0	0.20	109	28.0	0.030	49	16	80
235	GAP-TV-028	Fluvi-eutric Gleysol	A	7.3	0.10	117	31.0	0.040	56	18	107
236	GAP-TV-029	Eutric Gleysol	A	5.8	0.40	125	36.0	0.060	52	29	92
237	GAP-TV-032	Fluvi-eutric Gleysol	A	6.1	0.20	101	22.0	0.010	36	19	87
238	GAP-TV-039	Eutric Gleysol	A	7.3	0.40	120	21.0	0.060	42	28	115
239	GAP-TV-043	Fluvi-eutric Gleysol	A	6.9	0.30	99	18.0	0.030	37	16	83
240	GAP-TV-055	Eutric Gleysol	A	5.4	0.30	125	27.0	0.040	45	25	79
241	GAP-TV-064	Dystric Regosol	A	12.0	0.80	111	21.0	0.020	37	73	175
242	GAP-TV-086	Ranker	A	6.0	0.10	118	11.0	0.020	37	14	50
243	GAP-TV-113	Eutric Gleysol	A	8.2	0.30	126	24.0	0.090	41	23	106
244	GAP-TV-115	Fluvi-eutric Gleysol	A	6.3	0.30	103	25.0	0.080	36	20	78
245	GAP-TV-116	Fluvi-eutric Gleysol	A	9.5	0.50	125	39.0	0.110	56	34	135
246	GAP-TV-122	Eutric Gleysol	A	10.4	0.40	141	34.0	0.100	43	35	106
247	GAP-TV-123	Eutric Gleysol	A	8.7	0.50	119	31.0	0.140	44	34	134
248	GAP-TV-130	Eutric Gleysol	A	10.5	0.50	141	37.0	0.120	63	22	100
249	GAP-TV-133	Eutric Gleysol	A	9.5	0.50	108	34.0	0.140	49	27	101
250	GAP-TV-141	Albo-gleyic Luvisol	A	8.4	0.10	107	19.0	0.030	36	15	53
251	GAP-VK-180	Eutric Cambisol	A	3.8	0.40	36	40.0	0.080	14	32	78
252	GAP-VV-021	Ranker	A	9.1	0.20	250	32.0	0.080	140	16	77
253	GAP-VV-026	Rendzina	A	9.9	0.30	164	37.0	0.060	113	18	76
254	GAP-VV-029	Ranker	A	11.2	0.20	356	29.0	0.210	237	19	80
255	GAP-VV-032	Ranker	A	10.3	0.10	125	23.0	0.070	45	15	69
256	GAP-VV-042	Stagno-gleyic Cambisol	A	5.1	0.30	144	17.0	0.150	48	18	69
257	GAP-VV-056	Eutric Cambisol	A	5.8	0.30	192	15.0	0.100	63	16	51
258	GAP-ZA-006	Stagno-gleyic Cambisol	A	18.2	0.60	108	46.0	0.130	68	24	88
259	GAP-ZA-009	Stagno-gleyic Cambisol	A	6.4	0.30	127	30.0	0.070	35	29	92
260	GAP-ZA-011	Stagno-gleyic Cambisol	A	7.8	0.40	96	27.0	0.060	43	30	94

No.	Sample	Soil unit FAO (1970)	Hor.	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
261	GAP-ZA-015	Stagno-gleyic Cambisol	A	7.8	0.40	92	31.0	0.080	50	27	89
262	GAP-ZA-019	Stagno-gleyic Cambisol	A	6.4	0.30	126	17.0	0.040	42	18	57
263	GAP-ZA-023	Stagno-gleyic Cambisol	A	6.8	0.50	122	48.0	0.090	117	42	142
264	GAP-ZA-024	Calcaric Cambisol	A	6.2	0.50	114	35.0	0.070	97	29	109
265	GAP-ZA-025	Stagno-gleyic Cambisol	A	6.6	0.20	74	19.0	0.040	35	16	61
266	GAP-ZA-029	Stagno-gleyic Cambisol	A	6.3	0.40	90	42.0	0.090	39	24	110
267	GAP-ZA-030	Dystric Cambisol	A	6.2	0.30	258	20.0	0.080	70	23	78
268	GAP-ZA-031	Dystric Cambisol	A	6.9	0.40	134	27.0	0.100	60	29	87
269	GAP-ZA-034	Stagno-gleyic Cambisol	A	5.4	0.20	136	17.0	0.060	45	23	67
270	GAP-ZA-054	Dystric Planosol	A	15.4	0.50	103	43.0	0.130	72	18	70
271	GAP-ZH-003A	Luvic Cambisol	A	7.0	0.30	57	22.0	0.100	15	111	198
272	GAP-ZH-010	Fluvi-eutric Gleysol	A	121.0	0.20	34	49.0	1.320	7	84	62
273	GAP-ZH-023	Fluvi-eutric Gleysol	A	23.5	0.90	57	106.0	0.580	22	147	197
274	GAP-ZH-043	Eutric Cambisol	A	72.2	0.40	62	24.0	1.040	7	141	58
275	GAP-ZH-055	Eutric Cambisol	A	7.6	0.50	31	20.0	0.080	6	85	91
276	GAP-ZH-056	Eutric Cambisol	A	19.1	0.60	28	23.0	0.110	7	146	123
277	GAP-ZH-057	Eutric Cambisol	A	4.4	0.90	26	32.0	0.220	6	161	146
278	GAP-ZH-058	Eutric Cambisol	A	12.4	1.20	34	25.0	0.350	6	243	135
279	GAP-ZH-060	Stagno-gleyic Cambisol	A	4.9	0.60	39	32.0	0.140	8	118	122
280	GAP-ZH-062	Fluvi-eutric Gleysol	A	30.0	4.50	34	259.0	0.380	3	1572	910
281	GAP-ZH-063	Eutric Cambisol	A	39.0	0.80	22	21.0	0.080	7	103	143
282	GAP-ZH-064	Eutric Cambisol	A	26.2	0.40	45	9.0	0.670	3	121	36
283	GAP-ZH-065	Stagno-gleyic Cambisol	A	17.3	8.90	27	179.0	0.350	3	2122	1139
284	GAP-ZH-067	Eutric Cambisol	A	4.7	0.30	32	12.0	0.070	3	101	62
285	GAP-ZH-077	Eutric Cambisol	A	19.3	0.40	62	24.0	0.260	17	133	70
286	GAP-ZH-083	Eutric Cambisol	A	17.3	2.70	32	39.0	0.210	10	251	447
287	GAP-ZV-001	Eutric Fluvisol	A	7.3	7.30	73	92.0	0.130	7	789	967
288	GAP-ZV-012	Stagno-gleyic Cambisol	A	5.5	0.30	100	23.0	0.110	41	23	135
289	GAP-ZV-059	Eutric Cambisol	A	25.0	0.30	74	39.0	0.090	13	231	95
290	GAP-ZV-060	Eutric Cambisol	A	31.2	0.70	87	64.0	0.290	43	33	149
291	GAP-ZV-076	Fluvi-eutric Gleysol	A	4.8	1.40	47	11.0	0.070	13	22	96
292	GAPE-LV-125	Haplic Chernozem	A	29.4	0.50	72	86.0	0.990	19	50	106
293	GAPE-NZ-041	Eutric Fluvisol	A	18.7	0.50	65	44.0	0.190	17	38	91
294	GAPE-NZ-053	Fluvi-mollic Gleysol	A	11.2	0.50	133	57.0	0.060	47	29	128
295	GAPE-PO-001	Gleyic Planosol	A	9.5	0.40	153	29.0	0.150	47	24	99
296	GAPE-PP-020	Eutric Cambisol	A	9.8	0.20	128	26.0	0.150	39	17	71
297	GAPE-PP-027	Eutric Cambisol	A	11.8	0.30	136	30.0	0.130	42	19	77
298	GAPE-PP-028	Eutric Cambisol	A	12.1	0.30	127	31.0	0.090	48	17	146
299	GAPE-PP-033	Ranker	A	10.2	0.30	111	19.0	0.160	36	16	66
300	GAPE-PP-040	Ranker	A	7.9	0.60	140	31.0	0.120	44	21	87
301	GAPE-PP-042	Ranker	A	8.4	0.70	130	30.0	0.110	38	25	99
302	GAPE-PP-050	Rendzina	A	3.3	1.10	43	4.0	0.120	3	39	29
303	GAPE-SL-002	Ranker	A	10.4	0.30	120	24.0	0.120	39	17	79
304	GAPE-SL-008	Ranker	A	7.9	0.60	167	25.0	0.120	55	21	77
305	GAPE-VK-029	Stagno-gleyic Cambisol	A	5.7	0.10	99	40.0	0.060	26	13	73
306	GAPE-VV-006	Dystric Planosol	A	15.0	0.30	132	36.0	0.100	49	16	111

