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Heavy metals in Dutch field soils: an experimental and theoretical study on equilibrium partitioning

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CONTENTS

ABSTRACT

The prediction of the effects of metals on biotic species, communities and ecosystems is at present seriously hampered by a lack of (quantitative) understanding of the factors that modulate metal bioavailability. Bioavailability needs to be dealt with as a dynamic process, comprising a physico-chemically driven desorption process, and a physiologically driven uptake process. In this report the physico-chemical aspects of bioavailability in a typical Dutch field situation are studied. 49 Dutch soils, selected with the aim of covering a wide range of soil types occurring in the Netherlands, were sampled and the partitioning of 6 metals (Cd, Cr, Cu, Ni, Pb, Zn) and the metalloid As over the soil solid matrix and the pore water was studied. The main soil characteristics determining metal partitioning were quantified and statistical models were derived to describe the partitioning process on the basis of a limited number of easily determinable soil properties. As there is evidence for predominant pore water uptake of metals by organisms living in the soil, the models thus derived provide the first step in predicting the availability for uptake, and hence prediction of toxic effects, of the metals studied.

SUMMARY

The prediction of the effects of metals on biotic species, communities and ecosystems is at present seriously hampered by a lack of (quantitative) understanding of the factors that modulate metal bioavailability. Bioavailability needs to be dealt with as a dynamic process, comprising a physico-chemically driven desorption process, and a physiologically driven uptake process. In this report the physico-chemical aspects of bioavailability in a typical Dutch field situation are studied. 49 Dutch soils, selected with the aim of covering a wide range of soil types occurring in the Netherlands, were sampled and the partitioning of 6 metals (Cd, Cr, Cu, Ni, Pb, Zn) and the metalloid As over the soil solid matrix and the pore water was studied. The main soil characteristics determining metal partitioning were quantified and models were derived to describe the partitioning process on the basis of a limited number of easily determinable soil properties. As there is evidence for predominant pore water uptake of metals by organisms living in the soil, the models thus derived provide the first step in predicting the availability for uptake, and hence prediction of toxic effects, of the metals studied.

Experimentally determined partition coefficients are shown to vary strongly, both among soils and among metals. Addition of metal salts is shown to increase the bioavailability of the metals added; with the exception of arsenic, metal partitioning can be quantified by models that combine one or more of the metal binding soil phases, like amorphous iron- and aluminumoxy-hydroxide, organic matter and clay, and one of the soil characteristics that modulate metal partitioning. Especially soil pH is a dominant factor in this respect, as it was found that pH explained a high percentage of the variation in the values of the partition coefficients (K_p) for all metals.

The best models were obtained for K_p-values that are based upon total metal concentrations in both the soil solid phase and the pore water; in general in between 70 and 90 % of the data variance was explained. The standard errors of prediction K_p-values are in the range of a factor of 2 - 3 in an absolute sense. As this is in line with experimental uncertainties in determining K_p, this is quite acceptable. The explained variance was significantly increased by taking the activity of the free metal ion into account. Thereupon it was found that metal partitioning in soils containing carbonate as an additional sorption phase differs significantly from metal partitioning in soils that do not contain detectable carbonate levels. Exclusion of the carbonate containing soils further increased the predictive capability of the models thus derived.

SAMENVATTING

Het kwantificeren van het effect van metalen op organisme-, populatie- en ecosysteem-niveau wordt op dit moment bemoeilijkt door een gebrek aan kennis over de factoren die de biobeschikbaarheid van de metalen bepalen. Bij het in kaart brengen van deze factoren is het van belang om rekening te houden met het feit dat biobeschikbaarheid beschouwd dient te worden als een dynamisch proces dat zowel fysisch-chemische alsook fysiologische aspecten omvat. In dit rapport zijn de fysisch-chemische aspecten van biobeschikbaarheid voor de Nederlandse veldsituatie bestudeerd. Dit is gedaan aan de hand van een bemonstering van 49 landbodems, die werden geselecteerd met het primaire doel om een dwarsdoorsnede te verkrijgen van de verschillende bodemtypes die in Nederland voorkomen. Na bemonstering is de verdeling van 6 metalen (Cd, Cr, Cu, Ni, Pb, Zn) en het metalloïde As over de vaste bodemmatrix en het poriewater bestudeerd. De belangrijkste bodemeigenschappen waarvan verondersteld wordt dat zij het partitiegedrag beïnvloeden, zijn voor elke bodem gekwantificeerd en modellen zijn afgeleid voor het beschrijven van het partitieproces op basis van een aantal eenvoudig te bepalen bodemeigenschappen. De modellen zijn geschikt voor het berekenen van metaalgehaltes in het poriewater. Aangezien de meeste organismen die in de bodem leven, metalen via het poriewater opnemen zijn de modellen bruikbaar voor het voorspellen van de beschikbaarheid van metalen voor opname door deze organismen.

De in het rapport gepresenteerde resultaten laten zien dat gemeten partitiecoëfficiënten sterk verschillen tussen zowel bodems onderling als tussen de verschillende metalen. Het in het laboratorium toevoegen van metaalzouten verhoogt de biobeschikbaarheid van metalen. Verder wordt aangetoond dat, met uitzondering van arseen, metaalpartitie kan worden gekwantificeerd middels modellen die een combinatie zijn van een of meerdere van de metaalbindende bodembestanddelen (zoals bijvoorbeeld amorf ijzer- en aluminiumoxide, organisch koolstof en klei), en één van de bodemeigenschappen die metaalpartitie moduleren. Met name de pH van de bodem is in deze een belangrijke factor en een groot gedeelte van de variantie in de partitiedata kon dan ook met behulp van de pH worden verklaard.

De beste modellen werden verkregen voor partitiecoëfficiënten die gebaseerd zijn op totaalgehaltes in zowel de vaste fase als in het poriewater. In het algemeen kon tussen de 70 en 90 % van de variantie in deze partitiecoëfficiënten worden verklaard, met een absolute fout in de voorspelde K_p-waardes van een factor 2 - 3. Aangezien dit overeenkomt met de experimentele onzekerheid bij het bepalen van partitiecoëfficiënten, is deze marge acceptabel. De verklaarde variantie werd significant verbeterd door in plaats van het totaalgehalte in het poriewater de (berekende) activiteit van het vrije metaalion in het poriewater als basis voor de berekening van de partitiecoëfficiënten te nemen.

Tenslotte kon worden waargenomen dat metaalpartitie in bodems die carbonaat als extra metaal-adsorberende bodemfase bevatten, significant afwijkt van metaalpartitie in bodems waarin geen detecteerbare carbonaatgehaltes aanwezig zijn. Het niet meenemen van de carbonaat-bevattende bodems in de statistische analyse leidde dan ook tot een aanzienlijke verhoging van het voorspellend vermogen van de ontwikkelde partitiemodellen.

1 INTRODUCTION

1.1 General

Environmental quality objectives for toxic substances are derived on the basis of risk considerations, where "risk" usually has the meaning of the extent of an adverse effect. It is the purpose of ecotoxicological risk assessment to distinguish between soils or sediments that will or will not produce effects. In the case of metals, total concentrations in soils and sediments commonly span several orders of magnitude. Organisms, however, do not respond to total concentrations, and hence soil quality criteria that are based on total concentrations are unlikely to be predictive of adverse biological effects. The total amount of a substance may not be toxicologically meaningful as it may partly be non-available for uptake by organisms. This would not be important as long as availability would be a constant factor. This, however, is not the case and it is the variation in some crucial soil properties that results in a substantially different availability for uptake of compounds by organisms in different soils. This variation should be taken into account to improve the accuracy in predicting (no) effects. For hydrophobic organic compounds this has to a large extend been achieved by developing and validating a procedure for normalisation of the contaminant concentration to the amount of particulate organic carbon present in the system (DiToro *et al.*, 1991, Belfroid *et al.*, 1996).

Especially in the case of soils there has been little consideration of the factors that modulate the bioavailability of metals. In this respect it is necessary to develop methods which contain qualitative and quantitative descriptions of differences in bioavailability:

- Between soils typically used for laboratory testing and field soils.
- Between contaminated and non-contaminated (natural background) soils.
- Among contaminated field soils.

It should be noted that (bio)availability needs to be dealt with as a dynamic process, comprising at least two distinct phases: a physico-chemically driven desorption process, and a physiologically driven uptake process requiring identification of specific biotic species as endpoint (Peijnenburg *et al.*, 1997). As shown by Van Wensem *et al.* (1994) and Van Straalen (1996) it eventually is the body concentration that is critical in many organisms, as this is directly related with organ-effect levels. Soil organisms potentially have different uptake routes. It is thought that most organisms which live *in* the soil (i.e. including plants) are primarily exposed via pore water (e.g., Allen *et al.* (1993), and references cited therein), organisms which live *on* the soil are exposed indirectly via their food. There is evidence for predominant pore water uptake of organic substances by soft-bodied animals, but due to their complex physico-chemical behaviour such evidence is at present only circumstantial for metals (Spurgeon and Hopkin, 1996; Belfroid, 1994). Free metal ions in pore water are often considered to be the toxic species that can actually be taken up by organisms. Clearly, both abiotic (soil characteristics) and biotic (species-dependent) aspects determine "bioavailability".

In the Netherlands, maximum permissible and negligible concentrations (MPCs and NCs, respectively) for metals were first derived by Van de Meent *et al.* (1990) on the basis of the available ecotoxicological information without taking into account that metals are naturally present in the different environmental compartments. In most cases the methodology resulted in MPCs and/or NCs lower than what was considered the natural background situation. In those cases the environmental quality objectives were set equal to the background concentration, but this was not considered as an acceptable solution at the longer term. It was later realised that in the methodology proposed by Van de Meent *et al.* (1990), some additional discrepancies were present, as differences in bioavailability were insufficiently taken into account, and as no attention was paid to the fact that some metals are essential for optimal functioning of living organisms.

As a first step towards solving the methodological problems identified, the so-called "added risk approach" was proposed by Struijs *et al.* (1997) and implemented by Crommentuijn *et al.* (1997) for the calculation of maximum permissible concentrations and negligible concentrations, taking existing background concentrations in the Netherlands into account. The starting point for this approach is the calculation of a maximum permissible addition (MPA) on the basis of data from laboratory toxicity tests. This MPA is considered as the maximum concentration on top of the background concentration due to anthropogenic activities, taking the effects of the bioavailable fraction of the metals in the background into account. In the added risk approach, fixed values are used to correct for differences in (bio)availability of the metal under consideration. It was, however, recognised that it is necessary to derive and validate methods for calculating and measuring potentially and actually bioavailable metal concentrations in soils to enable a more realistic estimate of the risks imposed by heavy metals in the near future. Amongst others, a definition study was therefore carried out by De Rooij *et al.* (1997), aimed at the development of an improved methodology for the determination of heavy metal standards. In addition to a feasibility assessment for such a methodology, a research and development programme was initiated (De Rooij *et al.*, 1998). This programme encompasses the development of empirical models relating actually available metal concentrations to potentially available fractions, methods for measuring these concentrations, procedures for extrapolation of data, as well as an uptake model which relates actually bioavailable metal concentrations to the concentrations in (a number of test) organisms. The programme is anticipated to be based upon a selection of field soil samples, selected with the aim of covering a wide range of soil types occurring in the Netherlands. The results of initial studies carried out by Van den Hoop *et al.* (1995), and Janssen *et al.* (1996) on metal partitioning in unpolluted (heavy metals at background levels) and moderately contaminated Dutch field soils were used in the design of the improved methodology for the determination of heavy metal standards.

1.2 Equilibrium partitioning

As a large fraction of soil organisms is directly or indirectly exposed via the pore water, and as metal concentrations and metal activities in the pore water are dependent upon both the metal concentration in the solid phase and the composition of both the solid and the liquid phase, it is of great practical interest and importance to have a quantitative understanding of the distribution of heavy metals over the solid phase and pore water in soils. A relatively simple approach for calculating the distribution of heavy metals in soils is the so-called equilibrium partitioning (EP) concept (Shea, 1988; Van der Kooij *et al.*, 1991). The EP concept assumes that chemical concentrations among environmental compartments are at equilibrium and that the partitioning of metals among environmental compartments can be predicted based on partition coefficients. The partition coefficient, K_p, used to calculate the distribution of heavy metals over solid phase and pore water is defined as:

$$K_p = \frac{[Metal]_{solid\,phase}}{[Metal]_{pore\,water}} \quad (l/kg) \qquad (1)$$

K_p is not a constant and may vary of several orders of magnitude. It is affected by element properties and both solid phase and pore water characteristics. Knowledge of the relationship between soil characteristics and K_p values enables a calculation of the distribution of heavy metals over the solid phase and pore water for different soils. When coupled to an uptake model for metals by biota that are directly or indirectly exposed via the pore water, the relationships for predicting K_p values may be used to predict metal uptake for these organisms on the basis of the metal concentration in the solid phase, a property that in general is relatively easily determinable. It should be noted that in the formula for calculating K_p, several expressions for the metal concentrations in the pore water and in the solid phase may be used. In this study, metal levels in the pore water are expressed in terms of total concentrations, thereupon the calculated metal activities are used as the denominator in equation 1. Metal concentrations in the nominator are expressed in terms of total concentrations obtained after digestion of the soil matrix with either *aqua regia* or concentrated nitric acid. Thereupon 0.01 *M* $CaCl_2$-extraction was used as an expression of metal levels in the solid phase.

1.3 Aim of this report

The main aim is to provide additional experimental data on *in-situ* partitioning of 6 metals (Cd, Cr, Cu, Ni, Pb, and Zn) and As in Dutch field soils, to be used in the validation and extrapolation stages of the research and development programme proposed by De Rooij *et al.* (1997). The data collected will in part supplement the database on metal partitioning in Dutch field soils that was established by Van den Hoop (1995), and Janssen *et al.* (1996), and will provide the basis for deriving a bioavailability model for organisms predominantly exposed via the pore water. In addition to data on metal partitioning, the study was aimed at determining a number of soil and pore water characteristics expected to influence metal partitioning. To that end, 46 sites were selected for the sampling campaign. In order to get insight into possible changes of metal partitioning over time, the 46 sites selected encompass the 20 soils sampled by Janssen *et al.*, as well as 3 out of the 13 soils sampled by Van den Hoop (1995). For reference purposes, OECD-artisoil (OECD, 1984) was included in the dataset, and for one soil duplicate sampling was carried out to get insight into the reproducibility of the experimental procedures. OECD-artisoil is an artificial soil that is regularly used in toxicity studies, and was included in the dataset to enable comparison of metal partition in this artificial soil to partitioning in the field, with the aim of investigating possibilities to extrapolate results of toxicity and partitioning studies carried out in a typical lab setting, to realistic field conditions. With the aim of getting insight into differences in metal partitioning of (aged) field soil samples and samples to which metals salts were added shortly before analysis, the final number of 49 soil samples was obtained by addition of an aqueous solution of metal salts to one of the field soil samples collected. It should be noted that although in this report often is referred to a sampling campaign of “Dutch” field soils, also two samples taken from a highly polluted site in Belgium (Maatheide), and one sample taken in Germany are included in the dataset. As the latter sample was expected to contain high natural lead levels, these three samples significantly broaden the range of metal levels included in this study.

A secondary aim of the study reported here was to derive models for predicting metal partitioning in Dutch soils, based upon easily determinable soil and pore water characteristics. The multivariate regression models are aimed to be used to predict metal pore water levels or, preferably, metal activities in the pore water, on the basis of easily determinable total metal concentrations in the solid matrix and a limited number of soil characteristics. The results obtained need to be regarded as a first attempt towards deriving bioavailability models for orga-

nisms exposed via pore water and will be further extended according to the research and development program mentioned above (De Rooij *et al.*, 1998).
Within the concept of bioavailability, it is important to develop methods for calculating the non-available fraction of the metals present in the soil matrix. The difference in metal levels found between on the one hand either digestion of the soil matrix with *aqua regia* or concentrated nitric acid, and on the other hand 0.01 M $CaCl_2$-extraction may give a first, pragmatic, indication of the immobile or non-available metal fraction. In this report models are presented for calculating the non-available fraction thus defined.

The methodological details are described in chapter 2 of this report, whereas the results of the sampling campaign are shown in chapter 3. In chapter 4 the relations between the soil characteristics are presented, whereas the partitioning models derived for each of the metals included in the sampling campaign are given in chapter 5. Finally, the main conclusions that can be drawn from this study and some additional recommendations are given in chapter 6.

2 EXPERIMENTAL: METHODS AND MATERIALS

2.1 Soil sampling

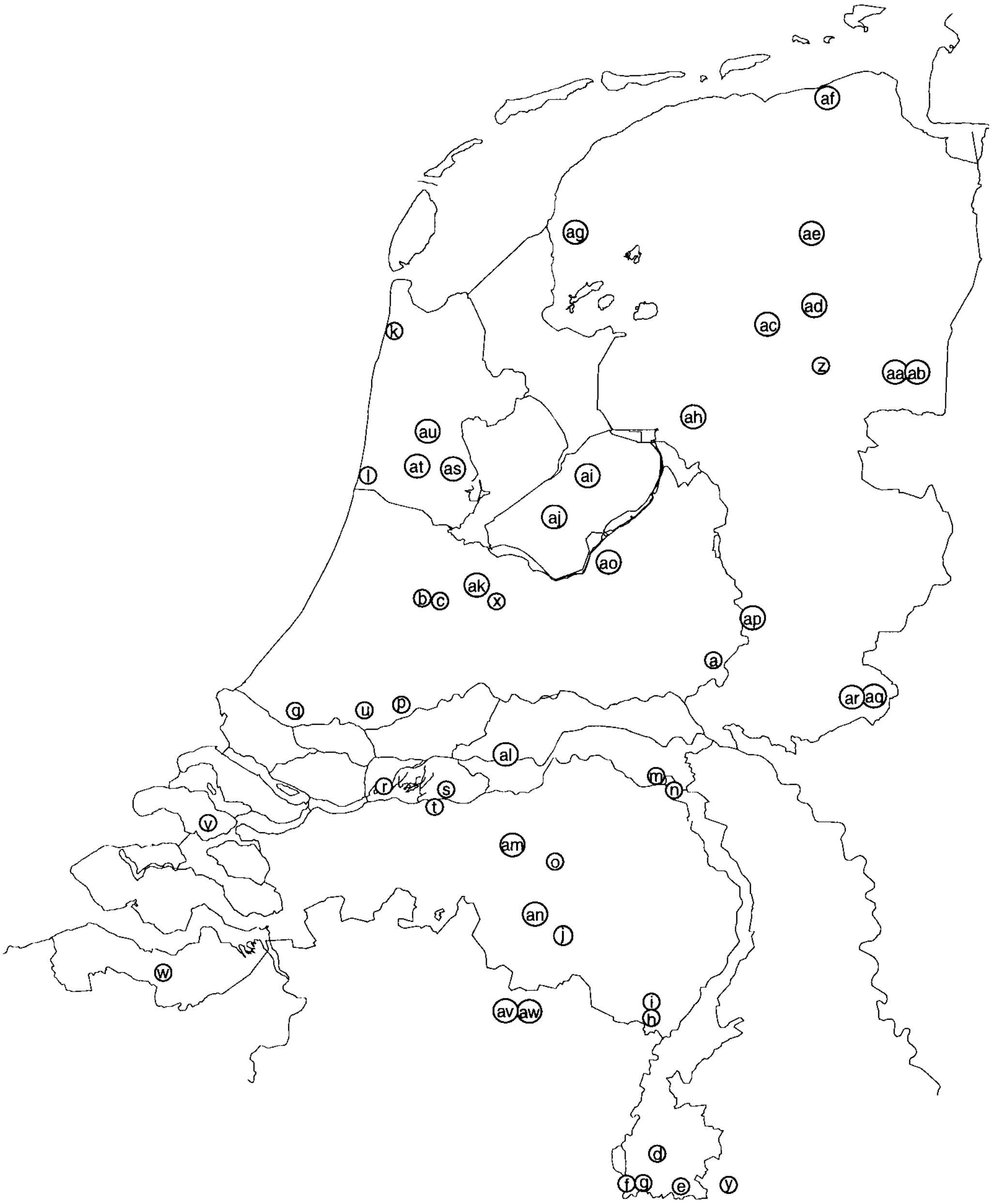

Figure 2.1 Map of the Netherlands showing the locations of the sampling sites. For site codes see Table 2.1.

Between September and December 1997, soil samples were collected at 46 different sites. 43 of these were located in the Netherlands, two Belgian sites (both located at Maatheide, one of which was highly polluted), and one German site (Stolberg, a site expected to contain relatively high background levels of lead) were also sampled. Thereupon, the sampling procedure was duplicated at the sites 'Veenoord' and 'Winterswijk'. To one of the latter samples (the sample encoded AR), an aqueous solution of a mixture of metal salts was added. Similarly, an aqueous solution of a mixture of metal salts was added to the OECD-artisoil (sample X). Figure 2.1 shows the locations sampled, whereas the site codes are given in Table 2.1. The soils were classified according to the Dutch classification scheme (Kuipers, 1984), in which a soil containing less than 8 % clay is classified as a sandy soil. Soil is classified as light clay in case of a clay content in between 8 and 35 %, and as a heavy clay in case the clay content exceeds 35 %. A humus poor soil contains less than 2.5 % OM and a humic soil in between 2.5 and 15 % OM.

