GEOLOGICA ULTRAJECTINA

Mededelingen van de
Faculteit Aardwetenschappen der
Universiteit Utrecht

No. 129

Evidence for groundwater contamination by heavy metals through soil passage under acidifying conditions

Berend J. Wilkens

GEOLOGICA ULTRAJECTINA

Mededelingen van de
Faculteit Aardwetenschappen der
Universiteit Utrecht

No. 129

Evidence for groundwater contamination by heavy metals through soil passage under acidifying conditions

Cover photo Melani Reumers

CIP-GEGEVENS KONINKLIJKE BIBLIOTHEEK, DEN HAAG

Wilkens, Berend Jan

Evidence for groundwater contamination by heavy metals through soil passage under acidifying conditions / Berend Jan Wilkens - Utrecht : Faculteit Aardwetenschappen, Universiteit Utrecht. - (Geologica Ultraiectina, ISSN 0072-1026; no 129)
Proefschrift Universiteit Utrecht - Met lit. opg. - Met samenvatting in het Nederlands.
ISBN 90-71577-83-X
Trefw.: grondwater / waterverontreiniging / zware metalen.

Evidence for groundwater contamination by heavy metals through soil passage under acidifying conditions

Bodempassage als route voor grondwaterverontreiniging door zware metalen onder verzurende omstandigheden

(MET EEN SAMENVATTING IN HET NEDERLANDS)

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
AAN DE UNIVERSITEIT UTRECHT
OP GEZAG VAN DE RECTOR MAGNIFICUS,
PROF. DR. J.A. VAN GINKEL,
INVOLGE HET BESLUIT VAN HET COLLEGE VAN DEKANEN
IN HET OPENBAAR TE VERDEDIGEN OP
MAANDAG 11 SEPTEMBER 1995 DES NAMIDDAGS OM 12:45 UUR.

Door

BEREND JAN WILKENS
geboren op 10 juni 1962, te Utrecht

PROMOTOR:	PROF. DR. C.H. VAN DER WEIJDEN
CO-PROMOTOR:	DR. IR. J.P.G. LOCH

Dit proefschrift werd mede mogelijk gemaakt met financiële steun van
het Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer,
Directie Drinkwater, Water en Bodem.

Aan mijn ouders

Summary

Sandy soils, in the border area of Belgium and the Netherlands (the Kempen region), are heavily contaminated with cadmium and zinc by atmospheric deposition from nearby smelters. Groundwater contamination by leaching from low adsorption soils is subject of this study. There are reports of high cadmium and zinc concentrations in groundwater in the area, but in most cases the direct sources are unknown. In an attempt to predict present or future risk of groundwater contamination by soil leaching, metal binding processes (retardation) that are specific for these soil types under the existing acidifying conditions were studied.

Four sampling fields were selected in this region. The fields have dimensions of 60 x 60 m^2 and are part of larger soil-units in nature reserves. The fields are located 1.4 to 3.5 km in the down wind direction (N-E) from the zinc smelters at Overpelt (B) and Budel (NL). At each of the four fields nine soil profiles and four groundwater observation tubes were sampled. Soil profiles were sampled at ten or eleven depths down to 1.30 m, whereas the groundwater tubes were monitored during one year (November 1991 to November 1992) at a filter depth of approximately 2.5 m.

The soil samples were analyzed for cadmium, copper, lead, nickel and zinc. Average soil contents of 131 $\mu g.g^{-1}$ zinc and 1.6 $\mu g.g^{-1}$ cadmium with maximum contents in the O-horizon of 2989 $\mu g.g^{-1}$ respectively 16.3 $\mu g.g^{-1}$ were found. In addition pH and contents of organic matter, aluminium, iron, and manganese were determined. The relative importance of these soil parameters for metal adsorption is derived from the profiles. The data show that the content of organic matter is the most important soil component for binding cadmium and zinc. Adsorption of cadmium and zinc on aluminium, iron and manganese (hydro) oxides appears to be of minor importance at low pH (< 5.5).

High concentrations of zinc (up to 12,900 $\mu g.l^{-1}$) and cadmium (up to 126 $\mu g.l^{-1}$) were observed in most of the groundwater samples. These metals are originating from the soil above the groundwater and entered the groundwater by soil passage. These soils have a low pH (4.0-4.5) and low contents of organic matter. The average pH in the groundwater is about 4.5. Soils of low pH and low content of organic matter have a minor groundwater protecting ability against infiltrating cadmium and zinc. The groundwater concentrations of cadmium and zinc exceed the Dutch intervention limits over 5 times, whereas the topsoil contents of both cadmium and zinc are 5 times lower than their intervention limits. If the soil and groundwater concentrations of these metals are directly influenced by each other the Dutch intervention values for soil and groundwater are not consistent.

Batch adsorption experiments were carried out with samples from an A, Bh and C-horizon of contaminated soil. Cadmium sorption was studied at 3 different pH-levels (3.6, 4.3 and soil buffered pH) and 3 different additions of zinc (0-40 $mg.l^{-1}$). Desorption data do not fit the proposed regression model for adsorption. Not all the cadmium, initially present in the polluted soil, will desorb reversibly. Adsorption of cadmium by acid sandy soils can be described by the Freundlich adsorption isotherm. The cadmium adsorption coefficient (K_F) decreases considerably at increasing proton activity in the sorption experiments. Although zinc also competes with cadmium for the sorption sites, we observe a two to three times stronger competition effect of the H^+ ion, which is explained by the chemical properties of both ions. Organic matter content largely explains the variation of the scaled Freundlich adsorption coefficients of the three soil samples.

A model is designed to calculate accumulation and leaching of heavy metals in the fields. Based on the Freundlich adsorption equation, sorption characteristics are achieved from the soil data, by using multiple linear regression techniques. The required partition coefficients are therefore exclusively acquired from soil and groundwater observations.

Leaching of cadmium and zinc from topsoil to groundwater can be explained by soil type. Sandy soils of relatively low organic matter content (arenosols) demonstrate a low retardation capacity. Leaching of these metals is extremely fast. Carbic podzols, of relatively high organic matter content in the topsoil (4 to 10%) have a higher capacity to adsorb cadmium and leaching to the groundwater is delayed. In spite of differences in type and vulnerability of both soils the groundwater is heavily polluted by cadmium and zinc after a century of diffuse industrial immission and breakthrough is complete for these metals. Copper has an extremely high retardation; the leaching of this metal is limited.

If Freundlich adsorption parameters and subsequent leaching are calculated from individual profiles of soil macro parameters, large field dispersion is predicted. Field dispersion is dependent on the variance in the retardation factors between the individual profiles. Using average retardation factors and their standard deviations to calculate breakthrough in time is an acceptable method to obtain the field dispersion coefficient. This coefficient is orders of magnitude larger than the molecular-diffusion/hydrodynamic-dispersion coefficient derived from grain size and soil structure.

An additional study was carried out to investigate the impact of short distance soil heterogeneity and preferential flow on copper, lead and zinc distribution in these soils. A soil site, close to one of the research fields, was sampled in a vertical plane of 150 cm width and 60 cm depth, in a grid providing 362 samples. The samples were analyzed for the contents of organic matter, aluminium, calcium and the heavy metals copper, lead and zinc. Soil heterogeneity was made visible by vertical contour profiles of these variables. Preferential flow was not observed with the used methods. Organic matter is the major soil parameter responsible for the distribution of copper and lead. Zinc has a lower correlation with organic matter content. Most organic matter is found in the topsoil, but bio-turbation by soil fauna is an important process for organic matter dispersion, and consequently for heavy metal distribution. Eluviation and illuviation processes of the major elements aluminium and calcium have not resulted in redistribution of heavy metals.

Samenvatting

Zandgronden in het Nederlands-Belgische grensgebied (Kempen), zijn zwaar vervuild met cadmium en zink door atmosferische depositie vanuit de nabij gelegen zinkfabrieken. Grondwatervervuiling door uitspoeling van gronden met lage adsorptie is onderwerp van deze studie. Hoge cadmium en zink concentraties in het grondwater zijn voor dit gebied al bekend, maar in de meeste gevallen zijn de directe bronnen onbekend. In een poging om een voorspelling te doen van huidige of toekomstig risico van grondwater vervuiling door bodemuitloging, zijn metaalbinding processen (retardatie) die specifiek zijn voor deze bodems onder de heersende verzurende omstandigheden bestudeerd.

Vier monsterveldjes zijn geselecteerd in dit gebied. De veldjes hebben de afmetingen 60 bij 60 m^2 en zijn een deel van een groter bodemsysteem in natuurgebieden. De veldjes liggen 1,4 tot 3,5 km van de zinkfabrieken te Overpelt (B) en Budel (NL) en in de richting van de overheersende windrichting. In elk van de vier veldjes negen bodemprofielen en vier grondwaterbuizen zijn bemonsterd. Bodem profielen zijn op tien of elf dieptes bemonsterd tot een diepte van 1,30 m en de grondwaterbuizen zijn gedurende één jaar bemonsterd op een gemiddelde filterdiepte van ongeveer 2,50 m.

De bodemmonster zijn geanalyseerd op cadmium, koper, lood, nikkel en zink. Gemiddelde bodemgehaltes van 131 $\mu g.g^{-1}$ zink en 1,6 $\mu g.g^{-1}$ cadmium met maximum gehaltes in de O-horizon van 2989 $\mu g.g^{-1}$ zink en 16,3 $\mu g.g^{-1}$ cadmium zijn in dit gebied gevonden. Als aanvulling hierop zijn de pH en de gehaltes organisch materiaal, aluminium, ijzer en mangaan bepaald. Het relatieve belang van deze bodemparameters voor metaal adsorptie is aan de hand van bodemprofielen bepaald. De gegevens tonen aan dat het gehalte organisch materiaal belangrijkste bodem parameter is voor de vastlegging van cadmium en zink. Adsorptie van cadmium en zink aan aluminium, ijzer en mangaan (hydr-) oxides blijkt een minder belang te hebben bij lage pH waarden (pH $<$ 5,5) .

Hoge concentraties zink (tot 12900 $\mu g.l^{-1}$) en cadmium (tot 126 $\mu g.l^{-1}$) zijn in de meeste grondwatermonsters gemeten. Deze metalen zijn afkomstig van de bodem boven het grondwater en bereiken het grondwater door bodempassage. Deze bodems hebben een lage pH (4,0-4,5) en een laag gehalte organisch materiaal. De gemiddelde pH in het grondwater is ongeveer 4,5. Bodems met een lage pH en een laag gehalte organisch materiaal hebben een kleinere grondwaterbeschermende functie tegen infiltrerend cadmium en zink. De grondwater concentraties cadmium en zink overschrijden de Nederlandse

interventie limieten meer dan 5 maal, terwijl de bovengrond gehaltes cadmium en zink vijf keer lager zijn dan deze interventie limieten. Als de bodem- en grondwatergehaltes van deze metalen direct door elkaar beïnvloed worden, dan zijn de Nederlandse interventie waarden voor bodem en grondwater niet met elkaar in overeenstemming.

Batch adsorptie experimenten zijn uitgevoerd met een monster van een A-, Bh- en C-horizon van vervuilde bodems. Cadmium sorptie was bestudeerd bij drie verschillende pH-niveaus (3,6, 4,3 en bodem gebufferde pH) en drie verschillende zink toevoegingen (0-40 $mg.l^{-1}$). Desorptie voldoet niet aan de voorgestelde regressiemodel voor adsorptie. Niet alle cadmium, aanwezig in de vervuilde bodem, zal reversibel desorberen. Adsorptie van cadmium aan zure zandgronden kan beschreven worden door de Freundlich adsorptie isotherm. De cadmium adsorptie coëfficiënt (K_F) wordt aanzienlijk lager bij hogere proton activiteit in de adsorptie experimenten. Ofschoon ook zink concurreert met cadmium voor de sorptieplaatsen, rapporteren wij een twee tot drie keer sterker verdringingseffect voor de H^+ ion, wat verklaart kan worden uit de chemische eigenschappen van beide cationen. Het gehalte organisch materiaal verklaart voor een groot gedeelte de variatie in de geschaalde Freundlich adsorptie coëfficiënt van de drie bodemmonsters.

Een model is ontworpen voor de berekening van de accumulatie en uitloging van zware metalen in de veldjes. Het model is gebaseerd op de Freundlich adsorptie vergelijking, en de sorptie eigenschappen worden verkregen van de bodem en grondwater getallen zelf gebruik makend van regressie analyses.

Uitloging van cadmium en zink van de bovengrond naar het grondwater kan verklaard worden aan de hand van het bodemtype. Zandgronden met een relatief laag organisch stof gehalte (arenosol) bezitten een lage retardatie capaciteit. Uitloging van deze metalen is dan ook zeer snel. Een carbic podzol, een bodem met relatief hoog organisch stof gehalte in de bovengrond (4-10%), heeft een grotere capaciteit om cadmium te adsorberen en uitspoeling naar het grondwater zal trager verlopen. Ondanks de verschillen in type en kwetsbaarheid van beide bodems, is het grondwater is zwaar vervuild met cadmium en zink na een ruim eeuw van diffuse industriële immissies en doorbraak naar het grondwater in volledig voor deze metalen.

Als Freundlich adsorptieparameters en de daaropvolgende uitspoeling karakteristieken worden berekend van individuele profielen van bodemparameters, wordt een grote velddispersie voorspeld. Velddispersie is afhankelijk van de variantie in de retardatie factoren tussen de individuele profielen binnen een veldje. Met de gemiddelde retardatie factor en de standaard deviatie binnen deze factor kan een velddispersie coëfficiënt berekend worden. Deze coëfficiënt ook kan bepaald worden uit de veld doorbraak curve in de tijd, deze beide komen goed met elkaar overeen. De velddispersie coëfficiënt is vele malen groter dan de moleculaire-diffusie / hydrodynamische-dispersie afgeleid van korrelgrootte en bodemstructuur.

Een aanvullende studie is uitgevoerd, om te onderzoeken wat het effect is van korte afstand bodemheterogeniteit en voorkeursstroming op de verdeling van koper, lood en zink in de Kempen bodem. Een bodem, nabij een van de onderzoeksveldjes is bemonsterd in een verticaal vlak van 150 cm breed en 60 cm diep, het ontstane grid bevat 362 monsters. De bodemmonsters zijn geanalyseerd op de gehaltes organisch materiaal, aluminium, calcium, en de zware metalen koper, lood en zink. Bodemheterogeniteit is zichtbaar gemaakt met behulp van zogenaamde verticale contourprofielen van deze variabelen. Voorkeursstroming is niet waargenomen met de gebruikte methode. Organisch materiaal is de belangrijkste bodemparameter verantwoordelijk voor de verdeling van koper en lood. Zink toont een lagere correlatie met het organisch stof gehalte. Bodem organische stof bevindt zich voornamelijk in de bovengrond, maar bio-turbatie door bodemfauna is een belangrijk mechanisme voor de herverdeling van organisch materiaal, en ook de daaraan gekoppelde metaal verdeling. In- en uitspoeling processen van de hoofd elementen aluminium en calcium hebben niet geleid tot de herverdeling van de metalen koper, lood en zink.

Table of contents

1

Introduction

1.1. Formulation of the problem

The research reported here is aimed at improving the knowledge of the mobility of the heavy metals cadmium and zinc in vulnerable soil types. We use the term vulnerable with reference to vulnerability of groundwater for contamination by soil leaching. At diffuse soil immissions of heavy metals, accumulation is often supposed to occur mainly in the topsoil. Binding of heavy metals in this soil compartment is relatively strong, because of de presence of soil organic matter, clay-minerals and sesquioxides. If soil contains little organic matter and no clay minerals a reduced accumulation in the topsoil and an increased leaching of heavy metals to the groundwater is expected. Also the pH of the soil is of influence on this leaching.

Cadmium contamination of the environment has drawn attention since the sixties. The most important occasion was an environmental calamity in Japan where rice paddy was irrigated by cadmium contaminated river water. The pollution was originated from an upstream situated mine. Also in the Netherlands concern exists about pollution of the environment by cadmium. Especially in the Dutch-Belgian Kempen elevated cadmium contents are found in soils and plants, as a result of industrial pollution. This study particulary addresses the questions whether or when the diffuse metal immissions breakthrough in the groundwater of the Kempen.

1.2. Approach to the problem and thesis outline

To study long term heavy metal mobilities in natural soils a diffusely polluted area around metal industries was required. A major source of cadmium is smelting and refining of non-ferrous metals. Another requirement for this study is the presence of vulnerable soils. The Kempen region satisfies these requirements. In the remainder of this introduction general information about the Kempen, soils, metal immissions and metal properties will be presented.

Distribution of heavy metals between soil and groundwater is investigated by field observations, adsorption batch experiments and model calculations. Soil profiles and groundwater are sampled to obtain field data for model validation. Sampling strategy, methods, results and immediate interpretations are reported in chapters 2 and 3 respectively. Adsorption batch experiments are carried out to study *in situ* partitioning of cadmium in soil at different level of zinc concentrations and imposed pH. Adsorption parameters are related to soil composition. This work is described in chapter 4. Chapter 5 describes model calculations of leaching and accumulation to gain insight on travel-times of cadmium and zinc from the topsoil down to the groundwater. To study the degree of lateral inhomogeneity of the soil profile and of heavy metal penetration in the soil at short distance, a pit wall was intensively sampled. Whereas chapters 2, 3 and 5 present heavy metal behaviour at field scale (60x60 m^2), chapter 6 describes distributions of heavy metals in this vertical plane of dimensions 1.5x0.6 m^2.

1.3. Research area

1.3.1. Geography

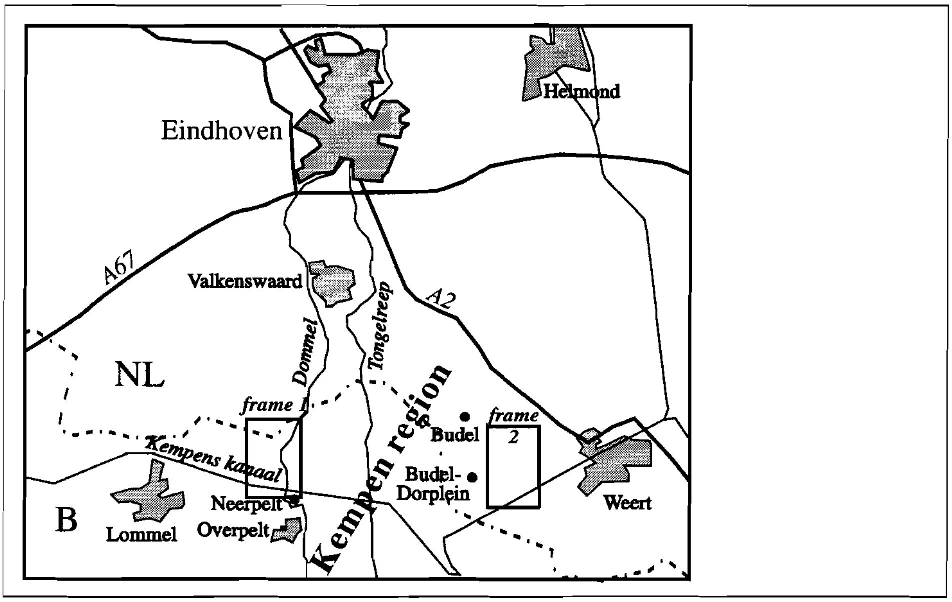

Figure 1.1. Map of the border area between the Netherlands (NL) and Belgium (B). The frames are enlarged in Figures 1.2. and 1.3.

Figure 1.1 shows a map of the south of the Netherlands and the north of Belgium. The frames in Figure 1.1 are enlarged in Figures 1.2 and 1.3, which are focused on the areas just around the zinc smelters and the research fields. The Kempen area is a flat lowland and consists mainly of aeolic coversands, with an elevation of 35-40 m above sea-level. Soils in this area are sandy and acidic. The climate of the area is humid and temperate with mean July and January temperatures of 19 and 4°C, and an annual precipitation averaging 800 mm, and the net infiltration rate is approximately 150-200 mm.y^{-1} (Boumans and Meinardi, 1986).

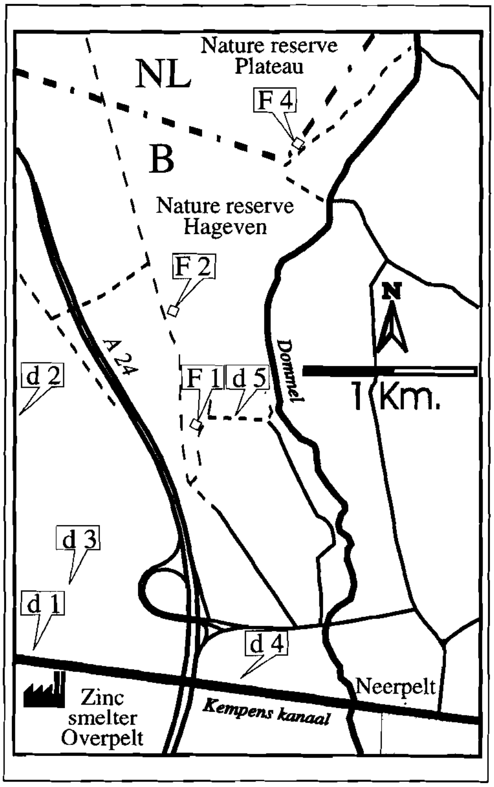

Figure 1.2. Map of the research area near zinc smelter Overpelt (Belgium).
F = soil and groundwater sampling field, listed in Table 1.II,
d = atmospheric deposition sampling point (LISEC, 1989), listed in Table 1.I.

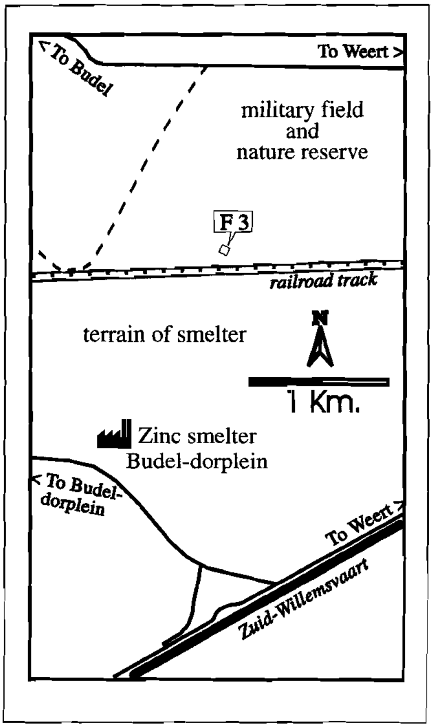

Figure 1.3. Map of the research area near zinc smelter Budel-Dorplein (the Netherlands).
F = soil and groundwater sampling field, listed in Table 1.II.

━━━	Motorway
───	Seconderary road
- - - - - -	Unpaved road
▬ ▬ ▪ ▬	Border
━━━	Canal or river

Legend by Figures 1.2 and 1.3.

1.3.2. Zinc smelters

At the end of the last century a number of zinc producing plants settled down in this area. Three zinc smelters are still active, i.e. at Overpelt (B), Balen (B) and Budel-Dorplein (NL). Beside these plants there were important former non-ferro smelters in the region, especially the zinc smelter Lommel.

The mostly used zinc ore in these smelters is sphalerite (ZnS), which contains a wide range of other trace metals. The most abundant are, in decreasing order manganese, cadmium, copper, arsenic, tin, gallium, antimony and thallium (Levinson, 1974). Zinc recovery, can be either by thermal or electrolytic extraction. The old, pyrometallurgic zinc plants employing thermal smelting are a major cadmium emission source. Hutton (1982), studying cadmium behaviour in the environment, suggests cadmium emission factors from 10-100 $g.ton^{-1}$ produced zinc, in the pyrometallurgic zinc production, to 0.20 g Cd ton^{-1} in the electrolytic process. The cadmium emissions from primary copper and lead production are lower than the cadmium emissions from pyrometallurgic zinc plants (Pacyna, 1987). In the late sixties and early seventies a change was made from thermal process technology to electrolytic process technology. The major chemical species evolved during non-ferrous metal production are cadmium-oxides and cadmium-sulphides. Condensation of cadmium takes place preferentially on fine particles in the 0.1 to 1.0 μm diameter range. Small particles from high-temperature processes are very easily transported by air masses over long distances. Cadmium concentration on the larger particles will be low and the particles in air decreases rapidly with distance from the smelter. At a distance of 30 km from the source the cadmium concentration will reach the background level in soil. High contents of heavy metals can be expected in the soils around zinc smelters. Within 1 km from a zinc smelter in Palmerton (Pa, U.S.), 13.5% $(g.g^{-1})$ zinc, 1750 $\mu g.g^{-1}$ cadmium, 2000 $\mu g.g^{-1}$ copper and 2000 $\mu g.g^{-1}$ lead are measured in the O-horizon (Buchauer, 1973).

1.3.3. Atmospheric deposition in the Kempen

An important variable for behaviour of heavy metals in soils is their concentration in solution. Speciation, adsorption and precipitation are functions of the solute concentration. In the Kempen area the heavy metal input concentrations in the soil are controlled mostly by the atmospheric immissions and the net rainwater infiltration. Some atmospheric deposition data are available for the situation around the zinc smelter Overpelt (Belgium). The atmospheric deposition of trace metals has a great spatial variability (Table 1.I) and decreases strongly with the distance from the zinc smelter. The concentrations of heavy metal entering the soil can be calculated from total deposition and net infiltration (150-200 $mm.y^{-1}$).

Table 1.I. Total atmospheric deposition (mg/m^2/y) for the elements Cd, Cu, Pb and Zn at points north, east and north-east of the zinc smelter Overpelt (Belgium) (Lisec, 1989).

Nr	distance from source	Cd	Cu	Pb	Zn
1	0.4 km North-East	202	168	364	8267
2	1.5 km North	4	14	67	492
3	0.8 km North-East	20	30	142	1448
4	1.5 km East	12	38	180	1277
5	2.1 km North-East	4	14	69	601

The deposition is an annual average for the period 1988-1989. Nickel deposition is not measured.

1.3.4. Soil and groundwater sampling at the research sites

We choose four sampling fields in this region. The fields are located in the direction of the prevailing wind (N-E) from the zinc smelters at Overpelt (B) and Budel (NL). Both soil profiles and groundwater were sampled on these fields. The four fields are indicated on the maps in Figures 1.2 and 1.3. The soil names and distances from the emission points are listed in Table 1.II.

Table 1.II. Soil and groundwater sampling sites, with the distance from the nearest emission point.

field	distance	emission point	soil type (F.A.O.)
1	1.9 km	Overpelt smelter (B)	arenosol
2	2.3 km	Overpelt smelter (B)	carbic podzol
3	1.4 km	Budel smelter (NL)	arenosol
4	3.5 km	Overpelt smelter (B)	carbic podzol

Soil was sampled in August and September 1990. Samples were taken from four fields in the Kempen. All sites were situated in a nature reserve. In every field of 60 x 60 m^2 soil profiles were sampled at nine locations in a regular square grid. Each soil profile was sampled down to a depth of 130 centimetres including the litter layer.

From November 1991 to November 1992 groundwater was sampled at 16 sites divided over the same four fields. A sampling sequence was made over 8 periods. In every field of 60 x 60 m^2 four groundwater samples were taken in a square using piezometric tubes. This sampling scheme enables us to relate the groundwater composition to the overlaying soil in each field. The tubes vary in length from 2.10 to 5.00 meter below soil surface. The filter screens of 1 meter length were placed just below the *in situ* estimated groundwater level in sandy layers. Details of the soil and groundwater sampling are presented in chapter 2 and 3.

1.4. Chemical characterization of the heavy metals

Table 1.III presents chemical properties of the heavy metals, which are involved in this research. Emphasis in this work is on the metals cadmium and zinc. These metals are mobile in soil-systems. The following sections present a short descriptions of the heavy metals considered in this research, e.g. minerals, use, toxicology and soil behaviour.

Table 1.III. Some major chemical properties of Cd, Cu, Ni, Pb and Zn.

Property	Cadmium	Copper	Lead	Nickel	Zinc
Atomic number	48	29	82	28	30
Atomic mass	112.41	63.54	207.19	58.71	65.39
Abundance world-wide in soil [$\mu g.g^{-1}$][1]	0.06-1.10	6-80	10-84	4-55	17-125

1) McBride, 1994.

1.4.1. Cadmium

Cadmium most often occurs in small quantities associated with zinc ores, such as sphalerite (ZnS). Greenockite (CdS) is the only cadmium sulphide mineral of importance. Almost all cadmium is obtained as a by-product in the treatment of zinc, copper and lead ores. Geochemically cadmium is in many respects similar to zinc (Weast, 1986).

The geochemical relationship between cadmium and zinc makes that both elements usually occur together in environment. Thus zinc smelters may have large emissions of fumes containing both ZnO and CdO. The higher volatility of CdO as compared to ZnO causes a relative enrichment of cadmium in these fumes as compared to the ores. In these ores the zinc/cadmium ratio is in the order of magnitude of 400 (Buchauer, 1973) or 130 to 650 reported by Levinson (1974). Sixty percent of the cadmium is used as coating material. Also in paint pigments and plastics industries extensive use is made of cadmium compounds. It is applied in batteries, in photography and in fungicides (de Haan and Zwerman, 1978).

The toxic effects of cadmium received widespread attention as a result of the Itai Itai disease in Japan. Death was attributed to kidney failure, when a cadmium content of 200 $\mu g.g^{-1}$ wet weight is reached in the kidney cortex. The victims were mainly post menopausal woman suffering from malnutrition, low vitamin-D intake and calcium deficiency (O'Neill, 1985).

Because of the predominant occurrence of cadmium as divalent cation electrostatic adsorption on negatively charged soil particles probably acts as the main bonding mechanism. Cadmium may also form complexes with hydroxyl and chloride ions. It was shown by Hahne and Kroontje (1973) and Boekhold (1992) that such complexes increase the mobility of cadmium in the environment.

Table 1.IV. Speciation of cadmium in water with inorganic species at different pH-levels.

pH	3	4	5	6	7
Cd^{2+}	0.781	0.781	0.781	0.781	0.776
$CdCl^+$	0.215	0.215	0.215	0.215	0.214
$CdCO_3$	0	0	0	0	0.002
$CdHCO_3^+$	0	0	0	0	0.001
CdOH	0	0	0	0	0.003
$CdSO_4$	0.004	0.004	0.004	0.004	0.004

Σ Cl 516 μm/l, Σ HCO_3^- 426 μm/l, Σ SO_4 610μm/l, Σ Cd 0.1 μm/l, (Pedroli, 1990).

With a computer model the speciation of cadmium and zinc is calculated in a solution with the most important pore-water anions. The pore-water composition is derived from the groundwater composition data-set of 412 samples (Pedroli, 1990), and calculated with the speciation model CHARON (1989). Table 1.IV presents the most important inorganic complexes for cadmium.

1.4.2. Copper

The discovery of copper dates from prehistoric times; it has probably been mined for more than 5000 years. Copper occasionally occurs in native form, and is found in many minerals such as cuprite, malachite, azurite, chalcopyrite and bornite. The most important copper ores are sulphides, oxides and carbonates. The electric industry is one of the greatest users of copper (Weast, 1986).

Copper, at trace concentration levels is an essential nutrient for plants. The effects of high copper contents of soil on the uptake of other micronutrients by plants are well known. High copper level may cause iron deficiency, which is demonstrated as typical chlorosis features (de Haan and Zwerman, 1978). Normal copper contents of soil are around 20 $\mu g.g^{-1}$ with variation over the range 2-100 $\mu g.g^{-1}$. Mobility and displacement of copper in soils is low. Copper is strongly bound by soil organic matter.

1.4.3. Lead

Native lead occurs in nature, but is rare. Lead is obtained from galena (PbS) by a roasting process. Anglesite ($PbSO_4$), cerussite ($PbCO_3$) and minium (Pb_3O_4) are other lead minerals (Weast, 1986).

Too high lead intake by human (and animals) may result in toxic effects following accumulation in the liver, kidneys and bones. Gasoline combustion being the main lead source, most of the lead will be deposited on soil and will form relatively insoluble compounds like cerussite ($PbCO_3$). Because of the formation of these solids and of the adsorption of lead when present as divalent cation, leaching of lead in soils in mostly small. Environmental concern for lead poisoning has resulted in new regulations to reduce the concentration of lead emitted by gasoline.

1.4.4. Nickel

Nickel is discovered by Cronstedt in 1751 in kupfernickel (niccolite). It is extensively used for making stainless steel and other corrosion-resistant alloys (Weast, 1986). Toxicity of nickel to plants is found in acid soils formed from serpentine or other ultrabasic rocks. Bio-accumulation of nickel in humus is pronounced and, like copper, nickel favours bonding to "softer" organic ligands containing nitrogen and sulphur. High organic matter levels in nickel rich soils can solubilize nickel as organic complexes, at least at higher pH (McBride, 1994).

1.4.5. Zinc

Centuries before zinc was recognized as a distinct element, zinc ores were used for making brass. An alloy containing 87% zinc has been found in prehistoric ruins in Transsylvania. The metal was discovered in Europe by Marggraf in 1746, who showed that it could be obtained by reducing calamine with charcoal. The principal ores of zinc are sphalerite (sulphide), smithsonite (carbonate), calamine (silicate), and franklinite (zinc, manganese, iron oxide)

(Weast, 1986). The most important use of zinc is as a metal coating and in alloys. Galvanized pipes are used in domestic water supply systems whereas galvanized metals used to be an important material for gutters and rainpipes.

At trace concentration zinc is an essential element for plants, animals and humans. Zinc toxicity has also been reported, normal zinc levels in plants are 25-150 $\mu g.g^{-1}$, concentrations above 400 $\mu g.g^{-1}$ are toxic for plants (O'Neill, 1985).

Table 1.V. Speciation of zinc in water with inorganic species at different pH-levels.

pH	3	4	5	6	7
Zn^{2+}	0.878	0.878	0.877	0.781	0.776
$ZnCl^+$	0	0	0	0	0
$ZnCO_3$	0	0	0	0.001	0.023
$ZnHCO_3^+$	0	0	0.001	0.008	0.030
$ZnOH^+$	0	0	0	0.001	0.010
$ZnSO_4$	0.122	0.122	0.122	0.121	0.114

Σ Cl 516 μm/l, Σ HCO_3^- 426 μm/l, Σ SO_4 610μm/l,
Σ Zn 18 μm/l, (Pedroli, 1990).

Prediction of zinc behaviour in soil is complicated by the occurrence of a great number of complexes which have cationic character like $Zn(OH)^+$ or an anionic character like the zincate anions $Zn(OH)_3^-$ at high pH. Moreover, chelation may influence zinc-soil interactions. Table 1.V presents the most important inorganic complexes for zinc, calculated with the CHARON model (1989).

1.4.6. Heavy metal precipitation

Precipitation of heavy metal minerals is a function of the solute concentrations. In an acid and oxic soil system with normal cadmium, copper, lead, nickel and zinc concentration domain, the heavy metal concentration is controlled by adsorption and desorption and not by precipitation (Harmsen, 1977; Brümmer et al., 1983). Under acid conditions the carbonate and hydroxide concentrations are very low and under oxic conditions the concentration of sulphide is negligible. Only in anoxic conditions sulphide may form and heavy metals could precipitate in sulphide minerals. Table 1.VI presents the solubility products of the most common cadmium, copper, lead, nickel and zinc minerals in soils.

Table 1.VI. Solubility products of cadmium, copper, lead, nickel and zinc species (Weast, 1986).

Substance	Formula	S.P.
Cadmium hydroxide	$Cd(OH)_2$	$5.33\ 10^{-15}$
Cadmium sulphide	CdS	$1.40\ 10^{-29}$
Cadmium carbonate	$CdCO_3$	$6.20\ 10^{-12}$
Copper(II) sulphide	CuS	$1.28\ 10^{-36}$
Nickel(II) hydroxide	$Ni(OH)_2$	$5.54\ 10^{-16}$
Nickel(II) sulphide	NiS	$1.08\ 10^{-21}$
Lead(II) hydroxide	$Pb(OH)_2$	$1.40\ 10^{-20}$
Lead(II) sulphide	PbS	$8.81\ 10^{-29}$
Zinc hydroxide	$Zn(OH)_2$	$7.68\ 10^{-17}$
Zinc sulphide	ZnS	$2.91\ 10^{-25}$

1.5. Soil components

When studying acid sandy soils, knowledge about soil material is essential. The soils in the Kempen region consist of poor aeolic coversands with scattered dune formation. The pH of these soils is rather low (between pH=3.5 and pH=5.5), therefore no carbonates are expected. Clay-minerals play also no role as binding component in this type of soil, because there are hardly any clay-minerals present. The main adsorption substrates in these soil for heavy metals are expected to be soil organic matter and minor amounts of important oxides of aluminium, iron and manganese.

1.5.1. Soil organic matter

One of the most important properties of soil humic substances is their ability to act as ion exchangers. The exchange capacity of humic materials is very high compared with most mineral components (Hayes & Swift, 1978). Characteristic reactive groups of the polymeric chains of organic matter are hydroxyl, carboxyl, phenolic and carbonyl groups, all of which may dissociate depending on the pH of the system. The dissociation equilibria of the different types of OH-groups can be expected to cover a fairly continuous range of pK-values. Considering a full range of carboxyl-groups present in many different configurations along the polymeric chain, it is clear that no particular pK-value of humic materials can be given.

Another important feature of the chemical structure of these heteropolymer chains is the occurrence of particular combinations of different reactive groups which are able to form inner-sphere surface complexes (Sposito, 1989) with certain metal cations, in particular transition metals. Such complexes involve chemical bonds, and are much stronger and less reversible compared to regular coulombic adsorption of cations in a double layer. The bond between humic acids and cations of the transition elements has a covalent character (Van Dijk, 1971). A cation present in a chemical bond complex is not readily exchangeable. As a result cation exchange equations are inapplicable at low concentrations where surface complex formation prevails and the surface charge, i.e. cation exchange capacity (C.E.C.) varies with the degree of surface complexation. These features are of great importance with regard to the retention by soil of heavy metal ions present as pollutants (Bolt et al., 1978).

1.5.2. Oxides and hydroxides

Adsorption of metals onto oxide surfaces is expected to be an important process affecting trace metal transport in natural systems. Hydroxides of iron, aluminium and manganese appear in aerated soils, mostly as coating on clay-minerals and sand-grains. In aerated soils, iron can be present as τ-Fe_2O_3 (hematite), α-FeOOH (goethite) or amorphous $Fe_{10}O_{15}.9H_2O$ (ferrihydrite) (Sposito, 1989). In temperate regions the solubility of Fe in soils is largely controlled by the solubility of amorphous hydrous ferric oxides (Novozamski and Beek, 1978). The most commonly found manganese mineral in soils is birnessite (δ-MnO_2) and gibbsite (α-$Al(OH)_3$) is the most important aluminium mineral (Sposito, 1989).

The surface hydroxyl groups of iron, aluminum and manganese oxides (e.g. Fe-OH) have two free electron pairs and a dissociable proton, indicating that these groups are ampholytes. Adsorption of H^+ and OH^- ions is thus based on protonation and deprotonation of surface hydroxyls (Harmsen, 1977; Schindler & Stumm, 1989; Farley et al., 1985). At a pH below the zero point of charge (pH_{zpc}) (Table 1.VII) an oxide surface has a positive charge so mostly anion adsorption will occur and at pH above pH_{zpc} cation adsorption will prevail.

As for adsorption on organic matter, metal cations may adsorb highly selectively to oxides-surfaces. This can be a partly irreversible reaction by inner-sphere complexation.

Table 1.VII. Zero points of charge for metal oxides (Stumm and Morgan, 1981 and Sposito 1984 (between brackets)).

Mineral	pH_{zpc}	Mineral	pH_{zpc}	Mineral	pH_{zpc}
τ-Fe_2O_3	6.7	α-Al_2O_3	9.1	δ-MnO_2	2.8 (1.7)
α-FeOOH	7.8 (6.1)	τ-Al_2O_3	(8.7)		
$5Fe_2O_3.9H_2O$	8.5	τ-AlOOH	8.2		
		α-$Al(OH)_3$	5.0		

At low pH, hydroxides of iron, aluminium are sensitive for dissolution. When complete dissolution occurs the basis for heavy metal adsorption will disappear. In Table 1.VIII. the solubility products of some metal-hydroxides are presented.

Table 1.VIII. Solubility products of some metal hydroxides (Novozamski and Beek, 1978; Weast, 1986).

Substance	Formula	S.P.
aluminium hydroxide	$Al(OH)_3$	$2.29x10^{-33}$
iron hydroxide	$Fe(OH)_3$	$3.16x10^{-38}$
goethite	FeOOH	$1.00x10^{-44}$

References

Boekhold, A.E. (1992).
Field scale behaviour of cadmium in soil.
Thesis, Agricultural University Wageningen, the Netherlands.

Bolt, G.H., M.G.M. Bruggenwert and A. Kamphorst (1978).
Adsorption of cations by soil. In: *Soil chemistry, A. Basic elements.* Ed. G.H. Bolt and M.G.M. Bruggenwert. Elsevier Scientific Publishing Company, Amsterdam, the Netherlands. p. 54-90.

Boumans, L.J.M. and C.R. Meinardi (1986).
Hoge zink gehalten in het ondiepe grondwater van een natuurgebied in de Peel.
H2O **19**(12): 263.

Brümmer, G., K.G. Tiller, U. Herms and P.M. Clayton (1983).
Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils.
Geoderma **31**: 337-354.

Buchauer, M.J. (1973).
Contamination of soil and vegetation near a zinc smelter by zinc, cadmium, copper and lead.
Environmental Science and Technology **24**: 543-549.

de Haan, F.A.M. and P.J. Zwerman (1978).
Pollution of soil. In: *Soil chemistry, A. Basic Elements*. Ed. G.H. Bolt and M.G.M. Bruggenwert. Elsevier scientific publishing company, Amsterdam, the Netherlands. p. 192-271.

CHARON 5.02 (Speciation model), 1989. de Rooij, N.M., Delft Hydraulics, Delft, the Netherlands.

Farley, K.J., D.A. Dzombak and F.M.M. Morel (1985).
A surface precipitation model for the sorption of cations on metal oxides.
Journal of Colloid and Interface Science **106**(1): 226-242.

Hanhe, H.C. and W. Kroontje (1973).
Significance of pH and chloride concentration on behaviour of heavy metal pollutants: mercury, cadmium, zinc and lead.
Journal of Environmental Quality **2**: 444-450.

Harmsen, K. (1977).
Behaviour of heavy metals in soils.
Thesis, Agricultural University Wageningen, the Netherlands.

Hayes, M.H.B. and R.S. Swift (1978).
The chemistry of soil organic colloids. In: *The chemistry of soil constituents*. Ed. D.J. Greenland and M.H.B. Hayes. John Wiley & Sons, New York, U.S.

Hutton, M. (1982).
Cadmium in the European community. In: *Monitoring and assessment research centre*. MARC, London, U.K.

Levinson, A.A. (1974).
Introduction to exploration geochemistry.
Applied Publishing Ltd, Wilmette, Illinois, U.S.A.

LISEC (1989).
Werkgroep zware metalen Noorder Kempen, subgroep lucht, LISEC, studiecentrum voor ecologie en bosbouw.

McBride, M.B. (1994).
Environmental chemistry of soils.
Oxford University Press, New York, U.S.

Novozamsky, I. and J. Beek (1978).
Common solubility equilibria in soils. In: *Soil chemistry, A. Basic elements*. Ed. G.H. Bolt and M.G.M. Bruggenwert. Elsevier Scientific Publishing Company, Amsterdam, the Netherlands.

O'Neill, P. (1985).
Environmental chemistry.
Chapman & Hall, London, U.K.

Pacyna, J.M. (1987).
Atmospheric emissions of arsenic, cadmium, lead and mercury from high temperature processes in power generation and industry. In: *Lead, mercury, cadmium and arsenic in the environment*. Ed. T.C. Hutchinson and K.M. Meema. John Wiley and Sons, Londen, U.K.

Pedroli, G.B.M., W.A.C. Maasdam and J.M. Verstraten (1990).
Zinc in poor sandy soils and associated groundwater. A case study.
The Science of the Total Environment **91**: 59-77.

Schindler, P.W. and W. Stumm (1989).
The surface chemistry of oxides, hydroxides, and oxide minerals. In: *Aquatic surface chemistry*.
Ed. W. Stumm. John Wiley and Sons, New York, U.S.A. p. 83-109.

Sposito, G. (1984).
The surface chemistry of soils.
Oxford University Press, New York, U.S.A. Pages 234.

Sposito, G. (1989).
The chemistry of soils.
Oxford University Press, New York, U.S.A. Pages 277.

Stumm, W. and J.J. Morgan (1981).
Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters.
John Wiley & Sons, New York, U.S. Pages 780.

van Dijk, H. (1971).
Cation binding of humic acids.
Geoderma **5**: 53-67.

Weast, R.C. (1986).
Handbook of chemistry and physics.
C.R.C. Press, Boca Raton, Florida, U.S.

2

Accumulation of cadmium and zinc from diffuse immission on acid sandy soils, as a function of soil composition

Co-Author: J.P.G. Loch

Accepted for publication in "Water, Air and Soil Pollution".

Abstract

Sandy soils, in the border area of Belgium and the Netherlands (the Kempen region), are heavily contaminated by atmospheric deposition from nearby smelters of cadmium and zinc. Groundwater contamination by leaching from these low retention soils is subject of study. There are reports of high cadmium and zinc concentrations in groundwater in the area, but in most cases the direct sources are unknown. In an attempt to predict present or future risk of groundwater contamination by soil leaching, metal binding processes (retardation) were studied that are specific for these soil types under the existing acidifying conditions.