Annex 4 Protocol for the determination of in-situ partition coefficients of heavy metals and their relationship with soil properties

Introduction

The assessment of in-situ partition (adsorption) constants for heavy metals and their relationship with soil properties requires the simultaneous assessment of:

- Total contents (aqua regia) and reactive contents (EDTA) of the relevant metals (Pb, Cd, Cu and Zn and possibly Ni).
- Major soil characteristics influencing the bioavailability of the metals, viz. pH, organic matter content, clay content and content of oxalate extractable Al and Fe.
- Dissolved contents of the relevant metals (Pb, Cd, Cu and Zn and possibly Ni).
- The electric conductivity (EC) and major ions in soil solution with preference for pH, Ca and DOC followed by Mg, K, Na, Al, NH_4, SO_4, NO_3, Cl and alkalinity (HCO_3).

The various aspects related to the derivation of the partition coefficients are given below.

Sampling

It is implicitly assumed that the metal contents in crops (wheat and maize) are also measured. This implies that it is necessary to derive reliable plot-averaged information on the soil properties and the solid and dissolved metal concentrations. This is reflected in the sampling numbers and sampling scheme. When no wheat or maize is available, the same sampling numbers and sampling scheme is considered relevant (see also the minutes of the meeting of meeting in Budapest).

Sampling devices

Sampling can be done by an auger that does allow a precise sampling of fixed depths. The amount of sample should be such that at least 1 kg of sample is available for centrifugation. When the samples are also used for adsorption and/or complexation experiments, another kg of soil sample is needed.

Sampling numbers

The spatial variability in soil and soil solution chemistry requires that at least 25 samples should be taken to derive either one pooled sample. To gain some insight in the spatial variability four pooled samples of 25 subsamples each will be taken. Using an auger, it may be necessary to take extra samples to at each measuring point (see sampling scheme) to get enough soil for the analyses.

Sampling scheme

One simple approach that is often used in the Netherlands is to sample in a fixed grid of 5 x 5 sampling points that are situated at regular intervals from each other.

The interval should be related to the plot area that is considered homogeneous in soil type and crop. One may consider interval of e.g. 5 meters or 10 meters apart leading to a plot area of 25 x 25 m or 50 x 50 m.

Sampling depths

The sampling will be limited to the plough layer where most effects on solute uptake (and ecology) are to be expected, i.e.:0-10 cm and 10-20 cm. Note that the total number of samples is equal to 20 (plots) x 2 (depths) x 4 (replicates) = 160.

Conservation and analyses of soil samples

Soil samples should be cooled in a refrigerator at 4°C, preferably for no longer than 1 or 2 days. This is due to possible changes in the solution chemistry, specifically with respect to NO_3 and NH_4 and thus to pH and thereby on the metal concentrations. In general centrifugation should be done as soon as possible.

Analyses of soil samples include:
- pH: use a 1 : 5 soil to solution ratio using both water and 0.01 M. $CaCl_2$ as an extractant.
- Total contents of heavy metals: use an aqua regia extraction method.
- Reactive content of heavy metals: use an EDTA extraction method.
- Organic matter and clay content: use the methods that are standard in the laboratory (please provide the details).
- Oxalate extractable Al and Fe content: an extraction and analyses method can be provided if this method is not yet used.

Centrifugation

Centrifugation should be performed with a centrifuge that does allow tubes of approximately 500 ml (about 0,5 kg of soil). This is necessary to get enough solution from the soil sample. At the bottom of the tube one should preferably use a 0,45 µ membrane filter. If one uses a filter with a high porosity (in mm), a separate filtration step over a 0,45 µ membrane filter is needed.
Experience in the Netherlands has led us to use a centrifugation speed of 7000rpm during 20 minutes at a room temperature of 20°C. At least 25 ml, but preferably 30-40 ml is needed for a complete analyses of the soil solution chemistry, assuming that ICP, AAS and FIA are available (see below). This may require several centrifugation rounds of 20 minutes. Another possibility used in the Netherlands is to use two centrifugation tubes of the same soil sample (about 1 kg of soil). In a moist period, this should give enough solution for the analyses.

Conservation and analyses of soil solution samples

Soil solution samples should be analysed as soon as possible. This refers specifically for pH, EC, NO_3 and NH_4, that should be analysed within one day, without conservation (see below).

