

RIJKSINSTITUUT VOOR
VOLKSGEZONDHEID EN MILIEU
BILTHOVEN

Rapport nr. 719101013

**Metal speciation in Dutch soils:
Field-based partition coefficients for heavy
metals at background levels**

M.A.G.T. van den Hoop

December 1995

Dit onderzoek werd verricht in opdracht en ten laste van het Directoraat-Generaal Milieubeheer, Directies Bodem en Stoffen, Veiligheid en Straling van het Ministerie voor Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer, in het kader van het project 719101. This investigation has been performed in order and for account of the Directorate-General for Environmental Protection, Directorates for Soil and for Chemicals, External Safety and Radiation Protection of the Ministry of Housing, Physical Planning and Environment.

Rijksinstituut voor Volksgezondheid en Milieu, Postbus 1, 3720 BA Bilthoven
tel. 030-2749111, fax 030-2742971

MAILING LIST

- 1 Directoraat-Generaal Milieubeheer, Directie Bodem
- 2 Directoraat-Generaal Milieubeheer, Directie Stoffen, Veiligheid, Straling
- 3 Plv. Directeur-Generaal Milieubeheer, Dr. ir. B.C.J. Zoeteman
- 4 Dr. J.H.M. de Bruijn (DGM/SVS)
- 5 Drs. C.A.J. Denneman (DGM/Bo)
- 6 Prof. dr. C.J. van Leeuwen (DGM/SVS)
- 7 Mw. Ir. J. Robberse (DGM/Bo)
- 8 Drs. P. del Castilho, AB-DLO-Instituut voor Bodemvruchtbaarheid
- 9 Dr. R.N.J. Comans, Energieonderzoek Centrum Nederland
- 10 Ir. Th. Edelman, Gedeputeerde Staten van Gelderland
- 11 Drs. E.H.G. Evers, Directoraat-Generaal RWS, Rijksinstituut voor Kust- en Zeeonderzoek
- 12 Dr. ir. C.A.M. van Gestel, Vrije Universiteit, Amsterdam
- 13 Drs. C. van de Guchte, Directoraat-Generaal RWS, Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling
- 14 Ir. Th.M. Lexmond, Landbouwniversiteit Wageningen
- 15 Dr. ir. J.P.G. Loch, Instituut voor Aardwetenschappen, Rijksuniversiteit Utrecht
- 16 Dr. H.N. Kerdijk, Waterloopkundig laboratorium
- 17 Ir. M. Paalman, Milieudienst Amsterdam
- 18 Ir. B. Palsma, Instituut voor Milieuwetenschappen, TNO
- 19 Prof. dr. W.H. van Riemsdijk, Landbouwniversiteit Wageningen
- 20 Drs. N.M. de Rooij, Waterloopkundig Laboratorium
- 21 Dr. S.M. Schrap, Directoraat-Generaal RWS, Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling
- 22 Drs. T.E.M. Ten Hulscher, Directoraat-Generaal RWS, Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling
- 23 Dr. P.C.M. van Noort, Directoraat-Generaal RWS, Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling
- 24 Drs. R. Wijland, Technische Commissie Bodembescherming
- 25 Mr. J. Pretorius, CSIR, Pretoria (South-Africa)
- 26 Dr. H.E. Allen, University of Delaware, Newark (USA)
- 27 Dr. E. Jenne, Battelle Pacific Northwest Laboratories, Richland (USA)
- 28 Depôt van Nederlandse publicaties en Nederlandse bibliografiën
- 29 Directie RIVM
- 30 Sectordirecteur Stoffen en Risico's, Dr. ir. G. de Mik
- 31 Hoofd Laboratorium voor Ecotoxicologie
- 32 Hoofd Laboratorium voor Bodem- en Grondwateronderzoek
- 33 Hoofd Laboratorium voor Anorganische Chemie
- 34 Hoofd Afdeling Voorlichting en Public Relations, Mw. Drs. J.A.M. Lijdsman-Schrijvenaar
- 35 Dr. ir. W.J.G.M. Peijnenburg (ECO)

-
- 36 Dr. P. van Beelen (ECO)
 - 37 Drs. R. Ritsema (LAC)
 - 38 Dr. ir. R.F.M.J. Cleven (LAC)
 - 39 Mw. A.I. Lesquillier (LAC)
 - 40 Ir. D. Fraters (LBG)
 - 41 Dr. J.F.M.M. Lembrechts (LSO)
 - 42 Dr. ir. D. van de Meent (ECO)
 - 43 Dr. ir. J. Notenboom (ECO)
 - 44 Ir. C.J. Roghair (ECO)
 - 45 Dr. J. Struijs (ECO)
 - 46 Drs. D. de Zwart (ECO)
 - 47 Dr. G.H. Crommentuijn (ACT)
 - 48 Drs. E. van de Plassche (ACT)
 - 49 Auteur
 - 50 Bureau rapportregistratie
 - 51-52 Bibliotheek RIVM
 - 53-60 Reserve-exemplaren LAC
 - 61-81 Reserve-exemplaren t.b.v. Bureau Rapportenbeheer

CONTENT	
MAILING LIST	2
CONTENT	4
ACKNOWLEDGEMENTS	5
SUMMARY	6
SAMENVATTING	7
1. INTRODUCTION	8
1.1 Speciation of heavy metals in soils	8
1.2 Soil and sediment quality criteria	8
1.3 Framework and approach	9
1.4 Aim	10
2. EXPERIMENTAL	11
2.1 Soils: sampling and pretreatment	11
2.2 Characterization of soil samples	11
2.3 Element analysis of soil and pore water	11
2.4 Extraction experiments	12
2.5 Calculations	12
3. RESULTS AND DISCUSSION	13
3.1 Soil characterization	13
3.2 Metal content of soils	14
3.3 Pore water composition	16
3.4 Field-based partition coefficients	16
3.5 Extractable amounts of heavy metals	22
4. CONCLUDING REMARKS	27
REFERENCES	28
APPENDIX A: Area, sample code and coordinates of soil samples	30

ACKNOWLEDGEMENTS

The author is grateful to the people of the Laboratory for Inorganic Chemistry, the Laboratory for Soil and Groundwater Research and the Department of Physical and Chemical Techniques of the Laboratory for Ecotoxicology for carrying out part of the experimental work. I thank Eric Meuffels, Henri den Hollander and Hans Verboom for their assistance in collecting the soil samples. I am also grateful to the advisory board for helpful discussions and comments on the report. The advisory board consisted of: J.H.M. de Bruijn, C.A.J. Denneman, J. Robberse (all Directorate General for Environmental Protection), P. del Castilho (Institute of Soil Fertility), R.N.J. Comans (Netherlands Energy Research Foundation), Th. Edelman (County Aldermen of Gelderland), E.H.G. Evers (Directorate General for Public Works and Water Management, Tidal Waters Division), R. Wijland (Technical Committee on Soil Protection), C.A.M. van Gestel (Vrije Universiteit, Amsterdam), C. van de Guchte, P.C.M. van Noort (both Institute for Inland Water Management and Waste Water Treatment), N.M. de Rooij (Delft Hydraulics), S.M. Schrap (Research Institute for Toxicology, University Utrecht), W.H. van Riemsdijk, Th. M. Lexmond (both Department of Soil Science and Plant Nutrition, Wageningen Agricultural University), J.P.G. Loch (Institute for Earth Science, University Utrecht), M. Paalman, (City department for the Environment, Amsterdam) B. Palsma (Institute for Environmental Science-TNO), R. van den Berg, D. Fraters, J.F.M.M. Lembrechts, D. van de Meent, J. Struijs, D. de Zwart (all National Institute of Public Health and the Environment).

SUMMARY

For 13 Dutch soil samples, total concentrations in the solid phase and in the soil solution were determined for the heavy metals Cd, Cu, Ni, Pb and Zn. The soils were characterized in terms of organic carbon content, pH, clay content and cation exchange capacity. Average field-based partition coefficients (K_p) were calculated as the ratio of the metal concentration in the solid phase and the soil solution and were 706, 241, 1337, 10785 and 1175 l kg⁻¹ for Cd, Cu, Ni, Pb and Zn, respectively. These values are approximately two orders of magnitude smaller than partition coefficients proposed for the harmonization of integrated quality objectives for the compartments soil, sediment and water.

For the present set of samples, the variability of K_p was in the same order of magnitude as its average value, due to variations in soil and pore water composition. For all metals, K_p -values could be well correlated to a Freundlich modified isotherm with respect to the cation exchange capacity of the soil, which is a measure for the amount of available binding sites.

SAMENVATTING

Van 13 Nederlandse bodemonsters zijn de totaalgehalten bepaald van de zware metalen Cd, Cu, Ni, Pb en Zn, zowel in de vaste fase als in het poriewater. De bodems zijn gekarakteriseerd in termen van organisch koolstofgehalte, pH, kleigehalte en kationuitwisselcapaciteit. Partiticoëfficiënten (K_p) zijn gedefinieerd als de verhouding van de metaal concentratie in de vaste fase en in het poriewater. Gemiddelde K_p -waarden waren 706, 241, 1337, 10785 en 1175 l kg⁻¹ voor respectievelijk Cd, Cu, Ni, Pb en Zn. Deze waarden zijn ongeveer twee orden van grootte kleiner dan de partiticoëfficiënten, die voorgesteld zijn bij de harmonisatie van milieukwaliteitsdoelstellingen voor de compartimenten bodem, sediment en water.