From four fields nine profiles were sampled and analyzed for cadmium and zinc. Average concentrations of 131 $\mu g.g^{-1}$ zinc and 1.6 $\mu g.g^{-1}$ cadmium with maximum values of 2989 $\mu g.g^{-1}$ respectively 16.3 $\mu g.g^{-1}$ were found. In addition pH and contents of organic matter, aluminium, iron, and manganese were determined. The relative importance of these soil parameters for metal retardation is derived from the profiles. The data show that organic matter is the most important soil component for binding cadmium and zinc. Adsorption of cadmium and zinc on aluminium, iron and manganese (hydr) oxides appears to be of minor importance at low pH (< 5.5).

2.1. Introduction

Cadmium, zinc, nickel and manganese are the most mobile and bioavailable metals in oxic environments (Scheffer & Schachtschabel, 1989). This paper describes the filter function of the soil for atmospheric deposition of zinc and cadmium, as protection for the groundwater in the Kempen. The soils of the Kempen region are developed in poor aeolic coversands. The area stretches across the Dutch-Belgian border, in the Belgian provinces of Antwerp and Limburg, and the Dutch province of North Brabant.

Heavy metal contamination of soils in the Kempen region is on a large spatial scale (Harmsen, 1977; Bosman and Paenhuys, 1980; Scokart et al., 1983, Pedroli et al., 1990, Boekhold, 1992). Exhaust fumes from three zinc smelters in this area contain oxides of heavy metals, which reach the soil either by dry deposition or with rainfall. Zinc concentrates are stored near the plant in the form of fine powder, and the dust may be blown directly onto the soils in the vicinity of the smelters.

Total cadmium emission from zinc production in Europe in 1979 was 1050 tons and the major cadmium species emitted in this process is cadmium oxide (Pacyna, 1987). The smelters in this region have a contamination history of hundred years. Twenty years ago the zinc smelters reduced their emissions five to ten times when a change was made from thermo to electric process technology. Cadmium emission in the thermo-metallurgic zinc production reaches from 10 to 100 g Cd/ton produced zinc and up to 0.20 g Cd/ton in the electrolytic process (Hutton, 1982).

In the past some research was done on leaching of heavy metals to the groundwater in the Kempen region. In the Dutch Kempen no correlation was found between the cadmium concentrations in the topsoil and in the groundwater, nor when samples were split into two groups of different soil pH. Processes responsible for high concentrations of cadmium and zinc in the Kempen groundwater are unknown (Maasdam et al., 1990, Pedroli et al., 1990).

The aim of this research is to investigate, which soil components are responsible for the binding of cadmium and zinc in these soils, e.g. oxides of aluminium, iron and manganese, organic matter, clay minerals or carbonates.

2.2. Cadmium and zinc sorption in soils

In general, organic matter, pH, clay minerals, carbonates and hydro-oxides of aluminium, iron and manganese are the main factors governing adsorption of cadmium and zinc in soils of temperate climate regions (Gerritse & van Driel, 1984, Miller et al., 1983, Chardon, 1984, Sims, 1986, Christensen, 1989). Other important soil processes are complexation of cadmium and zinc with organic (Harmsen, 1977) and inorganic soluble species (Sposito, 1989) and precipitation of cadmium and zinc minerals (Brümmer et al., 1983).

The Kempen soils, which are sandy, contain very small amounts of clay minerals (<1%), which therefore play only a minor role. No carbonates are present, because of the low pH (< pH 5.5) (Harmsen, 1977). At low pH the oxides of aluminium and iron have a positive surface charge. Consequently only surface complexation on the oxide will occur, but at low degree. Therefore pH is a more meaningful soil parameter to predict sorption than the content of oxides.

pH is an important factor controlling cadmium distribution in soils (Anderson & Christensen, 1988, Christensen, 1984). When pH decreases the amount of sorbed cadmium and zinc decreases. Freundlich adsorption parameters are found to be good indications of the relative cadmium sorption affinities at all pH values (García-Miragaya & Page, 1978). The adsorption of cadmium approximately doubles for each increase in pH of 0.5 unit in the pH interval from 4 to 7 (Christensen, 1989). This is caused by the effect of decreasing of proton activity and aluminium concentration in solution, both of which compete with cadmium and zinc for ion sorption sites on the soil sorbent surfaces and by the increase of the negative charge of the adsorbate (García-Miragaya & Page, 1978). Another cause of pH-effect may be the formation of hydroxy metal complexes $M(OH)^+$ at pH above 6, which increase the total amount of metal in solution (Scheffer & Schachtschabel, 1989). These complexes are easer to dissolve in the adsorption process than free metal cations (Sposito, 1989). Therefore soil pH is a critical factor in governing the distribution of cadmium and zinc between soil and solute (Scokart et al., 1983; Christensen, 1984; Ghanem & Mikkelsen, 1988; Eriksson, 1988, Christensen, 1989).

Zinc competes effectively for cadmium sorption sites. The cadmium distribution coefficient drops at increasing zinc solute concentrations (Benjamin & Leckie, 1981). A solute concentration above 100 $\mu g.l^{-1}$ zinc may significantly effect cadmium distribution between solid and liquid phases. In the presence of zinc at pH 5.5 the distribution coefficients of cadmium are 2 to 14 times lower than in absence of zinc. This may have implications for interpreting cadmium leaching. Competition by zinc for cadmium sorption sites was observed in topsoils as well as in subsoils (Christensen, 1987). Calcium present in the soil solution is found to compete very effectively with cadmium for sorption sites in the soil (Boekhold, 1992). Other transition metals are also found to compete with cadmium as well, especially copper.

2.3. Materials and methods

Soils were sampled in August and September 1990. Samples were taken from four fields in the Kempen. All fields were situated in a nature reserve. Fields 2 and 4 are abundantly covered with *Molinia caerulea* species whereas fields 1 and 3 have a very poor vegetation of the same species. In the summer of 1990 the groundwater table in all fields was approximately 1.5 meters below soil surface. In every field of 60 x 60 m^2 soil profiles were sampled at nine locations in a regular rectangular grid according Figure 2.1.

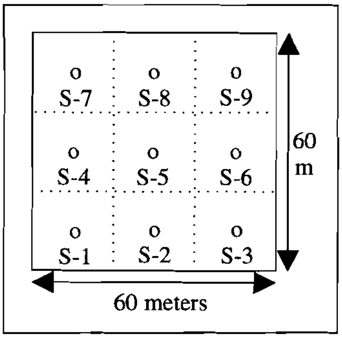

Figure 2.1. Field schematization. S-1 to S-9 are soil sampling sites.

Each soil profile was sampled at the average depth of 1 (0-2), 5 (4-6), 10 (9-11), 15 (14-16), 20 (19-21), 35 (34-36), 50 (49-51), 75 (74-76), 100 (99-101) and 130 (129-131) centimetres, and field 4 also at 25 (24-26) cm below soil surface in addition to the litter-layer, in total 405 samples (between brackets the actual depths are given). To sample the profile a pit was dug to a depth of 80 cm and the depths 1 to 75 cm were sampled by hand with a poly-propylene sample spoon. The depths 100 and 130 cm. were sampled with a foil-sampler. Using a foil-sampler an undisturbed soil core can be taken below soil surface.

Table 2.I. Soil sampling sites, with the distance from the nearest emission point.

field	distance	emission point of Cd end Zn	soil type (F.A.O.)
1	1.9 km	Overpelt smelter(B)	arenosol
2	2.3 km	Overpelt smelter(B)	carbic podzol
3	1.4 km	Budel smelter(NL)	arenosol
4	3.5 km	Overpelt smelter(B)	carbic podzol

The term "field profiles" is being introduced, which is defined by an average of nine soil profiles in one field previously mentioned. Field locations and soil names are listed in Table 2.I. The fields were located in the direction of the prevailing wind (N-E) from the zinc smelters at Overpelt (B) and Budel (NL).

The samples were stored up to 1 week in 500 ml HPTE boxes. All samples consisted of a well sorted very fine sand. The samples were air dried at room temperature (20 ^{0}C) and sieved over a 2 mm nylon sieve in the laboratory. Almost the whole sample passed the sieve and only some organic particles were retained.

0.5 gram of sample was destructed in 10 ml concentrated acid mixture ($HClO_4$:HNO_3 = 3:2) and 10 ml concentrated HF. The sample-solution was evaporated at 180^{0}C, re-dissolved in 10 ml concentrated HNO_3 at 90^{0}C and diluted with distilled water to 50 ml (Förstner & Wittman, 1981). For cadmium analysis 1 g of sample was destructed and diluted with water to 50 ml. The extracts were analyzed by ICP-AES (ARL 34000 instrument) for aluminium, iron and manganese. Zinc was analyzed by flame AAS (Perkin-Elmer 460 instrument) and cadmium was analyzed by graphite furnace AAS (Perkin-Elmer 5000 instrument). The detection limit of cadmium in soil material is 0.05 $\mu g.g^{-1}$.

Additional analyses were carried out with 22 samples to obtain free aluminium and free iron from soil to compare it with the former total destruction. The ratio between free and total aluminium and iron is respectively 0.1 and 0.3. By a fit through origin the correlation between the two analyses for aluminium and iron is 0.76 and 0.91 respectively. This correlation was used to derive the free iron and aluminium out of total content.

Soil pH was determined with 10 gram of soil in 25 ml double distilled water after equilibration of 24 h. pH was measured with a Knick Portamess 752 Calimatic. In the litter-layer the pH was not determined. The total content of organic matter was analyzed according to the Walkley and Black method (Black, 1965).

2.4. Results and discussion

2.4.1. Soil characteristics

in Table 2.II a general statistic review of all soil samples. It gives an indication of the soil characteristics of all soil profiles. It is obvious these soils have a low content of organic matter, low pH and low contents of oxides.

Figures 2.2 to 2.6 present depth profiles, exclusive the O-horizons, of organic matter content, H_3O^+ concentration, the contents of aluminium oxide,

Table 2.II. Basic statistics of the soil major components.

	mean	s.d.	min	max	n
O.M.	1.89	2.59	0.03	20.75	369
H_3O^+ (pH)	7.04E-5 (4.15)	5.43E-5	2.95E-6 (3.46)	3.47E-4 (5.53)	369
Al_2O_3	1.68	0.80	0.23	6.32	401
Fe_2O_3	0.42	0.26	0.05	1.63	401
MnO_2	0.0064	0.0040	0.0014	0.0287	401

mean = arithmetic average,
s.d. = standard deviation,
min = minimum value,
max = maximum value,
n = number of observations.

iron oxide and manganese oxide of the four sampled fields. Because of the low soil pH ($<$ 5.5) no carbonates are present in the soil. The soil samples contain less than 0.5% of the fraction below 2 μm. Consequently the amount of clay minerals is negligible. Most soil particles are in the fraction 125 to 250 μm (Table 2.III).

Table 2.III. Grainsize distribution of a representative soil sample.

fraction μm	[%]	fraction μm	[%]
1000-2000	0.3	105-125	19.5
500-1000	1.7	50-105	12.8
250-500	14.1	16-50	2.2
125-250	48.3	2-16	0.8
		<2	0.5

Fields 1 and 3 are both arenosols, having very low content of organic matter, about 1.5%. Field 3 is extremely poor in organic matter in the whole profile less than 1%. The pH of field 3 is somewhat higher than that of the other fields, which is also reflected in a higher amount of oxides present. The larger standard deviation of the oxides in the lower part of the profile is a result of an inhomogeneous process of dune formation in the past.

Fields 2 and 4 are well developed podzol profiles with a humic B-horizon including a zone of iron oxide accumulation in field 4. The illuviation of humic substance is located at 10 to 25 cm below soil surface. The standard deviation of the contents of organic matter in the topsoil in fields 2 and 4 is the effect of a different depth of the illuviation horizon in the different profiles within these fields. In fields 2 and 4 the soil pH increases with the depth. Iron and aluminium are partially removed from the topsoil probably due to a decrease in pH. In general the contents of aluminium, iron and manganese are low and increase with the depth, which may be a result of acidification. The correlation of the H_3O^+ activity with the total contents of aluminium, iron and manganese is negative (Table 2.IV). This can be explained by the increased solubility of aluminium, iron and manganese, at lower pH. In fields 2 and 4 the soil pH increases with depth. In the Kempen region the pH has decreased about 0.6 pH units in the upper layers of sandy soils (up to 30 to 40 cm depth) in the last 25 years (Ronse et al., 1988).

Table 2.IV. Correlation coefficients (R) of the soil macro parameters.

	O.M.	H_3O^+	Al_2O_3	Fe_2O_3	MnO_2
O.M.	1.00				
	369				
H_3O^+	0.68	1.00			
	369	369			
Al_2O_3	-0.30	-0.37	1.00		
	369	369	405		
Fe_2O_3	0.30	-0.33	0.76	1.00	
	369	369	405	405	
MnO_2	-0.21	-0.34	0.51	0.67	1.00
	369	369	405	405	405

n = 405 all samples.
n = 369 all samples without litter layer, O.M. and pH not analyzed.

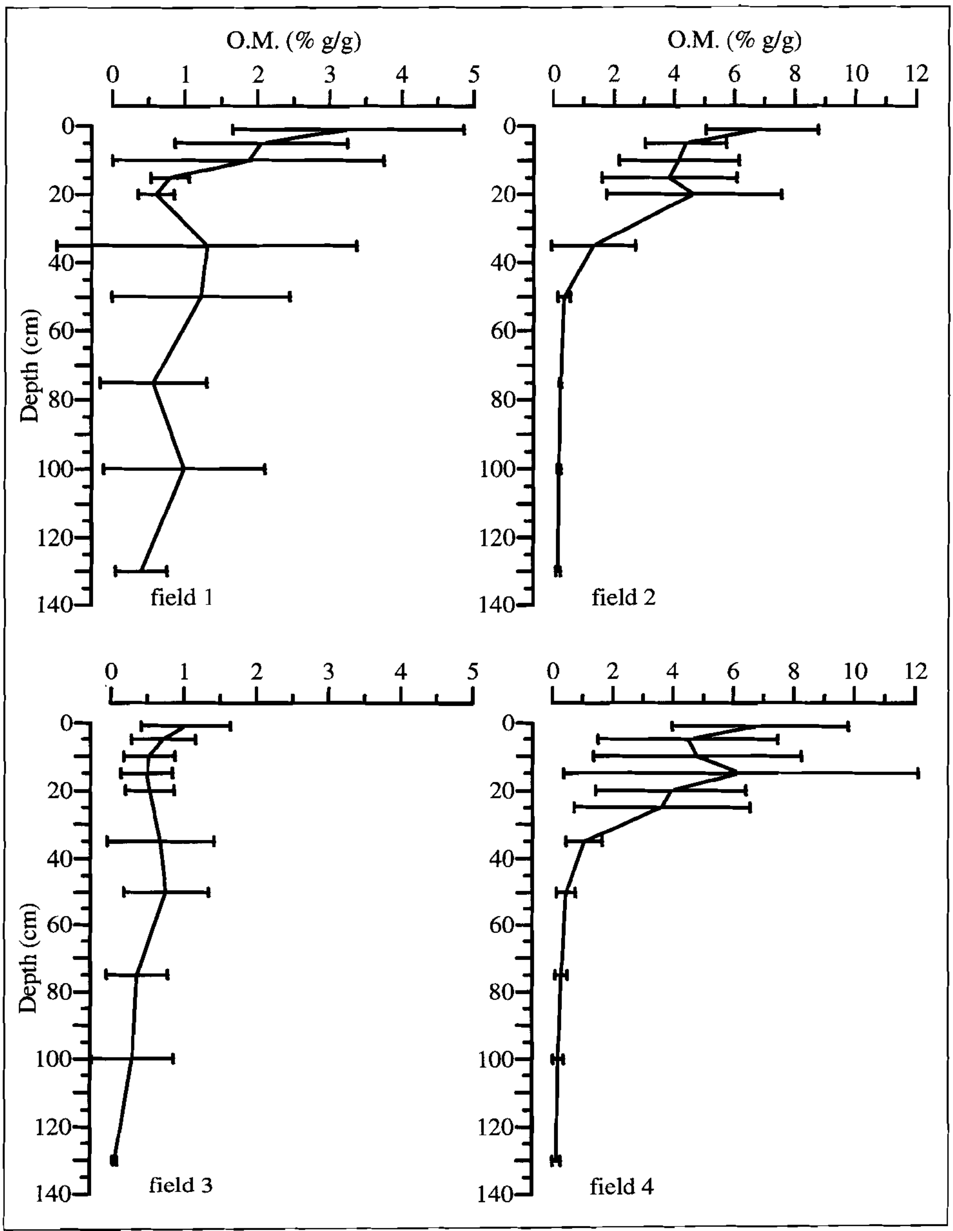

Figure 2.2. Field profiles of the average organic matter content [% g.g^{-1}] in the soil, exclusive of the O-horizon. The horizontal bars are the calculated standard deviations at each depth.

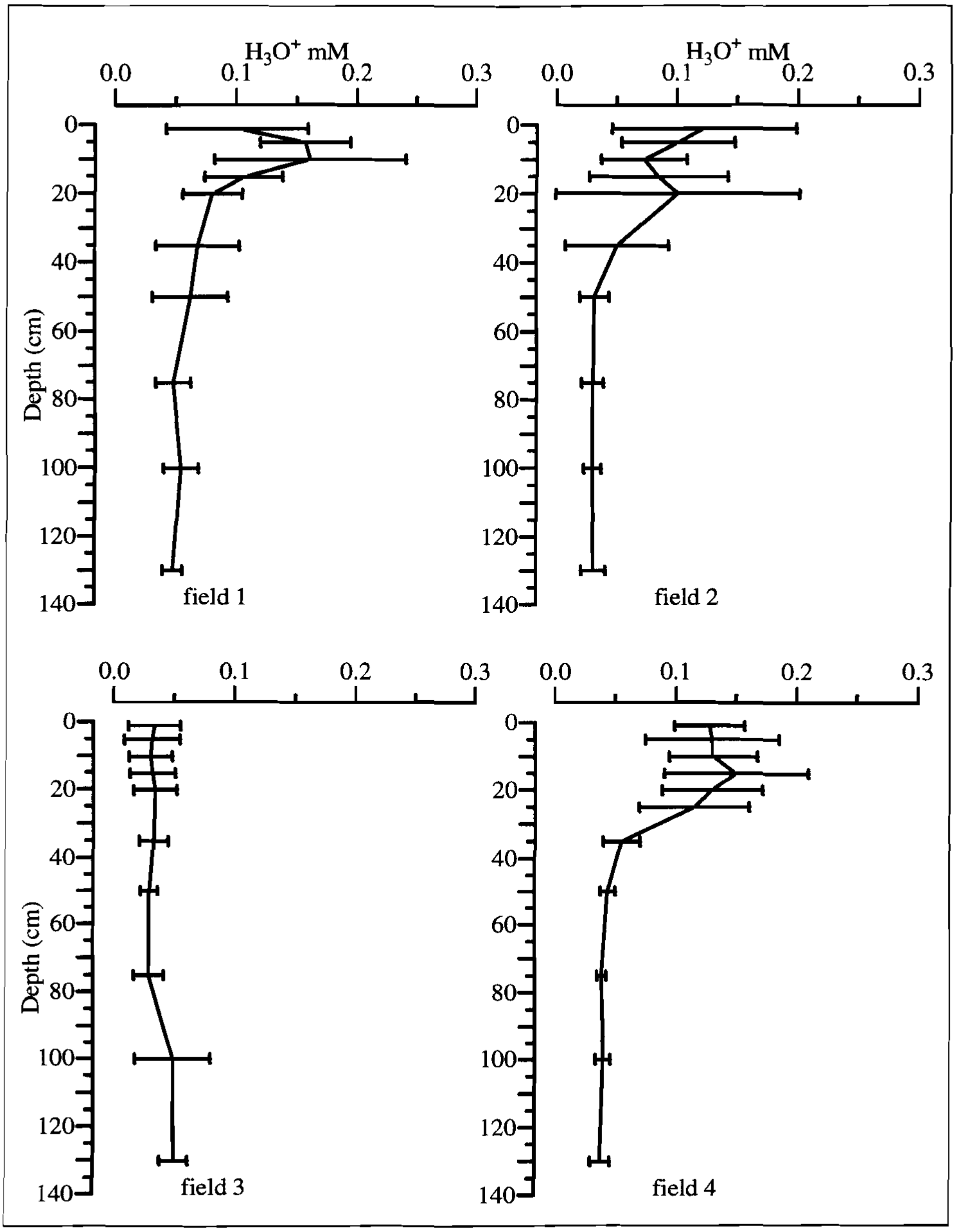

Figure 2.3. Field profiles of the average H_3O^+ activity in the soil, exclusive of the O-horizon. The horizontal bars are the calculated standard deviations at each depth.

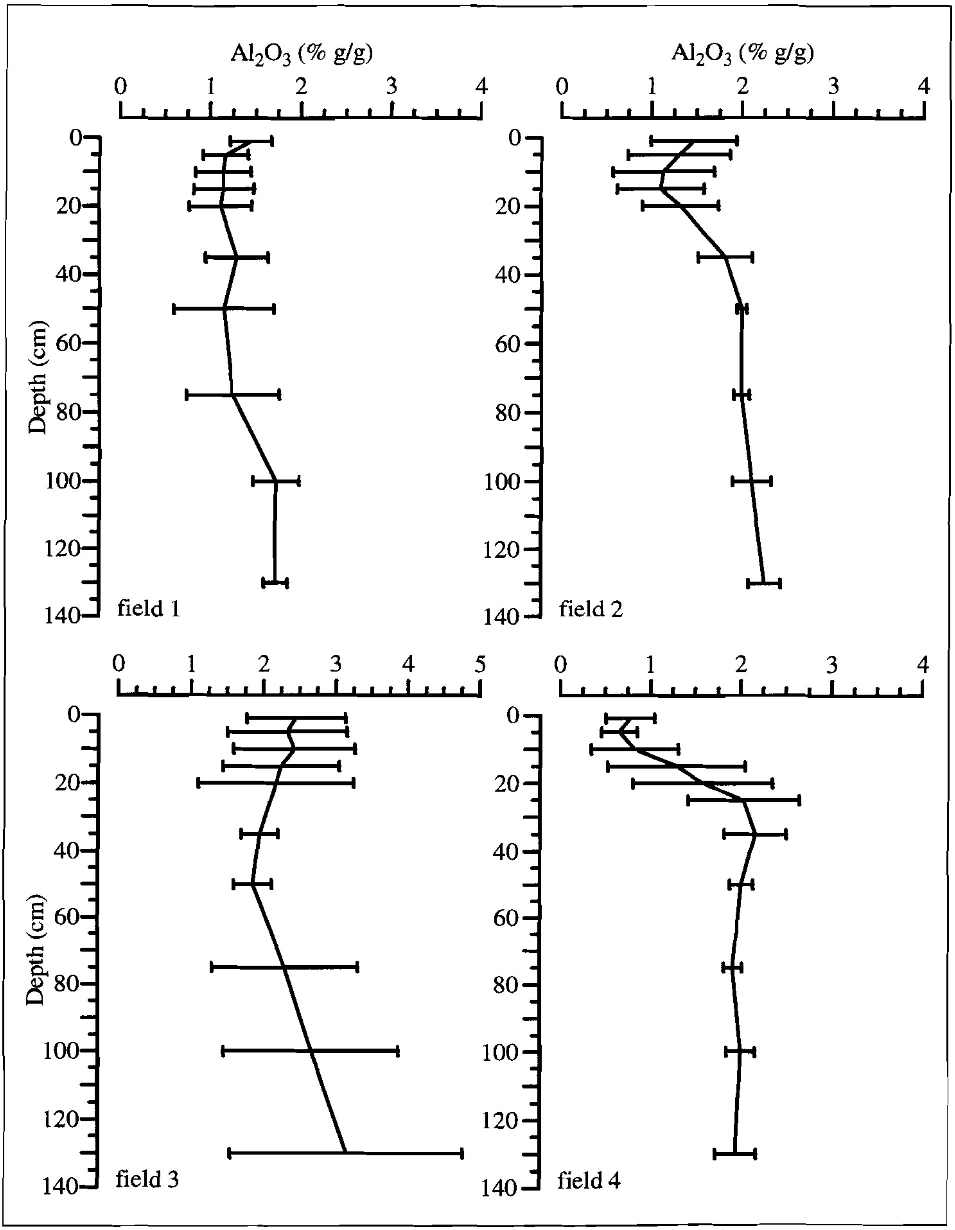

Figure 2.4. Field profiles of the average aluminium oxide content [% g.g^{-1}] in the soil, exclusive of the O-horizon. The horizontal bars are the calculated standard deviations at each depth.

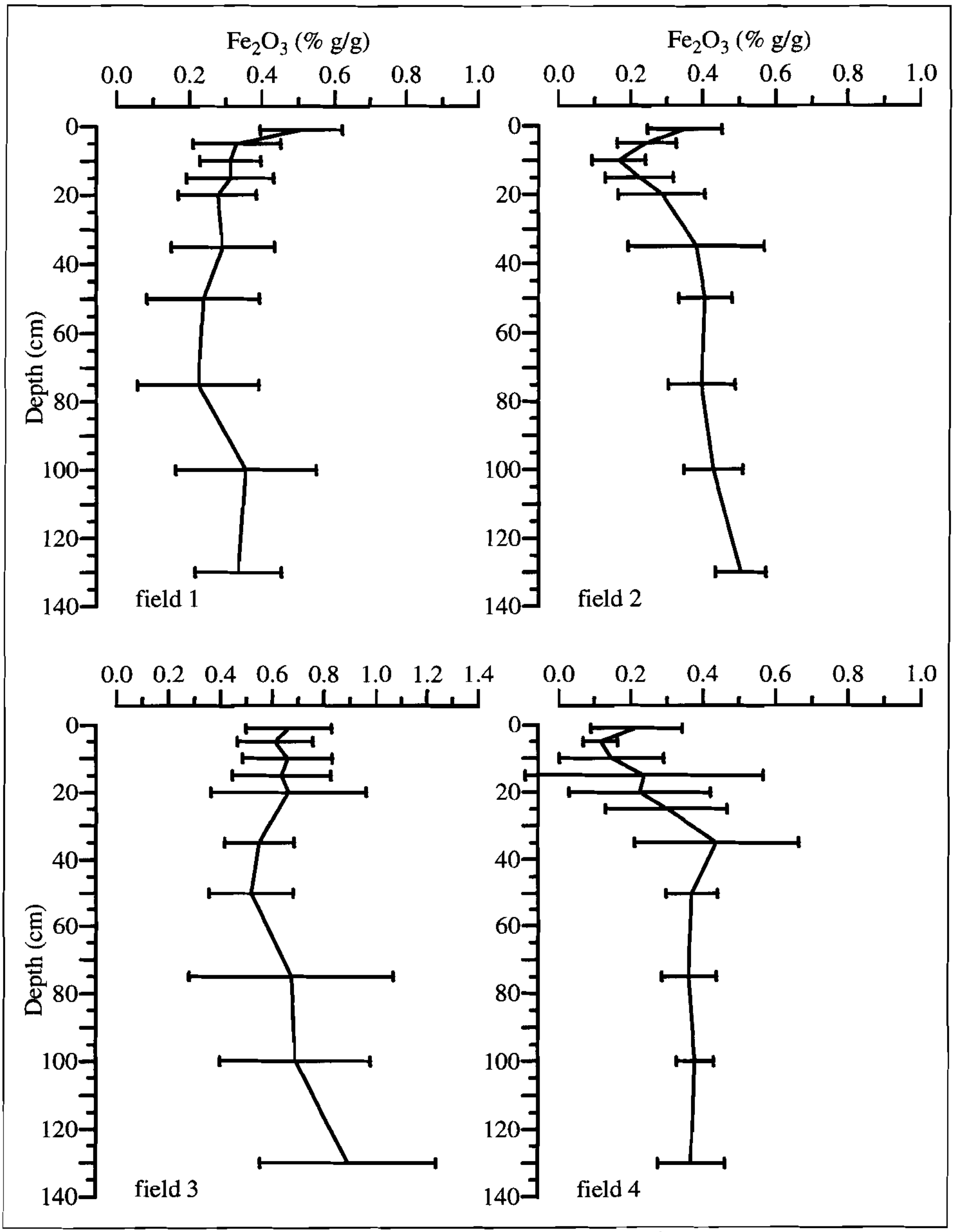

Figure 2.5. Field profiles of the average iron oxide content [% $g.g^{-1}$] in the soil, exclusive of the O-horizon. The horizontal bars are the calculated standard deviations at each depth.

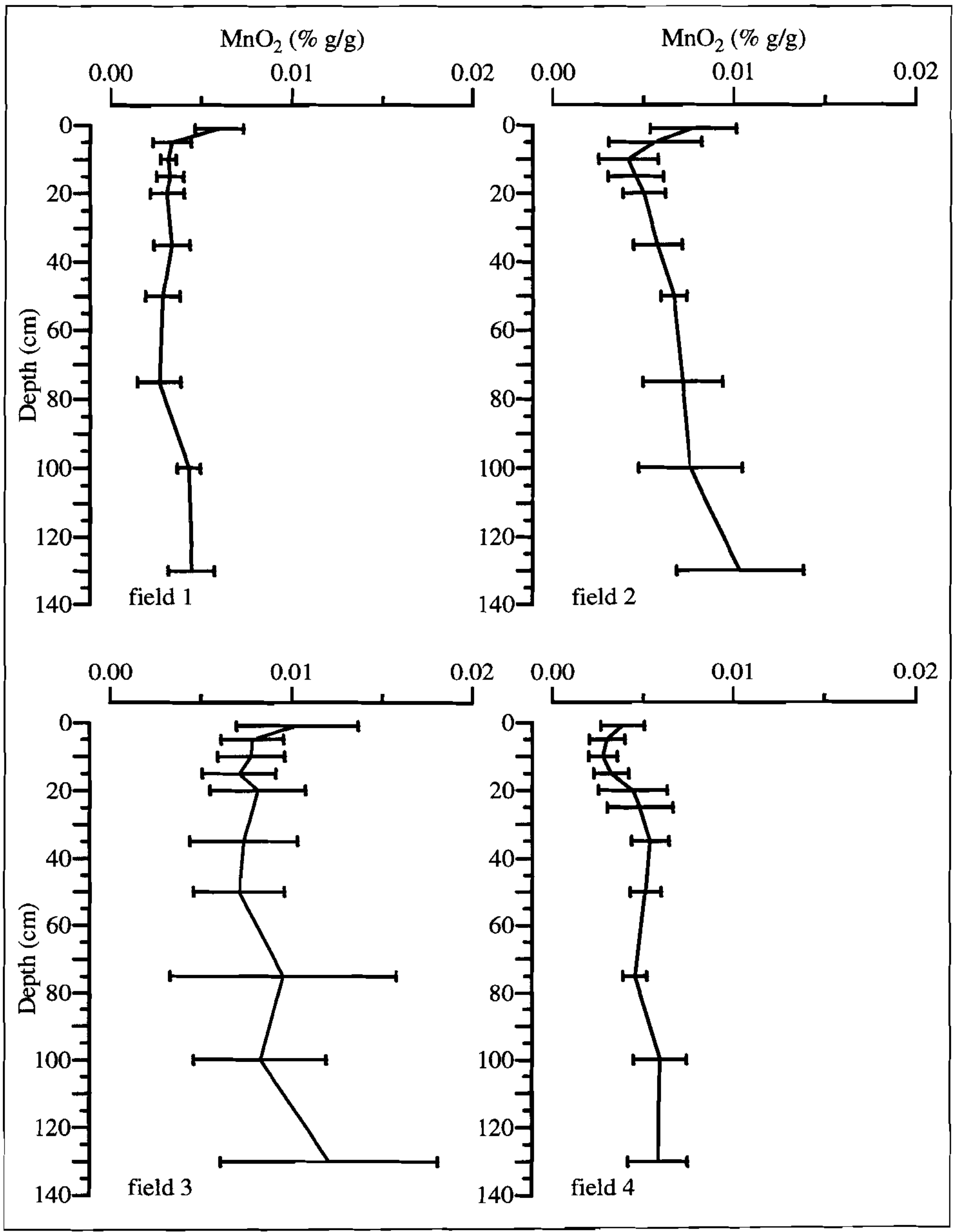

Figure 2.6. Field profiles of the average manganese oxide content [$\mu g.g^{-1}$] in the soil, exclusive of the O-horizon. The horizontal bars are the calculated standard deviations at each depth.

2.4.2. Behaviour of cadmium and zinc and their correlation with soil parameters

There is a clear enrichment of cadmium and zinc in the topsoil (Figures 2.7 and 2.8). This is due to atmospheric immission and these elements accumulate in the A-horizon, induced by its high binding capacity. The average content of cadmium in the topsoil of the four fields is between 0.3 and 3.0 $\mu g.g^{-1}$ and for zinc between 80 and 300 $\mu g.g^{-1}$. The natural background contents of the Kempen region in the topsoil (0-6 cm) are 0.15-0.45 $\mu g.g^{-1}$ for cadmium and 5-15 $\mu g.g^{-1}$ for zinc (Bosman & Paenhuys, 1980). Some basic statistics, including the average contents of cadmium and zinc of all samples are tabulated in Table 2.V.

Table 2.V. Basic statistics of cadmium and zinc contents in the soil samples. All the data are used.

	mean	s.d.	min	max	n
Cd [$\mu g.g^{-1}$]	1.60	2.64	0.05	16.3	291
Zn [$\mu g.g^{-1}$]	131	386	2	2989	405

mean = arithmetic average,
s.d. = standard deviation,
min = minimum value,
max = maximum value,
n = number of observations.

In field 3 hardly any accumulation of cadmium and zinc. In many cases cadmium contents just below topsoil are below the detection limit. Adsorption of cadmium and zinc onto soil particles is extremely low, because there is almost no organic matter present in the soil profile and the pH is too low for adsorption on (hydr)oxides of iron and aluminium. From 5 cm below soil surface to the groundwater this soil profile consists of a C-horizon, which has a low adsorption capacity for cadmium and zinc in general.

In fields 2 and 4 maximum content of adsorbed cadmium in the profile coincides with the horizon of organic matter illuviation. These maxima can be associated with the soluble organic matter migration from the A-horizon to the B-horizon in podzolic soils in accordance with Scokart et al. (1983). In addition a decrease of pH in the topsoil will have enhanced leaching of cationic cadmium and zinc.

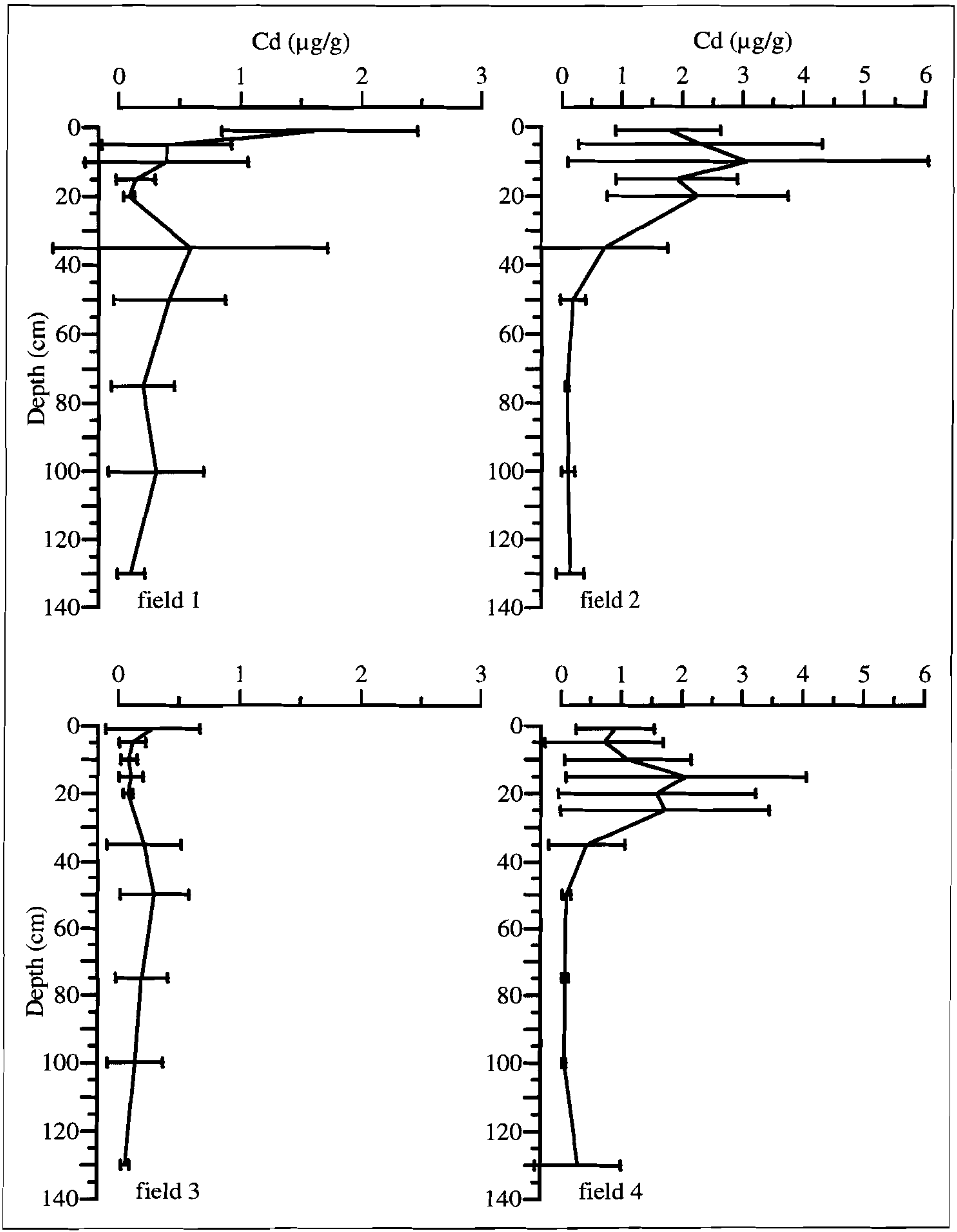

Figure 2.7. Field profiles of the average cadmium concentrations [$\mu g.g^{-1}$] in the soil, exclusive of the O-horizon. The horizontal bars are the calculated standard deviations at each depth.

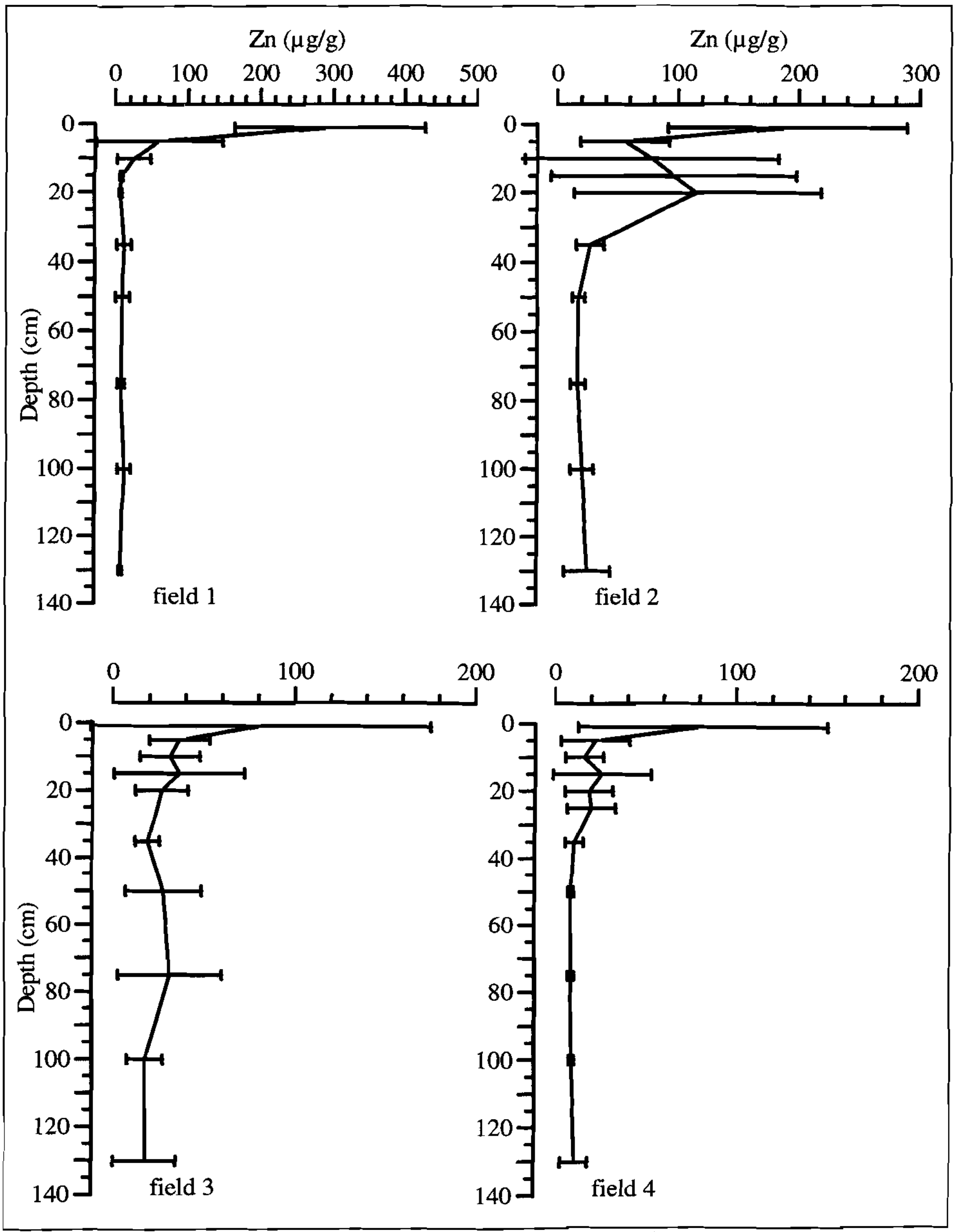

Figure 2.8. Field profiles of the average zinc concentrations [$\mu g.g^{-1}$] in the soil, exclusive of the O-horizon. The horizontal bars are the calculated standard deviations at each depth.

Table 2.VI. Correlation coefficients (R) of zinc and cadmium with soil components.

	O.M.	H_3O^+	Al_2O_3	Fe_2O_3	MnO_2	Cd	Zn
Cd	0.68	0.34	-0.25	0.10	0.37	1	0.89
	256	256	291	291	291	291	291
Zn	0.49	0.23	-0.21	0.19	0.44	0.89	1
	369	369	405	405	405	405	405

Small numbers are amount of observations involved in the correlation,
n = 405: all samples,
n = 369: all samples without litter layer (O.M. and pH not analyzed),
n = 291: only Cd concentration greater than d.l. 0.05 $\mu g.g^{-1}$,
n = 256: only Cd concentration greater than d.l. and without litter layer.

In general the contents of cadmium and zinc decrease with depth and they show a relation with organic matter, which must be the major adsorbent. The correlation of cadmium with organic matter is 0.68 (Table 2.VI). The correlation of the organic matter with cadmium is also evident from Figures 2.2 and 2.7. The profiles of organic matter and cadmium coincide with each other.

The correlation of cadmium and zinc with the oxides of aluminium and iron is low or negative. The correlation with manganese oxide indicates that cadmium and zinc are somewhat associated with MnO_2. Manganese oxide has a z.p.c. of 2.8 (Schindler and Stumm, 1989). At low pH therefore manganese oxide still may have some importance in cation sorption processes. Aluminium and iron (hydr) oxides play no role in the sorption processes at low pH, they have z.p.c. 5.0 ($Al(OH)_3$) and 7.8 (FeOOH) respectively.

The correlation of cadmium with zinc is very high, 0.89, indicating simultaneous deposition in this area and an almost similar behaviour in the soil of these metals. The average mass ratio between cadmium and zinc in these soils is 1:100. This is lower than the ratio in sphalerite (ZnS), the most common zinc ore, which has a ratio of cadmium and zinc of 1:130 to 1:650 (Levinson, 1974). The atmospheric deposition of cadmium and zinc in this area is in the ratio of 1:112 (LISEC, 1989). Thus it can be concluded that cadmium is a little concentrated during the smelting process and air transport. The higher volatility of CdO as compared to ZnO causes a relative enrichment of cadmium in soils as compared with the original ores.

In all mineral soils it is obvious that the important retardation processes take place in the A, E and B-horizons and not in the C-horizon. In the sandy soils of the Kempen the unsaturated zone is mainly occupied by the C-horizon.

2.4.3. Cadmium and zinc in the O-horizon

Table 2.VII shows the metal and oxide contents in the O-horizon. There is an extremely high accumulation of cadmium and zinc in the O-horizons of the soils. In most cases the O-horizon consists of more than 50 % [$g.g^{-1}$] organic matter (dead grass) and is very reactive in surface complexation with cadmium and zinc. The O-horizon contains 3 to 10 times more cadmium and zinc than the mineral A-horizon. The importance of this soil compartment might be large for retardation of cadmium and zinc. Nevertheless the total storage of this compartment is not as high as for the A-horizon, because the total mass of the O-horizon is rather low.

Table 2.VII. Contents of Al, Fe, Mn, Zn and Cd in the O-horizon (litter layer)

F	Th	Al_2O_3 [%]		Fe_2O_3 [%]		MnO_2 [%]		Zn [μg/g]		Cd [μg/g]	
	cm	avg	s.d.	avg	s.d.	avg	s.d.	avg	s.d.	avg	s.d.
1	1	1.38	0.20	0.75	0.25	0.013	0.005	1173	807	6.29	4.47
2	3	0.72	0.63	0.44	0.38	0.016	0.006	1773	610	11.02	3.56
3	1	2.76	0.54	0.99	0.36	0.018	0.003	320	191	1.32	0.77
4	3	0.54	0.19	0.37	0.08	0.008	0.002	1010	176	6.23	0.80

F = field number,
Th = thickness of the litter layer [cm],
avg = average contents in a field,
s.d. = standard deviation in samples.