When the other ions are not analysed within one day, conservation is needed by using one drop of concentrated HNO_3 (of course not to be used when pH, EC, NO_3 and NH_4 are measured).
The following procedure of moisture division may be used to allow the measurement of the various ions :

- Use 5 ml. of sample for the immediate measurement of pH, EC and of, NH_4 and NO_3 with the Flow Injection Analyser (FIA).
- Use 1 ml of sample and dilute this ten times and conserve this with one drop of concentrated HNO_3 for the measurement of Cl (FIA) and DOC using a TOC analyser.
- Use 15 ml of sample and conserve this with one drop of concentrated HNO_3 for the measurement of the major ions Al, Ca, Mg, K, Na and SO_4 and the heavy metals Cu and Zn using an ICP-AES. When the concentrations of Zn and Cu are too low, the analyses has to be repeated on an oven-AAS (see below).
- Use the remaining sample for the analyses of Pb and Cd (and possibly Ni) on an oven-AAS.

In a situation in which centrifugation causes a lot of problems (e.g. in very dry soils or in heavy clay soils), use can be made of a 0.01 M. $CaCl_2$ extraction method.

Calculation

Partition coefficients can be calculated by relating:

- Total dissolved contents of the relevant metals to total (aqua regia extracted) soil metal contents
- Total dissolved contents of the relevant metals to reactive (EDTA extracted) soil metal contents
- Calculated free metal ion activities of the relevant metals to total (aqua regia extracted) soil metal contents
- Calculated free metal ion activities of the relevant metals to reactive (EDTA extracted) soil metal contents

For a good interpretation of the results it is necessary to calculate the free metal ion activities using a chemical equilibrium model. This model is available at SC-DLO and uses the information on (i) total dissolved contents of the relevant metals and (ii) the macro-ion chemistry, viz. the major ions in soil solution (at least pH, Ca and DOC and preferably Mg, K, Na, Al, NH_4, SO_4, NO_3, Cl and alkalinity/HCO_3). Most preferably, the free metal ion activity is also measured with ion-specific electrodes to compare the measured and calculated free metal ion activities.

It is most relevant to assume a non-linear (Freundlich) relationship between the solid and dissolved metal concentrations according to :

$$Q = K_f \cdot c^n \text{ or } \log Q = \log K_f + n \log c \qquad (1)$$

The partition coefficients can then be related to the soil properties using linear regression analyses, according to :

$$\log K_f = a_0 + a_1 \cdot \log OM + a_2 \cdot \log clay + a_3 \cdot pH + a_4 \cdot \log (Al + Fe)_{ox} + a_5 \cdot \log Ca \quad (2)$$

Combination of Eq. (1) and Eq. (2) leads to one single relationship that can be derived by linear regression analyses according to :

$$\begin{aligned} \log Q = a_0 + a_1 \cdot \log OM + a_2 \cdot \log clay + a_3 \cdot pH + a_4 \cdot \log (Al + Fe)_{ox} + \\ a_5 \cdot \log Ca + n \log c \end{aligned} \quad (3)$$

Required instruments

Centrifuge with that does allow tubes of approximately 500 ml (about 0,5 kg of soil). TOC analyser, ICP or AAS and FIA (preferably) or another instrument with which NO_3, NH_4 and Cl can be measured.

Required methods

Extraction of heavy metals by aqua regia
Extraction of heavy metals by EDTA
Extraction of heavy metals by 0.43 N HNO_3
Extraction of heavy metals by 0.01 M $CaCl_2$
Methods to determine pH-H_2O and pH-$CaCl_2$
Methods to determine organic matter and clay content
Methods to determine the oxalate extractable content of aluminium and iron.
Measuring method for DOC
Measuring methods for all major cations and anions.

Programs

Chemical equilibrium program to calculate free metal ion activities (e.g. EPIDIM)
Statistical program to perform multiple regression analyses (e.g. GENSTAT)

Annex 5 Protocol for the calculation of free ion activities

Introduction

Within several tasks of the INCO-project (i.e. adsorption studies for transfer functions, in situ field partition and metal uptake by crops) free ion activities of heavy metals have to be assessed. For some cases free ion activities will be measured using a ion selective electrode (see protocol adsorption studies). When the free ion activity is not measured it has to be calculated. There are two possibilities to calculate metal ion activities (see also figure 1):

- Calculation of activities from measured concentrations of heavy metals and macro-chemistry using a chemical speciation model.
- Calculation of activities from reactive metal contents in the solid phase using transfer functions (sorption model).

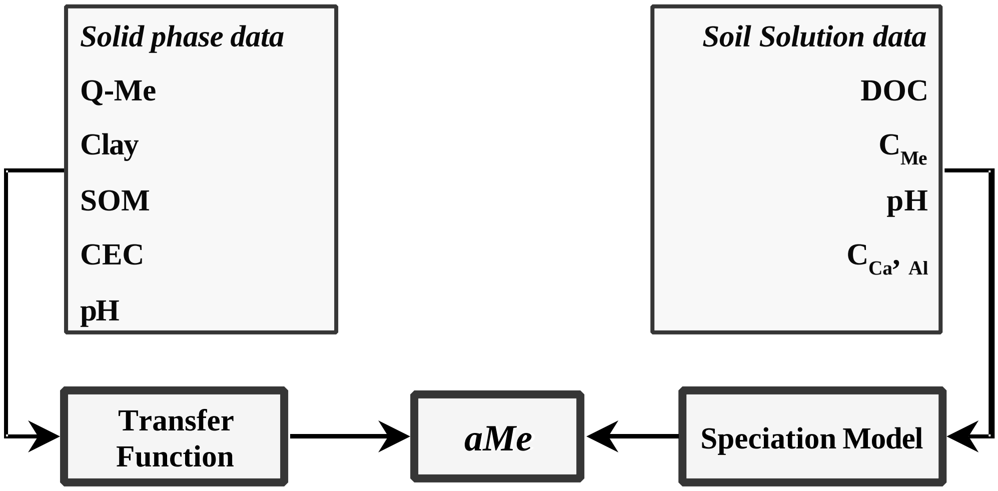

Figure 1 Schematic presentation calculation methods activities

In case of determination of activities for use in the derivation/validation of adsorption constants only the first method has to be used, whereas in deriving complexation constants (see protocol in Annex 7) only the second method is allowed. For other cases (e.g. the derivation of in-situ field partition constants based on total dissolved metal concentrations) both methods can be used to derive the free metal ion activity.

Calculation of free metal ion activities using a chemical speciation model

The activity of heavy metal species can be calculated if (i) concentrations of heavy metals are available, (ii) concentrations of the macro elements and DOC are available and (iii) formation constants of the relevant species are available. Formation constants of inorganic complexes are available from several compilations (see Appendix 1 for list of relevant formation constants of inorganic complexes). However for heavy metals complexation with dissolved organic carbon is most important.