De variatie in K_p bleek in de zelfde orde van grootte te zijn als de gemiddelde waarde van K_p . Dit is het gevolg van variatie in bodem- en poriewatersamenstelling. Voor alle metalen kon de K_p waarde goed gecorreleerd worden aan een gemodificeerde Freundlich isotherm voor de kationuitwisselcapaciteit, hetgeen een maat is voor het aantal beschikbare bindingsplaatsen in de bodem.

1. INTRODUCTION

1.1 Speciation of heavy metals in soils

The binding of heavy metals in soils is a function of the soil components, such as clay minerals and organic matter, the soil chemistry, which includes pH, ionic strength and ion composition, and the characteristics of the metal. Often several (soil/chemistry) parameters play an important role in the sorption behaviour of metals in soils at the same time. For example, Christensen (1989) observed that the binding of cadmium onto 63 Danish soils depends on both the pH of the soil solution as well the organic carbon content of the solid phase. Differences in sorption behaviour of cadmium in 12 different Dutch soils could be explained by taken into account the variation of pH and calcium activity (Chardon, 1984).

With respect to the bio-availability of (heavy) metals, knowledge of their speciation is of great significance, both from the viewpoint of their essentiality for various life forms, which is the case for e.g. zinc, potassium and calcium, and with respect to their toxicity, as is the case of e.g. cadmium and lead. It is now widely accepted for a number of heavy metals that ecotoxicity is more related to the concentrations of "labile" forms, rather than to total concentration. For example, several studies have shown that toxic effects of heavy metals are reduced in the presence of complexing agents (Sunda and Lewis, 1978; Chau et al., 1974; Khangarot and Ray, 1989; Corp and Morgan, 1991).

Although knowledge about speciation in natural systems has been increased significantly during the last two decades (Buffle, 1988; Stumm, 1987), the application with respect to the derivation of soil and sediment quality criteria is still a preliminary matter. In the Netherlands, the government has set target values for soils and sediments on the basis of total metal content. For the water compartment, quality criteria were derived separately from toxicity tests also based on total metal concentrations. Presently, much attention is given to the harmonization of quality objectives. The equilibrium partitioning concept is one of the approaches proposed to harmonize quality criteria in the different compartments. A major assumption of the equilibrium partitioning concept is that the concentration of a chemical in water can be predicted from the concentration in the solid phase by using a measured or calculated equilibrium partition coefficient. Measured partition coefficients for heavy metals reported in the literature are mainly obtained under controlled laboratory conditions which, however, do not necessarily reflect the conditions observed in the field.

1.2 Soil and sediment quality criteria

After the discovery of some severe soil pollution situations at the end of the seventies, the Dutch government started the setting of soil and sediment quality criteria for a number of heavy metals. This was first done by developing reference or target values that indicate good soil quality. These values are based on measurements of total metal content in Dutch natural environments. The areas were thought to be negligibly influenced by human activities. Hence, soils in these areas have probably a metal content close to the "natural" background level. Edelman (1984) found that the total metal content in these 40 soils was highly correlated with

clay content and organic matter content. Target values were derived by first applying multiple linear regression analysis on the data set in order to obtain the best relationship between the total metal content and clay content and/or organic matter content. The resulting slope was then shifted along the ordinate axis in such a way that approximately 90% of the samples were situated below the line. This has led to so-called reference lines, which are presented in the form:

$$c_s = a + b * \text{clay} + c * \text{organic matter} \quad (1)$$

where c_s denotes the total metal content; a represents the intercept and, b and c are coefficients related to the slope. Presently, utilized Dutch target values for various heavy metals in soils and sediments are collected in Table 1 (MILBOWA, 1991).

Table 1: Dutch target values for various heavy metals and As in soils presented as a mathematical expression (i.e. reference lines), which depends on the content of organic matter and clay minerals (MILBOWA, 1991).

[Cr]	= 50 + 2*clay
[Ni]	= 10 + clay
[Cu]	= 15 + 0.6*(clay + organic matter)
[Zn]	= 50 + 1.5*(2*clay + organic matter)
[Cd]	= 0.4 + 0.007*(clay + 3*organic matter)
[Hg]	= 0.2 + 0.0017*(3*clay + organic matter)
[Pb]	= 50 + clay + organic matter
[As]	= 15 + 0.4*(clay + organic matter)

[] = total content in mg.kg-1 dry soil

1.3 Framework and approach

Prior to the present research, a pilot study was performed consisting of a literature research and consulting experts in the field on an individual basis and during plenary meetings. The results of this pilot study are reported by Van den Hoop (1993). The purpose of this preliminary study was to define a framework for the validation of the equilibrium partitioning method, which resulted in the following set of criteria:

- (1) the continuing research should as yet be related to heavy metals;
- (2) the concentration levels of metals should be close to "natural" background concentrations;
- (3) partition coefficients should be obtained under field conditions;
- (4) attention should be paid to possible differences in physico-chemical behaviour of heavy metals in soils and sediments;
- (5) if possible, connection should be made with ecotoxicological research activities;
- (6) the possibilities to calculate an overall partition coefficient of heavy metals for the natural system from thermodynamic data should be investigated.

With this set of criteria including boundary conditions such as available time, equipment and manpower, an experimental validation program was developed and discussed with the advisory board in a plenary meeting on March 24, 1993. The present report contains the results of the experimental validation study with respect to criteria (1) to (3). In a separate report, experimental activities with respect to item (4) will be presented. The relation between the current activities and eco-toxicological research (criterion 5) will be reported elsewhere (Roghair et al., 1996). Criterion (6) appeared to be too difficult to fulfil within the given time. However, with the help of a visiting researcher from South-Africa, activities within this field are presently conducted.

1.4 Aim

The objectives of the present report are (1) to quantify heavy metal concentrations in solid phase and soil solution in soils under field conditions in order to obtain field partition coefficients (K_p) and (2) to compare the partition coefficients obtained with values proposed for the harmonization of quality criteria for heavy metals in the Netherlands. The results are meant to support the setting of "Integrated environmental quality objectives" (Van der Plassche and De Bruijn, 1992).

2. EXPERIMENTAL

2.1 Soils: sampling and pretreatment

Soil samples were collected from 14 different sites in the Netherlands between April 23 and July 20, 1993. In Appendix A, detailed information is given with respect to area and corresponding coordinates. The sites were selected on the next set of criteria: (1) the heavy metal content should be close to "background" levels, and (2) the soil samples should vary with respect to organic carbon content, clay content, pH and carbonate content. Most sites have been sampled before by Edelman (1984) and by Van Gestel et al. (1992). In the Netherlands, the samples collected by Edelman (1984) are known as reference soils. After removing the litter layer, about 8 litres of soil were collected from the toplayer (0-20 cm). The samples were stored in a polyethylene container and transferred to the laboratory. Pore water was obtained by centrifugation the soils at 7500 rpm (gx9739). To that end, home-made teflon tubes with a volume of 280 ml were used consisting of two compartments divided by an ashless (<0.007%) cellulose filter (Whatman 42). The particle retention diameter reported by the manufacturer is 2.5 mm. Approximately 1.5 kg of soil was treated. Centrifugation was continued until about 100 ml of soil solution was collected. The water content of one soil sample appeared to be too less to obtain enough soil solution and, hence, this sample is disregarded in the present study. For the remaining soils, the pH of the soil solution was measured immediately after collection. The collected soil solution was divided into two parts: one for anion analysis, and one for metal analysis. The pH of the latter was set to 2 by adding an appropriate aliquot of concentrated nitric acid (Suprapur). After centrifugation the soils were dried for one week at room temperature. Then, the dried soil was ground with a mill of either agate or porcelain and homogenized by hand.

2.2 Characterization of soil samples

The pH of the soil has been determined at a solid:liquid ratio of 1:5 with H₂O and 1 mol l⁻¹ KCl. For soils with pH(H₂O)>6.5, the carbonate content was determined by adding HCl and measuring the amount of gas developed. Total carbon was determined by dry combustion at approximately 1030°C with thermal conductivity detection of CO₂. The organic carbon content (oc) is calculated as the difference between total carbon content and calcium carbonate content. The clay content was determined by the pipet method (Andreasen, 1928) after dissolving cementing substances (Fe, Al and CaCO₃) in HCl and oxidizing organic matter by addition of hydrogen peroxide. The cation exchange capacity (CEC) was measured according to Gillman (1979) at soil pH and ionic strength similar to that encountered in the field.