Table 2.1 Codes, locations and main sources of metal pollution (when appropriate) of the sites sampled.

Site code	Location	Main source of metals	Soil type
A	Rozendaal	Secondary lead smelter	Sandy soil, humus poor
B	Woerden	Moterway traffic	Heavy clay soil, humic
C	Woerden	Railway	Heavy clay soil, humic
D	Houthem, river bank (De Geul)	Lead/zink mining	Light clay soil, humic
E	Epen, river bank (De Geul)	Lead/zink mining	Light clay soil, humic
F	Eijsden	Zinc oxide factory	Light clay soil, humic
G	Eijsden, river bank (De Maas)	Sources upstream	Light clay soil, humic
H	Budel	Zinc factory	Sandy soil, humus poor
I	Budel	Zinc factory	Sandy soil, humic
J	Valkenswaard, river bank (De Dommel)	Sources upstream	Sandy soil, humic
K	Callantsoog	Former shooting range	Sandy soil, humus poor
L	Wijk aan Zee	Blast-furnace steelworks	Sandy soil, humic
M	Heumen	Power line pylon	Sandy soil, humus poor
N	Mook	Zinc plating factory	Sandy soil, humus poor
O	Boxtel, river bank (De Dommel)	Sources upstream	Sandy soil, humic
P	Bergambacht, river bank (De Lek)	Sources upstream	Sandy soil, humic
Q	Vlaardingen	Waste incinerator	Light clay soil, humic
R	Kop van het Land, river bank (Merwede)	Sources upstream	Light clay soil, humic
S	Hank, estuarine river bank (Biesbos)	Sources upstream	Light clay soil, humic
T	Drimmelen, river bank (Amer)	Sources upstream	Sandy soil, humic
U	Ouderkerk a/d ijssel		Light clay soil, humic
V	Nieuwerkerk		Light clay soil, humic
W	Sluiskil		Light clay soil, humic
X	OECD	Metals added in the laboratory	Light clay soil, humic
Y	Stolberg (D)	Natural lead background at elevated level	Light clay soil, humic
Z	Stuifzand		Sandy soil, humic
AA	Veenoord	Galvanisation factory	Sandy soil, humic
AB	Veenoord	Galvanisation factory, duplicate of AA	Sandy soil, humic
AC	Lheebroekerzand		Sandy soil, humic
AD	Westerbork		Sandy soil, humic
AE	Norgerholt		Sandy soil, humic
AF	Noord Polder		Sandy soil, humus poor
AG	Schraard		Heavy clay soil, humic
AH	Genemuiden		Light clay soil, humic
AI	Larserbos		Light clay soil,humic
AJ	Zenderpark		Sandy soil, humus poor
AK	Maarssen	Galvanisation factory	Sandy soil, humic
AL	Eendenkooi	Natural zinc background	Heavy clay soil, humic
AM	Zandelei		Sandy soil humic
AN	Knegsel		Sandy soil, humic
AO	Ermelo		Sandy soil, humic
AP	Zutphen		Sandy soil, humic
AQ	Winterswijk geaddeerd	Metals added to sample AR	Sandy soil, humic
AR	Winterswijk		Sandy soil, humic
AS	Purmerend		Sandy soil, humic
AT	Krommenie		Sandy soil, humic
AU	De Rijp		Light clay soil, humic
AV	Maatheide (B)	Former zinc smelter	Sandy soil, humus poor
AW	Maatheide (B)	Former zinc smelter	Sandy soil, humic

The criteria used for the selection of sampling sites were: (i) cover both elevated metal concentrations and metal levels in soils considered to contain metals at natural background concentrations, (ii) little or no impact from agricultural practices, (iii) to a certain extent cover the Netherlands in a geographical sense, and (iv) the soil characteristics had to vary amongst sites. To get insight into time related changes of metal partitioning in undisturbed and slightly polluted soils, the 20 sites sampled by Janssen *et al.* (1996), and 3 sites sampled by van den Hoop (Lheebroekerzand (AC), Norgerholt (AE), Eendenkooi (AL)) were re-sampled.

2.2 Pre-treatment of the soils

At each site the upper litter or grass layer was removed and a total of 30 L of soil from the top layer (0-20 cm) was collected. The samples were transferred to the laboratory and stored in three 10 L polyethylene containers at 5 ^{0}C for further handling and analysis.

All roots present in the samples were removed in the laboratory and agglomerates were broken by hand or machine. Particles larger than 4 mm were removed by sieving, after which the remaining soil was homogenized. One third of the soil material collected was used for further pretreatment to enable chemical analyses, the remaining soil material was stored at 5 ^{0}C.

The soil material to be used for chemical analyses was air-dried, particles lager than 2 mm were removed by sieving, and the remaining soil was stored at room temperature. The moisture content of air-dry soil was determined from the weight loss of approximately 10 g of soil heated at 105 ^{0}C for about 12 hours.

2.3 Collection of pore water

For pragmatic reasons, a somewhat modified procedure was applied for the collection of pore water, as compared to the procedure used by Janssen *et al.*. For pragmatic reasons (collection of sufficient amounts of pore water, even for relatively dry soils), an electrolyte solution (2 m*M* $Ca(NO_3)_2$) was added to the soils prior to centrifugation: Two kg of soil of each location were moistened with a 2 m*M* solution of $Ca(NO_3)_2$ to get a pF-value of 2. Subsequently the soils were stored for three weeks at 5 ^{0}C (Houba and Novozamsky, 1997). After this equilibrium period, pore water was obtained by centrifugation of the soils at 7500 rpm (6000 g) at 5 °C. Centrifugation was continued until about 150 mL of pore water was collected. If insufficient quantities of pore water could be collected, another portion of two kg of soil was centrifuged. After centrifugation, the pore water collected was filtered over a 0.45 μm pore size filter, and the pH was measured (pH(pw)). The percentage of pore water collected, as related to the moisture content of the soil ranged from 2 to 76 percent (w/w).

The pore water collected was divided over two polyethylene bottles: One bottle of 30 ml of pore water was acidified with concentrated nitric acid to set the pH to 2, and used for metal analyses. The second bottle of 100 ml pore water was used for the determination of anions, pH and DOC.

2.4 Extractions and digestion

$CaCl_2$ extraction

Ca. 10.0 g of air-dry soil was weighed into a 250 ml plastic bottle and 100 ml of a 0.01 *M* $CaCl_2$ solution was added to each bottle. The bottles were shaken for about 24 hours at 150 rpm. The supernatants were passed through a 0.45 μm filter. The pH in the extracts was measured (pH($CaCl_2$)) and the extracts were acidified with concentrated nitric acid to set the pH to 2, prior to metal analysis. Four blanks were prepared and treated in the same way as the soil samples.

Nitric acid digestion

Ca. 0.2 g of ground air-dry soil was weighed into a microwave digestion bomb and 4 ml concentrated nitric acid were added to each bomb. The soil samples were digested in a microwave oven (CEM corporation-MDS 2000) for 30 minutes at 180 psi. After the samples were cooled, the solution was quantitatively transferred into a volumetric flask, diluted to a final volume of 50 mL with milli-Q water, and passed through a 0.45 μm filter. For reference purposes, seven blanks and seven standard soils were digested simultaneously.

Aqua regia digestion

Ca. 1.0 g of ground air-dry soil was weighed into a microwave digestion bomb and 4 ml concentrated nitric acid and 12 ml concentrated hydrochloric acid were added to each bomb. The soil samples were digested in a microwave oven (CEM corporation-MDS 2000) for 1 hour at 180 psi. Following cooling of the samples, the solution was quantitatively transferred into a volumetric flask and diluted to a final volume of 100 mL with milli-Q water. This solution was passed through a 0.45 µm filter. For reference purposes, seven blanks and seven standard soils were digested simultaneously.

Ammonium oxalate - oxalic acid extraction

Ca. 1.0 g of air-dry soil was weighed into a 250 ml plastic bottle and 60 ml of a 0.175 *M* ammonium oxalate-0.1 *M* oxalic acid solution was added to each bottle (Sparks *et al.*, 1996). The bottles were shaken in the dark for two hours at room temperature. The supernatants were passed through a 0.45 µm filter. Three blanks were prepared and treated in the same way as the soil samples.

2.5 Chemical analysis

Pore water

cations

The pore water cation concentrations were obtained for several elements. Cd, Cr, Ni and Pb were analysed by graphite furnace AAS (Perkin Elmer-4100 and Zeeman background correction). Cu and Zn were analysed by flame AAS (Perkin Elmer-2100 and deuterium background correction). As was analysed by FI-AAS (Perkin Elmer-2100, with FIAS-200). Ca, Mg, Na, K, Zn, Fe, Mn, Al were analysed by ICP-AES (Spectro Analytical Instruments).

anions

The pore water was analysed for the following anions: Cl^-, $NO_3^-$and SO_4^{3-} (all determined by ion chromatography), and PO_4^{3-} (continuous flow analysis).

Dissolved organic carbon

Dissolved organic carbon (DOC) was determined with a Dohrmann DC-190, TOC-analyzer.

Extracts and digests

The $CaCl_2$-extracts (as a matter of course with the exception of Ca), and the HNO_3- and *aqua regia*-digests were analysed for the same cations as the pore water. The ammonium oxalate - oxalic acid extracts were analysed for Al and Fe by ICP-AES.

2.6 Characterisation of the solid phase

The soils have been characterised in terms of pH(pw), pH(KCl), pH($CaCl_2$), loss-on-ignition (indicated as: LOI, in units of: %), organic carbon content (OC, %), clay content (clay, %), granules between 2 and 38 µm (fraction, %), cation exchange capacity (CEC, $cmol.kg^{-1}$), and amount of Al-/Fe-oxyhydroxides (Al-ox and Fe-ox respectively, $mmol.kg^{-1}$). Only for soils exceeding pH($CaCl_2$) = 5.5, the carbonate content was determined with an Element Analyzer (Model EA 1108, Fisons Instruments) after heating at 450°C for 3 hours.

Two expressions of LOI were obtained: LOI-1 and LOI-2 respectively. LOI-1 is considered representative of the organic matter content of the solid phase and was determined from the weight loss of approximately 5 g of dried soil (105°C), heated at 550°C for 3 hours. LOI-2 is considered representative of the inorganic matter content of the solid phase and was determined from the weight loss of the sample used for determining LOI-1, after additional heating at 900°C for 3 hours. The carbon and nitrogen content were determined with an Element Analyzer (Model EA 1108, Fisons Instruments). The organic matter content (OM, %) was calculated from the carbon content by multiplying with a value of 1.7. pH(pw) was determined directly in the pore water. pH(KCl) was determined at a 2:5 soil:liquid ratio (w/v) with 1 *M* KCl. pH($CaCl_2$) was determined in the 0.01 *M* $CaCl_2$ extract. CEC of the soil was determined in an unbuffered $BaCl_2$ extract (based on NEN 5780). The amount of soil that was used for the determination of CEC was made soil-type dependent: 20 g of air-dried soil material was used for sandy soils, and 7 g of air-dried material for the remaining soils was weighed into a centrifuge tube. Several portions of 100 mL of 0.5 *M* $BaCl_2$ were added, the suspension was shaken for 1 hour and the cation exchange sites were loaded with Ba. Eventually, 100.0 ml 0.02 *M* $MgSO_4$ was added upon which $BaSO_4$ precipitated and the cation exchange complex was fully occupied by Mg. The amount of Mg which remained in the supernatant was determined with capillary zone electrophoresis. The CEC was calculated from the difference between the added amount of Mg and the amount of Mg determined in the extract. The clay content was determined according to NEN 5753.

2.7 Chemical speciation calculations

The different forms (species) in which heavy metal ions (Me) and other ions may be present in the pore waters (i.e., Me^{2+}, $MeCl^+$, $MeOH^+$, $Fe(OH)^{2+}$, $CaNO_3^+$, $MgHCO_3^+$, $Al(OH)^{2+}$, HCO_3^-, MeDOC, etc.), were calculated by chemical speciation calculations using the MINTEQ program (Allison *et al.*, 1991). Next to the measured pore water characteristics (DOC, cation- and anion concentrations, and pH), the following provisions were made before MINTEQ calculations were executed:

1. Chemical equilibrium constants between many of the possible inorganic species that may occur in water solutions were taken from the NIST database (1993).
2. According to program characteristics, MINTEQ was allowed to predict precipitation, which implies that finely dispersed particles may be formed under the prevailing conditions. In that case, pore water metal concentrations are lower than under non-precipitative conditions.
3. The average binding site concentrations of the DOC, relevant for the degree of metal complexation, were calculated by the RANDOM program (Murray and Linder, 1983; Woollaard, 1995), under the assumptions of Pretorius *et al.* (1996) on the composition and functional group content of the DOC:
   - (i) all DOC is present as humic and fulvic type materials
   - (ii) only R-COOH, R-OH, Ø-COOH and Ø-OH are available to form binding sites
   - (iii) average values for elemental composition and function contents is representative of the DOC in the samples.

   Ligands binding less than 1% metal at each pH value were disregarded. The eight remaining ligands were: malic acid, acetylacetone, catechol, succinic acid, 2-hydroxy-2-methylpropionic acid, phthalic acid and propionic acid.
4. The influence on metal speciation of the redox potential (*pe*), which was not measured in the pore waters, was assumed to be negligible in view of simulation results obtained for each soil using the lower and upper limits for (*pe*+pH) (Lindsay, 1979). The redox potential is important for Fe(II)/Fe(III) equilibria and for the formation and dissolution of ferric precipitates. Especially for soils having a relatively high pH($CaCl_2$), precipitation potential was found. Amongst others, chloropyromorphite ($Pb_5(PO_4)_3Cl$), octavite ($CdCO_3$),

and malachite ($Cu(OH)_2.CuCO_3$) were predicted to be formed. These precipitates could play a role in controlling the solubility of the cations involved.

Speciation calculations were carried out for all metals included in this study; insufficient data were available for As.

2.8 Principal Component Analysis (PCA) and Partial Least Squares (PLS)

Principal component analysis (PCA) was used to determine meaningful patterns among the soils and relations between the soil characteristics. Details of this method are provided by Geladi and Kowalski (1986). Geometrically the data points can be represented as points in a multidimensional space with the variables as axes (in our case the soil characteristics). Distances and clusterings of points can be interpreted as similarities and dissimilarities among the objects. PCA calculates vectors (principal components) which fit best through the multidimensional data points. The first principal component is the vector of best fit for the data points. Subsequently, principal components can be calculated orthogonal to each other creating a plane or hyperplane and retain increasingly smaller R^2. To get an overview of the data set, a few (2 or 3) principal components are often sufficient. Subsequently identified principal components are characterised by a decreasing correlation coefficient, which usually becomes insignificant at the level of the third, fourth (or higher level) component. The number of significant components is determined via cross-validation criteria given within the programme. A principal component consists of a score, which summarises the X-variable (soil sample) and a loading, showing the influence of the variables (soil characteristics). In a score plot defined by 2 principal components, soil samples that have similar characteristics plot out near each other. This can give an indication of the similarity of soils. A loading plot defined by 2 principal components can give relationships among the soil characteristics. As in a score plot, soil characteristics that plot out near each other on the loading plot may be closely related.

Partition coefficients were related to soil characteristics using the partial least squares (PLS) projection to latent structures method. PLS is a multivariate projection method which finds relationships between predictor variables (here: soil characteristics) and a response variable (here: the partition coefficient) through regression modelling in latent variables in a similar way as PCA. As a measure of goodness-of-fit, we used the adjusted R^2. This is the variance of all the Y's explained by the principal components. By using the adjusted R^2 instead of a non-adjusted R^2, the R^2 values are corrected for the influence of the number of X's entered in the model. R^2 has a maximum value of 1, and the higher this value, the better the model is considered to be. R^2 values adjusted calculated with PLS are not sensitive for correlation between the descriptors when determining the relation between predictors and response. SIMCA-S 6.0 for Windows (Umetri AB, 1994) was used for the PLS and PCA-analyses.

Because the raw soil characteristics and K_p data showed a log-normal distribution, the data sets used in this study were log transformed (except pH) before PLS and PCA analyses were carried out to meet the assumption of homoscedasticity required for the regression models (Draper and Smith, 1981). The final models were derived by means of stepwise multiple regression analysis.

3 EXPERIMENTAL FINDINGS

3.1 General

In this chapter, the results of the soil analyses are given. Apart from the soil and pore water characteristics assumed to dominate metal partitioning, metal concentrations in the solid and liquid phase, calculated metal activities in the pore water, and values of the partition coefficients of the metals included in this study are reported. As three different expressions for the metal levels in the solid phase (*aqua regia-* and concentrated HNO_3-digestion and $CaCl_2$-extraction), and two expressions for metal levels in the pore water (total concentrations and activities) were measured, six different partition coefficients could be calculated for each metal (three in case of arsenic, due to a lack of calculated arsenic activities in the pore water). In addition, the differences in metal levels obtained by means of the two methods of digestion used in this study on the one hand and $CaCl_2$-extraction on the other hand, were calculated. These differences might be indicative of the non-available metal fraction in the soil. In most cases it turned out that in an absolute sense, the values thus obtained did not deviate significantly from the total metal concentrations. Therefore these differences will not be reported. On the other hand, $CaCl_2$-extraction can be seen as an operationally defined expression of the available metal fraction present in the soil matrix. In this report the operationally defined available metal fraction is expressed as the percentage of the total metal content (*aqua regia-* and HNO_3-digestion) that is extractable by means of 0.01 *M* $CaCl_2$-extraction.

3.2 Solid phase characteristics

For all soils studied, the main solid phase characteristics assumed to influence metal partitioning are given in Table 3.1. Apart form the experimental findings for each soil, also the minimum, maximum and average values are included in this table. The large variation of soil properties reflects one of the main criteria used for selecting the sampling sites, i.e. that the soil samples should vary with respect to their physico-chemical composition.

Table 3.1 Characterisation of the solid phase of the soils sampled.

Site	W_1 (%)	W_2 (%)	pH ($CaCl_2$)	pH (KCl)	Fe-ox (mmol.kg^{-1})	Al-ox (mmol.kg^{-1})	LOI_1 (%)	LOI_2 (%)	OM (%)	Clay (%)	Fraction (%)	CO_3^{2-} (mol.kg^{-1})
A	6.8	9.7	4.09	3.57	11.5	15.9	2.6	0.2	2.4	2.0	6.6	n.d.
B	27.7	56.5	5.60	4.71	136	70.1	15.1	1.1	15.0	39.1	19.5	n.d.
C	29.0	56.6	5.07	5.13	200	93.0	13.2	1.2	10.3	46.7	14.3	n.d.
D	17.2	29.2	7.26	6.93	41.8	18.3	4.5	2.9	4.7	11.0	35.2	0.7
E	26.6	33.6	6.65	6.30	100.1	36.6	6.0	0.9	5.2	8.9	25.2	0.2
F	18.2	36.0	7.38	6.92	43.1	28.1	6.2	3.2	8.7	13.3	40.7	1.2
G	15.1	41.0	7.24	7.20	184.8	37.9	4.8	5.9	6.8	10.0	30.3	1.5
H	2.9	8.2	3.97	3.98	3.9	11.3	2.0	0.1	2.2	0.5	1.7	n.d.
I	11.8	17.8	3.81	2.85	22.3	53.0	5.0	0.1	4.8	1.3	2.0	n.d.
J	2.8	18.7	4.55	3.98	8.2	20.7	2.1	0.2	2.6	1.3	1.2	n.d.
K	1.4	2.1	4.49	4.37	2.0	1.1	0.3	0.1	< 0.5	0.2	0.3	n.d.
L	6.3	6.8	7.12	7.80	10.0	4.2	1.6	1.9	2.7	0.8	0.6	0.6
M	6.7	7.7	3.99	3.42	27.0	22.1	1.9	0.2	1.9	3.0	2.1	n.d.
N	5.6	8.8	7.12	5.93	33.2	8.0	0.8	0.5	0.9	2.1	0.1	n.d.
O	18.9	25.1	6.09	n.d.	134	18.2	4.7	0.5	4.7	5.8	5.5	n.d.
P	22.9	30.9	7.22	7.34	146	26.1	3.5	5.6	6.0	4.4	7.9	1.4
Q	22.2	36.4	7.43	6.91	109	26.8	10.2	3.1	12.0	12.5	13.5	n.d.
R	12.8	19.2	7.36	7.16	46.7	15.1	4.1	2.6	4.7	8.2	10.6	0.5
S	33.8	65.7	7.08	6.52	214	66.1	15.0	1.9	16.8	24.6	35.9	0.7
T	21.3	29.0	7.36	7.00	48.7	10.5	3.2	0.7	3.8	6.7	5.5	0.2
U	48.8	68.1	4.88	4.36	234	248.0	35.2	1.9	32.3	27.3	22.9	n.d.