Metal-DOC complexation

For heavy metal-DOC complexation several models exist from simple mass action relations to complex models including electrostatic interactions and a distribution of binding strengths. Parameterisation of these complex models is however a large problem. Within this project use will be made of a simple model for metal-DOC complexation using a diprotic acid analogue for DOC (Bril in Reinds et al., 1995; Römkens, 1998). Dissociation of the diprotic acid analogue is described by:

$$H_2FA \Leftrightarrow HFA^- + H^+ \qquad [HFA^-] = K_{a,1} \cdot \frac{[H_2FA]}{[H^+]} \tag{1}$$

$$HFA^- \Leftrightarrow FA^{2-} + H^+ \qquad [FA^{2-}] = K_{a,2} \cdot \frac{[HFA^-]}{[H^+]} \tag{2}$$

where:

$K_{a,1}$ = the first dissociation constant for fulvic acid (mol.l^{-1})

$K_{a,2}$ = the second dissociation constant for fulvic acid (mol.l^{-1})

Equation (1) represents the dissociation of carboxylic groups (p$K_{a,1}$ around 4.5) and equation (2) represents the dissociation of phenolic groups at higher pH (p$K_{a,2}$ around 9.5). Heavy metals and major cations can form complexes with both the monovalent and divalent species according to:

$$aM + bL \Leftrightarrow M_aL_b \tag{3}$$

where a and b are the stoichiometric constants in the complexation of metal M with ligand L.

The activity of the complexed species can be expressed as:

$$(M_aL_b) = K_{ML} \cdot (M)^a \cdot (L)^b$$

where K_{ML} is the formation constant of species ML. The concentrations of the complexed species can thus be expressed in concentrations of the free metal and ligand ions. For each metal and ligand a mass balance can be set up expressed in the concentration of the free metal and ligand species. This set of mass balances can be solved using a chemical speciation program (see calculation method)

The formation constants of the organic complexes are listed in table 1.

Table 1 Logarithmic values of formation constants of heavy metal complexes at 25 ^{0}C and ionic strength = 0

Logarithmic values of formation constants of heavy metal complexes at 25 ^{0}C and ionic strength = 0

L	Log K_{ML}[1]									
	H	Al	Ca	Mg	Pb	Cd	Cu	Zn	Ni	Cr
HFA	4.4[1]	7[2]	3.7[1]	3.5[1]	5.5[1]	4.1[1]	5.7[1]	4.3[1]	4.3[1]	7[2]
FA	9.4	14[2]	6.1[1]	6.0[1]	10.0[1]	6.8[1]	10.7[1]	7.2[1]	7.3[1]	14[2]

[1] Bril (1996; using data of Sanders, 1982, Bril and Römkens, 1996, Mantoura et al., 1978, and Stevenson, 1976)

[2] Bril (pers. comm.)

Calculation method

Calculation of chemical speciation can easily be done using available computer programs (e.g. EPIDIM (Groenendijk, 1995), MINEQL (..) and CHARON (..)). In these models the chemistry of the soil solution is defined by a set of chemical components (such as Ca^{2+} and SO_4^{2-}) and a set of ion species (such as $CaSO_4$) with their associated specific formation constants. The formation of a certain species out of the components can be written as:

$$a_{1,j} \cdot A_1 + \ldots + a_{i,j} \cdot A_i + \ldots + a_{n,j} \cdot a_n = B_j \qquad (4)$$

where:

$a_{i,j}$ = the stoichiometric coefficient of component A_i in the formation of species B_j

n = the number of components.

If a species contains a component A_i, the associated stoichiometric coefficient is greater or equal to one; if the species does not contain the component A_i, the stoichiometric coefficient equals zero.

The set of components has to be chosen such that:

- all species can be build from this set
- no component can be build from a combination of other components.

Annex 1 lists the most important species to be used for the calculation of the speciation of the metals of interest within the project. In this table the stoichiometric coefficients $a_{i,j}$ are given with i = column number (components) and j = row number (species), the last column contains the formation constants K^0_j. All stoichiometric coefficients that are equal to zero are left blank in this table.

In EPIDIM the activity of each species is expressed in the activities of the components according to:

$$(B_j) = K_j^0 \cdot \prod_{i=1}^{n} (A_i)^{a_{ij}} \qquad (5)$$

where:

(B_j) = the activity of species j

(A_i) = the activity of component i

K_j^0 = the thermodynamic formation constant of species j

When the formation constant is corrected for non-ideal behaviour of the components equation 5 can be written in terms of concentrations according to:

$$[B_j] = K_j \cdot \prod_{i=1}^{n} [A_i]^{a_{ij}} \tag{6}$$

where:

$[B_j]$ = the concentration of species j

$[A_i]$ = the concentration of component i

K_j = the formation constant of species j corrected for ionic strength

For each component the total concentration equals:

$$[A_k]^T = \sum_{j=1}^{m} a_{kj} \cdot K_j \cdot \prod_{i=1}^{n} [A_i]^{a_{ij}} \tag{7}$$

where:

$[A_k]^T$ = the total concentration of component k

m = the number of species.

If the total concentrations are known, we have a set of N equations with N unknowns, the component concentrations. This set of equations can be solved numerically with a Newton Raphson iteration scheme (see e.g. Press et al., 1986).

To correct for non ideal behaviour of the ions, the formation constants K_j used have to be corrected for the ionic strength in the soil solution. These modified constants can be calculated from the thermodynamic formation constants of the species and activity coefficients of the species and components according to:

$$K_j = K_j^0 \cdot \frac{\prod_{i=1}^{n} \gamma_i^{a_{ij}}}{\gamma_j} \tag{8}$$

where:

$?_i$ = activity coefficient of component i

$?_j$ = activity coefficient of species j

K_j = formation constant corrected for ionic strength

K_j^o = thermodynamic formation constant (T = 25 C, I=0)

Activity coefficients can be calculated with the Davies equation (Stumm and Morgan, 1981):

$$\log \gamma_i = -0.5 \cdot z_i^2 \cdot \left(\frac{\sqrt{I}}{I + \sqrt{I}} - 0.3I \right) \tag{9}$$

where:
I = ionic strength
z_i = valence of ion i

The ionic strength is calculated according to:

$$I = \frac{1}{2} \sum_{j=1}^{m} z_j^2 \cdot [B_j] \tag{10}$$

Calculation of heavy metal activities using a transfer function

In cases for which not all or no soil solution concentrations are available, which are needed to calculate the activities from chemical speciation, the activity of heavy metals can be calculated using a transfer function. Such a transfer function relates the reactive metal content in the soil with the activity of the metal in the soil solution depending on soil and soil solution properties such as the CEC, clay content, organic matter content and pH. An example of a transfer function is given in equation 11 (Reinds et al., 1995).

$$\log M = a_0 + a_1 * pH + a_2 * \log(\% OC) + a_3 * \log CEC + a_4 * \log(\% clay) + n \log(a_M / a_{Ca}^{0,5}) \tag{11}$$

with:
M = reactive metal content solid phase ($mol.kg^{-1}$)
%OC = organic carbon content (%)
CEC = Cation Exchange Capacity ($mol_c.kg^{-1}$)
%clay = clay content (%)
n = Freundlich exponent

The Freundlich exponent and coefficients of the transfer function are listed in Table 2. The reactive metal content is not equal to the total metal content in the soil as part of this metal pool may be inert. Reactive metal contents can be assessed using extractions with EDTA or 0.43 N HNO_3. Furthermore at least the clay and organic carbon content and the pH should be known. When the transfer function according to equation 1 is used also the Ca-activity should be known or estimated.