2.3 Element analysis of soil and pore water

Total metal concentrations of the solid phase were obtained by means of GFAAS or ICP-AES after digesting the soils samples with concentrated nitric acid (Suprapur). In the resulting solution and the pore water, Cd, Ni, Cu and Pb were analyzed by GFAAS (Standard

Operating Procedures: LAC/M025; LAC/M030; LAC/M035; LAC/M032). Radial ICP-AES was used for the determination of Zn, Ca, Mg, Na, K, Fe and Mn (Standard Operating Procedure: LAC/M259). Nitrate, chloride and sulphate were measured in the pore water using ion chromatography (Standard Operating Procedure: LAC/M210). Fosfaat was determined using continuous flow analysis according to Standard Operating Procedures LAC/M064. The amount of dissolved organic carbon (DOC) and non purgeable organic carbon (NPOC) in the pore water were analyzed according to Standard Operating Procedures LAC/M049 and ECO/034, respectively.

2.4 Extraction experiments

In order to obtain information about the potential and actual availability of various metals, the soil samples were extracted with an acid solution and with an calciumchloride solution, respectively. Extractions were performed by adding 50 ml 0.1 mol l⁻¹ HNO₃ (Suprapur) to 5 g of soil or by adding 100 ml 0.01 mol l⁻¹ CaCl₂ solution to 10 g of soil in 250 ml polyethylene flasks. The suspensions were shaken for 24 hours at 21±1°C and then centrifuged for 20 min at 13000 rpm. The supernatant was used for element analysis without further treatment in case of the acid extraction. In case of the calciumchloride extraction, the pH of the supernatant was set to 2 by adding an appropriate aliquot of concentrated nitric acid (Suprapur). Ca, Mg, K, Na, Fe, Mn, Zn, Cd, Ni, Cu and Pb were measured in the supernatant as described above.

2.5 Calculations

Field partition coefficients (K_p in l kg⁻¹) have been calculated as the quotient of the metal mass concentration in the solid phase (c_s in mg kg⁻¹) and the total mass concentration of the metal in the soil solution (c_w in mg l⁻¹):

$$K_p = \frac{c_s}{c_w} \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Soil characterization

Table 2 summarizes some physical and chemical characteristics of the soils. The pH(H₂O), pH(KCl), the clay content, the organic carbon content and the CEC varied over broad ranges: 4.0 to 7.8 (pH(H₂O)), 3.1 to 7.1 (pH(KCl)), 1.4 to 64.9% (clay), 0.0 to 43.1% (organic carbon) and 4.6 to 51.5 cmol kg⁻¹ (CEC), respectively. The different types of samples (sandy, loamy, clay and peat) represent quite well the variety of Dutch soils.

Table 2: Characterization of soils in terms of pH(H₂O), pH(KCl), organic carbon content (oc), granular size distribution, cation exchange capacity (CEC) and carbonate content.

Sample	pH(H ₂ O)	pH(KCl)	oc %	LOI %	<2 μm %	2-16 μm %	38-63 μm %	>63 μm %	CEC cmol/kg	CaCO ₃ %
E930423A	6.0	4.6	4.1	12.6	64.9	23.3	1.3	1.7	43.2	n.d.
E930423B	4.7	4.2	43.1	76.3	19.4	6.2	2.7	4.1	46.1	n.d.
E930611C	7.8	7.1	5.2	8.1	23.6	19.6	16.7	12.4	35.3	7.4
E930624D	6.0	5.0	23.0	42.7	35.8	14.5	1.1	3.3	51.5	n.d.
E930624E	4.0	3.1	1.5	2.7	2.1	3.2	20.7	65.1	5.3	n.d.
E930629F	5.1	4.2	0.3	1.0	1.4	3.3	1.0	83.2	4.6	n.d.
E930707G	6.5	5.1	2.6	9.7	62.6	24.5	0.9	2.1	43.1	<0.2
E930707I	4.2	3.3	1.6	2.8	2.0	2.6	1.9	89.2	4.6	n.d.
E930715J	7.8	7.0	2.7	6.3	21.0	10.8	15.0	31.0	28.3	3.0
E930715K	6.7	5.2	3.2	9.2	41.6	23.6	7.4	11.4	39.0	<0.2
E930715L	4.5	3.4	4.5	11.8	37.3	22.1	3.4	17.9	23.8	n.d.
E930720M	5.5	4.5	2.3	4.8	5.9	3.8	5.9	75.8	8.6	n.d.
E930720N	6.0	5.0	2.6	6.7	19.0	16.0	19.9	24.0	20.3	n.d.

n.d.= not determined

In Table 3, pH, clay content and organic carbon content of the soil samples are compared with the results obtained by Edelman (1984) and Van Gestel et al. (1992). Analysis of this data set shows that:

- 1) for the various soil parameters different results are obtained by different researchers for the same area;
- 2) compared to the results of Edelman (1984) the present study shows either an increased or decreased value for the various soil parameters;
- 3) in the present study, for almost all soils a higher pH value is observed compared to the results of Van Gestel et al. (1992).

Van Gestel et al. (1992) argued that a lowered pH value compared to Edelman's observations could be the result of the progressing influence of acid rain. According to Van Gestel et al. (1992) the increased levels of organic carbon compared to the data of Edelman could be due to (i) inhibition of mineralization by acid rain or (ii) differences in the sampling procedure between researchers. Considering our own data, we mention that the observed differences might be due mainly to the consequences of soil heterogeneity, which was also briefly mentioned by Van Gestel et al. (1992).

Table 3: Comparison of soil characteristics of reference soils. The first number results from the present study. Included are the results obtained by Edelman (1984; second number in row) and Van Gestel *et al.* (1992; third number in row).

Area	Sample code	pH(H ₂ O)	pH(KCl)	oc %	<2 μm
Linschoten	E930423A	6.0 - 4.6 - 5.4	4.6 - 3.8 - 3.7	4.1 - 4.7 - 4.5	64.9 - 53.0 - 40.8
Zegveld	E930423B	4.7 - 4.5 - 4.3	4.2 - 3.6 - 3.3	43.1 - 26.0 - 27.3	19.4 - n.d. - 16.0
Almere	E930611C	7.8 - n.d. - n.d.	7.1 - n.d. - n.d.	5.2 - n.d. - n.d.	23.6 - n.d. - n.d.
Lettelberter Petten	E930624D	6.0 - 5.1 - 4.4	5.0 - 4.2 - 3.7	23.0 - 19.0 - 17.7	35.8 - 51.0 - 25.5
Norgerholt	E930624E	4.0 - 3.7 - 3.6	3.1 - 2.8 - 2.5	1.5 - 9.1 - 12.1	2.1 - 12.1 - 1.3
Lheerbroeker zand	E930629F	5.1 - n.d. - n.d.	4.2 - n.d. - n.d.	0.3 - n.d. - n.d.	1.4 - n.d. - n.d.
Eendekooi Het Broek	E930707G	6.5 - 6.7 - 5.6	5.1 - 6.2 - 4.4	2.6 - 5.5 - 6.5	62.6 - 54.0 - 47.0
Hernensche Bosch	E930707I	4.2 - 4.1 - 3.6	3.3 - 3.6 - 2.8	1.6 - 0.6 - 3.8	2.0 - 0.0 - 2.7
Koudekerkse Inlaag	E930715J	7.8 - 7.3 - n.d.	7.0 - 7.1 - n.d.	2.7 - 1.7 - n.d.	21.0 - 14.0 - n.d.
Lingedijk	E930715K	6.7 - 7.1 - n.d.	5.2 - 6.9 - n.d.	3.2 - 5.4 - n.d.	41.6 - 43.0 - n.d.
Beverweerd	E930715L	4.5 - 4.9 - 5.3	3.4 - 3.8 - 3.8	4.5 - 2.5 - 3.0	37.3 - 28.0 - 28.2
Oude Mirdumerklif	E930720M	5.5 - 7.0 - n.d.	4.5 - 6.7 - n.d.	2.3 - 3.7 - n.d.	5.9 - 19.0 - n.d.
Grote Wetsinge	E930720N	6.0 - 6.4 - n.d.	5.0 - 6.0 - n.d.	2.6 - 4.8 - n.d.	19.0 - 22.0 - n.d.

n.d. not determined

3.2 Metal content of soils

Total metal contents differ considerably from soil to soil (see Table 4). For example, for soil E930629F (sandy) the total copper content is approximately 50 times smaller for soil E930707G (clay). In general, with increasing content of clay and organic carbon, the metal content increases too, which is in agreement with the results of Edelman (1984). Geometric mean values were found to be 0.18, 8.71, 13.96, 25.91 and 49.3 mg kg⁻¹ for Cd, Cu, Ni, Pb and Zn, respectively, which is comparable for background levels observed in Europe and China (Van den Hoop, 1995). We note that soil sample #11 has been collected outside the reference area close to a road. Hence, an elevated Pb level in this sample reflects the anthropogenic influence.

Table 4: Content of metals of solid phase (mg per kg dry soil).