The difference in the contents of cadmium and zinc in the O-horizon of fields 2 and 4 can be explained by the distance of the sampled field from the zinc plant Overpelt (2.4 and 3.5 km. respectively). The O-horizon of field 3 was very difficult to sample in most cases. Because there was only a very thin layer of dead material of dusty appearance, the samples contained probably some of the mineral top-layer. The elevated levels of aluminium and iron support these observations. The average concentrations of cadmium and zinc in the O-horizon of field 3 are significantly lower than in fields 1, 2 and 4, although this field is nearest to an emission point (1.4 km). The litter-layer in field 1 was in some cases difficult to sample. There is also some relief in this field, causing the heavy metals to be removed from the higher places on a slope by surface run-off. That is the reason why the average contents are higher than for field 3, but the variation is also higher. Although field 1 is closer to the Overpelt plant than field 2, field 1 has lower zinc and cadmium contents in its litter-layer.

2.5. Conclusions

The studied soils have a high acidification as concluded from the removal of aluminium and iron from the topsoil, and an extremely low pH in the topsoil, i.e. a value between 3.5 and 4.

In the soil studied the organic matter is mostly present in the topsoil up to 30 cm. Organic matter is the most important binding component for cadmium and zinc. The profiles of cadmium content and organic matter content coincide with each other and the peak of cadmium content corresponds with the organic matter illuviation horizon. At low pH (pH below 5.5), the oxides of aluminium, iron and manganese are of minor importance as binding components for these metals.

Most adsorption of cadmium and zinc takes place in the O-, A-, E- and B-horizon. In the soils studied, the C-horizon takes up most of the soil profile between soil surface and groundwater table. Of all horizons the O-horizon is the most effective in retardation of cadmium and zinc, but this layer is at most 3 cm thick and has a low mass. For assessment of the retardation of cadmium and zinc the topsoil is of great importance. Below this topsoil, in the C-horizon adsorption of cadmium and zinc is nearly absent.

References

Anderson, P.R. and T.H. Christensen (1988).
Distribution coefficients of Cd, Co, Ni, and Zn in soils.
Journal of Soil Science **39**: 15-22.

Benjamin, M.M. and J.O. Leckie (1981).
Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxy-hydroxide.
Journal of Colloid and Interface Science **79**(1): 209-221.

Black, C.A. (1965).
Methods in soil analysis, Part two, chemical and microbiological properties.
American Society of Agronomy, Madison, Wisconsin, U.S.A.

Boekhold, A.E. (1992).
Field scale behaviour of cadmium in soil.
Thesis, Agricultural University Wageningen, the Netherlands.

Bosman, H. and J. Peanhuys (1980).
The distribution of heavy metals in the soils of the Kempen.
Pedologie **30**(2): 59-77.

Brümmer, G., K.G. Tiller, U. Herms and P.M. Clayton (1983).
Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils.
Geoderma **31**: 337-354.

Chardon, W.J. (1984).
Mobiliteit van cadmium in de bodem.
Thesis, Agricultural University Wageningen, the Netherlands.

Christensen, T.H. (1984).
Cadmium soil sorption at low concentrations: I. Effect of time, cadmium load, , and calcium.
Water, Air, and Soil Pollution **21**: 105-114.

Christensen, T.H. (1987).
Cadmium soil sorption at low concentrations: V. Evidence of competition by other heavy metals.
Water, Air, and Soil Pollution **34**: 293-303.

Christensen, T.H. (1989).
Cadmium soil sorption at low concentrations: VIII. Correlations with soil parameters.
Water, Air, and Soil Pollution **44**: 71-82.

Eriksson, J.E. (1988).
The effect of clay, organic matter and time on adsorption and plant uptake of cadmium added to the soil.
Water, Air, and Soil Pollution **40**: 359-373.

Förstner, U. and G.T.W. Wittman (1981).
Metal pollution in the aquatic environment.
Springer Verlag, Berlin, Germany.

García-Miragaya, J. and A.L. Page (1978).
Sorption of trace quantities of cadmium by soils with different chemical and mineralogical composition.
Water, Air, and Soil Pollution **9**: 289-299.

Gerritse, R.G. and W. van Driel (1984).
The relationship between adsorption of trace metals, organic matter, and pH in temperate soils.
Journal of Environmental Quality **13**(2): 197-204.

Ghanem, S.A. and D.S. Mikkelsen (1988).
Sorption of zinc on iron hydrous oxide.
Soil Science **146**(1): 15-21.

Harmsen, K. (1977).
Behaviour of heavy metals in soils.
Thesis, Agricultural University Wageningen, the Netherlands.

Hutton, M. (1982).
Cadmium in the European community. In: *Monitoring and assessment research centre.* MARC, London, U.K.

LISEC (1989).
Werkgroep zware metalen Noorder Kempen, subgroep lucht, LISEC, studiecentrum voor ecologie en bosbouw. Genk, Belgium.

Levinson, A.A. (1974).
Introduction to exploration geochemistry.
Applied Publishing Ltd, Wilmette, Illinois, U.S.A.

Maasdam, W.A., G.B.M. Pedroli and A.J. van Wijk (1990).
Hoge zinkgehalten in grondwater strijper Aa-gebied, vervolg: de relatie bodem grondwater.
H2O **23**(26): 732.

Miller, W.P., W.W. McFee and J.M. Kelly (1983).
Mobility and retention of heavy metals in sandy soils.
Journal of Environmental Quality **12**(4): 579-584.

Pacyna, J.M. (1987).
Atmospheric emissions of arsenic, cadmium, lead and mercury from high temperature processes in power generation and industry. In: *Lead, mercury, cadmium and arsenic in the environment.* Ed. T.C. Hutchinson and K.M. Meema. John Wiley and Sons, Londen, U.K.

Pedroli, G.B.M., W.A.C. Maasdam and J.M. Verstraten (1990).
Zinc in poor sandy soils and associated groundwater. A case study.
The Science of the Total Environment **91**: 59-77.

Ronse, A., L. de Temmerman, M. Guns and R. de Borger (1988).
Evolution of acidity, organic matter content, and CEC in uncultivated soils of north Belgium during the past 25 years.
Soil Science **146**: 453-460.

Scheffer F. and Schachtschabel, P. (1989).
Lehrbuch der Bodenkunde.
Enke Verlag, Stuttgart, Germany.

Schindler, P.W. and W. Stumm (1989).
The surface chemistry of oxides, hydroxides, and oxide minerals. In: *Aquatic surface chemistry.* Ed. W. Stumm. John Wiley and Sons, New York, U.S.A. p. 83-109.

Scokart, P.O., K. Meeus-Verdinne and R. de Borger (1983).
Mobility of heavy metals in polluted soils near zinc smelters.
Water, Air, and Soil Pollution **20**: 451-463.

Sims, J.T. (1986).
Soil pH effect on the distribution and plant availability of manganese, copper, and zinc.
Soil Science Society of America Journal **50**: 367-373.

Sposito, G. (1989).
The chemistry of soils.
Oxford University Press, New York, U.S.A. Pages 277.

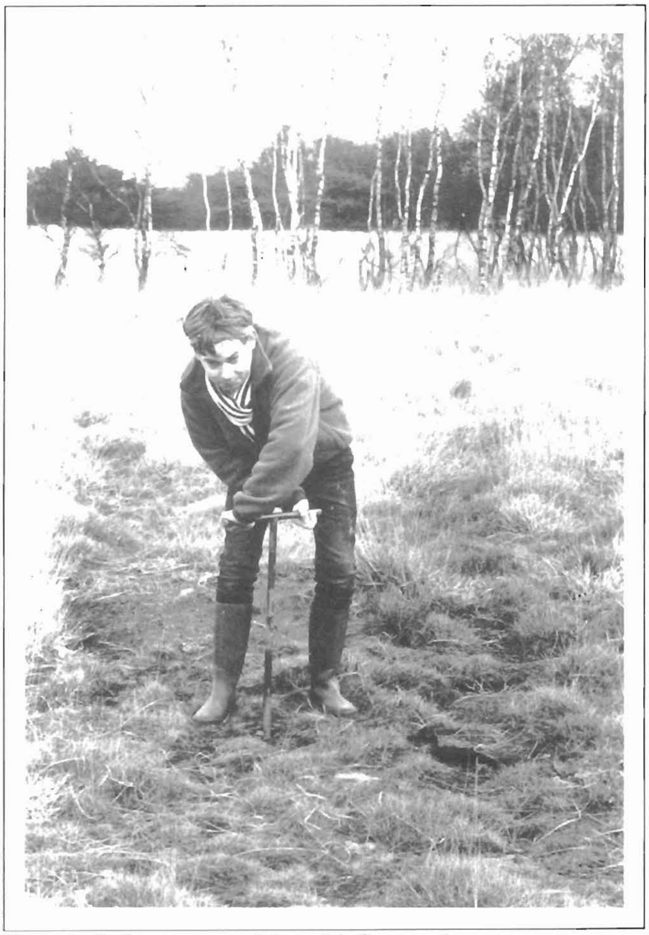

Photo 1 Soiltype survey (photo M. Reumers)

3

Heavy metal contamination in recharge groundwater under poor acid sandy soils

Co-Author: J.P.G. Loch

Abstract

Sandy soils in the border area of Belgium and the Netherlands (the Kempen region) are in use as nature reserve. They are heavily contaminated with cadmium and zinc, caused by atmospheric deposition from nearby zinc smelters. Groundwater threat by leaching from these low retention soils is subject of study. Four fields of 60 by 60 meters with each four groundwater sampling tubes located in a square were monitored during one year (November 1991 to November 1992).

High concentrations of zinc (up to 12,900 $\mu g.l^{-1}$) and cadmium (up to 126 $\mu g.l^{-1}$) were observed in most of the groundwater samples. These metals are originating from the soil above the groundwater and entered the groundwater by soil passage. These soils have a low pH (4.0-4.5) and low contents of organic matter. The average pH in the groundwater is about 4.5. Soils of low pH and low content of organic matter have a minor groundwater protecting ability against infiltrating cadmium and zinc. The groundwater concentration of cadmium and zinc exceed the Dutch intervention limits over 5 times, whereas the topsoil contents of both cadmium and zinc are 5 times lower than their intervention limits, i.e. a little above the target values. The Dutch intervention values for soil and groundwater are therefore not consistent.

3.1. Introduction

Groundwater contamination can take place by different pathways and different sources. One can distinguish point sources and diffuse sources. Diffuse sources are e.g. agricultural additives, polluted river-water and polluted precipitation. Contamination of rain-water is caused by air pollution and is a major problem in the vicinity of industrial areas.

Trace metal contamination of soils in the Kempen region is extensive (Scokart et al., 1983, Pedroli et al., 1990, Wilkens and Loch, 1995a). Exhaust fumes from three active zinc smelters in this area contain heavy metal oxides, which reach the nearby soil both by dry and wet deposition. These smelters started their activities in 1880. Twenty years ago the zinc smelters reduced their emissions five to ten times when a change was made from thermo to electric process technology.

In this period of more than a century heavy metals have accumulated in the topsoil. Topsoil contents of 1 to 10 $\mu g.g^{-1}$ cadmium and 100 to 1000 $\mu g.g^{-1}$ zinc were observed in this area (Wilkens and Loch, 1995a). Soil of the Kempen region are developed in rather poor aeolic coversands. Organic matter is the main binding component of cadmium and zinc. The heavy metal contents in the topsoil (0-20 cm) are related to the concentrations in the groundwater. Leaching of cadmium and zinc to the groundwater is to be expected, because these soils have an extremely low retardation capacity. The low adsorption is caused by a low pH and low contents of organic matter and almost no clay minerals are available.

Cadmium together with zinc are the most mobile and available trace metals in an oxic environment (Scheffer and Schachtschabel, 1989). As trace metals can be toxic at low concentration levels, the Dutch authorities have introduced target values and intervention limits for drinking-water, soil and groundwater. The target values are the soil contents and groundwater concentrations in the situation of durable soil quality. An excess of the intervention limit is officially considered to be serious pollution, in the situation that actual or potential risk is likely to occur. In Table 3.I a general compilation is given of trace metal concentrations in some aquatic compartments in the environment and of Dutch standards for trace metals.

High zinc concentrations in the shallow groundwater in poor sandy soils in this region were reported by Boumans and Meinardi (1986) and Maasdam et al. (1990). The latter authors reported zinc concentrations up to 15000 $\mu g.l^{-1}$. Acidic atmospheric deposition can drastically increase the mobility of heavy metals,

Table 3.I. A general compilation of trace metal and aluminum concentrations and quality criteria in the aquatic environment in the Netherlands, all concentrations in $\mu g/l$.

	Aquatic environment			Dutch quality criteria		
	Average values		range	drinking-water[3]	Groundwater	
Trace metal	rain-water[1]	sea-water[2]	groundwater[2] pH < 6.2		Target value[4]	Intervention limit[4]
Al (aluminium)	-	5	20-39000	200	-	-
Cd (cadmium)	0.23	0.11	0.1-6.4	5	0.4	6
Cr (chromium)	-	0.2	0.2-7.2	50	1	30
Cu (copper)	5.7	0.9	<1-90	100	15	75
Ni (nickel)	0.55	0.7	0.5-980	50	15	75
Pb (lead)	10.4	0.03	<0.5-12	50	15	75
Zn (zinc)	26	2	<2-830	100	65	800

1) KNMI/RIVM, location Breehey (1987),
2) Stuyfzand (1991),
3) Dutch legal standard for drinking water (Waterleidingbesluit, 1984), intervention limits for Cd, Cr, Ni and Pb and target values for Cu and Zn,
4) Dutch legal standard for groundwater (Alders, 1994).

especially in these low adsorption capacity soils (Karssemeijer et al., 1991). This paper describes the groundwater threat by soil leaching of cadmium, copper, nickel and zinc.

3.2. Materials and methods

3.2.1. Study area

The study area was situated in the Kempen on the Dutch-Belgian border. This area is a flat lowland, with an elevation of 35-40 m above sea-level, used as a nature reserve. Soils in this area are all sandy and acidic. The groundwater in this area is 0.5 to 3 meter below soil surface, depending on the season and topography.

The climate of the area is humid and temperate with mean July temperatures of 19 and in January 4°C. Annual precipitation averaging 800 mm, and net precipitation of 150-200 $mm.y^{-1}$ taking evapotranspiration into account (Boumans and Meinardi, 1986). Local chemical composition of the precipitation on our research sites was determined using KNMI/RIVM data (1988). These data are tabulated for the major elements, pH and Ec in Table 3.II.

All four groundwater sampling fields were situated at the same place as the soil sampling-fields of Wilkens and Loch (1995a). The soils of fields 2 and 4 are

Table 3.II. Chemical composition of precipitation (KNMI/RIVM, 1988).

Year	Precipitation	pH	Ec	Na	K	Ca	Mg	Cl
1988	800	4.9	50	1.1	0.29	0.69	0.15	2.5

Precipitation in mm.y^{-1},
Ec = electro conductivity in μS.cm^{-1},
Concentration of the elements in mg.l^{-1}.

abundantly covered with *Molinia caerulea* species (grass) whereas fields 1 and 3 have a very poor vegetation of this species. The fields are located in the direction of the prevailing wind (N-E) from the zinc smelters. Field locations and soil names are given in Table 3.III.

Table 3.III. Groundwater sampling sites, with the distance from the nearest emission point.

field	distance	emission point of Cd end Zn	soil type (F.A.O.)
1	1.9 km	Overpelt smelter(B)	arenosol
2	2.3 km	Overpelt smelter(B)	carbic podzol
3	1.4 km	Budel smelter(NL)	arenosol
4	3.5 km	Overpelt smelter(B)	carbic podzol

The region around fields 1, 2 and 4 (nature reserve Hageven) is studied by Bleuten (Dept. of Physical Geography, University of Utrecht, personal communication, 1994), who concludes that all sampled fields are infiltration areas. Data obtained from van Tiel (1992) show that the area around field 3 is an infiltration area. It is important to know whether we deal with groundwater infiltration areas or upwelling areas, because later in this text a comparison will be made between metal concentrations in topsoil and groundwater.

3.2.3. Sampling

From November 1991 to November 1992 groundwater was sampled at 16 sites divided over 4 fields. A sampling sequence was made over 8 periods. The spatial sampling strategy is presented in Figure 3.1. In every field of 60 x 60 m^2 four groundwater samples were taken in a square using piezometric tubes. This sampling scheme enables us to relate the groundwater composition to the overlaying soil in each field.

The piezometric tubes are made of high density poly-ethylene (h.p.t.e.). The tubes have a diameter of 41 mm and vary in length from 2.10 to 5.00 meter below soil surface. Filter screens of 1 meter length were placed below the expected local range of water-table levels. Figure 3.2. gives an indication of the seasonal groundwater-level variation during one year.

The groundwater was pumped up with a 12 Volts dc peristaltic pump. After measuring pH and Ec on site, an inline membrane filter (0.45 μm) was used to filter the water. Groundwater samples were stored in 100 ml hpte bottles and acidified to pH 1-2 with nitric acid. Samples were stored at 4°C. In the laboratory all metals were analyzed by ICP-AES (ARL 34000 instrument). The chloride concentration was determined by ion selective electrode (Orion), after adding an ISAB buffer (pH = 3).

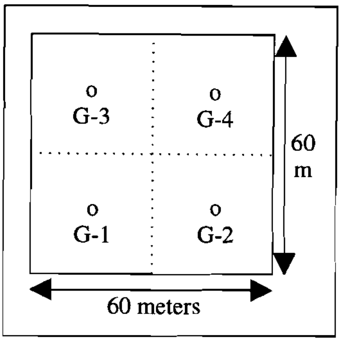

Figure 3.1. Field schematization. G-1, G-2, G-3 and G-4 are groundwater sampling sites

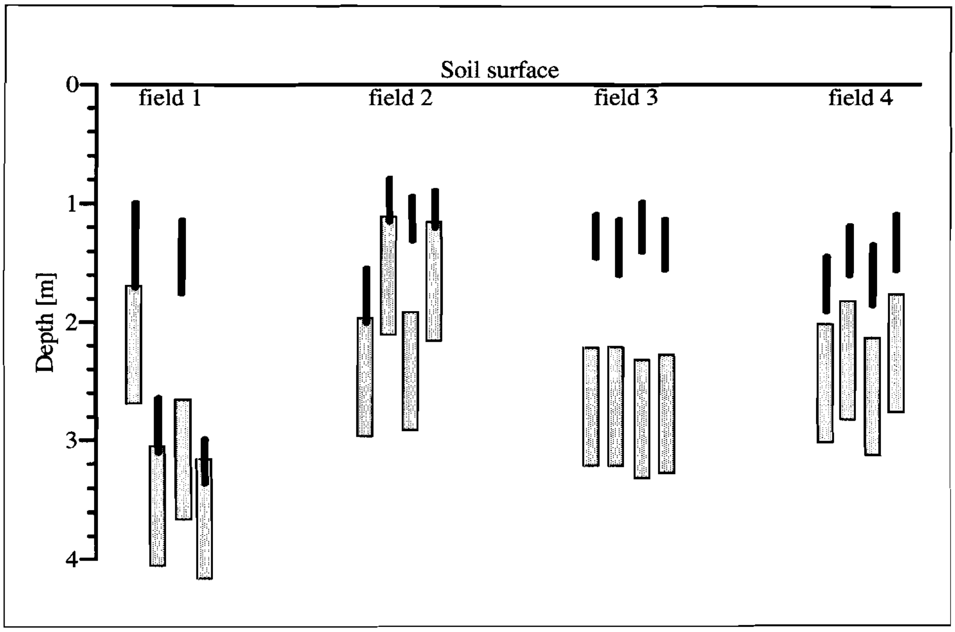

Figure 3.2. Groundwater-level in meters below soil surface (range indicated by the black lines), and the positions of the filter screens (dotted rectangles).

The soil samples were taken in the same fields in a regular grid at nine locations. In this study only the top samples (0-20 cm) of the soil profiles are used. Soil sampling and analytic procedures were described by Wilkens and Loch (1995a).

3.3. Results and discussion

3.3.1. Groundwater characterization

Table 3.IV. Basic statistics of the sampled groundwater (major elements), Ec is expressed in μS.cm^{-1}, Al, Fe, Mn, Si, Na, K, Ca, Mg, Cl, S, and P in mg/l.

	mean	min	max	s.d.	n	D
Ec	161	11	480	59	124	L
pH	4.59	3.76	5.74	0.43	112	N
Al	3.25	0.11	9.34	2.18	128	N
Fe	0.34	(0.00)	5.84	1.05	128	L
Mn	0.32	0.02	2.93	0.52	128	L
Si	3.39	1.22	5.98	1.17	128	L
Na	6.01	2.01	41.81	4.59	128	L
K	1.78	0.19	10.04	1.56	128	L
Ca	5.63	1.28	34.13	4.93	128	L
Mg	1.02	0.36	5.08	0.69	128	L
Cl	10.47	3.3	36	5.65	128	L
S	13.06	5.85	40.61	3.96	128	L
P	0.10	(0.03)	0.56	0.12	128	L

mean = arithmetic average,
s.d.: = standard deviation in population,
n: = number of observation or samples,
D: = distribution type, N = normal distribution, L = log-normal distribution,
values between brackets are below detection limit.

In Table 3.IV ranges and average values are given for the concentrations of the observed major elements, pH and Ec in the groundwater. The data from all four fields and the whole time series, i.e. a total number of 128 groundwater samples, were used in these statistical calculations. When a concentration is below the detection limit, we use the detection limit in the statistics. Striking are the low pH and the high aluminium concentration. In most cases the iron concentration is below the detection limit, only in field 4 we observe some iron in the groundwater. Therefore the groundwater in fields 1, 2 and 3 is oxic. Field 4 has in some cases a sub-oxic groundwater environment.

The dissolution of amorphous aluminium hydroxide appears to be dependent strongly on the pH (Table 3.V). Dissolved aluminium, however has a distinct tendency to form hydroxy complexes (in addition to organo-complexes), which may increase the solubility of amorphous aluminium hydroxide significantly. The stability of the most important dissolved Al-hydroxy complexes are listed in Table 3.V.

Table 3.V. The water solubility of solid Al-hydroxide at 25°C and the stability of dissolved Al-hydroxy complexes at 25°C (Ball et al, 1980).

Reaction:		log K
$Al(OH)_3$	$\longleftrightarrow Al^{3+} + 3\ OH^-$	-32.64
$Al^{3+} + H_2O$	$\longleftrightarrow Al(OH)^{2+} + H^+$	-4.99
$Al^{3+} + 2\ H_2O$	$\longleftrightarrow Al(OH)_2^+ + 2\ H^+$	-10.13
$Al^{3+} + 3\ H_2O$	$\longleftrightarrow Al(OH)_3^0 + 3\ H^+$	-16.00
$Al^{3+} + 4\ H_2O$	$\longleftrightarrow Al(OH)_4^- + 4\ H^+$	-22.05

The total amount of aluminium in solution consists of both complexed and uncomplexed aluminium and can be described by the mole balance Equation 3.1, which includes the anorganic hydroxide species.

$$\sum Al = m_{Al^{3+}} + m_{Al(OH)^{2+}} + m_{Al(OH)_2^+} + m_{Al(OH)_3^0} + m_{Al(OH)_4^-} \qquad (3.1)$$

At the prevailing low pH, high concentrations of aluminium can be expected in the groundwater. Figure 3.3 gives the total dissolved aluminium concentration plotted versus pH. The used model gives a good description of the aluminium solubility at the various pH-values in our groundwater samples. It is therefore obvious that the aluminium concentrations are determined by dissolution of aluminium hydroxide. The data points on the right hand side of the modelled curve demonstrate a too high solubility. This is probably caused by dissolved organic ligands, which form complexes with dissolved aluminium and increase the aluminium solubility.

3.3.2. Chloride

In soils and groundwater of moderate climates chloride is a conservative anion. Therefore we can make a comparison between the chloride concentration in groundwater and rain-water. By partial evapotranspiration of rain-water, concentrations in remaining soil solution will increase. An increase in the chloride concentration is an indication for the amount of evapotranspiration. On average the chloride concentration in rain-water is about 2.5 $mg.l^{-1}$ (KNMI, 1988). In the groundwater samples at the research sites an average chloride concentration of 10.47 $mg.l^{-1}$ was measured (Table 3.IV). The ratio between groundwater and rain-water concentration is about 4. Consequently, at average annual precipitation of 800 mm, 191 mm reaches the groundwater, which is in the range of 150-200

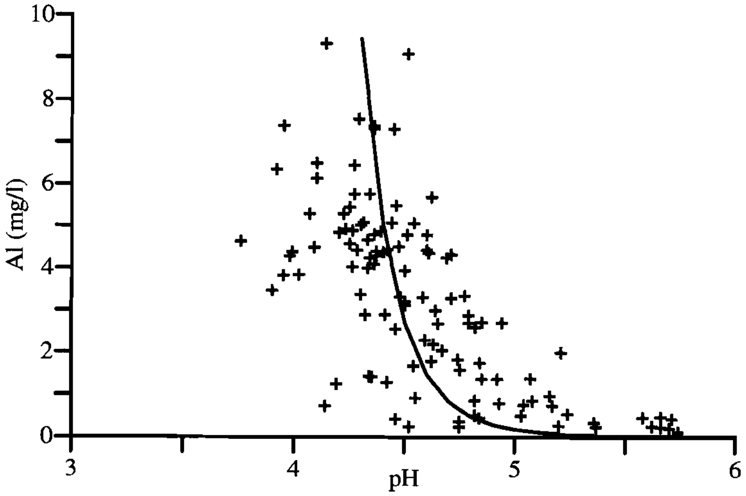

Figure 3.3. Scatter plot of dissolved aluminium and pH, and a calculation with the CHARON speciation model (1989), using the stability constants in Table 3.V.

mm.y^{-1} reported by Boumans and Meinardi (1986).

3.3.4. Heavy metals

Table 3.VI presents average concentrations of all groundwater samples, we report high average concentrations of cadmium and zinc. The field average groundwater concentrations of cadmium, copper, nickel and zinc are listed in Table 3.VII. The field averages are calculated according to equation 3.2.

$$\overline{c}_f = \frac{\Sigma_{t=1}^{8} \Sigma_{s=1}^{4} c_{t,s,f}}{32} \qquad (3.2)$$

where:

$\overline{c}_f$ = average concentration of heavy metal in groundwater in field f [μg.l^{-3}],

$c_{s,t,f}$ = heavy metal concentrations in groundwater on site s, at time t, and in field f [μg.l^{-3}].

The velocity of metal movement depends strongly on soil type and soil structure. The measured groundwater concentrations are the result of 110 years of solute movement through the soil (start of the industries in 1880).

Fields 2 and 4 both are soils of a podzolic character, allowing us to compare these fields with each other. In field 2 higher concentrations of all heavy metals in the groundwater than in field 4 have been observed. This is mainly caused by the distance from the emission point, respectively 2.3 and 3.5 km. The

Table 3.VI. Basic statistics of the sampled groundwater (trace elements), Cd, Cu and Ni are expressed in $\mu g.l^{-1}$ and Zn is expressed in $mg.l^{-1}$.

	mean	Min	Max	S.D.	n	D
Cd	45	(1.8)	126	27	128	N
Cu	5.4	(1.1)	39.4	7.20	128	L
Ni	17.2	(6.5)	192	24.0	128	L
Zn	5.18	1.36	12.97	2.89	128	N

mean = arithmetic average,
S.D. = standard deviation in population,
n = number of observation or samples,
D = distribution type, N = normal distribution, L = log-normal distribution,
values between brackets are below detection limit.

Table 3.VII. Average groundwater concentrations and quality criteria of Cd, Cu and Ni in $\mu g.l^{-1}$ and Zn in $mg.l^{-1}$ in the four fields.

	Groundwater			
	Cd	Cu	Ni	Zn
Target value	0.4	15	15	0.065
Intervention limit	6	75	75	0.80
Field 1	48	3.1	23	4.62
Field 2	71	10.2	16	6.54
Field 3	33	4.6	23	7.49
Field 4	26	3.0	8	2.08

The concentrations of cadmium and zinc are an average in time over four groundwater tubes per field. The target values and intervention limits are obtained from Alders (1994).

cadmium and zinc immissions on field 2 are larger than on field 4, because of their distance from the emission point (smelter Overpelt, Belgium). Comparing the groundwater concentrations with the Dutch soil quality criteria (Alders, 1994), the concentrations of cadmium and zinc in all fields are on an average 5 times higher than the intervention limits (Table 3.VII). This is the combined effect of low pH of soil and rain-water, a low retardation capacity of the overlaying soil, high and lasting immissions of metals and metal properties itself.

Contrary to cadmium and zinc, for all fields the average concentrations of nickel are around the target value and far below the intervention limit (Table 3.VII). For copper the average concentrations are all below the target value. This means that copper is not at an elevated level in the groundwater, and is probably at the natural background concentration.

Besides adsorption processes, leaching of heavy metals can be influenced by precipitation of heavy metals. Retardation by precipitation of cadmium, copper, nickel or zinc minerals ($Cd(OH)_2$ CdS, CuS, $Ni(OH)_2$, $Zn(OH)_2$, ZnS and $ZnCO_3$) is a function of the solute concentration. Under acid conditions the carbonate and hydroxide concentrations are very low ($[OH^-] = 10^{-10}$ at pH = 4) and under oxic conditions the concentration of sulphide is negligible. The solubility products of these precipitates will not be exceeded in these heavy metal concentration domains. In an acid, oxic soil system cadmium and zinc concentrations in the solution are controlled by adsorption (Harmsen, 1977; Brümmer et al., 1983).

3.3.5. Time trend analysis

Figures 3.6 and 3.7 give the groundwater concentration variation of cadmium respectively zinc in time. Common statistics used in time trends is the nonparametric Spearman rank correlation coefficient (Frapporti, 1994). The confidence of a trend test statistic parameter is low if only a few measurements in time are available. However, through study of the distribution of a trend statistic parameter, combining the individual statistics from a group of groundwater wells, the low-confidence individual-well information can be used to arrive at high-confidence group information. The basic concept is that, in a homogeneous group, wells may show a vague individual trend that, when tested together, will prove significant (Frapporti, 1994). For the time trend analysis we used the Spearman package designed by Frapporti (1994). The Kolmogorov-Smirnov test statistic is used to indicate the deviations of zero correlation (Davis, 1986) and its significance.

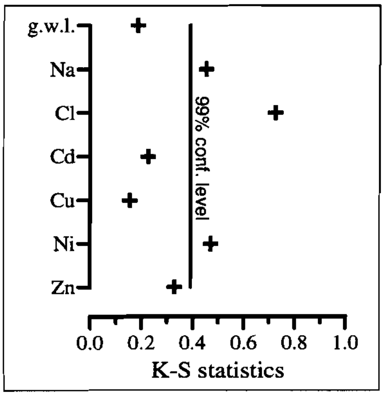

Figure 3.4. Kolmogorov-Smirnov (K-S) statistics, with critical value for the 99% confidence level.

The Kolmogorov-Smirnov statistic parameters for the period November 1991 to November 1992 are shown in Figure 3.4. The Spearman rank correlation coefficients are given in Figure 3.5. Significant time trends are found for chloride, sodium and nickel. The Kolmogorov-Smirnov statistic parameter of these elements is above the critical value of 0.392 by 99% confidence level (Davis, 1986) (Figure 3.4). Figure 3.5 shows that the time trends of Cl, Na and

Ni are negative, i.e. most Spearman rank correlation coefficients are negative. An explanation for this negative time trend is not found; no correlation with the groundwater-level is observed. Therefore the negative time trend is not caused by changing groundwater table.

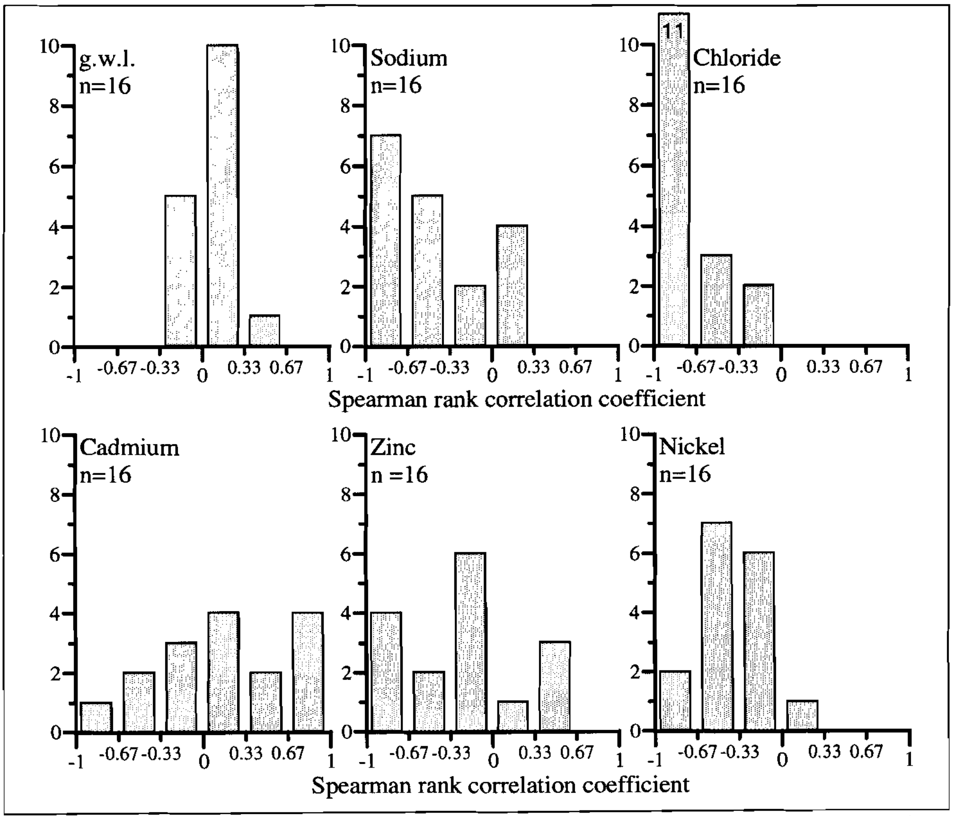

Figure 3.5. Distribution of Spearman rank correlation coefficients of Na, Cl, Cd, Ni Zn, and groundwater-level (g.w.l.). If the Spearman rank correlation is negative, there will be a negative time trend and vice versa for positive correlation.

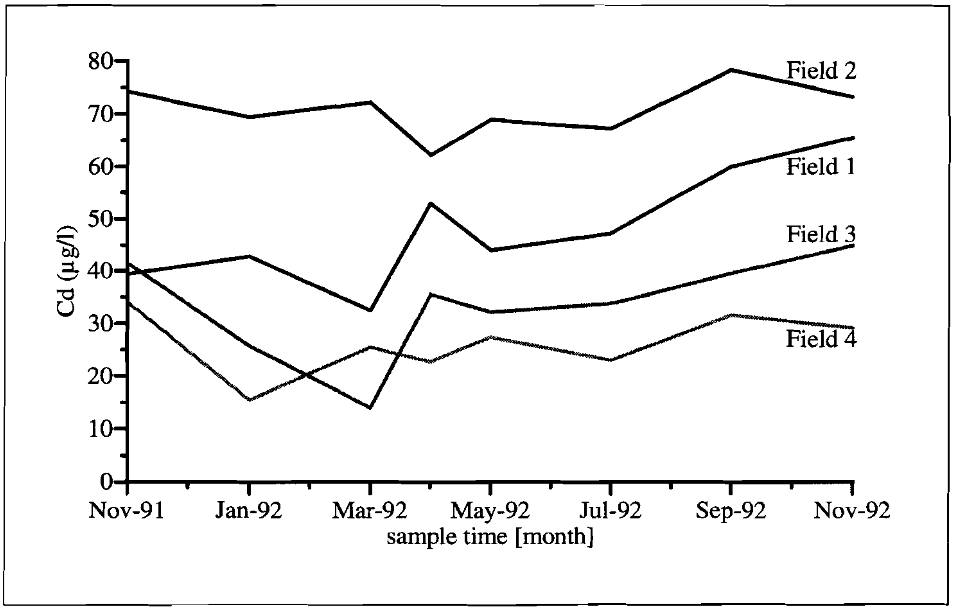

Figure 3.6. Average cadmium concentrations in the groundwater of fields 1, 2, 3, and 4 at different times for the period November 1991 to November 1992.

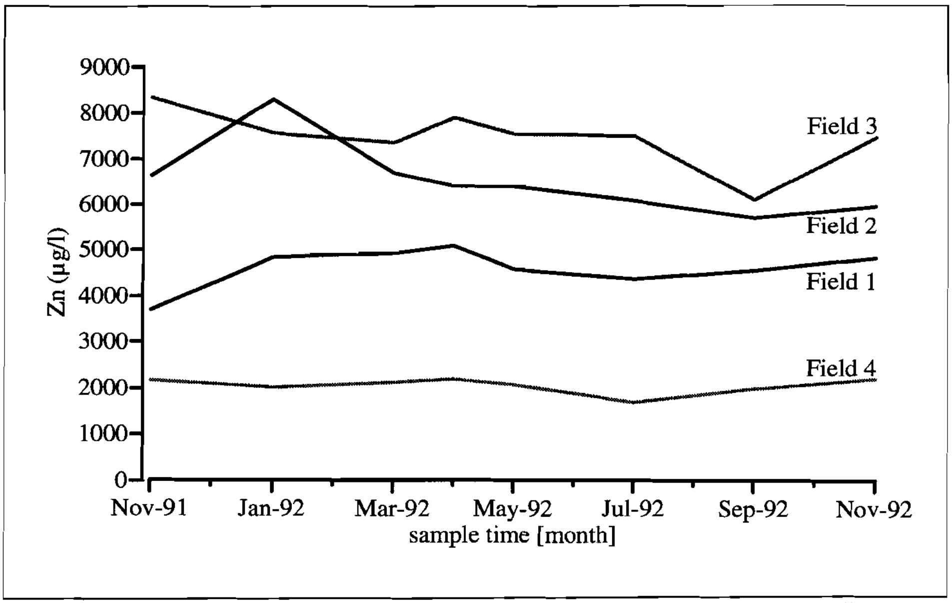

Figure 3.7. Average zinc concentrations in the groundwater of fields 1, 2, 3 and 4 at different times for the period November 1991 to November 1992.

No significant time trend is found for cadmium and zinc concentrations in groundwater, the Kolmogorov-Smirnov statistic parameters are below the critical value of 0.392. The decreasing atmospheric cadmium and zinc deposition in the last decades is not reflected by decreasing cadmium and zinc concentrations in the groundwater. Two possible explanations may be considered: the concentration drop took place in the past, or will take place in the future, since metal release from the topsoil is slow. Considering the scarce immission data and average groundwater concentration, the second option is the most likely. The actual cadmium immission in the year 1988, close to field 1, is about 25 $\mu g.l^{-1}$ (chapter 1), corrected for evapotranspiration. The observed average groundwater cadmium concentration is 48 $\mu g.l^{-1}$. The atmospheric cadmium immission and the groundwater concentration show a discrepancy, which points at a decrease in the cadmium concentration in the groundwater in the future. This observation is also valid for zinc immissions in relation to average groundwater concentrations, which are respectively 3,000 $\mu g.l^{-1}$ and 4,616 $\mu g.l^{-1}$. Even though the statistics of a group of wells are combined, a period of one year may be too short period to observe time trends, especially for long term processes like heavy metal leaching.

3.3.6. Heavy metal partition

From balance calculations using immission data and soil composition, it is clear that the infiltrated cadmium and zinc fronts have reached the groundwater (see also chapter 5 of this thesis). Since the composition of the topsoil and upper groundwater are linked together by sorptive processes during long term percolation of soil-water a relation might be made of these two compartments.

To quantify a field mobility of heavy metals for transport from the topsoil to the groundwater, we introduce an operational partition coefficient, K_p. This is the ratio between the content of heavy metal in the topsoil (0-20 cm) and the heavy metal concentration in the groundwater according to Equation 3.3.

$$K_p = \frac{q}{c} \tag{3.3}$$

where:

K_p = partition coefficient [$ml.g^{-1}$],

q = content in the top soil [$\mu g.g^{-1}$],

c = concentration in groundwater [$\mu g.ml^{-1}$].

The average soil contents used for the partition calculations are given in Table 3.VIII. These data are compiled from previously published (Wilkens and

Loch, 1995a) and unpublished data. The average content of organic matter in the topsoil is about 3.1% ($g.g^{-1}$)

Table 3.VIII. Contents of Cd, Cu, Ni and Zn in the top soil (0-20 cm).

	Top soil (0-20 cm)			
	Cd	Cu	Ni	Zn
Target value at: 4% organic matter, 0% clay (< 2 μm).	0.46	16.8	10.0	52
Intervention limit	12	190	210	720
Field 1	0.53	16.1	3.6	80
Field 2	2.26	15.7	5.4	107
Field 3	0.13	6.0	6.5	42
Field 4	1.29	6.8	2.1	33

All contents are in $\mu g.g^{-1}$. These soil contents are averages over the upper 20 cm, sampled at 0, 5, 10, 15 and 20 cm depth, and over nine profiles per field. Target value and intervention limits are derived from Alders (1994).

The K_p-values presented in Table 3.IX may reflect the *in situ* equilibrium partition coefficients. From the data in Table 3.IX it is easy to conclude that cadmium and zinc are the most mobile metals under the mentioned conditions. For the carbic podzols (fields 2 and 4) cadmium has a higher partition than zinc, whereas for the arenosols (fields 1 and 3) zinc has the higher partition coefficient. A continued deposition resulted in leaching of cadmium and zinc from the topsoil to the groundwater, whereas copper remains in the topsoil, as was also found by Miller et al. (1983). The K_p-values for cadmium derived in the way they are comparable with the partition coefficient obtained from batch experiments with soil samples from the same area, which ranged from 1.5 to 22.8 (Wilkens et al., 1995b).

As for in the groundwater, the soil contents of copper are comparable to the target values. Their K_p values represent long term contact between percolate and soil with natural contents of copper. Copper demonstrates a high ratio between topsoil and groundwater, which is caused by a strong binding to organic matter (McBride, 1989).

The discrepancy between field K_p-values (mobilities) obtained by this study and the ratio's of the Dutch target values and intervention limits is obvious for the elements cadmium and zinc (Table 3.IX). The Dutch soil protection policy is based on a significantly lower mobility for these metals, i.e. the cadmium partition in these soils is actually 20 to 200 times lower than implied in the target

Table 3.IX. Partition coefficients (K_p) derived from topsoil contents and groundwater concentrations. All partition coefficients are in ml.g^{-1}.

	Partition coefficient			
	Cd	Cu	Ni	Zn
Ratio of target values	1150	1120	667	800
Ratio of intervention limits	2000	2533	2800	900
Field 1	11.0	5131	160	17.2
Field 2	31.9	1539	339	16.4
Field 3	3.9	1302	285	5.6
Field 4	49.4	2295	281	15.7

The ratio's of target values and the intervention limits are obtained from table 3.VI and table 3.VIII.

and intervention values. An explanation may be that the Kempen soils have a low pH and this parameter is not incorporated in the Dutch criteria. The copper and nickel partition in our soils and the target and intervention values are in harmony which each other (Table 3.IX).

The environmental impact of these observations is clear. Cadmium and zinc deposited on these soils are very mobile, move down with infiltrated rain-water to the groundwater and will exceed the groundwater intervention limits.

Table 3.X gives the observed order of mobilities of the heavy metals. This sequence is found also by other authors, e.g. Brown (1983). For the arenosol we found a reverse order for cadmium and zinc as for the carbic podzol. The carbic podzol contains more organic matter than the arenosol (Wilkens and Loch, 1995a). An increased content of organic matter may enhance cadmium retardation more than that of zinc, this was confirmed by Elliott et al. (1986).

Table 3.X. A qualitative comparison of the mobility between the heavy metals in different soil types.

soil type	mobility	Reference
Arenosol	Cd > Zn >> Ni >> Cu	this study
Carbic Podzol	Zn > Cd >> Ni >> Cu	this study
oc < 2%	Cd > Zn > Cu > Pb	Elliott (1986)
oc = 2-4%	Zn > Cd > Cu > Pb	Elliott (1986)
adsorption on organic matter at pH=5	Zn > Ni > Cu	McBride (1989)

3.4. Conclusions

Introducing a heavy metal concentration ratio between topsoil and groundwater is a good way to determine their *in situ* partition coefficient, K_p, in these soils. The field K_p values of cadmium and zinc in poor acid sandy soils are extremely low, which reflects a low retardation and a high mobility. With a history of diffuse pollution of a hundred years, high concentrations of cadmium and zinc are found in the groundwater under these soils in large areas. They exceed the Dutch intervention limits over 5 times, whereas the topsoil contents of both cadmium and zinc are 5 times lower than their intervention limits, a little above target values. Dutch intervention values for soil and groundwater are therefore not consistent.

Almost no copper was found in the groundwater. The mobility of copper is very low, reflected by a very high K_p value. There will be no short term risk for copper leaching to groundwater.

For cadmium and zinc no significant time trend in the groundwater concentrations within the period of one year was observed. A decrease in the cadmium and zinc deposition will not result in a significant short time change in groundwater concentrations of these metals. There will be a slow release of cadmium and zinc from the topsoil to the groundwater, consequently a slow decrease in groundwater zinc and cadmium concentration levels.

At the prevailing low pH not only heavy metals become mobile, but also aluminium dissolves significantly. The measured aluminium concentrations satisfy the modeled dissolution of aluminium hydroxide and formation of its dissolved complexes.

References

Alders, J.M.G. (1994).
Interventiewaarden bodemsanering.
Staatscourant Koninkrijk der Nederlanden **95**(24th of May 1994).

Ball, J.W., D.K. Nordstrom and E.A. Jenne (1980).
Additional and revised thermodynamical data and computer code for WATEQ2 - a computerized chemical model for trace and major element speciation and mineral equilibria of natural waters (No. Water Supply Inv.), US Geol Survey.

Boumans, L.J.M. and C.R. Meinardi (1986).
Hoge zink gehalten in het ondiepe grondwater van een natuurgebied in de Peel.
H2O **19**(12): 263.

