

Field Scale Behaviour of Cadmium in Soil

CENTRALE LANDBOUWCATALOGUS



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Field Scale Behaviour of Cadmium in Soil

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Ter nagedachtenis aan mijn oma

Augusta Wanda Hanewacker

5 december 1904 - 29 maart 1991

Stellingen

1. Door bodemheterogeniteit kan kennis over bodemprocessen niet op dezelfde wijze worden toegepast op verschillende schaalgroottes.

Dit proefschrift.

2. In het algemeen wordt aan bodemonderzoek bij bodemsanering te weinig geld besteed.

Dit proefschrift.

3. De uitgebreide Freundlichvergelijking (Van der Zee & Van Riemsdijk, 1987) geeft een goede beschrijving van de invloed van de pH en het organische stofgehalte van de bodem op de adsorptie van cadmium aan zandgrond.

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

Dit proefschrift.

4. Alhoewel de resultaten van Chardon (1984) de indruk wekken dat de vormingsconstanten voor cadmiumchloride-complexen zoals vermeld door Hahne & Kroontje (1973) de juiste constanten zijn, is dit niet het geval.

Chardon, W.J., 1984. Mobiliteit van cadmium in de bodem. Proefschrift, Landbouwniversiteit Wageningen.

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

Dit proefschrift.

5. De theorie van geregionaliseerde variabelen is niet consistent, omdat de formules die worden gebruikt om de ruimtelijke afhankelijkheid van waarnemingen te schatten, zijn gebaseerd op de aanname dat de waarnemingen ruimtelijk onafhankelijk zijn.

6. Zolang niet bekend is of de voorgestelde nieuwe C-waarden van Van den Berg & Roels (1991) een betere indicatie geven van de risico's van bodemverontreiniging, is het af te raden de huidige C-waarden uit de Leidraad Bodembescherming te vervangen.

Van den Berg, R. & J.M. Roels, 1991. Beoordeling van risico's voor mens en milieu bij blootstelling aan bodemverontreiniging, integratie van deelaspecten. Rapport nr. 725201007, RIVM, Bilthoven.

7. Dat een semivariogram kan worden gebruikt voor de ontwikkeling van een bemonsteringsstrategie is van weinig nut bij bodemverontreinigingsonderzoek, omdat een semivariogram pas kan worden opgesteld nadat de monsters zijn geanalyseerd.
8. Al reageert de politiek nog zo snel, de vervuiling achterhaalt haar wel.
9. De voordelen van gewasrotatie ten opzichte van een monocultuur gelden evenzeer voor de levenswijze van mensen.
10. Don't fight pollution by dilution.
11. Versterking van de winterdijken werpt in ieder geval een dam op tegen werkeloosheid bij Rijkswaterstaat.
12. De snelheid op de fiets bij een afdaling met haarspeldbochten wordt niet zozeer bepaald door de helling van de weg, maar veel meer door de angst van de fietser voor het onverwachte.
13. Dat vrouwelijke wetenschappelijke medewerkers regelmatig worden gevraagd om waar te nemen op het secretariaat doet vermoeden dat zij breder inzetbaar worden geacht dan hun mannelijke collega's.
14. Gelijk bestaat niet.

Stellingen behorende bij het proefschrift van Sandra Boekhold:

"Field scale behaviour of cadmium in soil"

Wageningen, 17 november 1992

Voorwoord

Op deze plaats wil ik een aantal mensen bedanken, die hebben bijgedragen aan de totstandkoming van dit proefschrift.

Mijn begeleider en co-promotor Sjoerd van der Zee: Door stimulerende discussies en de grote mate van zelfstandigheid die je mij al in een vroeg stadium hebt gelaten, heb ik naast vakinhoudelijke kennis ook veel doorzettingsvermogen en zelfvertrouwen opgedaan. Dat had ik nodig, mede daarom ben ik uitermate tevreden over de wijze waarop je mij hebt begeleid. Groot is mijn dank voor de mogelijkheden die je mij hebt gegeven om veel te reizen. Ik hoop dat we ook in de toekomst zullen blijven samenwerken.

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Ondersteuning in de privésfeer is broodnodig, pannekoeknodig en kwarktaartnodig. Jacob, bedankt voor alles.

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Abstract

Boekhold, A.E., 1992. Field scale behaviour of cadmium in soil.
Doctoral thesis, Wageningen Agricultural University, the Netherlands.
ISBN 90-5485-038-8, 192 pages

Although total heavy metal contents of soil are often used to express the degree of contamination, they are of little value to judge environmental effects. The main objective of this thesis was to develop and test methodologies with which environmental risks of cadmium pollution of field soils can be evaluated. A method to determine the mobile and bioavailable fraction of the total Cd content may be soil extraction with 0.01 M CaCl_2 . Chemical processes that control the cadmium activity in such an extract were quantified. This is relevant information when Cd contents in CaCl_2 -extracts need interpretation in terms of bioavailability and leachability.

Cadmium behaviour at the field scale was studied using soil samples taken from an arable field in the Dutch Kempen region. Spatial variability of total Cd contents, CaCl_2 -extractable Cd contents, soil-pH, and organic matter content was distinct and different for all parameters. Spatial variability of soil-pH and organic matter content explained a major proportion of the variability of Cd contents.

Due to spatial variability, a high sampling density was needed for reliable estimation of pollution boundaries. When polluted soil needs remedial action, reduction of the research effort by minimizing the sampling density may well lead to an overall increase in sanitation costs because the area where concentrations exceed a critical threshold level becomes larger.

The long-term effect of soil heterogeneity on cadmium behaviour in soil was evaluated using a stochastic simulation model. Predicted uptake of Cd by barley and leaching of Cd to groundwater was much higher in a heterogeneous field as compared to an equivalent homogeneous field. Variability of soil hydraulic properties as well as soil chemical parameters caused these differences. This demonstrated the importance of soil heterogeneity for environmental impact assessment of soil contamination.

Additional index words: contamination, pH, soil chemistry, sorption, spatial variability, heterogeneity, geostatistics, barley, Kempen.

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Chapter 1

General Introduction

General Introduction

The high level of development of modern society is in many aspects beneficial to mankind, but there is a reverse to this medal. Industrial, agricultural, and domestic activities have led to environmental contamination which may affect the quality of life. The impact of discharging chemicals into the environment has been ignored for a long time. This may be (partly) understood by considering the buffering capacity of the environment. Buffering in this sense can be described as storage without (direct) occurrence of negative effects. Of the three environmental compartments soil, water, and air, soil typically has the largest buffering capacity per unit of volume.

Soil can immobilize chemicals by sorption, precipitation, or (bio)transformation, and as such acts as a natural filter for these compounds. However, soil has a finite capacity for retaining chemicals. Exceedance of this capacity may be harmful to the environment because it implies increased mobility and bioavailability of contaminants in the soil system. Not only overloading of the retention capacity of soils may lead to negative effects; also triggering events can result in release of previously stored chemicals in soils. Delayed effects of stored chemicals in soils may result from changes in land use, soil acidification caused by acid atmospheric deposition, or other future events that induce changes in the capacity of soils to store chemicals (Stigliani *et al.*, 1991). Understanding the behaviour of contaminants in soil is necessary to prevent adverse changes to occur in the future. This knowledge may give rise to investments in proper measures that reduce the inputs to acceptable levels.

This thesis is intended to add to the understanding of contaminant behaviour in soil. Particular attention is given to field scale behaviour in view of risk assessment of soil contamination with cadmium. In this introductory chapter, a general background of cadmium is given and its toxicity is described. The Dutch soil protection policy is summarized to illustrate the need for reliable predictions of exposure of human beings and ecosystems to chemicals in soils. Current knowledge on cadmium behaviour in soils is examined, and sorption models for cadmium are discussed. For prediction of environmental risks of soil pollution, soil heterogeneity and the scale problem are introduced as major aspects that need to be taken into account. Finally, the main objectives of this thesis are outlined.

Cadmium

Cadmium was first identified in 1817 in zinc carbonate (calamine). The name cadmium emanates from *cadmia*, the ancient Greek name for calamine (Nriagu, 1980). The chemical symbol is Cd; the molecular weight equals 112.41. Cadmium is a silvery white heavy metal, relatively weak, flexible, and very corrosion persistent in an alkaline environment. It is a rare element in the Earth's crust. The primary source of Cd dissemination into the environment is the exploitation of heavy metal ores that contain trace amounts of Cd. Cadmium is used for nickel-cadmium batteries and accumulators, pigments, stabilizers, and in the electroplating and alloy industries (Ros and Slooff, 1990).

The toxicity of Cd became well known due to a Japanese disaster. After World War 2, it became apparent that inhabitants along the lower reaches of the Jinzu river in Japan suffered from a very painful osseous disease, which was called itai-itai (ouch-ouch) disease (Kitagishi and Yamane, 1981). Patients endured intense pain in their bones. These symptoms are believed to reflect a disturbed calcium-phosphorus metabolism secondary to kidney damage due to Cd toxicity. Dietary deficiencies (lack of calcium and vitamin D) were possible contributing factors. Females were especially sensitive. The total number of patients having itai-itai disease reached 490 persons, all females. Cadmium-induced renal malfunction is widespread in a large number of inhabitants irrespective of sex.

The free Cd^{2+} -ion is the most toxic chemical species, the kidney appears to be the most sensitive organ for humans. Symptoms of acute Cd intoxication which occur following ingestion are severe nausea, vomiting, stomach-ache, muscular cramps, abdominal pain and diarrhoea. These symptoms may be followed by shock due to loss of liquid and death within 24 hr, or by acute renal failure and cardiopulmonary depression and death within 7-14 days (Yasumura *et al.*, 1980). Symptoms after chronic exposure of test animals and humans are proteinuria, osteoporosis, gastritis, high blood pressure, lung emphysema, and damage to liver, kidneys and testes. Chronic intoxication for humans is irreversible.

Because of the toxicity of Cd, its dissemination became an environmental issue. Cadmium is highly persistent in the environment and, when compared to other heavy metals, relatively mobile with respect to plant uptake and leaching. Mobility in the soil system may lead to groundwater contamination, which in turn may lead to deterioration of drinking water quality. Cadmium can accumulate in plants without causing physiological damage at concentrations that exceed acceptable concentrations in terms of Acceptable Daily Intake (ADI)

standards given by the WHO. Moreover, intake is already at the highest percentage of the Provisionable Tolerable Daily Intake for Cd in the average human diet (De Haan *et al.*, 1989). Bioavailability of Cd in soils may seriously disturb the functioning of ecosystems. These risks of soil contamination with Cd illustrate that evaluation of Cd behaviour in soils is necessary to help prevent repetition of the Japanese experience.

Soil pollution with Cd in the Netherlands is scattered throughout the country. Besides small scale soil pollution caused by point sources, diffuse source deposition caused soil pollution with Cd in the South of the Dutch Province of Limburg. The flood plains of the rivers Geul and Meuse are contaminated due to high Cd concentrations in the river water during many decades. These high concentrations were caused by heavy metal ore exploitation at the upper reaches of the Geul and Meuse in the Netherlands and Belgium (Harmsen, 1977; Leenaers, 1989). In the western part of the country Cd contamination of soil is the result of elevation of land with contaminated harbour sludge (CCRX, 1985). Arable land that received large amounts of phosphate fertilizers is enriched with Cd as well. Phosphate fertilizers contain trace amounts of Cd. The concentration depends on the origin of the rock phosphate used for fertilizer production, and may range from 50 - 170 mg kg⁻¹ of fertilizer (Williams and David, 1976).

The largest area in The Netherlands that experiences a Cd problem is the Kempen area. This area extends from the South of the Netherlands in the Province of Noord Brabant to the North of Belgium. In the Netherlands, an area of 350 km² is contaminated with Cd (Klitsie, 1988). Besides contamination with Cd, high contents of Zn are found. During almost a century, zinc smelters in this area used a thermic procedure to extract Zn from its ores. This resulted in high emissions of Zn and Cd into the atmosphere. Deposition in the vicinity of these zinc smelters caused accumulation of Zn and Cd in the soils. In the Seventies, an electrolytic process was introduced to extract Zn from its ores, and since then emissions have decreased considerably. In this thesis, field scale analysis of Cd behaviour was studied in an agricultural field in the Kempen area.

Dutch Soil Protection Policy

The discovery of severe soil pollution under a newly built residential area in Lekkerkerk in 1980 was a major incentive in the Netherlands for the development of legislation to protect the soil. The concept of multifunctionality plays a central role in the Dutch environmental legislation (Von Meijenfeldt, 1991). This

concept implies that now and in the future, soil quality must be such that the natural functions of soil must remain possible. To make this concept operational, reference values were developed for different pollutants that indicate good soil quality.

These reference values are based on measurements of pollutant contents in soils of Dutch natural environments, and include a differentiation according to organic matter content and clay content for heavy metals. This was done because high correlations were found between these soil parameters and the natural content of heavy metals. The fact that clay minerals naturally contain more heavy metals than other soil constituents, and organic matter content influences the soil bulk density, may explain these correlations (Lexmond and Edelman, 1987; De Haan *et al.*, 1990).

The Dutch environmental policy aims at protection of men and the environment against adverse effects of environmental contamination. The so-called risk approach is now in development, which aims at quantification of the chance of adverse effects (Anonymous, 1989). The individual risk of death due to exposure is starting point for the development of boundary values for maximum admissible risks for humans. For ecosystems, models are used to extrapolate results of standard toxicity tests for individual organisms to maximum admissible risks for the whole ecosystem. It is assumed that the functioning of ecosystems is protected when 95% of the ecosystem's species are protected against adverse effects of pollutants (Denneman *et al.*, 1989).

Van den Berg and Roels (1991) have proposed a method with which maximum admissible risks can be quantified by so-called C-values. These C-values are toxicologically based, and are supposed to give an indication of the possibility of an unacceptable risk for man and environment, when all potential exposure routes would be operational. In this proposal, the C-values for heavy metals are scaled with regard to organic matter content and clay content, in a way similar to the scaling of the reference values. This was done because clay and organic matter are known to be important factors in the retention capacity of soil for heavy metals, and to develop a consistent legislation. Note, however, that the arguments for accounting for clay content and organic matter content in both the reference values and the C-values are different. Moreover, it is well known, although not quantified for all contaminants, that retention of heavy metals in soils is regulated by other soil factors as well. When these other soil factors are important, they should be included in values that indicate maximum admissible risks.