Soil sample	K	Na	Ca	Mg	Fe	Mn
E930423A	15131	918	7676	10630	57592	714
E930423B	3690	273	16802	3087	16142	131
E930611C	10532	686	37019	9881	31548	648
E930624D	8597	827	14059	5602	33075	145
E930624E	1499	177	586	227	2556	37
E930629F	685	148	411	248	1927	32
E930707G	16809	980	7791	12431	43631	775
E930707I	915	129	218	339	3823	49
E930715J	6867	593	16559	5935	23829	315
E930715K	12728	771	8169	10187	41135	2837
E930715L	12206	619	4111	8172	29621	539
E930720M	2390	197	1887	1589	7102	167
E930720N	7622	487	6085	4487	20456	662
mean±stdev	7667±5562	524±309	9336±10148	5601±4348	24034±17541	543±745

Soil sample	Cd	Cu	Ni	Pb	Zn
E930423A	0.34	31.04	66.13	38.55	130.48
E930423B	0.35	9.99	19.22	22.62	41.58
E930611C	0.13	15.16	32.19	28.16	89.40
E930624D	0.63	12.71	24.12	16.85	75.02
E930624E	0.02	0.68	0.67	9.48	10.98
E930629F	0.02	0.70	1.27	6.05	5.42
E930707G	0.23	34.83	55.75	44.12	144.79
E930707I	0.03	2.91	2.00	8.84	10.20
E930715J	0.34	8.29	13.69	26.44	58.78
E930715K	0.46	23.75	53.28	32.09	121.58
E930715L	0.58	22.28	39.23	443.40	136.32
E930720M	0.15	6.53	17.33	16.48	28.62
E930720N	0.44	20.12	16.48	41.33	114.10
mean±stdev	0.29±0.21	14.54±11.20	26.26±21.69	24.25±13.06	74.41±51.87

3.3 Pore water composition

Total concentrations of various (heavy) metals, anions, DOC and the pH of the pore water (abbreviated as pw) are presented in Table 5. The range of metal concentrations found varies from sample to sample and from metal to metal and increases in the order $Cd < Pb < Ni < Cu \approx Zn$. Influence of human activities is again reflected in sample E930715L which has an exceptionally high concentration of lead. Analysis of the relation between pH(pw) and pH(KCl), and pH(pw) and pH(H₂O) shows that:

- for pH(pw) values smaller than 5, $pH(pw) < pH(H_2O)$ and $pH(pw) \approx pH(KCl)$;
- for pH(pw) values greater than 5, $pH(pw) > pH(KCl)$ and $pH(pw) \approx pH(H_2O)$.

This means that for acid soils pH(KCl) roughly reflects the pH of the pore water, whereas for alkaline soils the pH(H₂O) is a better estimate of the pH of the pore water. These observations are not in agreement with the results of Van Gestel et al. (1992). In the study of Van Gestel et al. (1992), pore water was collected after the performance of a bio-assay experiment with earthworms on reference soils. They found that in most cases the pH of the pore water was greater than the pH(H₂O) of the soil. Van Gestel et al. (1992) gave as possible explanation that this observation might be due to an increase of the carbonate concentration during the experimental procedure used to obtain pore water by centrifugation. However, considering our results, it seems more likely that the increase in pH in the pore water observed by Van Gestel et al. (1992) is due to:

- (1) the addition of a nutrient solution with a pH larger than the pH(H₂O) of the majority of the soils. Soil pH values after addition were found to be larger than before (Dirven-van Breemen, pers. comm.).
- (2) the presence of earthworms, which lead also to an increase of the pH of the soil (Dirven-van Breemen, pers. comm.).
- (3) in the bio-assay experiments a small amount of cow-manure with a pH-value of approximately 8 was added to the soil as food for the earthworms, which lead also to an increase of the pH of the soil (Van Gestel, pers. comm.).

3.4 Field-based partition coefficients

For Cd, Cu, Ni, Pb and Zn partition coefficients K_p were calculated according to equation (2) using the data from Tables 4 and 5 and are presented in Table 6. Partition coefficients appear to vary considerably from soil to soil. For the present set of samples, the standard deviation in K_p is approximately equal to its mean value, which is most likely due to differences in soil and porewater composition. In Figure 1, the corresponding average K_p values are presented. Average partition coefficients reported in or deduced from the literature are included. Presently derived average field-based partition coefficients are in the same order of magnitude as mean values for 11 American soils reported by Buchter et al. (1989), who studied the sorption behaviour of various metals using batch experiments. Buchter et al. (1989) fitted their data according to a Freundlich equation from which, partition coefficients were deduced at equilibrium concentrations of approximately 0.01 mg l⁻¹.

Table 5: Pore water composition with respect to pH, DOC, anions and cations.

Sample	pH (pw)	DOC mg/l	PO ₄ µg/l	Cl mg/l	NO ₃ mg/l	SO ₄ mg/l	K mg/l	Na mg/l
E930423A	4.75	15.16	24.70	39.48	283.67	30.70	0.90	29.10
E930423B	4.36	36.01	72.20	26.87	46.55	1070.48	2.78	18.95
E930611C	7.72	28.80	18.05	21.89	132.72	155.91	7.74	10.86
E930624D	5.82	47.17	40.85	57.59	12.68	113.43	0.43	33.21
E930624E	3.20	n.d.	1975.05	26.97	70.22	24.46	18.18	15.85
E930629F	4.19	n.d.	61.75	8.53	8.23	15.22	4.61	8.40
E930707G	4.56	65.42	114.00	53.84	14.47	71.64	1.17	29.62
E930707I	3.19	n.d.	n.d.	n.d.	n.d.	n.d.	7.31	12.63
E930715J	7.85	80.88	1109.60	136.06	28.57	143.65	1.21	31.44
E930715K	6.50	39.95	14.25	13.21	20.66	62.52	0.39	9.50
E930715L	4.14	53.35	804.65	19.27	407.23	42.89	21.19	18.29
E930720M	5.39	53.35	22.80	84.82	299.68	250.58	2.46	47.13
E930720N	5.35	53.29	11792.35	33.75	12.92	34.16	5.00	14.28

Sample	Ca mg/l	Mg mg/l	Fe mg/l	Mn µg/l	Cd µg/l	Cu µg/l	Ni µg/l	Pb µg/l	Zn µg/l
E930423A	85.12	13.88	0.65	36.51	0.42	105.81	44.79	1.24	84.99
E930423B	388.22	45.03	0.26	2591.00	0.60	179.53	13.56	7.25	150.37
E930611C	143.06	7.53	0.17	0.82	0.21	16.84	12.27	1.66	32.69
E930624D	60.57	5.76	6.14	85.92	0.22	55.61	14.79	7.46	45.77
E930624E	7.69	2.96	1.22	220.97	2.12	281.21	46.84	6.42	261.52
E930629F	3.69	0.97	0.70	119.41	1.10	47.34	10.51	14.50	71.92
E930707G	40.79	6.63	0.25	62.86	0.32	53.06	19.08	3.73	39.23
E930707I	9.62	4.25	1.05	913.81	5.88	91.19	43.32	3.52	464.20
E930715J	166.56	17.06	0.30	6.86	0.39	148.39	11.97	1.66	45.77
E930715K	35.63	3.86	0.21	27.72	0.38	64.50	12.74	1.24	65.38
E930715L	107.06	19.63	0.53	4761.00	6.95	130.60	112.29	262.11	333.44
E930720M	169.86	31.78	0.69	416.97	2.15	124.24	24.36	3.32	235.37
E930720N	33.19	4.67	0.35	20.59	0.34	65.14	22.42	1.86	71.92

n.d.=not determined (due to not enough porewater for analysis)

Table 6: Field-based partition coefficients (K_p in l/kg) for Cd, Cu, Ni, Pb and Zn.

Soil sample	Cd	Cu	Ni	Pb	Zn
E930423A	799	293	1477	31011	2735
E930423B	583	56	1418	3119	1535
E930611C	633	900	2624	16991	276
E930624D	2887	229	1631	2258	1639
E930624E	10	2	14	1477	42
E930629F	18	15	121	417	75
E930707G	728	656	2923	11829	3691
E930707I	5	32	46	2510	22
E930715J	867	56	1144	15953	1284
E930715K	1211	368	4183	25809	1860
E930715L	84	171	349	1692	409
E930720M	71	53	712	4971	122
E930720N	1279	309	735	22162	1587
mean±stdev	706±798	241±273	1337±1260	10785±10572	1175±1158