Brown, K.W., J.C. Thomas and J.F. Slowey (1983).
The movement of metals applied to soils in sewage effluent.
Water, Air, and Soil Pollution **19**: 43-54.

Brümmer, G., K.G. Tiller, U. Herms and P.M. Clayton (1983).
Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils.
Geoderma **31**: 337-354.

Davis, J.C. (1986).
Statistics and data analysis.
John Wiley & Sons, New York, U.S.

CHARON 5.02 (Speciation model), 1989. de Rooij, N.M., Delft Hydraulics, Delft, the Netherlands.

Elliott, H.A., M.R. Liberati and C.P. Huang (1986).
Competitive adsorption of heavy metals by soils.
Journal of Environmental Quality **15**(3): 214-219.

Frapporti, G. (1994).
Geochemical and statistical interpretation of the dutch national groundwater quality monitoring network.
Thesis, Utrecht University, the Netherlands.

Harmsen, K. (1977).
Behaviour of heavy metals in soils.
Thesis, Agricultural University Wageningen, the Netherlands.

Karssemeijer, P.L., P.G.M. Kaasenbrood and M.C. Rang (1991).
Spore-elementen in het ondiepe grondwater: depositie of verzuring?
H2O **24**(12): 323.

KNMI/RIVM (1987).
Chemische samenstelling van de neerslag over Nederland, KNMI/RIVM, De Bilt, the Netherlands.

KNMI/RIVM (1988).
Chemische samenstelling van de neerslag over Nederland, KNMI/RIVM, De Bilt, the Netherlands.

Maasdam, W.A., G.B.M. Pedroli and A.J. van Wijk (1990).
Hoge zinkgehalten in grondwater strijper Aa-gebied, vervolg: de relatie bodem grondwater.
H2O **23**(26): 732.

McBride, M.B. (1989).
Reaction controlling heavy metal solubility in soils. In: *Advances in soil science.* Springer Verlag, New York, U.S.

Miller, W.P., W.W. McFee and J.M. Kelly (1983).
Mobility and retention of heavy metals in sandy soils.
Journal of Environmental Quality **12**(4): 579-584.

Pedroli, G.B.M., W.A.C. Maasdam and J.M. Verstraten (1990).
Zinc in poor sandy soils and associated groundwater. A case study.
The Science of the Total Environment **91**: 59-77.

Scheffer, F. and P. Schachtschabel (1989).
Lehrbuch der Bodenkunde.
Enke Verlag, Stuttgart, Germany.

Scokart, P.O., K. Meeus-Verdinne and R. de Borger (1983).
Mobility of heavy metals in polluted soils near zinc smelters.
Water, Air, and Soil Pollution **20**: 451-463.

Stuyfzand, P.J. (1991).
Sporenelementen in grondwater in Nederland.
H2O **24**(26): 757.

van Tiel, I. (1992).
Monitoring van de grondwatersamenstelling in de provincie Noord-Brabant, een multidisciplinaire aanpak.
H2O **25**(26): 746.

Waterleidingsbesluit (1984).
Dutch legal standard for drinking water.
Staatsblad Koninkrijk der Nederlanden, Den Haag, the Netherlands.

Wilkens, B.J. and J.P.G. Loch (1995a).
Accumulation of cadmium and zinc from diffuse immission on acid sandy soils, as a function of soil composition.
Water, Air, and Soil Pollution (Submitted for publication).

Wilkens, B.J., N. Brummel and J.P.G. Loch (1995b).
Influence of pH and zinc concentration on cadmium sorption in acid, sandy soils.
Water, Air, and Soil Pollution (Submitted for publication).

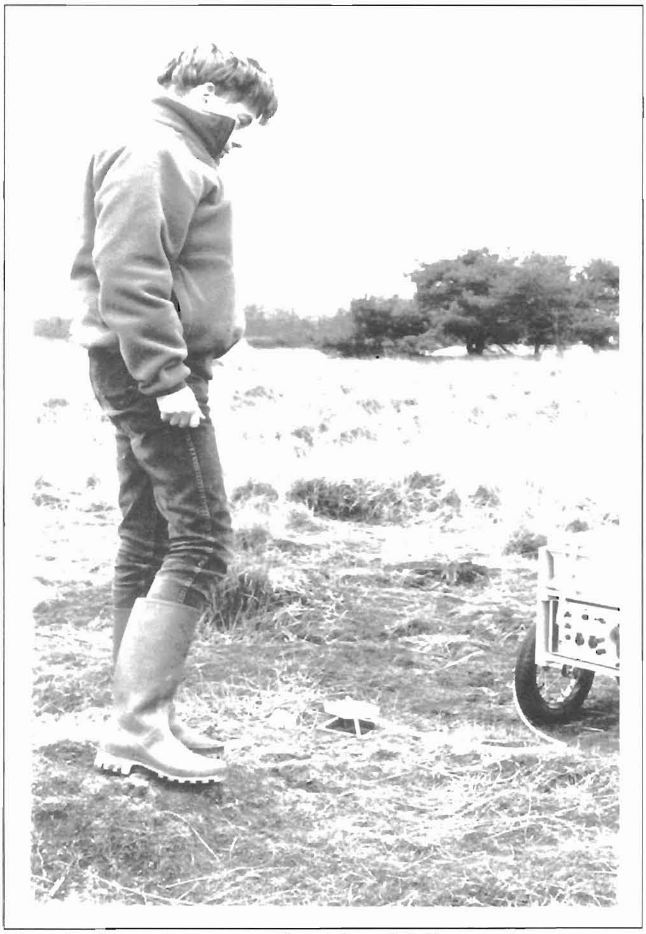

Photo 2 Groundwater sampling (photo M. Reumers)

4

Influence of pH and zinc concentration on cadmium sorption in acid, sandy soils

Co-Authors: N. Brummel
J.P.G. Loch

Abstract

Batch adsorption experiments were carried out with samples from an A-, Bh- and C-horizon of contaminated sandy soil of podzolic character from the Kempen region at the Dutch-Belgian border. Cadmium sorption was studied on 3 soil samples at 3 different pH-levels (3.6, 4.3 and soil buffered pH) and 3 different additions of zinc (0-40 $mg.l^{-1}$).

Adsorption of cadmium by acid sandy soils can be fitted by a Freundlich adsorption isotherm. Although zinc competes with cadmium for the sorption sites, we observe a two to three times stronger competition effect of the proton cation, which is explained by the chemical properties of both ions. The cadmium adsorption coefficients (K_F) decrease considerably by an increase of the proton activity used in the sorption experiments. Organic matter contents explain for a large part the variation of the Freundlich adsorption coefficients of the three soil samples. Desorption data do not fit the proposed regression model for adsorption. Not all the cadmium, initially present in the polluted soil, will desorb reversibly. The assumption of absence of irreversible bound cadmium may be not correct.

4.1. Introduction

Heavy metal contamination of soils in the Kempen, at the Dutch-Belgian border, is known for years and is spread over a large region. It is caused by emissions of zinc smelters in the area, founded 110 years ago. The zinc smelter involved in our study emitted zinc together with cadmium, which resulted in soil immissions in the mass ratio 50 to 150 (Wilkens and Loch, 1995). The aim of this research is to study adsorption of cadmium on acid sandy soils and the influence of pH and solute concentration of zinc.

4.1.1. Cadmium sorption

Most natural soils are heterogeneous media, i.e they provide a wide range of adsorption sites with different bonding properties and they also contain a wide range of ionic and non-ionic aqueous species taking part in adsorption processes. The mobility of cadmium in soils is dependent on the concentration of the equilibrium cadmium in dissolved form. When solubility products are not exceeded, the content of cadmium in the solid phase is a function of the concentration in the solution. This function is usually described by either a linear equation or by a Freundlich equation.

The linear adsorption equation is the most simple sorption model. It describes a constant partition between the amount sorbed and the amount in the solution. For cadmium this equation is

$$q = K_d [Cd^{2+}] \tag{4.1}$$

Where:

q = adsorption density of cadmium in the solid phase [$\mu g.g^{-1}$],
K_d = distribution coefficient [$ml.g^{-1}$],
$[Cd^{2+}]$ = cadmium concentration in solution [$\mu g.ml^{-1}$].

The Freundlich adsorption isotherm is an empirical relation between the adsorption density of cadmium on a solid phase and the aqueous concentration of cadmium, described by Equation 4.2.

$$q = K_F [Cd^{2+}]^n \tag{4.2}$$

Where:

K_F = Freundlich adsorption coefficient [$\mu g^{1-n}.ml^n.g^{-1}$],
n = a parameter depending on the degree of heterogeneity of the sorption surface, usually $0 \leq n \leq 1$ [-].

Sorption affinity varies across the surface, because the surface is heterogeneous. The high affinity sorption sites will be occupied at low concentrations, whereas also sites of lower affinity are occupied at higher concentrations. The Freundlich isotherm predicts no adsorption maximum.

At low cadmium concentrations sorption follows the behaviour of a Freundlich isotherm (García-Miragaya & Page, 1978; Chardon, 1984, Christensen, 1984, Barrow et al., 1989). The value of the adsorption K_F parameter is not a constant, but depends on the conditions in the solid and the solution. In general, in sandy soils, organic matter, pH and oxides (of Al, Fe, and Mn) are the main factors governing adsorption of cadmium (Gerritse & van Driel, 1984; Miller et al., 1983; Sims, 1986; Christensen, 1989). At low pH (below pH 5) the oxides of Al and Fe mainly have a positive surface charge and adsorption is of minor importance. Therefore pH is a major soil parameter determining sorption and the oxide content is of less importance.

Soil pH markedly alters the distribution of cadmium (Christensen, 1984). When the pH decreases the amount of adsorbed cadmium decreases (García-Miragaya, 1978). The K_F value for cadmium sorption approximately doubles for each increase in pH of 0.5 unit in the pH interval from 4 to 7 (Christensen, 1989). Therefore it can be concluded that soil pH is the most critical controlling factor for the distribution of cadmium between soil and solute (Scokart et al., 1983; Christensen, 1984; Eriksson, 1989, Christensen, 1989).

Zinc competes effectively for cadmium sorption sites; at increasing zinc concentrations in solution the cadmium distribution coefficient decreases (Benjamin & Leckie, 1981). A solute concentration above 100 μg Zn l^{-1} may significantly effect cadmium distribution between solid and liquid phases. In the presence of zinc at pH 5.5 the distribution coefficients of cadmium are 2 to 14 times lower than in absence of zinc, which has implications for interpreting cadmium leaching (Christensen, 1987).

4.1.2. Soil-dependent Freundlich sorption models

K_d and K_F in Equations 4.1 respectively 4.2 are dependent on several soil parameters, which can be divided in two groups. The first group consists of the solution properties, including pH, calcium concentration, chloride concentration and other competing or complexing species. The second group is the solid properties, including organic matter content, C.E.C., particle fraction $< 2\mu$m and oxide content. To predict the sorption behaviour under various soil and solute conditions, many authors tried to describe K_d or K_F as an empirical function of these properties. The next examples of cadmium sorption models are all primarily based on the linear or Freundlich isotherm.

For a wide range of Dutch soil types De Haan et al. (1987) found an exponential dependency of K_F on the proton activity and calcium concentrations (Eq. 4.3). They derived this equation from a simplified data set from Chardon (1984).

$$K_F = K_{sc}\{H^+\}^{-0.48}[Ca^{2+}]^{-0.41} \tag{4.3}$$

where:

K_{sc} = scaled Freundlich adsorption parameter, obtained from regression and independent of calcium concentration and proton activity,

$\{H^+\}$ = proton activity in solution [M],

$[Ca^{2+}]$ = calcium concentration in solution [mM].

According to the exponents of H^+ and calcium the competition effect of these ions on the cadmium adsorption are almost equal. For the same soils they also found an empirical relation between K_F and $[H^+]$ and organic matter content (Eq. 4.4). Boekhold (1992) used a similar equation to explain the variation in K_F values, for sandy soils of the Kempen with a pH between 5 and 6.

$$K_F = K_{sc}\{H^+\}^{-0.48}\,oc \tag{4.4}$$

where:

oc = organic carbon contents in the solid phase [% $g.g^{-1}$].

For a simple proton-cadmium exchange reaction Anderson and Christensen (1988) derived a pH dependence of K_d by regression:

$$K_d = 0.030\cdot\{H^+\}^{-0.64} \tag{4.5}$$

More complex regression equations of K_F and soil characteristics were derived from the data set by Chardon (1984). Del Castilho and Chardon (1993) used the equation describing the dependence of K_F on pH:

$$K_F = -0.3281 + 0.0528\cdot(10^{0.2598\cdot pHsoil}) \tag{4.6}$$

4.2. Materials and methods

4.2.1. Sampling sites

Different soil-horizons were sampled from two contaminated soil profiles at two different locations in the vicinity of a zinc smelter. We used the samples, from three horizons with representative soil properties, for sorption experiments. The horizons are part of sandy soils of podzolic character located in a nature reserve with grass vegetation in the Belgian Kempen. Soil-horizons 1 and 3 are located 2.3 km North-East from the zinc smelter near Overpelt (Belgium). Soil-horizon 2 is located 3.5 km North-East from this smelter. Horizon 1 is an A-horizon (topsoil), 2 is a Bh-horizon (organic matter illuviation) and 3 is a C-horizon (an unaltered subsoil).

4.2.2. Soil sample characterization

Soil characterization was carried out according to standard procedures. Total content of cadmium was determined by taking 0.25 g of soil samples. This was digested in 10 ml of a 3:2 mixture of concentrated $HClO_4$ and HNO_3 and 10 ml concentrated HF. The solution was evaporated at 180 °C and redissolved at 90 °C in a mixture of 10 ml water and 3 ml concentrated HNO_3. When the residue was dissolved, the sample was transferred to a 50 ml volumetric flask and adjusted to volume. All samples were analyzed for cadmium and zinc, respectively with graphite furnace AAS (Perkin-Elmer 5000 instrument) and with flame AAS (Perkin-Elmer 460 instrument).

Organic matter content was determined by reduction of $Cr_2O_7^{2-}$ by organic compounds and subsequent determination of unreduced $Cr_2O_7^{2-}$ by oxidation-reduction titration with Fe^{2+} (Walkley-Black method) as described by Black (1965) using a multiplication factor of 100/77 to calculate the total organic matter.

A combined glass calomel electrode (Ingold) was used for measuring the soil pH in water (soil:water = 1:2.5 $g.g^{-1}$). The samples were stirred by hand several times. After one day equilibrium was assumed and the pH was measured.

4.2.3. Sorption experiments

To study the effect of zinc competition on the sorption of cadmium, sorption isotherms were determined at three different zinc concentrations and at three different initial pH levels. Zinc concentrations were: 0 μg.ml^{-1}, 0.4 or 4 μg.ml^{-1} and 4 or 40 μg.ml^{-1}. To obtain required final pH levels, preliminary experiments were done with the soil samples to determine at which initial pH a final pH was reached. This examination was done for the pH = 3.6 and pH = 4.3. Three final pH-levels were pursued: pH = 3.6, pH = 4.3 (addition of HCl or NaOH) and pH where the pH is soil buffered (pH_{sb}) and not altered by addition of HCl or NaOH; see Table 4.I. The batch experiments were done mainly according to Chardon (1984). Solutions of cadmium and other cations and anions were made in varying concentrations with an ionic strength of 7 mM as described in Table 4.II. For each sorption isotherm 8 cadmium levels were used: 10, 25, 50, 100, 200, 400, 800 and 1600 μg Cd.l^{-1}. To the plastic tubes, containing 2 grams of air dry soil sample, 0.8 ml of distilled water was added, corresponding with 40% soil moisture. The tubes were placed in a refrigerator (2 °C) for equilibration for three days. After equilibration, 40 ml of a solution with the composition given in Table 4.2 was added to the tubes (soil:water = 1:20). The suspensions were shaken in the dark for 24 hours. After equilibration, pH was measured and soil and solution were separated by centrifugation (4000 rpm for 10 min.). The supernatant was filtered (cellulose nitrate filter, pore size: 0.45 μm) and acidified by concentrated HCl to approximately pH 1.

Table 4.I. Equilibrium pH and initial zinc levels in batch experiments.

pursued equilibrium pH-level	initial zinc concentrations [μg.ml^{-1}]			actual equilibrium pH		
				s1	s2	s3
pH_{sb} not altered	0	4	40	3.92 0.19	3.60 0.10	4.22 0.29
pH = 3.6	0	0.4	4	3.64 0.10	3.53 0.06	3.78 0.11
pH = 4.3	0	0.4	4	4.33 0.10	3.87 0.11	4.57 0.10

s1, s2, s3 = soil samples 1, 2 and 3,
the small numbers are the variations in the equilibrium pH.

The concentration of zinc in the supernatant was determined by flame AAS (Perkin-Elmer 460 instrument; detection limit: 20 μg.l^{-1}). The concentration of cadmium in the supernatant was determined by either flame AAS (Perkin-Elmer 460 instrument; detection limit: 20 μg.l^{-1}) or graphite furnace AAS (Perkin-Elmer

Table 4.II. Batch solute composition.

species	concentration ($mg.l^{-1}$)	concentration (M)
$Ca(NO_3)_2$	246 $mg.l^{-1}$	1.5 mM
KCl	75 $mg.l^{-1}$	1.0 mM
Na_2SO_4	71 $mg.l^{-1}$	0.5 mM
$Cd(NO_3)_2$	10 - 1600 $\mu g\ Cd^{2+}.l^{-1}$	0.09 μM - 14 μM
$Zn(NO_3)_2$	0 - 40 mg $Zn^{2+}.l^{-1}$	0.0 mM - 0.6 mM

5000 instrument; detection limit: 0.2 $\mu g.l^{-1}$). Which instrument was used depended on the cadmium concentration in the supernatant. The total amount of cadmium in the solid phase was calculated by the difference between the initial concentration in the solution plus the initial soil content, and the final concentration in the solution, according to Equation 4.7.

$$q = \frac{(v_i c_i + m q_i) - v_e c_e}{m} \qquad (4.7)$$

where:

v_i = volume of added solution [ml],
c_i = cadmium concentration in added solution [$\mu g.ml^{-1}$],
q_i = initial content of cadmium in solid phase [$\mu g.g^{-1}$],
v_e = total moisture volume [ml],
c_e = equilibrium concentration of cadmium in solution [$\mu g.ml^{-1}$],
m = added soil mass in batch experiment [g].

4.2.4. Statistical analysis

The basic Freundlich isotherm parameters (K_F and n) were determined from regression with the linearized Freundlich equation (Eq. 4.8).

$$\ln q = \ln K_F + n \cdot \ln[Cd^{2+}] \qquad (4.8)$$

The varying solute concentrations of cadmium and zinc and proton activity are further used in a regression analysis. We propose Equation 4.8 to describe the dependence of K_F (Eq. 4.2) on zinc concentration and proton activity in solution.

$$K_F = K_{sc}\,[Zn^{2+}]^a\,\{H^+\}^b \qquad (4.9)$$

where:

K_{sc} = scaled Freundlich adsorption coefficient, which is independent from the zinc concentration and proton activity,

$[Zn^{2+}]$ = zinc concentration in solution [mg.l^{-1}],

$\{H^+\}$ = proton activity in solution [mol.l^{-1}],

a,b = regression parameters [-].

Describing this equation as Freundlich equation:

$$q = K_{sc}\,[Zn^{2+}]^a\,\{H^+\}^b\,[Cd^{2-}]^n \qquad (4.10)$$

where:

q = content of cadmium in the solid phase [μg.g^{-1}],

$[Cd^{2+}]$ = cadmium concentration in solution [μg.ml^{-1}],

n = Freundlich exponent [-].

To interpret adsorption data we used multiple linear regression analysis (m.l.r.a.). The m.l.r.a. calculations were carried out using Quatro Pro (Borland, 1992). The sorption data can be divided in two groups, i.e. batch experiments where adsorption occurs and experiments where desorption occurs. We only used the data from batch experiments where *adsorption* occurred, the desorption experiments were initially discarded. First we carried out a regression analysis of adsorbed cadmium as a function of only the cadmium concentration in solution, next we added the proton activity and zinc concentration to the regression equation. The multiple linear regression was calculated according to the linearized Equation 4.11:

$$\ln q = \ln K_{sc} + a.\ln[Zn^{2+}] + b.\ln\{H^+\} + n.\ln[Cd^{2+}] \qquad (4.11)$$

Cadmium in the soil may be partly present in an irreversibly bound form, e.g. in the lattice of minerals. This quantity will be designated q_0. A method of trial and error is used to predict q_0, with q_0 assumed equal in all experiments with one soil sample. All q values are recalculated by subtracting q_0. With the corrected q values a regression analysis is carried out according to equation 4.11. With the calculated regression parameters new q values can be calculated using equation 4.10. Comparing measured and calculated q in an x-y graph, two conditions must be satisfied in the x-y regression ($y = a{\cdot}x + b$): parameter 'a' must be one and the parameter 'b' must be zero. By trial and error a q_0 is found for which these conditions are satisfied. The thus obtained q_0 appears to be very inaccurate and in most cases larger than the actual solid phase cadmium-content, which is not permitted. Therefore we rejected this method for estimation of q_0.

The second best option is to take q_0 equal zero. Probably q_0 is not zero in our soil samples. The initial cadmium content before pollution, 100 years ago, is very low. The soil is contaminated with cadmium till present. Presumably the additional adsorbed cadmium is more or less reversibly bound in the soil. If q_0 is taken zero the parameters K_F and 'n' in batch experiments will predict a higher K_F-value and a lower 'n'-value than when q_0 has a finite value.

4.3. Results and discussion

4.3.1. Soil characterization

The chemical characteristics of the three samples are presented in Table 4.III. Adsorption of cadmium on oxides of aluminium, iron and manganese is not expected. The clay fraction (particles below 2 μm) is less than 0.5 percent. Most particles are in the fraction 125 to 250 μm (Wilkens and Loch, 1995).

Table 4.III. Soil sample characterization.

	Sample 1 (A-horizon)	Sample 2 (Bh-horizon)	Sample 3 (C-horizon)
o.m. [% $g.g^{-1}$]	3.98	6.73	0.31
pH_{soil}	4.76	4.17	5.12
Al_2O_3 [% $g.g^{-1}$]	1.58	1.94	1.91
Fe_2O_3 [% $g.g^{-1}$]	0.22	0.18	0.32
MnO_2 [% $g.g^{-1}$]	0.0050	0.0037	0.0039
Cd [$\mu g.g^{-1}$]	3.12	3.64	0.37
Zn [$\mu g.g^{-1}$]	41.89	27.55	15.67

o.m. = organic matter content.

4.3.2. Sorption experiments

In Figures 4.1, 4.2 and 4.3 the sorption data of the batch experiments are presented. Adsorption of cadmium by acidic sandy soils can be described by the Freundlich isotherm (Eq. 4.2). The solid lines are the best fitting adsorption isotherms according to Freundlich's model. The values of K_F and n are tabulated in Table 4.IV.

The competition effect of zinc is evident in the experiments at pH_{sb} (the Figures 4.1a, 4.2a and 4.3a). Higher zinc concentrations up to 40 $\mu g.ml^{-1}$ are used in these experiments. Zinc addition to the batch solution will cause lower K_F adsorption parameters.

Table 4.IV. K_F and n values for Cd derived from sorption batch experiments (K_F in [$\mu g^{1-n}.ml^n.g^{-1}$], n [-]).

		Sample 1		Sample 2		Sample 3	
	Zn μg/ml	K_F	n	K_F	n	K_F	n
pH_{sb} not altered	0	9.36	0.50	15.38	0.45	1.93	0.45
	4	8.16	0.55	13.95	0.45	1.66	0.58
	40	6.47	0.66	11.82	0.51	1.57	0.43
pH=4	0	16.05	0.60	22.80	0.58	6.33	0.67
	0.4	16.46	0.66	22.79	0.59	6.26	0.70
	4	14.42	0.63	22.81	0.70	6.15	0.74
pH=3	0	9.13	0.67	15.64	0.66	2.64	0.55
	0.4	8.95	0.60	16.69	0.67	2.91	0.61
	4	8.69	0.63	17.31	0.77	2.66	0.66

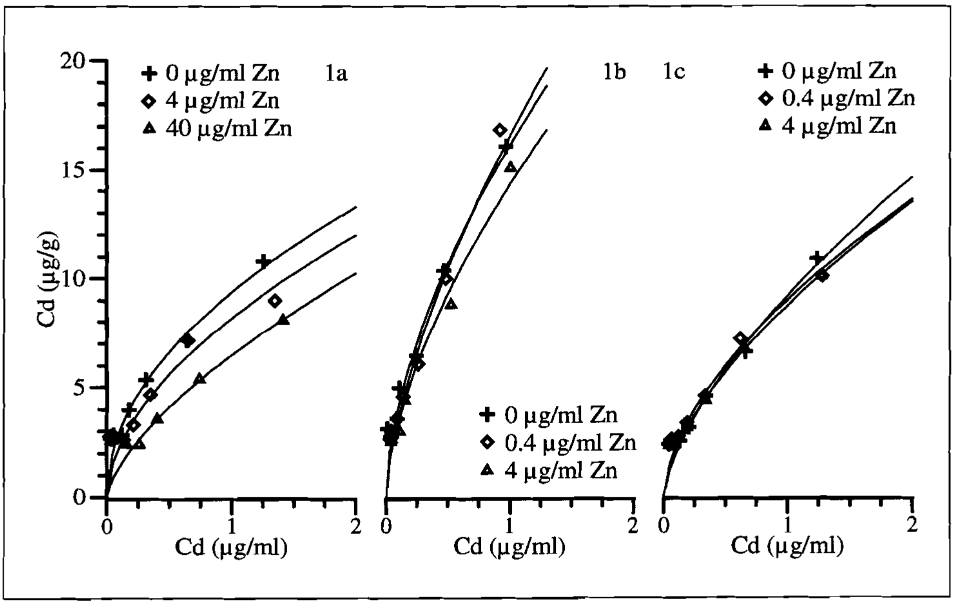

Figure 4.1. Sorption of cadmium on soil sample 1 at different pH and zinc levels in solution. Graph a, pH = pH_{sb}; graph b, pH = 4.3; graph c, pH = 3.6.

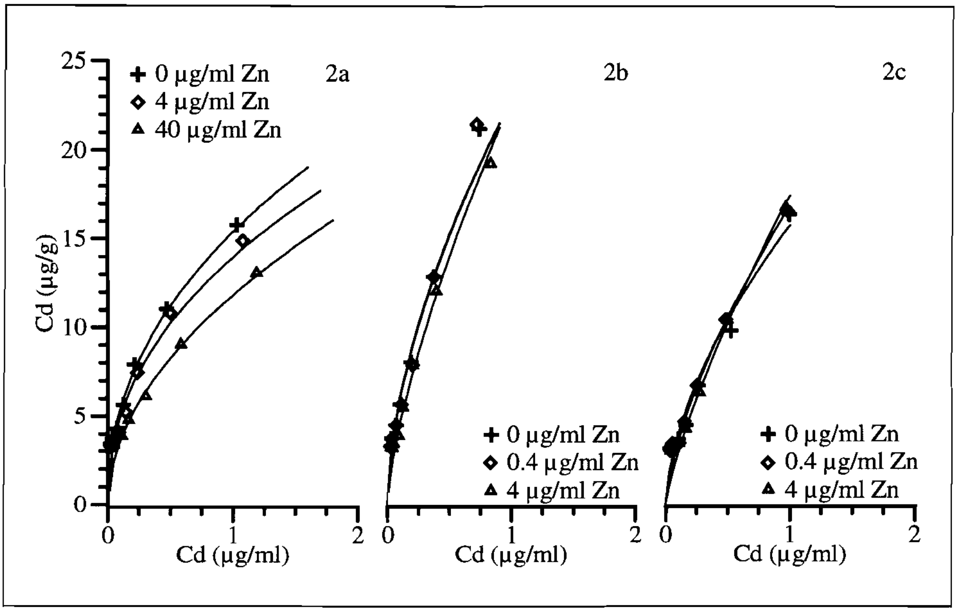

Figure 4.2. Sorption of cadmium on soil sample 2 at different pH and zinc levels in solution. Graph a, pH = pH_{sb}; graph b, pH = 4.3; graph c, pH = 3.6.

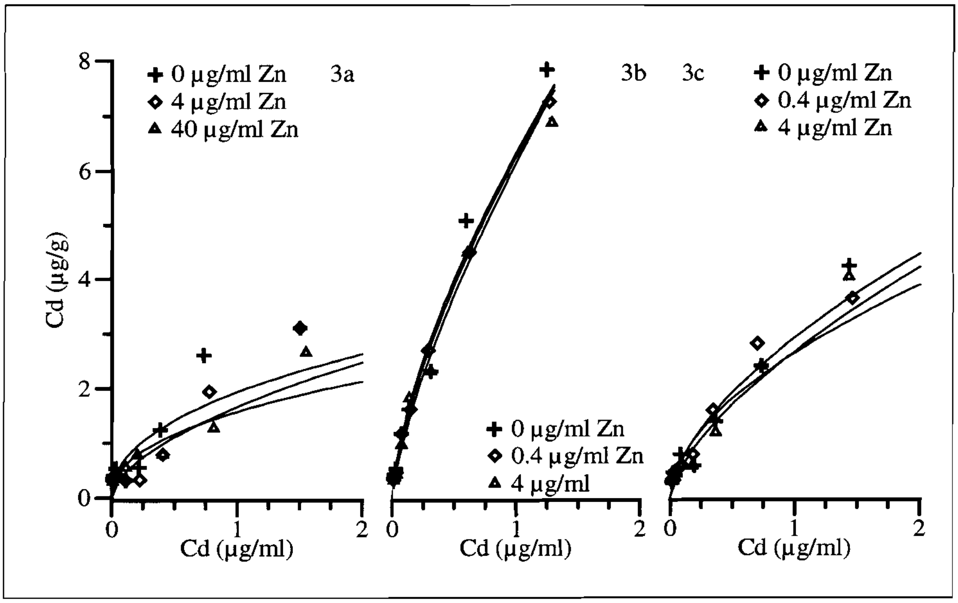

Figure 4.3, Sorption of cadmium on soil sample 3 at different pH and zinc levels in solution. Graph a, pH = pH_{sb}; graph b, pH = 4.3; graph c, pH = 3.6.

The pH effect is experimentally introduced in the batch solutions. The results of the sorption experiments are presented in Figures 4.1, 4.2 and 4.3, the experiments at pH = 4.3 demonstrate larger cadmium adsorption than at pH = 3.6. This is reflected in the K_F values in Table 4.IV. A lower pH decreases the amount of cadmium sorbed on the soil. This is caused by increasing proton activity and concentrations of aluminium in solution, which compete with cadmium for sorption sites on the solid surface. In addition an increasing proton activity results in a decrease of the negative charge of the adsorbate (Garcia-Miragaya & Page, 1978). The pH-values at the individual data points of graphs 'a' of Figures 4.1 to 4.3 are not constant. Higher cadmium addition led to lowered equilibrium pH. This influenced curvature of the sorption isotherms.

The differences in sorption behaviour between the samples can be ascribed to the difference in organic matter content. Sample 2 (Bh horizon) exhibits the largest adsorption, which corresponds with the highest organic matter content. Sample 3 (C-horizon) has the lowest K_F value and the lowest organic matter content.

4.3.3. Standardization of the K_F parameter

The sorption data are divided in the two groups mentioned before. When plotting the data of Figures 4.1 to 4.3 on a larger scale at low concentrations it can be seen that the desorption data points are not very well described by the Freundlich equation. Therefore only the adsorption data are used in the regression analysis to obtain the parameters of Equation 4.10 with the linearized regression Equation 4.11. To determine K_{sc} and the exponents a, b and n, we carried out a m.l.r.a. by computer. The pH is converted to the proton activity.

The results of the m.l.r.a. are plotted in Figure 4.4, 4.5 and 4.6 and tabulated in Table 4.V. The difference in the number of observations (N in Table 4.V) is caused by the difference in the number of batch experiments where adsorption actually is observed. The calculated cadmium adsorption is plotted versus the measured cadmium content in the three soil-horizons. We also added the previously discarded desorption data in the figures. For samples 1 and 2 the "fit" of the regression is fairly good, for both soils correlations in the *adsorption* data of 0.96 are calculated. The fit for sample 3 is not as good. An explanation is, that the adsorption on sample 3 is not as high as on samples 1 and 2, as a result of low organic matter content. Any error in the measurements or an inhomogeneous sample have a big impact on the final results of sample 3.

Table 4.V. Results of the m.l.r.a.

	m.l.r.a.	R	a	b	n	K_{sc}
			Zn^{2+}	H^+	Cd^{2+}	
Sample 1 (N=35)	I	0.62			0.44 0.06	9.42
	II	0.90		-0.39 0.04	0.62 0.04	0.31
	III	0.96	-0.13 0.02	-0.36 0.03	0.64 0.02	0.49
Sample 2 (N=42)	I	0.84			0.56 0.04	16.46
	II	0.94		-0.47 0.05	0.63 0.02	0.33
	III	0.96	-0.06 0.02	-0.39 0.05	0.63 0.02	0.64
Sample 3 (N=54)	I	0.74			0.54 0.04	3.01
	II	0.85		-0.35 0.06	0.58 0.04	0.12
	III	0.88	-0.11 0.03	-0.34 0.05	0.61 0.03	0.14

a, b, n = regression parameters,
N = number of observations involved in the regression,
I, II, III = three types of regression:
I only cadmium concentration is used in l.r.a.,
II concentrations of cadmium and H^+ are used in m.l.r.a.,
III the whole regression Equation 4.11 is used,
The small numbers are the errors in the regression estimations.

The data points below the line "initial cadmium", the *desorption* data points, show a deviation from the "1:1 fit" (Figures 4.4 to 4.6). This indicates that another mechanism is active when desorption occurs instead of adsorption. This may be ascribed to a phenomenon of hysteresis, since the cadmium which is adsorbed for some decades has made a tight bond with the soil, i.e. by relocation of the cadmium cation. This can be lattice bound or specifically bound cadmium, but these bond-types can not be distinguished by the used experiments.

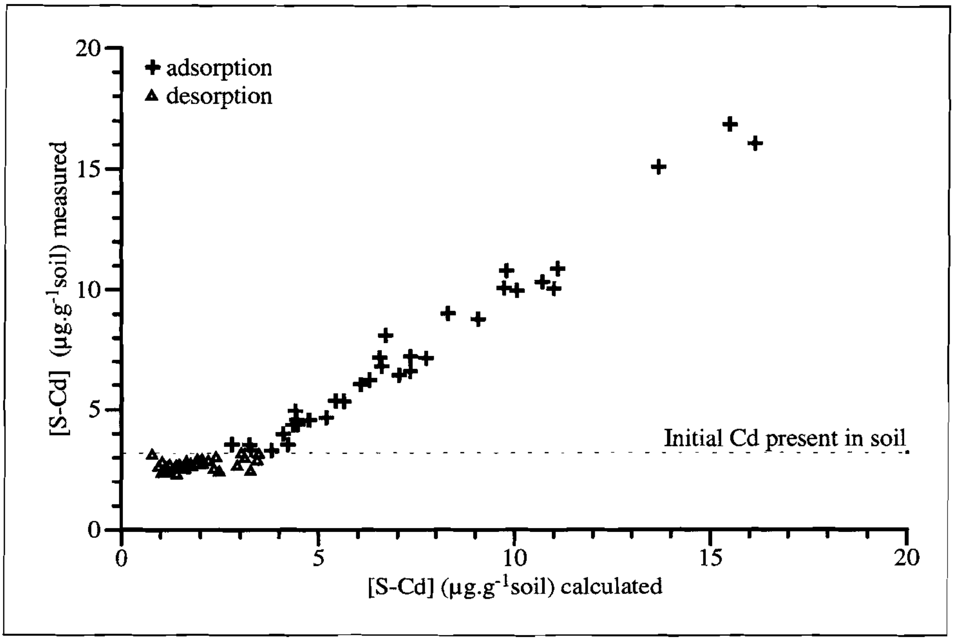

Figure 4.4. Results of regression of soil sample 1 (A-horizon). Calculated data are plotted versus the measured data. S-Cd is the adsorbed amount of cadmium.

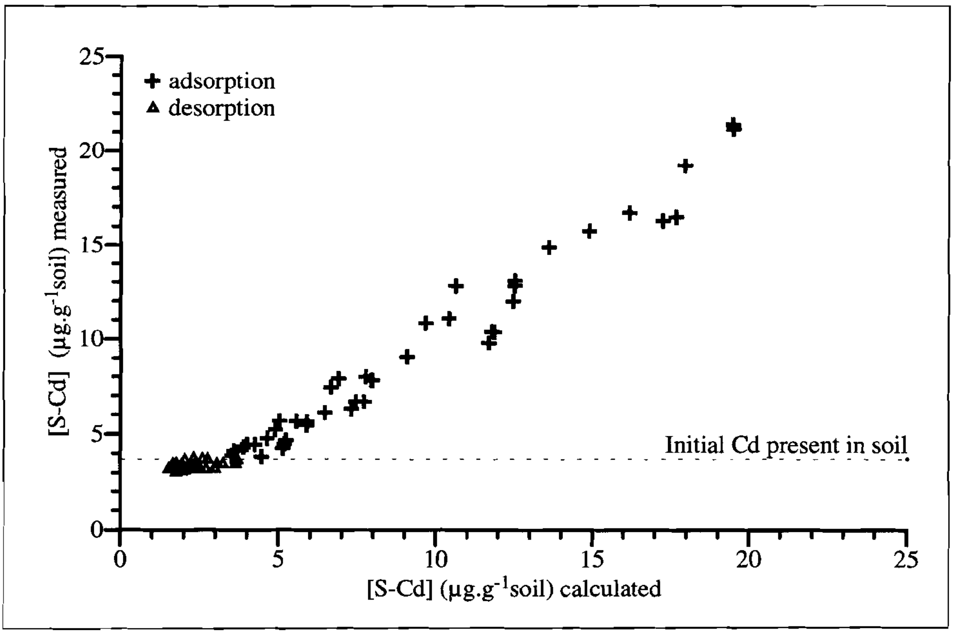

Figure 4.5. Results of regression of soil sample 2 (Bh-horizon). Calculated data are plotted versus the measured data. S-Cd is the adsorbed amount of cadmium.

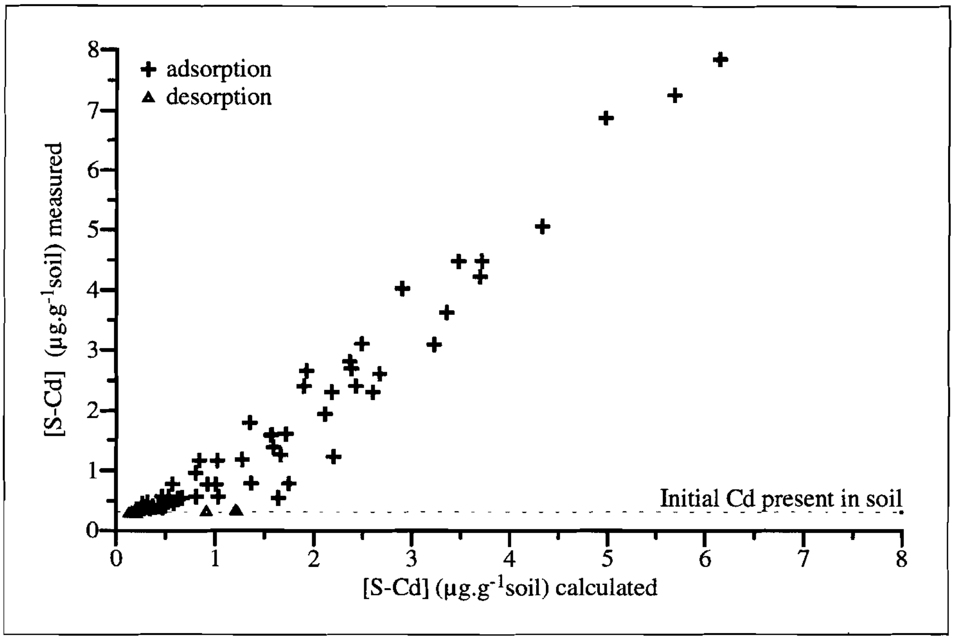

Figure 4.6. Results of regression of soil sample 3 (C-horizon). Calculated data are plotted versus the measured data. S-Cd is the adsorbed amount of cadmium.

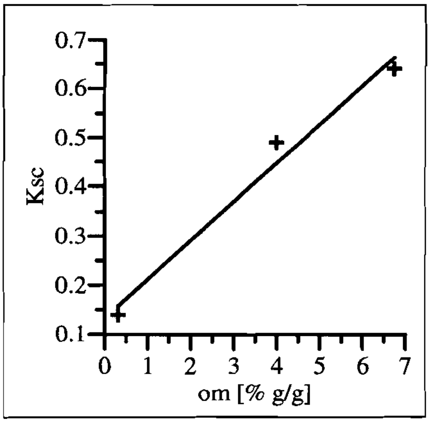

Figure 4.7. Relation between organic matter content and K_{sc}.

Whereas the exponents in Equation 4.10 (a, b and n) are very similar for the different soil-horizons, the K_{sc}-values are different. This is caused by differences of solid organic matter content of the three soil-horizons. Soil sample 2 has the highest organic matter content, which reflects the highest K_{sc}, and vice versa for soil sample 3 (Figure 4.7). In these sandy soils of low pH, organic matter is the most important sorption substrate (Wilkens and Loch, 1995). Other substances are not very important, since clay minerals are almost absent in these soils and at a low pH oxides mostly have a positive surface charge. The organic matter content is not incorporated in Equation 4.10, because only three soil samples are used, consequently three levels of organic matter content are available.

The negative values for a and b indicate a competing effect in the adsorption of cadmium in these soils. The proton competition is stronger than that of zinc. This can be explained by the different bonding types with these ions. For a pH drop of one unit a decrease in K_F of respectively. 56, 59 and 54 % is calculated for the three soil samples according to Equation 4.9. For a tenfold increase of the zinc concentration, K_F decreases with only 26, 13 and 22 % for samples 1, 2 and 3 respectively.

4.4. Conclusions

Adsorption data almost perfectly fit the presented model. An increase in the zinc solute concentration or proton activity will result in a decrease in sorption density of cadmium. Zinc and protons compete for the cadmium sorption sites. The proton competition is almost 2 to 3 times stronger than of zinc. The organic matter content of the three soil-horizons can explain the variation in magnitude of the scaled Freundlich adsorption coefficients; both are positively correlated.

Desorption data do not fit well to the proposed model. This may be explained by different causes. The assumption that no irreversibly bound cadmium is present in the soil solid may be not correct. Nevertheless it is obvious that the total cadmium initially present in the contaminated soil solids, will not reversibly desorb according to the Freundlich adsorption model.

References

Anderson, P.R. and T.H. Christensen (1988).
Distribution coefficients of Cd, Co, Ni, and Zn in soils.
Journal of Soil Science **39**: 15-22.

Barrow, N.J., J. Gerth and G.W. Brümmer (1989).
Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. II. Modelling the extent and rate of reaction.
Journal of Soil Science **40**: 437-450.

Benjamin, M.M. and J.O. Leckie (1981).
Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide.
Journal of Colloid and Interface Science **79**(1): 209-221.

Black, C.A. (1965).
Methods in soil analysis, Part two, chemical and microbiological properties.
American Society of Agronomy, Madison, Wisconsin, U.S.A.

Boekhold, A.E. (1992).
Field scale behaviour of cadmium in soil.
Thesis, Agricultural University Wageningen, the Netherlands.

Borland (1992).
Quatro pro 4, computer program. Borland International Inc, U.S..

Chardon, W.J. (1984).
Mobiliteit van cadmium in de bodem.
Thesis, Agricultural University Wageningen, the Netherlands.

Christensen, T.H. (1984).
Cadmium soil sorption at low concentrations: I. Effect of time, cadmium load, , and calcium.
Water, Air, and Soil Pollution **21**: 105-114.

Christensen, T.H. (1987).
Cadmium soil sorption at low concentrations: VI. A model for zinc competition.
Water, Air, and Soil Pollution **34**: 305-314.

Christensen, T.H. (1989).
Cadmium soil sorption at low concentrations: VIII. Correlations with soil parameters.
Water, Air, and Soil Pollution **44**: 71-82.

de Haan, F.A.M., S.E.A.T.M. van der Zee and W.H. van Riemsdijk (1987).
The role of soil chemistry and soil physics in protecting soil quality: variability of sorption and transport of cadmium as an example.
Netherlands Journal of Agricultural Science **35**: 347-359.

del Castilho, P. and W.J. Chardon (1993).
Effect of pH on cadmium uptake by some field crop.
Conference proceeding: heavy metals in the environment, Toronto, Canada.

Eriksson, J.E. (1989).
The influence of pH, soil type and time on adsorption and uptake by plants of Cd added to the soil.
Water, Air, and Soil Pollution **48**: 317-335.

García-Miragaya, J. and A.L. Page (1978).
Sorption of trace quantities of cadmium by soils with different chemical and mineralogical composition.
Water, Air, and Soil Pollution **9**: 289-299.

Gerritse, R.G. and W. van Driel (1984).
The relationship between adsorption of trace metals, organic matter, and pH in temperate soils.
Journal of Environmental Quality **13**(2): 197-204.

Miller, W.P., W.W. McFee and J.M. Kelly (1983).
Mobility and retention of heavy metals in sandy soils.
Journal of Environmental Quality **12**(4): 579-584.

Scokart, P.O., K. Meeus-Verdinne and R. de Borger (1983).
Mobility of heavy metals in polluted soils near zinc smelters.
Water, Air, and Soil Pollution **20**: 451-463.

Sims, J.T. (1986).
Soil pH effect on the distribution and plant availability of manganese, copper, and zinc.
Soil Science Society of America Journal **50**: 367-373.