Table 2 Values for the Freundlich exponent (n) and coefficients in equation 11

M	N	a_0	a_1	a_2	a_3	a_4
Pb	0.55	-4.40	0.60	0.62	0.46	-
Cd	0.82	-3.15	0.50	1.00	-	-0.24
Cu	0.55	-3.85	0.70	0.52	0.46	-0.14
Zn	0.75	-3.42	0.75	1.30	-	-

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Annex. 1 Species table used in EPIDIM

Species 1)	Components 2)						$\log K_{j0}$ 3)
	H^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	HFA^-	M^{2+}	
OH^-	-1						-14.00
$CaHCO_3^+$	-1	1					-8.41
$CaCO_3$	-2	1					-16.69
$CaSO_4$		1		1			2.31
$CaHFA^+$		1			1		2.20
CaFA	-1	1			1		-4.90
$MgHCO_3^+$	-1		1				-8.44
$MgCO_3$	-2		1				-16.61
$MgSO_4$			1	1			2.31
Al^{3+}	3						7.00 4)
$AlOH^{2+}$	2						2.01
$Al(OH)_2^+$	1						-3.10
$Al(OH)_4^-$	-1						-15.70
$AlSO_4^+$	3			1			10.02
$Al(SO_4)^-$	3			2			11.92
HCO_3^-	-1						-9.51 5)
CO_3^{2-}	-2						-19.84 5)
H_2FA 6)	1				1		4.30
FA^{2-}	-1				1		-9.50
$MHCO_3^+$	-1					1 7)	$KMHCO_3^+$
MCO_3	-2				1		$KMCO_3$
MOH^+	-1					1 7)	$KMOH^+$
$MHFA^+$					1	1 7)	$KMHFA^+$
MFA	-1				1	1 7)	KMFA
M_{ads}						n 8)	$\log K_F$ 9)

[1] Species which consist of only one component (e.g. H^+) are not in this table, their formation constants are equal to 1.

[2] The components Na^+,K^+,Cl^-,NH_4^+ and NO_3^- are not in this table because no complexes of these ions were taken into account.

[3] Values of K^0 for inorganic species are derived from the WATEQX database (Van Gaans, 1989). Values for complexes with FA were derived from Reinds et al (1995).

[4] Derived with the assumption that Al^{3+} is in equilibrium with an Al-hydroxide according to the reaction $Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$

[5] Derived from equilibrium with gaseous CO_2

[6] Organic acids are modelled as a diprotic acid schematically represented by H2FA

[7] See Table 1 for formation constants for each of the metals

[8] Freundlich exponent

[9] Freundlich constant calculated in EPIDIM

Annex 6 Protocol for the assessment of adsorption constants in relation to soil properties and the use of the copper ion selective electrode

Introduction and background

From thermodynamic equilibrium, combined with the principle of electro-neutrality, and introducing an activity relation for the heterogeneity of sorption sites (a/o. Langmuir, 1981), we expect the sorption of trace metals onto soils to follow Freundlich type of behaviour. The Freundlich exponent *nf* is a measure of the width of the distribution of ΔG of binding to the available sites, and the Freundlich constant is a function of the Freundlich exponent *nf* and the *average* value of ΔG (ΔG_{av}), the co-adsorbing anions, the competing cations and the number of sites available (Bril, 1995). This theory also shows that all relations have to be taken as log-log rather than linear (or curvy-linear as the Langmuir isotherm assumes).
Of course the relation does *not* include concentrations (which thermodynamically have no meaning), but the activity of the metal in the soil solution.

The resulting overall equation for the sorption of a trace metal onto soils can be given as (Bril, 1995)

$$\log(M_{Me}) = \log(N_s) + nf * [\log(K_{eq}) + n*\log(aL) - z*\log(aE_p)] + nf * \log(aMe) \quad (1)$$

Here
M_{Me} = the metal concentration in the adsorbent (the solids) in $mol.kg^{-1}$
N_s = the number of adsorption sites in $mol.kg^{-1}$
K_{eq} = $\exp(-\Delta G_{av}/RT)$
aE_p = the activity of competing cations in $mol.l^{-1}$
aL = the activity of the co-adsorbing anions in $mol/.l^{-1}$
aMe = the activity of the adsorbing metal ion in $mol/.l^{-1}$
n,z = stoichiometric constants

The assumptions underlying this model are:
1) Constant stoichiometry of the sorption reaction,
2) The introduction of the power function to describe surface heterogeneity,
3) Neglecting the effect of adsorption of the trace metal Me on the mole-fraction of the sorbed macro-elements.

Equation (1) can be re-arranged to give a general form

$$\log(M_{Me}) = C_0 + \log(N_s) + C_2*\log(aE_p) + C_3 * \log(aL) + C_4* \log(aMe) \quad (2)$$

Here $C_0 - C_4$ are constants, which can be fitted against measured adsorption data. When we assume that

$$\text{Log } Ns = C_{11}* \log S_1 + C_{12} * \log S_2 \ldots. + C_{1m} * \log S_m$$

Where S_1 .. S_m are the individually distinguishable potential sorption sites, and

$\log(aE_p) = (1/C_2) * (C_{21}*\log (CA_1) + C_{22}*\log(CA_2) .. + C_{2m}*\log(CA_m))$

Where CA_1 .. CA_m are the individually distinguishable potentially competing cations, then equation (2) can be fitted to sorption data and should give good relations for different metals.

Relations found up to now

The next paragraph gives the relations as they are available at the moment at AB-DLO. Note that all equations are still under development, and will be changed due to the results of the experimental work which is currently being performed.