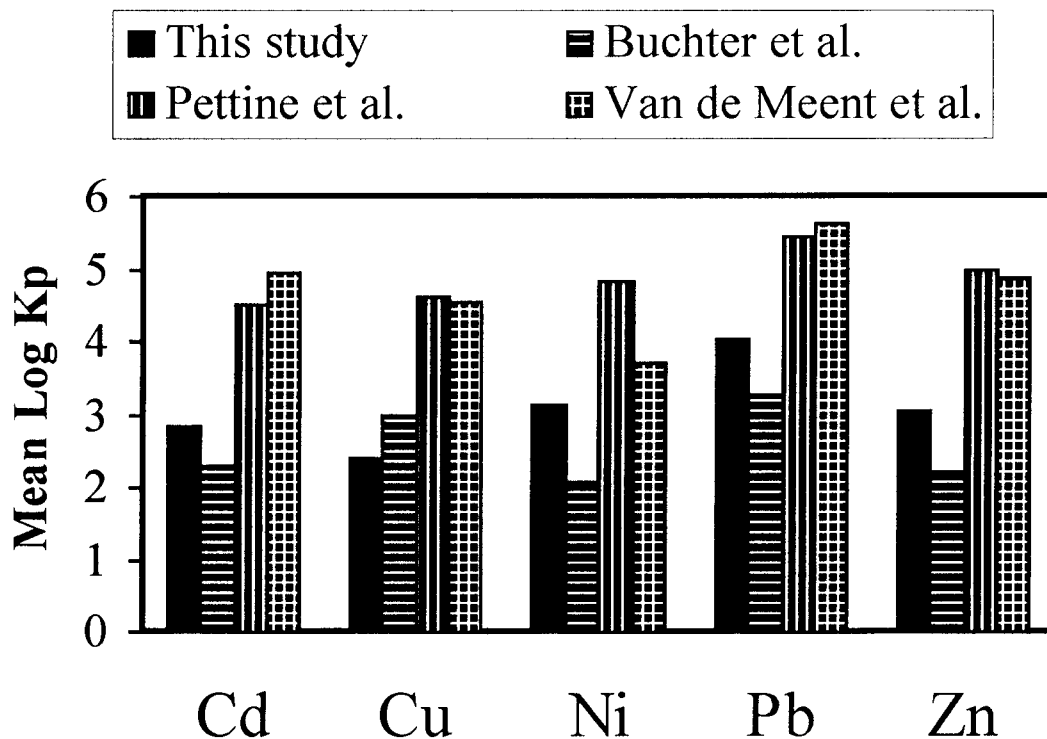


Figure 1: Average partition coefficients for heavy metals for soils and suspended matter.

Furthermore, Figure 1 clearly shows that partition coefficients for the soil system are significantly smaller, i.e. approximately two orders of magnitude independent the metal, than for suspended matter (Pettine et al., 1994; Van de Meent et al., 1990). We should add that the data of Pettine et al. (1994) are based on actual measurements in the River Po, whereas the results of Van de Meent et al. (1990) are deduced from literature data. The data of Van de Meent et al. (1990) were proposed as values for the harmonization of integrated Dutch environmental quality objectives for the compartments soil, sediment and water. From our data, however, it can be concluded that application of K_p -values derived for suspended matter to the soil system leads to erroneous results.

At this point it seems useful to analyze in more detail the variation in K_p by considering various soil characteristics. Since our data should be of help by the harmonization of integrated Dutch environmental quality objectives, K_p -values have been linearly correlated with respect to the organic matter content and clay mineral content by taking the same combinations of organic matter and clay as used for the derivation of the target values (see Table 1). The results are presented in Table 7 and Figure 2. The organic matter content is estimated by multiplying the organic carbon content by a factor 1.7. For the various metals, the partition coefficient seems to increase with increasing content of organic matter and/or clay minerals. However, the correlation is not very gratifying as is expressed by the small values of r^2 . The relation between the partition coefficient and the fractions of organic matter and clay minerals seems questionable.

Table 7: Results of linear regression of measured partition coefficients and the organic matter content and clay mineral content for Cd, Cu, Ni, Pb and Zn.

Metal	function	r^2
Cd	$K_p = 377.8 + 5.41 * (\text{clay} + 3 * \text{organic matter})$	0.21
Cu	$K_p = 160.0 + 2.18 * (\text{clay} + \text{organic matter})$	0.06
Ni	$K_p = 383.0 + 36.8 * \text{clay}$	0.40
Pb	$K_p = 8055 + 72.9 * (\text{clay} + \text{organic matter})$	0.05
Zn	$K_p = 958 + 4.42 * (2 * \text{clay} + \text{organic matter})$	0.03

In order to obtain the best possible correlation between the partition coefficient and soil parameters one might try to fit K_p to a single soil parameter or to a combination of parameters (Janssen et al., 1995). Application of the latter procedure results usually in a better correlation because more variables are taken into account. The nature of this approach can become quite empirical if binding models are considered. We will not survey all possible relationships between K_p and various combinations of soil parameters to obtain the best correlation. Starting point in our strategy is to recall that the binding of metals onto soil components can be described quite satisfyingly by a Freundlich type isotherm (Van den Hoop, 1993):

$$c_s = k c_w^n \quad (3)$$

where n is a measure for the linearity of the isotherm. Since the metal concentrations in the

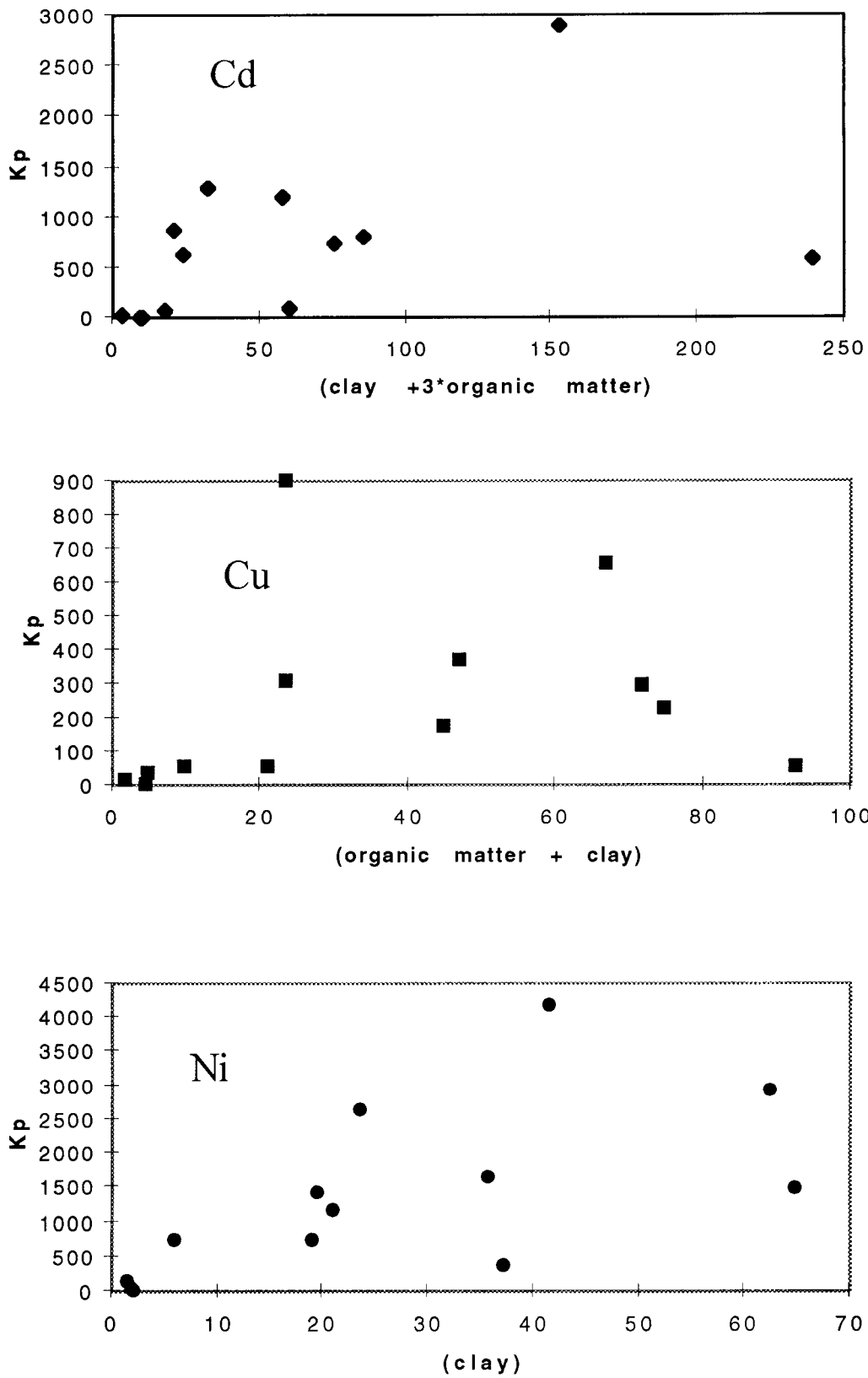


Figure 2: Field-based partition coefficients for Cd, Cu and Ni plotted as a function of the corresponding reference lines from Table 1 (continued at next page).