Exposure

Interpretation of the impact of elevated Cd contents in soil on 'man and the environment' needs relationships between a certain dose or exposure and possible health effects (both on humans and on ecosystems), which is studied by (eco)toxicologists. However, this knowledge cannot be used directly, because a certain soil Cd content should be translated to exposure first. This translation is very complicated. Exposure of humans to Cd in contaminated soil is mostly indirect, by consumption of contaminated drinking water or contaminated food that was grown on contaminated soil. The only route for direct exposure is ingestion of contaminated soil, mostly by children that play at contaminated sites. The indirectness of exposure imposes many uncertainties on the final estimation of exposure.

Plants are exposed to Cd in the soil solution via their roots, or from airborne particles via their leaves. No consensus is (yet) established on relationships between Cd contents in soils and Cd concentrations in edible parts of plants. It is well known that soil factors influence plant uptake. The main factors are soil pH, clay and organic matter content, and Cd content of the soil, particularly the true exchangeable fraction of the metal in the soil (Häni and Gupta, 1985). Also the presence of cations like Zn influences Cd uptake by plants (Smilde *et al.*, 1992). Concentrations of Cd in plants vary among species and cultivars if grown on the same soil. Different plant parts accumulate different amounts of Cd (Busch, 1985). Moreover, the concentration depends on the physiological state and age of the plant. Because the concentration in the soil liquid phase is continuously changing as a result of soil water dynamics, the problem of indirect exposure can be formulated as two different problems, one related to the plant and its uptake mechanisms, and one related to the soil, because it needs to be defined which effective concentrations plant roots are exposed to.

Although total heavy metal contents in soil are often used to express the degree of contamination, total contents are of little value to judge biological effects. Extraction of soil with neutral salt solutions of NaNO_3 or CaCl_2 have been recommended as a method to obtain soil data that are at least more indicative of expected effects of soil pollution with heavy metals than total contents. Greenhouse experiments showed that uptake of Cd by plants correlated well with CaCl_2 -extractable Cd, but did not correlate with total Cd contents (Styperek, 1985; Salt, 1988). Eriksson (1990) found that in Sweden, concentrations in grains correlated well with CaCl_2 -extractable Cd contents. However, only correlative relationships between CaCl_2 -extractable Cd contents of soil and Cd concentra-

tions in plants have been established. No information is available (yet) on the applicability of this method to predict exposure of crops grown on contaminated soil, as mechanistic understanding is still lacking.

Sorption Models for Cadmium

A quantitative interpretation of soil contamination with heavy metals in terms of possible effects on crop and groundwater quality needs insight into the behaviour of heavy metals in the soil system. Behaviour is controlled by the combined effects of chemical, physical and biological processes. Chemical behaviour of Cd is primarily governed by sorption and precipitation reactions in soil. In acid and neutral soils, precipitation of Cd is unlikely to occur, except in calcitic soils or soils with a high concentration of phosphates and/or sulphates (Lindsay, 1979). Because measurements and experiments described in this thesis were done for acid sandy soils, this aspect of Cd behaviour in soils is not given further attention.

To study Cd sorption in soils, laboratory measurements can be done with homogenized and sieved soil, so that reproducible results can be obtained. Adsorption experiments involve equilibration of soil with water of a particular ionic composition (electrolyte solution) and Cd concentration in a batch experiment. After separation of the liquid and the solid phase, the change in Cd concentration as compared to the added solution concentration can be measured in the liquid phase by various analytical techniques. Changes in the Cd concentration after equilibration with soil are then indicative of the Cd retention capacity of the soil. Adsorption isotherms can be measured with a large degree of reproducibility. However, the measurements are very sensitive to changes in either the soil composition or the electrolyte composition. This restricts the applicability of both sorption models and parameter values derived from these kinds of experiments.

Two different approaches can be distinguished in the modelling of heavy metal adsorption by soils. In the molecular approach, the sorption behaviour is described as the formation of surface complexes between ions in solution and functional groups of the soil solid phase. The binding depends on the types of functional groups, the type of ion, electrostatic effects, and composition of the soil solution. The molecular approach strives at a mechanistic description of the sorption process, and the factors that influence sorption. Its model parameters are usually derived for individual solid phase components (e.g. goethite:

Hiemstra and Van Riemsdijk, 1990; organic matter: De Wit *et al.*, 1990)). Compilation of submodels for the individual soil components into one model for use in real soils is still a challenge for the future (Nederlof, 1992).

The macroscopic approach uses empirical expressions to describe observed sorption behaviour of heavy metals. The macroscopic approach is used for systems that are not very well characterized, such as soils. Because field soils are poorly defined media in terms of the nature of available sorption sites and their reactivity, macroscopic sorption models are used in this thesis to describe Cd sorption in field soils.

Adsorption of Cd in the environmentally relevant concentration range can often be described by a simple equation that relates the adsorbed amount (q in mg kg^{-1}) to the concentration in solution (c in mg L^{-1}): $q = kc^n$; where k and n are model parameters and $0 < n \leq 1$. This adsorption equation was suggested first by Van Bemmelen (1888), although it is often attributed to Freundlich (1909) (Sposito, 1981). In this thesis it is referred to as the Freundlich equation.

The Freundlich equation describes the observation that an increase in the concentration in solution does not result in a proportional increase in the adsorbed amount, but that the adsorbed amount levels off. The Freundlich equation is valid for a limited concentration range only, because the soil solid phase has a finite capacity to adsorb chemicals. This adsorption maximum is not included in the Freundlich equation. Because Cd contents in soils are already environmentally relevant far below the adsorption maximum, it is important to focus on an accurate description of Cd sorption in the relevant concentration range, instead of a description of the entire adsorption curve.

Besides the fact that the Freundlich equation describes a limited concentration range, its parameters k and n are only valid for the system from which they are derived. To expand its applicability it has been tried to develop extensions of the Freundlich equation. Chardon (1984) studied the sorption behaviour of Cd in soils, and he derived an adjusted Freundlich equation that explicitly accounts for the effect of pH and Ca activity on the sorption behaviour of Cd. This equation described Cd sorption in 12 different soil types and under varying values of pH and Ca-activity fairly well, using constant values for the model parameters. Van der Zee and Van Riemsdijk (1987) derived an extension, using the data of Chardon (1984), that includes the effect of pH and organic matter content.

The use of the Freundlich equation implicitly assumes sorption equilibrium. However, when the time needed to reach sorption equilibrium exceeds the contact time between the sorption sites and the sorbing chemical, model parameters

derived from equilibrium experiments cannot be applied directly. When sorption kinetics are of relevance, this should be incorporated in the sorption model for an adequate description of observed sorption behaviour.

Soils, Soil Heterogeneity and Scale

The theory of heavy metal sorption is still in development, and only recently the effect of the inherent heterogeneous character of soils has been acknowledged. Different scales of heterogeneity can be distinguished, involving different problems and possible solutions. Some of these scales and related problems are briefly introduced to illustrate the relevance of scale and soil heterogeneity for behaviour of contaminants in soils.

Soil consists of a mixture of organic and inorganic constituents. The inorganic fraction may contain silica (SiO_2), metal(hydr)oxides of iron, aluminium, and manganese, clay minerals, calcium carbonates, and primary minerals like feldspars (Bolt and Bruggenwert, 1981). Clay minerals exhibit a constant negative surface charge, whereas the metal oxides are amphoteric, i.e. be either positively or negatively charged depending on the pH of the system. The organic fraction, known as organic matter or humus, is very poorly defined, and formed by chemical or (micro)biological degradation of dead plant and animal residues. Soil organic matter exhibits variable charge characteristics similar to the metal oxides, although its overall charge is negative (Stevenson, 1982).

At the molecular scale, heavy metal sorption is a chemical reaction at the soil-water interface. The overall charge of soil particles leads to the formation of a diffuse double layer, in which charged ions are attracted to the surface by electric forces on the one hand, and tend to distribute evenly in the solution because of enthalpic and entropic forces. Because of the heterogeneity of the surface sites of the solid phase, the electric forces are not evenly distributed over the surface. The binding of chemicals to a soil is then the overall result of the binding of individual molecules to sites of different binding energy. Methods with which overall binding characteristics can be translated to surface heterogeneity were described by Nederlof (1992).

Another scale of observation may be soil aggregates. The irregular shape and packing structure of soil aggregates results in a distribution of pore sizes in soil, and variability of length scales (Brusseau *et al.*, 1989; Rappoldt, 1992). Accessibility of reactive surface sites in the center of the aggregates is diffusion controlled. The sorption capacity as observed in batch experiments, with optimal

accessibility of reactive surface sites in the soil-water suspension, may then not be indicative for the retention capacity of undisturbed soils.

At still larger scales, the porous system is heterogeneous due to cracks, root channels and other relatively large pores that may induce preferential flow (Bouma, 1981; Schulín *et al.*, 1987; Van Ommen, 1988; Brusseau and Rao, 1990). In that case, part of the soil solution containing the chemicals passes the solid matrix without interaction. When the scale of observation is extended further, differences in geologic origin and soil formation processes cause variability of soil types.

The effect of field scale heterogeneity is that observations done in one part of an area do not necessarily reflect contaminant behaviour in the entire area. This implies that a carefully designed sampling strategy is necessary to understand spatial variability of soil processes in the entire field. Another effect of field scale heterogeneity is that predictions based on soil homogeneity can be markedly different from predictions based on soil heterogeneity (Herr *et al.*, 1989). Van der Zee (1988) showed that predictions of phosphate transport in agricultural field soils, based on the assumption of soil homogeneity, underestimated the moment of first breakthrough of phosphate towards groundwater. This underestimation was partly due to soil heterogeneity which caused accelerated leaching in some areas in the field as compared to the average leaching. Furthermore, the fate of phosphate in soil was controlled by nonlinear processes. Nonlinearity implies that predictions of average behaviour in a heterogeneous soil are different from predictions done for a homogeneous soil with the same average properties. In risk assessment of soil contamination these aspects are of prime concern, because they determine the vulnerability of the soil system.

From this brief outline of the scale problem, it is evident that each scale of observation involves different, scale-specific problems with respect to the modelling of heavy metal behaviour. The model that is used to describe heavy metal behaviour in soil needs to be developed for the scale at which it is applied, including scale-relevant aspects of heterogeneity. Parameter values for the model need to be appropriate at that scale. Only then the model can be conceived as a representation of the system that is modelled.

Objectives

As was outlined in the previous paragraphs, the environmental risk of a contaminant at a given total content is highly dependent on the properties of the soil.

Quantification of this dependency is difficult because of the large number of soil properties involved. This complication, together with the relatively large variations in soil properties at various scales, causes risk assessment of soil contamination and the development of a relevant system of soil quality standards to be a delicate task.

The main objective of this thesis was to develop methodologies with which the environmental risks of Cd pollution of field soils can be evaluated. One of the methods that seems to be promising with respect to bioavailability and leachability is soil extraction with CaCl_2 . Because little is known about the chemical behaviour of Cd in CaCl_2 -suspensions of soil, an important incentive was to clarify this method with respect to the effect of soil pH and electrolyte composition on the Cd sorption equilibrium.

Furthermore, this study was aimed at validating the assumption that field scale heterogeneity of Cd behaviour is an important factor in risk assessment of soil contamination with Cd. Derivation of an accurate Cd sorption model for field scale applications, including methods of parameterization and validation of this model was an important goal. Insight into the relationship between CaCl_2 -extractable soil Cd, total soil Cd contents, and soil properties as pH and organic matter content is intended to lead to a better understanding of the effects that may be expected from soil pollution with Cd.

Risk assessment of soil pollution involves distinction between 'clean' and 'contaminated' locations as well, in view of effective remedial action of contaminated sites. In this context, one of the objectives of this study was to evaluate the ability of spatial interpolation methods to delineate observed spatial patterns of Cd contamination of a field soil. Besides prediction of spatial patterns of Cd in contaminated soils, the ability of models to predict effects of long-term Cd deposition onto soils is relevant for interpretation of various scenarios for emission reductions. This thesis addresses the importance of spatial variability of soil chemical properties for these kinds of predictions. Finally, this study aims at testing the ability of CaCl_2 -extractable Cd contents of soil to indicate field scale variability of Cd concentrations in plants.

Layout of this thesis

In this thesis articles are compiled, in their current state slightly modified, that were published in or submitted to international scientific journals. In the next chapter, the chemical behaviour of Cd in 0.01 M CaCl_2 is examined, as influenced

by the composition of the electrolyte solution. The effect of pH on Cd sorption is quantified by the extended Freundlich equation of Van der Zee and Van Riemsdijk (1987), and explained by assuming that protons and Cd sorb onto the same sorption sites.

In Chapter 3, the extended Freundlich equation is applied to Cd sorption in both batch experiments, in a soil column transport experiment, as well as along a transect in an arable field. In this way, Cd sorption is studied at different scales of observation. To interpret data that were taken along a transect in a field, spatial patterns of Cd contents, pH, and organic matter content along the transect are compared using methods from time series analysis in Chapter 4. In Chapter 5, a two-dimensional sampling procedure is used to assess spatial patterns and correlation scales for different soil parameters using geostatistical theory.

In Chapter 6, kriging is evaluated as a spatial interpolation method that quantifies pollution boundaries in a heterogeneous field soil. Chapter 7 presents a model with which the long-term effects of diffuse Cd deposition onto a heterogeneous soil can be evaluated. Both heterogeneity with respect to soil physical parameters as soil chemical parameters is analyzed. To investigate the ability of the CaCl_2 extraction method to indicate Cd concentrations in the economic product of crops, Cd concentrations in barley grains are compared with CaCl_2 -extractable Cd contents of soil in Chapter 8. These field data on Cd accumulation and bioavailability to crops are used to validate the developed model on long-term effects of Cd deposition onto soils.

In Chapter 9, the results of the work described in the previous chapters is integrated in view of the objectives of this study. The implications for future research as well as soil protection policy are discussed.