Wilkens, B.J. and J.P.G. Loch (1995).
Accumulation of cadmium and zinc from diffuse immission on acid sandy soils, as a function of soil composition.
Water, Air, and Soil Pollution (Submitted for publication).

Photo 3. Landscape seriously affected by pollutants (photo M. Reumers)

5

A one-dimensional approach to predict heavy metal leaching in layered and spatially variable soils

Co-Author: J.P.G. Loch

Abstract

A model is designed to calculate accumulation and leaching of heavy metals in soils. Based on the Freundlich adsorption equation, sorption characteristics are achieved from the soil data, by using linear multiple regression techniques.

Leaching of cadmium and zinc from topsoil to groundwater can be explained by soil type. Sandy soils of relatively low organic matter contents (arenosols) demonstrate a low retardation capacity. Leaching of these metals is extremely fast. Carbic podzols of relatively high organic matter content in the topsoil (4 to 10%) have a higher capacity to adsorb cadmium and leaching to the groundwater is delayed. In spite of differences in type and vulnerability of both soils the groundwater is heavily polluted by cadmium and zinc after more than a century of diffuse industrial immission and breakthrough is complete for these metals. Copper has an extremely high retardation; the leaching of this metal is limited. Breakthrough of copper to the groundwater is not expected within 4000 years of metal percolation. No difference in retardation of copper is observed between arenosol and carbic podzol.

A large field dispersion is observed, if Freundlich adsorption parameters and subsequent leaching are calculated from individual profiles of soil macro parameters. The field dispersion is dependent of the variance in the retardation factors of the individual profiles. Using average retardation factors and their standard deviations to calculate breakthrough in time is an acceptable method to obtain the field dispersion coefficient. This coefficient is orders of magnitude larger than the molecular-diffusion/hydrodynamic-dispersion coefficient derived from grain size and soil structure.

5.1. Introduction

Vulnerability of groundwater for pollution may be defined by the capability of contaminating substances to penetrate through the soil column to the groundwater. On their way down from the soil surface heavy metals will adsorb on soil particles, which will retard their leaching. The continued input of heavy metals on soil through atmospheric deposition will result in an excessive accumulation in the topsoil or an increased leaching to the groundwater. Immission on the soil is both by direct wet and dry deposition and deposition of plant foliage and other dead organic material.

When calculating leaching and accumulation of heavy metals in a soil column, more or less empirical expressions have to be used. Furthermore, still not all complexes, which can be formed, are known. This is especially true for the metal-organic species. Heavy metals in the soil are present in solids and solutions. The solid phases of the metals are precipitates and adsorbed metals. In solution metals exist both as charged and uncharged complexes and free ions.

In the Dutch-Belgian Kempen region three zinc smelters contaminated the surrounding soils heavily with cadmium and zinc (Scokart et al., 1983, Pedroli, 1990, Wilkens and Loch, 1995). The zinc smelters have been active during 110 years.

The aim of this study is to make a quantitative assessment of the heavy metal leaching and mobility. As tool for this assessment a model for vertical metal transport is used. The soil-specific adsorption coefficients are mostly unknown. A model scheme is designed to obtain the soil-specific adsorption coefficients in heterogeneous soils. Subsequently heavy metal leaching can be calculated.

Since only vertical soil passage is considered, a one-dimensional approach is sufficient. Analytical solutions for the one-dimensional convection-dispersion-adsorption equation are available only for linear adsorption isotherms assuming a constant distribution of species between solids and solution and a soil profile with homogeneous adsorption properties. For that reason a numerical technique for solving the transport equation is chosen.

5.2. Model description

The immission fluxes are unknown for the period before 1980. This early period is characterized by high zinc and cadmium emissions from the pyrometallurgic zinc plants. For the period after 1980 some immission data are available (LISEC, 1989), including immissions close to one of our research field. The lacking immission data for the model calculations can be obtained by the following procedure.

The model scheme (Figure 5.1) is based on the assumption that the whole soil profile is in equilibrium and has reached steady state with respect to metal distribution through the profile, which implies that the metal input is equal to the metal output. This hypothesis is tested in the model scheme. If the hypothesis is valid, the heavy metal concentration in the groundwater (metal output) is assumed to be equal to the heavy metal in the infiltrating water (metal input).

We use the data sets of chapters 2 and 3. Chapter 2 describes the soil and chapter 3 the groundwater. The soil and groundwater are sampled in four fields. Each field contains nine soil profiles and four groundwater sample points arranged in respectively a quadrangular grid (grid: 20 meters) and a square (30 meters). The soil is sampled at ten depths (field 1, 2 and 3) or eleven depths (field 4) and the groundwater is sampled eight times within one year. We distinguish site profiles and field profiles: a **site profile** is an individual sampled profile at ten or eleven depths, a **field profile** is an average profile based on nine individual site profiles.

The collected data are passed through the model scheme of Figure 5.1 to obtain adsorption profiles and leaching characteristics of the heavy metals cadmium, copper, nickel and zinc. The adsorption profiles present the Freundlich constant K_F versus depth. For cadmium the Freundlich isotherm (Equation 5.9) is taken, with exponent n of 1.00 and 0.75 respectively. Cadmium at low concentration is found to adsorb according to the Freundlich isotherm, where n is set to 0.75 (Christensen, 1985, chapter 4 of this thesis). For the metals copper, nickel, and zinc the parameter n is set at 1.

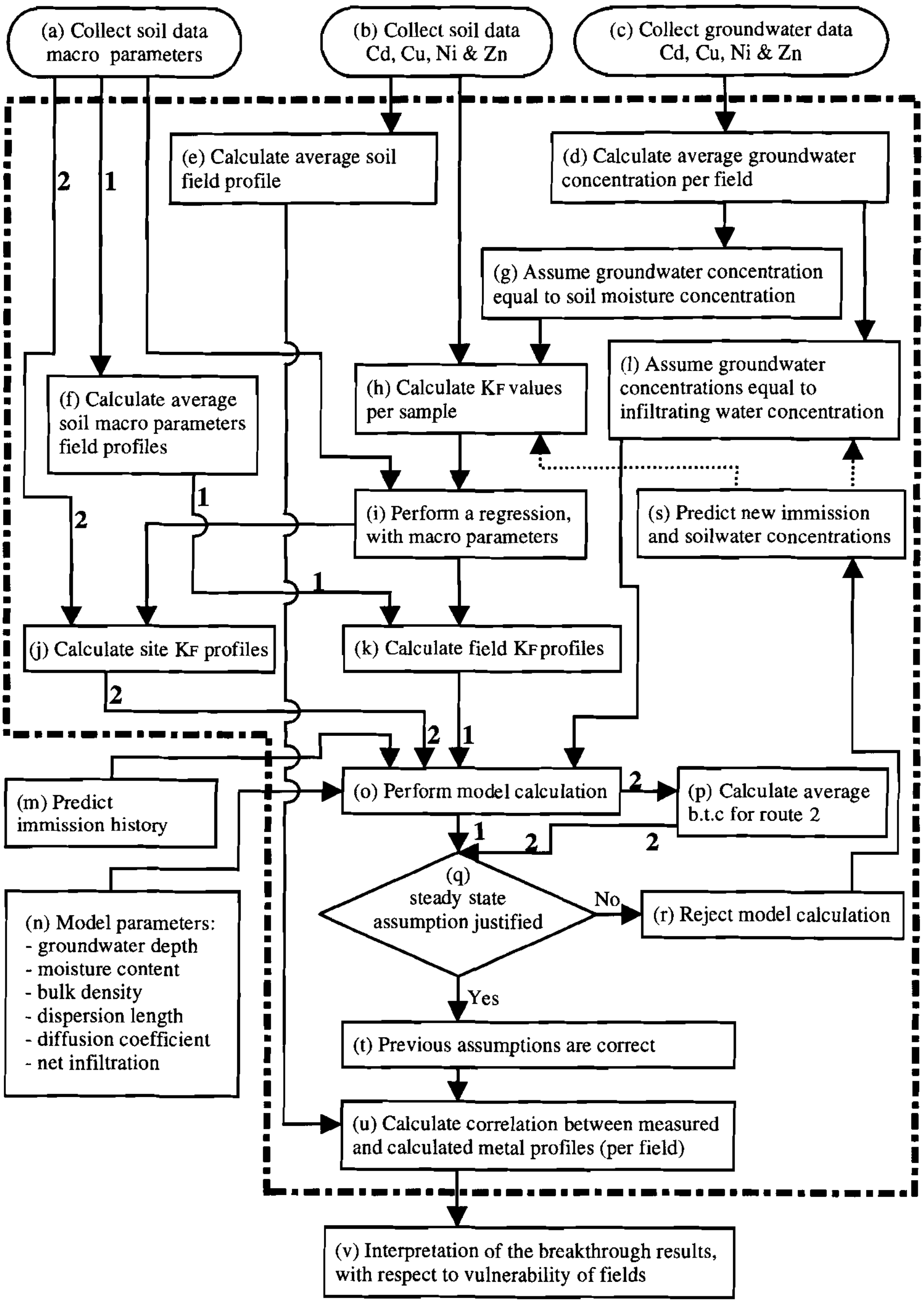

Figure 5.1. Flowchart to obtain adsorption and leaching characteristics.

Description and explanation of the elements in Figure 5.1.

a The soil macro parameters used here are described in chapter 2 of this thesis; they include the aluminium, iron and manganese oxide contents, organic matter content and pH-soil.
(4 fields, 9 sites, 10-11 depths, total 369 values)

b The used cadmium and zinc soil contents are described in chapter 2. The copper and nickel soil contents used are not previously described.
(4 fields, 9 sites, 10-11 depths, total 369 values)

c The groundwater concentrations of heavy metals are described in chapter 3; they include cadmium, copper, nickel and zinc.
(4 fields, 4 sites, 8 times, total 128 values)

d Average groundwater concentration of heavy metals are calculated for all metals and each field (Table 5.I). These concentrations are acquired by taking an average of four sites and eight sampling times (Eq. 5.1).

$$\overline{c}_f = \frac{\Sigma_{t=1}^{8} \Sigma_{s=1}^{4} c_{t,s,f}}{32} \qquad (5.1)$$

where:

$\overline{c}_f$ = average concentration of heavy metal in groundwater in field f [μg.cm^{-3}],

$c_{s,t,f}$ = concentration of heavy metals in groundwater on site s, at time t, and in field f [μg.cm^{-3}].

(4 fields, total 4 values, Table 5.I)

Table 5.I. Average groundwater concentrations of Cd, Cu, Ni and Zn [μg.cm^{-3}] in fields 1 to 4, in the period November 1991 to November 1992.

field	Cd	Cu	Ni	Zn
field 1	0.048	0.0031	0.023	4.6
field 2	0.071	0.0101	0.016	6.5
field 3	0.033	0.0046	0.023	7.5
field 4	0.026	0.0030	0.008	2.1

e Average soil contents of heavy metals are calculated for each depth and for all heavy metals, within a field, i.e. an average at all depths of nine sites (see also chapter 2).

$$\overline{m}_{z,f} = \frac{\Sigma_{s=1}^{9} m_{s,z,f}}{9} \tag{5.2}$$

where:

$\overline{m}_{z,f}$ = average heavy metal content at depth z and in field f [μg.g^{-1}],

$m_{s,z,f}$ = heavy metal content on site s, at depth z and in field f [μg.g^{-1}].

(4 fields, 10-11 depths, total 41 values)

f Average soil macro parameter contents are calculated, within a field, i.e. an average at all depths of nine sites (see also chapter 2).

$$\overline{x}_{z,f} = \frac{\Sigma_{s=1}^{9} x_{s,z,f}}{9} \tag{5.3}$$

where:

$\overline{x}_{z,f}$ = average content of soil macro parameter x at depth z and in field f,

$x_{s,z,f}$ = content of soil macro parameter x on site s, at depth z and in field f.

(4 fields, 10-11 depths, total 41 values)

g At the assumption of a steady state soil profile of heavy metals, the soil moisture concentration may be taken constant (c) (Table 5.I) in the whole soil profile within a field (Equation 5.1).

(4 fields, total 4 values, Table 5.I)

h For each soil sample the *in situ* K_F is calculated, using the logarithmic form of the Freundlich equation with the assumption for the value of n (i.e. n=1.00 or n=0.75).

$$\ln K_F = \ln q - n \times \ln(c) \tag{5.4}$$

where:

K_F = Freundlich adsorption parameter,

q = metal content in solid phase [μg.g^{-1}],

n = Freundlich exponent [-],

c = metal moisture concentration [μg.cm^{-3}].

(4 fields, 9 sites, 10-11 depths, total 369 values)

i A multiple linear regression analysis is carried out with the soil macro parameters and K_F, using all data. The regression equation has the form:

$$\ln K_F = \ln K_{sc} + a \cdot \ln(om) + b \cdot \ln\{H^+\} + c \cdot \ln(Al_2O_3) + d \cdot \ln(Fe_2O_3) + e \cdot \ln(Mn) \qquad (5.5)$$

where:
K_{sc} = scaled adsorption parameter, i.e. independent of the soil parameters,
a, b, c, d, e = regression parameters,
om = organic matter content [% g.g^{-1}],
$\{H^+\}$ = proton activity [mol.l^{-1}] rewritten from pH_{soil},
Al_2O_3 = aluminium oxide content in the soil [% g.g^{-1}],
Fe_2O_3 = iron oxide content in the soil [% g.g^{-1}],
MnO_2 = manganese oxide content in the soil [% g.g^{-1}].

If a regression parameter is below 0.2, the soil macro parameter is dropped from the regression equation and the regression analysis is repeated without this parameter. The results of the regression analysis are presented in Table 5.II.

(4 fields, 9 sites, 10-11 depths, total 369 values)

Table 5.II. Parameters and correlations of the regression analysis.

	n	K_{sc}	a (o.m.)	b (H^+)	c (Al_2O_3)	d (Fe_2O_3)	e (MnO_2)	R
Cd	0.75	0.271	1.077	-0.239	-	-	-	0.842
Cd	1.00	0.645	1.084	-0.230	-	-	-	0.841
Cu	1.00	1376	0.501	-	-	0.619	-	0.590
Ni	1.00	4285	-	-	-	-	0.458	0.345
Zn	1.00	131	0.586	-	-	0.306	0.540	0.791

The regression parameters of o.m., H^+, Al_2O_3, Fe_2O_3 and MnO_2 are the exponents in equation 5.6, respectively a, b, c, d and e. The factor (n) in Eq. 5.4 is 0.75 non-linear or 1.00 linear adsorption.

j The K_F value is calculated for every depth on each site with the regression parameters obtained under step i. K_F profiles are calculated for every site and for all four heavy metals using Equation 5.6.

$$K_F(z) = K_{sc} \cdot (\{H^+\}(z))^a \cdot (om(z))^b \cdot (Al_2O_3(z))^c \cdot (Fe_2O_3(z))^d \cdot (MnO_2(z))^e \qquad (5.6)$$

where:
$K_F(z)$ = adsorption parameter at depth z.

(4 fields, 9 sites, 10-11 depths, total 369 values)

k The K_F value is calculated on every depth in the field profile with the regression parameters obtained under i using the average soil macro

parameters obtained by Equation 5.3. A K_F profile is calculated for every field and for all four heavy metals, using Equation 5.6.
(4 fields, 10-11 depths, total 41 values)

l At the assumption of a steady state heavy metal soil profile the groundwater concentrations (Table 5.I) may be taken equal to the heavy metal concentration in the infiltrating water (C_{bound}). C_{bound} is the upper boundary concentration in the soil column calculations.
(4 fields, total 4 values, Table 5.I)

m The immission history is hard to trace. We know the zinc industry in this region has been active for 110 years. We assume the emission period of cadmium and zinc and, although with less confidence copper and nickel, also has a length of 110 years.

n The general model parameters are obtained from different sources

- Average groundwater depth is obtained from chapter 3. The distance from topsoil to groundwater level is taken as column length in the model calculations.
- The net infiltration is obtained from meteorological data (chapter 3). A precipitation of 800 $mm.y^{-1}$ is reported, of which 20 % to 25% will finally reach the groundwater. Therefore the net infiltration is taken 0.054 $cm.day^{-1}$.
- The initial heavy metal soil contents are taken zero, this is the situation before pollution. The actual initial content is not zero, but low. The natural background contents of the Kempen region in the topsoil (0-6 cm) are 0.15-0.45 $\mu g.g^{-1}$ for cadmium and 5-15 $\mu g.g^{-1}$ for zinc (Bosman & Paenhuys, 1980).
- Soil moisture content and bulk density are obtained from field measurements, according to standard procedures and are taken constant with depth and time.
- Diffusion coefficient is obtained from Weast (1986) and corrected for tortuosity ($\tau=2$) (Koorevaar et al., 1993) and moisture content (θ). The dispersion coefficient is estimated (Bolt, 1982) on the basis of the soil structure and grain size distribution (Wilkens and Loch, 1995). Total diffusion/dispersion is calculated according to equation 5.7.

$$D = \alpha \frac{Q}{\theta} + \frac{D_{mol}\theta}{\tau} \tag{5.7}$$

where:

D = total diffusion/dispersion coefficient [$cm^2.day^{-1}$],
α = dispersion length [cm],
Q = net infiltration rate [$cm.day^{-1}$],
θ = soil moisture content [$cm^3.cm^{-3}$],
D_{mol} = molecular diffusion coefficient [$cm^2.day^{-1}$],
τ = tortuosity [-].

The general model parameters of physical nature needed for the model calculations are summarized in Table 5.III.

Table 5.III. Physical model parameters.

Parameter	value	units
net infiltration rate	0.054	[$cm.day^{-1}$]
dispersion length	1.0	[cm]
diffusion coefficient	0.864	[$cm^2.day^{-1}$]
moisture content	0.2	[$cm^3.cm^{-3}$]
bulk density	1.5	[$g.cm^{-3}$]
column length	150	[cm]

o The transport of heavy metals in soil is calculated by a one-dimensional transport model. The used model is a slight modification of the model described by Appelo and Postma (1993). Their model describes transport of solutes in a vertical homogeneous soil column. We made some adaptations to the model to serve our purposes. Our altered model can handle adsorption profiles, i.e. it assigns to each node a particular K_F value. A short description and a listing of the changes are given in appendix C.1. The model input consists of the calculated adsorption profile (j or k) (obtained along two different routes, as indicated in Figure 5.1 by the numbers *1* and *2*), the immission data (l), immission history (m) and physical model parameters (n). The calculations will result in a breakthrough curve in time at 150 cm below soil surface (average groundwater level).

p The field breakthrough curve is calculated from nine individual breakthrough curves along route *2*, according to Equation 5.8:

$$\overline{c}_{t,f} = \frac{\sum_{s=1}^{9} c_{s,t,f}}{9} \tag{5.8}$$

where:

$\overline{c}_{t,f}$ = average concentration in breakthrough curve at time t and in field f [μg.cm^{-3}],

$c_{s,t,f}$ = concentration in breakthrough curve on site s, at time t, and field f [μg.cm^{-3}].

q If complete breakthrough is established within the period of immission till present, the assumption of steady state metal profile is justified (i.e. the flux into the column is equal to the flux out of the column). Thus immission is equal to leaching to the groundwater. This statement can be true or false.

r If the statement [q] is false, the steady state assumptions [g] "groundwater concentration is equal to soil moisture concentration" and [l] "groundwater concentration is equal to net infiltration concentration" are not correct. Then model calculations are not suitable and must be rejected.

s New immission data must be obtained from literature (e.g. LISEC, 1989). Also sorption data for heterogeneous or layered soils must then be achieved in other ways (e.g. Boekhold, 1992). The purpose of the subsequent simulation then is not verifying steady state, but to predict breakthrough time.

t If statement [q] is true, the steady state assumptions [g] "groundwater concentration is equal to soil moisture concentration" and [l] "groundwater concentration is equal to net infiltration concentration" are correct. The model calculation can be accepted.

u With the K_F profiles obtained under j and k the heavy metal profiles are calculated using Freundlich adsorption Equation 5.9.

$$q_z = K_F(z) \cdot c_z^n \tag{5.9}$$

where:
$K_F(z)$ = Freundlich adsorption parameter at depth z,
q_z = metal content in solid phase at depth z [μg.g^{-1}],
c_z = metal moisture concentration at depth z[μg.cm^{-3}].

The calculated heavy metal profiles can be compared with the measured soil profiles (Figures 5.5, 5.6, 5.9 and 5.10).

v The interpretation of the model data will be described in section 5.3

Two pathways through the scheme (Figure 5.1) are distinguished to calculate field breakthrough curves: route *1*, via [a] [f] [k] [o], route *2*, via [a] [j] [o] [p]. In route *1* the transport model used the field K_F profiles. In route *2* the transport model used the individual site K_F profiles; this is the most extensive route. Copper and nickel are only calculated according to route *1* and cadmium and zinc are calculated along routes *1* and *2*. If the condition of steady state in the whole field profile must be satisfied, all individual sites must be in steady state. Therefore route *2* is the only valid route to determine complete breakthrough, for steady state at all individual sites.

5.3. Results and discussion

5.3.1. Mobility of cadmium and zinc

Figures 5.2 and 5.3 present the field breakthrough curves (b.t.c.) for cadmium for linear and non-linear adsorption for all four fields. Figure 5.4 presents the field breakthrough curves for zinc for all fields. For each field average field breakthrough curves are calculated along route *1* (thin line) and along route *2* (bold line). Breakthrough is established within the immission time for both cadmium and zinc (Figures 5.2 to 5.4). The breakthrough of zinc is complete along route *2* (zinc reaches its immission concentration). Therefore the steady state assumptions for the model calculations of zinc are accepted. For cadmium the breakthrough along route *2* in field 3 is complete, breakthrough in fields 2 and 4 is beyond 95%.

In field 1 the field breakthrough is 89% of its immission concentration after 110 years of percolation. This is acceptable for our purpose, and the steady state assumptions for the cadmium model calculations are not rejected. Eight individual sites have reached complete breakthrough. In one individual site of field 1 even initial breakthrough according to route *2* is not yet established. At this site the breakthrough at $c = \frac{1}{2}c_0$ will be expected after 160 years of percolation and final breakthrough after 200 years. Therefore field breakthrough is 89% after 110 years of percolation.

The differences in final breakthrough concentrations are caused by the differences in the immission concentrations, which actually are the average groundwater concentrations in the particular field. Therefore the differences in the final breakthrough concentrations between the fields may not be interpreted.

Compared with the thin lines the bold line b.t.c.'s demonstrate an increased field dispersion, which is caused by a variation in the total retardation between the nine soil profiles within a field. This variance adds an additional dispersion to the hydro-dynamic dispersion coefficient (see also section 5.3.3). It is obvious that, by taking average K_F-profiles along route *1*, the original soil heterogeneity will be smoothed.

The cadmium breakthrough time at $c = \frac{1}{2}c_0$, along route *2*, for linear adsorption is 70 years after start of percolation for both fields 2 and 4. For non-linear adsorption this breakthrough point occurs at 65 and 85 years respectively. For field 1 this point is earlier, 60 years after the start of percolation and for field 3 only 35 years in both adsorption models. Consequently field 3 is the most vulnerable soil for groundwater pollution with respect to cadmium. Leaching in this soil is extremely rapid. This observation is explained by the soil type. The soil in field 3 is classified as an arenosol and has a remarkably low organic matter content in the whole soil profile, which is the main adsorption substrate for cadmium (see regression parameters in Table 5.II). The soils of fields 2 and 4 are both carbic podzols, with relatively high organic matter content in the topsoil (4 to 10%). Consequently the carbic podzols demonstrate a higher capability to adsorb cadmium in the topsoil and a delayed leaching to the groundwater. However, in almost all soil profiles the cadmium front (at $c = \frac{1}{2}c_0$) has reached the groundwater level at 1.5 meters below soil surface. In spite of the differences in soil type and vulnerability the groundwater is heavily polluted after 100 years of percolation.

The same observations apply for zinc along routes *1* and *2*. The zinc breakthrough time, where $c = \frac{1}{2}c_0$, is between 40 and 50 years of percolation for all four fields. Complete breakthrough is established within 90 years of percolation for all fields, consequently the groundwater is contaminated with high concentrations zinc. No significant differences in leaching behaviour are observed between the fields or soil types.

Another remarkable point is the extremely rapid first breakthrough in fields 1 and 3 for both cadmium and zinc calculated along route *2*. A couple of individual sites in these fields have reached complete breakthrough within a percolation period of 25 years.

The differences in behaviour, along route *1*, at linear and non-linear cadmium adsorption are the shape of the breakthrough curves and in some cases the time when $c = \frac{1}{2}c_0$. The b.t.c. at linear adsorption is symmetric relative to the point $c = \frac{1}{2}c_0$. The b.t.c. at non-linear adsorption is not symmetric, low concentrations exhibit a higher retardation (initial breakthrough is later than for linear adsorption) and high concentrations exhibit a lower retardation. This results in a breakthrough curve with a steeper slope, which is obvious in field 2 and 4. Along route *2*, the differences are limited to the angular shape in the b.t.c. at non-linear adsorption and a more smoothed b.t.c. at linear adsorption.

Figures 5.5 and 5.6 represent the field soil profiles of respectively cadmium and zinc. The measured contents are compiled from chapter 2 (Wilkens and Loch, 1995). The lines are the new calculated contents according to the previously described model along route *2*. For both cadmium and zinc the fit is satisfactory, this is also confirmed by high regression correlations (Table 5.II).

In the field profiles of cadmium (Figure 5.5) small discrepancies are observed between the linear and non-linear adsorption model profile calculations. The explanation might be that the linearization of the Freundlich equation ($n=1$ in Equation 5.4) is done in the narrow concentration domain 0.026 to 0.071 $\mu g.cm^{-3}$. These are maximum concentrations, which the solute can reach and at these maximum concentrations the linearization is done. The calculated K_F at $n = 1.00$ is different from K_F at $n = 0.75$, resulting in other regression parameters (Table 5.II). The two sorption models have their point of intersection between 0.026 to 0.071 $\mu g.cm^{-3}$. At cadmium solute concentrations below this point the non-linear model predicts more adsorbed cadmium than the linear model, and vice versa for concentrations above this point. This phenomenon is clearly visible in the field profiles (Figure 5.5): at the highest solute concentration (Field 2, 0.071 $\mu g.cm^{-3}$) the non-linear model predicts less adsorbed cadmium than the linear model. At the lowest solute concentration (Field 4, 0.026 $\mu g.cm^{-3}$) the non-linear model predicts more adsorbed cadmium than the linear model, in accordance with our previous remark.

Table 5.IV presents the total measured and calculated soil accumulation (along route *2*) for the elements cadmium and zinc. For both elements the model calculates an under-estimation of the metal accumulation in the total soil profile. Only calculated zinc in field 3 results in an over-estimation in comparison to the measured contents. The under-estimation of cadmium and zinc is pronounced at high heavy metal contents in the profiles (Figures 5.5 and 5.6).

Table 5.IV. Total cadmium and zinc accumulation measured and calculated.

field	1		2		3		4	
	M	C	M	C	M	C	M	C
Cd	72	61	139	108	36	23	100	52
Zn	4879	4448	8956	8160	5962	8387	3286	2121

Accumulation in $\mu g.cm^{-2}$, for the depth: 0 to 150 cm below soil surface,
M = measured field accumulation,
C = calculated field accumulation.

5.3.2. Mobility of copper and nickel

Figures 5.7 and 5.8 present the field breakthrough curves for copper and nickel for all four fields calculated only along route *1*. Most obvious is the extremely high retardation of both metals. Copper retardation is about the same in all fields: first breakthrough occurs after 4000 years of percolation and complete breakthrough after 9000 years. If we assume the copper and nickel immission starts with the foundation of the local industry, it is clear that breakthrough is not established within the immission time (110 years). Consequently the steady state assumptions and model calculations must be rejected. Nevertheless a qualitative assessment of copper and nickel mobility can be made. The relatively high copper and nickel adsorption parameters will result in high retardation factor and low mobility. Leaching of nickel and copper to the groundwater will not cause environmental problems in the near future.

Figures 5.9 and 5.10 represent the field soil profiles of respectively copper and nickel. The lines are the calculated profiles according to the previously described rejected assumptions, calculated along route *1*. The field profiles of copper fit reasonably at greater depth with the measured field profiles, but not as good as for cadmium and zinc. The mismatch between copper calculated and measured is striking in the topsoil, there is a systematic under-estimation of the copper soil content (Figure 5.9).

A new approach to this problem will be introduced. The assumption "the whole profile is in steady state" is abandoned. The copper contents in the lower part of the profiles and the groundwater are assumed both natural background values. The model calculations for copper are done with immission concentrations, which are actually background concentrations. These background contents and concentrations exist probably for thousands of years. The measured contents of copper in the topsoil are much higher than the calculated soil contents (natural background), this may point at raised immissions in the last 110 years. If the soil immission is five to ten times higher and starts 110 years ago, the model will fit well in the topsoil and the subsoil, consequently the last assumption of non-steady state is true. The infiltrating front of elevated copper concentration has reached approximately the layer 5 to 10 cm below soil surface.

The fits between nickel measured and nickel calculated are unsatisfactory, which is expected, because the assumptions of steady state are not true for all fields. Another explanation is that the nickel correlation in the regression equation is very low, i.e. 0.345 (Table 5.II) and nickel has a regression parameter only for the manganese contents (Table 5.II), whereas the manganese content in the soil are extremely low. Therefore manganese content is not a robust soil parameter.

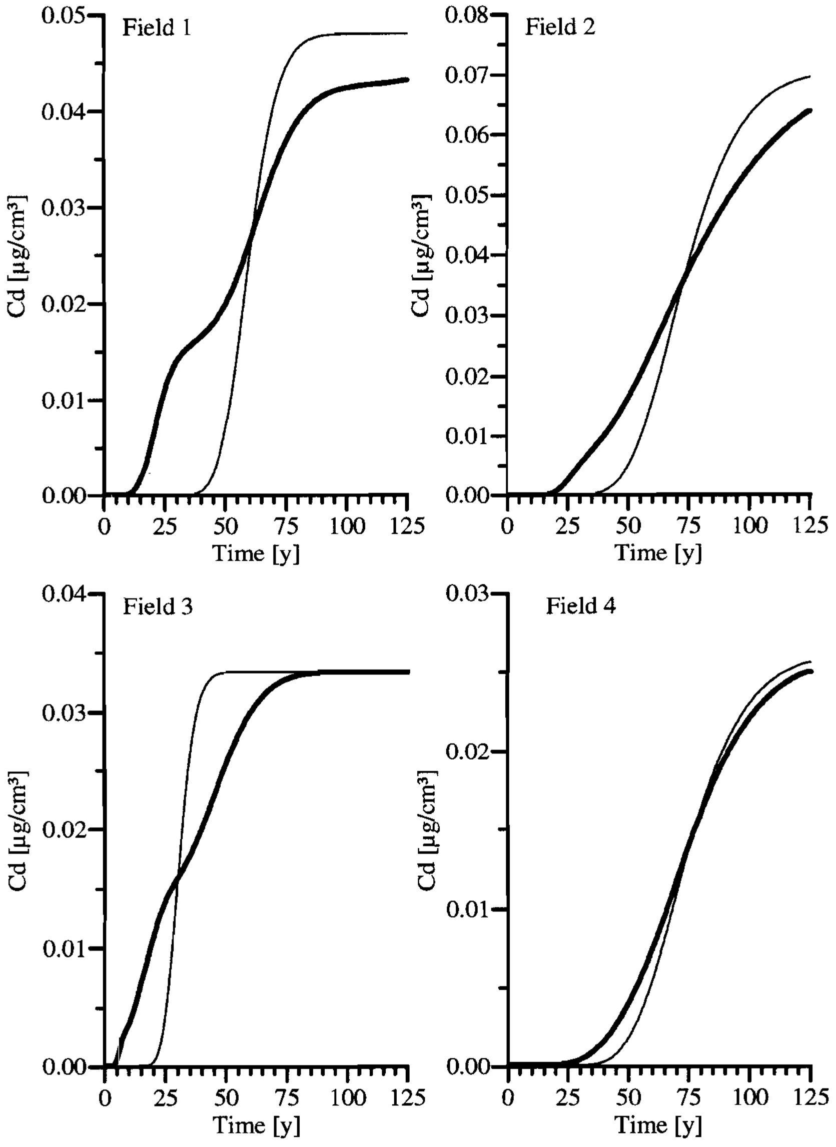

Figure 5.2. Cadmium field breakthrough curves, for the case of linear adsorption (Eq. 5.9), for fields 1-4. Solute concentration at depth 150 cm. The thin lines are calculated according to route 1, and the bold lines are calculated according to route 2.

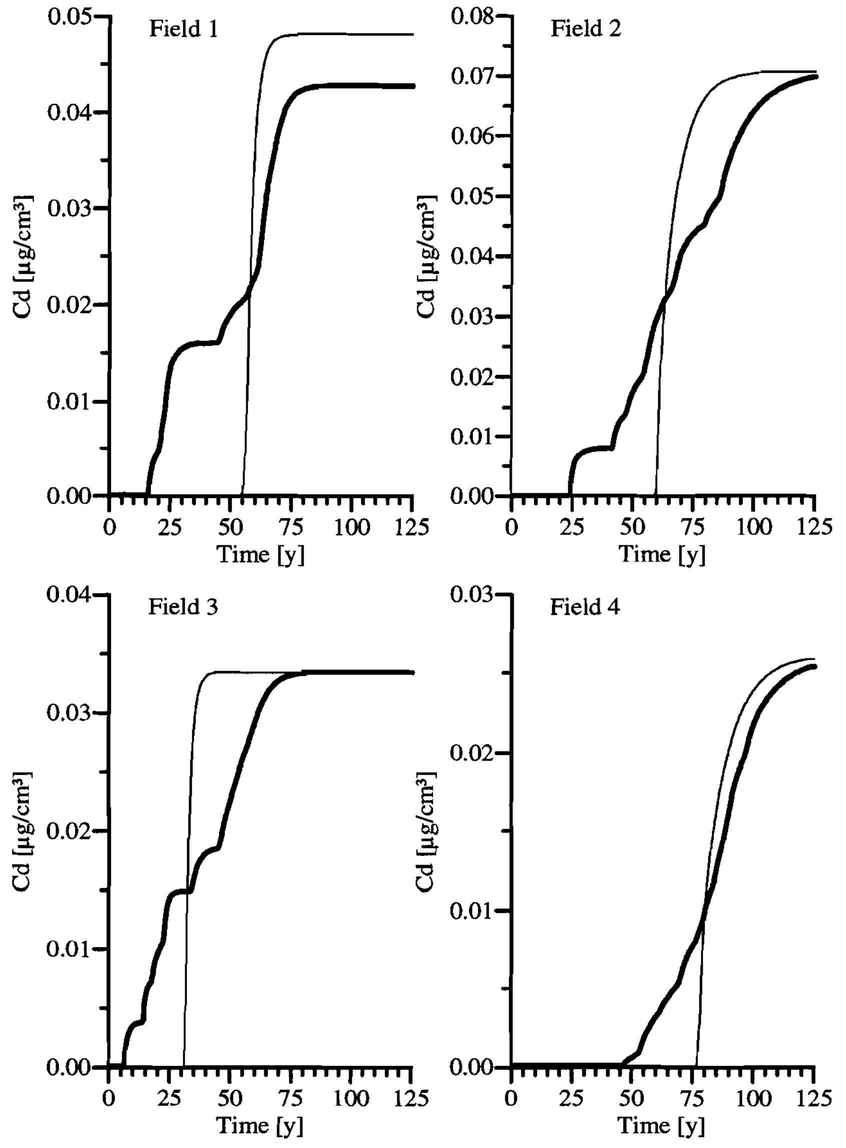

Figure 5.3. Cadmium field breakthrough curves, for the case of non linear adsorption (Eq. 5.9), for fields 1-4. Solute concentration at depth 150 cm. The thin lines are calculated according to route 1, and the bold lines according to route 2.

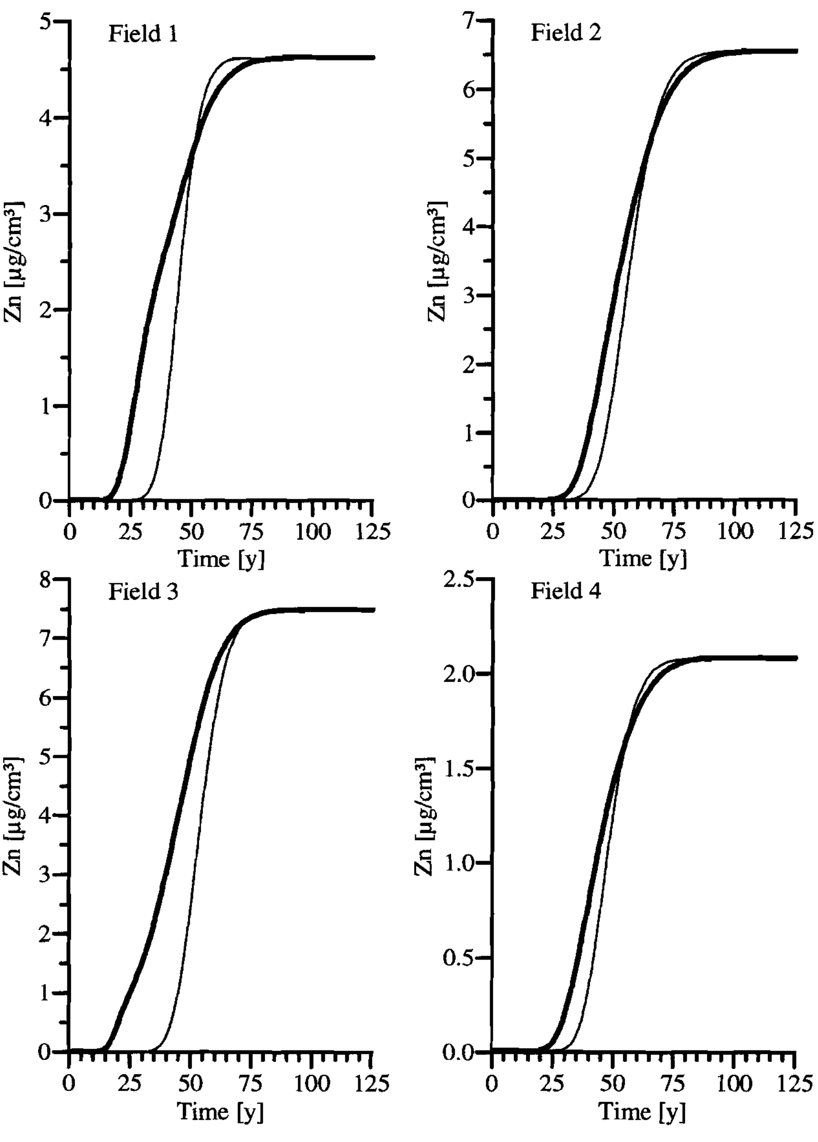

Figure 5.4. Zinc field breakthrough curves, for fields 1-4. Solute concentration at depth 150 cm. The thin lines are calculated according to route 1, and the bold lines according to route 2.

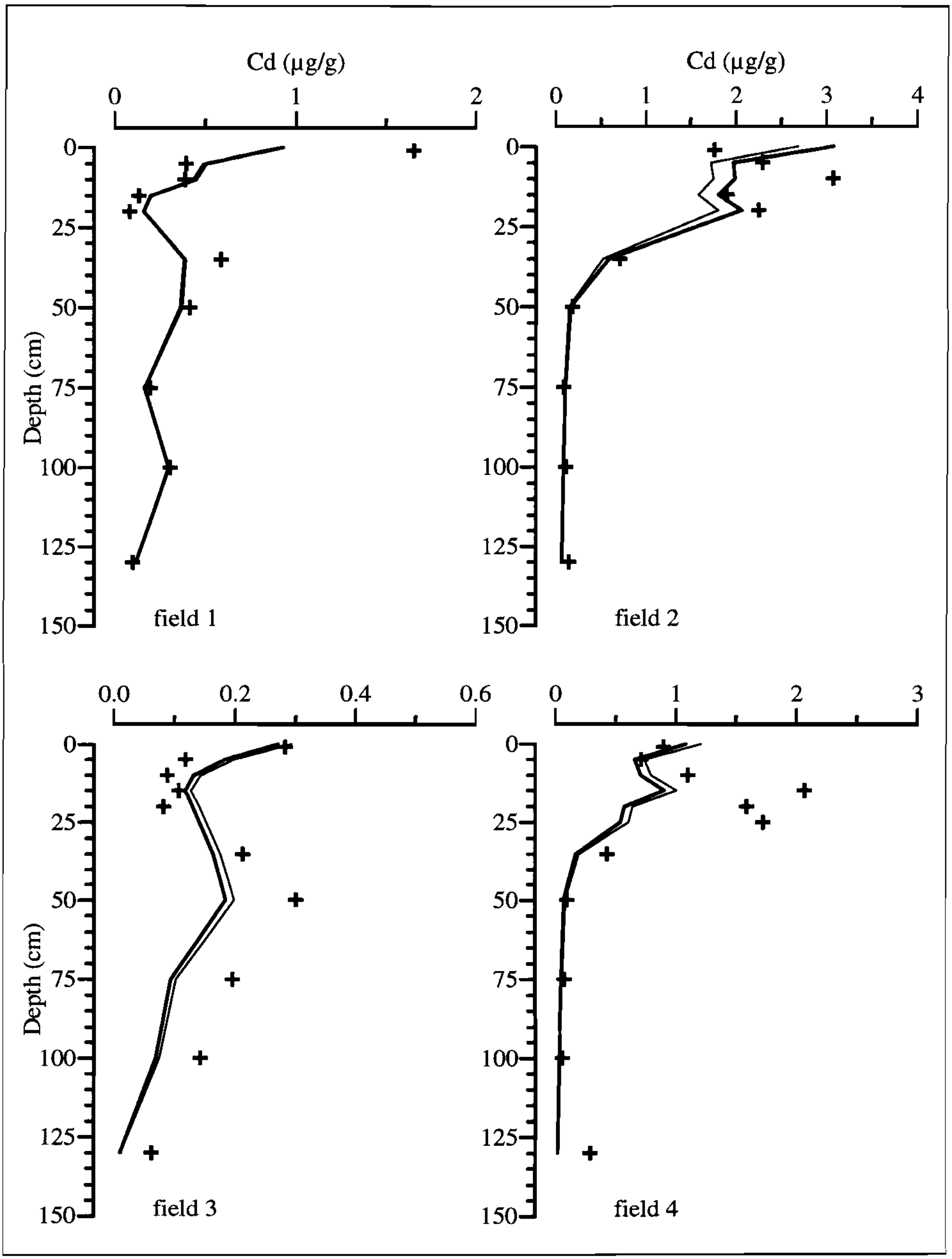

Figure 5.5. Field profiles of the cadmium soil contents [$\mu g.g^{-1}$].

The observed cadmium contents in soil are indicated by the symbol plus. The bold lines are calculated according to the linear adsorption model (n=1.00), and the thin lines are calculated according to the non-linear adsorption model (n=0.75), both according to route *2*.

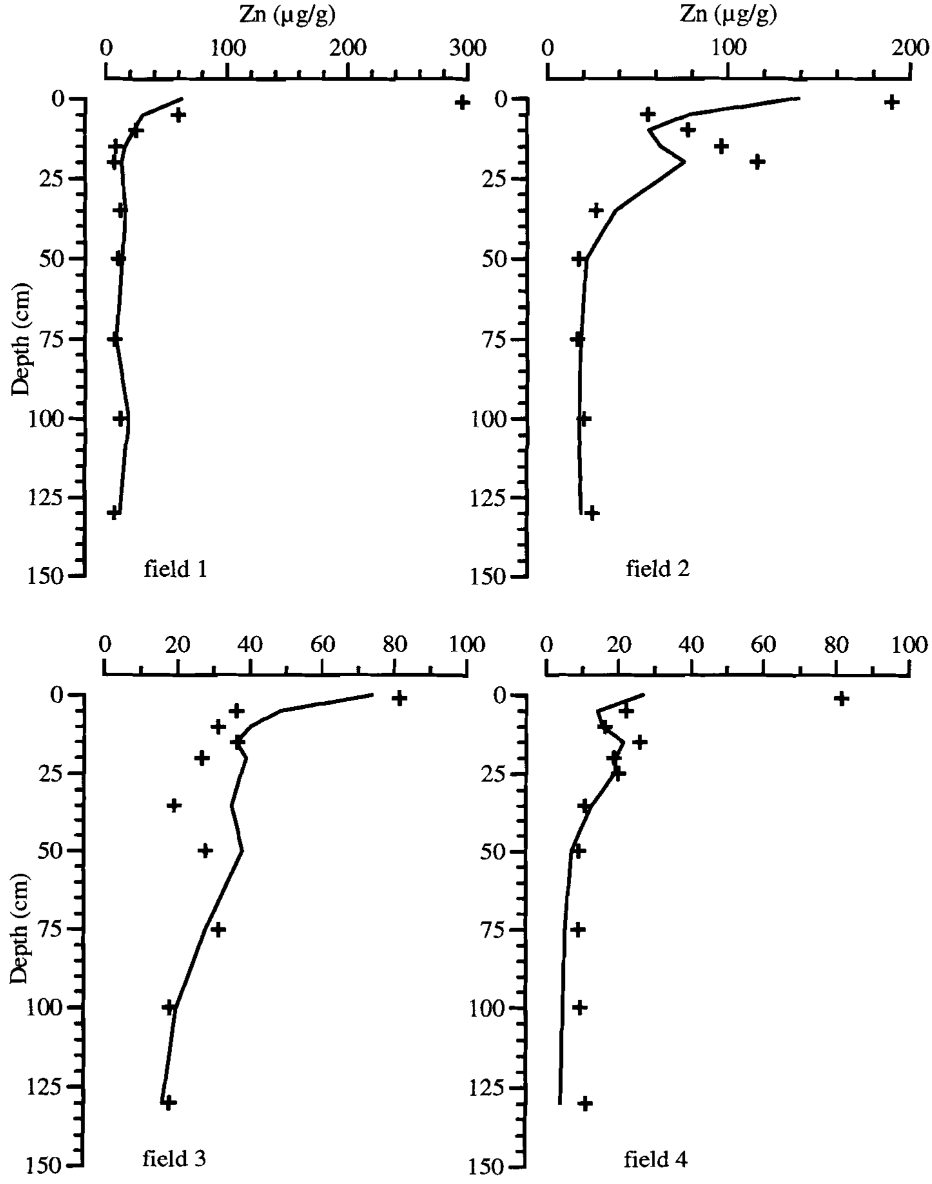

Figure 5.6. Field profiles of the observed zinc contents [$\mu g.g^{-1}$] in soil, indicated by the symbol plus. The drawn line represents the zinc contents according to the route 2 model calculations.