V	16.0	31.7	7.35	7.55	34.3	6.9	3.2	3.2	4.2	11.2	9.3	0.7
W	17.2	30.4	7.12	7.37	46.3	10.9	3.9	2.5	4.3	11.2	11.7	1.0
X	31.8	49.6	4.84	n.d.	1.7	7.0	11.1	0.5	6.7	11.8	8.1	n.d.
Y	22.9	36.4	4.19	n.d.	81.8	41.7	7.2	0.7	6.4	15.8	46.0	n.d.
Z	8.6	22.7	4.96	5.40	22.1	22.0	4.6	0.5	3.8	1.7	2.6	n.d.
AA	11.0	21.6	5.50	6.00	16.6	40.5	4.3	0.2	5.2	1.7	3.0	0.2
AB	10.9	21.1	5.35	n.d.	16.0	40.4	4.4	0.2	3.8	1.9	2.3	n.d.
AC	37.3	60.4	3.59	3.06	24.1	80.0	10.5	0.2	9.3	1.4	1.3	n.d.
AD	11.8	30.5	3.65	3.22	14.8	28.6	4.9	0.1	5.3	1.1	1.9	n.d.
AE	23.5	40.8	3.09	2.36	19.0	11.0	6.8	0.2	5.8	2.3	3.7	n.d.
AF	11.3	29.6	7.30	7.63	18.7	4.2	1.1	3.1	1.9	5.4	5.7	0.6
AG	33.9	65.1	5.87	7.35	99.3	23.1	8.6	2.7	7.6	39.8	33.0	n.d.
AH	36.9	76.1	4.75	n.d.	389	51.6	26.7	1.6	23.4	29.3	30.8	n.d.
AI	22.4	50.3	7.23	n.d.	108	19.0	7.9	4.0	7.9	22.3	34.5	0.9
AJ	13.8	17.6	7.31	n.d.	27.6	5.8	3.0	0.6	2.1	4.7	4.3	n.d.
AK	17.8	25.3	6.60	5.64	64.8	36.0	5.8	0.5	5.8	3.3	4.8	n.d.
AL	30.3	68.4	5.59	n.d.	111	63.9	10.2	1.3	6.4	51.6	31.5	n.d.
AM	23.3	43.1	3.20	2.59	60.9	28.1	8.0	0.4	6.8	3.8	10.2	n.d.
AN	11.6	30.1	4.20	3.82	28.8	49.2	4.4	0.3	4.2	2.5	8.8	n.d.
AO	10.8	22.6	3.41	2.85	5.4	13.2	4.3	0.1	4.2	0.2	0.5	n.d.
AP	13.0	21.3	7.25	7.20	76.9	12.5	3.2	2.5	3.3	4.1	4.3	0.6
AQ	21.6	33.9	4.45	n.d.	34.7	41.1	6.7	0.3	6.4	2.2	3.1	n.d.
AR	11.9	29.6	4.36	3.92	40.7	47.5	6.4	0.3	6.1	2.3	3.4	n.d.
AS	20.7	25.5	7.21	7.67	57.2	16.2	4.5	1.9	5.0	6.2	3.6	0.5
AT	24.2	35.3	7.15	7.15	77.7	21.4	9.6	2.2	10.8	7.0	5.8	0.6
AU	37.5	73.8	7.16	7.45	132	23.4	14.8	2.1	16.2	15.0	9.0	0.4
AV	6.5	16.2	3.68	3.53	2.5	9.2	2.6	0.1	1.4	0.7	1.5	n.d.
AW	10.5	19.9	6.33	4.75	133.3	62.0	6.4	1.8	12.6	1.2	1.8	1.0
Min.	1.4	2.1	3.09	2.36	1.7	1.1	0.3	0.1	0.9	0.2	0.1	0.2
Max.	48.9	76.1	7.43	7.80	389.2	248.0	35.2	5.9	32.3	51.6	46.0	1.5
Av.	18.5	33.4	5.68	5.47	71.5	33.6	6.9	1.4	7.0	10.0	11.6	0.7

W_1 = moisture content of the soil, W_2 = moisture content of the soil after centrifugation, Fe-ox/Al-ox = Amount of iron and aluminum extracted by ammonium oxalate/oxalic acid. This is assumed to be present as "active"or "amorphous" Fe and Al (oxyhydr)oxide (Sparks *et al.*, 1996), OM = organic matter, Clay = soil particles <2 mm, fraction = granules between 2 and 38 mm , CEC = cation exchange capacity. n.d. = not detectable, min. = minimum value, max = maximum value, av. = average value.

For most parameters determined in these soils, the values found were well-reproducible and duplication of the whole procedure (soils AA and AB) showed that in general deviations of less than 2 % were observable. However, in some cases (like for instance the OM-content of the soils and the percentage of granules between 2 and 38 mm) large deviations of over 10 % were detectable. This might be due to the fact that the data given represent point samples which not necessarily reflect the pollution status of a larger area; even samples that are basically taken at the same site might deviate slightly.

3.3 Metal concentrations in the solid phase

The concentrations of some elements displaced by the *aqua regia-* and HNO_3-digests, as well as by $CaCl_2$-extraction are given in Tables 3.2 - 3.4. The data are expressed on a dry weight basis and the elements extracted by $CaCl_2$ have been corrected for the amount of each element that was supposed to be present in the pore water at the moment of sampling. $CaCl_2$ extraction releases only part of the metals from the solid phase, especially metals sorbed onto the oxide phases will not be released. As expected much higher concentrations of elements were found in the digests than in the $CaCl_2$ extracts.

In addition to the total metal levels reported in Tables 3.2 and 3.3, also a comparison is made with the maximum permissible and negligible concentrations derived by Crommentuijn *et al.* (1997), using the added risk approach. This is done for metal concentrations determined by both *aqua regia* and HNO_3-digestion.

Table 3.2 Total metal concentrations in the solid phase (*aqua regia*-digestion). Underlined values represent samples containing metal levels in between the negligible metal concentration and the maximum permissible metal concentration, values given with a dark background represent samples exceeding the maximum permissible metal concentration (Crommentuijn *et al.*, 1997).

Site	Cu (mmol .kg^{-1})	Cr (mmol .kg^{-1})	Ni (mmol .kg^{-1})	As (mmol .kg^{-1})	Cd (µmol .kg^{-1})	Pb (mmol .kg^{-1})	Zn (mmol .kg^{-1})	Al (mmol .kg^{-1})	Fe (mmol .kg^{-1})	Mn (mmol .kg^{-1})	Mg (mmol .kg^{-1})	Ca (mmol .kg^{-1})	K (mmol. kg^{-1})	Na (mmol .kg^{-1})
A	0.07	0.67	***0.21***	0.07	0.60	0.17	0.26	159	89	1.85	18	9	13	1.73
B	0.43	1.51	0.72	0.16	2.98	0.18	1.52	1515	443	6.18	262	175	204	25.43
C	1.65	2.01	0.83	0.20	3.85	0.31	1.92	1868	560	8.28	289	128	247	25.25
D	0.20	1.12	***0.40***	0.09	***14.16***	***0.52***	7.07	464	257	6.75	92	600	71	4.89
E	0.41	0.76	0.45	0.23	72.42	4.28	47.69	628	318	10.70	118	120	107	35.58
F	0.48	1.26	***0.42***	0.29	23.98	0.47	13.58	685	330	10.75	108	503	110	12.50
G	***0.75***	1.28	0.45	0.18	42.95	n.d.	9.14	737	492	13.04	354	907	127	21.53
H	0.05	0.08	n.d.	0.02	1.79	0.09	0.20	37	17	0.45	3	2	11	3.79
I	0.05	0.47	0.16	0.05	3.13	0.15	0.23	88	37	0.27	5	2	7	0.84
J	0.07	0.19	0.03	0.07	***8.58***	0.11	0.84	159	50	1.86	14	14	32	6.34
K	0.01	0.27	0.09	0.02	n.d.	0.27	0.11	39	24	0.76	7	8	5	0.90
L	0.09	0.26	0.09	0.07	1.70	0.11	0.74	94	110	2.39	43	399	18	4.12
M	0.09	0.40	0.11	0.03	0.40	0.07	0.29	151	76	1.49	16	6	17	1.95
N	1.61	1.37	0.45	0.10	2.72	***0.66***	3.05	238	174	3.25	56	54	36	3.87
O	0.31	0.89	0.17	0.20	63.52	0.12	2.28	268	223	5.32	39	55	25	3.73
P	0.84	2.90	0.42	0.32	37.61	n.d.	8.92	548	394	11.29	264	1140	100	21.98
Q	***0.81***	1.17	0.53	0.11	5.57	1.09	2.29	613	370	10.46	129	594	109	63.78
R	0.54	1.32	0.40	0.26	***14.23***	0.44	5.06	424	232	7.78	169	542	69	14.84
S	2.15	3.06	0.98	***0.66***	164.21	1.83	20.04	1206	636	23.48	210	224	159	30.49
T	0.39	0.92	0.27	0.23	17.83	0.37	4.05	328	207	8.04	115	152	48	7.07
U	0.78	2.33	0.73	0.23	9.57	***0.90***	2.54	1259	394	3.69	168	193	104	14.28
V	0.10	0.70	0.17	0.18	1.92	0.06	0.69	492	234	n.d.	160	680	100	11.29
W	0.24	0.82	0.22	0.33	3.56	0.17	1.30	504	275	n.d.	176	437	105	42.95
X[1]	0.61	0.65	**0.39**	0.17	59.45	***0.70***	7.97	980	21	0.23	16	52	56	4.21
Y	0.26	0.80	0.22	0.18	8.08	1.27	1.88	887	265	3.54	70	30	119	20.98
Z	0.50	0.15	0.06	0.06	1.42	0.16	0.79	117	75	2.39	16	36	16	2.32
AA	0.28	0.23	0.19	0.02	2.31	0.18	6.09	184	69	1.60	22	40	27	6.23
AB	0.18	0.35	0.12	0.02	2.32	0.17	5.01	165	60	1.23	19	33	17	2.13
AC	0.03	0.12	0.04	0.02	2.15	0.11	0.16	104	30	0.58	7	8	10	2.05
AD	0.04	0.07	n.d.	0.02	0.71	0.04	0.12	77	29	0.47	5	6	6	1.43
AE	0.02	0.15	0.02	0.02	n.d.	0.07	0.10	91	44	0.74	9	11	16	3.01
AF	0.04	0.37	0.12	0.07	0.79	0.03	0.31	238	136	3.07	135	556	43	4.36
AG	0.22	2.65	1.10	0.24	3.21	0.14	1.24	1274	555	9.37	314	142	248	44.49
AH	0.43	1.27	0.55	0.25	6.47	0.25	1.47	911	506	12.28	180	143	121	23.40
AI	0.29	1.34	0.52	0.22	6.31	0.22	2.53	880	435	14.10	321	828	163	17.01
AJ	0.06	0.26	0.12	0.03	0.83	0.03	0.33	184	92	2.30	59	119	30	2.32
AK	0.54	0.25	0.17	0.07	***10.22***	***0.62***	19.14	224	157	3.31	46	135	27	5.71
AL	0.46	1.89	0.99	0.18	4.26	0.18	1.68	1768	595	9.48	356	145	220	51.56
AM	0.09	0.26	0.05	0.05	0.73	0.13	0.20	215	103	1.14	23	19	15	2.34
AN	0.17	0.23	0.04	0.05	4.67	0.15	0.56	146	52	3.00	12	17	11	1.62
AO	0.01	0.07	n.d.	0.01	1.75	0.04	0.09	32	12	0.20	2	3	4	1.16
AP	0.22	0.61	***0.26***	0.10	4.62	0.20	1.71	289	210	6.78	132	515	50	5.00
AQ[1]	0.47	0.56	0.24	0.14	27.74	0.58	3.92	227	118	6.67	26	50	23	3.87
AR	0.21	0.66	0.19	0.05	2.95	0.23	0.69	187	105	5.79	22	39	17	2.22
AS	0.26	0.31	0.16	0.10	0.84	1.79	0.77	267	135	3.38	83	381	42	6.11
AT	0.54	0.47	0.22	0.09	7.23	0.47	***2.53***	320	223	5.87	111	421	63	13.11
AU	0.37	0.83	0.27	0.20	4.28	0.54	2.24	584	241	5.30	112	291	107	25.11
AV	0.11	0.07	0.03	0.03	5.28	0.21	0.68	42	16	0.24	3	2	6	1.52
AW	5.13	0.39	0.48	0.67	188.83	7.11	115.67	142	201	3.82	18	28	14	17.91
Min.	0.01	0.07	0.02	0.01	0.40	0.03	0.09	32	12	0.20	2	2	4	0.84
Max.	5.13	3.06	1.10	0.67	188.83	7.11	115.67	1868	636	23.48	356	1140	248	63.78
Av.	0.48	0.83	0.32	0.15	17.97	0.60	6.36	470	213	5.21	101	224	67	12.86

[1]: metals added in the laboratory, therefore no comparison made to risk levels, n.d. = not detectable, min. = minimum value, max. = maximum value, av. = average value.

Table 3.3 Total metal concentrations in the solid phase (HNO_3-digestion). Underlined values represent samples containing metal levels in between the negligible metal concentration and the maximum permissible metal concentration, values given with a dark background represent samples exceeding the maximum permissible metal concentration (Crommentuijn *et al.*, 1997).

Site	Cu mmol.kg^{-1}	Cr mmol.kg^{-1}	Ni mmol.kg^{-1}	As mmol.kg^{-1}	Cd µmol.kg^{-1}	Pb mmol.kg^{-1}	Zn mmol.kg^{-1}
A	0.04	0.66	***0.21***	0.07	n.d.	0.23	0.18
B	0.46	1.57	0.77	0.23	n.d.	0.15	1.73
C	1.68	1.87	0.75	0.30	0.69	0.34	2.69
D	0.19	1.24	0.32	0.13	***11.14***	0.48	7.95
E	0.39	0.58	0.42	0.23	56.94	3.62	46.66
F	0.50	1.34	0.45	0.39	***20.51***	0.44	15.52
G	***0.78***	1.39	0.57	0.20	***35.01***	n.d.	10.90
H	n.d.	0.24	n.d.	n.d.	1.41	0.09	0.27
I	n.d.	0.21	n.d.	0.06	2.48	0.13	0.40
J	n.d.	0.18	n.d.	0.06	6.23	0.08	0.73
K	n.d.	0.06	n.d.	0.04	n.d.	0.26	0.15
L	0.03	0.37	0.10	0.08	1.01	0.11	0.86
M	0.03	0.54	0.15	0.05	n.d.	0.06	0.15
N	7.86	1.28	0.42	0.28	2.56	0.74	3.44
O	0.30	0.63	0.13	0.25	44.99	0.17	2.31
P	0.89	3.36	0.40	0.37	29.13	n.d.	9.01
Q	0.70	0.91	***0.46***	0.15	3.36	***0.55***	2.63
R	0.51	1.42	0.39	0.31	***11.12***	0.39	4.99
S	2.19	3.57	0.94	0.81	135	1.82	23.58
T	0.35	0.90	***0.29***	0.25	***15.38***	0.33	4.01
U	0.84	2.08	0.77	0.36	7.12	***0.85***	2.77
V	0.06	0.49	0.16	0.21	n.d.	0.06	0.71
W	0.21	0.71	0.20	0.39	2.18	0.15	1.19
X[1]	0.48	0.46	0.32	0.22	46.99	***0.51***	5.37
Y	0.23	0.77	0.21	0.22	6.05	1.09	2.38
Z	0.07	0.17	n.d.	0.06	0.50	0.12	0.71
AA	0.10	0.15	n.d.	0.03	2.60	0.16	5.50
AB	0.11	0.14	n.d.	0.04	1.71	0.14	5.37
AC	n.d.	0.12	n.d.	0.05	1.70	0.10	0.14
AD	n.d.	0.07	n.d.	0.02	n.d.	0.03	0.04
AE	n.d.	0.17	n.d.	0.02	n.d.	0.08	0.07
AF	n.d.	0.39	n.d.	0.08	n.d.	0.02	0.32
AG	0.16	2.81	0.94	0.31	n.d.	0.11	1.45
AH	0.54	0.98	0.49	0.37	3.48	0.23	2.35
AI	0.24	1.03	0.43	0.31	2.65	0.18	2.66
AJ	n.d.	0.32	0.13	0.07	n.d.	0.03	0.50
AK	0.50	0.48	0.17	0.11	***9.62***	***0.61***	23.33
AL	0.58	2.84	1.04	0.38	1.39	0.19	2.48
AM	0.04	0.33	n.d.	0.08	n.d.	0.12	0.20
AN	0.17	0.25	n.d.	0.07	3.76	0.13	0.65
AO	n.d.	0.09	n.d.	n.d.	1.61	0.03	0.12
AP	0.17	0.50	0.19	0.13	3.06	0.17	1.95
AQ[1]	0.27	0.38	0.15	0.11	18.2	0.37	3.12
AR	0.23	0.43	n.d.	0.09	3.10	0.27	1.11
AS	0.24	0.29	0.15	0.12	0.00	1.77	1.02
AT	0.54	0.51	0.19	0.14	5.41	0.44	2.94
AU	0.35	0.59	0.24	0.23	2.40	0.48	3.27
AV	0.06	0.10	0.01	n.d.	4.42	0.20	0.84
AW	6.93	0.57	0.50	0.83	190	7.88	142
Min.	0.01	0.06	0.01	0.01	0.00	0.02	0.04
Max.	7.86	3.57	1.04	0.83	189.85	7.88	142
Av.	0.75	0.83	0.28	0.19	16.57	0.56	7.19

[1] : metals added in the laboratory, therefore no comparison made to risk levels, n.d. = not detectable, min. = minimum value, max. = maximum value, av. = average value.

Table 3.4 0.01 *M* $CaCl_2$-extractable metal concentrations in the solid phase.

Site	Cu	Cr	Ni	As	Cd	Pb	Zn	Al	Fe	K	Mg	Mn	Na
	µmol .kg^{-1}	µmol .kg^{-1}	µmol .kg^{-1}	µmol .kg^{-1}	µmol .kg^{-1}	µmol .kg^{-1}	µmol .kg^{-1}	µmol .kg^{-1}	µmol .kg^{-1}	mmol .kg^{-1}	mmol .kg^{-1}	µmol .kg^{-1}	mmol .kg^{-1}
A	0.99	0.20	3.67	0.06	0.19	5.33	17.0	1219	50.2	0.55	0.32	411	0.30
B	0.91	0.67	3.17	0.05	0.12	n.d.	6.58	41.1	14.0	0.61	8.25	141	3.54
C	3.74	0.18	8.59	0.03	0.23	0.06	28.3	87.2	14.8	14.5	12.81	167	1.87
D	0.49	n.d.	0.29	0.17	0.12	0.12	7.03	n.d.	n.d.	2.48	2.10	n.d.	0.44
E	0.86	n.d.	2.36	0.11	3.02	0.14	757	n.d.	2.00	0.70	3.44	11.4	0.44
F	0.87	n.d.	0.31	0.30	0.19	n.d.	11.9	n.d.	2.01	0.64	1.79	2.21	0.40
G	1.72	0.05	0.29	0.18	0.24	n.d.	5.73	8.03	5.02	0.49	1.97	1.49	0.26
H	0.29	0.09	2.42	0.08	0.95	3.41	68.0	1061	19.0	0.28	0.14	7.22	0.10
I	0.39	0.27	4.04	0.30	2.29	5.32	73.6	3219	108	0.43	0.28	15.9	0.12
J	0.19	n.d.	2.77	0.12	2.46	0.49	201	357	8.03	0.26	0.38	69.9	0.12
K	0.10	n.d.	0.42	0.09	0.02	63.23	3.38	146	35.2	0.13	0.16	4.77	0.17
L	0.29	n.d.	n.d.	0.18	0.02	n.d.	2.00	n.d.	2.99	0.33	1.02	1.40	0.34
M	2.30	0.17	3.84	0.08	0.19	1.29	26.5	1138	101	0.47	0.24	70.8	0.20
N	3.58	n.d.	0.27	0.02	0.07	0.06	2.71	n.d.	2.00	0.28	1.36	22.3	0.15
O	1.18	0.16	1.68	0.08	3.79	n.d.	82.5	9.03	5.02	3.37	5.97	136	1.63
P	1.95	0.07	0.64	0.44	0.26	n.d.	9.12	n.d.	n.d.	0.24	2.73	12.3	6.08
Q	1.20	n.d.	0.49	0.22	0.01	n.d.	2.10	n.d.	2.99	3.44	6.33	1.40	6.88
R	1.52	0.09	0.34	0.27	0.10	n.d.	2.50	n.d.	n.d.	3.51	3.03	5.61	2.59
S	1.22	0.11	0.95	0.21	0.97	n.d.	21.2	n.d.	n.d.	0.98	8.56	0.60	5.44
T	0.80	0.07	0.28	0.09	0.21	n.d.	4.22	n.d.	n.d.	0.62	3.33	4.42	4.09
U	2.05	0.55	4.68	0.12	0.55	1.39	49.7	500	61.3	1.51	9.88	744	2.27
V	0.27	n.d.	0.33	1.55	0.01	n.d.	n.d.	n.d.	2.01	1.08	1.85	n.d.	0.55
W	0.66	n.d.	0.27	2.71	0.02	n.d.	n.d.	n.d.	2.01	1.57	1.57	n.d.	0.74
X	4.56	8.40	131	14.0	27.6	3.79	3898	97.5	44.2	1.48	3.50	37.8	1.72
Y	1.35	0.15	3.82	0.01	4.06	22.6	231	605	20.2	1.45	2.73	209	0.27
Z	0.55	0.06	0.51	0.25	0.15	0.11	103	56.2	9.99	3.36	3.51	121	0.97
AA	0.29	n.d.	0.75	0.04	0.39	0.09	962	36.1	5.99	0.91	1.68	17.4	0.86
AB	0.48	0.06	0.91	0.04	0.44	0.11	989	26.0	9.01	1.07	1.68	21.3	0.96
AC	n.d.	0.08	1.90	0.06	1.31	4.41	40.5	2768	30.3	0.33	0.27	20.2	0.40
AD	0.18	0.11	1.19	0.05	0.37	0.70	33.8	1723	31.7	0.32	0.66	60.6	0.34
AE	0.17	0.12	1.18	0.13	0.10	3.51	14.5	761	42.0	0.63	0.73	52.7	0.22
AF	0.19	n.d.	n.d.	0.55	0.00	n.d.	n.d.	n.d.	1.85	1.27	1.13	0.60	0.43
AG	0.37	0.10	3.35	0.12	0.13	n.d.	2.71	10.0	8.04	5.56	21.89	200	4.37
AH	0.45	0.09	4.09	0.01	0.36	0.06	39.9	63.6	24.1	1.23	14.30	156	2.23
AI	0.48	n.d.	0.50	0.49	0.02	n.d.	1.81	n.d.	3.01	6.85	6.52	n.d.	2.06
AJ	0.10	n.d.	n.d.	0.09	0.00	n.d.	n.d.	n.d.	n.d.	1.19	1.18	n.d.	0.24
AK	0.70	n.d.	0.65	0.12	0.34	n.d.	435	13.0	3.98	0.88	2.56	2.01	1.34
AL	0.73	0.04	5.07	0.03	0.31	n.d.	3.82	14.8	2.85	0.55	13.16	372	1.92
AM	1.10	0.31	2.89	0.11	0.26	5.09	33.5	1901	98.5	0.79	0.95	75.7	0.23
AN	0.58	0.14	2.11	0.23	2.78	0.46	120	607	9.70	0.19	1.45	205	0.27
AO	0.08	n.d.	1.57	0.10	1.24	1.73	48.2	1110	5.99	0.25	0.52	6.92	0.21
AP	1.03	n.d.	0.20	0.12	0.02	n.d.	n.d.	n.d.	2.99	5.23	2.77	1.91	0.42
AQ	3.61	0.87	49.2	1.40	10.9	1.43	1851	445	29.7	1.32	1.66	791	0.67
AR	1.08	0.20	3.26	0.19	0.83	0.34	159	499	23.1	0.98	1.52	274	0.52
AS	0.51	0.08	n.d.	0.22	0.01	0.08	n.d.	n.d.	1.99	0.80	1.67	n.d.	0.81
AT	1.22	n.d.	0.59	0.51	0.02	0.09	3.72	n.d.	7.02	7.54	9.75	1.40	3.07
AU	0.59	n.d.	n.d.	0.13	0.01	n.d.	3.52	n.d.	2.01	0.60	8.19	n.d.	8.09
AV	1.67	0.10	1.78	0.31	3.55	13.4	255	1436	25.2	0.33	0.14	8.90	0.15
AW	2.51	n.d.	8.77	0.06	28.9	5.51	6404	16.8	4.01	0.15	0.07	7.54	0.12
Min.	0.08	0.04	0.20	0.01	0.00	0.06	1.81	8.03	1.85	0.13	0.07	0.60	0.10
Max.	4.56	8.40	131	14.03	28.9	63.2	6404	3219	107.6	14.5	21.89	791	8.09
Av.	1.09	0.47	6.07	0.55	2.05	4.98	396	666	20.6	1.71	3.71	107	1.46