Chapter 2

Influence of electrolyte composition and pH on cadmium sorption by an acid sandy soil

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Influence of electrolyte composition and pH on cadmium sorption by an acid sandy soil

Summary

Extraction of soil with CaCl_2 has been recommended as a measure of bioavailability of heavy metals. Interpretation of soil extraction data in terms of plant uptake potential may improve when the chemical behaviour of heavy metals in these extracts is ascertained. The effect of pH, Cd-complexation by Cl, and competition between Cd and Ca on Cd sorption was studied at an ionic strength of 0.03 M. Sorption of cadmium was measured in 0.01 M CaCl_2 , in 0.01 M $\text{Ca}(\text{NO}_3)_2$, in a mixture of 0.02 M NaCl and 0.01 M NaNO_3 , and in 0.03 M NaNO_3 , at different values of pH ranging from 3.8 to 4.9. Adsorption isotherms were all linear, with a negative intercept at the y-axis. This intercept indicated (linear) desorption of only part of the initial soil Cd content. About 50% of the Cd in solution was complexed in the presence of 0.02 M Cl at ionic strength of 0.03. Due to competition between Cd and Ca, sorption of Cd was reduced by 80% in the Ca-electrolytes as compared with the Na-electrolytes. Sorption was highly sensitive to pH as each 0.5 unit increase in pH resulted in twice as much sorption of Cd. An empirical factor in the sorption equation that accounts for this pH-effect showed a similar response to changes in pH as a mechanistic factor. This mechanistic factor was developed by assuming that Cd and protons sorb onto the same sites and that a two-site Langmuir sorption isotherm for protons was able to describe the titration curve of the soil. This similarity may explain the successful application of the empirical factor in this and previous studies.

Introduction

Risk assessment of heavy metal pollution of soils aims at predicting the fate of these potentially harmful compounds in the environment. Risks for exceedance of quality standards for crops may be evaluated using the plant itself as an extracting agent. Then, heavy metal uptake is a direct indicator of the availability of metals in the soil. The use of plants for determining the metal status of a soil is a time consuming process, because it requires experiments for all possible combinations of soils and plant species. Laboratory-scale column experiments may give insight into the leaching behaviour, which may indicate the risks of groundwater contamination. Both greenhouse experiments and soil column studies are costly and laborious activities. An alternative approach to assess the hazards of soil contamination with heavy metals may be offered by soil measures. This may reduce the effort involved in risk assessment considerably.

The total content of a heavy metal in soil is not a good soil measure, rather the metal concentration in the soil solution is the parameter that controls mobility and bioavailability. Several soil measures have been proposed that supposedly reflect the soluble and easily exchangeable heavy metal fraction of soil. Good correlation between plant uptake and the so-called extractable heavy metal concentration of the soil has been found by Häni & Gupta (1980). Extraction with a CaCl_2 -solution was recommended as a measure of bioavailability, since it not only reflected soil type dependent differences in availability, but also the influence of soil pH (Sauerbeck & Styperek, 1985). Concentrations in a 0.01 M CaCl_2 -extract appeared to be a good measure of nutrient availability in soils (Houba *et al.*, 1986). There is evidence that this is also the case for heavy metal uptake (Sanders *et al.*, 1987).

Interpretation of Cd solution concentrations in terms of bioavailability is not straightforward. Cadmium uptake by plants is mainly regulated by the free Cd^{2+} -activity in solution (Bingham *et al.*, 1984). Hatch *et al.* (1988) found that although dissolved Cd in the soil solution is larger at low pH, the extent to which Cd uptake by plants increases with decreasing pH in soil will be less than expected based on solution concentrations alone. During vegetative growth, absorption of Cd by plants is suppressed at low pH due to increased competition between Cd and protons. The same tendency can be expected in the presence of other competing cations in solution, e.g. Zn. Interpretation of Cd solution concentrations may improve when the chemical behaviour of Cd in a CaCl_2 -extract of soil is ascertained.

Chemical behaviour of Cd in soils is primarily regulated by sorption reactions and precipitation/dissolution of Cd species. In neutral and acid soils, precipitation of Cd is unlikely to occur, other than in soils which are calcitic or very high in phosphate or sulfate (Lindsay, 1979). Sorption of Cd mainly involves the free divalent cation Cd^{2+} (Neal & Sposito, 1986). Chloride may form soluble complexes with Cd (Hahne & Kroontje, 1973), thereby enhancing the dissolved fraction whilst calcium can compete with Cd for sorption sites (Chardon, 1984; Christensen, 1984). Moreover, since the total Cd-concentration, pH, CEC, ionic strength, concentration of other competing cations (e.g. Zn), and soil texture influence the concentration in solution as well, the equilibrium Cd-concentration measured in a 0.01 M CaCl_2 -extract of soil will be the result of the combined influence of all these processes.

In the following, we consider adsorption of Cd in an acid sandy soil under various experimental conditions to quantify the relative importance of three processes that regulate the Cd-concentration in a 0.01 M CaCl₂-extract of a sandy soil, i.e. complexation of Cd²⁺ by Cl⁻, competition between Cd²⁺ and Ca²⁺, and the influence of pH on Cd sorption.

Theory

Sorption of Cd

Adsorption of Cd in the low concentration range (0-1 μmol dm⁻³) can be adequately described by the Freundlich equation:

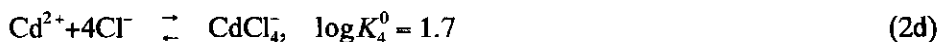
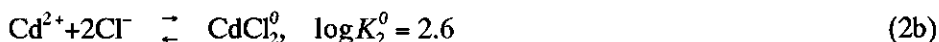
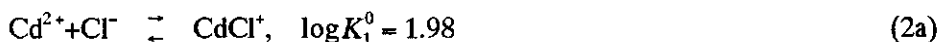
$$q = k_{Cd}^c c^n \quad (1)$$

where q is the adsorbed amount (mol kg⁻³), c is the total Cd-concentration in solution (mol dm⁻³), and k_{Cd}^c and n are Freundlich parameters. In this equation, q and c are operational variables. By monitoring the change in c when a solution of known initial concentration is added to a given amount of soil, q is calculated as the difference after correction for the soil-solution ratio. Often the soil already contains a certain amount of Cd. This initial content of the soil can be measured analytically, or it can be estimated by fitting the sorption data to the sorption model.

The value of parameter k_{Cd}^c is not a constant, but depends on soil type and experimental conditions (De Haan *et al.*, 1987). The presence of calcium in solution influences sorption of Cd. Cadmium is preferentially adsorbed over Ca at low Cd concentrations (Milberg *et al.*, 1978). Homann & Zakoski (1987) reported a decrease in adsorbed Cd by an average of 81% when final free Ca²⁺ increased from an average of 0.09 mM to 4.0 mM. Christensen (1984) found that an increase in Ca-concentration from 0.001 mol dm⁻³ to 0.01 mol dm⁻³ reduced Cd sorption by a factor of three.

Complexation of Cd with Cl

Chloride can form soluble complexes with Cd, hence reducing the Cd²⁺-activity in solution:



Values for the equilibrium complexation constants (K^0 s) are from Smith & Martell (1981), given for an ionic strength (I) of zero. García-Miragaya & Page (1976), Chardon (1984), Christensen (1984), and Christensen & Lun (1989) used other values, cited by Hahne & Kroontje (1973), for the complexation constants in their calculations ($\log K_1 = 1.32$, $\log K_2 = 2.22$, $\log K_3 = 2.31$, and $\log K_4 = 1.86$). It is unclear why these authors did so, since Hahne & Kroontje (1973) obtained their values from Sillén and Martell (1964), who gave these particular values for Cd complexation by Cl in a 4.5 M NaClO₄ background electrolyte, instead of for zero ionic strength. Therefore, we did not consider the values of Hahne and Kroontje (1973) any further.

The K -values at zero ionic strength (K^0) were converted into K -values valid for other values of ionic strength (K^I) by using the appropriate activity coefficient: $K^I = K^0 \cdot f(\text{reactants}) / f(\text{products})$. The activity coefficient for each species was calculated with the 'Davies' extension of the Debye-Hückel equation (Bolt & Bruggerwert, 1978) for charged species:

$$-\log f_z = 0.5 |z_+ \cdot z_-| \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (3)$$

For uncharged species the activity coefficient was calculated using $-\log f_0 = 0.5 I$ (Long & Angino, 1977). For the fraction of the total Cd-concentration as Cd^{2+} in solution, F , the expression can be derived:

$$F = \frac{\text{Cd}^{2+}}{\text{Cd}_T} = \frac{1}{1 + K_1^I[\text{Cl}^-] + K_2^I[\text{Cl}^-]^2 + K_3^I[\text{Cl}^-]^3 + K_4^I[\text{Cl}^-]^4} \quad (4)$$

When the free Cd^{2+} species is the dominant sorbing Cd-species, sorption of Cd should be expressed as a function of Cd^{2+} -activity (a) instead of total concentration in solution (c). Hence, Equation (1) can be rewritten into:

$$q = k_{\text{Cd}}^c \left(\frac{a}{F f_{2+}} \right)^n = k_{\text{Cd}}^a a^n \quad (5)$$

Effect of pH

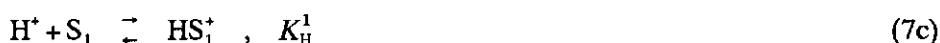
In field experiments (Boekhold *et al.*, 1991; Boekhold & Van der Zee, 1992) the effect of pH on the sorption equilibrium of Cd in an acid sandy soil was described well by including an empirical factor for this pH effect, as derived by Chardon (1984), in the sorption equation:

$$q = k_{Cd}^a a^n = k_{Cd}^* (H^+)^m a^n \quad (6)$$

with $m = -0.5$. The same empirical factor was used by Van der Zee & Van Riemsdijk (1987), and Gerritse & van Driel (1984) derived an equivalent correction factor for an acid sandy soil.

Another approach is to consider adsorption of protons and Cd^{2+} simultaneously. Then, the number of sites available for Cd^{2+} on the adsorption complex is not a constant, but depends on the number of sites occupied by protons (Kuo & Jellum, 1991). The adsorption complex can be conceived of as an ensemble of different sorption sites, each having their own affinity constant, K . This implies a distribution of K -values instead of a single value (Van Riemsdijk *et al.*, 1990). Often it is possible to define one 'effective' K -value for a limited pH-range. This effective K -value is an operational constant, and speculation about the chemical structure of the presumed adsorption sites is unwarranted (Perdue & Lytle, 1983). For the pH-range of 3.5 to 6.5 it sufficed for our soil to distinguish two different sites, as is shown in the sequel.

We assume that Cd^{2+} and protons compete for the same sites,



where S_1 and S_2 represent two different sites of unspecified valence and counter ion. By further assuming that a constant number of sites is available:

$$S_1 + CdS_1^{2+} + HS_1^+ = S_1^{tot} \quad (8a)$$

$$S_2 + CdS_2^{2+} + HS_2^+ = S_2^{tot} \quad (8b)$$

simple manipulation yields the competitive two-site Langmuir equation for Cd sorption:

$$q = \{CdS_1 + CdS_2\} = \frac{K_{Cd}^1 S_1^{tot} a}{1 + K_H^1 (H^+) + K_{Cd}^1 a} + \frac{K_{Cd}^2 S_2^{tot} a}{1 + K_H^2 (H^+) + K_{Cd}^2 a} \quad (9)$$

In the linear part of the Langmuir isotherm, i.e. at low Cd activities, $K_{Cd}^1 \cdot a$ and $K_{Cd}^2 \cdot a$ are small as compared to 1 in the denominator of Equation (9), which renders a relationship linear in a . By defining that $K_{Cd}^1 = K_{Cd}^2 = K_{Cd}$, we assume that Cd has the same affinity for the two sorption sites, thus eliminating one of the fitting parameters in the model:

$$q = K_{Cd} \left[\frac{S_1^{tot}}{1 + K_H^1(H^+)} + \frac{S_2^{tot}}{1 + K_H^2(H^+)} \right] a \quad (10)$$

The term between brackets is a factor that accounts for the effect of pH on Cd sorption, hereafter referred to as the mechanistic factor. With Equation (10), a model is developed that accounts for the effect of pH on Cd sorption in a mechanistic way rather than by the empirically derived factor $(H^+)^m$ of Chardon (1984).

Materials and Methods

Adsorption isotherms were measured in an acid sandy soil for a concentration range of 0-1.2 $\mu\text{mol Cd dm}^{-3}$ at a solid:solution ratio of 1:10. Table 1 gives some characteristics of the experimental soil. The soil suspension was shaken end-over-end for 20 h at 20° C. Then pH was measured in the suspension. After centrifugation at 10,000 g the Cd-concentration in the supernatant was measured using an atomic absorption spectrophotometer (Instrumental Laboratory AA/AE spectrophotometer S11 with Smith-Hieftje background correction) with scale expansion. An air-acetylene flame was used to measure Cd-absorption at a wavelength of 228.8 nm. The detection limit was approximately 0.1 $\mu\text{mol dm}^{-3}$.

The initial Cd content of the soil is measured using 0.43 M HNO_3 as an extractant at a solid:solution ratio of 1:10. This acid extraction is assumed to yield the total extractable Cd content. After two hours of shaking the suspension was centrifuged and the Cd-concentration in the supernatant was measured.

To separate the effects of chloride complexation on the one hand, and competition of Ca with Cd on the other hand, sorption isotherms were measured in 0.01 M CaCl_2 , 0.01 M $\text{Ca}(\text{NO}_3)_2$, a mixture of 0.02 M NaCl and 0.01 M NaNO_3 , and 0.03 M NaNO_3 . These four solutions have the same ionic strength and the activity of Cl or Ca is either the same as in the reference 0.01 M CaCl_2 -solution or zero.

Sorption isotherms of Cd were measured at pH-values of 3.8, 4.0, 4.2, 4.7, and 4.9 by adding 0.1 M HNO_3 or 0.1 M NaOH to the soil suspensions and equilibrating for 24 hours before adding Cd. Adjustment of pH affected ionic strength by 2% maximum.

Sorption of H^+ or OH^- was measured by adding HNO_3 or NaOH solution in a range of 0 to 0.4 mmol of H^+ or 0 to 1 mmol of OH^- to the soil. By adding 10 cm^3 0.105 M NaNO_3 a soil solution ratio of 1:10 was used at an ionic strength of 0.03. The suspension was shaken for 20 h at 20°C , and pH determined.

The model of Kinniburgh (1989) was used to fit the adsorption data using a nonlinear least square approach. Cadmium sorption data were fitted to Equation (1), (2), and (6). To obtain parameter values for the mechanistic factor of Equation (10), proton titration data were fitted to a two-site Langmuir equation.