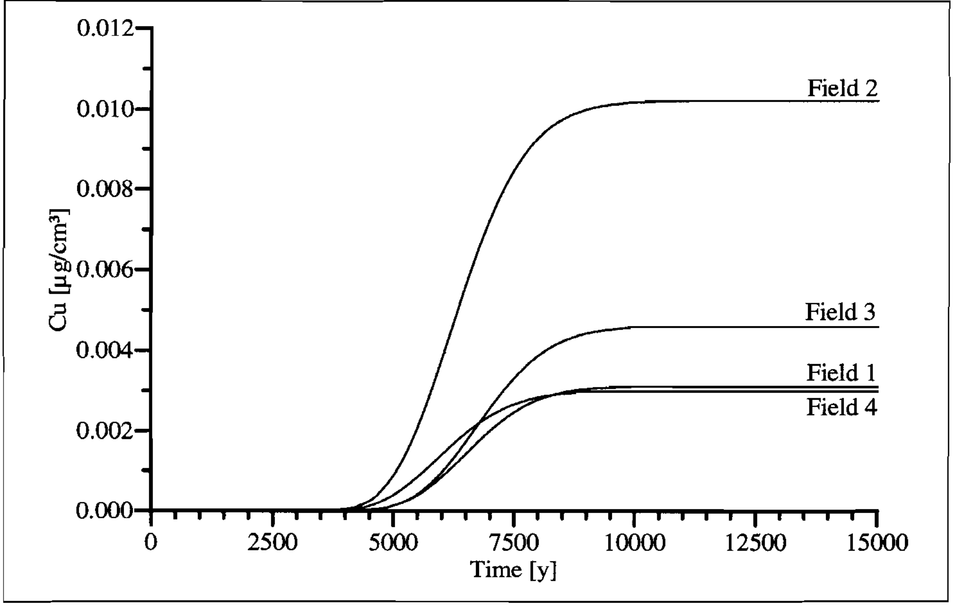

Figure 5.7. Copper field breakthrough curves, for fields 1-4. Solute concentration at depth 150 cm. Only route *1* is calculated.

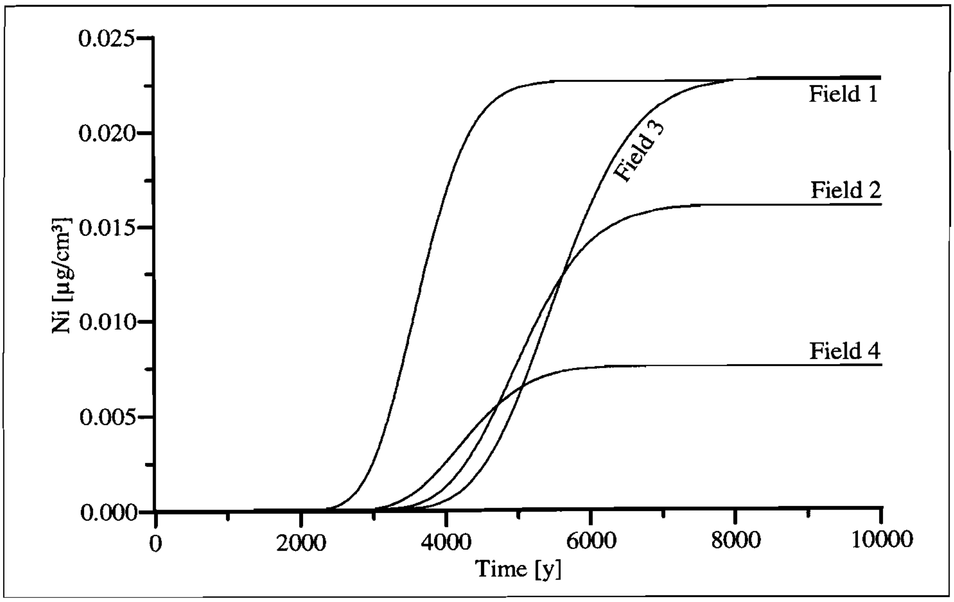

Figure 5.8. Nickel field breakthrough curves, for fields 1-4. Solute concentration at depth 150 cm. Only route *1* is calculated.

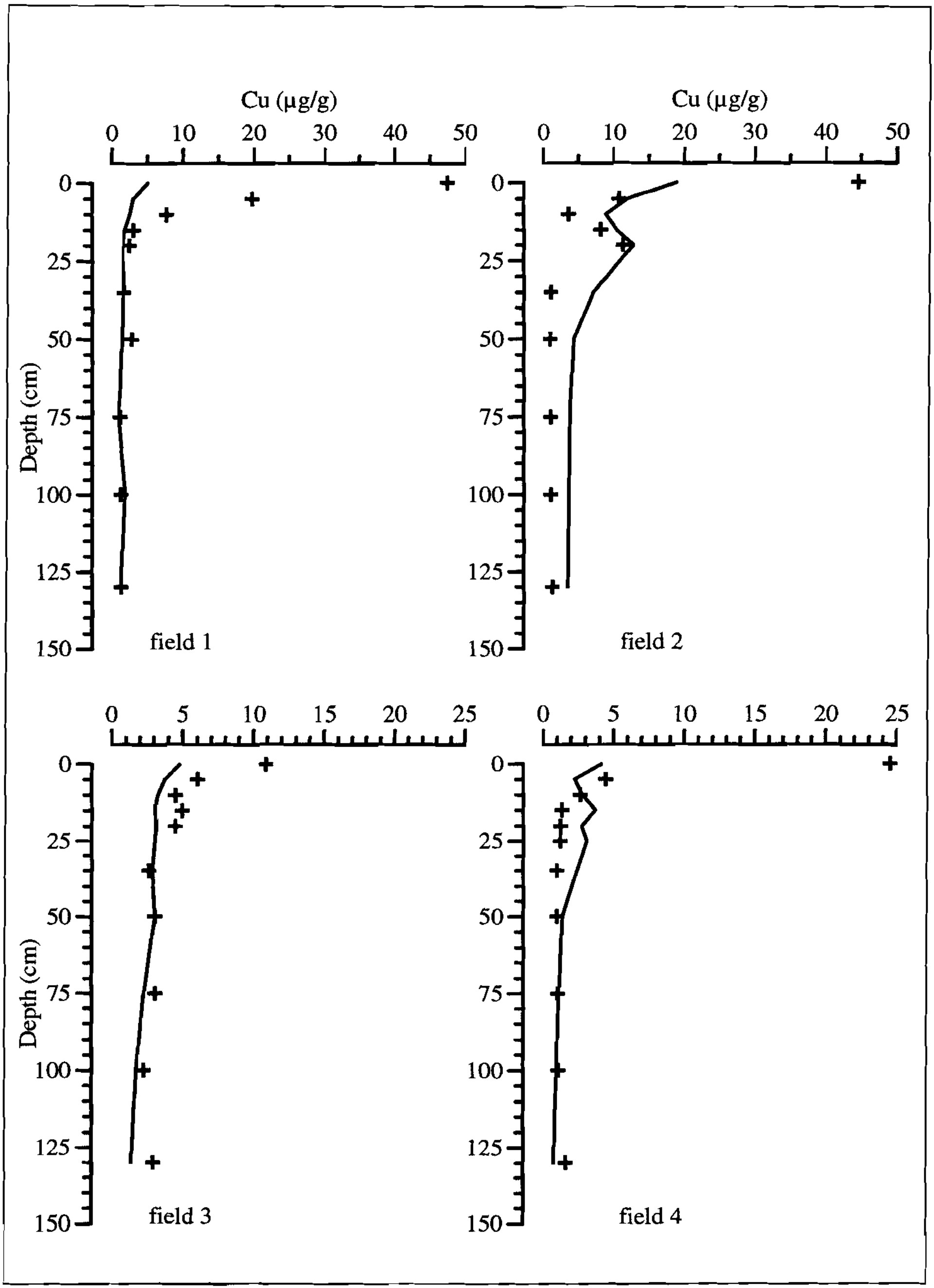

Figure 5.9. Field profiles of the observed copper contents [$\mu g.g^{-1}$] in soil, indicated by the symbol plus. The drawn line represents the copper contents according to the model calculations (route *1*).

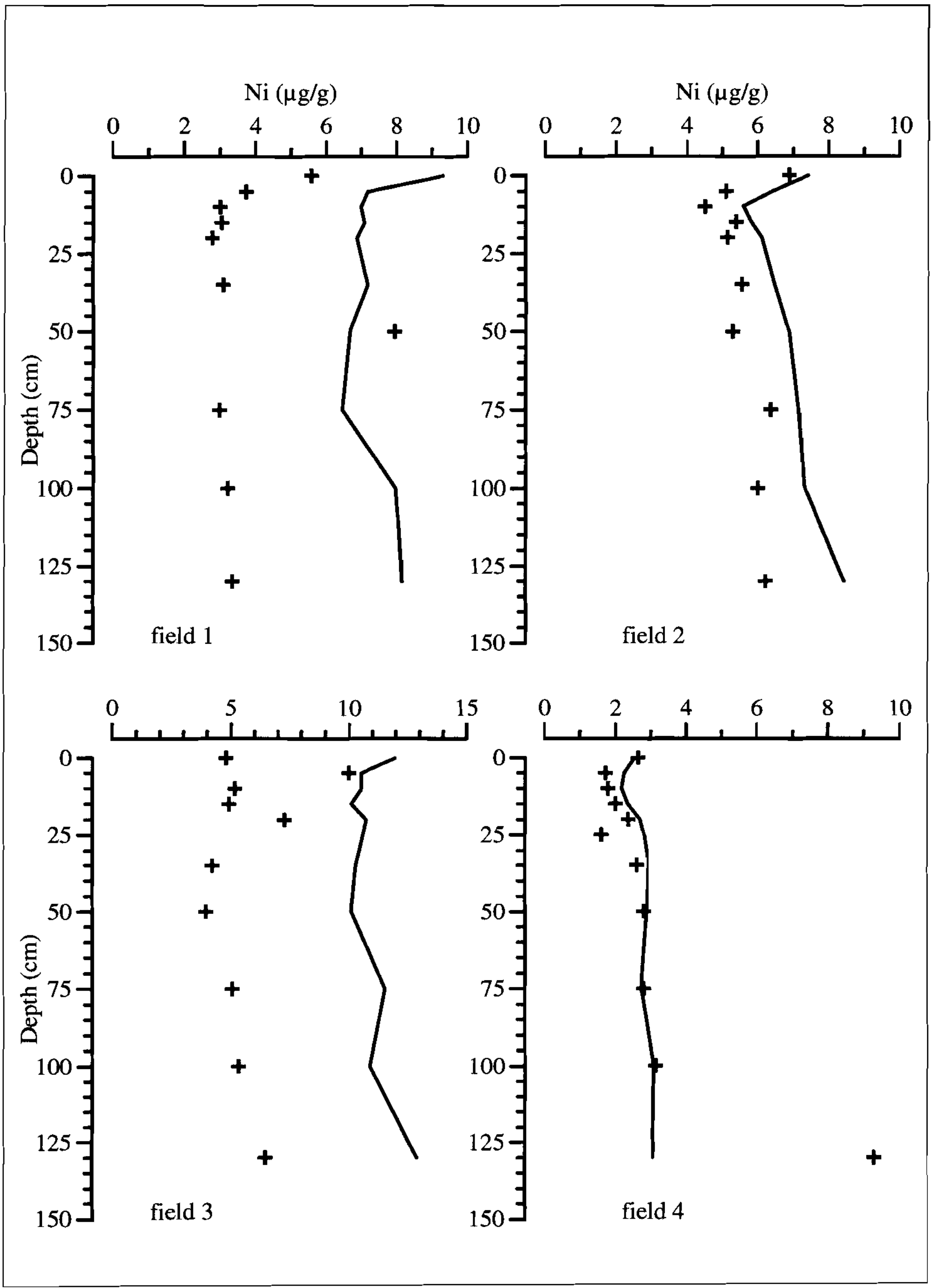

Figure 5.10. Field profiles of the observed nickel contents [$\mu g.g^{-1}$] in soil, indicated by the symbol plus. The drawn line represents the nickel contents according to the model calculations (route *1*).

5.3.3. Field dispersion from soil heterogeneity

Variations in the retardation factors between the soil profiles within one field will result in broadening of the breakthrough curve according to route *2*. The effect of variation in retardation characteristics is lost when averages are taken along route *1*. This variation can be interpreted as a supplementary field dispersion. In this section a quantification will be made of the field dispersion.

Dispersion in the breakthrough curve

In a solute infiltration case without sorptive retardation Appelo and Postma (1993) found a relation between the variance σ_z^2 in the depth of the concentration fronts and the diffusion-dispersion coefficient:

$$\sigma_z^2 = 2Dt \tag{5.10}$$

where:
σ_z^2 = concentration front variance in z (distance at time = t) [cm^2],
D = combined diffusion and hydro-dynamic dispersion coefficient [$cm^2.day^{-1}$],
t = time [day].

In the following analysis sorptive retardation will be incorporated in equation 5.10. Dispersion in the column profile (concentration versus depth at time = t) (Eq. 5.10) will be transformed into dispersion in the breakthrough curve (concentration versus time at depth = z). An equation for dispersion in a b.t.c. is more applicable to our objective than an equation describing the dispersion in a column profile.

The retardation factor at linear adsorption (n=1.00) is defined as:

$$R = 1 + \frac{\rho}{\theta} K_F \tag{5.11}$$

where:
R = retardation factor [-],
ρ = soil bulk density [$g.cm^{-1}$],
θ = moisture content [$cm.cm^{-1}$],
K_F = adsorption coefficient [$cm.g^{-1}$].

A retardation factor acts on the dispersion coefficient in Equation 5.10, therefore this equation is rewritten to:

$$\sigma_z^2 = 2\frac{D}{R}t \tag{5.12}$$

The relation between time (t) and depth (z) for constant R and v, is given by:

$$\bar{t} = \frac{R}{v}\bar{z} \qquad (5.13)$$

where:

$\bar{t}$ = average breakthrough time [day],
$\bar{z}$ = average front depth [cm],
v = pore water velocity [cm.day^{-1}].

The relation between the variance in z and the variance in t is:

$$\sigma_z^2 = \frac{\sigma_t^2}{\bar{t}^2}\bar{z}^2 \qquad (5.14)$$

where:

σ_t^2 = variance in breakthrough time at depth = z [day^2].

Rearranging equation 5.12 for the variance in t, with the assumptions:
$\bar{z}$ = L and t = $\bar{t}$

where:

L = column length [cm].

and with the use of equations 5.13 and 5.14 gives:

$$\sigma_t^2 = D\frac{2LR^2}{v^3} \qquad (5.15)$$

Equation 5.15 gives the variance in breakthrough times at z=L as a result of diffusion/dispersion.

The dispersion/diffusion coefficient can also be obtained from the breakthrough times themselves:

$$D_{btc} = \frac{\sigma_t^2 v^3}{2LR^2} \qquad (5.16)$$

where:

D_{btc} = dispersion observed in the breakthrough curve [cm^2.day^{-1}].

A breakthrough curve is a cumulative frequency distribution of breakthrough times. The variance in breakthrough times at depth z = L is obtained from the breakthrough curve and is given by (Davis, 1986):

$$\sigma_t^2 = \frac{(t_{0.842} - t_{0.158})^2}{4} \qquad (5.17)$$

where:

$t_{0.158}$ = time where c(t)/c(0) = 0.158,
$t_{0.842}$ = time where c(t)/c(0) = 0.842.

Equation 5.16 and 5.17 are combined to:

$$D_{btc} = \frac{v^3(t_{0.842} - t_{0.158})^2}{8LR^2} \tag{5.18}$$

The time of half breakthrough ($c = \frac{1}{2}c_0$) is:

$$\bar{t} = t_{0.5} = R\frac{L}{v} \tag{5.19}$$

where:

$t_{0.5}$ = time when $c(t)/c_o = 0.5$.

Substituting 5.19 in 5.18 gives:

$$D_{btc} = \frac{vL(t_{0.842} - t_{0.158})^2}{8 \cdot t_{0.5}^2} \tag{5.20}$$

Equation 5.20 is used to obtain the total dispersion coefficient from the breakthrough curve.

Field dispersion

In the case of parallel soil profiles, which conduct the recharge of the same perfectly mixed aquifer, the differences in adsorption are of influence on the average groundwater concentration as a function of time. Spatial variance in the retardation characteristics will result in an additional dispersion in the field breakthrough curve. We assume linear adsorption, i.e. the retardation is independent of the solute concentration. The relation between the variance in time (at z=L) and the variance in retardation factors is:

$$\sigma_t^2 = \frac{\sigma_R^2}{\bar{R}^2}\bar{t}^2 \tag{5.21}$$

where:

σ_t^2 = variance in breakthrough times as a result of the variance in retardation factors [day^2],

σ_R^2 = variance in retardation factors [-],

$\bar{R}$ = average retardation factor [-].

Rewriting equation 5.16 by substituting of 5.19 and 5.21 results in a relation for the dispersion caused by variance in the retardation factors. At z = L, constant v and R = $\bar{R}$ this dispersion is given by:

$$D_R = \frac{\sigma_R^2 v L}{2\overline{R}^2} \tag{5.22}$$

where:

D_R = dispersion coefficient as a result of variance in retardation factors [$cm^2.day^{-1}$].

D_R is the dispersion coefficient only caused by the variance in the retardation factors. The total field dispersion is given by:

$$D_f = D + D_R \tag{5.23}$$

where:

D_f = total field dispersion coefficient [$cm^2.day^{-1}$].

The total field dispersion is caused by the heterogeneity in adsorption characteristics in addition to hydrodynamic dispersion and diffusion. The parameter D_R will introduce a supplementary dispersion in the breakthrough curve at depth L.

For each column an average or substituted retardation factor is calculated, which is representative for the whole soil profile. Thus each field is described by 9 retardation factors, from which an average and a standard deviation is calculated for the case of linearly adsorbing cadmium (see table 5.V). A normal distribution is assumed for these statistical calculations, although in most cases this is not true and may cause deviations in the model calculations.

A simple stochastic model (Appendix C.2) is designed to calculate field breakthrough curves from the average retardation factor and its standard deviation (σ). This model gives a symmetric breakthrough curve at high dispersion levels, as opposed to the previously used numeric method. Calculation of the variance or standard deviation assumes a symmetric distribution in the population, consequently resulting in a symmetric breakthrough curve. From the average retardation factors (Table 5.V) and their standard deviations, 4000 randomly generated retardation factors are calculated with a normal distribution. Randomness of the retardation factor causes a variation in both front shape and front velocity (Bosma and van der Zee, 1993).

With the retardation data from Table 5.V ($\overline{R}$ and σ_R) and the general model parameters from Table 5.III a distribution of front velocities is calculated using the stochastic model described in appendix C.2. From the 4000 front velocities, a cumulative frequency distribution is constructed, which is actually an average breakthrough curve. The field dispersion coefficient is calculated from this b.t.c. using Equation 5.20. Field dispersion coefficients are also calculated from the average b.t.c. along route 2 and the stochastic model, using Equation 5.20. The

Table 5.V. Average field retardation factor, standard deviation for linear adsorbing cadmium and different types of dispersion.

field	$\bar{R}$	σ_R	D_R	D_f	D_{btc}^{I}	D_{btc}^{II}
field 1	42.0	26.2	7.91	8.27	8.38	6.24
field 2	54.9	18.2	2.23	2.59	2.43	4.64
field 3	23.1	11.8	5.23	5.59	5.73	8.90
field 4	53.8	8.7	0.56	0.92	0.97	2.27

$\bar{R}$ = average retardation factor in a field,
σ_R = standard deviation in population of retardation factors,
D_R = dispersion coefficient calculated according to Equation 5.22,
D_f = dispersion coefficient calculated according to Equation 5.23,
D_{btc}^{I} = dispersion in b.t.c. from the stochastic model, using Equation 5.20 (Figure 5.11, thin line),
D_{btc}^{II} = dispersion in b.t.c. according to route *2*, using Equation 5.20 (Figure 5.11, bold line).

field dispersion can also be calculated from the retardation average and variance at once, using Equations 5.22 and 5.23 (Table 5.V).

The results of the calculations are presented in Figure 5.11. The modeled breakthrough curve of field 3 satisfactory describes the field breakthrough curve along route *2*. Field 1 has an extraordinarily large dispersion since one site has a much larger retardation factor. Consequently the population of retardation factors for field 1 does not have a normal distribution, causing the mismatch between the modeled field dispersion in the b.t.c. and field b.t.c according to route *2*. This is also the explanation for the high field dispersion coefficient of, 8.38 (Table 5.V), using the variance in the retardation compared with dispersion in the b.t.c., i.e. 6.24 (Table 5.V). The dispersion in the b.t.c.'s (along route *2*) are fields 2, 3 and 4 are higher than based on the variance in the retardation factors; this is probably caused by the same phenomenon.

5.4. Conclusions

Model calculations according to the proposed flow scheme and model are satisfactory for the metals cadmium and zinc. These metals have an extremely high mobility. Nearly complete breakthrough to groundwater is within the past 100 years of immission. The leaching of copper is small, no high groundwater concentrations of copper are to be expected in the near future.

When field breakthrough curves are calculated from individual site b.t.c's, a large dispersion is observed in the field b.t.c. If breakthrough curves are calculated from average soil macro parameters they demonstrate smaller field

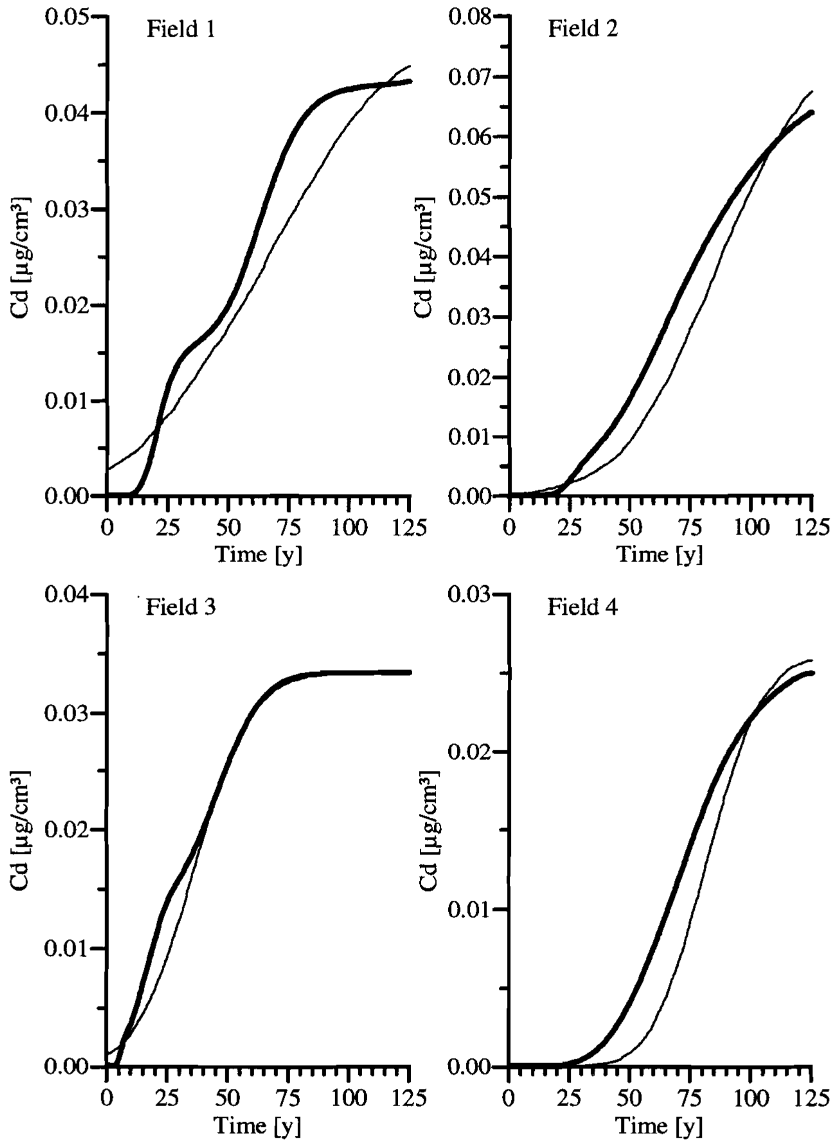

Figure 5.11. Cadmium field breakthrough curves (linear adsorption) for fields 1-4. Solute concentration at depth is 150 cm. The bold line is the modeled breakthrough along route 2. The thin line is the stochastic modeled field dispersion.

dispersion. When taking average soil macro parameters, the initial soil heterogeneity is smoothed. Therefore the procedure followed along route *1* is incorrect. Using average retardation factors and their standard deviations to calculate breakthrough in time is a satisfactory method to obtain the field dispersion coefficient.

References

Appelo, C.A.J. and D. Postma (1993).
Geochemistry, groundwater and pollution.
Balkema, Rotterdam, the Netherlands.

Boekhold, A.E. (1992).
Field scale behaviour of cadmium in soil.
Thesis, Agricultural University Wageningen, the Netherlands.

Bolt, G.H. (1982).
Soil chemistry, B. physico-chemical models.
Elsevier Scientific Publishing Company, Amsterdam, the Netherlands.

Bosma, W.J.P. and S.E.A.T.M. van der Zee (1993).
Transport of reacting solute in a one-dimensional, chemically heterogeneous porous medium.
Water Resources Research **29**(1): 117-131.

Bosman, H. and J. Peanhuys (1980).
The distribution of heavy metals in the soils of the Kempen.
Pedologie **30**(2): 59-77.

Christensen, T.H. (1985).
Cadmium soil sorption at low concentrations: III. Prediction and observation of mobility.
Water, Air, and Soil Pollution **25**: 255-264.

Davis, J.C. (1986).
Statistics and data analysis in geology.
John Wiley & Sons, New York, U.S.

Koorevaar, P., G. Menelik and C. Dirksen (1983).
Elements of soil physics.
Elsevier, Amsterdam, the Netherlands.

LISEC (1989).
Werkgroep zware metalen Noorder Kempen, subgroep lucht, LISEC, studiecentrum voor ecologie en bosbouw. Genk, Belgium.

Pedroli, G.B.M., W.A.C. Maasdam and J.M. Verstraten (1990).
Zinc in poor sandy soils and associated groundwater. A case study.
The Science of the Total Environment **91**: 59-77.

Scokart, P.O., K. Meeus-Verdinne and R. de Borger (1983).
Mobility of heavy metals in polluted soils near zinc smelters.
Water, Air, and Soil Pollution **20**: 451-463.

van der Zee, S.E.A.T.M. and W.H. van Riemsdijk (1987).
Transport of reactive solute in spatially variable soil systems.
Water Resources Research **23**(11): 2059-2069.

Weast, R.C. (1986).
Handbook of chemistry and physics.
C.R.C. Press, Boca Raton, Florida, U.S.

Wilkens, B.J. and J.P.G. Loch (1995).
Accumulation of cadmium and zinc from diffuse immission on acid sandy soils, as a function of soil composition.
Water, Air, and Soil Pollution (Accepted for publication).

6

Influence of heterogeneity in the vertical plane on the copper, lead and zinc distribution in an acid, sandy soil

Co-Authors: R.A. Rikers
J.P.G. Loch

Abstract

In the Belgian Kempen a study was carried out to investigate the impact of soil heterogeneity and preferential flow on copper, lead and zinc distribution in acid sandy soils. The area has been polluted for a century by the zinc producing industry. A soil site was sampled in a vertical plane of 150 cm width and 60 cm depth, in a grid providing 362 samples. The samples were analyzed for the contents of organic matter, aluminium, manganese, calcium and the heavy metals copper, lead and zinc.

Soil heterogeneity was made visible by vertical contour profiles of organic matter content, aluminium, calcium, copper, lead and zinc. Preferential flow was not observed with the used methods. Organic matter is the major soil parameter responsible for the distribution of copper and lead. Zinc has a lower correlation with organic matter content. Most organic matter is found in the topsoil, but bioturbation by soil fauna is an important process for organic matter dispersion, and consequently for heavy metal distribution. Eluviation and illuviation processes of the major elements aluminium and calcium have not resulted in redistribution of heavy metals.

6.1. Introduction

Soil heterogeneity and preferential solute transport may have an impact on solute transport models. Transport of heavy metals can be underestimated by the models when these phenomena are not taken into account. The retardation of the soil is lower than predicted, resulting in underestimation of the leaching to the groundwater level and consequently of the heavy metal groundwater concentration.

Preferential transport can be divided into macropore flow or funnelling (Kung, 1990) and fingering. Macropore flow is due to root channels, wormholes and cracks which occur in soil. Cracks are known to be present especially in clay soil. In a sandy soil macropores will only exist as roots or wormholes, cracks are mostly absent. Flow paths start in a macropore. Where the macropore ends a finger may develop, because in the macropore relatively high flow rates are present compared to its surroundings.

Fingers will also develop when a wetting front is unstable (Bronswijk et al., 1990). When the hydraulic conductivity of an upper layer is smaller than in the layer below, lateral contraction of a percolating fluid-body takes place, because its velocity grows with distance but its volume remains the same (Hillel and Baker, 1988). In soil, the water pressure at the soil surface may be more negative than at the lower wetting part of the front (Raats, 1973). This means that fingering may develop in layered and non-layered sandy soils when water infiltrates as unsaturated flow. Fingers may also develop when pressure differences arise along the wetting front (Raats, 1973). This is particularly so when water-repellent soils are present and parts in the terrain are wetter than other parts, because of differences in repellency.

Soil heterogeneity with respect to its chemical composition, such as content of organic matter, oxide content and pH will have an impact on heavy metal distribution and leaching. Variability of Cd and Zn contents are related to soil chemical variability, especially pH and contents of organic matter (Boekhold and van der Zee, 1992). At locations of low adsorption the heavy metal leaching will be favoured over places of average adsorption characteristics, consequently soil chemical variability will lead to an underestimation of the moment of first breakthrough at the groundwater level (van der Zee and van Riemsdijk, 1987). This process will introduce an additional dispersion, which is based on variance in the retardation factors over different locations (chapter 5) The aim of this study is to make a qualitative assessment of soil heterogeneity and preferential transport in metal contaminated acid sandy soils. We also focus on the processes which are responsible for spatial soil chemical variability.

6.2. Materials and methods

6.2.1. Sampling site

According to the F.A.O. classification the sampling site is an arenosol. A preliminary study showed that finger formation is possible in this soil. Very close to the site a sprinkling test was carried out with a food dye (0.1 % Brilliant Blue FCF). On the sprinkled site a pit was dug after three days. Finger formation was observed with finger length of 20 cm and width of approximately 4 cm. The site is located 1.9 km north-east of the zinc smelter at Overpelt (Belgium), near field 1 referred by Wilkens and Loch (1995). The flora on the site has clearly been affected by heavy metal immissions, including cadmium.

At the sampling site a pit of 2 m length, 2 m width and 1 m depth was dug. A profile-wall was shaped in the vertical plane by scraping off soil. The profile wall was sampled in the vertical plane with 5 cm spacing creating a grid with horizontal dimension of 31 samples (0, 5, 10 ... 145 and 150 cm). This line was sampled at 12 different depths (0, 5, 10 ... 50 and 60 cm below soil surface). From top to bottom the grid provided 372 sample points. Care was taken to avoid contamination of samples by traces from layers above. During sampling bio-turbation and tunnels were observed in the form of holes made by soil fauna. In some of these places it was impossible to take a soil sample. From the 372 initial sample points, 362 soil samples could be actually taken.

6.2.2. Sample analysis

All samples were weighted and air dried at 50 °C for five days. The content of organic matter was determined after ashing for 2 hours at 900 °C. An extraction with 25% nitric acid (HNO_3) for 1 hour at 100 °C in PFTE bombs was done to free all but lattice-bound metals. The resulting solution was prepared for ICP-AES metal analyses (Al, Ca, Mn, Cu, Pb and Zn).

6.2.3. Statistical analysis

The data obtained by chemical analyses were translated into vertical contour profiles using computer contouring by gridding. A vertical contour profile is a map of the chemical content in a vertical plane. This kind of maps is easy to interpret with respect soil heterogeneity.

Gridding is the process of determining values of the plane at a set of locations that are arranged in a regular pattern, which completely covers the mapped area. In general, values of the surface are not known at these uniformly spaced points and so they must be estimated from the irregularly located control points where values are known. The locations where estimates are made are referred to as "grid nodes" (Davis, 1986).

The control points used in estimating the value at a grid node are weighted. The weighting varies with the distance between the grid node and the control points. As weight function, we used

$$\omega = \frac{1}{D^2} \qquad (6.1)$$

where:

ω = weight,

D = distance.

The nearest-neighbour search is used to select the data points within the local neighbourhood around a grid location. Five nearest data points are used in the search.

6.3. Results and discussion

6.3.1. General

Table 6.I presents general statistic information about the measured contents of metals and organic matter in the samples. Striking are the low average contents of organic matter. With the same data a correlation table is calculated (Table 6.II). All heavy metals are positively correlated with the content of organic matter. For all heavy metals organic matter appears to be the binding substrate. The correlation of copper and lead with organic matter is very significant, i.e. respectively 0.75 and 0.82. Strong adsorption of copper and lead on organic matter explains these observations.

Table 6.I. Contents of organic matter (OM), Al, Fe, Mn, Ca and some heavy metals in $\mu g.g^{-1}$.

	mean	min	max	s.d.	n
O.M.	1.36	0.50	3.77	0.76	352
Al	1324	45	3393	464	362
Fe	1457	15	4577	624	362
Mn	3.34	0.65	22.5	1.96	361
Ca	16.1	3.42	85.2	15.3	362
Cu	5.33	0.06	50.7	8.41	326
Pb	40.2	0.77	266	50.3	329
Zn	14.4	0.79	246	24.7	362

Concentrations below detection limit are discarded, therefore n is sometimes below 362.

mean = arithmetic average,
min = minimum value,
max = maximum value,
s.d. = standard deviation.

Table 6.II. Correlation coefficients of organic matter (OM), Al, Fe, Mn, Ca and some heavy metals.

	OM	Al	Fe	Mn	Ca	Cu	Pb	Zn
OM	1							
Al	-0.32 350	1						
Fe	0.29 350	0.55 362	1					
Mn	0.25 349	0.41 361	0.47 361	1				
Ca	0.18 350	0.51 362	0.37 362	0.73 361	1			
Cu	0.75 314	-0.25 326	0.28 326	0.68 325	0.60 326	1		
Pb	0.82 318	-0.36 329	0.20 329	0.47 328	0.29 329	0.94 294	1	
Zn	0.55 350	-0.09 362	0.26 362	0.78 361	0.48 362	0.80 326	0.69 329	1

2-tailed significance = 0.001 for all correlations, Al-Zn correlation is worse than 0.01. The small numbers are (n) samples involved in the correlations.

6.3.2. Vertical contour profiles

The data are plotted in vertical contour profiles, as explained in section 6.2.3. Contour profiles are presented of the organic matter, aluminium, calcium, copper, lead and zinc contents.

Organic matter

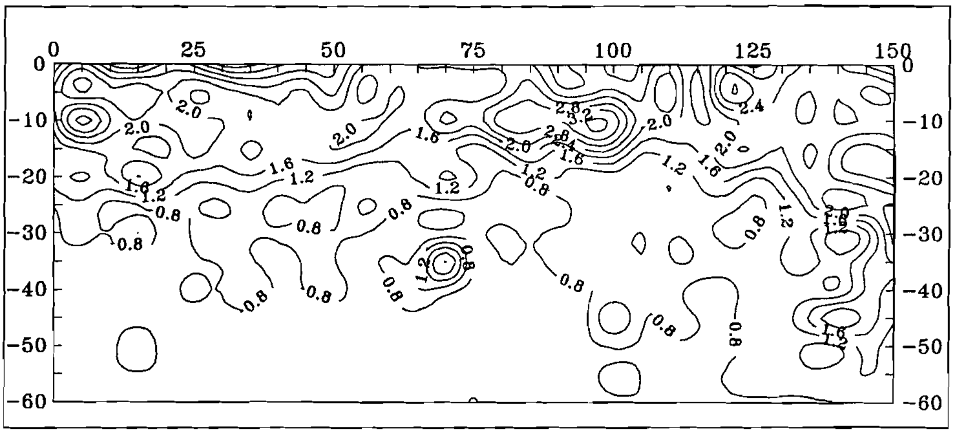

Figure 6.1. Vertical contour profile of organic matter content, contents in percentage g.g^{-1}.

The organic matter profile (Figure 6.1) is not homogeneous and shows irregularly spaced areas of high contents of organic matter. As to be expected the topsoil contains more organic matter than the subsoil (30 - 60 cm). In the lateral direction the contents of organic matter is not constant either. The effect of bio-turbation is clearly visible in the middle and right side of the contour profile (Figure 6.1). Here spots of relatively high content of organic matter are probably caused by downward transport from the topsoil by (soil) animals.

Aluminium

The content of aluminium in the topsoil is lower than in the middle of the contour profile (Figure 6.2). At 25 cm below soil surface a discontinuous layer of aluminium accumulation is observed. Two regions with rather high aluminium contents are located left and right in the contour profile at 25 to 30 cm below soil surface. These are clear indications that a podzolization process is still active. The accumulation of aluminium is independent of the organic matter distribution, indicating the absence of organic illuviation in the profile.

No effect of bio-turbation on the Al distribution is visible. An explanation may be that on the time scale of Al-eluviation/illuviation bio-turbation was not important.

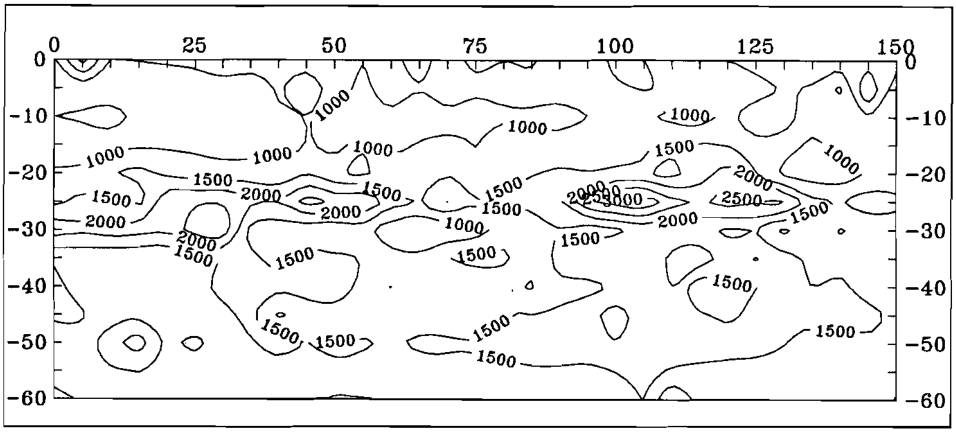

Figure 6.2. Vertical contour profile of aluminium content, contents in $\mu g.g^{-1}$.

Calcium

A clear illuviation horizon for calcium at 25 to 30 cm below soil surface is observed (Figure 6.3). The difference with aluminium is the contrast in contents of calcium between the illuviation horizon and the surrounding soil. The ratio of Ca-contents in the illuviation horizon and the surrounding soil is about 48:8, which is two times higher than for aluminium, where a ratio of 2500:1000 is observed.

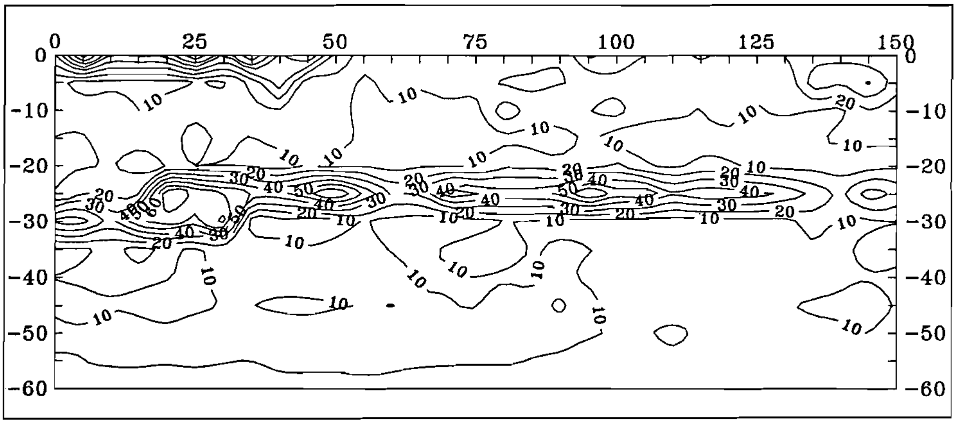

Figure 6.3. Vertical contour profile of calcium content, contents in $\mu g.g^{-1}$.

Heavy metals (copper, lead and zinc)

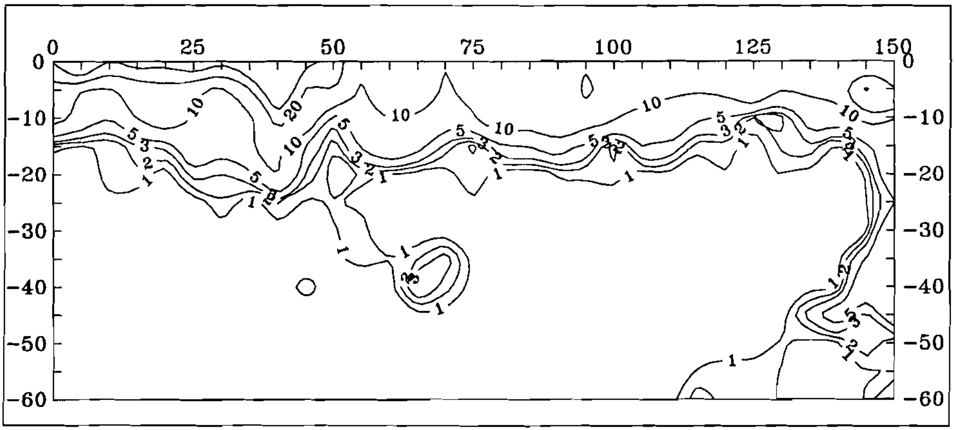

Figure 6.4. Vertical contour profile of copper content, contents in $\mu g.g^{-1}$. Contour intervals at 1, 2, 3, 5, 10, 20 and 30 $\mu g.g^{-1}$.

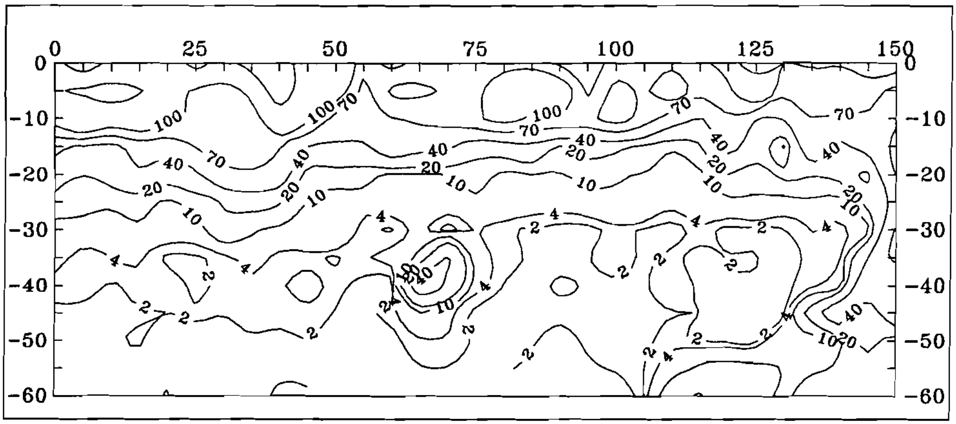

Figure 6.5. Vertical contour profile of lead content, contents in $\mu g.g^{-1}$. Contour intervals at 2, 4, 10, 20, 40, 70, 100 and 200 $\mu g.g^{-1}$.

The copper contour profile shows high contents of copper in the upper 20 cm (Figure 6.4). The same observation is valid for the lead contour profile (Figure 6.5). The contents of copper and lead are closely associated with the contour profile of organic matter (Figure 6.1), which confirms the high correlation coefficients discussed before. Association with organic matter is not as strong for the content of zinc in the profile: although irregular, the contents of zinc below 20 cm are generally low (Figure 6.6). The correlation of the zinc content with content of organic matter is lower (0.55), i.e. than for copper and lead. The retardation of zinc in the profile appears to be lower in its contour profile. The copper and lead distributions (Figures 6.4. and 6.5) reflect a lower mobility than the zinc distribution (Figure 6.6). Almost all copper and all lead remain in the topsoil, leaching of these elements seems to be minimal.