n.d. = not detectable, min. = minimum value, max. = maximum value, av. = average value.

As can be deduced from Tables 3.2 and 3.3, in various samples the negligible and the maximum permissible metal concentrations are exceeded and some soils contain more than one metal at levels exceeding the risk levels indicated. Again it should be noted that the aim of this study was not to obtain soil samples representative for a specific area. Instead the data given represent point samples, which not necessarily reflect the pollution status of the whole area.

As can be seen from Table 3.2, 21 out of the 46 soils sampled independently contain one or more metals at total concentrations (*aqua regia* digestion) exceeding the MPC; 25 out of the 46 soils sampled independently contain one or more metals at total concentrations (*aqua regia* digestion) exceeding the NC (comparable numbers are derived for total metal concentrations obtained by means of HNO_3-destruction). 14 Samples contain Zn-levels above the MPC, in addition one sample contains a Zn-level in between the NC and the MPC. For Ni these numbers are 10 and 5 respectively, for Cd: 9 and 4, Pb: 6 and 5, Cr: 6 and 0, Cu: 5 and 2, only one sample contained As at levels exceeding the MPC (Sample AW, a heavily polluted Belgium site), whereas one sample contained As at a total level in between the NC and the MPC. 13 samples contained more than one metal at levels exceeding the MPC, and in addition in 4 soils the NC for more than one metal was exceeded.

In Tables 3.5 and 3.6 the operationally defined available metal fraction is given, expressed as the percentage of the total metal concentration (*aqua regia*- and HNO_3-digestion) that is extractable by means of 0.01 *M* $CaCl_2$-extraction. As can be deduced from these tables, the operationally defined available metal fraction expressed as the percentage of the total metal concentration that is extractable by means of 0.01 *M* $CaCl_2$-extraction, varies greatly both among metals and among soils. On average, this fraction is lowest for Cr (about 0.1 %), followed by As and Cu (less than 1 %), Pb (about 2 %), Ni (about 3 %), Zn (about 12 %) and Cd (in between 18 and 27 %). Also, as illustrated in Figure 3.1 for Zn, there is no direct relationship between the operational defined available metal fraction and the total metal concentration in the solid phase. This is despite the apparent trend of increasing extractable metal levels upon increasing total metal concentrations: as can be seen from Figure 3.1, deviations of extractable metal concentrations of over 3 orders of magnitude at similar total levels, were measured. At first glance a certain clustering might be deducible of the data presented in Figure 3.1. However, a further analysis learned that this is not the case: the data are distributed randomly over the different soil types.

Table 3.5 Operationally defined available metal fraction, expressed as the percentage of the total metal concentration (*aqua regia* digestion) that is extractable by means of 0.01 *M* $CaCl_2$-extraction.

Site	Cu	Cr	Ni	As	Cd	Pb	Zn
A	1.42	0.03	1.78	0.09	31.87	3.12	6.41
B	0.21	0.04	0.44	0.03	4.16	n.d.	0.43
C	0.23	0.01	1.04	0.01	5.88	0.02	1.47
D	0.25	n.d.	0.07	0.19	0.87	0.02	0.10
E	0.21	n.d.	0.53	0.05	4.17	0.00	1.59
F	0.18	n.d.	0.07	0.10	0.80	n.d.	0.09
G	0.23	0.00	0.06	0.10	0.55	n.d.	0.06
H	0.59	0.11	n.d.	0.49	53.28	3.64	33.38
I	0.77	0.06	2.58	0.62	73.35	3.66	32.24
J	0.27	n.d.	8.97	0.17	28.71	0.46	23.80
K	0.99	n.d.	0.45	0.50	n.d.	23.85	3.01
L	0.33	n.d.	n.d.	0.25	1.36	n.d.	0.27
M	2.58	0.04	3.49	0.24	47.40	1.94	9.25
N	0.22	n.d.	0.06	0.02	2.45	0.01	0.09
O	0.39	0.02	0.98	0.04	7.09	n.d.	3.61
P	0.23	0.00	0.15	0.14	0.69	n.d.	0.10
Q	0.15	n.d.	0.09	0.19	0.21	n.d.	0.09
R	0.28	0.01	0.09	0.10	0.70	n.d.	0.05
S	0.06	0.00	0.10	0.03	0.59	n.d.	0.11
T	0.20	0.01	0.10	0.04	1.17	n.d.	0.10
U	0.26	0.02	0.60	0.05	5.78	0.15	1.96
V	0.27	n.d.	0.19	0.88	0.32	n.d.	n.d.
W	0.27	n.d.	0.13	0.83	0.65	n.d.	n.d.
X	0.75	1.30	33.26	8.02	46.48	0.54	48.88
Y	0.52	0.02	1.76	0.00	50.21	1.78	12.29
Z	0.11	0.04	0.81	0.44	10.51	0.07	12.96
AA	0.10	n.d.	0.39	0.21	16.92	0.05	15.79
AB	0.27	0.02	0.76	0.21	18.85	0.06	19.74
AC	n.d.	0.07	5.41	0.29	60.91	3.89	25.40
AD	0.46	0.17	n.d.	0.31	52.07	1.64	28.33
AE	0.81	0.08	6.97	0.60	n.d.	4.89	14.83
AF	0.47	n.d.	n.d.	0.78	0.37	n.d.	n.d.
AG	0.17	0.00	0.31	0.05	3.91	n.d.	0.22
AH	0.11	0.01	0.74	0.00	5.55	0.02	2.71
AI	0.16	n.d.	0.10	0.22	0.27	n.d.	0.07
AJ	0.15	n.d.	n.d.	0.26	0.49	n.d.	n.d.
AK	0.13	n.d.	0.37	0.18	3.36	n.d.	2.27
AL	0.16	0.00	0.51	0.02	7.30	n.d.	0.23
AM	1.16	0.12	6.14	0.25	35.51	3.89	16.37
AN	0.33	0.06	5.46	0.42	59.66	0.31	21.70
AO	0.74	n.d.	n.d.	0.74	71.13	4.00	53.68
AP	0.46	n.d.	0.08	0.13	0.45	n.d.	n.d.
AQ	0.77	0.16	20.8	1.03	39.27	0.24	47.22
AR	0.51	0.03	1.74	0.37	28.18	0.15	23.08
AS	0.19	0.03	n.d.	0.23	0.62	0.00	n.d.
AT	0.22	n.d.	0.27	0.56	0.31	0.02	0.15
AU	0.16	n.d.	n.d.	0.06	0.30	n.d.	0.16
AV	1.52	0.14	6.86	1.23	67.25	6.38	37.65
AW	0.05	n.d.	1.81	0.01	15.32	0.08	5.54
Min.	0.05	0.00	0.06	0.00	0.21	0.00	0.05
Max.	2.58	1.30	33.26	8.02	73.35	23.85	53.68
Av.	0.44	0.09	2.84	0.44	18.45	2.24	11.80

n.d. = not detectable, min. = minimum value, max. = maximum value, av. = average value.

Table 3.6 Operationally defined available metal fraction, expressed as the percentage of the total metal concentration (HNO_3-digestion) that is extractable by means of 0.01 *M* $CaCl_2$-extraction.

Site	Cu	Cr	Ni	As	Cd	Pb	Zn
A	2.25	0.03	1.79	0.09	n.d.	2.35	9.25
B	0.20	0.04	0.41	0.02	n.d.	n.d.	0.38
C	0.22	0.01	1.14	0.01	32.90	0.02	1.05
D	0.26	n.d.	0.09	0.14	1.11	0.03	0.09
E	0.22	n.d.	0.56	0.05	5.31	0.00	1.61
F	0.17	n.d.	0.07	0.08	0.94	n.d.	0.08
G	0.22	0.00	0.05	0.09	0.67	n.d.	0.05
H	n.d.	0.04	5.57	0.35	67.82	3.99	25.26
I	n.d.	0.13	8.62	0.50	92.55	4.06	18.63
J	3.54	n.d.	4.79	0.19	39.56	0.63	27.51
K	n.d.	n.d.	1.12	0.25	n.d.	24.44	2.23
L	0.93	n.d.	n.d.	0.22	2.28	n.d.	0.23
M	8.33	0.03	2.63	0.16	n.d.	2.25	17.33
N	0.05	n.d.	0.06	0.01	2.60	0.01	0.08
O	0.40	0.03	1.32	0.03	8.43	n.d.	3.58
P	0.22	0.00	0.16	0.12	0.89	n.d.	0.10
Q	0.17	n.d.	0.10	0.14	0.35	n.d.	0.08
R	0.30	0.01	0.09	0.09	0.89	n.d.	0.05
S	0.06	0.00	0.10	0.03	0.72	n.d.	0.09
T	0.23	0.01	0.10	0.04	1.36	n.d.	0.11
U	0.24	0.03	0.61	0.03	7.77	0.16	1.80
V	0.42	n.d.	0.21	0.75	1.64	n.d.	n.d.
W	0.32	n.d.	0.14	0.69	1.06	n.d.	n.d.
X	0.96	1.83	40.52	6.40	58.80	0.74	73.21
Y	0.59	0.02	1.86	0.00	67.10	2.08	9.73
Z	0.79	0.03	0.78	0.44	29.66	0.09	14.37
AA	0.29	n.d.	1.10	0.11	14.98	0.05	17.48
AB	0.43	0.04	1.60	0.10	25.60	0.08	18.41
AC	n.d.	0.07	8.28	0.12	77.16	4.58	29.10
AD	n.d.	0.16	9.13	0.21	87.93	2.05	83.49
AE	n.d.	0.07	2.97	0.52	n.d.	4.20	21.36
AF	n.d.	n.d.	n.d.	0.68	n.d.	n.d.	n.d.
AG	0.23	0.00	0.36	0.04	35.00	n.d.	0.19
AH	0.08	0.01	0.84	0.00	10.30	0.02	1.70
AI	0.20	n.d.	0.12	0.16	0.64	n.d.	0.07
AJ	n.d.	n.d.	n.d.	0.14	1.66	n.d.	n.d.
AK	0.14	n.d.	0.37	0.11	3.56	n.d.	1.87
AL	0.13	0.00	0.49	0.01	22.41	n.d.	0.15
AM	2.47	0.09	3.37	0.15	n.d.	4.26	17.06
AN	0.35	0.05	4.60	0.34	74.02	0.35	18.53
AO	n.d.	n.d.	5.81	0.89	77.43	5.15	41.88
AP	0.61	n.d.	0.11	0.09	0.67	n.d.	n.d.
AQ	1.34	0.23	32.95	1.31	59.85	0.38	59.31
AR	0.46	0.05	4.20	0.22	26.82	0.13	14.26
AS	0.21	0.03	n.d.	0.18	113.21	0.00	n.d.
AT	0.22	n.d.	0.30	0.38	0.42	0.02	0.13
AU	0.17	n.d.	n.d.	0.05	0.53	n.d.	0.11
AV	2.78	0.09	14.26	1.30	80.49	6.75	30.29
AW	0.04	n.d.	1.76	0.01	15.24	0.07	4.53
Min.	0.04	0.00	0.05	0.00	0.35	0.00	0.05
Max.	8.33	1.83	40.52	6.40	113.21	24.44	83.49
Av.	0.78	0.11	3.76	0.37	27.44	2.38	13.18

n.d. = not detectable, min. = minimum value, max. = maximum value, av. = average value.

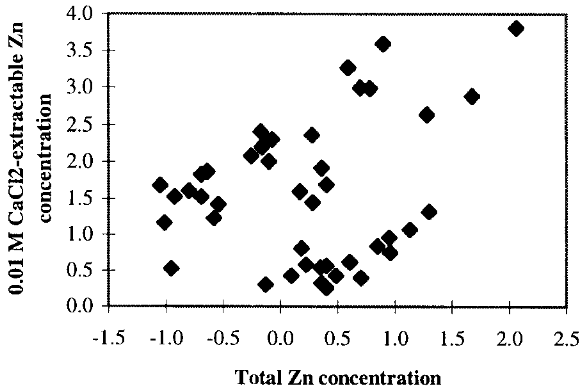

Figure 3.1 Plot of the log-transformed 0.01 *M* $CaCl_2$-extractable Zn-concentration (μmol.kg^{-1}, *aqua regia* digestion) for each of the soil samples included in this study, versus the log-transformed total metal concentration (mmol.kg^{-1}).

As all soils sampled by Janssen *et al.* (1996), were re-sampled within the framework of this study, it is obvious to compare the data on total metal concentrations reported in both studies. HNO_3-digestion was employed by Janssen *et al.* (1996) as the sole method for liberating the metals from the solid phase. As a typical result of the comparison of both sets of data, in Figure 3.2 the log-transformed total Zn-concentrations are plotted. As is obvious from this Figure, and despite the fact that in some cases not exactly the same spot was re-sampled, total metal concentrations reported in general correspond well.

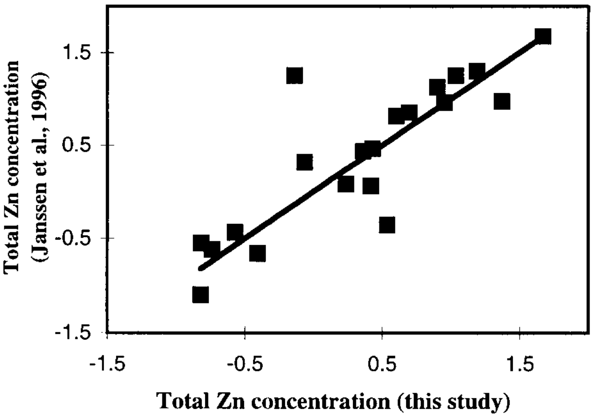

Figure 3.2 Plot of the (log-transformed) total Zn levels (HNO_3-digestion) found in the soil solid phase by Janssen *et al.* (1996) versus the (log-transformed) total concentration of Zn in the solid phase, as reported in Table 3.3 (soils A-T). Zn-levels are in units of mmol.kg^{-1}.

3.4 Pore water characteristics

In Table 3.7 the composition of the pore water is given in terms of pH(pw), conductivity, DOC, anions and major cations. Thereupon in Table 3.8 the MINTEQ-calculated (log-transformed) free metal concentrations and metal activities are given for each of the soils included in this study.

Table 3.7 Pore water composition with respect to pH, EC (conductivity), DOC, anions and major cations.

Site	pH (H_2O)	CO_3^{2-} $(mmol.l^{-1})$	DOC $(mmol.l^{-1})$	EC $(\mu S.cm^{-1})$	NO_3^- $(mmol.l^{-1})$	SO_4^{2-} $(mmol.l^{-1})$	PO_4^{3-} $(\mu mol.l^{-1})$	Cl^- $(mmol.l^{-1})$	K $(mmol.l^{-1})$	Mg $(mmol.l^{-1})$	Mn $(mmol.l^{-1})$	Na $(mmol.l^{-1})$	Ca $(mmol.l^{-1})$	Fe $(\mu mol.l^{-1})$	Al $(\mu mol.l^{-1})$	Cu $(\mu mol.l^{-1})$	Cr $(\mu mol.l^{-1})$	Ni $(\mu mol.l^{-1})$	As $(\mu mol.l^{-1})$	Cd $(\mu mol.l^{-1})$	Pb $(\mu mol.l^{-1})$	Zn $(\mu mol.l^{-1})$
A	4.23	0.02	8.38	431	2.67	0.27	1.3	0.43	0.40	0.19	89.4	0.63	0.46	15.5	65.6	1.67	0.11	0.83	0.02	0.03	0.11	5.9
B	6.10	0.23	7.25	1350	9.35	1.79	1.9	0.95	0.06	0.89	8.65	2.81	5.15	10.6	29.2	0.73	0.16	0.53	0.01	0.01	0.03	8.6
C	5.88	0.06	5.45	760	4.33	1.16	3.0	0.48	1.64	0.74	12.5	0.85	1.92	44.7	53.8	3.12	0.14	0.72	0.05	0.01	0.12	2
D	7.54	1.45	4.86	1750	15.48	0.48	0.7	0.36	0.95	0.54	0.07	0.73	7.83	1.2	2.3	0.79	0.03	0.35	0.02	0.01	0.01	1.4
E	6.96	1.96	2.54	1201	8.01	2.34	5.0	0.19	0.13	0.77	1.56	0.50	5.71	1.4	2.6	1.37	0.02	0.56	0.01	0.15	0.03	63
F	7.69	3.78	3.52	1460	11.08	0.26	1.2	0.11	0.05	0.39	0.32	0.33	7.53	0.6	3.6	1.02	0.02	0.33	0.04	0.01	0.01	1
G	7.33	2.74	2.52	909	3.90	0.81	4.5	0.10	0.06	0.39	2.98	0.25	4.95	1.1	2.5	1.64	0.03	0.39	0.03	0.01	n.d.	0.6
H	4.26	0.04	10.1	436	2.99	0.16	1.8	0.18	0.50	0.13	2.9	0.25	0.43	12.2	59	1.79	0.13	0.81	0.02	0.06	0.15	14.8
I	4.25	0.01	12.3	533	3.69	0.28	0.8	0.13	0.53	0.29	12.4	0.24	0.59	13.2	180.3	1.44	0.11	0.80	0.02	0.23	0.21	22.5
J	5.26	0.06	4.94	592	5.11	0.13	1.0	0.13	0.38	0.48	14.9	0.49	1.66	3.4	30.2	1.47	0.05	0.72	0.02	0.20	0.02	50.9
K	5.10	0.01	5.29	474	3.71	0.10	13.1	0.26	0.24	0.35	8.7	0.51	1.15	9.3	38.5	1.39	0.08	1.19	0.04	0.04	4.38	5.8
L	7.32	1.57	3.23	1440	11.74	0.39	6.2	0.78	0.23	0.70	0.98	1.15	6.25	4.2	5.3	1.54	0.03	0.40	0.05	0.01	0.05	1.2
M	4.63	0.01	10.2	538	3.78	0.20	11.2	0.20	0.45	0.23	27.0	0.43	0.76	21.85	78.75	1.97	0.11	0.81	0.02	0.04	0.06	12.85
N	7.16	2.17	4.79	1144	9.43	0.49	0.4	0.13	0.07	0.93	0.41	0.30	5.08	1.8	3.6	2.04	0.04	0.29	0.01	0.01	0.04	0.8
O	6.21	0.14	4.74	2710	15.97	7.43	1.6	1.65	2.18	3.77	2.4	3.33	10.39	1.3	3.4	2.03	0.08	0.77	0.01	0.27	0.01	16
P	7.12	3.63	2.03	2370	3.15	4.96	8.1	10.13	0.09	1.24	1.62	9.09	8.51	0.5	1.9	0.98	0.04	0.45	0.05	0.04	n.d.	5.4
Q	7.08	0.91	4.23	3700	10.70	14.83	7.9	7.71	1.17	2.89	0.59	8.21	18.43	3.5	4.8	1.22	0.02	0.32	0.02	0.02	0.01	1.5
R	7.16	2.05	3.68	3740	15.06	5.97	0.5	13.51	2.64	2.18	3.3	5.40	16.77	3.9	8.6	2.05	0.16	0.75	0.03	0.02	0.03	1.7
S	7.17	2.71	2.23	1095	4.53	1.36	0.6	2.27	0.12	0.75	0.15	2.79	3.84	1.3	2.2	0.97	0.07	0.28	0.03	0.02	0.01	1.1
T	7.09	1.51	2.75	2370	7.57	2.87	n.d.	9.99	0.26	1.39	1.17	7.11	8.27	4.2	4.3	0.84	0.07	0.47	0.02	0.02	0.02	1.3
U	5.60	0.02	9.51	2210	11.85	6.78	1.7	0.95	0.10	2.18	108	1.23	11.31	5.6	60.3	3.9	0.12	1.59	0.02	0.07	0.07	14.4
V	7.54	4.42	2.43	773	3.82	0.45	8.9	0.61	0.15	0.25	n.d.	0.62	3.70	0.4	1.4	2.02	0.04	0.72	0.38	0.01	0.01	1.4
W	7.50	3.17	3.32	663	1.37	0.50	13.0	1.23	0.21	0.16	n.d.	0.81	3.15	0.4	0.6	1.36	0.05	0.68	0.82	0.03	0.01	2.9
X	5.30	0.12	44.6	4000	7.08	0.53	1.4	31.71	0.84	2.07	12.5	1.43	17.83	4.5	17.2	8.18	5.15	44.1	28.8	9.62	1.00	1247
Y	5.08	0.02	4.80	369	1.87	0.41	2.5	0.52	0.27	0.35	41.8	0.41	1.03	136	176	1.84	0.58	0.48	0.18	0.18	1.59	18.1