Results and Discussion

Fig. 1 shows sorption isotherms of Cd at pH 3.8, 4.2, and 4.9. For pH 4.0 and 4.7 sorption isotherms were fully consistent, and therefore not shown. The sorption isotherms are linear, with a negative intercept at the y-axis, indicating desorption at low concentrations. The fitted intercept value is different for each isotherm and ranges from nearly zero to 50% of the initial Cd content of the soil as measured in 0.43 M HNO_3 . Apparently, only part of the Cd originally present in the soil obeyed to the linearity of sorption as observed for the added Cd in the experiments. This suggests that newly added Cd interacted with another type of binding site than the bulk of the initial Cd present in this soil, resulting in a negative intercept at the y-axis. Since this newly added Cd is of interest in view of soil pollution, attention is focussed on the linearity of the sorption isotherm, thus n equals one in Equations (1), (5), and (6).

Sorption isotherms were different for all electrolyte solutions and all values of pH. Equilibrium calculations showed that only 48% of the dissolved Cd is present as Cd^{2+} in 0.02 M Cl solutions at $I = 0.03$. The majority of Cd^{2+} present in solution is complexed as CdCl^+ , only small amounts are complexed by more than one Cl^- ion. By assuming that only Cd^{2+} is able to adsorb in significant quantities, the adsorption isotherms measured in the Cl and NO_3 -electrolytes should coincide when Cd^{2+} -activities instead of Cd-concentrations are considered. In Fig. 2 it is shown that for pH 3.8, 4.2, and 4.9, the Cd sorption data measured in the Cl and NO_3 -electrolytes indeed join into one line. For pH 4.0 and 4.7 the same applied, which justifies the assumption of Neal & Sposito (1986)

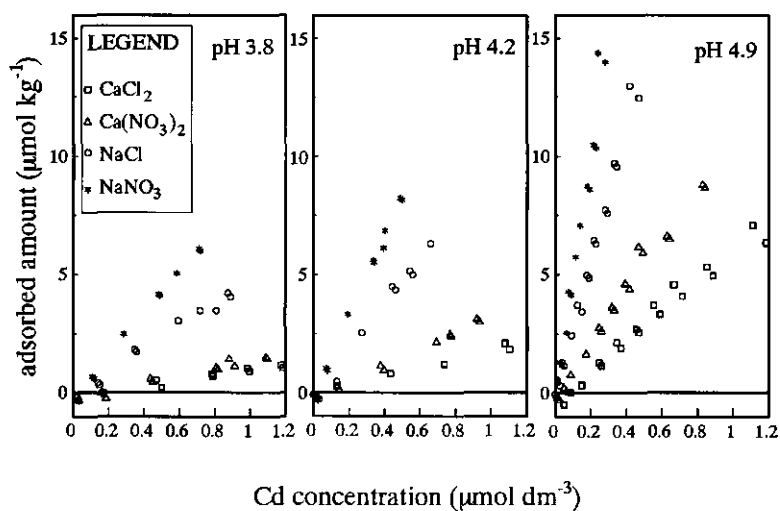


Fig. 1. Adsorbed amount of Cd ($\mu\text{mol kg}^{-1}$) as a function of the total Cd concentration in solution ($\mu\text{mol dm}^{-3}$) at pH 3.8, 4.2, and 4.9, using different background electrolyte solutions.

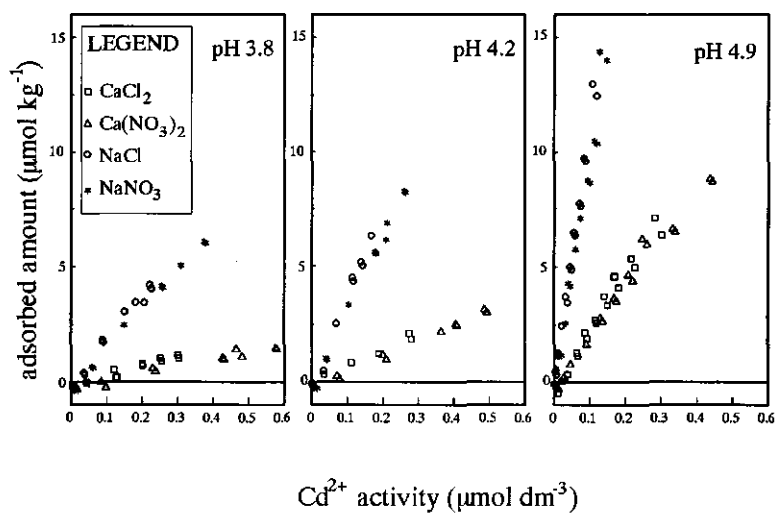


Fig. 2. Adsorbed amount of Cd ($\mu\text{mol kg}^{-1}$) as a function of the free Cd^{2+} -activity in solution ($\mu\text{mol dm}^{-3}$) at pH 3.8, 4.2, and 4.9, using different background electrolyte solutions.

that other species than Cd^{2+} do not significantly sorb. The difference in Fig. 2 between the Na- and the Ca-electrolytes is only due to the difference between Ca and Na with respect to competition with Cd for sorption sites. For all pH-values, sorption of Cd is reduced by approximately 80% in the Ca-electrolytes, as compared with the Na-electrolytes (Table 2).

Table 2. Slope and intercept value of the Cd adsorption isotherms from Fig. 2, goodness-of-fit (r^2), and relative slope in Ca-electrolytes as percentage of Na-electrolytes.

pH	electrolyte cation	slope ($\text{dm}^3 \text{ kg}^{-1}$)	intercept ($\mu\text{mol dm}^{-3}$)	r^2	Ca/Na *100%
3.8	Ca	3.0	-0.12	0.86	
3.8	Na	17.7	-0.23	0.97	17
4	Ca	5.0	-0.51	0.84	
4	Na	24.1	-0.03	0.97	21
4.2	Ca	6.4	-0.05	0.97	
4.2	Na	34.8	-0.30	0.97	18
4.7	Ca	14.7	-0.28	0.91	
4.6	Na	71.9	-0.23	0.96	21
4.9	Ca	22.3	-0.25	0.97	
4.9	Na	100.4	-0.07	0.97	22

To analyze the validity of the empirical factor $(\text{H}^+)^m$ that accounts for pH-effects on Cd sorption, the Cd sorption data measured in the Na- and Ca-electrolytes were put into separate graphs. Using the adsorbed amount of Cd as y-axis, and the product of Cd^{2+} -activity and $(\text{H}^+)^m$ as x-axis, in each graph a straight line with a slope that equals k^* should develop. When m (Equation (6)) is set to -0.5, a value found in previous Cd sorption studies, the scatter in the data is still considerable (Fig. 3). A trend in pH is still noticeable, as at increasing pH the corresponding data show higher adsorbed amounts. This implies that the effect of pH is not completely accounted for. Comparison of the fitted slopes (for the Ca-electrolytes k^* equals 0.061 ± 0.001 ($r^2 = 0.86$) and for the Na-elec-

trolites k^* equals 0.308 ± 0.006 ($r^2 = 0.89$)), indicated the same competitive effect of Ca (80% reduction of Cd sorption), as observed for the individual Cd adsorption isotherms.

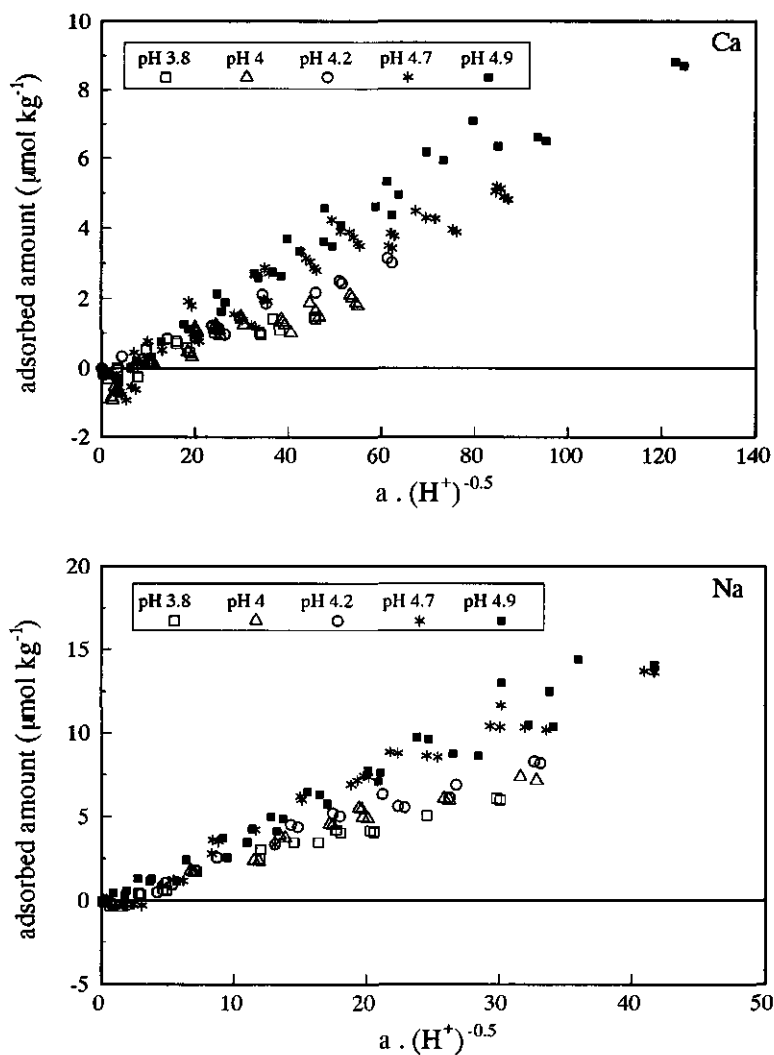


Fig. 3. Adsorbed amount of Cd ($\mu\text{mol kg}^{-1}$) in a) Ca-electrolytes and b) Na-electrolytes as a function of the product of the Cd^{2+} -activity in solution (a) and $(\text{H}^+)^{-0.5}$.

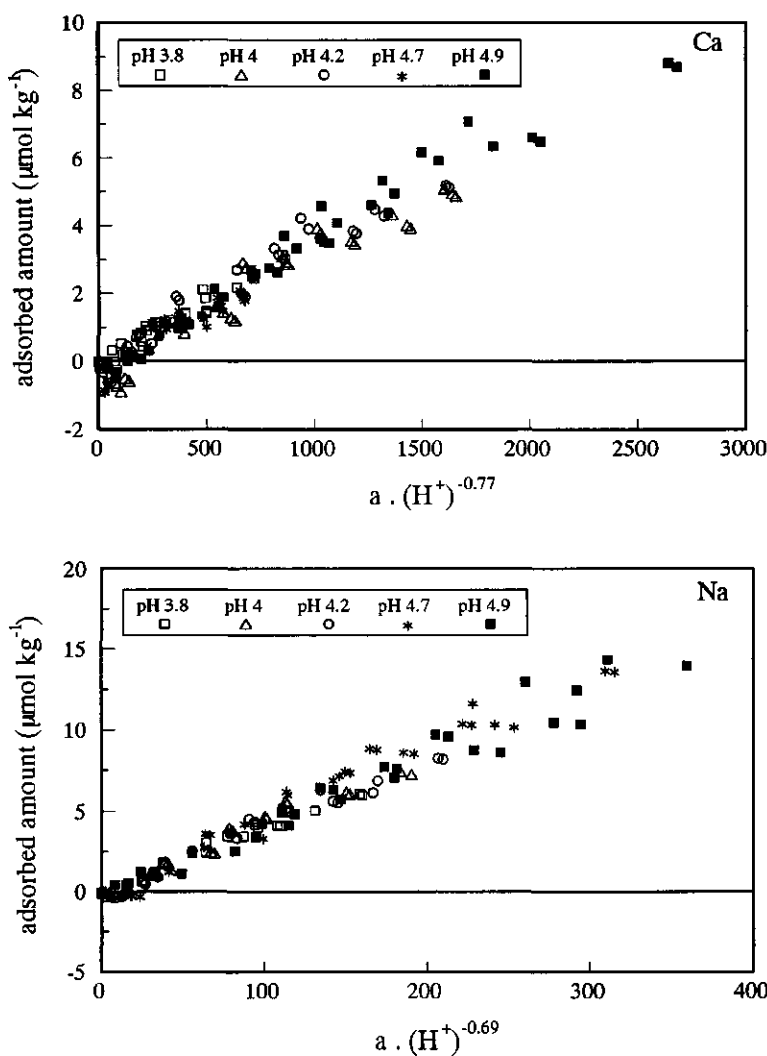


Fig. 4. Adsorbed amount of Cd ($\mu\text{mol kg}^{-1}$) in a) Ca-electrolytes ($m = -0.77$) and b) Na-electrolytes ($m = -0.69$) as a function of the product of the Cd^{2+} -activity in solution (a) and $(\text{H}^+)^m$ where m is fitted to the data.

By fitting m to the sorption data, substantially less scatter is left and the trend in pH is eliminated (Fig. 4). Different values for m were obtained, for the Na-electrolytes $m = -0.69 \pm 0.01$ and for the Ca-electrolytes $m = -0.77 \pm 0.02$. These values of m are considerably more negative than -0.5 , as found in previous

studies. When we consider m as a stoichiometric coefficient, indicating the relative replacement ratio of H by Cd, $|m|$ mole of protons are replaced by one mole of Cd when Cd adsorbs onto the soil. Then, more protons are released when Cd is adsorbed onto our soil than onto the soils used in previous studies. This may be due to differences in sorption mechanisms or sorption surface characteristics between different soils. Anderson & Christensen (1988) found an average calculated proton replacement of 0.65 for each mole of Cd adsorbed, which corresponds with our findings.

Due to the difference in value of m , sorption of Cd is now reduced by 92% in the Ca-electrolytes ($k^* = 0.0036$ ($r^2 = 0.95$)) as compared with the Na-electrolytes ($k^* = 0.044$ ($r^2 = 0.96$)). This apparent increase in competition between Ca and Cd when the effect of pH is accounted for, may be due to interference between Ca and protons during their competition with Cd. Protons not only compete with Cd, they compete with Ca as well. Therefore, changes in pH affect not only Cd sorption, but also Ca sorption, and therewith the competitive effect of Ca on Cd sorption. The effect of Ca on Cd sorption is not formulated explicitly in Equation (6). When interference between Ca and protons is important, its effect will be hidden in the value of m after fitting the data to Equation (6). This may explain the difference in value of m between the Ca- and the Na-electrolytes. To derive a mathematical formulation of the effect of Ca on Cd-sorption, more data are needed than given here.