1: Cadmium:

$\log M_{Cd}$ ($mol.kg^{-1}$) = (-1.90 ± 0.30) + 1.00 * log (CEC, $eq.kg^{-1}$, Bascomb) + 0.50 * pH – 0.24 * log(%clay) - 0.41 * log [aCa, $mol.l^{-1}$] + 0.82 * log [aCd ($mol.l^{-1}$)]

2: Copper:

$\log M_{Cu}$ ($mol.kg^{-1}$) = (-3.0 ± 0.1) + 0.52 * log (CEC) + 0.70 * pH – 0.14 * log(%clay) + 0.46 * log (%OM) - 0.3 * log [aCa ($mol.l^{-1}$)] + 0.6 * log [aCu ($mol.l^{-1}$)]

3: Zinc:

a: Without Fe-oxalate included

$\log M_{Zn}$ ($mol.kg^{-1}$) = -2.30 + 1.30 * log (CEC) + 0.75 * pH
+ 0.75 * log [aZn ($mol.l^{-1}$) / $aCa^{0.5}$ ($mol.l^{-1}$)]

b: With Fe-oxalate included

$\log M_{Zn}$ ($mol.kg^{-1}$)= -0.80 ± 0.132 + 0.623 * pH + 0.329 * log Fe-ox ($mol.kg^{-1}$) + 0.69 * log CEC
+ 0.7 * log (aZn $mol.l^{-1}$)

4: Lead:

1: Only %OC, CEC in the model
$\log M_{Pb}$ ($mol.kg^{-1}$) = -3.55 + 0.624 * log (CEC) + 0.60 * pH
+ 0.462 * log (%OC) + 0.55 * log [aPb ($mol.l^{-1}$) / $aCa^{0.5}$ ($mol.l^{-1}$)]

2: With many solid parameters, based on new dataset

$\log M_{Pb}$ ($mol.kg^{-1}$) = -2.3 + 0.68 * log (%OM) + 0.58 * pH – 0.22 * log aCa ($mol.l^{-1}$)

$$-0.19 * \log(\%Clay) + 0.41 * \log(Al\text{-}ox,\ mol.kg^{-1}) + 0.6 * \log[\ aPb\ (mol.l^{-1})]$$

These relations are based on Dutch and/or UK soils and are not verified for any other part of the world. Also, many of these relations are based on only a very limited number of soils (e.g. cadmium, 14 soils) which makes them quite unreliable. It is therefore the aim to produce better relations for these elements, especially with respect to Slovakian and Hungarian soils, thus validating the relations for a much broader applicability.

A second flaw in the current relations is that they are based mainly on data which are gathered with pH values above 5 and below 7. Thus the calibrated pH dependency is only valid for a relatively small pH range. It is necessary to increase the pH range to make the transfer functions more generally applicable.

Finally, most of these relations are based on calculated activities of the elements studied (the activities are calculated with a speciation model).

A protocol for quantifying adsorption parameters.

Purpose of the study is to calibrate transfer functions (relation 2). Therefore it must be made certain that all (possibly) relevant parameters are measured. Furthermore, the relevant parameters should have a range which is big enough to ensure the possibility of fitting the coefficients of relation (2). Therefore, the following protocol is suggested:

1. Use 10 - 15 (12) soils with a variety of soil characteristics. Important variables to select the soils are: %OM, %clay, pH (water or KCl), Fe- and Al-oxide content and the metal content (EDTA extractable or 0.43 N HNO_3 extractable).
2. Since the competing cations are an essential part of the transfer functions, the concentration of the background electrolyte is an important variable. Also, the composition of the background electrolyte is extremely important. Therefore, use different concentrations of calcium nitrate. $Ca(NO_3)_2$ is chosen because the nitrate does not form any complexes with the heavy metals. Proposed electrolyte concentrations are: 0.002 M, 0.01 M and 0.05 M. This gives a range of a factor 25 in calcium concentration, and thus the background electrolyte effects can be quantified. Another advantage of using background electrolytes of Ca is that no large dispersion of humic acids occurs, and therefore the separation of liquid and solid after equilibration is much easier.
3. In the experiments, adjust pH with saturated $Ca(OH)_2$ (which is about 0.1 N OH^-) and 0.1 N HNO_3. This assures that no large quantities of other cations and/or anions enter the experiment.
4. Make a stock solution of 50 mg $Cd.l^{-1}$ and 400 mg $Cu.l^{-1}$ (both as nitrate) in 0.01 N HNO_3 (to prevent precipitation of metal oxides).
5. Make for each soil-electrolyte combination 16 centrifuge tubes with 10.0 g soil and 90 ml electrolyte, and equilibrate on a slow shaker overnight (at least 16 hours). The reason for this step is, that we work with dried soil samples. It is known from literature that re-wetting takes time. Therefore, the soils are pre-adjusted to the electrolyte. It is assumed that after overnight equilibration the soil is conditioned enough.

6. Split the tubes into 2 groups of 3 tubes. Now add of the stock metal solution (4) to group I nothing and group II 2 ml. Within each group, add to the first tube 2.5 ml 0.1 N HNO_3, to the second tube 1 ml 0.1 N HNO_3 and to the third tube nothing. Finally, adjust all volumes to 100 ml with the appropriate background electrolyte. The 2*3 design should assure a reasonable pH and metal concentration range in the final solutions. Equilibrate 24 hours at a constant temperature (20 degrees ?). Record the temperature.
7. Measure the pH in the tubes (this is the equilibrium pH), and Ec (conductivity).
8. Centrifuge and filter the liquids over 0.45 µm filter. The solutions should be split into 3 (2) portions: 1- About 25 ml for total Cd, Cu, Ca and Al (+ Mg, K, Na, Fe, Mn, S, P, Cl, NO_3) determination with ICP (AAS) measurement. The first four are essential information. Without these values it is impossible to use the results. The other elements are 'useful' information which might be of interest to quantify possible competition, and complexation. 2- About 20 ml for determination of TOC and IC (gives IC and DOC). This information is essential input for the speciation model. 3- About 50 ml for measurement of pCu with ISE. When the ISE method as described in the next chapter is not operational, the last portion can be skipped.
9. Storage of the samples: The sample for ICP/AAS can be stored and transported when strongly acidified (e.g. with 1 ml conc. HNO_3). The DOC sample (2) and the pCu sample (3) should not be acidified, and therefore, should be stored in the refrigerator, and analysed a.s.a.p.

This protocol gives for 12 soils a total of 216 samples to analyse (12 soils x 3 Ca levels x 3 pH levels x 2 metal concentration levels). The results should be sufficient to calibrate the transfer functions. The data can further be used to calculate DOC complexation constants for copper, when ISE measurements are performed. When Mg, K and Na are also measured, cation exchange coefficients for the soils (K-Gapon and/or K-Vanselov) can be calculated, which is useful model input for SEKTRAS.

A protocol for measuring Copper activity with an ISE.

In order to derive adsorption constants, free metal ion activities should be known. In case of Cd and Zn (where no reliable methods exist to determine those activities), this can be done reasonably well with a chemical speciation model (see the protocol described in Annex 5). In case of Cu and Pb, it is however to be preferred strongly to directly measure the activity of the free metal ion.