Z	5.47	0.04	6.91	1390	9.48	0.75	166	2.52	2.84	1.24	1.99	2.05	3.42	10	27.6	3.96	0.07	0.62	0.10	0.02	0.07	9.5
AA	6.03	0.12	3.43	793	6.00	0.37	2.8	0.51	0.43	0.47	4.21	1.55	2.58	7.3	17.4	0.54	0.03	0.19	0.01	0.01	0.05	57.8
AB	6.04	0.45	3.13	860	6.71	0.40	3.1	0.57	0.50	0.52	2.04	1.63	2.75	7.1	17.6	0.46	0.05	0.18	0.01	0.01	0.05	67.7
AC	4.05	0.05	4.52	165	0.27	0.20	5.5	0.39	0.14	0.04	1.86	0.29	0.16	131	238	1.31	0.30	0.34	0.14	0.03	0.44	2.7
AD	3.95	0.08	5.32	428	3.09	0.17	0.9	0.34	0.13	0.36	26.6	0.69	1.03	69.9	91.5	1.37	0.06	0.39	0.01	0.03	0.10	9.6
AE	3.49	0.03	10.0	482	1.89	0.18	136	0.35	0.41	0.21	11.0	0.34	0.38	41.4	79.7	2.49	0.09	0.41	0.10	0.04	0.32	5
AF	7.42	3.39	2.33	571	1.31	0.16	15.3	0.91	0.38	0.23	1.08	0.69	2.67	24	19.1	1.08	0.07	0.24	0.25	0.00	0.02	0.4
AG	6.28	0.40	4.23	2760	0.64	18.99	0.7	2.32	1.15	6.42	53.4	3.17	12.79	1.7	3.2	0.71	0.05	0.82	0.01	0.01	0.01	1.3
AH	5.35	0.27	8.45	321	0.07	0.87	4.6	0.62	0.08	0.47	18.7	0.75	1.23	147	114	1.79	0.30	0.95	0.07	0.02	0.13	2.3
AI	7.50	5.12	3.99	1181	1.34	0.72	23.1	2.41	1.64	0.88	0.24	1.77	4.99	1.2	2.4	0.83	0.03	0.28	0.15	0.00	0.01	0.2
AJ	7.34	2.03	2.29	819	4.25	0.27	4.6	0.43	0.52	0.29	0.06	0.41	3.81	1.3	3.1	0.22	0.01	0.16	0.03	0.00	0.01	1.8
AK	6.83	0.65	3.12	750	5.55	0.37	10.4	0.48	0.21	0.33	0.49	1.54	2.70	5.8	8.7	0.63	0.03	0.19	0.03	0.01	0.07	16.3
AL	6.44	0.25	4.85	364	0.24	0.78	1.2	0.72	0.04	0.38	23.9	0.73	1.31	23.9	47	1.35	0.11	0.64	0.02	0.01	0.01	0.6
AM	3.65	0.02	3.92	659	4.14	0.29	6.5	0.33	0.40	0.45	28.9	0.30	1.23	15.3	136	1.14	0.09	0.51	0.02	0.04	0.15	17.9
AN	5.58	0.03	3.84	126	0.03	0.26	16.7	0.23	0.05	0.12	39.0	0.33	0.34	52	113	1.69	0.27	0.30	0.27	0.02	0.23	4.4
AO	4.60	0.02	4.08	354	2.01	0.18	0.8	0.42	0.33	0.27	2.69	0.48	0.38	6.2	42.7	0.86	0.05	0.43	0.06	0.16	0.21	63.2
AP	7.07	1.17	3.24	1246	7.29	0.52	8.4	0.81	3.07	0.67	0.14	0.68	4.12	4	2.9	0.61	0.04	0.19	0.04	0.00	0.03	1.2
AQ	4.80	0.11	22.6	2310	0.32	0.53	15.4	19.67	1.08	1.17	605	1.22	5.95	505	80.6	1.34	0.46	9.07	0.30	1.59	0.36	355
AR	5.31	0.02	5.28	885	6.89	0.42	17.3	0.72	0.44	0.58	36.0	0.67	3.35	11.9	59	2.07	0.10	0.78	0.03	0.05	0.07	20.7
AS	7.30	2.18	2.87	760	1.36	1.28	3.0	0.91	0.23	0.26	0.19	0.94	3.77	3.1	5.4	0.28	0.04	0.11	0.07	0.00	0.13	0.4
AT	7.40	2.42	6.74	1790	6.63	3.34	10.9	3.54	2.65	1.80	0.57	2.99	5.98	3.5	4	0.66	0.04	0.26	0.10	0.00	0.03	0.9
AU	7.50	4.12	4.76	1460	0.07	4.88	0.6	3.12	0.12	1.13	0.34	5.42	5.66	0.8	1.3	0.7	0.01	0.29	0.04	0.00	0.01	0.2
AV	3.94	0.01	3.98	485	3.32	0.20	0.6	0.34	0.48	0.22	8.19	0.50	0.92	4.5	143	1.63	0.06	0.64	0.05	0.75	0.70	73.8
AW	6.16	0.12	1.32	395	2.41	0.54	0.4	0.22	0.04	0.18	0.42	0.29	0.93	2.1	44.6	0.65	0.01	1.06	0.01	1.34	0.25	837
Min.	3.49	0.01	1.32	126	0.03	0.10	0.40	0.10	0.04	0.04	0.06	0.24	0.16	0.40	0.6	0.22	0.01	0.11	0.01	0.00	0.01	0.20
Max.	7.69	5.12	44.6	4000	15.97	18.99	166	31.71	3.07	6.42	605	9.09	18.43	505	238	8.18	5.15	44.1	28.8	9.62	4.38	1247
Av.	6.04	1.14	6.02	1191	5.17	1.87	11.5	2.60	0.63	0.88	26.00	1.62	4.59	28.2	43.6	1.55	0.20	1.60	0.67	0.31	0.24	62.3

n.d. = not detectable, min. = minimum value, max. = maximum value, av. = average value.

Table 3.8 Log-transformed free metal concentrations (between brackets) and metal activities (between square brackets) of six heavy metals in Dutch soils. All data in units of mol.l^{-1}.

Site	[Cu^{2+}]	(Cu^{2+})	[Cr^{2+}]	(Cr^{2+})	[Ni^{2+}]	(Ni^{2+})	[Cd^{2+}]	(Cd^{2+})	[Pb^{2+}]	(Pb^{2+})	[Zn^{2+}]	(Zn^{2+})
A	-6.02	-6.14	-6.97	-7.10	-6.14	-6.27	-7.61	-7.74	-7.08	-7.20	-5.27	-5.40
B	-6.85	-7.10	-6.80	-7.05	-6.39	-6.64	-8.02	-8.27	-7.77	-8.02	-5.14	-5.39
C	-6.03	-6.23	-6.87	-7.06	-6.24	-6.44	-8.14	-8.33	-7.10	-7.29	-5.77	-5.96
D	-7.97	-8.25	-7.51	-7.78	-7.53	-7.80	-8.03	-8.31	-9.48	-9.75	-5.99	-6.26
E	-7.75	-8.00	-7.72	-7.97	-7.63	-7.88	-7.14	-7.39	-9.28	-9.53	-4.44	-4.69
F	-8.00	-8.26	-7.64	-7.90	-7.85	-8.11	-8.40	-8.65	-9.96	-10.22	-6.21	-6.47
G	-7.10	-7.31	-7.47	-7.68	-7.18	-7.39	-8.08	-8.29	n.d.	n.d.	-6.31	-6.52
H	-6.11	-6.23	-6.90	-7.02	-6.17	-6.29	-7.26	-7.38	-6.95	-7.07	-4.87	-4.99
I	-6.07	-6.21	-6.95	-7.08	-6.16	-6.29	-6.66	-6.80	-6.81	-6.94	-4.69	-4.82
J	-6.31	-6.47	-7.28	-7.45	-6.22	-6.38	-6.74	-6.90	-7.73	-7.90	-4.33	-4.50
K	-6.35	-6.49	-7.08	-7.23	-6.00	-6.15	-7.47	-7.62	-5.45	-5.60	-5.28	-5.42
L	-9.50	-9.75	-7.48	-7.73	-7.11	-7.36	-8.25	-8.50	-8.39	-8.64	-5.99	-6.25
M	-6.30	-6.44	-6.95	-7.09	-6.19	-6.33	-7.39	-7.53	-7.33	-7.47	-4.95	-5.09
N	-6.99	-7.23	-7.42	-7.65	-7.04	-7.28	-8.31	-8.54	-8.19	-8.42	-6.17	-6.40
O	-6.13	-6.47	-7.12	-7.46	-6.24	-6.58	-6.73	-7.07	-8.37	-8.70	-4.91	-5.25
P	-6.87	-7.17	-7.36	-7.66	-6.78	-7.08	-7.63	-7.94	n.d.	n.d.	-5.37	-5.68
Q	-6.90	-7.29	-7.62	-8.01	-6.88	-7.26	-8.01	-8.40	-8.83	-9.21	-5.99	-6.37
R	-6.71	-7.08	-6.80	-7.17	-6.56	-6.93	-7.90	-8.28	-8.27	-8.64	-5.87	-6.24
S	-7.05	-7.27	-7.15	-7.37	-7.09	-7.31	-7.79	-8.02	-8.70	-8.92	-6.04	-6.26
T	-7.00	-7.30	-7.14	-7.44	-6.71	-7.02	-7.88	-8.18	-8.43	-8.73	-5.96	-6.27
U	-5.92	-6.24	-6.94	-7.26	-5.93	-6.25	-7.32	-7.64	-7.39	-7.70	-4.96	-5.28
V	-7.36	-7.55	-7.39	-7.58	-7.28	-7.48	-8.45	-8.64	-9.81	-10.00	-6.00	-6.19
W	-7.61	-7.79	-7.35	-7.53	-7.25	-7.44	-7.76	-7.94	-9.37	-9.55	-5.68	-5.86
X	-6.41	-6.79	-5.29	-5.68	-4.51	-4.90	-5.41	-5.79	-6.34	-6.72	-3.00	-3.38
Y	-5.81	-5.95	-6.24	-6.38	-6.34	-6.48	-6.79	-6.93	-5.88	-6.02	-4.77	-4.91
Z	-5.99	-6.23	-7.15	-7.39	-6.30	-6.54	-7.82	-8.06	-7.29	-7.53	-5.08	-5.32
AA	-6.70	-6.89	-7.57	-7.76	-6.79	-6.98	-7.77	-7.96	-7.44	-7.63	-4.28	-4.47
AB	-6.72	-6.92	-7.30	-7.50	-6.82	-7.02	-7.88	-8.08	-7.39	-7.58	-4.21	-4.40
AC	-5.92	-6.02	-6.52	-6.61	-6.49	-6.58	-7.60	-7.70	-6.41	-6.50	-5.58	-5.68
AD	-5.92	-6.06	-7.21	-7.36	-6.43	-6.57	-7.52	-7.66	-8.08	-8.22	-5.04	-5.18
AE	-5.66	-5.78	-7.07	-7.19	-6.41	-6.52	-7.40	-7.51	-6.58	-6.69	-5.32	-5.44
AF	-7.43	-7.61	-7.14	-7.32	-7.56	-7.75	-8.59	-8.77	-9.13	-9.31	-6.51	-6.70
AG	-6.59	-6.96	-7.32	-7.68	-6.29	-6.66	-8.11	-8.47	-8.25	-8.61	-6.09	-6.46
AH	-6.32	-6.47	-6.53	-6.68	-6.13	-6.28	-7.84	-7.99	-7.06	-7.21	-5.71	-5.86
AI	-7.84	-8.07	-7.48	-7.71	-7.58	-7.81	-8.81	-9.04	-9.49	-9.72	-6.83	-7.06
AJ	-7.99	-8.19	-7.92	-8.12	-7.59	-7.79	-8.83	-9.03	-9.44	-9.64	-5.82	-6.02
AK	-7.04	-7.23	-7.52	-7.71	-6.96	-7.14	-8.18	-8.37	-7.59	-7.78	-4.84	-5.03
AL	-6.68	-6.82	-6.97	-7.11	-6.35	-6.49	-8.28	-8.42	-8.34	-8.48	-6.30	-6.44
AM	-5.98	-6.13	-7.04	-7.19	-6.31	-6.47	-7.47	-7.63	-6.89	-7.05	-4.76	-4.92
AN	-5.91	-6.00	-6.57	-6.66	-6.56	-6.65	-7.67	-7.77	-6.72	-6.81	-5.38	-5.47
AO	-6.24	-6.36	-7.33	-7.44	-6.41	-6.53	-6.83	-6.94	-6.75	-6.87	-4.23	-4.34
AP	-7.27	-7.50	-7.38	-7.60	-7.13	-7.36	-8.71	-8.94	-8.26	-8.48	-5.98	-6.20
AQ	-6.78	-7.07	-6.34	-6.63	-5.16	-5.45	-6.12	-6.41	-6.70	-6.99	-3.52	-3.81
AR	-5.99	-6.19	-7.02	-7.23	-6.17	-6.37	-7.34	-7.55	-7.28	-7.49	-4.72	-4.93
AS	-7.91	-8.11	-7.42	-7.62	-7.71	-7.91	-9.11	-9.31	-7.97	-8.16	-6.50	-6.69
AT	-7.96	-8.24	-7.36	-7.64	-7.43	-7.71	-8.55	-8.83	-8.68	-8.96	-6.19	-6.47
AU	-7.97	-8.23	-7.85	-8.12	-7.55	-7.81	-8.77	-9.03	-9.26	-9.53	-6.23	-6.50
AV	-5.82	-5.96	-7.23	-7.37	-6.21	-6.35	-6.15	-6.29	-6.21	-6.35	-4.15	-4.29
AW	-6.33	-6.48	-7.92	-8.07	-6.02	-6.17	-5.91	-6.06	-6.72	-6.87	-3.11	-3.25

As can be deduced from Table 3.7 the pore water composition varies strongly among soils, which is obvious given the variance among soil types and soil properties. Similar as for total metal concentrations, the data reported in Table 3.7 were compared to the data reported by Janssen *et al.* (1996). As a typical result of this comparison, in Figure 3.3 a plot of the (log-transformed) total Cd levels found in the pore water by Janssen *et al.* (1996), are plotted as a function of the (log-transformed) total concentration of Cd in the pore water for soils A-T, as reported in Table 3.7. As can be deduced from Figure 3.3, Cd-levels reported in this study systematically exceed the values reported by Janssen *et al.* (1996). On the one hand, this finding is surprising in view of the fact that in this study the pore water was filtered over a 0.45 μm filter prior to analysis, whereas in case of Janssen *et al.* (1996), a 2.5 μm filter was used. On the other hand, however, this finding may well reflect the addition of a 2 m*M* aqueous solution of $Ca(NO_3)_2$ to the soils in order to generate sufficient quantities of pore water in all soils, as was done in this study.

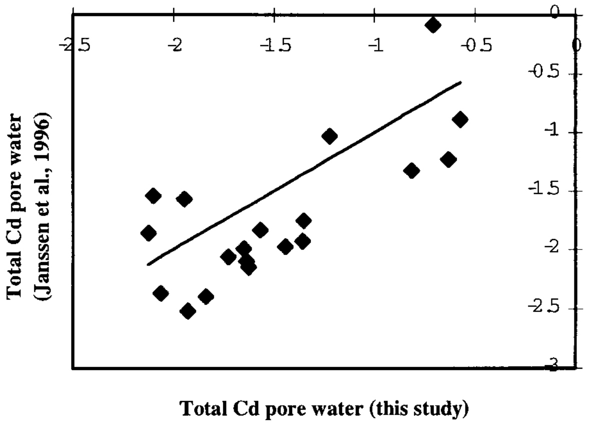

Figure 3.3 Plot of the (log-transformed) total Cd levels found in the pore water by Janssen *et al.* (1996), versus the (log-transformed) total concentration of Cd, as reported in Table 3.7 (soils A-T). Cd-levels are in units of $nmol.l^{-1}$.

3.5 Partition coefficients

In Tables 3.9 - 3.11 calculated partition coefficients are given. The values of partition coefficients defined as the ratio of the metal concentration in the solid phase to the calculated metal activity in the pore water, will not be given.

Table 3.9 Calculated partition coefficients for 13 metals and As in Dutch soils (K_p, $L.kg^{-1}$), defined as the ratio between the total metal concentrations in the solid phase (*aqua regia* destruction) and the pore water.