Table 3. Parameter values for correction factor in Equation (10).

$\log(K_H^1)$ ($\text{dm}^3 \text{ mol}^{-1}$)	$\log(K_H^2)$	S_1^{tot} (mol kg^{-1})	S_2^{tot}
7.10	4.82	0.0085	0.0028

To obtain insight into the physical meaning of the empirically derived correction factor for the effect of pH on Cd sorption, a mechanistic approach was developed as described in the theory section. By fitting proton titration data for our soil to a two-site Langmuir sorption isotherm, parameters values for the mechanistic factor of Equation (10) were obtained (Table 3). The model fits the titration data well (Fig. 5), whereas assuming one sorption site yielded a poor fit (not shown). The mechanistic correction factor was compared with the empirical correction factor $(\text{H}^+)^m$, for $m = -0.5$, -0.69 , and -0.77 in a pH-range

of 3.5 to 6.5 (Fig. 6). Absolute values were all different, but since we are interested in the relative response of the correction factor to changes in pH, values were scaled to give the same order of magnitude.

The overall response of the mechanistic factor to changes in pH is similar to the response of the empirical factor. In the full pH-range, the mechanistic factor corresponds best with the empirical factor when $m = -0.5$. When $m = -0.69$ or -0.77 , the value of the empirical factor is much higher than the mechanistic factor above pH 5. However, when the pH range of 3.8 - 4.9 is considered, the mechanistic factor corresponds best with the empirical factor using the values of m fitted to our adsorption data. This may explain why, for our data, other values of m gave a better fit to the data than the value of -0.5 found in previous studies.

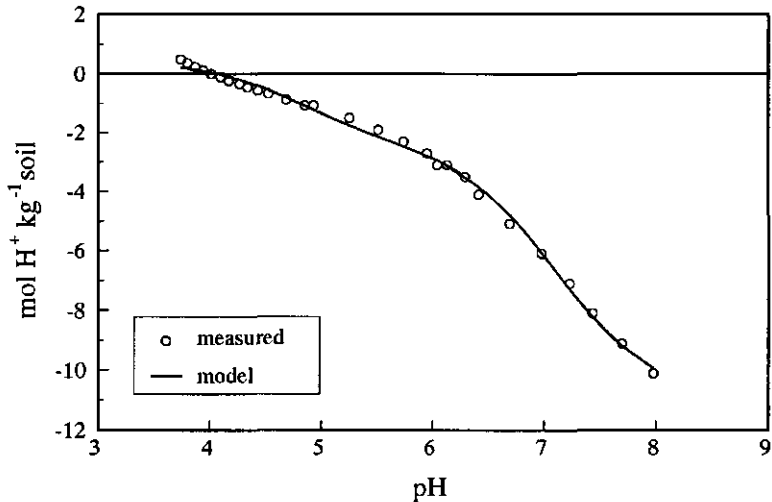


Fig. 5. Titration data for protons onto the sandy soil.

The similarity in relative change over the relevant range of pH between the mechanistic factor and the empirical factor may explain the applicability of the empirically derived correction factor that accounts for the influence of pH on Cd sorption, in this study as well as in previous studies. By assuming that Cd and protons sorb onto the same sites, and that a two-site Langmuir equation was able to describe sorption of Cd and pH, the influence of pH on Cd-sorption is explained successfully.

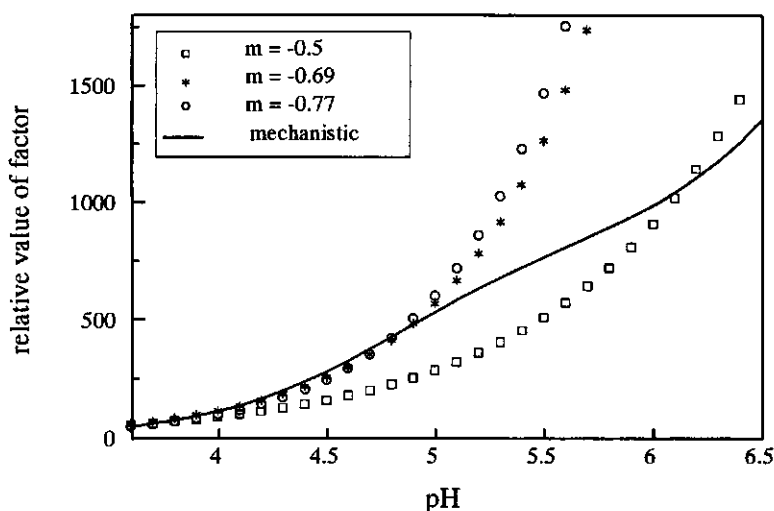


Fig. 6. Empirical and mechanistic correction factors for pH as a function of pH.

Conclusions

Sorption isotherms of Cd in suspensions of an acid sandy soil and electrolytes at $I = 0.03$ M were linear. Only part of the Cd initially present in the soil showed linear sorption behaviour similar to the added Cd in the experiments. In the Cl-electrolytes 48% of the Cd ions were present in their free divalent cation form. When the sorption isotherms were expressed in terms of Cd^{2+} -activity instead of Cd-concentration, sorption of Cd in the Cl-electrolytes was similar to sorption in NO_3 -electrolytes for values of pH ranging from 3.8 to 4.9. Apparently, only the Cd^{2+} species is able to adsorb in significant amounts. Differences in sorption behaviour after correction for complexation with Cl were now due to differences between the Ca- and the Na-electrolytes. Sorption of Cd was reduced by 80% in the Ca-electrolytes as compared with the Na-electrolytes. Measured Cd-concentrations are very sensitive to pH in all electrolyte suspensions.

When 0.01 M CaCl_2 -extraction of soil is employed for risk assessment of Cd pollution of acid sandy soils, one should realize that the presence of Ca and Cl increases the amount of Cd desorbed from contaminated soil by a factor 10 as compared with a NaNO_3 -extract of the same ionic strength, assuming that Cd sorption is fully reversible. This increase in desorbed concentration facilitates

analytical determination of Cd in a 0.01 M CaCl_2 -extract of soil. Interpretation of Cd-concentrations measured in a 0.01 M CaCl_2 in terms of bioavailability and leachability of Cd should take these features of Cd behaviour into account.

When the empirically derived correction factor for the influence of pH on Cd sorption, $(\text{H}^+)^m$, with $m = -0.5$, was used to quantify the pH-effect on Cd sorption, the scatter in the data was still considerable. Fitting of m improved the correction for pH, resulting in values for m of -0.69 for the Na-electrolytes, and $m = -0.77$ for the Ca-electrolytes. Interference between Ca and protons during their competition with Cd may explain the difference in the value of m between the two electrolytes.

By assuming that Cd and protons adsorb onto the same binding sites of the soil, another approach to account for the effect of pH on Cd sorption was developed. This mechanistic correction factor showed a similar relative change in value over a pH range of 3.5 to 6.5 as the factor $(\text{H}^+)^m$ with $m = -0.5$, whereas the fitted values for m corresponded best with the mechanistic factor in the pH range of our measurements (pH 3.8 to 5). Although the mechanistic factor is still based on operationally defined variables, it is derived using a physical model of the sorption process. Therefore, it may explain the success of the factor $(\text{H}^+)^m$ in this and previous studies.

Chapter 3

A Scaled Sorption Model Validated at the Column Scale to Predict Cadmium Contents in a Spatially Variable Field Soil

Co-author: Sjoerd E.A.T.M. Van der Zee

A Scaled Sorption Model Validated at the Column Scale to Predict Cadmium Contents in a Spatially Variable Field Soil

Abstract

Sorption of Cd is described with an extended Freundlich equation, that accounts explicitly for effects of pH and organic matter content. Parameters for this scaled sorption model were estimated using batch experiments with soil taken from an arable field. The sorption model explained differences in sorption between two soil samples from the same field that differed in pH and organic matter content. For validation of the sorption model predictions, a transport model was developed for cadmium in soil. Predictions of solute breakthrough were made that were in good agreement with measurements, using sorption parameter values that were derived from batch experiments that used the same background electrolyte concentration. With the validated sorption model total soil Cd contents along a transect in the field were predicted using measured values of pH, organic carbon content, and Cd concentration in soil solution. Although spatial variability of these parameters is distinct and not identical to the spatial variability of the total Cd content of the soil, model predictions showed good agreement with the observed spatial pattern. Spatial variability of pH and of organic matter content appeared to be an important factor which explained a large proportion of the heterogeneity of Cd contents in this soil. The scaled sorption model described Cd sorption well in both batch experiments, column scale experiments, and at the field scale, when all (scale dependent) relevant processes were taken into account.

Introduction

Contaminants that enter soil may be subject to accumulation, uptake by plants, (bio)degradation, and leaching. Whereas leaching poses a threat to groundwater quality, accumulation of contaminants may have an adverse effect on soil biological processes. The effect of the presence of contaminants depends not only on quantity, but also on local environmental conditions, e.g. soil type, land use, climate, etc. Once a site is contaminated, field measurements may reveal the impact of contamination on crop quality or groundwater quality. Laboratory and greenhouse experiments may yield insight into the relevance of different processes that determine the environmental fate of the contaminants in soil. Prediction of the effect of contamination in soil requires the use of a model that accounts for all relevant processes that regulate the behaviour of contaminants in soil. The applicability of (small scale) laboratory results to (large scale) field situations is then of paramount importance.

The fate of cadmium in the terrestrial environment is to a large extent determined by its chemical interactions with the soil solid phase because this determines the amount of Cd available for leaching and plant uptake. In most situations sorption is the main process that regulates the Cd concentration in the soil solution. For soils high in pH precipitation of Cd needs to be considered as well. In general, it is of paramount importance to give an accurate description of the sorption process when the environmental impact of Cd contamination of soil needs to be assessed.

One of the main difficulties in modelling transport through soil is its heterogeneity. When transport models are applied to field soils the behaviour of water and solutes is often not adequately described because soil physical (Biggar and Nielsen 1976) as well as soil chemical (Van der Zee and Van Riemsdijk 1987) parameters are highly variable in natural soils. By assuming spatial variability of pH in a field soil it was shown that field average behaviour of Cd did not correspond with behaviour predicted with average soil parameters (Boekhold and Van der Zee 1991). Therefore, the variability of soil chemical parameters needs to be reflected by the sorption model when field scale behaviour of Cd is of interest.

The purpose of this contribution is to validate a Cd sorption model that explicitly accounts for the effects of pH and organic matter content of the soil on Cd sorption. Parameter values for this scaled sorption model are obtained using batch experiments. The sorption model is combined with a transport model, and used to predict column transport of Cd. In this way the validity of the sorption model for a different scale of analysis and under different dynamics is assessed. The scaled sorption model is then applied to a heterogeneous field soil. Cadmium contents of the field were predicted and compared with measured data, and the ability of the scaled sorption model to predict the variability of Cd contents in the field is discussed.

Theory

Sorption isotherms of Cd in the low concentration range that is realistic for field situations have been shown to be well described by the Freundlich adsorption equation (García-Miragaya and Page 1977, 1978; Christensen 1984; Chardon 1984):

$$q = kc^n \quad (1)$$

where q is sorbed amount (mg kg^{-1}), c is concentration in the soil solution (mg L^{-1}), and k ($\text{mg}^{1-n} \text{ L}^n \text{ kg}^{-1}$) and n (-) are the Freundlich model parameters.

Many soil parameters have been reported that significantly affect the behaviour of Cd in soil. Soil pH appears to be the most important property that determines Cd availability to plants (Adriano 1986). By decreasing the soil pH also the amount of sorbed Cd was decreased (García-Miragaya and Page 1978). Organic matter is known to adsorb considerable amounts of inorganic cations (Adriano 1986), and is therefore an important soil constituent with regard to Cd sorption. Another factor is the type of exchangeable cations present (García-Miragaya and Page 1977). Calcium and also other heavy metals have been found to compete with Cd for sorption sites (Christensen 1984, 1987; Chardon 1984). Since the free divalent Cd ion is the most important Cd species that interacts with the soil solid phase, the extent to which Cd complexes are formed influences the sorption equilibrium. Next to dissolved organic matter the chloride ion also forms complexes with Cd. Chloride is more selective than many organic complexing agents and does not complex strongly with cations like Al^{3+} , Ca^{2+} and Mg^{2+} (Hahne and Kroontje 1973).

Chardon (1984) found that the value of the parameter n (Eq. (1)) is approximately constant for 12 different soils and different experimental conditions. However, the value of k varied considerably. Part of the variation in k could be explained deterministically by variation of pH and calcium activity. This corresponds with findings of Christensen (1989b) who observed that for linear adsorption the distribution coefficient approximately doubled for each 0.5 unit increase in pH. For the 63 different soils he used differences in organic matter content were also responsible for the variability of k . Van der Zee and Van Riemsdijk (1987) used a Freundlich sorption equation that accounts for variability of both pH and organic carbon content:

$$q = k^* oc (\text{H}^+)^{-0.5} c^n \quad (2)$$

in which k^* is the scaled sorption parameter ($\text{mg}^{1-n} \text{ L}^n \text{ kg}^{-1}$), oc is the organic carbon content of the soil (% by mass), and (H^+) is the proton activity in the soil solution (mol L^{-1}). Eq. (2) is used in this paper, and applied to a field soil that shows significant variability in both pH and organic matter content in the horizontal plane.

The validity of the Freundlich-type representation of the sorption process was examined using column experiments. The scale of observation is then expanded from individual soil samples in batch experiments to a larger soil volume under continuous flow of water and solutes. Transport of Cd in soil is primarily controlled by convective displacement of soil water. Additionally, diffusion and

dispersion processes affect the shape of the infiltrating solute front. When steady state water flow is assumed and production terms are neglected, the transport equation for one dimensional transport of reactive solutes in soil is given by:

$$\rho \frac{\partial q(c)}{\partial t} + \theta \frac{\partial c}{\partial t} = \theta D \frac{\partial^2 c}{\partial z^2} - \theta v \frac{\partial c}{\partial z} \quad (3)$$

where ρ is the soil bulk density (kg m^{-3}), t is time (year), θ is volumetric water content of the soil ($\text{m}^3 \text{m}^{-3}$), D is diffusion-dispersion coefficient ($\text{m}^2 \text{year}^{-1}$), z is soil depth (m), and v is water flow velocity (m year^{-1}).