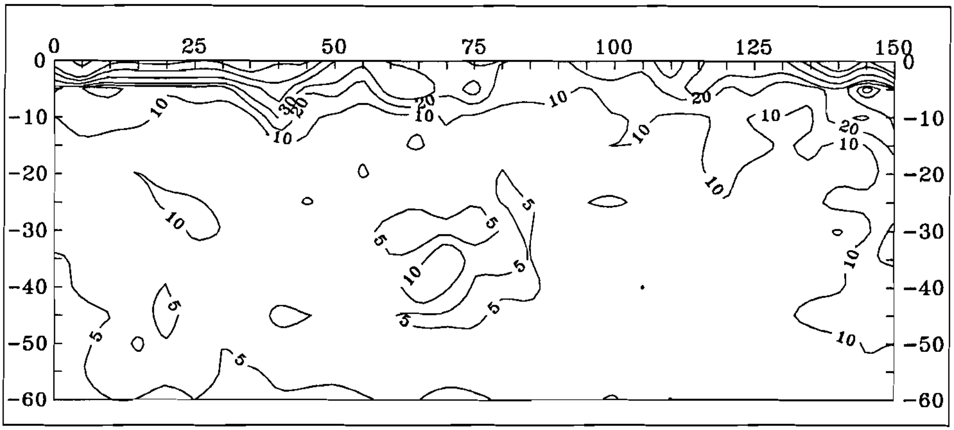

Figure 6.6. Vertical contour profile of zinc content, contents in $\mu g.g^{-1}$. Contour intervals at 5, 10, 20, 30, 50, 75 and 100 $\mu g.g^{-1}$.

There is an area at the right side and a spot in the middle of the contour profiles with relatively high contents of heavy metal, especially for copper and lead (Figures 6.4 and 6.5). This is probably caused by bio-turbation. Redistribution of heavy metals by bio-turbation might happen in two ways. First, heavy metal polluted organic matter in the topsoil is moved down by soil animals. Second, unpolluted organic matter from the topsoil is transported downwards by soil animals before the start of soil contamination. In a later phase the organic matter is polluted by adsorption of copper and lead, from heavy metal contaminated percolation water.

The aluminium illuviation layer is situated just below the layer of highest contents of organic matter and matches the layer with calcium peaks. There is no match with the zinc, copper and lead contents, which indicates that the distribution of Al-oxides plays no role in the distribution of these heavy metals.

From these contour profiles two major processes can be distinguished, i.e. bio-turbation of the soil and eluviation/illuviation of some major soil elements. The contour profiles of aluminium and calcium give a strong indication that eluviation and illuviation took place after bio-turbation had occurred, because the bio-turbation has not acted on the illuviation horizons.

6.3.3. One-dimensional heavy metal profiles

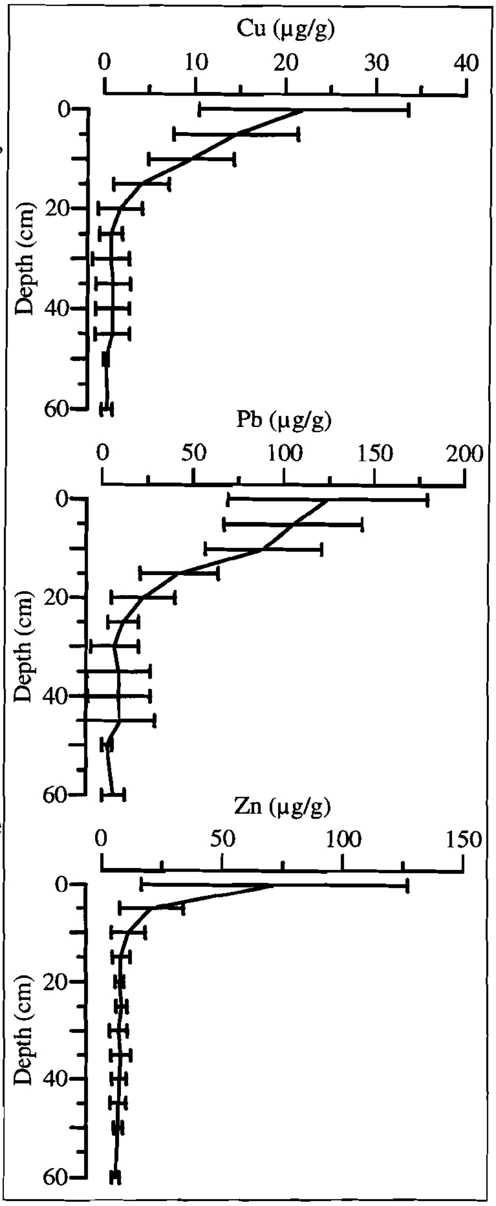

Figure 6.7. One-dimensional heavy metal soil profiles of copper, lead and zinc.

Figure 6.7 represents the copper, lead and zinc profiles of the sample site. The average contents were calculated from 31 samples at every depth. The variation bar is the standard deviation within 31 samples.

The shape of the zinc content profile is comparable with the zinc profile of Wilkens and Loch (1995) near this sample site, but the contents presented here are much lower. The absolute variation is highest in the topsoil.

Copper and lead have a different soil content profile; most striking is the relatively high standard deviation in the lower part of the profile. Also the average contents of copper and lead are slightly elevated in the lower part of the profiles. Both observations are consistent with the postulated redistribution mechanism.

The profiles presented here have almost the same standard deviation in the topsoil as presented by Wilkens and Loch (1995). The differences between the sampling methods are sample size and sampling distance. In this study we collected samples of about 25 grams on a spot with a diameter of 2 cm. In the former study by Wilkens and Loch (1995) we took samples of about 200 grams at a specific depth in a 2 cm thick horizontal layer. The sampling distance in this study is 5 cm in each layer, i.e. 31 samples on a line. The sampling distance in the former study is 20 meters, i.e. 9 samples in a grid. Therefore the variability on field scale seems to be explained by differences at a scale of decimeters, probably caused by bio-turbation.

6.4. Conclusions

Two processes are distinguished which are responsible for heterogeneity of soil macro parameters, i.e. bio-turbation of soil and eluviation and illuviation of aluminium and calcium. Eluviation/illuviation processes resulted in horizontal layers of these elements. Bio-turbation disturbed the original horizontal layering of organic matter in the soil and consequently the distribution of the trace metals, copper, lead. Because of its higher mobility zinc redistribution is only slightly affected by this process. The observed heterogeneity could not be ascribed to preferential flow phenomena. From comparison of data of this paper with data in chapter 2 of this thesis (Wilkens and Loch, 1995), it can be concluded that, the variability at the field scale seems to be explained by differences at a scale of decimeters, probably caused by bio-turbation.

References

Boekhold, A.E. and S.E.A.T.M. van der Zee (1992).
Significance of soil chemical heterogeneity for spatial behaviour of cadmium in field soils.
Soil Science Society of America Journal **56**: 747-754.

Bronswijk, J.J.B., L.W. Dekker and C.J. Ritsema (1990).
Preferent transport van water en opgeloste stoffen in de Nederlandse bodem: meer regel dan uitzondering.
H2O **23**(22): 594-597.

Davis, J.C. (1986).
Statistics and data analysis.
John Wiley & Sons, New York, U.S.A.

Hillel, D. and R.S. Baker (1988).
A descriptive theory of fingering during infiltration into layered soils.
Soil Science **146**(1): 51-56.

Kung, K.S. (1990).
Preferential flow in sandy vadose zone: 1 field observation.
Geoderma **46**: 51-58.

Raats, J.R. (1973).
Unstable wetting fronts in uniform and non-uniform soils.
Soil Science Society of America Journal **37**: 681-685.

van der Zee, S.E.A.T.M. and W.H. van Riemsdijk (1987).
Transport of reactive solute in spatially variable soil systems.
Water Resources Research **23**(11): 2059-2069.

Wilkens, B.J. and J.P.G. Loch (1995).
Accumulation of cadmium and zinc from diffuse immission on acid sandy soils, as a function of soil composition.
Water, Air, and Soil Pollution (Accepted for publication).

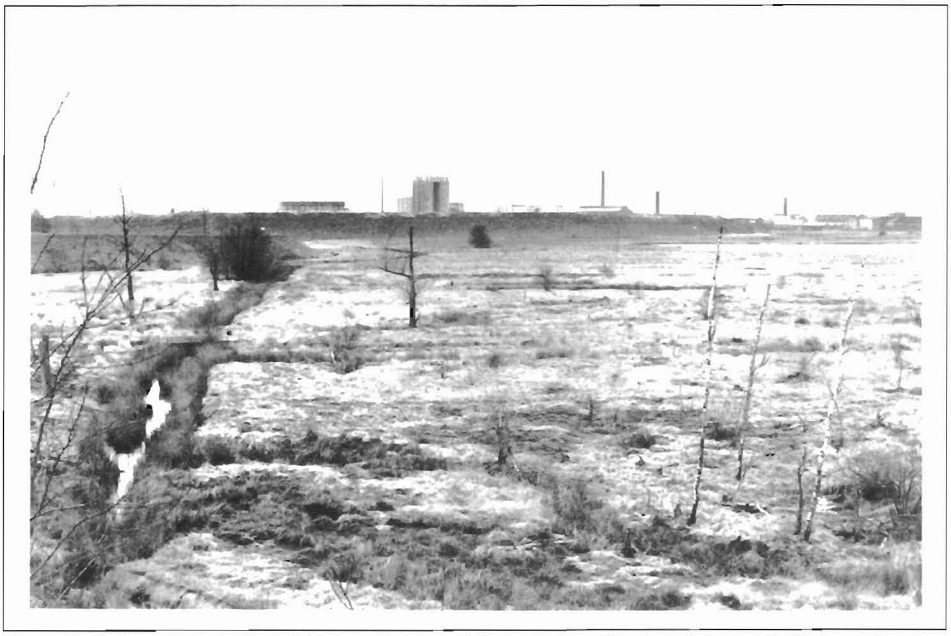

Photo 4. Soil and vegetation 1 km north-east of zinc smelter Overpelt (photo M. Reumers)

Appendix A
Soil sample characteristics

Explanations by Tables A.I. to A.VII
F = field,
S = site,
D = depth [cm],
pH = pH soil in pH units.
OM = organic matter content [% g.g^{-1}],
Al_2O_3 = aluminium oxide content [% g.g^{-1}],
Fe_2O_3 = iron oxide content [% g.g^{-1}],
MnO_2 = manganese oxide content [% g.g^{-1}],
Cd = cadmium content [μg.g^{-1}],
Cr = chromium content [μg.g^{-1}],
Cu = copper content [μg.g^{-1}],
Ni = nickel content [μg.g^{-1}],
Pb = lead content [μg.g^{-1}],
Zn = zinc content [μg.g^{-1}].

Table A.I. Soil sample characteristics.

F	S	D	pH	OM	Al_2O_3	Fe_2O_3	MnO_2	Cd	Cr	Cu	Ni	Pb	Zn
1	1	5	3.74	2.14	0.85	0.186	0.0027	0.20	6.5	12.5	3.9	156.2	23.0
1	1	10	3.70	3.48	0.36	0.119	0.0024	2.10	4.4	1.7	3.9	13.2	32.0
1	1	15	3.98	1.13	0.29	0.058	0.0019	0.56	4.1	1.2	4.1	19.2	8.6
1	1	20	4.07	0.33	0.33	0.048	0.0018	0.15	3.6	1.0	3.4	13.3	4.0
1	1	35	3.82	1.66	1.10	0.098	0.0037	1.30	6.2	1.2	4.7	10.3	19.0
1	1	50	3.86	2.07	1.71	0.201	0.0044	1.40	9.6	1.1	4.3	16.9	33.0
1	1	75	4.30	0.68	1.99	0.344	0.0055	0.30	11.1	1.0	4.0	21.1	14.6
1	1	100	4.21	0.92	2.07	0.331	0.0053	0.18	9.8	1.4	2.6	18.2	11.4
1	1	130	4.41	0.26	1.51	0.254	0.0037	0.06	8.9	1.1	2.6	20.1	5.8
1	2	0	4.50	1.55	1.16	0.350	0.0046	1.10	6.7	25.9	4.9	166.6	231.0
1	2	5	3.79	1.56	1.13	0.256	0.0032	0.15	6.7	8.5	2.8	85.3	22.0
1	2	10	3.82	0.93	1.18	0.271	0.0035	0.05	9.6	4.9	2.7	62.4	9.2
1	2	15	3.90	0.83	1.21	0.263	0.0035	0.05	8.7	4.3	4.9	59.4	8.4
1	2	20	3.95	0.55	1.24	0.248	0.0044	0.05	7.6	3.2	3.4	48.2	7.6
1	2	35	4.08	0.37	1.48	0.502	0.0032	0.05	8.7	1.5	3.4	10.5	11.0
1	2	50	4.12	0.18	1.59	0.499	0.0030	0.05	14.0	1.5	4.7	14.3	8.5
1	2	75	4.26	0.07	1.33	0.225	0.0016	0.05	4.3	0.9	3.4	18.7	4.3
1	2	100	4.41	0.08	1.67	0.303	0.0039	0.05	11.4	1.0	3.2	20.1	5.8
1	2	130	4.24	0.46	1.77	0.256	0.0049	0.05	10.2	1.3	4.1	9.8	7.8
1	3	0	3.85	5.26	1.51	0.594	0.0069	3.00	10.3	76.9	7.4	407.5	449.0
1	3	5	3.83	1.28	1.15	0.326	0.0035	0.07	8.2	9.0	2.5	83.6	11.7
1	3	10	3.82	0.73	1.16	0.371	0.0035	0.05	9.9	5.4	2.8	60.4	8.5
1	3	15	3.94	0.40	1.25	0.385	0.0034	0.05	8.3	4.2	4.1	47.5	6.3
1	3	20	4.03	0.41	1.31	0.389	0.0035	0.05	8.6	4.8	2.9	51.9	6.4
1	3	35	4.35	0.45	0.73	0.105	0.0018	0.05	4.8	3.7	1.4	30.7	3.3
1	3	50	4.15	3.34	1.46	0.354	0.0025	0.58	7.4	16.0	2.9	59.5	20.0
1	3	75	4.33	0.36	1.76	0.551	0.0027	0.06	7.3	1.2	4.6	10.5	14.3
1	3	100	4.35	0.13	1.61	0.462	0.0047	0.05	8.2	1.3	3.8	14.8	10.5
1	3	130	4.35	0.11	1.56	0.430	0.0038	0.05	7.7	1.2	4.6	19.0	8.5
1	4	0	3.67	5.68	1.60	0.594	0.0069	1.90	15.2	70.6	6.2	420.8	355.0
1	4	5	3.69	3.31	1.03	0.297	0.0033	0.58	6.4	36.3	3.6	334.0	85.0
1	4	10	3.47	6.19	1.10	0.294	0.0029	0.58	6.4	17.6	4.1	398.2	60.0
1	4	15	3.96	0.77	1.27	0.326	0.0028	0.16	6.2	2.8	3.4	46.2	11.6
1	4	20	4.12	1.00	1.45	0.319	0.0034	0.08	7.3	1.7	5.0	26.9	10.6
1	4	35	4.30	0.72	1.24	0.257	0.0024	0.11	6.5	1.1	2.5	17.5	9.5
1	4	50	4.35	0.71	0.36	0.052	0.0016	0.16	5.8	0.9	49.7	21.2	3.3
1	4	75	4.30	0.35	0.67	0.061	0.0027	0.11	7.8	0.9	1.9	31.1	3.0
1	4	100	4.17	1.29	1.84	0.299	0.0047	0.22	10.0	0.8	5.1	10.9	11.3
1	4	130	4.22	0.92	1.81	0.281	0.0058	0.13	9.1	1.0	4.0	13.6	9.7
1	5	0	4.20	2.90	1.72	0.618	0.0066	2.20	12.7	47.2	4.9	217.4	440.0
1	5	5	3.75	2.46	1.30	0.384	0.0038	0.60	7.4	24.4	4.0	203.1	87.0
1	5	10	3.78	1.79	1.26	0.369	0.0035	0.13	7.3	12.0	4.6	229.5	33.0
1	5	15	3.88	0.73	1.21	0.318	0.0029	0.05	6.3	3.4	2.1	83.7	7.3
1	5	20	3.98	0.54	1.26	0.352	0.0039	0.05	8.6	3.4	3.1	41.4	7.3
1	5	35	4.24	0.17	1.64	0.347	0.0049	0.05	12.0	2.1	4.1	16.8	7.6
1	5	50	4.37	0.08	1.53	0.315	0.0030	0.05	9.0	1.2	4.9	8.2	5.3
1	5	75	4.35	0.07	1.58	0.337	0.0029	0.05	7.1	1.3	5.2	12.4	5.8
1	5	100	4.33	0.05	1.57	0.285	0.0045	0.05	8.2	1.3	2.8	11.2	4.6
1	5	130	4.26	0.10	1.93	0.366	0.0066	0.05	12.4	1.4	2.6	7.7	6.5
1	6	0	4.12	1.40	1.19	0.350	0.0037	0.45	9.7	14.0	3.2	119.9	70.0
1	6	10	3.96	0.59	1.28	0.340	0.0030	0.07	9.4	5.5	2.3	35.1	8.7
1	6	5	3.86	1.01	1.13	0.324	0.0030	0.08	7.6	6.5	4.5	83.8	12.0
1	6	15	4.11	0.54	1.15	0.317	0.0036	0.09	9.0	1.8	2.3	19.2	8.1
1	6	20	4.26	0.28	1.04	0.258	0.0027	0.05	5.4	1.0	0.7	20.5	6.2
1	6	35	4.29	0.51	1.49	0.343	0.0046	0.10	9.4	1.2	3.9	17.3	8.2

Table A.II. Soil sample characteristics.

F	S	D	pH	OM	Al_2O_3	Fe_2O_3	MnO_2	Cd	Cr	Cu	Ni	Pb	Zn
1	6	35	4.29	0.51	1.49	0.343	0.0046	0.10	9.4	1.2	3.9	17.3	8.2
1	6	50	4.34	0.39	1.10	0.272	0.0028	0.09	5.8	0.9	0.8	11.1	6.0
1	6	75	4.28	0.88	0.68	0.112	0.0018	0.26	5.6	1.7	2.2	27.0	9.9
1	6	100	4.26	2.61	1.95	0.821	0.0037	1.20	8.9	1.3	1.4	17.0	31.0
1	6	130	4.34	0.25	1.84	0.605	0.0051	0.07	9.9	1.2	3.2	23.7	9.2
1	7	0	4.19	1.46	1.14	0.386	0.0044	0.75	12.2	18.0	3.3	115.2	138.0
1	7	5	4.12	0.70	0.95	0.262	0.0018	0.08	5.4	6.1	2.1	45.5	15.5
1	7	10	4.29	0.72	1.17	0.283	0.0027	0.05	7.2	4.2	3.0	25.5	8.8
1	7	15	4.28	0.77	1.11	0.256	0.0028	0.12	6.3	1.5	-0.6	14.6	8.5
1	7	20	4.34	0.72	0.83	0.188	0.0019	0.17	4.8	1.0	2.1	24.2	8.2
1	7	35	4.09	6.69	0.81	0.190	0.0030	3.40	6.9	1.7	1.9	18.9	36.0
1	7	50	4.31	1.35	0.65	0.076	0.0034	0.65	7.2	1.3	-0.6	20.3	5.4
1	7	75	4.13	2.37	1.25	0.097	0.0028	0.84	4.2	1.3	3.1	14.3	12.5
1	7	100	4.15	2.95	1.89	0.237	0.0043	0.69	11.2	2.4	4.7	17.2	23.0
1	7	130	4.36	1.07	1.70	0.249	0.0037	0.39	8.2	2.4	6.5	20.6	11.4
1	8	0	3.98	3.19	1.70	0.590	0.0064	1.40	10.7	45.2	6.2	248.9	294.0
1	8	5	3.74	4.42	1.72	0.615	0.0057	1.70	16.7	66.4	7.2	344.6	276.0
1	8	10	3.76	1.87	1.46	0.395	0.0035	0.41	8.9	15.5	2.6	110.1	63.0
1	8	15	3.80	1.24	1.38	0.500	0.0041	0.05	9.0	6.2	3.5	126.8	13.4
1	8	20	4.00	0.86	1.19	0.373	0.0039	0.05	11.6	4.7	2.3	59.3	9.4
1	8	35	4.32	0.28	1.67	0.447	0.0037	0.05	10.5	1.6	2.5	17.5	7.5
1	8	50	4.41	0.14	1.58	0.319	0.0038	0.05	10.4	1.2	3.1	13.7	6.2
1	8	75	4.46	0.07	1.41	0.243	0.0028	0.05	6.7	1.2	1.8	16.9	4.4
1	8	100	4.49	0.05	1.68	0.322	0.0046	0.05	9.1	1.2	3.9	12.1	5.9
1	8	130	4.36	0.14	1.73	0.311	0.0041	0.05	10.2	1.2	2.0	11.1	6.3
1	9	0	3.81	3.95	1.53	0.578	0.0071	1.80	13.3	61.4	6.7	308.0	285.0
1	9	5	3.84	1.59	1.19	0.321	0.0034	0.08	7.4	7.7	3.1	68.4	9.1
1	9	10	3.96	0.60	1.22	0.362	0.0035	0.06	11.5	2.2	1.1	31.4	6.8
1	9	15	4.11	0.71	1.40	0.385	0.0044	0.09	11.5	1.8	2.5	13.4	8.2
1	9	20	4.29	0.75	1.32	0.317	0.0025	0.10	7.6	1.2	2.2	14.2	8.2
1	9	35	4.34	0.92	1.46	0.340	0.0031	0.17	6.7	1.2	3.5	13.1	9.0
1	9	50	4.29	2.75	0.37	0.052	0.0015	0.70	3.6	1.0	-0.6	10.0	8.2
1	9	75	4.67	0.26	0.53	0.046	0.0014	0.05	4.8	0.9	-0.6	13.2	2.0
1	9	100	4.15	0.87	1.20	0.142	0.0032	0.26	4.5	0.8	1.5	12.7	7.4
1	9	130	4.43	0.34	1.63	0.254	0.0025	0.05	6.1	0.9	-0.6	14.9	5.0
2	1	0	3.60	8.46	1.32	0.531	0.0097	2.20	14.2	59.7	8.8	342.0	371.0
2	1	5	3.90	3.87	0.94	0.262	0.0053	4.00	12.4	11.2	4.7	101.8	46.0
2	1	10	4.13	3.42	0.71	0.158	0.0031	3.60	12.1	2.4	4.9	15.0	26.0
2	1	15	4.20	2.79	1.07	0.293	0.0044	3.10	12.0	1.6	5.7	27.5	27.0
2	1	20	4.35	1.68	1.32	0.464	0.0065	1.90	11.9	1.1	4.3	13.7	25.0
2	1	35	4.58	0.70	2.08	0.728	0.0065	0.13	21.0	1.1	6.3	19.4	31.0
2	1	50	4.64	0.32	2.09	0.568	0.0075	0.05	14.4	1.0	7.3	17.4	20.0
2	1	75	4.59	0.25	2.11	0.623	0.0089	0.06	23.1	1.1	6.4	16.8	23.0
2	1	100	4.66	0.13	2.07	0.503	0.0076	0.05	19.4	1.2	7.4	12.8	17.0
2	1	130	4.51	0.09	2.33	0.600	0.0101	0.05	20.8	1.3	6.7	21.6	21.0
2	2	0	4.35	6.77	0.97	0.332	0.0056	3.40	11.9	37.6	7.9	227.5	220.0
2	2	5	4.42	4.25	0.94	0.288	0.0050	1.90	17.6	23.8	6.3	113.0	92.0
2	2	10	4.50	2.51	0.84	0.125	0.0027	1.40	8.8	1.5	5.3	15.0	47.0
2	2	15	4.49	2.22	0.61	0.107	0.0025	1.80	8.4	1.1	6.0	13.5	34.0
2	2	20	4.36	5.41	0.63	0.162	0.0029	4.70	6.8	5.4	5.3	106.2	64.0
2	2	35	4.62	0.50	1.56	0.594	0.0051	0.18	11.3	1.2	6.7	16.1	10.1
2	2	50	4.75	0.29	1.98	0.426	0.0062	0.1	10.5	0.55	5.45	15.25	14
2	2	75	4.74	0.14	1.81	0.314	0.0079	0.05	16.4	1.0	4.4	14.1	8.0
2	2	100	4.53	0.17	2.03	0.490	0.0071	0.05	12.6	1.2	8.0	15.1	14.3
2	2	130	4.52	0.10	1.94	0.510	0.0070	0.05	16.5	1.0	5.5	23.5	19.0

Table A.III. Soil sample characteristics.

F	S	D	pH	OM	Al_2O_3	Fe_2O_3	MnO_2	Cd	Cr	Cu	Ni	Pb	Zn
2	3	0	4.14	7.50	2.15	0.384	0.0087	1.70	16.4	50.7	8.4	260.7	220.0
2	3	5	4.12	5.74	1.62	0.207	0.0051	1.30	17.1	6.1	7.5	88.5	46.0
2	3	10	4.14	4.74	1.35	0.155	0.0046	2.00	15.5	3.6	7.0	45.0	25.0
2	3	15	4.11	3.44	1.10	0.167	0.0042	1.40	19.1	4.3	5.7	106.9	26.0
2	3	20	4.10	2.92	1.04	0.186	0.0053	1.00	10.8	9.1	5.1	238.7	48.0
2	3	35	4.50	0.31	1.94	0.383	0.0071	0.13	9.9	1.1	9.6	13.1	12.0
2	3	50	4.43	0.05	2.01	0.419	0.0061	0.13	9.8	1.1	7.0	27.8	16.0
2	3	75	4.45	0.23	1.99	0.355	0.0049	0.12	9.8	1.2	5.0	15.0	17.0
2	3	100	4.51	0.18	2.14	0.335	0.0048	0.13	9.7	1.3	8.1	21.3	19.0
2	3	130	4.34	0.16	2.37	0.486	0.0099	0.06	16.2	1.3	7.7	25.7	20.0
2	4	0	3.87	5.81	0.94	0.258	0.0071	0.84	10.6	48.8	3.7	257.8	104.0
2	4	5	3.85	4.76	0.83	0.348	0.0034	0.50	7.6	11.5	2.7	183.0	28.0
2	4	10	3.92	6.52	0.72	0.124	0.0029	3.60	7.6	1.9	1.9	9.2	31.0
2	4	15	3.83	4.77	0.93	0.244	0.0045	3.20	9.3	14.9	3.6	315.9	167.0
2	4	20	4.11	3.58	1.09	0.178	0.0039	2.10	8.3	2.3	2.4	41.2	74.0
2	4	35	4.38	1.24	1.97	0.357	0.0067	0.69	9.3	0.5	2.2	5.5	33.0
2	4	50	4.56	0.55	1.97	0.399	0.0069	0.17	11.1	0.6	3.8	5.9	24.0
2	4	75	4.54	0.27	2.02	0.397	0.0087	0.12	14.1	0.5	1.9	6.5	18.0
2	4	100	4.36	0.33	2.41	0.476	0.0105	0.10	19.0	0.9	4.2	-5.3	20.0
2	4	130	4.46	0.28	2.52	0.526	0.0124	0.1	18.2	1.2	4.3	7.85	18
2	5	0	3.74	5.85	1.08	0.234	0.0049	0.93	11.2	36.0	4.0	260.5	107.0
2	5	5	3.84	2.98	0.70	0.114	0.0035	0.86	9.0	9.1	1.7	61.5	17.0
2	5	10	3.97	3.12	0.60	0.100	0.0031	0.87	8.2	5.3	2.7	42.2	16.0
2	5	15	4.03	1.90	0.55	0.097	0.0032	1.40	7.1	1.5	1.3	17.1	11.9
2	5	20	3.77	6.79	1.15	0.165	0.0041	4.70	8.8	8.8	2.9	145.8	93.0
2	5	35	4.06	1.39	1.92	0.266	0.0067	0.83	9.3	1.0	2.6	-5.2	24.0
2	5	50	4.39	0.28	1.89	0.347	0.0073	0.18	9.3	0.5	2.8	10.0	9.4
2	5	75	4.47	0.23	2.01	0.418	0.0091	0.11	10.8	0.8	3.3	8.7	12.6
2	5	100	4.49	0.19	1.84	0.351	0.0051	0.05	7.7	0.7	3.0	-5.1	13.5
2	5	130	4.44	0.22	2.30	0.465	0.0091	0.07	12.7	0.9	3.9	9.8	18.0
2	6	0	3.72	10.65	1.60	0.414	0.0106	2.40	23.8	58.6	10.7	361.3	291.0
2	6	5	3.97	7.10	1.63	0.257	0.0105	4.50	15.3	19.9	7.9	206.5	116.0
2	6	10	4.32	7.15	1.32	0.165	0.0052	9.50	9.5	2.7	6.6	18.4	238.0
2	6	15	4.16	5.38	0.91	0.170	0.0047	2.40	9.6	9.9	7.6	190.2	226.0
2	6	20	4.18	6.31	1.74	0.302	0.0060	2.10	13.8	32.1	8.4	479.0	312.0
2	6	35	4.51	1.46	1.25	0.204	0.0036	0.37	-0.6	1.2	4.0	-5.3	31.0
2	6	50	4.63	0.31	1.99	0.404	0.0075	0.11	11.1	1.3	6.7	7.4	18.0
2	6	75	4.57	0.25	1.95	0.343	0.0051	0.08	9.1	1.3	7.7	15.1	16.0
2	6	100	4.59	0.17	2.08	0.467	0.0105	0.07	16.3	1.3	8.0	14.4	21.0
2	6	130	4.59	0.17	2.26	0.523	0.0139	0.07	20.3	2.0	8.2	13.4	20.0
2	7	0	3.85	7.24	1.17	0.223	0.0046	1.30	12.9	26.4	4.9	170.2	119.0
2	7	5	3.80	4.18	0.88	0.120	0.0027	0.93	9.2	6.0	3.7	59.9	24.0
2	7	10	3.92	2.86	0.67	0.106	0.0027	0.48	10.8	2.4	3.1	24.8	9.9
2	7	15	3.69	5.01	0.95	0.249	0.0040	0.73	8.9	19.8	6.4	367.9	80.0
2	7	20	3.46	10.12	1.21	0.455	0.0054	1.60	12.0	29.0	6.5	600.4	178.0
2	7	35	3.82	4.85	1.50	0.112	0.0041	3.40	13.2	1.7	4.9	12.2	42.0
2	7	50	4.24	0.78	2.04	0.304	0.0068	0.74	13.6	1.3	3.8	25.1	11.9
2	7	75	4.30	0.23	2.01	0.340	0.0048	0.12	12.3	1.1	6.8	8.6	9.7
2	7	100	4.45	0.20	1.87	0.333	0.0047	0.07	11.4	1.1	3.8	15.8	11.4
2	7	130	4.49	0.21	2.29	0.430	0.0070	0.07	15.1	1.3	4.2	15.1	18.0
2	8	0	4.33	4.20	2.00	0.329	0.0078	0.89	19.9	28.7	6.6	142.8	74.0
2	8	5	4.04	2.78	2.27	0.304	0.0086	0.65	21.7	4.2	5.3	48.7	34.0
2	8	10	4.39	1.35	2.22	0.326	0.0066	0.53	17.7	1.3	4.7	6.1	25.0
2	8	15	4.44	0.91	1.85	0.327	0.0075	0.39	12.7	1.2	5.1	11.4	18.0
2	8	20	4.42	0.57	1.77	0.328	0.0057	0.34	11.0	1.0	6.0	9.4	19.0

Table A.IV. Soil sample characteristics.

F	S	D	pH	OM	Al_2O_3	Fe_2O_3	MnO_2	Cd	Cr	Cu	Ni	Pb	Zn
2	8	35	4.43	0.42	2.03	0.365	0.0053	0.12	13.6	1.0	7.2	20.9	22.0
2	8	50	4.50	0.19	1.96	0.365	0.0053	0.05	12.0	1.1	6.0	12.4	23.0
2	8	75	4.51	0.24	2.05	0.426	0.0103	0.06	15.0	1.2	7.3	23.8	25.0
2	8	100	4.51	0.17	2.47	0.540	0.0124	0.05	23.6	1.2	7.0	11.5	25.0
2	8	130	4.46	0.07	2.15	0.594	0.0168	0.05	28.5	1.5	8.4	25.0	18.0
2	9	0	4.42	5.84	1.95	0.440	0.0109	2.20	17.0	54.5	7.1	257.4	206.0
2	9	5	4.56	3.85	1.92	0.298	0.0068	6.00	15.0	5.0	6.3	28.2	99.0
2	9	10	4.39	5.83	1.69	0.249	0.0067	5.70	14.2	11.0	4.5	229.4	285.0
2	9	15	4.44	8.22	1.90	0.357	0.0064	2.70	15.0	19.4	7.2	333.4	280.0
2	9	20	4.41	4.58	1.94	0.330	0.0057	1.80	14.5	13.3	5.5	205.0	235.0
2	9	35	4.65	1.06	2.09	0.425	0.0072	0.52	14.8	1.1	6.6	15.6	41.0
2	9	50	4.62	0.33	2.01	0.413	0.0063	0.12	12.4	1.0	5.1	11.4	24.0
2	9	75	4.66	0.24	2.02	0.346	0.0050	0.07	11.8	1.0	14.6	15.5	23.0
2	9	100	4.72	0.18	2.08	0.362	0.0059	0.40	11.0	1.1	4.6	19.0	43.0
2	9	130	5.08	0.11	2.07	0.393	0.0066	0.77	13.5	1.2	7.2	17.8	76.0
3	1	0	4.52	0.98	3.19	0.858	0.0136	0.22	20.9	13.0	4.4	46.1	77.0
3	1	5	4.22	0.42	3.73	0.885	0.0097	0.05	26.9	4.2	5.2	17.6	28.0
3	1	10	4.30	0.27	3.09	0.644	0.0099	0.05	20.4	2.3	6.5	15.1	24.0
3	1	15	4.33	0.19	3.66	0.906	0.0107	0.05	24.3	2.4	5.2	6.5	25.0
3	1	20	4.23	0.17	4.98	1.440	0.0117	0.05	34.8	4.4	6.6	7.1	36.0
3	1	35	4.37	1.00	2.19	0.547	0.0072	0.25	13.5	3.1	3.4	27.4	29.0
3	1	50	4.67	1.20	1.88	0.476	0.0081	0.84	12.7	5.0	2.4	32.0	72.0
3	1	75	4.93	0.97	2.04	0.557	0.0072	0.50	13.4	7.7	4.2	41.8	77.0
3	1	100	4.57	0.235	2.45	0.827	0.0084	0.12	18.1	4.7	4.0	23.7	26
3	1	130	4.12	0.07	5.34	1.154	0.0140	0.05	37.0	4.4	6.0	15.3	16.3
3	2	0	4.10	0.83	2.27	0.623	0.0093	0.10	17.5	9.3	4.5	29.5	32.0
3	2	5	4.21	0.66	2.14	0.565	0.0089	0.05	13.6	4.9	3.5	16.4	19.0
3	2	10	4.25	0.55	2.23	0.639	0.0086	0.05	13.3	3.0	3.2	16.4	19.0
3	2	15	4.36	0.55	1.99	0.559	0.0073	0.07	13.6	3.3	4.7	26.8	17.0
3	2	20	4.38	0.59	2.08	0.582	0.0065	0.06	14.8	3.8	2.8	26.6	19.0
3	2	35	4.35	0.50	2.08	0.592	0.0074	0.10	16.2	3.3	4.0	20.7	16.6
3	2	50	4.50	0.26	1.99	0.483	0.0062	0.07	15.0	1.2	3.8	15.0	8.9
3	2	75	4.49	0.28	2.05	0.488	0.0069	0.08	13.9	1.1	3.1	12.9	10.7
3	2	100	4.37	0.20	2.25	0.453	0.0048	0.05	12.2	1.2	2.9	13.9	13.4
3	2	130	4.48	0.12	1.95	0.467	0.0056	0.05	13.7	1.2	3.3	22.9	12.5
3	3	0	4.36	1.39	2.12	0.679	0.0102	0.19	14.3	13.0	2.3	78.2	73.0
3	3	5	4.99	1.06	2.03	0.649	0.0087	0.12	14.0	8.9	3.6	50.4	53.0
3	3	10	4.76	0.93	1.86	0.632	0.0072	0.08	11.8	7.8	3.5	53.0	42.0
3	3	15	4.72	0.70	1.78	0.534	0.0067	0.06	12.8	5.9	3.4	41.1	24.0
3	3	20	4.51	0.67	1.77	0.503	0.0065	0.07	9.5	5.2	3.4	30.7	22.0
3	3	35	4.47	0.77	1.79	0.515	0.0061	0.11	11.0	5.6	4.3	34.2	23.0
3	3	50	4.38	1.15	1.78	0.486	0.0060	0.19	11.3	5.0	3.2	29.1	22.0
3	3	75	4.39	0.12	2.43	0.859	0.0103	0.05	14.2	2.0	4.9	13.3	12.8
3	3	100	4.42	0.08	2.16	0.601	0.0052	0.05	11.4	1.9	2.7	13.0	10.3
3	3	130	4.25	0.08	3.42	0.910	0.0104	0.05	23.4	2.9	5.9	15.0	18.0
3	4	0	4.46	0.40	2.74	0.732	0.0089	0.08	17.6	4.6	3.6	14.5	29.0
3	4	5	4.74	0.29	2.30	0.618	0.0086	0.05	15.4	3.8	3.8	11.2	27.0
3	4	10	4.62	0.22	3.73	1.044	0.0092	0.05	26.0	4.5	5.4	15.9	30.0
3	4	15	4.56	0.16	3.59	0.983	0.0085	0.05	23.6	3.8	5.0	9.2	24.0
3	4	20	4.61	0.86	2.16	0.586	0.0091	0.11	15.2	3.5	4.4	21.6	20.0
3	4	35	4.58	1.01	2.03	0.532	0.0059	0.24	13.2	3.1	2.4	15.7	24.0
3	4	50	4.63	1.13	1.61	0.381	0.0051	0.57	10.9	4.5	3.7	36.7	38.0
3	4	75	4.82	1.11	1.75	0.392	0.0051	0.57	10.4	3.9	2.5	29.6	45.0
3	4	100	4.83	0.06	2.60	1.026	0.0114	0.05	17.0	2.4	4.0	12.8	11.2
3	4	130	4.29	0.03	2.75	1.125	0.0115	0.05	16.1	3.6	4.7	6.2	10.9

Table A.V. Soil sample characteristics.

F	S	D	pH	OM	Al_2O_3	Fe_2O_3	MnO_2	Cd	Cr	Cu	Ni	Pb	Zn
3	5	0	4.63	1.13	1.65	0.522	0.0078	0.20	13.6	8.2	6.5	37.5	57.0
3	5	5	4.52	1.63	1.87	0.541	0.0070	0.36	9.1	15.3	7.0	123.0	67.0
3	5	10	4.68	0.96	1.81	0.508	0.0059	0.15	10.9	4.5	7.1	36.5	32.0
3	5	15	4.64	0.93	2.08	0.525	0.0062	0.13	13.1	2.0	6.9	14.8	24.0
3	5	20	4.60	1.06	1.76	0.513	0.0071	0.17	10.9	6.1	28.2	47.2	34.0
3	5	35	4.62	2.34	1.56	0.278	0.0044	1.00	7.5	1.2	5.7	10.3	25.0
3	5	50	4.57	1.28	1.68	0.429	0.0054	0.40	8.4	3.3	5.5	21.9	31
3	5	75	4.39	0.04	1.52	0.463	0.0083	0.05	6.3	0.9	5.9	6.1	8.4
3	5	100	4.27	0.05	3.39	0.939	0.0125	0.05	17.1	2.9	9.7	-5.3	17.0
3	5	130	4.34	0.07	6.32	1.564	0.0258	0.15	38.7	6.7	14.3	24.3	63.0
3	6	0	5.12	2.44	2.59	0.828	0.0171	1.30	19.7	35.8	7.6	115.9	327.0
3	6	5	5.03	0.26	1.47	0.469	0.0043	0.05	7.2	2.2	5.2	22.6	22.0
3	6	10	4.81	0.08	1.54	0.498	0.0043	0.05	8.2	1.2	5.1	17.7	13.7
3	6	15	4.69	0.06	1.51	0.468	0.0033	0.05	5.8	1.0	3.9	7.9	12.4
3	6	20	4.59	0.05	1.70	0.740	0.0132	0.05	15.3	0.9	5.4	19.5	11.8
3	6	35	4.55	0.04	2.11	0.637	0.0148	0.05	14.0	1.0	5.5	5.6	11.3
3	6	50	4.45	0.05	1.58	0.555	0.0081	0.05	9.0	1.1	3.1	14.1	7.8
3	6	75	4.39	0.04	2.12	0.572	0.0095	0.05	13.6	1.0	5.4	12.6	9.9
3	6	100	4.36	0.04	2.06	0.529	0.0064	0.05	12.3	0.9	6.0	-5.3	9.9
3	6	130	4.32	0.04	1.88	0.652	0.0114	0.05	4.4	1.7	5.5	9.4	9.0
3	7	0	4.44	0.45	3.69	0.808	0.0095	0.05	21.0	2.4	5.1	9.1	33.0
3	7	5	4.51	0.47	3.71	0.792	0.0093	0.05	20.6	2.0	53.1	-5.2	23.0
3	7	10	4.50	0.28	3.61	0.803	0.0091	0.05	20.6	2.5	5.9	9.9	19.0
3	7	15	4.42	0.29	2.03	0.590	0.0069	0.05	12.4	3.0	5.0	21.5	19.0
3	7	20	4.41	0.22	1.56	0.485	0.0057	0.05	8.9	2.9	4.3	36.5	16.0
3	7	35	4.36	0.32	1.51	0.497	0.0067	0.06	9.6	3.1	4.0	29.8	17.0
3	7	50	4.49	1.46	1.66	0.362	0.0046	0.44	8.3	1.7	2.9	10.5	20.0
3	7	75	4.42	0.59	2.01	0.548	0.0071	0.35	12.5	5.4	4.5	36.9	76.0
3	7	100	4.63	1.77	1.41	0.259	0.0046	0.74	8.1	1.2	3.7	7.4	35.0
3	7	130	4.32	0.05	2.37	0.856	0.0076	0.05	12.3	2.4	5.9	6.5	11.7
3	8	0	5.04	0.85	2.01	0.384	0.0095	0.27	15.0	4.0	4.5	13.6	49.0
3	8	5	5.23	0.93	1.98	0.475	0.0077	0.24	13.5	5.3	4.1	20.7	43.0
3	8	10	5.13	0.99	2.24	0.643	0.0089	0.25	13.8	8.6	5.7	28.8	68.0
3	8	15	5.46	0.49	1.69	0.460	0.0059	0.15	8.8	5.5	4.6	45.8	57.0
3	8	20	5.53	0.55	1.87	0.551	0.0065	0.07	10.8	4.2	5.0	39.5	23.0
3	8	35	5.00	0.05	2.15	0.789	0.0075	0.05	10.3	1.5	3.4	-5.2	8.7
3	8	50	4.71	0.05	2.38	0.906	0.0129	0.05	12.4	1.6	5.4	5.8	9.7
3	8	75	4.82	0.07	4.84	1.625	0.0247	0.06	31.8	4.6	11.0	15.6	32
3	8	100	4.23	0.06	5.57	1.155	0.0145	0.05	31.3	3.9	9.1	8.4	20.0
3	8	130	4.35	0.04	2.43	0.740	0.0151	0.05	13.8	2.1	6.2	8.0	12.1
3	9	0	4.43	0.75	1.71	0.522	0.0064	0.14	12.7	7.8	4.7	48.5	55.0
3	9	5	4.24	0.75	1.68	0.498	0.0063	0.09	8.8	7.9	4.5	61.1	45.0
3	9	10	4.30	0.44	1.70	0.513	0.0067	0.06	10.5	6.2	4.2	48.7	33.0
3	9	15	4.18	1.06	1.83	0.701	0.0083	0.35	10.7	17.8	5.5	121.7	126.0
3	9	20	4.23	0.61	1.68	0.568	0.0069	0.10	8.6	9.5	5.3	42.9	59.0
3	9	35	4.37	0.10	2.06	0.561	0.0062	0.05	11.7	1.6	5.2	22.6	19.0
3	9	50	4.49	0.28	2.08	0.577	0.0074	0.09	15.4	4.0	5.6	36.3	42.0
3	9	75	4.57	0.04	1.83	0.525	0.0060	0.05	10.0	1.2	4.2	11.2	12.0
3	9	100	4.39	0.05	2.39	0.601	0.0075	0.05	12.5	1.4	5.7	10.6	10.9
3	9	130	4.36	0.04	1.91	0.588	0.0074	0.05	10.8	1.4	6.4	5.6	8.4
4	1	0	3.87	3.83	0.97	0.151	0.0040	0.64	8.8	7.8	2.3	36.3	43.0
4	1	5	3.91	2.69	0.96	0.107	0.0027	0.44	8.5	3.2	1.5	16.0	18.0
4	1	10	4.12	1.02	0.73	0.067	0.0025	0.22	8.0	11.1	1.6	10.6	4.8
4	1	15	3.85	4.74	1.26	0.085	0.0034	2.30	7.7	1.4	2.4	13.6	25.0
4	1	20	3.81	4.52	1.48	0.107	0.0040	2.50	9.0	1.4	2.7	6.0	23.0

Table A.VI. Soil sample characteristics.