Site	Cu	Cr	Ni	As	Cd	Pb	Zn	Al	Fe	Mn	Mg	Ca	K	Na
A	42	6.35E+03	247	3.49E+03	22	1.57E+03	4.49E+01	2.42E+03	5.75E+03	2.07E+01	91	20	31	3
B	584	9.63E+03	1349	1.20E+04	253	6.55E+03	1.77E+02	5.19E+04	4.17E+04	7.14E+02	294	34	3284	9
C	528	1.48E+04	1151	4.50E+03	448	2.65E+03	9.60E+02	3.47E+04	1.25E+04	6.62E+02	392	67	150	30
D	249	3.60E+04	1146	4.65E+03	976	5.79E+04	5.05E+03	2.02E+05	2.14E+05	9.65E+04	172	77	75	7
E	296	4.02E+04	802	1.65E+04	473	1.48E+05	7.57E+02	2.42E+05	2.27E+05	6.86E+03	153	21	799	71
F	466	5.49E+04	1305	6.53E+03	3036	7.89E+04	1.36E+04	1.90E+05	5.50E+05	3.36E+04	279	67	2330	38
G	457	3.76E+04	1170	5.69E+03	3801	n.d.	1.52E+04	2.95E+05	4.48E+05	4.38E+03	919	183	2308	87
H	28	6.66E+02	n.d.	7.77E+02	30	6.28E+02	1.38E+01	6.19E+02	1.43E+03	1.54E+02	20	4	21	15
I	35	4.18E+03	196	2.13E+03	13	7.06E+02	1.01E+01	4.86E+02	2.78E+03	2.16E+01	17	4	12	4
J	48	3.70E+03	43	4.48E+03	44	4.64E+03	1.66E+01	5.27E+03	1.48E+04	1.25E+02	30	8	83	13
K	7	3.23E+03	78	4.69E+02	n.d.	6.06E+01	1.94E+01	1.02E+03	2.56E+03	8.73E+01	20	7	20	2
L	58	7.87E+03	216	1.41E+03	226	2.50E+03	6.19E+02	1.76E+04	2.62E+04	2.44E+03	61	64	75	4
M	45	3.52E+03	135	1.58E+03	9	1.03E+03	2.23E+01	1.92E+03	3.48E+03	5.51E+01	67	8	38	5
N	790	3.61E+04	1517	1.96E+04	453	1.57E+04	3.81E+03	6.60E+04	9.64E+04	7.92E+03	61	11	501	13
O	151	1.19E+04	221	1.98E+04	200	1.49E+04	1.43E+02	7.89E+04	1.72E+05	2.22E+03	10	5	11	1
P	860	6.60E+04	927	6.42E+03	861	n.d.	1.65E+03	2.88E+05	7.88E+05	6.97E+03	214	134	1087	2
Q	667	4.87E+04	1639	4.85E+03	298	1.56E+05	1.52E+03	1.28E+05	1.06E+05	1.77E+04	45	32	93	8
R	265	8.36E+03	534	8.25E+03	603	1.47E+04	2.97E+03	4.93E+04	5.95E+04	2.36E+03	77	32	26	3
S	2200	4.31E+04	3547	2.06E+04	7331	1.30E+05	1.82E+04	5.48E+05	4.89E+05	1.57E+05	282	58	1300	11
T	470	1.25E+04	573	1.07E+04	772	2.07E+04	3.12E+03	7.64E+04	4.92E+04	6.87E+03	83	18	184	1

U	201	2.03E+04	492	1.15E+04	144	1.22E+04	1.76E+02	2.09E+04	7.03E+04	3.41E+01	77	17	1080	12
V	50	1.72E+04	238	4.59E+02	315	1.25E+04	4.94E+02	3.52E+05	5.84E+05	n.d.	653	184	677	18
W	179	1.82E+04	319	3.99E+02	120	1.39E+04	4.47E+02	8.40E+05	6.87E+05	n.d.	1112	139	495	53
X	75	1.25E+02	9	6.06E+00	6	7.04E+02	6.40E+00	5.70E+04	4.71E+03	1.82E+01	8	3	67	3
Y	141	1.39E+03	448	9.74E+02	45	7.98E+02	1.04E+02	5.05E+03	1.95E+03	8.48E+01	198	29	447	52
Z	125	2.08E+03	101	5.47E+02	73	2.22E+03	8.33E+01	4.23E+03	7.47E+03	1.20E+03	13	10	6	1
AA	520	8.58E+03	997	2.34E+03	195	3.82E+03	1.05E+02	1.06E+04	9.39E+03	3.80E+02	46	16	64	4
AB	394	6.99E+03	671	2.33E+03	159	3.11E+03	7.40E+01	9.40E+03	8.39E+03	6.02E+02	37	12	34	1
AC	26	3.95E+02	103	1.55E+02	81	2.59E+02	5.91E+01	4.38E+02	2.28E+02	3.14E+02	171	50	69	7
AD	30	1.08E+03	n.d.	1.63E+03	22	4.38E+02	1.24E+01	8.36E+02	4.10E+02	1.78E+01	15	6	50	2
AE	8	1.74E+03	41	2.28E+02	n.d.	2.24E+02	1.95E+01	1.14E+03	1.07E+03	6.71E+01	41	29	38	9
AF	37	5.10E+03	513	2.87E+02	180	1.86E+03	7.85E+02	1.24E+04	5.65E+03	2.84E+03	584	208	115	6
AG	306	5.52E+04	1346	1.98E+04	217	1.01E+04	9.55E+02	3.98E+05	3.27E+05	1.76E+02	49	11	216	14
AH	239	4.27E+03	578	3.80E+03	378	1.92E+03	6.40E+02	8.00E+03	3.44E+03	6.56E+02	383	116	1453	31
AI	348	4.07E+04	1822	1.46E+03	2336	2.70E+04	1.26E+04	3.67E+05	3.63E+05	5.88E+04	364	166	100	10
AJ	285	2.18E+04	768	1.16E+03	417	6.47E+03	1.85E+02	5.94E+04	7.11E+04	3.83E+04	206	31	59	6
AK	851	8.19E+03	926	2.58E+03	1327	9.07E+03	1.17E+03	2.58E+04	2.70E+04	6.76E+03	142	50	126	4
AL	340	1.75E+04	1556	8.41E+03	666	2.24E+04	2.80E+03	3.76E+04	2.49E+04	3.96E+02	930	110	5236	71
AM	83	2.85E+03	92	2.69E+03	20	8.83E+02	1.14E+01	1.58E+03	6.72E+03	3.93E+01	50	15	37	8
AN	102	8.53E+02	131	2.02E+02	203	6.53E+02	1.26E+02	1.29E+03	9.92E+02	7.69E+01	103	48	211	5
AO	12	1.38E+03	n.d.	2.37E+02	11	2.06E+02	1.42E+00	7.42E+02	1.86E+03	7.49E+01	8	7	12	2
AP	362	1.46E+04	1362	2.40E+03	1925	7.44E+03	1.43E+03	9.97E+04	5.25E+04	4.84E+04	197	125	16	7
AQ	350	1.22E+03	26	4.47E+02	17	1.61E+03	1.10E+01	2.82E+03	2.33E+02	1.10E+01	22	8	21	3
AR	103	6.93E+03	241	1.60E+03	58	3.37E+03	3.32E+01	3.17E+03	8.81E+03	1.61E+02	39	12	38	3
AS	937	8.04E+03	1495	1.40E+03	763	1.40E+04	1.93E+03	4.94E+04	4.36E+04	1.78E+04	315	101	185	7
AT	822	1.07E+04	867	9.62E+02	1506	1.47E+04	2.82E+03	8.01E+04	6.36E+04	1.03E+04	62	70	24	4
AU	527	5.92E+04	938	4.78E+03	1298	4.18E+04	1.12E+04	4.49E+05	3.01E+05	1.56E+04	99	51	878	5
AV	67	1.15E+03	41	4.82E+02	7	2.98E+02	9.18E+00	2.96E+02	3.54E+03	2.95E+01	13	2	12	3
AW	7893	3.24E+04	458	4.78E+04	141	2.84E+04	1.38E+02	3.18E+03	9.55E+04	9.10E+03	105	30	385	62
Min.	7	1.25E+02	9	6.06E+00	6	6.06E+01	1.42E+00	2.96E+02	2.28E+02	1.10E+01	8	2	6	1
Max.	7893	6.60E+04	3547	4.78E+04	7331	1.56E+05	1.82E+04	8.40E+05	7.88E+05	1.57E+05	1112	208	5236	87
Av.	483	1.67E+04	726	5.74E+03	691	1.91E+04	2.17E+03	1.06E+05	1.24E+05	1.19E+04	190	51	502	15

n.d. = not detectable, min. = minimum value, max. = maximum value, av. = average value.

Table 3.10 Calculated partition coefficients for 6 metals and As in Dutch soils (K_p, $L.kg^{-1}$), defined as the ratio of the total metal concentrations in the solid phase (HNO_3 destruction) to the pore water.

Site	Cu	Cr	Ni	As	Cd	Pb	Zn
A	2.65E+01	6.23E+03	2.46E+02	3.49E+03	n.d.	2.08E+03	3.11E+01
B	6.34E+02	1.00E+04	1.46E+03	1.78E+04	n.d.	5.67E+03	2.01E+02
C	5.37E+02	1.38E+04	1.04E+03	6.78E+03	8.00E+01	2.92E+03	1.35E+03
D	2.41E+02	3.99E+04	9.17E+02	6.41E+03	7.69E+02	5.33E+04	5.68E+03
E	2.82E+02	3.03E+04	7.64E+02	1.63E+04	3.72E+02	1.25E+05	7.44E+02
F	4.88E+02	5.85E+04	1.39E+03	8.91E+03	2.60E+03	7.31E+04	1.55E+04
G	4.73E+02	4.08E+04	1.47E+03	6.39E+03	3.10E+03	n.d.	1.82E+04
H	n.d.	1.85E+03	n.d.	n.d.	2.35E+01	5.73E+02	1.82E+01
I	n.d.	1.89E+03	n.d.	2.63E+03	1.06E+01	6.37E+02	1.76E+01
J	n.d.	3.40E+03	n.d.	4.02E+03	3.19E+01	3.38E+03	1.44E+01
K	n.d.	6.77E+02	n.d.	9.31E+02	n.d.	5.91E+01	2.61E+01
L	2.05E+01	1.13E+04	2.55E+02	1.55E+03	1.35E+02	2.31E+03	7.17E+02
M	1.40E+01	4.79E+03	1.79E+02	2.33E+03	n.d.	8.87E+02	1.19E+01
N	3.85E+03	3.36E+04	1.44E+03	5.66E+04	4.27E+02	1.76E+04	4.30E+03
O	1.46E+02	8.44E+03	1.65E+02	2.45E+04	1.68E+02	2.08E+04	1.44E+02
P	9.09E+02	7.64E+04	8.97E+02	7.37E+03	6.67E+02	n.d.	1.67E+03
Q	5.70E+02	3.80E+04	1.44E+03	6.58E+03	1.80E+02	7.90E+04	1.75E+03
R	2.47E+02	9.02E+03	5.20E+02	9.75E+03	4.71E+02	1.29E+04	2.93E+03
S	2.26E+03	5.03E+04	3.43E+03	2.55E+04	6.02E+03	1.30E+05	2.14E+04
T	4.20E+02	1.23E+04	6.12E+02	1.21E+04	6.66E+02	1.82E+04	3.09E+03
U	2.15E+02	1.81E+04	4.83E+02	1.81E+04	1.07E+02	1.15E+04	1.92E+02
V	3.20E+01	1.19E+04	2.19E+02	5.42E+02	n.d.	1.18E+04	5.07E+02
W	1.53E+02	1.59E+04	2.93E+02	4.79E+02	7.33E+01	1.21E+04	4.09E+02
X	5.82E+01	8.90E+01	7.33E+00	7.63E+00	4.89E+00	5.12E+02	4.30E+00
Y	1.24E+02	1.34E+03	4.25E+02	1.23E+03	3.39E+01	6.85E+02	1.31E+02

Z	1.78E+01	2.46E+03	n.d.	5.48E+02	2.58E+01	1.62E+03	7.51E+01
AA	1.84E+02	5.70E+03	n.d.	4.36E+03	2.21E+02	3.39E+03	9.52E+01
AB	2.40E+02	2.84E+03	n.d.	5.08E+03	1.17E+02	2.62E+03	7.94E+01
AC	n.d.	4.06E+02	n.d.	3.87E+02	6.38E+01	2.20E+02	5.17E+01
AD	n.d.	1.16E+03	n.d.	2.42E+03	n.d.	3.50E+02	4.23E+00
AE	n.d.	1.95E+03	n.d.	2.60E+02	n.d.	2.61E+02	1.36E+01
AF	n.d.	5.41E+03	n.d.	3.29E+02	n.d.	1.23E+03	8.01E+02
AG	2.32E+02	5.86E+04	1.15E+03	2.61E+04	n.d.	8.17E+03	1.12E+03
AH	3.03E+02	3.32E+03	5.13E+02	5.51E+03	2.04E+02	1.80E+03	1.02E+03
AI	2.90E+02	3.11E+04	1.51E+03	2.07E+03	9.81E+02	2.22E+04	1.33E+04
AJ	n.d.	2.68E+04	8.00E+02	2.18E+03	.	6.67E+03	2.76E+02
AK	7.87E+02	1.59E+04	9.19E+02	4.16E+03	1.25E+03	8.90E+03	1.43E+03
AL	4.28E+02	2.63E+04	1.63E+03	1.82E+04	2.17E+02	2.32E+04	4.14E+03
AM	3.89E+01	3.58E+03	n.d.	4.43E+03	n.d.	8.07E+02	1.10E+01
AN	9.86E+01	9.38E+02	n.d.	2.49E+02	1.64E+02	5.62E+02	1.48E+02
AO	n.d.	1.92E+03	n.d.	n.d.	1.00E+01	1.60E+02	1.84E+00
AP	2.76E+02	1.18E+04	1.03E+03	3.30E+03	1.27E+03	6.24E+03	1.62E+03
AQ	2.02E+02	8.23E+02	1.65E+01	3.52E+02	1.15E+01	1.03E+03	8.79E+00
AR	1.13E+02	4.49E+03	n.d.	2.64E+03	6.11E+01	4.06E+03	5.38E+01
AS	8.74E+02	7.57E+03	1.39E+03	1.79E+03	4.17E+00	1.38E+04	2.56E+03
AT	8.25E+02	1.16E+04	7.60E+02	1.43E+03	1.13E+03	1.38E+04	3.27E+03
AU	4.95E+02	4.24E+04	8.33E+02	5.64E+03	7.28E+02	3.68E+04	1.64E+04
AV	3.68E+01	1.76E+03	1.96E+01	n.d.	5.93E+00	2.82E+02	1.14E+01
AW	1.07E+04	4.71E+04	4.72E+02	5.95E+04	1.42E+02	3.15E+04	1.69E+02
Min.	3.66E+00	8.90E+01	7.33E+00	7.63E+00	4.17E+00	5.91E+01	1.82E+00
Max.	1.07E+04	7.64E+04	3.43E+03	5.95E+04	6.02E+03	1.30E+05	2.14E+04
Av.	6.95E+02	1.66E+04	6.28E+02	8.02E+03	5.42E+02	1.65E+04	2.56E+03

n.d. = not detectable, min. = minimum value, max. = maximum value, av. = average value.

Table 3.11 Calculated partition coefficients for 13 metals in Dutch soils (K_p, $L.kg^{-1}$), defined as the ratio between the extractable metal concentrations in the solid phase ($CaCl_2$ extraction) and the pore water.

Site	Cu	Cr	Ni	As	Cd	Pb	Zn	Al	Fe	K	Mg	Mn	Na
A	0.60	1.89	4.40	3.17	7.07	48.91	2.87	18.58	3.24	1.36	1.66	4.60	0.48
B	1.25	4.29	5.98	4.04	10.52	n.d.	0.77	1.41	1.32	9.89	9.24	16.35	1.26
C	1.20	1.35	11.94	0.64	26.32	0.47	14.13	1.62	0.33	8.83	17.38	13.58	2.18
D	0.62	n.d.	0.82	8.72	8.49	13.70	5.02	n.d.	n.d.	2.60	3.92	n.d.	0.60
E	0.63	n.d.	4.24	7.80	19.76	4.78	12.01	n.d.	1.43	5.25	4.47	7.28	0.88
F	0.85	n.d.	0.95	6.77	24.31	n.d.	11.86	n.d.	3.35	13.69	4.61	6.91	1.22
G	1.05	1.50	0.75	5.78	20.86	n.d.	9.55	3.21	4.57	8.96	5.11	0.50	1.05
H	0.16	0.70	2.99	3.78	15.96	22.86	4.60	17.98	1.56	0.55	1.08	2.49	0.40
I	0.27	2.40	5.06	13.14	9.80	25.83	3.27	17.85	8.15	0.80	0.98	1.28	0.50
J	0.13	n.d.	3.83	7.46	12.60	21.21	3.95	11.82	2.36	0.68	0.79	4.71	0.24
K	0.07	n.d.	0.35	2.36	0.53	14.45	0.58	3.78	3.78	0.55	0.45	0.55	0.33
L	0.19	n.d.	n.d.	3.47	3.07	n.d.	1.67	n.d.	0.71	1.42	1.46	1.43	0.30
M	1.17	1.50	4.72	3.74	4.23	19.97	2.06	14.46	4.64	1.05	1.03	2.62	0.46
N	1.75	n.d.	0.90	4.09	11.09	1.46	3.39	n.d.	1.11	3.96	1.47	54.47	0.50
O	0.58	2.16	2.18	8.15	14.18	n.d.	5.16	2.66	3.86	1.55	1.58	56.84	0.49
P	1.99	1.63	1.41	8.88	5.91	n.d.	1.69	n.d.	n.d.	2.62	2.21	7.57	0.67
Q	0.98	n.d.	1.51	9.45	0.63	n.d.	1.40	n.d.	0.86	2.94	2.19	2.38	0.84
R	0.74	0.58	0.45	8.39	4.19	n.d.	1.47	n.d.	n.d.	1.33	1.39	1.70	0.48
S	1.26	1.60	3.45	6.42	43.37	n.d.	19.29	n.d.	n.d.	7.99	11.49	4.02	1.95
T	0.95	0.96	0.58	4.32	9.05	n.d.	3.24	n.d.	n.d.	2.36	2.39	3.78	0.57
U	0.52	4.74	2.95	5.91	8.33	18.77	3.45	8.29	10.95	15.71	4.53	6.87	1.84
V	0.14	n.d.	0.45	4.06	0.99	n.d.	n.d.	n.d.	5.02	7.27	7.55	n.d.	0.89
W	0.49	n.d.	0.40	3.30	0.77	n.d.	n.d.	n.d.	5.02	7.36	9.93	n.d.	0.92
X	0.56	1.63	2.97	0.49	2.87	3.79	3.13	5.67	9.83	1.76	1.69	3.03	1.20
Y	0.73	0.26	7.88	0.04	22.73	14.23	12.78	3.45	0.15	5.42	7.77	5.01	0.66
Z	0.14	0.84	0.82	2.41	7.65	1.46	10.80	2.03	1.00	1.18	2.84	60.91	0.47
AA	0.53	n.d.	3.89	4.92	33.05	1.83	16.65	2.07	0.82	2.14	3.61	4.13	0.56
AB	1.05	1.16	5.12	4.87	29.90	1.97	14.61	1.48	1.27	2.13	3.20	10.45	0.59
AC	n.d.	0.28	5.59	0.45	49.25	10.08	15.01	11.64	0.23	2.33	6.62	10.87	1.40
AD	0.13	1.81	3.04	5.05	11.48	7.20	3.52	18.83	0.45	2.47	1.85	2.28	0.49
AE	0.07	1.41	2.85	1.36	2.37	10.94	2.89	9.55	1.01	1.54	3.49	4.81	0.64
AF	0.17	n.d.	n.d.	2.23	0.67	n.d.	n.d.	n.d.	0.08	3.37	4.87	0.55	0.62

AG	0.52	2.04	4.11	9.95	8.46	n.d.	2.08	3.14	4.73	4.84	3.41	3.75	1.38
AH	0.25	0.31	4.30	0.14	20.99	0.44	17.36	0.56	0.16	14.78	30.43	8.36	2.96
AI	0.57	n.d.	1.77	3.25	6.25	n.d.	9.05	n.d.	2.51	4.18	7.40	n.d.	1.16
AJ	0.43	n.d.	n.d.	3.07	2.03	n.d.	n.d.	n.d.	n.d.	2.30	4.09	n.d.	0.58
AK	1.12	n.d.	3.42	4.57	44.53	n.d.	26.70	1.50	0.69	4.15	7.86	4.10	0.87
AL	0.54	0.40	7.96	1.44	48.63	n.d.	6.36	0.31	0.12	13.17	34.35	15.57	2.64
AM	0.96	3.37	5.66	6.74	7.18	34.39	1.87	13.97	6.44	1.98	2.10	2.62	0.77
AN	0.34	0.51	7.14	0.85	121.07	1.99	27.39	5.38	0.19	3.60	12.48	5.25	0.82
AO	0.09	n.d.	3.68	1.75	7.78	8.22	0.76	26.01	0.97	0.76	1.92	2.57	0.44
AP	1.68	n.d.	1.09	3.08	8.59	n.d.	n.d.	n.d.	0.75	1.70	4.14	13.65	0.62
AQ	2.69	1.91	5.43	4.61	6.87	3.93	5.21	5.52	0.06	1.22	1.42	1.31	0.55
AR	0.52	2.13	4.20	5.84	16.39	5.15	7.67	8.45	1.94	2.25	2.63	7.60	0.77
AS	1.83	2.16	n.d.	3.19	4.73	0.61	n.d.	n.d.	0.64	3.55	6.32	n.d.	0.86
AT	1.85	n.d.	2.31	5.42	4.71	2.88	4.13	n.d.	2.01	2.85	5.42	2.46	1.03
AU	0.85	n.d.	n.d.	3.09	3.88	n.d.	17.60	n.d.	2.51	4.94	7.23	n.d.	1.49
AV	1.02	1.66	2.79	5.94	4.77	19.02	3.46	10.05	5.58	0.69	0.64	1.09	0.29
AW	3.86	n.d.	8.32	4.48	21.59	22.04	7.65	0.38	1.91	4.07	0.40	17.96	0.41
Min.	0.07	0.26	0.35	0.04	0.53	0.44	0.58	0.31	0.06	0.55	0.40	0.50	0.24
Max.	3.86	4.74	11.94	13.14	121.07	48.91	27.39	26.01	10.95	15.71	34.35	60.91	2.96
Av.	0.84	1.63	3.51	4.55	15.52	11.81	7.63	7.72	2.52	4.12	5.41	9.24	0.88

n.d. = not detectable, min. = minimum value, max = maximum value, av. = average value.

As can be deduced from Tables 3.9 - 3.11, K_p-values vary strongly: not only among metals, but also for a single metal among soils. In most cases K_p-values differ by several orders of magnitude. Consistently higher K_p values were found with the two digestion methods used in this study, than with the 0.01 *M* $CaCl_2$ extraction. As the pore water concentrations in general are higher than the concentrations reported by Janssen *et al.* (1996), the K_p-values reported here for soils A-T are systematically lower than the K_p-values reported in the latter study.