Due to the nonlinearity of the sorption equation high concentrations display a higher apparent transport velocity through the soil column than low concentrations. This is the result of a decrease of the differential sorption capacity (dq/dc) when c increases, provided $0 < n < 1$ in Eq. (1). The spreading of the infiltrating solute front due to diffusion and dispersion is counterbalanced by this effect, which leads to the development of a relatively sharp front when a constant concentration is imposed at the column entrance that is higher than the initial concentration in the soil column. When the opposing influence on spreading of diffusion and dispersion on the one hand, and of adsorption nonlinearity on the other hand, are in equilibrium, the infiltrating solute front travels with a constant propagation velocity and invariant shape.

When a chemical is not adsorbed instantaneously during its transport through the soil, a kinetic sorption model is required for model predictions. To account for nonequilibrium sorption a first order rate equation is assumed:

$$\frac{\partial q}{\partial t} = k_r (k c^n - q) \quad (4)$$

Parameter k_r (year^{-1}) is a rate parameter and defines to what degree local equilibrium between solution concentration and adsorbed concentration is reached. When k_r reaches infinity equilibrium exists.

Nonequilibrium conditions may also occur when water fluxes are highly variable in the soil column. Then, the presence of relatively immobile water may cause differences in accessibility of sorption sites of the soil, which may be described with the dual porosity concept. In the case of nonlinear sorption in the immobile soil region and no sorption in the mobile soil region, this concept is mathematically equivalent with the concept of nonlinear sorption with first order sorption kinetics (Nkedi-Kizza *et al.* 1984). Thus, the model cannot distinguish which of these two processes is responsible for nonequilibrium effects. Moreover, with nonlinear sorption in the stagnant region and no sorption in the mobile region, the expression is mathematically indistinguishable from a similar

problem where the mobile region exhibits linear sorption. Mobile region sorption affects only the parameter values of the transport model and not the effect of nonlinearity of sorption (Vander Zee 1990). Therefore, it is assumed that sorption in the mobile region is zero.

A finite difference method based on the Crank-Nicholson scheme was used to solve Eq. (3) using the Newton-Raphson iteration method for the following initial and boundary conditions:

$$t = 0 \quad 0 \leq z \leq L \quad c = 0 \quad (5a)$$

$$t > 0 \quad z = 0 \quad \lim_{z \rightarrow 0^+} \left(D \frac{\partial c}{\partial z} - v c \right) = -v c_i \quad (5b)$$

$$t > 0 \quad z = L \quad \lim_{z \rightarrow L^-} \frac{\partial c}{\partial z} = 0 \quad (5c)$$

These conditions apply to steady state transport in a homogeneous soil column of finite length, L (m).

Materials and Methods

An arable field in the "Kempen" region in the south of the Netherlands was sampled. This area has received large amounts of Cd and Zn by atmospheric deposition during the past century due to the presence of zinc ore smelters. Soil was classified as a Typic Haplaquod, a sandy soil with a humic upper layer of 0.25 to 0.30 m. Cadmium contents in the parent material are negligible. At 1 m intervals two hundred 0-20 cm soil samples were taken with an auger along a transect in the field, with every point located at least 25 m away from the parcel boundaries. The soil samples were air dried and sieved to remove particles larger than 2 mm.

The Cd content of the soil was measured using a 0.43 M HNO_3 extract of the soil (Houba *et al.* 1988). Five g of soil was equilibrated with 50 ml 0.43 M HNO_3 for 2 hours. After filtration the Cd concentration in the filtrate was measured using flame-AAS. With this method the total Cd content of the soil is approximated, denoted as Cd_T (mg kg^{-1}). Destruction of the soil showed that more than 95% of the total content was extractable with 0.43 M HNO_3 .

The amount of Cd extracted with CaCl_2 from soil is suggested as a measure of bioavailability. Cadmium concentrations in this mild salt solution reflected soil dependent differences in availability of Cd and Zn in pot experiments with different plant species (Sauerbeck and Styperek 1985). With a CaCl_2 -extract of soil also the mobile fraction of the heavy metal content can be characterized (Brümmer *et al.* 1986). To obtain values that are indicative for mobility and bioavailability of Cd in our field, a five g soil sample was equilibrated with 50 ml 0.01 M CaCl_2 for 20 hours in an end-over-end shaker (Houba *et al.* 1988). The pH was measured with a glass-calomel electrode in the CaCl_2 -soil suspension. After centrifugation the Cd concentration in the supernatant, c (mg L^{-1}), was measured using flame AAS, denoted as Cd_s when expressed as mg kg^{-1} soil.

Organic matter content of the soil was determined as the organic carbon content, oc , by oxidation of organic matter with $\text{K}_2\text{Cr}_2\text{O}_7$ in a strong sulphuric acid medium (Houba *et al.* 1988).

Cadmium transport was examined in soil sample no. 115 from the transect. Soil columns of 0.11 m length and 0.016 m diameter were percolated with a 0.005 M CaCl_2 solution at a flow rate of approximately 1 m day^{-1} . To obtain breakthrough within a few weeks, relatively high Cd concentrations (2 and 20 mg Cd L^{-1}) were used. Breakthrough experiments were carried out in duplicate. To estimate the diffusion-dispersion coefficient, D , breakthrough curves of an inert solute (chloride as 0.005 M KCl) were determined.

The Freundlich parameters k and n for the transport model were derived for soil sample no. 115 using a 0.005 M CaCl_2 -electrolyte solution at a Cd concentration range of 0 - 12 mg L^{-1} (adsorption experiment I). Soil was shaken head over end for 20 hours to ensure sorption equilibrium. Because the Cd concentrations in solution of the 200 field samples were measured in a 0.01 M CaCl_2 -solution, this solution was used as background electrolyte to obtain the Freundlich parameters k^* and n for field-scale predictions. Sorption was measured for soil sample no. 35 and no. 115 using a Cd concentration range of 0 - 0.2 mg L^{-1} , (adsorption experiment II and III respectively), which is in the same order of magnitude as measured concentrations in the field. These two soil samples differed in organic carbon content and pH. Additionally, sorption was measured at Cd concentrations of 3 - 7 mg L^{-1} for soil sample no. 115 (adsorption experiment IV), to verify the validity of the Freundlich sorption parameters at Cd concentrations higher than 0.2 mg L^{-1} .

Results and Discussion

Equation (1) was fitted to the sorption data by nonlinear regression. All fitted sorption isotherms showed a goodness-of-fit (r^2) of 0.993 or more. The value of k is different for the two soil samples (sorption experiments II and III), whereas parameter n is of similar magnitude (Table 1). This is in accordance with findings from Chardon (1984). Parameter k^* is approximately equal for the two soil samples when the same background electrolyte concentration is used. This indicates that Eq. (2) gives a good description of the influence of soil pH and organic matter content on Cd sorption in this soil, parameters k^* and n are similar for two soil samples that differed in pH and organic matter content.

Table 1. Freundlich sorption parameters k and n , goodness-of-fit (r^2) of regression, k^* , pH and organic carbon content (oc) of the two soil samples from the transect that were used in batch and column experiments.

	I Sample no. 115 0.005 M CaCl_2	II Sample no. 35 0.01 M CaCl_2	III Sample no. 115 0.01 M CaCl_2
n	0.69	0.75	0.77
k ($\text{mg}^{1-n} \text{L}^n \text{kg}^{-1}$)	63.7	49.0	24.0
r^2	0.993	0.997	0.996
k^* ($\text{mg}^{1-n} \text{L}^n \text{kg}^{-1}$)	0.051	0.026	0.024
pH	5.4	5.6	5.2
oc ($\text{g g}^{-1} \%$)	2.5	3.0	2.5

The observed difference in k , k^* and n for soil sample no. 115 when another electrolyte concentration is used (adsorption experiments I and III; Table 1 and Fig. 1b), can be attributed to differences in ionic strength and in calcium and chloride concentrations. This induces differences in the Cd^{2+} -activity in the soil solution on the one hand, and may cause alteration of the surface charge/potential of the adsorbent on the other hand, causing a shift in the Cd sorption equilibrium. The lower electrolyte concentration in sorption experiment I is also responsible for the higher pH in this experiment as compared with sorption experiment III (Table 1). Because competition for sorption sites between H^+ and Ca^{2+} is less in

0.005 M CaCl_2 as compared with 0.01 M CaCl_2 , less protons reside in the solution phase, which implies a higher pH. When k and n are derived using different experimental conditions, these results show that they are not interchangeable.

In Fig. 1b the fitted adsorption isotherm for Cd in the 0.01 M CaCl_2 electrolyte solution stems from the sorption data in the low concentration range only (adsorption experiment III; 0-0.2 mg L^{-1} , Fig. 1a), while the points are measurements in the high concentration range (adsorption experiment IV; 3-7 mg L^{-1}). Cd sorption is described well in the high concentration range using sorption parameters that are derived from adsorption data in the low concentration range. Thus, the Freundlich sorption isotherm gives a good description of the sorption process in the whole range of Cd concentrations.

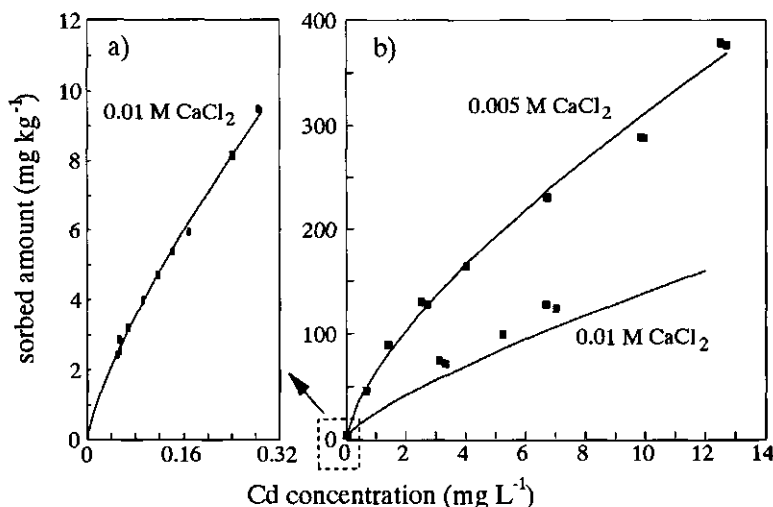


Fig. 1. Measured (points) and fitted (lines) adsorption isotherms for soil sample no. 115: (a) Using 0.01 M CaCl_2 as electrolyte in the low Cd concentration range, (b) Using two electrolyte concentrations in the high Cd concentration range. For 0.01 M CaCl_2 the fitted line is the same as in (a).

Although the sorption model (Eq. (1)) was fitted well to the sorption data, the model cannot be regarded as validated. For validation purposes we predicted Cd breakthrough, i.e. used the model for a quite different dynamic regime. The values of k and n obtained with the 0.005 M CaCl_2 -electrolyte were used for simulation of column scale transport of Cd, because these values correspond with experimental conditions. Fig. 2 shows the measured and simulated breakthrough curves of Cd. At the Cd concentration of 2 mg L^{-1} the model describes

measured breakthrough very well regarding the moment of first breakthrough as well as 50% breakthrough ($c/c_0=0.5$). Breakthrough of higher concentrations is described reasonably well. Breakthrough experiments using a 0.01 M CaCl_2 -electrolyte (not shown) yielded similar results.

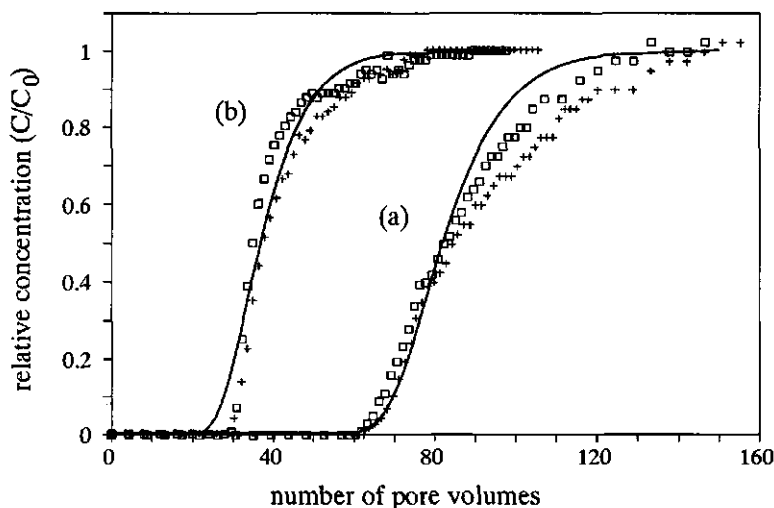


Fig. 2. Breakthrough curves of cadmium, measured in duplicate (symbols) and simulated (lines), for $c = 2 \text{ mg Cd L}^{-1}$ (a) and $c = 20 \text{ mg Cd L}^{-1}$ (b).

The asymmetric shape and width of the breakthrough curves indicate that nonequilibrium conditions prevailed. This may be illustrated with the dual porosity concept. In the presence of an immobile liquid phase the flow velocity will be larger than without a stagnant water phase due to a smaller effective flow domain. This leads to early breakthrough. Diffusion of Cd into the stagnant phase, where it will be subject to adsorption, continuously removes Cd from the mobile region, resulting in a "tailing" of the breakthrough curve. This effect becomes more pronounced when the difference between the feed and the initial concentration is larger, as is visible in Fig. 2b, where a Cd concentration of 20 mg L^{-1} was applied. Simulation of Cd breakthrough at this concentration is also in agreement with measured breakthrough, which validates the assumption of Freundlich type sorption. Due to the relatively high flow velocity in the column, nonequilibrium may also be due to slow sorption kinetics.

The rate parameter k_r was fitted simultaneously to both breakthrough experiments, because there was no reason to expect any differences in sorption kinetics or accessibility of sorption sites between the columns. When k_r was fitted individually, the simulation almost perfectly (within experimental error) matched measured breakthrough.

The Freundlich sorption equation gave a good description of Cd sorption in batch experiments and yielded a good prediction of Cd transport for different concentrations in column experiments, when the effect of nonequilibrium conditions was accounted for. The scale of observation is now further expanded from the soil column scale towards the field scale. Because the scaled sorption model (Eq. (2)) yielded a constant value of k^* for two soil samples from the field, the ability of the scaled sorption model to describe and predict Cd behaviour in the whole field was examined.