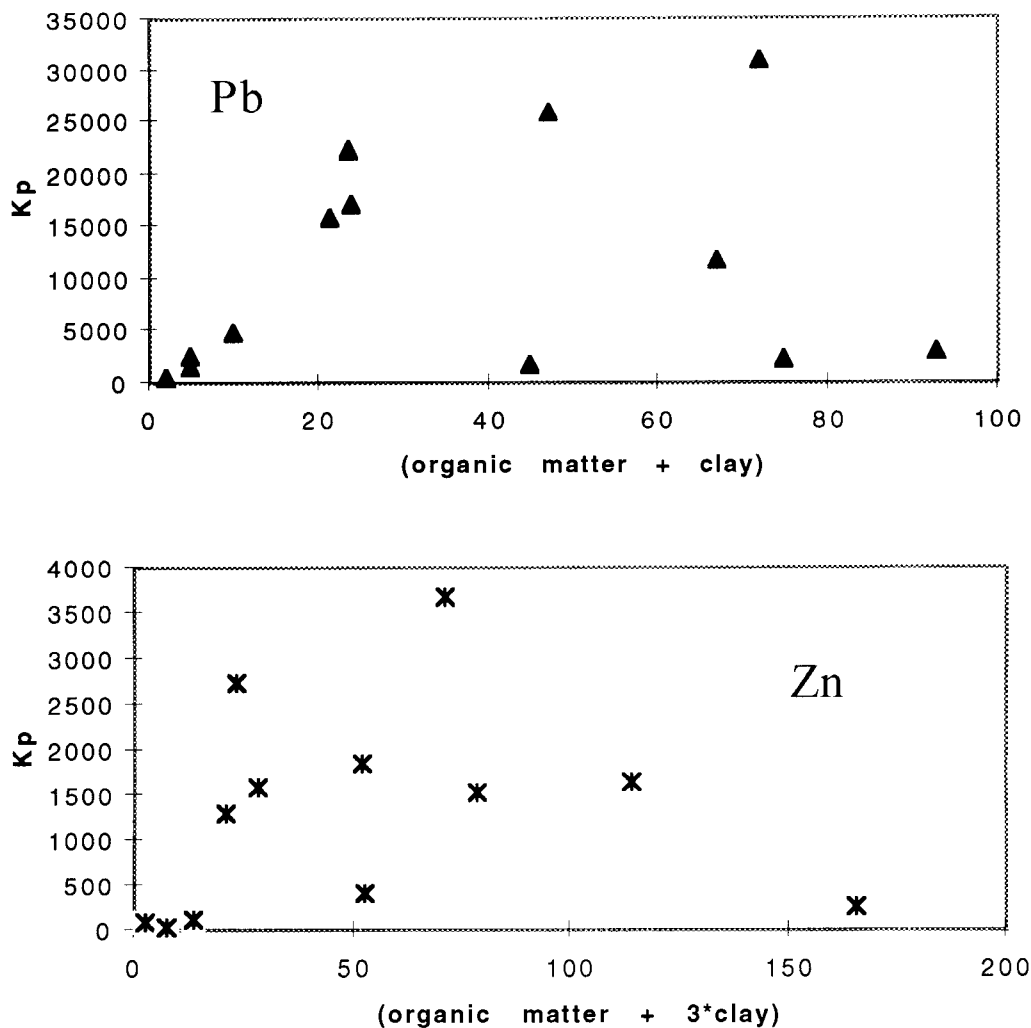


Figure 2: Field-based partition coefficients for Pb and Zn plotted as a function of the corresponding reference lines from Table 1 (continued from previous page).

present study are relatively small, we assume that the shape of the sorption isotherm is close to linearity ($n=1$). Then, equation (3) reduces to a form similar to equation (2). The parameter k is often interpreted as a measure for the strength of the binding. However, such a translation should be done with care. Nevertheless, k reflects in a certain way the binding behaviour under the experimental conditions employed. In several cases, it has been shown that variations in k can be minimized by taking into account soil parameters, such as pH and organic carbon (Chardon, 1984; Van der Zee and Van Riemsdijk, 1987). Following such a methodology, we have chosen to correlate the measured partition coefficient with respect to the cation exchange capacity (CEC). The reason for this is two-fold:

- 1) the CEC is a measure for the amount of available binding sites and, thus among others, incorporates the content of clay minerals and organic matter. Furthermore, the present CEC has not been measured under buffered conditions but at the pH of the soil. In this way, the influence of the pH on the binding behaviour is taken into account too.

- 2) for practical purposes, such as the evaluation of the "environmental" quality of soils, it is preferable to minimize the amount of soil analyses and to use relatively easy analytical methodologies, which is the case for the determination of the CEC.

The incorporation of CEC in equation (3) and assuming linear sorption behaviour leads to:

$$c_s = k' * CEC^p * c_w \quad (4)$$

Combination of equations (2) and (4) results in

$$K_p = k' * CEC^p \quad (5)$$

where the power p may be related to the number of sites involved in the binding process of a single metal ion. In Figure 3, plots are shown of the logarithm of the measured partition coefficient vs. the logarithm of the CEC of the soil for different heavy metals. For all metals, a linear relationship is observed in agreement with equation (5). Compared to the correlation between K_p and the fractions clay minerals and organic matter, the quality of the fits is considerably increased in the present approach. Regression data are listed in table 8.

Table 8: Results of linear regression of measured partition coefficients and the cation exchange capacity (CEC) for Cd, Cu, Ni, Pb and Zn.

Metal	function	r^2
Cd	$\log K_p = -0.33 + 2.08 \log CEC$	0.83
Cu	$\log K_p = 0.13 + 1.45 \log CEC$	0.61
Ni	$\log K_p = 0.65 + 1.65 \log CEC$	0.78
Pb	$\log K_p = 2.53 + 0.94 \log CEC$	0.41
Zn	$\log K_p = 0.53 + 1.67 \log CEC$	0.53

3.5 Extractable amounts of heavy metals

The partition coefficients given in section 3.4 have been calculated on the basis of the total metal content in solid and solute phase. By application of the equilibrium partitioning concept, it is presumed that the metals in solution are in equilibrium with the metals in the solid phase. However, part of the metals in solid phase are fixed. One may assume that this fraction is not involved in the exchange reaction of metals between the solute and solid phase. In general, sorption studies are based on batch experiments in which the metal is added to a solid/solute suspension. Partition coefficients are mainly derived from the amount sorbed (calculated as the difference in metal concentration initially and finally present in solute phase) and the concentration in the solute phase. Hence, the originally fixed metal in the solute phase is not considered in these experiments. Determination of this fraction is not simple. Alternatively, we have chosen to perform an extraction experiment with a displacer solution containing a high concentration of protons (0.1 mol l⁻¹). The extracted amount of metals may be seen as the potential available fraction (long term basis).

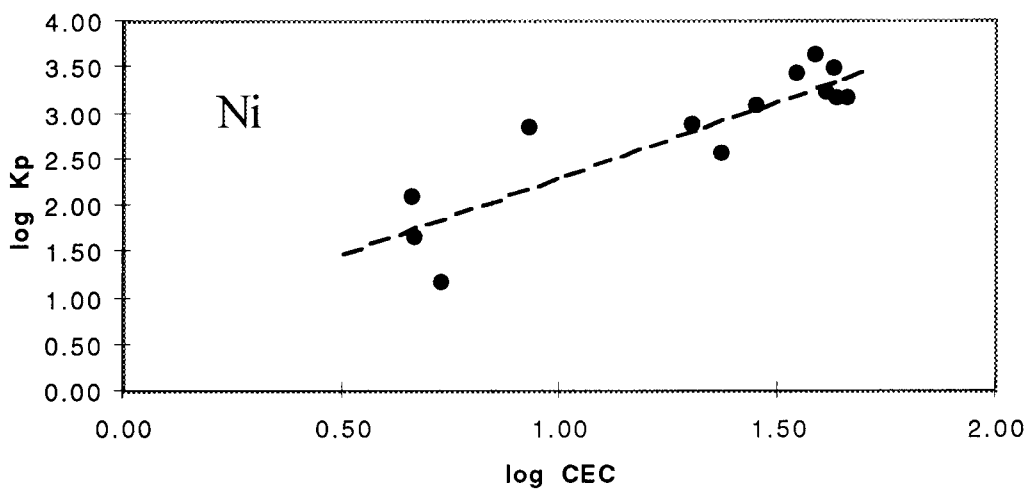
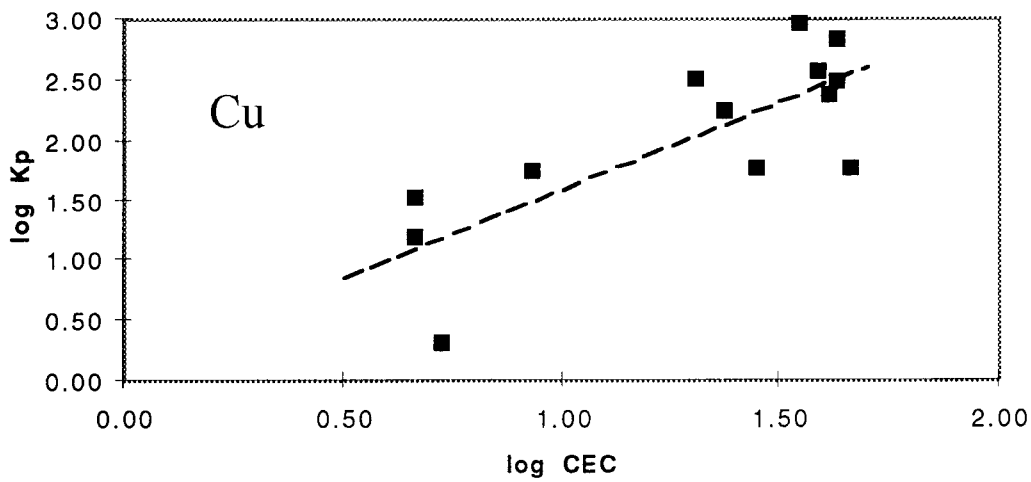
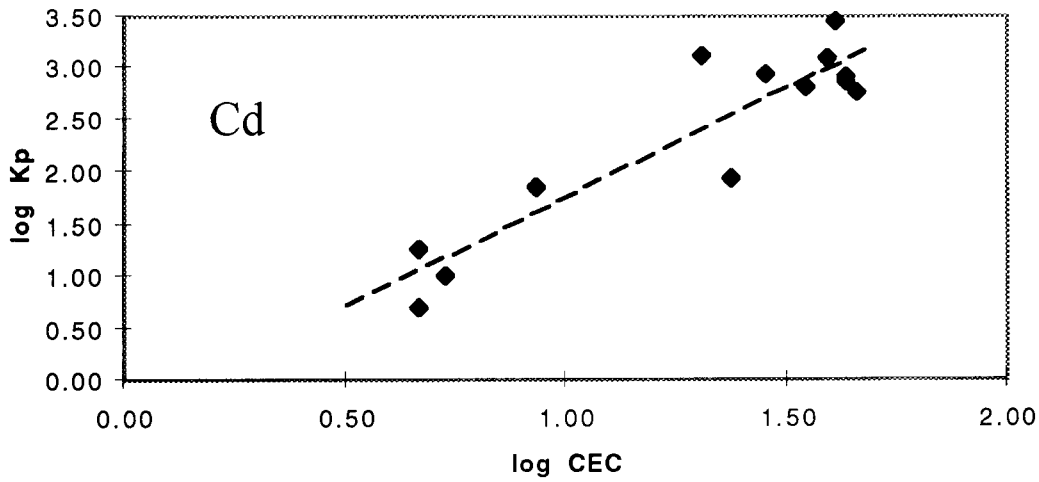