Copper can be measured with an Ion Selective Electrode (ISE). The use of these electrodes has been studied extensively (a/o Hansen, 1972, Avdeef, 1983, Sanders & Bloomfield (1981), Sanders (1982), Sauvé (1995)). For our protocol, especially the work of Avdeef (1983) is extremely important. The chosen method follows in broad lines the method described in that article.

The following equipment is used:

– a Metrohm combined glass electrode 6.0233.100 and

– a Metrohm Ion Selective Crystal Membrane Electrode Cu^{2+} 6.0502.140

However, other (combinations) of electrodes can also be used (see literature) and perform just as good. The copper electrode needs a reference electrode. The reference within the pH electrode is also used as reference for the copper electrode. This is essential, since otherwise no simultaneous measurements are possible. The copper electrode can best be used in a dark bottle/glass since the response is influenced by UV radiation.

The method uses ethylene-diamine (EN) for complexation of copper containing standard solutions. The total copper concentration used in the buffers equals 5.10^{-5} $mol.l^{-1}$, and an ethylenediamine concentration of 2.10^{-4} $mol.l^{-1}$ at different pH values. The following formula can be used to calculate the pCu of the mentioned ethylenediamine solutions:

For a solution of:
1) 0.2 *mmol* ethylenediamine/ l
2) 0.03 mol $NaNO_3$ / l and
3) 0.05 *mmol* $Cu(NO_3)_2$ / l

the pCu can be calculated ($5 < pH < 9$):

$$pCu = -21.7 + 4.72 * pH + (0.9*pH)/(pH-4) - 0.012335 * pH^3$$

pH has to be adjusted with 0.03 M HNO_3 or 0.03 N NaOH to keep ionic strength constant. The electrode is calibrated against different ethylenediamine solutions, and then used to measure soil solutions (about 5 minutes/sample, with total Cu concentration below 50 $\mu g.l^{-1}$ 10 minutes). After each soil solution a buffer with pH=7.32 is measured to give an indication of possible electrode drift. The copper activity can be measured down to pCu = 19. It is impossible to measure Cu activity when *total dissolved copper* falls below about 20 ppb (about 3.10^{-7} $mol.l^{-1}$), since the electrode doesn't give a meaningful response then. So before using the electrode with soil solutions, it is necessary to measure total dissolved copper with GFAAS or ICP, to insure that the total dissolved concentration is high enough to get a meaningful electrode response.

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Annex 7 Protocol for the determination of protonation and complexation constants for Dissolved Organic Carbon (DOC)

Introduction

Our goal is to describe metal binding to DOC that closely matches DOC from field samples. Therefore we do not extract DOC in a 0.1 N NaOH solution since this raises the extraction pH to 13 which has a profound effect on the chemical composition of the organic ligands extracted from soil. Instead we propose to use a mild extraction where pH does not exceed 8 (see section 'DOC extraction'). An inert background electrolyte is used (0.05 N $NaNO_3$) so that the ionic strength of various extracts is roughly the same. Further pretreatment steps such as acidification to pH 1 to separate humic from fulvic acids are not included either. An optional step is a purification step using cation resins in the Ca or Na form.

Two types of experiments are performed on the DOC to determine the total effective charge of DOC (see 'pH titration') and to determine the interaction between metals and DOC (i.e. Ca, Cu, Pb, Cd and Zn). In general, titrations are performed in solutions that contain approximately 150 – 250 mg $C.l^{-1}$. These solutions are prepared by dilution of the original stock solution using 0.05 N $NaNO_3$.

The further contents includes a description of:

- Model description
- DOC extraction from soils
- pH titration of DOC
- Titration of DOC with Ca
- Titration of DOC with Cu
- Titration of DOC with Cd, Zn, Pb and Ni (under construction)
- Derivation of complexation constants for metal-DOC interaction

Model description

In our model the dissociation of DOC is described by two reactive groups that roughly represent carboxyl and phenol type sites (Perdue, 1985):

$$H_2DOC \Leftrightarrow HDOC^- + H^+ \qquad pK_1 = \{3.5 - 4.8\} \qquad (2)$$

$$HDOC^- \Leftrightarrow DOC^{2-} + H^+ \qquad pK_2 = \{8.5 - 10.0) \qquad (3)$$

The titration curve of a bi-protic acid reveals two sharp buffering peaks whereas the heterogeneous composition of DOC in potentiometric titration curves is characterised by a rather smooth buffering curve. This points at the continuous dissociation of reactive groups that dissociate between pH 2 and 10 (De Wit, 1992). Therefore, the two-site DOC model cannot describe the dissociation behaviour correctly. Despite this limitation we feel that the discrete site approach still has its merits as a practical tool to describe metal binding to DOC. The approach was used previously to describe metal binding to SOM and DOC We use the apparent charge density from the potentiometric titrations for the conversion from gram carbon per liter to moles of charge. Based on the titration data, an average value of 10 meq.g^{-1} C was used which is close to previously reported values (Schecher and Driscoll, 1995). Metal complexation in solution for both Ca and Cu can be described by a 1:1 metal : ligand complex ratio for both reactive groups:

$$Me^{2+} + HDOC^{-} \Leftrightarrow MeHDOC^{+} \qquad pK_{Me-1} \tag{4}$$
$$Me^{2+} + DOC^{2-} \Leftrightarrow MeDOC^{0} \qquad pK_{Me-2} \tag{5}$$

The CHARON speciation program (De Rooij and Kroot, 1991) is used to calculate the speciation in solution. Aside from complexation with DOC, also inorganic complexation (NO_3^-, OH^-, CO_3^{2-}, HCO_3^-, and Cl^-) can be taken into account.

DOC extraction from soils

Stock solutions of DOC are prepared using 200 gram of air-dried, sieved (< 2 mm) soil that is equilibrated on a table-top shaker with 500 ml 0.05 N $NaNO_3$. Approximately 25 ml 0.05 N NaOH was added in portions of 1 ml to prevent extreme pH values in the supernatant (pH between 7 and 8). In total, the extraction equilibration lasts for 24 hours. Soil extracts are centrifuged at 3000 g for 30 minutes to remove all solid particles. The clear supernatant is filtered on a 0.4 µm Millipore GTTP filter. After filtration, aliquots of 0.05 N HNO_3 are added to bring the final solution pH down to 6.0 ± 0.1. Finally, small aliquots (< 2 ml) of a 2% NaN_3 solution are added to the stock solutions to prevent microbial degradation of DOC. Total- (TC) and inorganic carbon (IC) content of the extracts are measured on a Shimadzu Total Organic Carbon Analyser (TOC-500) immediately after extraction and prior to the experiments. DOC (calculated as TC–IC) concentrations in the extracts ranged from 600 to 1500 mg C.l^{-1}. Samples are stored in polypropylene bottles at 4°C until further use. Although the 'DOC' thus extracted is still not entirely equal to DOC present in soils, we feel that it bears a closer resemblance to DOC in soil solutions than purified humic or fulvic acids that have been subject to extreme chemical treatment (pH 0 to 14, drying and dissolution etc.).

pH titration of DOC

During the pH-titration, a solution is continuously stirred and N_2 gas is led through the reaction vessel. A solution (starting volume = ± 30 - 50 ml) that contains DOC (± 250 mg C.l^{-1}) is acidified to pH 3 using 0.05 N HNO_3. After stabilisation of the pH electrode, solution pH is slowly raised to 10 by addition of 50 µl aliquots of 0.05 N NaOH. Changes in pH are recorded after stabilisation of the pH electrode (drift of the pH electrode < 0.1 mV min^{-1}). In the concentration range studied, equilibration is usually reached within 5 minutes after base addition. Reversibility of the reaction is determined by back titration to pH 3 using 0.05 N HNO_3. Dilution of DOC concentration due to addition of acid/base during the titration has to be considered.