Table 2. Mean, standard deviation, minimum, and maximum values of the field data.

Parameter	Mean	S.D.	Min	Max
Cd_T (mg kg ⁻¹)	3.7	0.8	2.2	5.6
Cd_s (mg kg ⁻¹)	0.45	0.10	0.16	0.73
oc (g g ⁻¹ %)	2.6	0.3	1.8	3.1
pH	5.7	0.3	5.1	6.5

Statistical information on the field data can be found in Table 2. With an average Cd content of 3.7 mg Cd kg⁻¹ soil in this field, the official Dutch reference value for Cd in soil (0.5 mg kg⁻¹ for this soil type; Ministry of Housing, Physical Planning, and Environment 1987) is exceeded. Not only Cd contents are variable, also pH, organic carbon content and Cd concentration in the soil solution showed distinct spatial variability. The correlation between Cd_T and the soil parameters pH and oc was 0.33 and 0.44 respectively. Cd_s did not correlate significantly with Cd_T . Therefore, total Cd contents do not give a proper indication of the Cd content in a mild salt solution, which is thought to reflect bioavailability and leachability of a solute (Brümmer *et al.* 1986). There was no prominent spatial relationship visible between the various measured space series (Fig. 3).

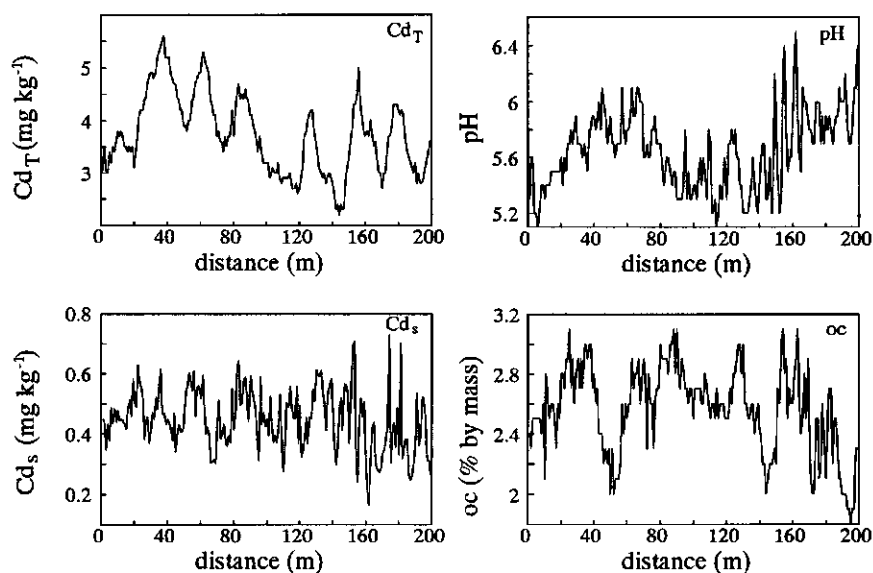


Fig. 3. Measured spatial pattern of Cd_T , Cd_s , pH and oc along the transect.

The scaled Freundlich parameters k^* and n obtained using 0.01 M $CaCl_2$ as a background electrolyte were used to predict Cd_T contents along the transect with Eq. (2), using measured values of pH, oc , and Cd_s for all 200 data points along the transect. The scaled sorption model predicts the spatial pattern of total soil Cd contents rather accurate along the main part of the transect (Fig. 4a), although the predicted pattern is much more erratic than the measured pattern. This is primarily induced by very erratic patterns of measured pH and Cd_s (Fig. 3). The correlation coefficient (r) between the measured and predicted points is 0.67. Figure 5 shows that values of Cd_T are in general overestimated. This suggests that k^* was biased, which is well possible since k^* was determined using two soil samples only. This may be too low a number for reliable prediction of k^* in this heterogeneous field.

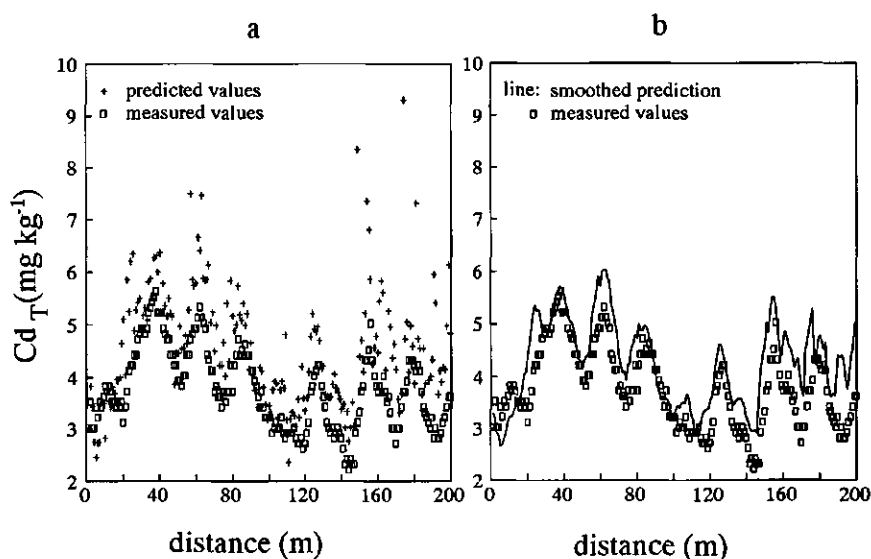


Fig. 4. Predicted and measured spatial pattern of cadmium contents along the transect, (a) predicted (crosses) and measured (squares) cadmium contents, (b) smoothed prediction (line) and measured (squares) cadmium contents.

Smoothing of the prediction using simple moving average with 2 points on either side of the target yields a spatial pattern that is very similar to the measured spatial pattern (Fig. 4b). Correlation between the measured points and the smoothed prediction ($r=0.82$) is much improved. Variation in pH, *oc*, and Cd_s explained 67% of the variation in total soil Cd contents after smoothing of the predicted spatial pattern. Apparently, Cd behaviour in the soil studied here is mainly regulated by pH and organic matter content. Deviations of the prediction from the measured spatial pattern may be induced by variability of other factors that influence Cd sorption, that are not included in the scaled sorption model. Regarding the fact that only spatial variability of Cd_s , pH and *oc* are accounted for, the prediction corresponds very well with the measured spatial pattern.

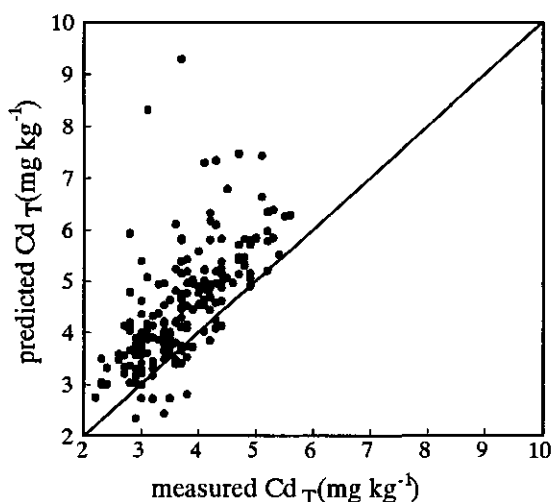


Fig. 5. Measured values of Cd_T vs. predicted values of Cd_T, using Eq. (2). The line shows where predicted Cd_T equals measured Cd_T.

Conclusions

Cadmium sorption in a sandy soil was described well with the Freundlich sorption equation. Parameter values for the sorption model that were fitted in the low concentration range described sorption in the high concentration range well. Different background electrolyte concentrations resulted in differences in sorption parameter values. Therefore, when batch derived parameter values are applied to transport experiments or to the field, they should be obtained using the same electrolyte concentration and composition. The scaled sorption model reflected effects of differences in pH and organic carbon content on Cd sorption in batch experiments. Parameter values for the model were consistent for different soil samples. The proposed transport model for one dimensional solute transport with Freundlich type sorption that accounts for nonequilibrium sorption predicted observed Cd transport in laboratory soil columns very well. Thus the Freundlich sorption equation is also appropriate for experimental conditions very different from the one used for Freundlich parameter fitting (batch experiments).

An arable soil was shown to be heterogeneous in pH, organic matter content, and Cd content in the horizontal plane. Extreme values may have a significant impact on the environmental effects of Cd pollution which are not recognized when only average values are accounted for. Although the spatial patterns of pH,

organic carbon content, total soil Cd content, and the Cd concentration in the soil solution are different from each other, prediction of total soil Cd contents along the transect with a scaled sorption model that accounts explicitly for effects of pH and organic carbon content is in good agreement with the measured spatial pattern. The scaled sorption model gave a good description of the Cd sorption process in batch experiments, as well as under flow conditions, as well as in the field. Apparently Cd behaviour in this soil is primarily regulated by sorption and pH and organic matter content are the main factors that govern Cd sorption in this soil. Because these soil parameters are spatially variable, soil chemical heterogeneity needs to be considered when the behaviour of Cd in the field is studied.

Chapter 4
**Spatial Patterns of Cadmium Contents Related to
Soil Heterogeneity**

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Spatial Patterns of Cadmium Contents Related to Soil Heterogeneity

Abstract

To investigate Cd behavior in a heterogeneous soil, soil samples were taken along a transect in a field. Total Cd content, Cd concentration in solution, and soil properties controlling Cd sorption were measured. The scale and degree of variability of these parameters were assessed using statistical and spectral analysis. No substantial correlation was found between total Cd and Cd in solution. However, with a scaled sorption model that accounts for effects of pH and organic matter content the variability of total Cd was predicted well as a function of measured concentrations and soil properties. Apparently, total Cd contents of this soil are primarily controlled by the organic matter content and pH.

Introduction

Heavy metal contamination of agricultural soils by atmospheric deposition or by disposal of waste (sewage sludge) constitutes a risk of either leaching of heavy metals which may reduce ground water quality, or excessive accumulation in the top soil. Heavy metal accumulation may induce harmful effects on terrestrial biota and may adversely affect the quality of agricultural products due to heavy metal uptake. Cadmium is probably the heavy metal of most environmental concern due to its high toxicity, relative high mobility in the terrestrial environment, and its occurrence in the human diet at the highest percentage of the Provisional Tolerable Weekly Intake (De Haan *et al.*, 1989).

The distribution of Cd between soil and solute is a key aspect in evaluating the environmental impact of Cd addition to land. Whereas total Cd contents are commonly used to indicate soil contamination, the Cd concentration in solution determines the actual environmental exposure. As soils consist of heterogeneous mixtures of different sorbates (clay minerals, oxides, organic matter), and a variety of soluble substances, the binding mechanisms for Cd in soils are manifold and vary with soil composition (Brümmer *et al.*, 1986).

Despite the complexity of possible reactions, several important soil factors controlling the distribution of Cd between soil and solutes have been identified. Among others, pH, the concentration of competing cations such as Ca or other heavy metals, and organic matter content significantly affect the sorption

equilibrium of Cd (Mahler *et al.*, 1980; Christensen, 1987; 1989b).

Information on the soil chemistry of Cd obtained from laboratory batch experiments can be used in solute transport models to estimate and predict behavior of Cd under flow conditions. Such models yield reasonable results for laboratory soil columns if the relevant processes and their interactions are accounted for (Jury *et al.*, 1986). However, the use of such models for prediction of Cd behavior in field situations is hampered by variability of both soil physical (Biggar and Nielsen, 1976) and soil chemical parameters (Van der Zee and Van Riemsdijk, 1987; Böttcher and Strebel, 1988). Spatial variability at the field scale may govern the actual fate of chemicals in the environment. Knowledge of the heterogeneity of Cd behavior in agricultural fields may contribute to proper risk assessment of soil contamination.

In this contribution the spatial pattern of Cd, pH and organic matter content along a transect in an arable field is analyzed. With a Cd sorption model that accounts for pH and organic matter effects explicitly, the spatial variability of total Cd is predicted and compared with measured Cd contents.

Sorption Model

The relationship between sorbed Cd (q , mg kg⁻¹) and the Cd concentration in soil solution (c , mg L⁻¹) can be described with the Freundlich sorption equation (Christensen, 1984; Chardon, 1984; Buchter *et al.*, 1989), given by

$$q = kc^n \quad (1)$$

where k and n are parameters. Whereas n was reasonably constant for 12 different soils and different experimental conditions, parameter k varied considerably (Chardon, 1984). However, variability of k could be drastically reduced by introducing soil pH and the Ca activity in soil solution into the sorption equation. For 63 different soils Christensen (1989b) found that besides pH also differences in organic matter content of the soil attributed to variability of k . For soils as considered here Cd sorption depends predominantly on pH and organic matter (De Haan *et al.*, 1987). A scaled sorption model for Cd was proposed by Van der Zee and Van Riemsdijk (1987) that accounts explicitly for effects of both pH and organic C content, oc (g g⁻¹ %) of the soil:

$$q = k^* oc(H^+)^{-0.5} c^n \quad (2)$$

in which (H^+) is the proton activity (mol L^{-1}). The scaled sorption parameter k^* now reflects the joint effects of all other factors that regulate Cd sorption. When variability of these other factors is small as compared to variability of pH and oc , k^* can be considered a field constant. Using data of pH, organic C content, and Cd concentration in soil solution, the scaled sorption model is used here to predict Cd contents of the soil.

Materials and Methods

Soil samples were taken in an arable field in a sandy soil in the 'Kempen' region in the southern part of the Netherlands. This area received large diffuse atmospheric deposition of zinc and cadmium due to emission by zinc ore smelters during the past century. At 1 m intervals 200 soil samples from 0 to 20 cm were taken with a sampling auger along a transect in the field. Samples were air dried, sieved through a 2 mm sieve, and analyzed for Cd content, pH, and organic matter content.

Cadmium was determined using two different procedures. Extraction with a 0.43 M HNO_3 -solution yielded the total reversibly sorbed Cd content, Cd_T (mg kg^{-1}), of the soil (Houba *et al.*, 1988). A measure of the Cd concentration in the soil solution was obtained by extraction of the soil with a 0.01 M CaCl_2 -solution (Houba *et al.*, 1988). Soil was shaken head over end for 24 hrs to ensure sorption equilibrium (Chardon, 1984; Christensen, 1984), at a soil solution ratio of 1:10. Immediately after shaking the pH of the suspension was determined with a glass-calomel electrode. The measured Cd concentration, c , was used to calculate the soluble Cd content of the soil, henceforth denoted as Cd_s (mg kg^{-1}). Organic matter content of the soil was measured as the organic C content, oc , and analyzed according to Kurmies (Houba *et al.*, 1988).