F	S	D	pH	OM	Al_2O_3	Fe_2O_3	MnO_2	Cd	Cr	Cu	Ni	Pb	Zn
4	1	25	3.91	2.61	1.58	0.161	0.0039	1.50	10.7	1.2	1.5	5.9	16.0
4	1	35	4.12	1.72	2.04	0.334	0.0059	0.82	14.0	1.0	3.7	9.6	14.0
4	1	50	4.27	1.19	2.04	0.364	0.0068	0.27	12.4	1.0	5.1	10.7	10.8
4	1	75	4.33	0.68	2.09	0.388	0.0060	0.21	11.9	1.1	2.9	10.6	9.5
4	1	100	4.28	0.57	1.94	0.353	0.0055	0.14	11.8	1.2	3.9	10.1	9.2
4	1	130	4.31	0.49	2.06	0.411	0.0087	2.20	14.0	4.3	3.4	6.8	30.0
4	2	0	3.83	11.35	0.69	0.172	0.0033	2.20	11.6	20.0	1.9	124.6	75.0
4	2	5	3.91	5.50	0.43	0.075	0.0018	1.40	7.5	1.9	1.3	12.0	24.0
4	2	10	3.97	2.97	0.45	0.071	0.0023	1.00	9.0	1.6	2.8	9.9	11.7
4	2	15	3.98	2.28	0.53	0.069	0.0023	0.65	7.9	1.2	-0.6	9.2	7.1
4	2	20	3.92	2.88	0.91	0.064	0.0023	0.70	10.7	1.2	2.4	13.0	11.2
4	2	25	3.89	7.05	1.92	0.167	0.0030	2.40	8.7	1.1	0.8	10.0	26.0
4	2	35	4.29	1.73	2.41	0.471	0.0060	0.29	12.3	1.2	2.1	11.4	10.2
4	2	50	4.42	0.52	2.18	0.279	0.0051	0.05	11.1	0.9	1.7	9.8	8.6
4	2	75	4.43	0.22	2.05	0.314	0.0042	0.05	10.4	0.9	2.1	5.3	11.3
4	2	100	4.35	0.13	2.01	0.352	0.0061	0.05	11.5	1.2	2.8	7.5	8.0
4	2	130	4.37	0.07	1.90	0.406	0.0062	0.05	13.0	1.4	3.1	8.0	7.5
4	3	0	4.00	9.60	0.95	0.390	0.0054	1.60	11.0	49.8	6.2	305.1	190.0
4	3	5	4.17	2.58	0.56	0.088	0.0053	0.09	6.3	3.2	2.1	31.5	10.8
4	3	10	3.76	12.45	1.91	0.525	0.0031	2.90	10.7	1.4	3.8	13.4	35.0
4	3	15	3.93	4.67	2.06	1.092	0.0039	1.10	12.2	0.9	3.8	9.9	14.0
4	3	20	4.30	0.49	2.51	0.620	0.0070	0.05	13.2	1.2	3.9	5.9	8.4
4	3	25	4.34	0.26	2.26	0.509	0.0068	0.05	11.8	1.1	4.1	9.7	9.7
4	3	35	4.38	0.17	1.96	0.409	0.0058	0.05	10.7	1.2	2.9	9.1	9.9
4	3	50	4.39	0.13	1.89	0.383	0.0047	0.05	11.7	1.2	3.6	13.9	10.0
4	3	75	4.39	0.12	1.82	0.357	0.0039	0.05	9.8	1.3	4.4	9.5	10.6
4	3	100	4.39	0.10	1.92	0.393	0.0058	0.05	12.7	1.1	4.2	11.8	12.2
4	3	130	4.37	0.08	1.83	0.443	0.0052	0.05	16.1	1.1	3.4	11.5	8.1
4	4	0	3.84	5.30	0.80	0.245	0.0034	0.47	8.7	24.0	1.9	126.1	72.0
4	4	5	3.77	6.30	0.86	0.174	0.0031	0.20	8.9	10.2	0.7	67.4	19.0
4	4	10	3.77	6.30	0.51	0.131	0.0022	0.65	5.5	1.1	-0.6	11.3	17.0
4	4	15	3.91	2.80	0.47	0.085	0.0019	0.25	5.6	1.0	1.1	11.8	6.9
4	4	20	3.89	2.24	0.52	0.096	0.0022	0.25	6.0	0.7	1.5	6.8	6.4
4	4	25	3.99	0.90	0.76	0.107	0.0025	0.10	7.9	1.0	-0.6	11.3	3.8
4	4	35	4.21	1.36	2.87	0.961	0.0062	0.14	14.7	0.9	2.3	6.6	14.0
4	4	50	4.32	0.22	2.11	0.526	0.0056	0.05	10.2	1.2	2.0	15.7	10.4
4	4	75	4.40	0.09	1.83	0.406	0.0044	0.05	8.9	1.0	2.2	5.8	7.9
4	4	100	4.45	0.08	1.80	0.343	0.0039	0.05	11.3	1.1	2.7	11.0	7.6
4	4	130	4.59	0.08	1.50	0.143	0.0044	0.05	6.5	1.4	1.6	13.5	3.3
4	5	0	3.86	5.31	0.89	0.245	0.0046	0.46	10.3	23.8	2.8	164.1	56.0
4	5	5	3.70	6.89	0.90	0.188	0.0034	0.58	6.6	5.7	2.1	88.5	21.0
4	5	10	3.79	6.45	0.46	0.141	0.0020	1.20	5.9	1.7	1.2	12.4	14.0
4	5	15	3.94	2.10	0.47	0.073	0.0024	0.29	6.7	1.3	0.9	11.5	4.2
4	5	20	4.05	0.89	0.62	0.071	0.0027	0.12	8.5	1.1	1.5	11.3	2.3
4	5	25	3.80	8.97	2.04	0.233	0.0032	3.60	10.5	1.1	1.1	5.3	29.0
4	5	35	4.15	1.13	2.43	0.586	0.0063	0.24	14.9	1.1	3.7	10.1	8.9
4	5	50	4.31	0.30	2.13	0.364	0.0052	0.06	11.5	1.1	2.4	8.7	8.2
4	5	75	4.40	0.28	1.94	0.258	0.0049	0.05	10.4	1.2	2.7	9.5	6.0
4	5	100	4.38	0.14	2.12	0.484	0.0082	0.05	17.3	1.1	4.2	6.1	11.2
4	5	130	4.34	0.10	2.27	0.444	0.0080	0.05	13.1	1.4	61.6	9.9	10.9
4	6	0	4.03	7.11	0.41	0.110	0.0029	0.60	7.2	22.8	2.2	190.0	37.0
4	6	5	4.08	2.26	0.48	0.072	0.0024	0.14	10.3	3.5	1.8	26.1	9.5
4	6	10	4.06	1.62	0.76	0.079	0.0028	0.09	9.2	2.0	2.3	7.5	8.1
4	6	15	3.53	20.75	2.42	0.317	0.0032	4.80	11.2	1.6	3.4	7.5	88.0
4	6	20	3.80	4.98	2.56	0.485	0.0072	1.10	16.4	1.1	3.8	14.2	18.0

Table A.VII. Soil sample characteristics.

F	S	D	pH	OM	Al_2O_3	Fe_2O_3	MnO_2	Cd	Cr	Cu	Ni	Pb	Zn
4	6	25	4.23	1.14	2.97	0.575	0.0075	0.07	16.3	1.2	2.5	8.4	10.9
4	6	35	4.46	0.31	1.88	0.386	0.0036	0.05	9.2	1.0	3.4	8.7	7.3
4	6	50	4.42	0.18	1.89	0.394	0.0039	0.05	10.5	0.9	4.0	8.7	11.3
4	6	75	4.46	0.13	1.92	0.356	0.0041	0.05	11.9	1.0	2.9	7.5	9.9
4	6	100	4.45	0.09	1.88	0.393	0.0050	0.05	9.6	1.1	3.7	13.2	10.5
4	6	130	4.47	0.09	1.79	0.394	0.0052	0.05	10.7	1.5	2.8	8.4	11.0
4	7	0	3.93	10.62	1.25	0.440	0.0060	1.30	10.4	48.7	3.2	278.9	207.0
4	7	5	3.65	10.45	0.64	0.172	0.0024	3.10	9.2	7.4	3.5	73.7	71.0
4	7	10	3.91	3.76	0.47	0.081	0.0027	0.38	9.6	1.3	1.0	7.7	8.4
4	7	15	3.91	3.17	0.76	0.100	0.0032	0.44	9.8	1.2	1.5	9.0	10.8
4	7	20	3.74	5.69	1.53	0.193	0.0041	1.60	9.9	1.2	1.5	13.2	26.0
4	7	25	3.76	3.76	2.13	0.416	0.0049	1.20	15.2	1.1	0.8	9.5	15.5
4	7	35	4.25	0.87	1.99	0.339	0.0059	0.10	9.8	0.9	1.8	10.7	6.3
4	7	50	4.34	0.50	2.10	0.381	0.0051	0.06	12.0	0.9	2.3	7.9	7.1
4	7	75	4.43	0.44	1.93	0.527	0.0048	0.05	10.9	1.0	1.5	-5.2	8.9
4	7	100	4.46	0.16	2.23	0.391	0.0070	0.05	12.5	1.1	2.0	6.4	9.4
4	7	130	4.50	0.16	2.11	0.409	0.0060	0.06	13.6	1.0	2.2	-5.2	10.8
4	8	0	4.02	4.11	0.55	0.095	0.0028	0.38	14.6	15.9	-0.6	123.7	29.0
4	8	5	4.09	1.79	0.57	0.089	0.0032	0.33	10.7	3.2	-0.6	36.9	15.8
4	8	10	3.80	5.44	1.21	0.122	0.0047	2.80	11.8	2.0	0.8	13.3	32.0
4	8	15	3.73	8.52	1.90	0.151	0.0046	5.20	13.6	2.3	1.1	11.5	46.0
4	8	20	3.77	8.14	1.98	0.160	0.0053	4.90	12.8	2.0	-0.6	-5.2	42.0
4	8	25	3.79	4.86	2.11	0.181	0.0053	5.10	15.4	2.3	-0.6	10.2	48.0
4	8	35	4.16	1.60	1.99	0.268	0.0054	2.00	11.6	1.1	-0.6	11.4	21.0
4	8	50	4.31	0.50	1.89	0.350	0.0058	0.10	8.1	1.0	0.8	8.0	7.0
4	8	75	4.40	0.54	1.81	0.321	0.0050	0.10	11.5	1.2	2.7	7.1	8.6
4	8	100	4.47	0.41	1.87	0.301	0.0045	0.05	9.4	1.1	0.8	7.0	8.7
4	8	130	4.54	0.10	1.94	0.326	0.0034	0.05	8.2	1.5	1.1	8.1	8.5
4	9	0	3.74	4.79	0.48	0.099	0.0026	0.44	10.0	8.1	2.7	137.6	24.0
4	9	5	3.99	2.03	0.54	0.081	0.0031	0.15	8.6	2.0	2.0	27.9	10.4
4	9	10	3.90	3.29	0.94	0.104	0.0030	0.69	9.5	1.7	2.1	13.6	14.2
4	9	15	3.83	7.11	1.72	0.167	0.0045	3.60	12.3	1.3	3.3	14.7	31.0
4	9	20	3.91	5.59	2.09	0.235	0.0054	3.10	14.2	1.5	3.4	15.4	31.0
4	9	25	4.05	3.25	2.52	0.350	0.0066	1.50	17.5	1.3	2.4	13.5	21.0
4	9	35	4.43	0.61	1.86	0.188	0.0037	0.20	8.3	0.9	3.0	9.2	5.5
4	9	50	4.45	0.56	1.86	0.286	0.0043	0.16	8.7	0.9	3.3	14.7	8.2
4	9	75	4.46	0.25	1.86	0.334	0.0040	0.05	9.4	1.1	3.8	9.4	8.1
4	9	100	4.35	0.18	2.24	0.407	0.0078	0.05	12.8	1.1	4.0	11.2	9.1
4	9	130	4.41	0.14	2.10	0.344	0.0056	0.05	11.3	1.3	4.4	10.2	9.8

Appendix B
Groundwater sample characteristics

Explanations by tables B.I. to B.III
F = field,
S = site,
T = sample time, month, November 1991 to November 1992,
D = groundwater table, depth below soil surface [cm],
pH = pH in pH units,
Ec = electro-conductivity [μS.cm^{-1}],
Cl = chloride concentration [mg.l^{-1}],
Si = silicium concentration [mg.l^{-1}],
Al = aluminium concentration [mg.l^{-1}],
Fe = iron concentration [mg.l^{-1}],
Mn = manganese concentration [mg.l^{-1}],
Na = sodium concentration [mg.l^{-1}],
K = potassium concentration [mg.l^{-1}],
Ca = calcium concentration [mg.l^{-1}],
Mg = magnesium concentration [mg.l^{-1}],
Cd = cadmium concentration [μg.l^{-1}],
Cu = copper concentration [μg.l^{-1}],
Ni = nickel concentration [μg.l^{-1}],
Zn = zinc concentration [μg.l^{-1}].

Table B.I. Groundwater sample characteristics.

F	S	T	D	pH	Ec	Cl	Si	Al	Fe	Mn	Na	K	Ca	Mg	Cd	Cu	Ni	Zn
1	2	Nov	2.80	4.14	93	7.1	4.72	0.72	0.525	0.133	2.52	1.70	2.70	0.89	9	5	50	1553
1	3	Nov	1.60	4.34	134	8.5	2.66	1.44	0.086	0.130	2.01	1.56	2.44	0.40	11	4	23	4266
1	4	Nov	3.10	4.75	87	6.8	5.59	0.36	0.918	0.176	3.56	2.59	4.47	1.29	12	2	31	1700
2	1	Nov	1.85	4.67	188	18.0	2.96	2.04	0.065	0.425	7.14	3.25	12.09	1.52	59	2	31	4304
2	2	Nov	1.05	4.54	139	12.0	2.59	1.68	0.036	0.212	4.76	7.57	7.13	0.89	44	1	192	5550
2	3	Nov	1.20	4.10	313	33.0	2.87	6.14	0.032	0.161	8.64	6.22	17.81	3.14	109	36	7	8263
2	4	Nov	1.15	4.41	187	18.0	2.05	2.89	0.013	0.409	9.60	1.49	8.60	1.11	85	6	22	8501
3	1	Nov	1.45	4.85	246	11.0	4.32	1.36	0.689	2.558	6.03	1.84	18.20	2.02	2	3	61	8429
3	2	Nov	1.50	4.19	116	9.3	3.41	1.24	0.006	0.358	3.80	1.09	3.99	0.59	69	3	12	7443
3	3	Nov	1.30	5.70	171	9.9	4.89	0.21	0.016	1.092	6.42	1.32	11.18	1.71	30	3	20	8781
3	4	Nov	1.55	4.52	119	7.3	5.66	0.24	0.004	0.366	3.87	1.13	4.99	1.34	65	4	17	8761
4	1	Nov	1.78	4.07	127	12.0	2.95	5.29	0.271	0.052	5.59	1.04	1.72	0.71	21	6	11	2376
4	2	Nov	1.45	4.20	116	12.0	2.17	4.84	0.010	0.029	5.61	0.48	1.69	0.56	50	2	7	2063
4	3	Nov	1.65	3.99	135	28.0	3.14	4.38	1.589	0.079	5.88	1.17	1.95	0.88	15	2	9	1525
4	4	Nov	1.40	4.22	142	15.0	2.24	5.30	0.027	0.061	8.79	0.62	2.37	0.73	50	4	10	2803
1	1	Jan	1.00	4.36	183	8.2	4.79	7.32	0.009	0.103	3.67	1.98	3.01	0.59	72	3	22	5847
1	2	Jan	2.65	4.31	157	6.9	3.89	5.08	0.088	0.066	3.68	1.26	2.27	0.76	42	9	27	4265
1	3	Jan	1.15	4.25	158	7.5	4.72	5.45	0.074	0.083	3.09	1.53	2.96	0.65	29	3	20	6202
1	4	Jan	3.00	4.32	140	7.2	4.68	2.89	0.075	0.072	3.47	1.89	3.05	0.89	28	6	12	3025
2	1	Jan	1.60	4.65	300	21.0	2.42	2.67	0.002	0.488	9.44	4.89	18.64	2.64	63	8	22	7537
2	2	Jan	0.80	4.92	196	13.0	2.01	1.36	0.002	0.350	10.08	2.78	8.86	1.18	50	3	7	8556
2	3	Jan	0.95	4.44	321	28.0	2.70	5.08	0.006	0.170	8.27	6.15	17.56	3.09	108	35	14	9471
2	4	Jan	0.90	4.85	173	14.0	1.64	2.71	0.010	0.239	10.13	1.16	6.63	0.87	57	6	24	7718
3	1	Jan	1.10	5.16	375	12.0	3.46	0.97	0.002	2.184	41.81	1.47	11.28	1.40	8	9	45	7659
3	2	Jan	1.20	4.55	115	6.9	2.76	0.91	0.002	0.355	4.15	1.53	5.03	0.63	38	6	11	5602
3	3	Jan	1.00	5.20	168	11.0	4.32	0.26	0.002	0.896	6.72	1.19	9.18	1.29	25	8	32	10697
3	4	Jan	1.30	4.75	116	6.4	4.70	0.24	0.007	0.227	4.04	1.00	5.90	1.29	32	6	8	6364
4	1	Jan	1.45	4.42	135	11.0	2.50	4.43	0.276	0.040	6.21	0.83	1.74	0.65	6	8	7	2206
4	2	Jan	1.20	4.50	121	12.0	1.86	3.93	0.004	0.016	6.66	0.33	1.72	0.52	24	4	11	1901
4	3	Jan	1.35	4.26	155	11.0	2.85	4.04	3.224	0.077	6.38	1.14	2.28	0.93	2	3	7	1433
4	4	Jan	1.10	4.69	160	11.0	1.98	4.24	0.017	0.035	12.56	0.37	2.53	0.62	30	5	8	2558
1	1	Mar	1.55	-1	183	7.5	5.51	8.31	0.144	0.090	3.46	1.75	2.58	0.57	48	1	31	5885
1	2	Mar	2.90	-1	156	6.8	4.05	4.71	0.171	0.073	3.32	1.25	2.32	0.74	41	1	8	4059
1	3	Mar	1.60	-1	150	11.0	4.43	3.98	0.100	0.115	3.14	1.72	3.66	0.69	23	1	19	7360
1	4	Mar	3.25	-1	112	9.0	4.68	1.10	0.011	0.084	3.82	2.32	4.17	1.31	18	1	7	2440
2	1	Mar	1.55	-1	130	9.8	2.41	1.43	0.006	0.261	4.90	2.05	6.67	0.78	50	1	7	5648
2	2	Mar	1.15	-1	149	12.0	2.41	2.21	0.009	0.175	4.31	2.04	6.46	0.83	63	1	11	7567
2	3	Mar	1.25	-1	285	25.0	2.70	3.96	0.023	0.137	6.55	5.55	16.77	2.82	87	28	16	6065
2	4	Mar	1.20	-1	150	14.0	1.65	3.39	0.009	0.157	5.56	0.98	4.65	0.81	89	1	7	7564
3	1	Mar	1.35	-1	210	7.0	3.47	1.02	0.073	2.047	16.12	0.69	8.25	1.08	2	1	56	9549
3	2	Mar	1.40	-1	110	7.2	2.48	0.75	0.002	0.258	3.52	0.87	6.21	0.69	38	1	7	4160
3	3	Mar	1.35	-1	170	9.1	4.24	0.27	0.038	0.865	8.01	1.09	7.80	1.33	2	3	43	12092
3	4	Mar	1.40	-1	194	8.2	3.65	0.23	0.010	0.438	15.80	1.24	9.12	1.36	14	1	7	3704
4	1	Mar	1.85	-1	129	12.0	2.65	4.70	0.379	0.045	4.54	0.78	1.58	0.67	15	1	7	2310
4	2	Mar	1.55	-1	118	10.0	1.88	4.38	0.005	0.023	5.17	0.34	1.48	0.58	46	1	9	2059
4	3	Mar	1.70	-1	170	14.0	2.92	4.35	4.880	0.094	5.86	1.31	2.72	1.16	7	1	7	1482
4	4	Mar	1.45	-1	131	8.9	2.00	4.85	0.015	0.048	5.92	0.27	2.04	0.55	34	1	7	2714
1	1	Apr	1.45	4.29	181	8.6	4.75	7.55	0.347	0.095	3.16	2.04	2.66	0.58	102	1	69	6008
1	2	Apr	2.85	4.27	166	6.5	4.05	5.77	0.178	0.086	3.16	1.34	2.46	0.81	56	4	44	4607
1	3	Apr	1.55	4.34	151	8.6	4.49	4.24	0.096	0.113	3.09	1.62	3.52	0.68	32	1	8	7107
1	4	Apr	3.15	4.35	117	7.2	4.68	1.42	0.022	0.084	3.65	2.23	3.87	1.21	22	1	7	2680
2	1	Apr	1.90	4.74	136	12.0	2.34	1.82	0.011	0.205	4.67	2.00	6.72	0.84	45	3	7	5167
2	2	Apr	1.10	4.63	150	10.0	2.34	2.19	0.063	0.152	4.33	2.16	6.11	0.78	62	2	7	7283
2	3	Apr	1.25	4.50	240	21.0	2.52	3.12	0.004	0.118	5.46	4.71	13.28	2.19	64	24	7	5671

Table B.II. Groundwater sample characteristics.

F	S	T	D	pH	Ec	Cl	Si	Al	Fe	Mn	Na	K	Ca	Mg	Cd	Cu	Ni	Zn
2	4	Apr	1.15	4.58	148	12.0	1.59	3.30	0.002	0.154	4.97	0.82	4.47	0.69	78	1	7	7547
3	1	Apr	1.25	4.84	202	7.8	3.54	1.75	0.008	2.311	11.54	0.86	7.39	1.21	39	3	38	10216
3	2	Apr	1.35	4.93	107	6.3	2.62	0.78	0.002	0.245	3.34	0.91	6.42	0.70	40	6	7	4023
3	3	Apr	1.20	5.62	162	11.0	4.27	0.25	0.002	0.856	7.87	1.11	6.99	0.99	33	1	18	12967
3	4	Apr	1.35	5.37	186	8.7	4.08	0.24	0.002	0.584	16.37	1.17	7.44	1.21	30	3	21	4502
4	1	Apr	1.75	4.39	129	11.0	2.68	4.87	0.390	0.049	4.30	0.91	1.68	0.69	14	6	7	2353
4	2	Apr	1.45	4.61	120	10.0	1.93	4.36	0.002	0.025	5.23	0.39	1.50	0.57	42	1	7	2106
4	3	Apr	1.65	4.28	177	16.0	2.90	4.43	5.150	0.100	5.68	1.34	2.70	1.19	3	1	7	1638
4	4	Apr	1.35	4.54	132	11.0	1.95	5.07	0.015	0.030	5.82	0.28	1.91	0.63	32	1	7	2805
1	1	May	1.50	4.51	182	7.8	5.01	9.09	0.051	0.097	3.39	2.39	3.05	0.69	95	6	7	5797
1	2	May	2.80	4.47	142	7.6	4.37	4.50	0.188	0.077	3.14	1.52	2.66	0.84	38	2	16	3449
1	3	May	1.55	4.71	149	9.6	4.50	4.33	0.160	0.122	3.31	1.98	4.00	0.74	25	1	12	6788
1	4	May	3.10	5.08	116	6.2	4.72	0.85	0.057	0.085	6.06	2.49	4.25	1.31	18	3	7	2301
2	1	May	1.70	4.94	191	12.0	2.41	2.70	0.028	0.310	5.98	3.22	10.94	1.55	60	4	9	5422
2	2	May	0.85	4.82	162	15.0	2.59	2.59	0.027	0.241	5.40	2.48	7.53	0.96	68	3	7	7918
2	3	May	1.05	4.60	291	26.0	2.69	4.42	0.034	0.142	6.94	6.34	18.63	3.09	70	36	7	5324
2	4	May	0.90	4.77	150	12.0	1.78	3.34	0.033	0.252	5.49	1.34	5.63	0.94	78	5	7	7010
3	1	May	1.20	4.79	-1	6.9	3.98	2.68	0.014	2.925	9.82	1.15	8.55	1.57	41	7	49	10281
3	2	May	1.35	5.04	-1	5.1	2.68	0.74	0.014	0.249	3.60	1.00	6.58	0.70	31	2	7	3470
3	3	May	1.15	5.36	-1	9.6	4.55	0.34	0.017	0.885	6.62	1.06	7.40	1.09	40	4	15	12545
3	4	May	1.40	5.74	-1	5.6	3.78	0.11	0.026	0.649	15.06	1.22	6.68	0.99	17	7	10	4004
4	1	May	1.75	4.46	130	10.0	2.71	5.48	0.475	0.084	4.66	0.90	1.94	0.77	17	6	8	2251
4	2	May	1.45	4.60	118	9.0	2.04	4.79	0.023	0.036	5.09	0.54	1.60	0.58	42	2	7	1885
4	3	May	1.65	4.30	170	12.0	3.04	5.03	4.756	0.107	5.91	1.54	2.93	1.31	7	1	7	1628
4	4	May	1.35	4.62	134	9.3	2.08	5.69	0.035	0.040	5.57	0.47	2.15	0.70	44	4	7	2588
1	1	Jul	1.70	4.36	182	6.6	4.77	7.39	0.017	0.086	3.10	2.46	2.83	0.61	98	3	7	5352
1	2	Jul	3.10	4.37	144	5.6	4.18	4.29	0.127	0.070	2.79	1.45	2.54	0.77	36	1	14	3303
1	3	Jul	1.75	4.37	153	8.0	4.64	4.40	0.102	0.109	3.05	1.89	3.71	0.67	33	2	16	6317
1	4	Jul	3.35	4.42	119	5.8	4.54	1.28	0.018	0.079	3.31	2.22	3.91	1.20	22	3	7	2541
2	1	Jul	2.00	5.07	122	8.7	2.48	1.38	0.015	0.232	4.19	1.62	5.19	0.59	44	3	7	4601
2	2	Jul	1.10	4.64	195	15.0	2.78	2.98	0.012	0.185	5.48	2.21	7.88	0.99	74	5	7	8221
2	3	Jul	1.30	4.51	346	26.0	2.56	4.78	0.015	0.136	8.07	7.08	20.70	3.49	68	35	7	4975
2	4	Jul	1.15	4.71	152	10.0	1.79	3.28	0.015	0.181	4.73	1.44	4.81	0.83	83	5	10	6589
3	1	Jul	1.45	4.75	202	7.2	4.12	1.57	0.004	2.325	6.92	0.95	8.08	1.29	43	4	46	10500
3	2	Jul	1.60	4.82	114	5.2	2.72	0.51	0.007	0.217	3.72	0.99	6.96	0.65	25	2	7	2681
3	3	Jul	1.40	5.58	166	19.0	4.77	0.46	0.003	0.905	5.74	1.23	7.73	1.12	43	7	15	12484
3	4	Jul	1.50	5.66	154	5.2	3.83	0.22	0.006	0.540	10.87	1.18	6.07	0.83	24	1	8	4451
4	1	Jul	1.90	4.36	140	8.9	2.70	4.80	0.481	0.054	3.92	0.80	1.90	0.58	17	1	7	2128
4	2	Jul	1.60	4.40	122	9.3	1.90	4.38	0.020	0.028	4.17	0.43	1.61	0.52	42	1	7	1825
4	3	Jul	1.85	4.33	178	11.0	2.93	4.00	5.840	0.103	4.77	1.60	2.83	1.21	6	2	7	1363
4	4	Jul	1.55	4.50	142	6.6	1.22	3.20	0.077	0.028	2.91	0.19	1.28	0.36	27	1	7	1534
1	1	Sep	1.50	3.95	175	5.9	5.87	7.39	0.077	0.081	2.85	2.41	2.69	0.54	100	5	7	4919
1	2	Sep	2.95	3.92	168	4.8	4.78	6.36	0.036	0.074	2.62	1.48	2.24	0.62	52	4	7	3974
1	3	Sep	1.55	3.98	152	7.3	5.24	4.29	0.131	0.108	3.09	1.94	3.75	0.67	43	3	18	6079
1	4	Sep	3.20	3.90	141	5.0	5.52	3.45	0.054	0.070	3.10	1.89	3.00	0.78	45	8	7	3276
2	1	Sep	1.95	5.21	144	10.0	2.86	1.99	0.021	0.191	4.46	2.47	7.83	1.01	56	8	7	4395
2	2	Sep	1.15	4.46	162	12.0	2.78	2.55	0.020	0.160	4.91	2.02	6.50	0.79	76	5	7	6975
2	3	Sep	1.30	4.10	480	20.0	2.85	6.51	0.019	0.186	11.54	10.04	34.13	5.08	85	39	7	4926
2	4	Sep	1.20	4.30	159	11.0	2.09	3.38	0.020	0.168	4.44	1.58	5.56	0.86	96	4	7	6574
3	1	Sep	1.45	5.24	187	5.9	4.20	0.54	0.098	0.897	24.91	0.98	3.01	0.55	15	9	7	3238
3	2	Sep	1.35	5.03	111	5.5	3.51	0.49	0.002	0.588	4.07	1.22	7.16	0.48	22	3	7	2184
3	3	Sep	1.35	4.84	154	7.9	5.38	0.44	0.002	0.796	6.57	1.31	5.33	0.74	68	8	13	12158
3	4	Sep	1.50	4.46	123	6.4	4.89	0.41	0.004	0.483	4.24	1.46	5.60	1.02	53	7	20	6888
4	1	Sep	1.85	3.76	136	9.8	2.96	4.62	0.388	0.044	4.21	1.01	1.85	0.60	19	3	7	2119
4	2	Sep	1.55	4.36	116	7.4	2.18	4.10	0.022	0.038	4.03	0.39	1.53	0.41	47	6	7	1787

Table B.III. Groundwater sample characteristics.

F	S	T	D	pH	Ec	Cl	Si	Al	Fe	Mn	Na	K	Ca	Mg	Cd	Cu	Ni	Zn
4	3	Sep	1.75	3.95	157	10.0	3.19	3.83	4.637	0.110	4.74	1.49	2.80	1.15	10	3	7	1638
4	4	Sep	1.45	4.26	137	9.0	2.35	4.90	0.048	0.041	5.53	0.38	1.95	0.52	50	1	7	2458
1	1	Nov	1.25	4.45	164	5.3	5.98	7.31	0.029	0.075	2.88	1.74	2.45	0.52	95	2	7	5189
1	2	Nov	2.65	4.27	157	3.6	4.52	6.46	0.067	0.073	2.44	1.39	2.24	0.67	64	3	158	4413
1	3	Nov	1.20	4.34	159	6.7	5.48	5.77	0.069	0.088	2.83	1.48	2.90	0.64	46	4	15	5537
1	4	Nov	3.00	4.33	148	4.6	5.33	4.66	0.122	0.066	3.09	1.33	2.45	0.69	57	2	10	4177
2	1	Nov	1.75	4.62	134	9.4	2.61	1.79	0.027	0.170	5.66	1.97	6.24	0.91	52	5	11	4519
2	2	Nov	0.90	4.59	138	8.1	2.49	2.29	0.030	0.130	4.47	2.04	4.74	0.68	76	2	11	7089
2	3	Nov	1.05	4.48	294	36.0	2.81	3.31	0.017	0.152	6.54	6.20	18.65	2.97	85	27	7	6032
2	4	Nov	0.95	4.79	129	9.0	2.09	2.86	0.037	0.135	4.27	1.16	4.38	0.72	80	5	13	6299
3	1	Nov	1.15	5.71	136	6.7	3.32	0.41	0.013	0.877	11.41	0.96	3.79	0.66	33	2	13	6812
3	2	Nov	1.15	5.66	99	4.1	3.11	0.47	0.413	0.572	2.94	1.15	6.20	0.59	27	7	62	4287
3	3	Nov	1.10	5.17	163	8.4	4.71	0.73	0.006	0.805	9.21	1.21	4.83	0.88	77	11	26	12847
3	4	Nov	1.15	4.82	11	3.3	4.20	0.85	0.006	0.299	4.41	1.34	3.99	1.03	42	7	18	6025
4	1	Nov	1.55	4.23	123	8.5	3.11	4.93	0.337	0.038	4.39	0.94	1.82	0.68	19	6	11	2849
4	2	Nov	1.25	4.09	108	6.6	2.15	4.50	0.013	0.024	4.25	0.28	1.35	0.49	41	1	7	1947
4	3	Nov	1.40	4.02	141	9.5	3.07	3.85	3.100	0.092	4.88	1.44	2.56	1.03	11	1	7	1882
4	4	Nov	1.20	4.25	114	5.2	2.32	4.58	0.033	0.016	4.61	0.40	1.54	0.44	46	8	14	2202

Appendix C
Pascal-sources

C.1. Pascal-source adaptations for one-dimensional transport in heterogeneous soils

The applied numerical model is a slight modification of the model "Columnperc2" described by Appelo and Postma (1993). This model is fairly simple and suitable for our purpose. The modification involves the possibility to assign to each cell or node a different adsorption parameter (K_F).

C.1.1. Variables and initialization

In Frames C.1 and C.3 the model parameters are read from disk-file using the procedures *ReadData* (read general model parameters) and *ReadProfile* (read the K_F profile). Frames C.2 and C.4 are listings of example input-files. Frame C.2 shows the input file for the procedure *ReadData*. Frame C.4 shows an example file with a K_F profile read by the procedure *ReadProfile*. Both procedures are implemented after line 4 in the main block of the program "Columnprec2".

```
procedure ReadData;
var F : text;
begin
  assign(F,'input.dat');
  reset(F);
  readln(F,Time);                          { Total simulation time }
  readln(F,TotX);                     { Total length of the column }
  readln(F,Cin);              { Concentration at the top boundary }
  readln(F,D);                            { Diffusion coefficient }
  readln(F,Disp);                             { Dispersion length }
  readln(F,Theta);                             { Moisture content }
  readln(F,Rho);                                   { Bulk density }
  readln(F,Infil);            { Net infiltration at top boundary }
  readln(F,nf);                             { Freundlich exponent }
  close(F);
  Veloc := Infil/Theta;          { calculate pore-water-velocity }
end;
```

Frame C.1. Procedure ReadData.

```
36500.0
  150.0
    1.0
    0.864
    1.0
    0.2
    1.5
    0.05
    0.75
```

Frame C.2. Example of the file: "input.dat".

```
const Nr_K_Ads  = 10;

var  K_D, K_P : array[1..Nr_K_Ads] of real;

procedure ReadProfile;
var F     : text;
    Ic, n : word;
begin
  assign(F,'K.INP');
  reset(F);
  readln(F,n);
  for Ic := 1 to n readln(F,K_D[Ic],K_P[Ic]);
  close(F);
end;
```

Frame C.3. Procedure ReadProfile.

```
10
  0  15.0
  5  10.0
 10   7.5
 15  10.0
 20  20.0
 35   5.0
 50   1.0
 75   1.0
100   0.5
130   0.5
```

Frame C.4. Example of the file: "k.dat".

C.1.2. Implementation of adsorption processes

The non-linear Freundlich adsorption model (Eq. C.1) is used in the model. The parameter K_F is variable in the z direction (depth).

$$q = K_F(z)\, c^n \tag{C.1}$$

where:

q_z = amount adsorbed at depth z [μg.g^{-1}],
$K_F(z)$ = Freundlich parameter variable of depth (z),
c_z = concentration in solution at depth z [μg.cm^{-31}],
n = Freundlich exponent [-].

The parameter K_F is made dependent on soil macro parameters like the organic matter content. These macro parameters are not constant, but highly variable with depth. Therefore a K_F profile is obtained from the soil macro parameters, as is described in chapter 5. This K_F profile is a sequence of K_F values at certain depth intervals. These intervals may be different from the model discretisation. The interpolation procedure *Set_K_Column* (Frame C.5) is used to calculate the actual K_F at each depth. The procedure *Set_K_Column* is incorporated in the main program block just after the procedure *ReadProfile*. Non-linear adsorption cannot be calculated at once, both Eq. C.1 and C.2 have to be solved simultaneously.

$$T_z = \rho\, q_z + \theta\, c_z \tag{C.2}$$

where:

T_z = total amount at depth z [μg.cm^{-3}],
ρ = bulk density [g.cm^{-3}],
θ = moisture content [cm^3.cm^{-3}].

If ρ, θ, K_F and T_z are known, q_z and c_z can be calculated using Newton's iterative method. The calculation of the adsorption take place in the Pascal procedure *Distri*. This procedure is a slight modification from the program "Columnperc2", the additional line (Frame C.6) is marked by the symbol "#".

```
procedure Set_K_Column;
var Ic, j : word;
    Ok    : boolean;
begin
  j := 2;                                                                             { K_D[1] = 0 }
  for Ic := 1 to NCel do
    repeat
      Ok := false;
      if (Ic-0.5)*delX <= K_D[j] then                             { K_D[j-1] < (Ic*0.5) <= K_D[j] }
        begin
          K[Ic] := (K_P[j]-K_P[j-1])/(K_D[j]-K_D[j-1])*((Ic-0.5)*delX-K_D[j-1])+K_P[j-1];
          Ok   := true;                                   { Calculate the actual K value in a cell }
        end
      else
        begin
          j := j + 1;
          if j > Nr_K_Ads then
            begin
              j     := Nr_K_Ads;
              K[Ic] := K_P[Nr_K_Ads];
              Ok    := True;
            end;
        end;
    until Ok;                                          { If Ok then a K value is assigned to a cell }
end;
```

Frame C.5. Procedure Set_K_Column.

```
procedure Distri;
var D, D1, D2, M1, M, T, Kf, nf . real,
    Ic, It                       : word;

function Freundlich(Kf, nf, C : real) : real,
begin
   if C > 1e-10 then
      Freundlich := Kf * exp(nf*ln(C))                     { implementation of Freundlich equation }
   else
      Freundlich := 0;
end;

begin
  for Ic := 1 to NCel do
    begin
#     Kf := K[Ic] * Rho / Theta;     { correction for rho and theta and assign specific KF to node }
      T  := Q[Ic] + Cwl[Ic];                                                { total present in a cel }
      M  := T / (Kf + 1);                               { first approach of concentration in solution }
      It := 0;
      if nf <> 1 then                               { if n = 1 then q and c can be calculated at once }
        repeat
          D2 := M;
          M1 := M;
          D  := Freundlich(Kf,nf,M1) + M1 - T;
          M1 := M + 1E-09;
          D1 := Freundlich(Kf,nf,M1) + M1 - T;
          if abs(D1-D) > 0 then M := M-D/((D1-D)/(1E-09));
          if M < 1E-09 then M := 0.0;
          if M > T     then M := T;
          It := It + 1;
          if It > 20 then                                               { max number of iterations }
            begin
              writeln('Freundlich equation, iteration > 20 Cel: ',i);
              Halt;
            end;
        until (abs(D) <= 1E-06) or ((D2+M) = 0);
      Cwl[Ic] := M;                                                                     { actual c }
      Q[Ic]   := T - Cwl[Ic];                                                           { actual q }
    end;
end;
```

Frame C.6. Procedure Distri.

C.2. Pascal source listing of the stochastic model

The stochastic model is implemented in the program *BTC*. The pascal listing of the program *BTC* is presented in Frame C.7. This program calculates breakthrough times with a normal distribution from the standard deviation in retardation factors and the standard deviation caused by diffusion/dispersion (Eq. 5.15). The function *RndNorm*, which generates a random normal distribution, is obtained from Rugg and Feldman (1987). The output of the program consists of a file which contains two columns of breakthrough times, where the first column are breakthrough times only caused by the variance in retardation factors and the second column are breakthrough times caused by total field dispersion.

```
program BTC;
uses  Crt;
const Max = 4000;
var
  i    . longint;
  F    : text;
  Theta, Alpha, Diffusion, Dispersion, Length, Retention, Velocity, Infil,
  AvgR, AvgT, SigmaR, SigmaT, Time1, Time2                                : real;

function RndNorm(Mean, StanDev : real) : real;
var RndA, RndB, Radius2, Deviate : real;
begin
   repeat
      RndA    := 2 * random - 1;
      RndB    := 2 * random - 1;
      Radius2 := sqr(RndA) + sqr(RndB);
   until Radius2 < 1;
   Deviate := RndA * sqrt((-2 * ln(Radius2)) / Radius2);
   RndNorm := Mean + Deviate * StanDev
end;

begin
  Alpha      := 1;                                                             { dispersion length }
  Diffusion  := 0.864;                                                     { diffusion coefficient }
  Theta      := 0.2;                                                            { moisture content }
  Infil      := 0.054;                                                 { net infiltration velocity }
  Velocity   := Infil / Theta;                                               { pore water velocity }
  Dispersion := Diffusion*Theta/2+Alpha*Velocity;                                   { equation 5.7 }
  Length     := 150;                                                               { column length }
  AvgR       := 41.98;                                              { average retardation factor }
  SigmaR     := 26.24;                              { standard deviation in the retardation factor }
  AvgT       := AvgR*Length/Velocity;                       { average breakthrough time, at c=½c0 }
  SigmaT     := sqrt(2*Dispersion*Length*AvgR*AvgR/(Velocity*Velocity*Velocity));
  assign(F,'OUT.DAT');                     { standard deviation in time according to Equation 5.15 }
  rewrite(F);
  randomize;
  for i := 1 to Max do
    begin
      Retention := RndNorm(AvgR, SigmaR);                      { sample from a normal distribution }
      Time1 := (Retention*Length/Velocity);   { calculate travel time from the retardation factor }
      write(F,Time1:10:2);                                                         { write to disk }
      Time2 := RndNorm(Time1, SigmaT);          { add hydro-dynamic dispersion to field dispersion }
      writeln(F,Time2:10:2);                                                       { write to disk }
    end;
  close(F);
end.
```

Frame C.7. Listing of pascal source of the program BTC.

The output of the program *BTC* is the input for the program *Histogram* (Frame C.8), this program calculates the frequency distribution of a population of breakthrough times. Breakthrough times below zero are set to zero and breakthrough times above the maximum of 50,000 days (137 years) are set equal to 50,100. The output of the program "*Histogram*" consists of three columns of which the first column is the time class. The second and third columns are frequency distributions of breakthrough times as a result of the variance in the retardation factors respectively the total field dispersion.

```
program Histogram;
const Max = 4000;
var
    i            : word;
    d            : longint;
    F            : text;
    Freq         : array[0..501,1..2] of word;
    Time1, Time2 : real;
begin
  for i := 0 to 501 do Freq[i,1] := 0;
  for i := 0 to 501 do Freq[i,2] := 0;
  assign(F,'OUT.DAT');
  reset(F);
  for i := 1 to Max do
    begin
      read(F,Time1);
      if Time1 > 0 then
        begin
          d := round(Time1/100+0.5);
          if d <= 500 then Freq[d,1]:=Freq[d,1]+1 else Freq[501,1]:=Freq[501,1]+1;
        end
      else Freq[0,1] := Freq[0,1]+1;
      read(F,Time2);
      if Time2 > 0 then
        begin
          d := round(Time2/100+0.5);
          if d <= 500 then Freq[d,2] := Freq[d,2]+1 else Freq[501,2] := Freq[501,2]+1;
        end
      else Freq[0,2] := Freq[0,2]+1;
    end;
  close(F);
  assign(F,'FREQ.DAT');
  rewrite(F);
  writeln(F,'0 ',Freq[0,1],' ',Freq[0,2]);
  for i := 1 to 500 do writeln(F,(i-0.5)*100,' ',Freq[i,1],' ',Freq[i,2]);
  writeln(F,'50000 ',Freq[500.1],' ',Freq[500.2]);
  close(F);
end.
```

Frame C.8. Program Histogram.

References

Appelo, C.A.J. and D. Postma (1993).
Geochemistry, groundwater and pollution.
Balkema, Rotterdam, the Netherlands. Pages 536.

Rugg, T. and P. Feldman (1987).
Turbo pascal program library.
Que corporation, Indianapolis, U.S. Pages 617.

Nawoord

Ik wilde bij deze gelegenheid verschillende mensen bedanken die hun inzet hebben getoond of mij gesteund hebben bij mijn promotie werk. In de eerste plaats hebben veel vrienden en kennissen mij geassisteerd met het veldwerk in de Kempen, te weten, Jodie Wilkens, Jan-Geert Koops, Iris Birnie, Andre van Veller, Cor de Boer, Hendrik-Jan Visser, Foeke Postma, Jan Drent, Ellis van Kessel, Ton Kroon, Tirza van Dalen, Harm van Lieshout én Gerard Wilkens. Laboratorium ondersteuning heb ik gekregen van Mark van Alphen voor de bodem analyses en Paul Anten voor de ICP-AES analyses. Doctoraal studenten, Nicoline Brummel en Ruud Rikers hebben een waarde volle bijdrage geleverd aan dit werk. Mijn kamergenoten op de faculteit, Bert Palsma en Thomas Keijzer, zijn voor mij van groot belang geweest en ik heb veel plezier met hun gehad. Ook veel plezier heb ik in de lunchpauzes gehad met Peter Pruisers, Ronald Jonckbloedt, Patrick van Sandvoort en Helen de Waard, zij konden je op een goede manier in de pauzes los maken van je wetenschappelijke werk. Ton van Hinte en Luc Lourens van de vakgroep geologie wisten mij altijd te helpen met problemen rond desktop publishing. Peter van der Linden wilde ik bedanken voor de layout adviezen van de werk. Gert-Jan Reichart wist altijd precies op het juiste moment met de wereldbol strandbal door de kamer te stuiteren en heeft in de laatste fase van dit werk voor gezelligheid gezorgd. Als laatste wilde ik wilde ik Guus Loch bedanken voor zijn inzet. Guus heeft mij altijd sterk gemotiveerd in mijn werk wat uiteindelijk tot dit proefschrift heeft geleid. Hij heeft mij ook goed begeleid bij het denk- én schrijfproces, en is de discussie over de inhoud van dit werk niet uit de weg gegaan of is deze zelfs aangegaan.

Curriculum vitae

Berend Wilkens werd op 10 juni 1962 geboren te Utrecht. Begon in augustus 1984 aan de studie geologie. In augustus 1985 werd het propaedeutisch examen afgelegd. In februari 1990 werd de studie voltooid met als hoofdvak exogene geochemie en de bijvakken milieukunde en informatica. In de periode maart 1990 tot en met maart 1994 was hij werkzaam bij de vakgroep geochemie als assistent in opleiding. In de periode maart 1994, mei 1994 was hij in functie als toegevoegd docent bij de zelfde vakgroep, met als taak het opzetten en doceren van een nieuw onderdeel in het onderwijsprogramma. Van juli 1995 tot heden is hij verbonden aan de vakgroep geochemie wederom als toegevoegd docent.

Photo 5. Groundwater sample equipment at sample field 1 (photo M. Reumers)