Figure 3: Field-based partition coefficients for Cd, Cu and Ni plotted vs the CEC (continued on next page).

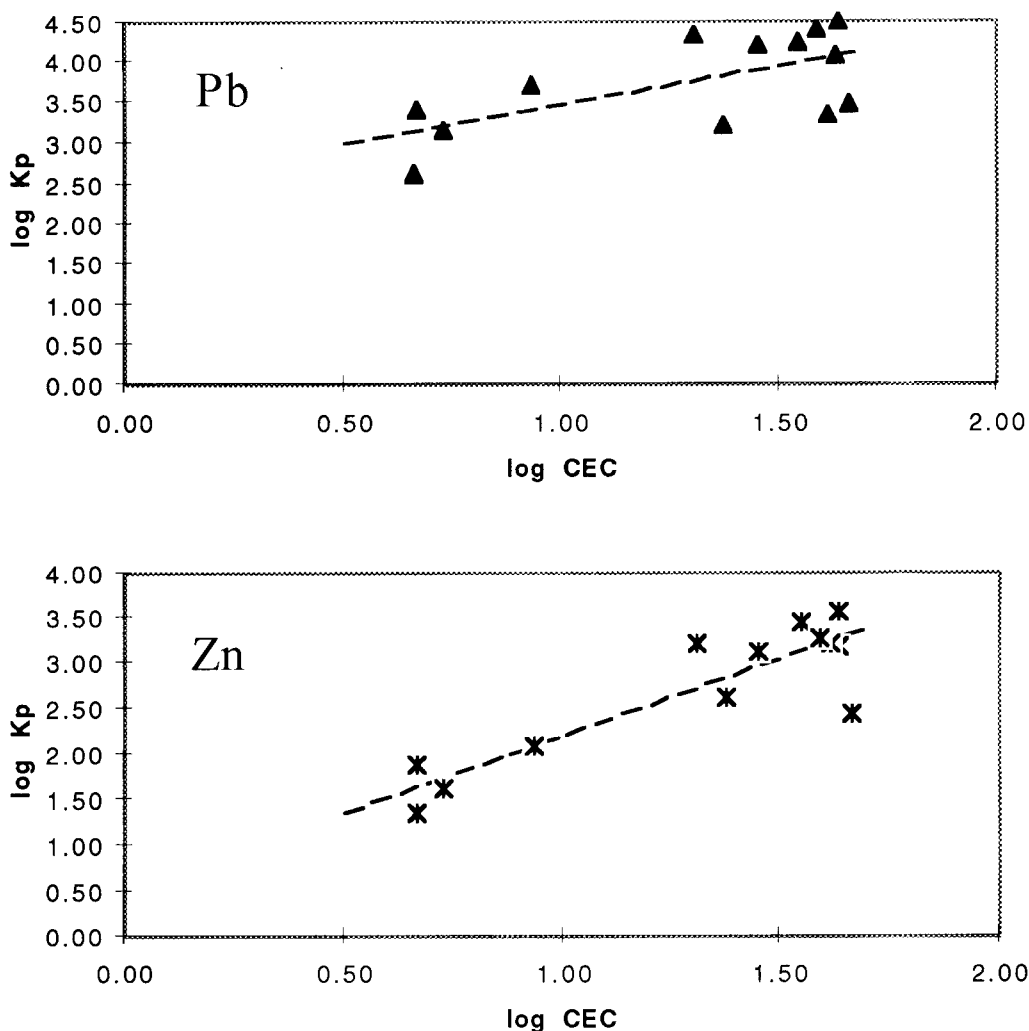


Figure 3: Field-based partition coefficients for Pb and Zn plotted vs the CEC (continued from previous page).

In Table 9, the mean ratio (c_H/c_s) of the amount of metals extracted by 0.1 mol l⁻¹ HNO₃ (c_H) and the total content of the solid phase (c_s) is listed for a series of elements. A ratio of 1 means that all metals in solid phase are available under these acidic conditions. We should mention that it is not possible to conduct from these data information with respect to the fraction fixed metal ions. However, the results might give some indication with respect to availability of metals on the long term. The mean ratio c_H/c_s increases in the sequence Cu≤Ni<Zn<Pb<<Cd. The relatively large value for the latter element may be related to the generally observed reversibility in binding behaviour of cadmium.

Table 9: Mean ratio c_H/c_s and c_{CaCl_2}/c_s of metal extracted by acid solution or calcium-chloride solution and total content of the solid phase for Cd, Cu, Ni, Pb and Zn.

Metal	Cd	Cu	Ni	Pb	Zn
Mean ratio c_H/c_s	0.62±0.21	0.15±0.11	0.16±0.09	0.30±0.28	0.23±0.12
Mean ratio c_{CaCl_2}/c_s	0.17±0.24	0.003±0.003	0.01±0.02	0.009±0.015	0.09±0.16

Furthermore, we have taken an 0.01 mol l⁻¹ CaCl₂ extraction solution as a measure of the actual metal availability. This procedure has been shown to predict reasonably well the uptake of Cd and Zn by various crops (Whitten and Ritchie, 1991; Novozamsky et al., 1993). In Table 10, the pH of and the Cd, Cu, Ni, Pb and Zn concentrations in the calciumchloride extraction solution are presented. The pH(CaCl₂) appears to be a good estimate of the pH of the original pore water (see Figure 4, r²=0.946). For the various heavy metals, however, calciumchloride extracted concentrations and field collected porewater concentrations could not be well correlated. This might be due to differences (i) in soil/solution ratios and (ii) with respect to pretreatment. We recall that the calciumchloride extractions are performed with dried and ground soil material, whereas the field collected pore water was in contact with a more heterogeneous soil composition.

Table 10: Heavy metal concentrations in an 0.01 mol l⁻¹ CaCl₂ extraction solution and pH for various soil samples. Soil:solution ratio = 1:10.