The apparent buffering capacity (in meq gC^{-1}) is calculated as the difference between the amount of H^+ or OH^- added and the amount needed to bring a blank solution (without DOC) to the same pH (pH 2.5 – 11.0). The values of pK_{a1} and pK_{a2} can be derived from the first derivative (α) of the amount of acid/base buffered between two points of the titration curve:

$$\alpha = \frac{d[\text{acid or base buffered}]}{d[\text{pH}]} \text{ (in meq g}^{-1}\text{ C)} \quad (1)$$

The values of $pK_{a\text{-}i}$ were derived from a graphical plot of α vs. pH (Baham and Sposito, 1986).

Titration of DOC with Ca

Derivation of standard curve for calcium

Ca activities in solution are measured with a Methrom Liquid Membrane ion selective electrode in combination with a Beckmann double junction reference electrode. The electrode shows a linear Nernstian response in the concentration range from $10^{-5.5}$ M to $10^{-1.5}$ M. Calibration curves can be obtained by addition of small aliquots of $Ca(NO_3)_2$ (from stock solutions of 10^{-3} M, 10^{-2} M and 10^{-1} M) to a solution containing 10^{-6} M $Ca(NO_3)_2$ and 0.05 M $NaNO_3$ as background electrolyte. The reaction vessel is continuously stirred with a magnetic stirring device, and the solution is kept oxygen-free by continuous bubbling with purified N_2. Calcium is added until the total Ca concentration approximately equals $10^{-1.5}$ M. The activity in solution is calculated using the Davies equation for correction of ionic strength. Complexation of Ca^{2+} with NO_3^- was taken into account. During the titration, the pH of the solution is maintained at 6.0 ± 0.1 by small (10 µl) additions of 0.05 N NaOH using an automated burette (Methrom).

Ca-DOC titrations

Two different experiments are performed to study calcium binding to DOC. The first experiment is a titration of solutions containing soil-derived DOC (150 – 250 mg $C.l^{-1}$) with $Ca(NO_3)_2$ similar to the approach described under Derivation of standard curve for calcium. The second experiment is a potentiometric titration of a solution with a fixed amount of DOC ($DOC_{soluition}$ approx. 200 mg $C.l^{-1}$) and Ca (ranging from 10^{-4} M to 10^{-3} M) between pH 3 and 10. The approach used here is similar to the one described under pH titration of DOC.

Titration of DOC with Cu

Derivation of Cu standard curve.

Avdeef et al. (1983) developed a method enabled them to measure Cu activity levels down 10^{-19} M. The approach is based on the addition of a strong complexing component (Ethylenediamine, EN) to a solution containing variable amounts of Cu. Complexation of EN with copper caused a decrease in the Cu activity down to 10^{-19} M at a copper total concentration of 10^{-6} M. The values of the stability constants of EN-Cu and H-EN complexes at I = 0 are shown in Table 2.

A calibration curve for Cu (pCu [10^{-13} to 10^{-5} M]) is obtained in a titration of a solution that contains $3.55{\cdot}10^{-4}$ M Ethylenediamine, $1.00{\cdot}10^{-6}$ M $Cu(NO_3)_2$ and 0.05 M $NaNO_3$. After an initial equilibration time of approximately 30 minutes the drift of the electrode is minimal (< 0.1 mV min^{-1}) and addition of copper is started. Copper is added in steps of 20 µl from an automated burette using 0.1 M $Cu(NO_3)_2$. Solution pH is measured simultaneously with an Orion pH electrode. The entire titration vessel is placed in a dark chamber. Addition of acid (0.05 N HNO_3) or base (0.05 N NaOH) is accomplished by an automatic burette. The solution is continuously stirred and bubbled with purified N_2 during the titration. The chemical equilibrium program CHARON (De Rooij and Kroot, 1991) is used to calculate the copper activity for each point of the titration curve. The electrode response in the calibration curve thus obtained, showed a Nernstian response from pCu 19 to pCu 5.

Values for logK^0 used to calculate Cu speciation in the EN-Cu titrations.

Component	Ionic strength (mol.l^{-1})	log K^0 (at 25 ° C)
ENH^+	0.092 – 0.286	10.008
ENH_2^{2+}	0.092 – 0.286	16.912
$EnCu^{2+}$	0.113 – 0.295	10.562
$Cu(EN)_2^{2+}$	0.113 – 0.295	19.646

Cu-DOC titrations.

Solutions containing DOC were titrated between pH 2.0 and 7.5 as described in the section on Ca-DOC titrations. No copper was added to the soil derived DOC solution. In order to obtain reliable Copper readings using the ISE, the total dissolved Copper concentration should at least be $10^{-6.8}$ to 10^{-6} M (between 10 and 64 µg.l^{-1}).

Titration of DOC with Pb, Cd, Zn, and Ni (under construction)

The method described earlier for copper is being tested for Pb, but currently no results are available. As of now, no reliable ISE exists for Ni and Zn, and the one for Cd is not suitable for complexation studies due to the relatively high solubility of CdS (compared to CuS). This implies that Cd activities can be measured only at high Cd activity levels ($Cd^{2+} > 10^{-4}$ M). Other methods to measure Cd and Zn activities involve cation exchange resins or membrane technology.

Derivation of complexation constants for metal-DOC interaction

The titrations described earlier enable us to derive the appropriate complexation constants by fitting the data to the previously defined model concept (two-pK model). The required input includes:

- total DOC level
- charge density of DOC (meq g^{-1} C)
- total dissolved metal concentration (measured by AAS, ICP or otherwise)
- measured metal activity (by ISE)
- pH
- total concentration of other ligands that form complexes with the metal of interest (e.g. Cl)
- Existing models such as FITEQL are available that are able to give estimates of the values of $\log K_{Me\text{-}DOC}$.

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