From the data presented in Tables 3.9 - 3.11, addition of heavy metals in general leads to significantly lower K_p-values, or in other words: metals added to the field soils show an increased bioavailability for organisms with predominant metal uptake via the pore water. When comparing the K_p-values obtained for soils AR and AQ (which is soil AR after addition of a mixture of metal salts), it becomes clear that with the exception of Cu (HNO_3-digestion) and As ($CaCl_2$-extraction, although it should be noted that As was not present in the metal mixture that was added to the soil), the values obtained for soil AQ are significantly lower. In addition, from the data presented it can be deduced that K_p-values for soil X (OECD artisoil, to which the same mixture of metal salts was added), for all metals studied are at the very low end of the range of partition coefficients found in this study, and in fact for Cr, Ni and As, the values obtained for soil X are the minimum values found for all soils studied.

4 RELATIONS BETWEEN SOIL CHARACTERISTICS

PCA (section 2.8) was performed on all soil characteristics for which experimental data were available, to study the correlation between the sampled soils. From the outcome of the score plot thus obtained an indication of the similarity and diversity of soils can be gained. Soils which plot out near each other on the score plot may be related. The first two principal components explained 73 % of the variance. The third principal component explained only a small percentage of the remaining variance (8 %) and did not add much more information. Figure 4.1 shows the scores of the soils for the first two principal components. As can be seen from this Figure, soils AA and AB (which represent duplicate sampling) plot out near each other, clearly indicating the similarity of these soils. Figure 4.1 also shows that only vaguely some clustering of the soil samples can be distinguished. The soils are distributed over the score plot, which is a reflection of variation of the soil characteristics amongst sites according to the criteria used for the selection of the sampling sites. Due to their high organic matter content, the soils U and AH do not fall within the 95 % confidence interval. Nevertheless, these soils were included in all statistical anlyses.

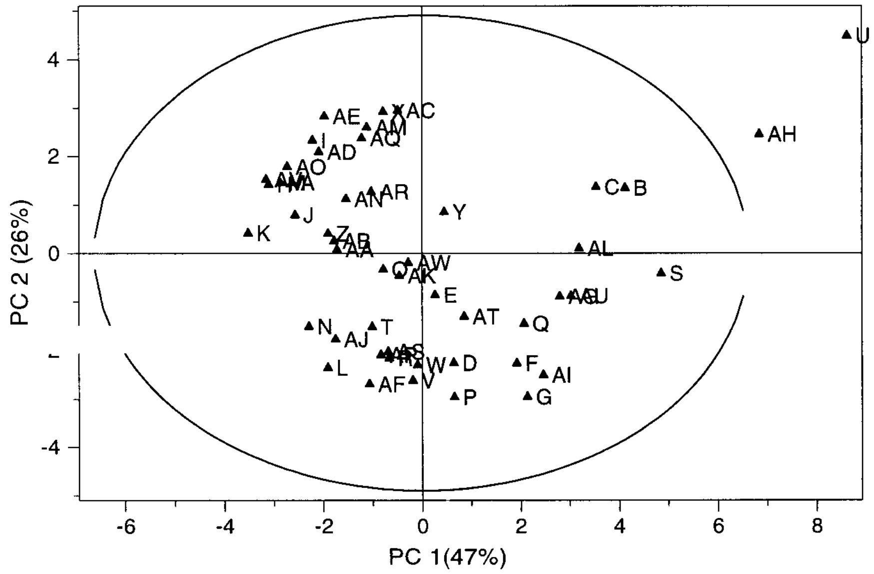

Figure 4.1 Principal component (PC) score plot of the soils sampled. The ellipsoid indicates the 95 % confidence interval.

The relation between K_p values and soil characteristics strongly depends on the relationships between soil characteristics. The most important soil characteristics that need to be taken into account are:

(i) The adsorption phases: clay, organic matter (OM) and Fe- and Al-oxyhydroxides.
(ii) Many studies have shown the importance of soil pH. In this study the pH was measured as pH(KCl), pH(pw), and pH($CaCl_2$).
(iii) Competitive sorbed ions, corresponding with the CEC, since the CEC is determined as the amount of desorbed ions upon a high concentration of cations. Especially Ca is an important cation at the exchange complex of soils in the Netherlands.

Among the pore water characteristics influencing metal adsorption, complex-forming anions are an important factor. Especially dissolved organic carbon (DOC) is known to complex metals and keep them into solution. Therefore, DOC was taken into account as an important soil characteristic. Figure 4.2 shows the loadings of the soil characteristics for the first two principal components. The loading plot shows two clusters of soil characteristics. The first cluster contains most of solid phase characteristics: LOI1, OM, N, Fe-ox, pF2, clay and CEC. Within this cluster a sub-cluster of Fe-ox, CEC and clay seems to be present. To a lesser extent this also hold for Al hydroxide. CEC is correlated with Al-ox, OM, clay and Fe-ox, since they provide the main adsorption phases in the soil.

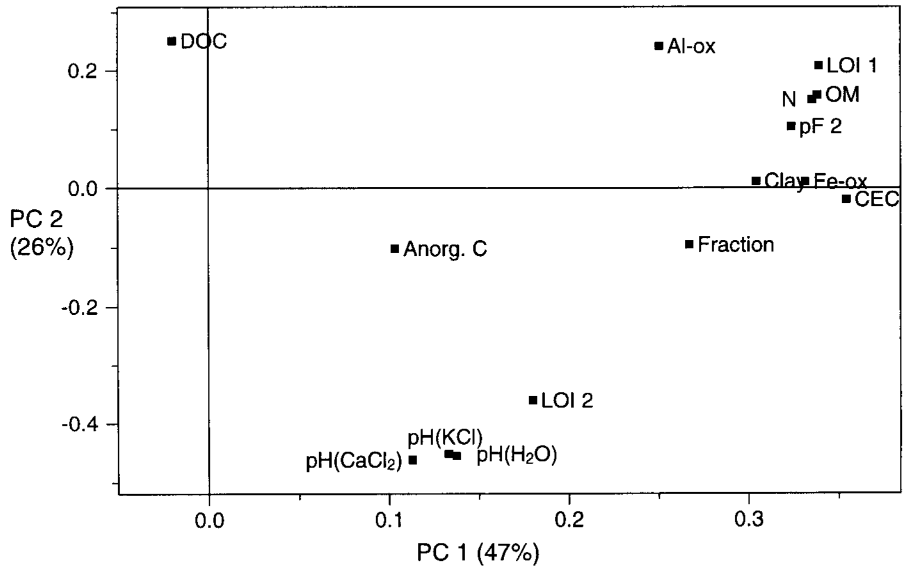

Figure 4.2 Principal component (PC) loading plot of the soils sampled.

The second cluster shows that the pH's are closely related. This suggests that no further information is gained when the pH's are measured in several ways. To study the relationship between K_p values and soil characteristics it is sufficient to use one type of pH measurement. For practical reasons the best choice seems pH($CaCl_2$), as the method to determine this pH is easy to carry out and already commonly used. Quantitatively, in Table 4.1 the correlation between the three pH's is given.

Table 4.1 Results of monovariate correlations between the three pH's determined in this study.

pH($CaCl_2$) = -1.15 + 1.13 * pH(pw)	R^2_{adj}=0.951, n=47, F=902, P<0.001
pH($CaCl_2$) = 1.17 + 0.83 * pH(KCl)	R^2_{adj}=0.905, n=40, F=373, P<0.001
pH(pw) = 2.12 + 0.72 * pH(KCl)	R^2_{adj}=0.891, n=40, F=319, P<0.001

5 CORRELATIONS BETWEEN PARTITION COEFFICIENTS AND SOIL CHARACTERISTICS

5.1 General

As indicated above, one of objectives of this study was to derive models for predicting metal partitioning in Dutch field soils, based upon a limited number of easily determinable soil and pore water characteristics. As soils X (OECD artisoil) and AQ (a soil sample to which metal salts were added in the laboratory), do not represent field soils, these two soils were left out of the data set used for the multivariate data analyses. Soil AB is a duplication of sample AA. To warrant an unbiased data set, soil AB too was left out of the data analysis, which left a data base of 46 field soils.

As indicated in chapter 1, six different sets of K_p values were obtained by combining three expressions for the metal concentrations in the solid phase and either total metal concentrations in the pore water or pore water activities. In addition, the non-available metal fraction in the solid matrix (in this study defined as the difference in metal levels found between either *aqua regia* or concentrated nitric acid destruction and 0.01 *M* $CaCl_2$ extraction) was correlated to soil characteristics. Finally, models are derived for calculating these non-available metal fractions.

5.2 Multivariate regression models for 46 soils

In Tables 5.1 - 5.8, the results of the multivariate regression analyses are given for each of the metals included in this study. Apart from the actual models, also the relevant statistical information is provided. In all cases the relevant soil and pore water characteristics are giving in decreasing order of importance.

Table 5.1 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, As, Cd, Pb, Zn (defined as the ratio of the total metal concentrations in the solid phase (*aqua regia* digestion) and the pore water), and soil and pore water characteristics.

Metal	Regression equation obtained	Statistics
Cu	log K_p = -0.20 + 0.28 * pH($CaCl_2$) + 0.89 * log Al-ox - 0.56 * log DOC	R^2_{adj}=0.742, n=46, F=45.0, P<0.001
Cr	log K_p = 2.16 + 0.25 * pH($CaCl_2$) + 0.40 * log CEC	R^2_{adj}=0.694, n=46, F=53.2, P<0.001
Ni	log K_p = 0.46 + 0.25 * pH($CaCl_2$) + 0.41 * log Al-ox + 0.22 * log CEC	R^2_{adj}=0.712, n=44, F=36.4, P<0.001
As	log K_p = 1.86 - 0.98 * log LOI_l + 0.95 * log Fe-ox + 0.52* log Al-ox	R^2_{adj}=0.385, n=46, F=10.6, P<0.001
Cd	log K_p = 1.38 + 0.49 * pH($CaCl_2$) + 0.80 * log Al-ox	R^2_{adj}=0.811, n=45, F=95.7, P<0.001
Pb	log K_p = -0.13 + 0.48 * pH($CaCl_2$) + 0.16 * log Fraction + 0.73 * log Al-ox	R^2_{adj}=0.837, n=45, F=76.5, P<0.001
Zn	log K_p = -1.07 + 0.51 * pH($CaCl_2$) + 0.55 * log Clay + 0.22 * log Al-ox	R^2_{adj}=0.838, n=46, F=80.6, P<0.001

Table 5.2 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, As, Cd, Pb, Zn (defined as the ratio of the total metal concentrations in the solid phase (nitric acid digestion) and the pore water), and soil and pore water characteristics.

Metal	Regression equation obtained	Statistics
Cu	log K_p = 0.90 + 0.10 * pH($CaCl_2$) - 0.37 * log Fraction + 1.00 * log Fe-ox - 0.91* log DOC	R^2_{adj}=0.548, n=36, F=11.9, P<0.001
Cr	log K_p = 1.88 + 0.25 * pH($CaCl_2$) + 0.38 * log Fe-ox	R^2_{adj}=0.697, n=46, F=54.0, P<0.001
Ni	log K_p = 0.85 + 0.15 * pH($CaCl_2$) + 0.54 * log Fe-ox	R^2_{adj}=0.568, n=32, F=21.4, P<0.001
As	log K_p = 2.18 - 0.34 * log Fraction + 0.99 * log Fe-ox	R^2_{adj}=0.294, n=44, F=9.96, P<0.001
Cd	log K_p = 1.41 + 0.46 * pH($CaCl_2$) + 0.80 * log Al-ox	R^2_{adj}=0.584, n=35, F=24.9, P<0.001
Pb	log K_p = -0.35 + 0.50 * pH($CaCl_2$) + 0.86 * log Al-ox	R^2_{adj}=0.818, n=45, F=99.7, P<0.001
Zn	log K_p = -1.18 + 0.52 * pH($CaCl_2$) + 0.55 * log Clay + 0.24 * log Al-ox	R^2_{adj}=0.832, n=46, F=80.6, P<0.001

Table 5.3 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, As, Cd, Pb, Zn (defined as the ratio of the total metal concentrations in the solid phase ($CaCl_2$-extraction) and the pore water) and soil and pore water characteristics.

Metal	Regression equation obtained	Statistics
Cu	log K_p = -0.61 + 0.41 * log Fe-ox - 0.51 * log DOC	R^2_{adj}=0.357, n=45, F=13.5, P<0.001
Cr	No significant correlation	--
Ni	log K_p = 0.26 - 0.14 * pH($CaCl_2$) + 0.64 * log Al-ox	R^2_{adj}=0.677, n=42, F=44.0, P<0.001
As	log K_p = -0.15 + 0.15 * pH($CaCl_2$) - 0.25 * log Clay	R^2_{adj}=0.149, n=46, F=5.03, P=0.011
Cd	log K_p = -0.01 - 0.38 * log LOI_2 + 1.01 * log Al-ox - 0.73 * log DOC	R^2_{adj}=0.585, n=46, F=22.6, P<0.001
Pb	log K_p = 1.79 - 0.20 * pH($CaCl_2$)	R^2_{adj}=0.170, n=27, F=6.31, P=0.019
Zn	log K_p = 0.22 + 0.55 * log Al-ox - 0.45 * log DOC	R^2_{adj}=0.262, n=41, F=8.11, P=0.001

Table 5.4 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, Cd, Pb, Zn (defined as the ratio of the total metal concentration in the solid phase (*aqua regia* digestion) and the metal activities in the pore water) and soil and pore water characteristics.

Metal	Regression equation obtained	Statistics
Cu	log K_p = -1.27 + 0.72 * pH($CaCl_2$) + 0.92 * log LOI_1 - 0.24 * log Fraction	R^2_{adj}=0.858, n=46, F=93.7, P<0.001
Cr	log K_p = 1.89 + 0.28 * pH($CaCl_2$) + 0.40 * log Fe-ox	R^2_{adj}=0.719, n=46, F=59.9, P<0.001
Ni	log K_p = 0.38 + 0.43 * pH($CaCl_2$) + 0.50 * log Clay	R^2_{adj}=0.865, n=44, F=138.3, P<0.001
Cd	log K_p = -1.48 + 0.55 * pH($CaCl_2$) + 0.58 * log LOI_1 + 0.40 * log Al-ox	R^2_{adj}=0.874, n=45, F=103.0, P<0.001
Pb	log K_p = 0.07 + 0.70 * pH($CaCl_2$) + 0.56 * log Fraction	R^2_{adj}=0.837, n=45, F=113.6, P<0.001
Zn	log K_p = -1.04 + 0.55 * pH($CaCl_2$) + 0.60 * log Clay + 0.21 * log Al-ox	R^2_{adj}=0.869, n=46, F=102.9, P<0.001

Table 5.5 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, Cd, Pb, Zn (defined as the ratio of the total metal concentration in the solid phase (nitric acid digestion) and the metal activities in the pore water) and soil and pore water characteristics.

Metal	Regression equation obtained	Statistics
Cu	$\log K_p = -1.53 + 0.74 * \mathrm{pH(CaCl_2)} + 1.23 * \log \mathrm{LOI_1} - 0.42 * \log \mathrm{Fraction}$	R^2_{adj}=0.809, n=38, F=53.1, P<0.001
Cr	$\log K_p = 1.88 + 0.28 * \mathrm{pH(CaCl_2)} + 0.42 * \log \mathrm{Fe\text{-}ox}$	R^2_{adj}=0.719, n=46, F=60.0, P<0.001
Ni	$\log K_p = 0.36 + 0.43 * \mathrm{pH(CaCl_2)} + 0.54 * \log \mathrm{Clay}$	R^2_{adj}=0.888, n=46, F=183.0, P<0.001
Cd	$\log K_p = -1.89 + 0.54 * \mathrm{pH(CaCl_2)} + 0.89 * \log \mathrm{Al\text{-}ox}$	R^2_{adj}=0.658, n=40, F=38.6, P<0.001
Pb	$\log K_p = 0.06 + 0.70 * \mathrm{pH(CaCl_2)} + 0.55 * \log \mathrm{Fraction}$	R^2_{adj}=0.832, n=45, F=110.0, P<0.001
Zn	$\log K_p = -1.15 + 0.56 * \mathrm{pH(CaCl_2)} + 0.61 * \log \mathrm{Clay} + 0.24 * \log \mathrm{Al\text{-}ox}$	R^2_{adj}=0.865, n=46, F=99.6, P<0.001

Table 5.6 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, Cd, Pb, Zn (defined as the ratio of the total metal concentration in the solid phase ($CaCl_2$-extraction) and the metal activities in the pore water) and soil and pore water characteristics.

Metal	Regression equation obtained	Statistics
Cu	$\log K_p = -2.26 + 0.54 * \mathrm{pH(CaCl_2)}$	R^2_{adj}=0.729, n=46, F=122.2, P<0.001
Cr	No significant correlation	--
Ni	$\log K_p = 0.63 + 0.38 * \log \mathrm{Fraction}$	R^2_{adj}=0.347, n=42, F=22.8, P<0.001
Cd	$\log K_p = -0.56 + 0.09 * \log \mathrm{Al\text{-}ox} + 1.34 * \log \mathrm{OM}$	R^2_{adj}=0.483, n=46, F=15.0, P<0.001
Pb	No significant correlation	--
Zn	$\log K_p = 0.56 + 0.57 * \log \mathrm{Al\text{-}ox} - 0.59 * \log \mathrm{DOC}$	R^2_{adj}=0.322, n=41, F=10.5, P<0.001

Table 5.7 Multivariate regression formulae describing the quantitative relationship between the log-transformed non-available fraction of Cu, Cr, Ni, As, Cd, Pb, Zn (naf_{aq}, defined as the difference in metal levels found between *aqua regia* digestion and 0.01 *M* $CaCl_2$ extraction) and soil and pore water characteristics.

Metal	Regression equation obtained	Statistics
Cu	$\log \mathrm{naf}_{aq} = -3.61 + 0.25 * \mathrm{pH(CaCl_2)} + 0.58 * \log \mathrm{Fe\text{-}ox} + 0.79 * \log \mathrm{Al\text{-}ox} - 0.56 * \log \mathrm{CEC}$	R^2_{adj}=0.740, n=46, F=33.7, P<0.001
Cr	$\log \mathrm{naf}_{aq} = -1.16 - 0.98 * \log \mathrm{LOI_1} + 0.30 * \log \mathrm{Clay} + 0.39 \log \mathrm{Fe\text{-}ox} + 0.48 * \log \mathrm{CEC}$	R^2_{adj}=0.774, n=46, F=32.5, P<0.001
Ni	$\log \mathrm{naf}_{aq} = -2.27 + 0.14 * \mathrm{pH(CaCl_2)} - 0.50 * \log \mathrm{LOI_1} + 0.52 * \log \mathrm{Clay} + 0.55 * \log \mathrm{Al\text{-}ox}$	R^2_{adj}=0.661, n=46, F=21.9, P<0.001
As	$\log \mathrm{naf}_{aq} = -1.63 + 0.40 * \log \mathrm{LOI_1} + 0.39 * \log \mathrm{Fe\text{-}ox}$	R^2_{adj}=0.724, n=46, F=61.2, P<0.001
Cd	$\log \mathrm{naf}_{aq} = 0.11 + 0.78 * \log \mathrm{Fe\text{-}ox} - 1.30 * \log \mathrm{DOC}$	R^2_{adj}=0.492, n=45, F=22.3, P<0.001
Pb	$\log \mathrm{naf}_{aq} = -2.85 + 0.21 * \mathrm{pH(CaCl_2)} + 0.45 * \log \mathrm{Fe\text{-}ox} + 0.67 * \log \mathrm{Al\text{-}ox} - 0.63 * \log \mathrm{DOC}$	R^2_{adj}=0.390, n=46, F=8.02, P<0.001
Zn	$\log \mathrm{naf}_{aq} = -4.05 + 0.51 * \mathrm{pH(CaCl_2)} + 0.31 * \log \mathrm{Fraction} + 1.33 * \log \mathrm{Al\text{-}ox} - 0.90 * \log \mathrm{CEC}$	R^2_{adj}=0.734, n=45, F=32.8, P<0.001

Table 5.8 Multivariate regression formulae describing the quantitative relationship between the log-transformed non-available fraction of Cu, Cr, Ni, As, Cd, Pb, Zn (naf_{HNO3}, defined as the defined as the difference in metal levels found between nitric acid digestion and 0.01 *M* $CaCl_2$ extraction) and soil and pore water characteristics.