Soil sample	pH	Cd (µg l ⁻¹)	Cu (µg l ⁻¹)	Ni (µg l ⁻¹)	Pb (µg l ⁻¹)	Zn (µg l ⁻¹)
E930423A	4.93	1.75	2.85	45.5	<0.5	32.7
E930423B	4.37	0.65	3.35	15.0	<0.5	104.6
E930611C	7.43	<0.1	1.60	2.0	<0.5	<6.5
E930624D	5.17	0.55	0.50	5.0	2.60	29.4
E930624E	3.33	1.40	<0.5	4.0	37.25	349.8
E930629F	4.36	1.10	<0.5	2.0	21.85	219.0
E930707G	5.75	1.45	0.70	22.0	<0.5	6.5
E930707I	3.63	1.55	<0.5	6.0	22.35	369.4
E930715J	7.31	<0.1	1.00	<1.0	0.5	<6.5
E930715K	5.82	1.15	3.80	20.5	<0.5	16.4
E930715L	3.91	12.35	13.35	141.5	323.85	425.0
E930720M	4.94	1.75	3.45	4.5	0.70	160.2
E930720N	5.36	0.70	0.80	7.5	<0.5	75.2

In Table 9, the mean ratio (c_{CaCl_2}/c_s) of the amount of metals extracted by 0.01 mol l⁻¹ CaCl₂ and the total content of the solid phase (c_s) is listed for various heavy metals. The mean ratio (c_{CaCl_2}/c_s) increases in the sequence Cu<Pb≤Ni<Zn<Cd and is smaller than using 0.1 mol l⁻¹ HNO₃ as an extractant. Although calcium chloride is a much weaker extractant than nitric acid, relatively large fractions are still extracted for cadmium and zinc. This is in line with results from the literature for the interaction of zinc and cadmium with dissolved organic carbon under conditions of excess calcium and can be explained in terms of competition (Van den Hoop et al., 1995).

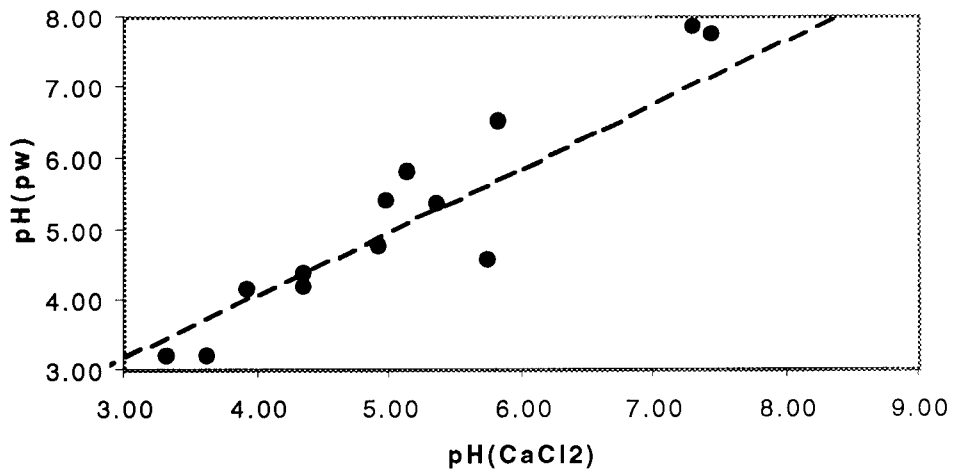


Figure 4: Relationship between pH obtained an 0.01 mol l⁻¹ CaCl₂ extraction solution and pH of the field collected pore water. Soil:solution ratio = 1:10.

4. CONCLUDING REMARKS

- Variation in absolute values of several soil parameters, like pH, organic matter and clay mineral content, at similar sample locations as reported by Edelman (1984), Van Gestel et al. (1992) reflects mainly the heterogeneity of the soil system.
- The mean field-based partition coefficients for Cd, Cu, Ni, Pb and Zn obtained in this study are significantly smaller than the ones proposed by Van de Meent et al. (1990) for the harmonization of integrated environmental quality objectives.
- For the present set of samples, the variation in K_p appeared to be in the same order of magnitude as the absolute value of K_p for various metals, due to variations in the composition of the soil solid phase and the pore water solution.
- Field-based partition coefficients are much less dependent on the combinations of contents of organic matter and clay minerals as compared to the total metal content as obtained by Edelman (1984).
- Field-based partition coefficients could quite well be correlated with the cation exchange capacity of the soil. Since this soil parameter is a measure for the amount of binding sites available at soil pH and easy to determine, it does not seem unreasonable to consider the CEC as a "correction" parameter for K_p by the harmonization of integrated environmental quality objectives.
- On the basis of using different extraction solutions, like nitric acid and calcium chloride, various fractions of heavy metals were obtained. These fractions might be related to long term and actual metal availability.

REFERENCES

- Andreasen, A.H.M., *Kolloidchem. Beihefte*, 27 (1928) 349.
- Buchter, B., B. Davidoff, M.C. Amacher, C. Hinz, I.K. Iskandar and H.M. Selim, *Soil Science*, 148 (1989) 370.
- Buffle, J., *Complexation reactions in Aquatic Systems: An Analytical Approach*, Ellis Horwood Ltd., Chichester, 1988.
- Chardon, W.J., *Mobiliteit van cadmium in de bodem*, dissertatie, Landbouwniversiteit Wageningen, 1984.
- Chau, Y.K., R. Gachter and K. Lum-Shue-Chang, *J. Fish Res. Board Can.*, 31 (1974) 1515.
- Christensen, T.H., *Water Air Soil Pollut.*, 44 (1989) 71.
- Corp, N., and A.J. Morgan, *Environ. Pollut.*, 74 (1991) 39.
- Edelman, Th., *Achtergrondgehalten van stoffen in de bodem*, Reeks Bodembescherming 34, Staatsuitgeverij Den Haag, 1984.
- Van Gestel, C.A.M., E.M. Dirven-van Breemen and J.W. Kamerman, *Beoordeling van gereinigde grond. IV. Toepassing van bioassays met planten en regenwormen op referentiegronden*, RIVM rapport no 216402004, februari 1992.
- Gillman, G.P., *Aust. J. Soil Res.*, 17 (1979) 129.
- Van den Hoop, M.A.G.T., *De toepasbaarheid van het evenwichtspartitieconcept bij de afleiding van integraal afgestemde milieukwaliteitsdoelstellingen voor bodem en sediment: een verkenningstudie*, RIVM rapport no 719101009, maart 1993.
- Van den Hoop, M.A.G.T., *Literatuurstudie naar achtergrondgehalten van zware metalen en arseen in bodem, sediment, oppervlaktewater en grondwater*, RIVM rapport no 719101019, augustus 1995.
- Van den Hoop, M.A.G.T., H.P. van Leeuwen, J.P. Pinheiro, A.M. Mota and M. de L. Simões Gonçalves, *Colloids Surfaces A: Physicochem. Eng Aspects* 95 (1995) 305.
- Janssen, R.P.T., P.J. Pretorius, W.J.G.M. Peijnenburg and M.A.G.T. van den Hoop, *Determination of field-based partition coefficients for heavy metals in Dutch soils and their relationships with soil characteristics*, RIVM report no 719101023, december 1995.
- Khangarot, B.S., and P.K. Ray, *Ecotoxicol. Environ. Saf.*, 18 (1989) 109.

Van de Meent, D., T. Aldenberg, J.H. Canton, C.A.M. van Gestel en W. Slooff, STREVEN NAAR WAARDEN. Achtergrondstudie ten behoeve van de nota "Milieukwaliteitsnormering water en bodem". RIVM rapport nr. 670101001, maart 1990.

Milbowa, Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer, Milieukwaliteitsdoelstellingen bodem en water, Tweede Kamer, 1990-1991, 21990 nr 1.

Novozamsky, I., Th.M. Lexmond and V.J.G. Houba, Intern. J. Environ. Anal. Chem., 51 (1993) 47.

Van de Plassche, E.J., and J.H.M. de Bruijn, Towards integrated environmental quality objectives for surface water, ground water, sediment and soil for nine trace metals, RIVM report no 679101005, december 1992.

Pettine, M., M. Camusso, W. Martinotti, R. Marchetti, R. Passino and G. Queirazza, Sci. Total Environ., 145 (1994) 243.

Stumm, W., (ed.), Aquatic Surface Chemistry: chemical processes at the particle-water interface, Wiley, New York, 1987.

Sunda, W.G., and J.A.M. Lewis, Limnol. Oceanogr., 23 (1978) 870.

Whitten, M.G., and G.S.P. Ritchie, Aust. J. Soil Res., 29 (1991) 215.

Van der Zee, S.E.A.T.M. and W.H. van Riemsdijk, Water Resour. Res., 23 (1987) 2059.

APPENDIX A: Area, sample code and coordinates of soil samples

Area	Sample code ^a	Coordinates
Linschoten	E930423A	453.2 x 121.1
Zegveld	E930423B	461.0 x 115.8
Almere	E930611C	481.7 x 148.6
Lettelberter Petten	E930624D	578.6 x 224.3
Norgerholt	E930624E	564.0 x 226.3
Lheebroeker zand	E930629F	539.0 x 226.0
Eendekooi Het Broek	E930707G	429.0 x 143.7
Hernensche Bosch	E930707I	426.8 x 176.0
Koudekerkse Inlaag	E930715J	411.9 x 43.4
Lingedijk	E930715K	431.3 x 136.9
Beverweerd	E930715L	449.4 x 145.8
Oude Mirdumerklif	E930720M	538.9 x 166.8
Grote Wetsinge	E930720N	591.5 x 231.1

- ^a The sample code starts with E from Equilibrium Partitioning followed by the date (in reverse order) of sampling ending with a running character.