Metal	Regression equation obtained	Statistics
Cu	$\log naf_{HNO3} = -1.91 - 0.38 * \log Fraction + 1.20 * \log Fe\text{-}ox - 0.73 * \log DOC$	$R^2_{adj}=0.547, n=38, F=15.9, P<0.001$
Cr	$\log naf_{HNO3} = -0.55 + 0.29 * \log LOI_2 + 0.44 * \log Clay$	$R^2_{adj}=0.713, n=46, F=58.1, P<0.001$
Ni	$\log naf_{HNO3} = -1.64 + 0.39 * \log LOI_2 + 0.30 * \log Clay + 0.40 * \log Fe\text{-}ox + 0.29 * \log Al\text{-}ox - 0.49 * \log OM$	$R^2_{adj}=0.773, n=46, F=31.6, P<0.001$
As	$\log naf_{HNO3} = -2.39 + 0.10 * pH(CaCl_2) + 0.58 * \log Fe\text{-}ox$	$R^2_{adj}=0.757, n=46, F=72.8, P<0.001$
Cd	$\log naf_{HNO3} = -0.04 + 0.74 * \log Fe\text{-}ox - 1.39 * \log DOC$	$R^2_{adj}=0.248, n=40, F=7.45, P=0.002$
Pb	$\log naf_{HNO3} = -2.84 + 0.16 * pH(CaCl_2) - 0.49 * \log Clay + 0.59 * \log Fe\text{-}ox + 0.48 * \log Al\text{-}ox$	$R^2_{adj}=0.367, n=45, F=7.38, P<0.001$
Zn	$\log naf_{HNO3} = -4.21 + 0.53 * pH(CaCl_2) + 0.31 * \log Fraction + 1.35 * \log Al\text{-}ox - 0.90 * \log CEC$	$R^2_{adj}=0.690, n=46, F=26.6, P<0.001$

Several conclusions may be drawn from the regression formulae for predicting K_p, as presented in Tables 5.1 - 5.6. In general, formulae are obtained that are a combination of one or more of the sorption phases present in the soil (metal sinks) and the soil related factors that modulate metal sorption (pH). Generally speaking, soil pH is the dominant factor regulating metal partitioning in soil, and pH explained a high percentage of the variation in K_p values for nearly all metals. Other researchers reported similar results (Anderson and Christensen, 1988; Buchter *et al.*, 1989). This can be explained by the fact that H^+ ions compete for binding sites. Further, the soil pH affects the surface charge and is important in regulating metal speciation in the pore water.

With regard to the elements included in this study, especially for the partition coefficients based upon the two digestion techniques employed, in general good correlations are obtained for the heavy metals studied. The standard errors of prediction are typically in the range of 0.2 - 0.4 log units. This corresponds to a standard error of prediction of K_p-values of a factor of 2 - 3 in an absolute sense. As this error is in line with experimental uncertainties in determining K_p, this is quite acceptable. The models for predicting partition coefficients that are based upon $CaCl_2$-extraction clearly perform less. The poor R^2_{adj}-values observed for the $CaCl_2$-extraction, suggest that K_p-values based on this extraction method can not explain the variation in K_p values by taking into account the determined soil characteristics. One reason for this may be that $CaCl_2$ is not successful in desorbing the metals from the adsorption phases. This is in line with the earlier observations of Janssen *et al.* (1996) for Ni and Zn, that the amount of metal extracted by 0.01 *M* $CaCl_2$ corresponds with metal pore water concentrations. The latter observation would also suggest that K_p-values for Ni and Zn can also be calculated as the ratio of the amount of metal digested by HNO_3 to the amount of metal extracted by 0.01 *M* $CaCl_2$.

Arsenic deviates from these general observations as no satisfactory models could be derived for this element. As arsenic is the only element studied that will predominantly be present in the field soils as a negatively charged species (arsenate), this finding most likely is a reflection of this deviating behaviour. Clearly more research is needed to better understand the partitioning of As in Dutch field soils. Such research is now in progress (De Rooij *et al.*, 1998).

When comparing Tables 5.1 and 5.2 to Tables 5.4 and 5.5, it can be deduced that in general the best models are obtained for partition coefficients based upon metal activities in the pore water. All models shown in Tables 5.4 and 5.5 have $pH(CaCl_2)$ as the dominant property determining

K_p-values. With respect to this finding it should be noted that calculated metals activities were used for the derivation of the underlying K_p-values. It will be clear that the pH of the pore water may strongly have affected the values of the activities thus obtained, which implies that the present covariation may result from autocorrelation. At present, methods for measuring the activity of free metal ions in pore water are grossly lacking. To confirm the correlations found it is essential that methods for actually measuring metal activities are developed. Such research is currently in progress (De Rooij *et al.*, 1998).

From Tables 5.7 and 5.8 it may be deduced that the non-available metal fraction is associated to a limited number of sorption phases in the soil. Especially Fe-ox, Al-ox, and LOI_l (which is a reflection of the organic matter content of the soil) are important factors in this respect. Again pH appears to have an impact on the non-available metal fraction. In general, the best models are derived for data based upon *aqua regia* digestion (Table 5.7), as compared to data based upon HNO_3-digestion (Table 5.8).

5.3 Multivariate regression models for non-carbonate containing soils

As shown in ables 5.1 - 5.8, pH is the dominant property modulating metal partitioning in soils. To illustrate the impact of pH on metal partitioning, log transformed K_p-values for Zn are plotted in Figure 5.1 as a function of $pH(CaCl_2)$.

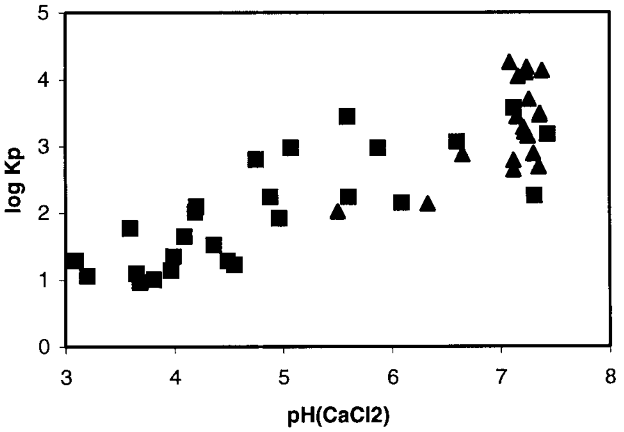

Figure 5.1 Plot of log-transformed K_p-values of Zn in 46 Dutch field soils versus $pH(CaCl_2)$. K_p-values ($L.kg^{-1}$) were derived on the basis of *aqua regia* digestion and total zinc concentrations in the pore water. Triangles represent K_p-values measured in carbonate containing soils.

From a close inspection of the data depicted in Figure 5.1 it became clear that metal partitioning in soils containing carbonate as an additional sorption phase deviates from partitioning in soils that do not contain carbonate, in the sense that Kp-values obtained for these soils appeared not to be no related to $pH(CaCl_2)$. This may be due to both metal sorption to the carbonate phase and to precipitation. We therefore decided to split the database of 46 soils into a set of 18 soils that do contain carbonate and a set of 28 soils that do not. Subsequently, multivariate regression analysis was carried out on both data sets.

For the carbonate-containing soils, no models could be derived for predicting metal partitioning. This not only implies that additional research on this type of soils is required, but these findings may also be a consequence of the precipitation processes taking place in these soils. Precipitation may give rise to relatively high metal levels in the solid phase which are not related to any of the soil constituents. In addition it should be noted that also a majority of the sediments underlying Dutch surface water are known to contain considerable amounts of carbonate, which implies that additional research should also take metal partitioning in these sediments into account.

In Tables 5.9 - 5.16 the results of the multivariate regression analyses are given for each of the metals included in this study, as carried out for the limited data set of all soils that do not contain detectable carbonate levels in the solid phase. Again, in all cases the relevant soil and pore water characteristics are giving in decreasing order of importance.

Table 5.9 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, As, Cd, Pb, Zn (defined as the ratio of the total metal concentrations in the solid phase (*aqua regia* digestion) and the pore water) and soil and pore water characteristics for soils that do not contain any detectable carbonate.

Metal	Regression equation obtained	Statistics
Cu	$\log K_p = -0.72 + 0.39 * \mathrm{pH(CaCl_2)} + 0.60 * \log \text{Al-ox}$	$R^2_{adj}=0.823$, n=28, F=63.8, P<0.001
Cr	$\log K_p = 2.41 + 0.22 * \mathrm{pH(CaCl_2)} + 0.95 * \log \mathrm{CEC} - 0.77 * \log \mathrm{OM}$	$R^2_{adj}=0.776$, n=27, F=31.0, P<0.001
Ni	$\log K_p = 0.68 + 0.27 * \mathrm{pH(CaCl_2)} + 0.35 * \log \text{Al-ox} + 0.15 * \log \mathrm{Clay}$	$R^2_{adj}=0.796$, n=25, F=32.2, P<0.001
As	$\log K_p = 3.10 - 1.35 * \log \mathrm{LOI_1} + 1.58 * \log \mathrm{CEC}$	$R^2_{adj}=0.528$, n=28, F=16.1, P<0.001
Cd	$\log K_p = 2.26 + 0.42 * \mathrm{pH(CaCl_2)} + 0.78 * \log \text{Al-ox} - 0.68 * \log \mathrm{DOC}$	$R^2_{adj}=0.799$, n=26, F=34.0, P<0.001
Pb	$\log K_p = 1.97 + 0.34 * \mathrm{pH(CaCl_2)} + 0.72 * \log \mathrm{LOI_2}$	$R^2_{adj}=0.774$, n=28, F=47.3, P<0.001
Zn	$\log K_p = -0.35 + 0.41 * \mathrm{pH(CaCl_2)} + 0.60 * \log \mathrm{Clay}$	$R^2_{adj}=0.795$, n=28, F=53.4, P<0.001

Table 5.10 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, As, Cd, Pb, Zn (defined as the ratio of the total metal concentrations in the solid phase (nitric acid digestion) and the pore water) and soil and pore water characteristics for soils that do not contain any detectable carbonate.

Metal	Regression equation obtained	Statistics
Cu	$\log K_p = 0.30 + 0.26 * \log \mathrm{CEC} + 0.30 * \log \text{Al-ox} - 0.88 * \log \mathrm{DOC} + 0.36 * \mathrm{pH(CaCl_2)}$	$R^2_{adj}=0.628$, n=19, F=8.6, P=0.001
Cr	$\log K_p = 2.11 + 0.31 * \log \mathrm{Clay} + 0.29 * \mathrm{pH(CaCl_2)}$	$R^2_{adj}=0.705$, n=28, F=33.2, P<0.001
Ni	$\log K_p = 2.84 + 0.92 * \log \mathrm{LOI_2}$	$R^2_{adj}=0.529$, n=15, F=16.7, P=0.001
As	$\log K_p = 3.31 - 0.91 * \log \mathrm{Fraction} + 1.31 * \log \mathrm{Clay}$	$R^2_{adj}=0.497$, n=25, F=12.8, P<0.001
Cd	$\log K_p = 2.07 + 0.40 * \mathrm{pH(CaCl_2)} + 0.52 * \log \text{Al-ox}$	$R^2_{adj}=0.668$, n=19, F=19.1, P<0.001
Pb	$\log K_p = 0.89 + 0.58 * \log \mathrm{CEC} + 0.41 * \mathrm{pH(CaCl_2)}$	$R^2_{adj}=0.806$, n=28, F=57.1, P<0.001
Zn	$\log K_p = -0.49 + 0.62 * \log \mathrm{Clay} + 0.44 * \mathrm{pH(CaCl_2)}$	$R^2_{adj}=0.789$, n=28, F=51.4, P<0.001

Table 5.11 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, As, Cd, Pb, Zn (defined as the ratio of the total metal concentrations in the solid phase ($CaCl_2$-extraction) and the pore water) and soil and pore water characteristics for soils that do not contain any detectable carbonate.

Metal	Regression equation obtained	Statistics
Cu	No significant correlation	--
Cr	No significant correlation	--
Ni	$\log K_p = 1.74 - 0.21 * \mathrm{pH(CaCl_2)} + 0.38 * \log \mathrm{Clay} - 0.59 * \log \mathrm{DOC}$	$R^2_{adj}=0.517$, n=27, F=10.3, P<0.001
As	No significant correlation	--
Cd	No significant correlation	--
Pb	No significant correlation	--
Zn	No significant correlation	--

Table 5.12 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, Cd, Pb, Zn (defined as the ratio of the total metal concentration in the solid phase (*aqua regia* digestion) and the metal activities in the pore water) and soil and pore water characteristics for soils that do not contain any detectable carbonate.

Metal	Regression equation obtained	Statistics
Cu	log K_p = -1.03 + 0.64 * pH($CaCl_2$) + 0.20 * log Clay + 0.35 * log Al-ox	R^2_{adj}=0.916, n=28, F=98.5, P<0.001
Cr	log K_p = 2.46 + 1.03 * log CEC + 0.26 * pH($CaCl_2$) - 0.85 * log LOI_1	R^2_{adj}=0.771, n=28, F=31.3, P<0.001
Ni	log K_p = 0.48 + 0.42 * pH($CaCl_2$) + 0.43 * log Clay	R^2_{adj}=0.883, n=25, F=91.8, P<0.001
Cd	log K_p = -0.68 + 0.43 * pH($CaCl_2$) + 0.28 * log Fe-ox + 0.54 * log Al-ox - 0.64 * log DOC	R^2_{adj}=0.888, n=26, F=50.5, P<0.001
Pb	log K_p = 0.43 + 0.55 * log CEC + 0.61 * pH($CaCl_2$)	R^2_{adj}=0.833, n=28, F=68.2, P<0.001
Zn	log K_p = 0.94 + 0.36 * pH($CaCl_2$) + 1.14 * log LOI_2	R^2_{adj}=0.836, n=28, F=69.7, P<0.001

Table 5.13 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, Cd, Pb, Zn (defined as the ratio of the total metal concentration in the solid phase (nitric acid digestion) and the metal activities in the pore water) and soil and pore water characteristics for soils that do not contain any detectable carbonate.

Metal	Regression equation obtained	Statistics
Cu	log K_p = -1.46 + 0.78 * pH($CaCl_2$) + 0.57 * log LOI_1 + 0.16 * log DOC	R^2_{adj}=0.737, n=20, F=18.8, P<0.001
Cr	log K_p = 2.83 + 0.27 * pH($CaCl_2$) + 0.61 * log LOI_2	R^2_{adj}=0.730, n=28, F=37.6, P<0.001
Ni	log K_p = 0.62 + 0.37 * pH($CaCl_2$) - 0.15* log Fraction + 0.61 * log Clay	R^2_{adj}=0.881, n=28, F=51.0, P<0.001
Cd	log K_p = -1.26 + 0.47 * pH($CaCl_2$) + 0.68 * log Al-ox	R^2_{adj}=0.792, n=22, F=41.0, P<0.001
Pb	log K_p = 0.42 + 0.56 * log CEC + 0.60 * pH($CaCl_2$)	R^2_{adj}=0.839, n=28, F=71.2, P<0.001
Zn	log K_p = -0.55 + 0.50 * pH($CaCl_2$) + 0.67 * log Clay	R^2_{adj}=0.839, n=28, F=71.4, P<0.001

Table 5.14 Multivariate regression formulae describing the quantitative relationship between log-transformed partition coefficients of Cu, Cr, Ni, Cd, Pb, Zn (defined as the ratio of the total metal concentration in the solid phase ($CaCl_2$-extraction) and the metal activities in the pore water) and soil and pore water characteristics for soils that do not contain any detectable carbonate.

Metal	Regression equation obtained	Statistics
Cu	No significant correlation	--
Cr	No significant correlation	--
Ni	log K_p = 7.46 - 7.03 * log LOI_2 + 11.01 * log Clay - 1.82 * log Fe-ox - 7.28 * log DOC	R^2_{adj}=0.691, n=27, F=15.5, P<0.001
Cd	No significant correlation	--
Pb	No significant correlation	--
Zn	No significant correlation	--

Table 5.15 Multivariate regression formulae describing the quantitative relationship between the log-transformed non-available fraction of Cu, Cr, Ni, As, Cd, Pb, Zn (naf_{aq}, defined as the difference in metal levels found between *aqua regia* digestion and 0.01 *M* $CaCl_2$ extraction) and soil and pore water characteristics for soils that do not contain any detectable carbonate.

Metal	Regression equation obtained	Statistics
Cu	log naf_{aq} = -0.69 + 1.39 * log LOI_2 + - 0.25 * log Fraction + 0.91 * log Al-ox - 1.03 * log OM	R^2_{adj}=0.725, n=27, F=18.2, P<0.001
Cr	log naf_{aq} = -0.66 - 0.37 * log Fraction + 0.91 * log Clay	R^2_{adj}=0.732, n=28, F=37.8, P<0.001
Ni	log naf_{aq} = -2.91 + 0.23 * pH($CaCl_2$) + 0.49 * log Clay + 0.91 * log DOC	R^2_{adj}=0.733, n=25, F=22.9, P<0.001
As	log naf_{aq} = -1.24 + 0.38 * log LOI_2 + 0.30 * log Clay	R^2_{adj}=0.768, n=28, F=45.6, P<0.001
Cd	log naf_{aq} = -1.09 + 0.16 * pH($CaCl_2$) + 0.40 * log Fe-ox	R^2_{adj}=0.385, n=26, F=8.81, P=0.001
Pb	log naf_{aq} = -0.56 + 0.49 * log LOI_2	R^2_{adj}=0.261, n=28, F=10.5, P=0.003
Zn	log naf_{aq} = -2.87 + 0.38 * pH($CaCl_2$) + 0.59 * log Al-ox	R^2_{adj}=0.679, n=28, F=28.4, P<0.001

Table 5.16 Multivariate regression formulae describing the quantitative relationship between the log-transformed non-available fraction of Cu, Cr, Ni, As, Cd, Pb, Zn (naf_{HNO3}, defined as the defined as the difference in metal levels found between nitric acid digestion and 0.01 *M* $CaCl_2$ extraction) and soil and pore water characteristics for soils that do not contain any detectable carbonate.

Metal	Regression equation obtained	Statistics
Cu	log naf_{HNO3} = -3.19 + 0.30 * pH($CaCl_2$) + 0.58 * log Fe-ox	R^2_{adj}=0.534, n=20, F=11.9, P=0.001
Cr	log naf_{HNO3} = -0.61 - 0.34 * log LOI_1 + 0.40 * log LOI_2 + 0.55 * log Clay + 0.42 * log DOC	R^2_{adj}=0.828, n=28, F=33.5, P<0.001
Ni	log naf_{HNO3} = -0.89 + 0.94 * log LOI_2 + 0.36 * log Clay - 0.46* log OM + 0.59 * log DOC	R^2_{adj}=0.854, n=27, F=39.1, P<0.001
As	log naf_{HNO3} = -1.77 + 0.48 * log LOI_2 + 0.54 * log Fe-ox + 0.37 * log Al-ox - 0.68 * log OM	R^2_{adj}=0.891, n=27, F=54.0, P<0.001
Cd	No significant correlation	--
Pb	No significant correlation	--
Zn	log naf_{HNO3} = -3.12 + 0.43 * pH($CaCl_2$) + 0.60 * log Al-ox	R^2_{adj}=0.585, n=28, F=20.0, P<0.001

Basically, the same conclusions may be drawn from the models presented in Tables 5.9 - 5.16, as for the corresponding data in Tables 5.1- 5.8. Despite the obvious reduction of the number of data points, in most cases higher values for the statistical parameters are found, indicating an improvement of the significance of the correlations obtained.

6 CONCLUSIONS AND RECOMMENDATIONS

The main conclusion to be drawn is that the aim of this study (providing a first set of data and models to be used in the validation and extrapolation stages of the research and development programme proposed by De Rooij *et al.* (1997)) has been met: *In-situ* partitioning of 6 metals (Cd, Cr, Cu, Ni, Pb, and Zn) and As in Dutch field soils was studied at 46 sites. For reference purposes, OECD-artisoil was included in the dataset, and for one soil duplicate sampling was carried out to get insight into the reproducibility of the experimental procedures. In addition, the impact of freshly added metal salts to the soil matrix was studied and finally, models were derived that enable the prediction of metal partitioning in Dutch soils on the basis of a limited number of easily obtainable soil characteristics. The models may be used to predict pore water concentrations of field soils, on the basis of measured metal concentrations in the solid phase.

Based upon the findings reported above, the following conclusions may be drawn:

- Partition coefficients of heavy metals and of As vary strongly among soils and among metals.
- Addition of metal salts to one of the soils leads to a decrease of the magnitude of the partition coefficients, which implies that the bioavailability of the metal salts added is increased for soil organisms whose dominant uptake route is via the pore water. This finding could be related to non-linearity of the sorption isotherm in these soil systems.
- Metal partitioning in soils containing carbonate differs form partitioning in which there are no detectable amount of carbonate present as an additional sorption phase.
- With the exception of arsenic, metal partitioning can be quantified by models that combine one or more of the metal binding soil phases, like amorphous iron- and aluminum-oxyhydroxide, organic matter and clay, and one of the soil characteristics that modulate metal partitioning. Especially soil pH is a dominant factor in this respect, as it was found that pH explained a high percentage of the variation in the values of the partition coefficients (K_p) for all metals.
- The 'best' models in terms of statistical significance are obtained for K_p-values that are based upon total metal concentrations in both the soil solid phase and the pore water; in general in between 70 and 90 % of the data variance is explained in this case. The standard errors of prediction of K_p are typically in the range of 0.2 - 0.4 log units, or a factor of 2 - 3 in an absolute sense. This is in line with experimental uncertainties in determining K_p.
- The explained variance is significantly increased by taking the activity of the free metal ion into account.
- Exclusion of the carbonate containing soils from the data analysis further increases the predictive capability of the models thus derived.

As indicated above, the results given in this report will provide the basis for additional research that is amongst others aimed at developing empirical models that relate actually available metal concentrations to potentially available fractions (de Rooij, 1998). In light of these activities foreseen, the following recommendations can be made on the basis of the results presented in this report:

1. To further investigate the factors that modulate metal partitioning in carbonate containing soils.
2. To further investigate the partitioning of negatively charged species (like arsenate) in soil-pore water systems.
3. To investigate the possibilities of using mild extraction methods, to replace quite expedious methods of pore water collection, which as shown in chapter 3 (2 m*M* $Ca(NO_3)_2$) do not always yield comparable results.

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