Parameter k^* of the scaled sorption model was determined in duplicate by fitting sorption data from batch experiments of two soil samples from the transect. These samples differ in organic C content and pH. Sorption isotherms were measured in a 0.01 M CaCl_2 -solution in a concentration range of 0 to 0.2 mg L^{-1} . This range is realistic for most contaminated sites (Christensen, 1984; De Haan *et al.*, 1987).

Statistical Analysis

The data were analyzed and interpreted using techniques from time series analysis. This requires second order stationary data, i.e. the expected value of the mean, m , and the variance, s^2 , along the transect are constant. In case of a significant linear trend of the mean this trend must be removed resulting in residuals with zero mean. In the absence of a trend, the mean value of the data was subtracted from each value in the data series.

For equally spaced data points the autocorrelation function expresses how the correlation between any two values of the sequence changes as a function of their separation interval or lag, h . The autocorrelation coefficient (r_h) is a normalized form of the autocovariance (cov_h), which is given by

$$cov_h = \frac{1}{N} \sum_{i=1}^{N-h} (y(x_i) - \bar{y})(y(x_{i+h}) - \bar{y}) \quad (3)$$

in which y is the value measured at position x , \bar{y} is the average value of y , and N is the number of observations (Davis, 1986). The autocovariance at lag zero, cov_0 , equals the variance of the data set. The autocorrelation coefficient is given by

$$r_h = \frac{cov_h}{cov_0} \quad (4)$$

The autocorrelation is calculated for lags not larger than $N/4$ to ensure a credible graph.

Spectral Analysis

In time series analysis it is assumed that a time or space series can be regarded as the sum of many sinusoidal waves, or harmonics, with different frequencies and amplitudes. The variance of the time series is then composed of the sum of the variances of the harmonics (Box and Jenkins, 1976). For a stationary time series that is continuous and sampled at discrete equally spaced points, the continuous power or variance spectrum may be calculated with the Fast Fourier Transform computer algorithm given by the software package STAT-GRAPHICS (Anonymous, 1985). Peaks in the variance spectrum indicate frequencies f (m^{-1}) or periods $p=1/f$ (m) of pronounced periodicities in the data series.

The variance spectrum is a Fourier transform of the autocorrelation function,

i.e. they are mathematically equivalent (Box and Jenkins, 1976). However, their representation of the data sheds light on different aspects of the data series. Therefore, both methods were applied here.

Results and Discussion

Statistical description of the data

Table 1. Mean (m), standard deviation (s), and standard deviation due to measurement errors (s_a) of the measured parameters along the transect

	Cd_T (mg kg ⁻¹)	Cd_s (mg kg ⁻¹)	pH	oc (g g ⁻¹ %)
m	3.7	0.45	5.7	2.6
s	0.8	0.10	0.3	0.3
s_a	0.08	0.04	0.04	0.08

Table 1 summarizes the statistics of Cd_T , Cd_s , pH and oc of the 200 soil samples. All values of Cd_T are much higher than the official Dutch reference value, which considers effects of organic matter and clay content explicitly (about 0.45 mg Cd kg⁻¹ soil, Ministry of Housing, Physical Planning and Environment, 1987). The pH indicates that the soil is slightly acidic. About 10% of the total Cd present was extractable with a 0.01 M CaCl₂-solution.

Table 2. Correlation matrix of the measured parameters

	Cd_T (mg kg ⁻¹)	Cd_s (mg kg ⁻¹)	pH	oc (g g ⁻¹ %)
Cd_T	1			
Cd_s	0.15*	1		
pH	0.33**	-0.59**	1	
oc	0.44**	0.10	-0.13	1

*: significance level of 0.05

**: significance level of 0.01

Observed variability of the four data series, expressed as the standard deviation, s , is much larger than the standard deviation due to measurement errors, s_a (Table 1). Thus, the observed variability of the four data series truly exists in the field.

Correlation may give an indication of similarity between the four soil parameters. Table 2 shows that pH and oc correlate positively with Cd_T at a significance level of 0.01. This suggests a functional relationship between pH and oc, and the total Cd content along the transect. The soluble Cd content of the soil, Cd_s , is only slightly correlated with Cd_T at a significance level of 0.05. Thus, total Cd content and soluble Cd content are not directly related. The pH correlates well with Cd_s , suggesting that the Cd concentration in the soil solution is to a large extent regulated by the proton activity.

Besides correlation based on 200 individual soil samples, also the spatial arrangement of the four parameters can give an indication of the analogy between the data series. On sight (Figure 1) there seems to be little resemblance between Cd_T , Cd_s , pH and oc. Methods from time series analysis may reveal underlying similarities between the measured parameters.

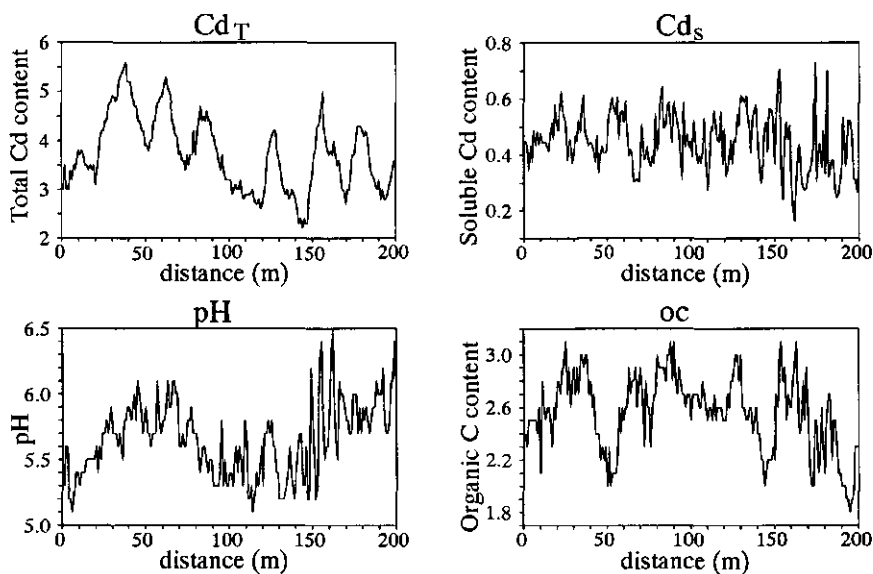


Fig. 1. The spatial pattern of total Cd content, Cd_T (mg kg^{-1}), soluble Cd content, Cd_s (mg kg^{-1}), pH, and organic C content, oc ($\text{g g}^{-1} \%$) along the transect in an arable field.

Autocorrelation

Before the data were used in time series analysis, stationarity of the data series was examined. Total Cd content, soluble Cd content, and *oc* showed a significant linear trend. This trend was removed from the data. No significant trend was detected in the data series of pH, therefore the mean value was subtracted from the data. The residuals were used in further analysis.

Figure 2 shows the value of the autocorrelation function for lags up to 50 m. The autocorrelation function of Cd_T shows a peak at $h = 25$ m, suggesting periodicity of total Cd contents with a frequency of 0.04 m^{-1} . Cd_s does not correlate with itself beyond the first few lags. This suggests randomness of the data series of the soluble Cd content. The autocorrelation function of pH indicates no pronounced periodicity. The organic C content shows a slowly descending autocorrelation with small peaks at every 6 to 7 lag distances. This may reflect periodicity of the data series of *oc* with frequencies of 0.14 to 0.17 m^{-1} .

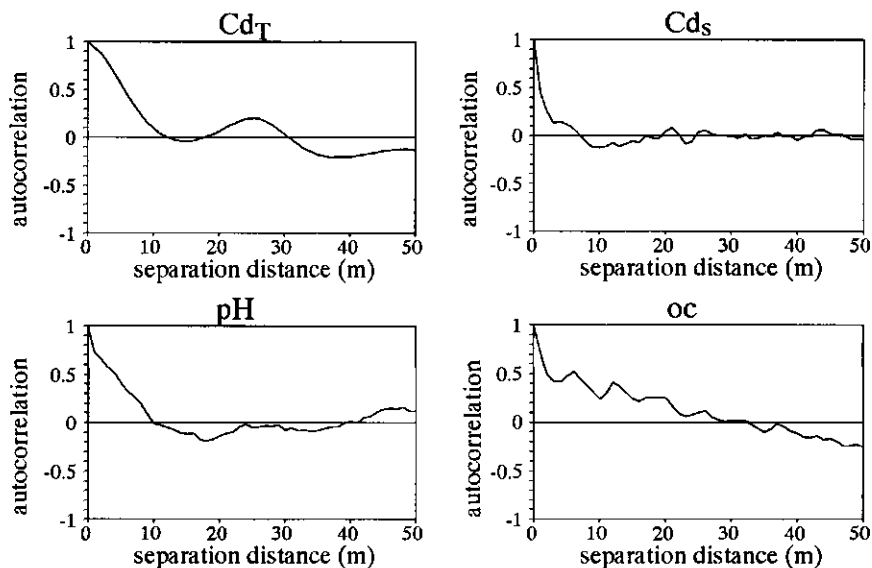


Fig. 2. The autocorrelation of total Cd content, Cd_T (mg kg^{-1}), soluble Cd content, Cd_s (mg kg^{-1}), pH, and organic C content, *oc* ($\text{g g}^{-1} \%$) as a function of the separation distance or lag, h (m).

Variance spectra

The variance spectra of the four soil parameters are shown in Figure 3. Total Cd content shows a peak at $f = 0.038 \text{ m}^{-1}$, which was already suggested by the autocorrelation function. The variance of the spectrum of Cd_s is never larger than 6.5% of the total variance, the signal appears to be erratic. This again implies randomness of the sequence, suggesting that the value of Cd_s is generated by a truly probabilistic process. The spectrum of oc contains peaks at $f = 0.015, 0.035, 0.08$, and 0.135 m^{-1} , of which only $f = 0.135 \text{ m}^{-1}$ ($p = 7.5 \text{ m}$) was suggested by the autocorrelation function. For pH no important periodicity can be observed, although at frequencies of $f = 0.025$ and 0.15 m^{-1} small peaks are visible.

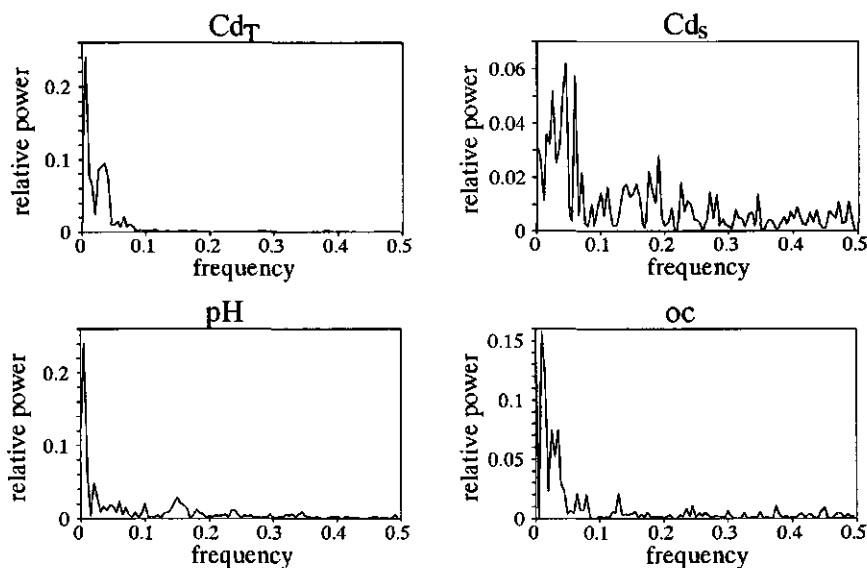


Fig. 3. The power spectrum of total Cd content, Cd_T (mg kg^{-1}), soluble Cd content, Cd_s (mg kg^{-1}), pH, and organic C content, oc ($\text{g g}^{-1} \%$).

The variance spectrum of oc resembles that of Cd_T at the low frequencies. Long term fluctuations of Cd_T thus correspond with long term fluctuations of oc . The variance spectrum of pH shows little similarity with Cd_T .

Bands of high frequency may be explained by fertilization methods or other agricultural management practices used by the farmer, which usually have a distinct width that imposes variability in the field along e.g. sowing direction (Böttcher and Strebel, 1988). The pH and oc show peaks at frequency bands

corresponding with periods that may be caused by field management. However, the larger scale variability at periods exceeding ca. 15 m can only be explained by other factors that are as yet unknown.

Prediction of cadmium contents

The scaled sorption model was fitted to the adsorption data of the two soil samples from the transect, and the results are summarized in Table 3. Whereas the value of k is rather different for the two soils, correction of k with pH and oc yields equivalent values of k^* for both soils. The value of n is similar in both cases, supporting findings of Chardon (1984). This indicates that the scaled sorption model gives a good description of the influence of pH and oc on Cd sorption in this soil.

Table 3. Fitted Freundlich parameters of the sorption isotherm, measured for two different soil samples along the transect

		soil 1	soil 2
Cd_T	(mg kg ⁻¹)	5.3	2.8
pH	-	5.6	5.2
oc	(g g ⁻¹ %)	3.0	2.5
k	(mg ¹⁻ⁿ L ⁿ kg ⁻¹)	49.0	24.0
n	-	0.75	0.77
k^*	(mg ¹⁻ⁿ L ⁿ kg ⁻¹)	0.026	0.024

Equation (2) was used to predict Cd sorption along the transect, using measured values of c , pH and oc , and the average k^* and n from the two sorption isotherms. Figure 4 shows the predicted Cd content Cd_p , together with the measured Cd content, Cd_T . The signals show a distinct similarity along the longest part of the transect. Comparison of the variance spectrum of Cd_p (Figure 5) with the spectrum of Cd_T shows that for low frequency bands the signals are comparable. Both signals show peaks at periods of 100 m and at bands from 22 to 33 m. The predicted signal contains some additional peaks at higher frequencies, comparable with the spectrum of pH, which are not present in the spectrum of Cd_T . This suggests that short range fluctuations in the predicted signal are

attributable to short range fluctuations in pH, that are not passed through to Cd_T in reality. There seems to be a stabilizing factor present, that prevents short range fluctuations of pH and oc to be transmitted to Cd_T .

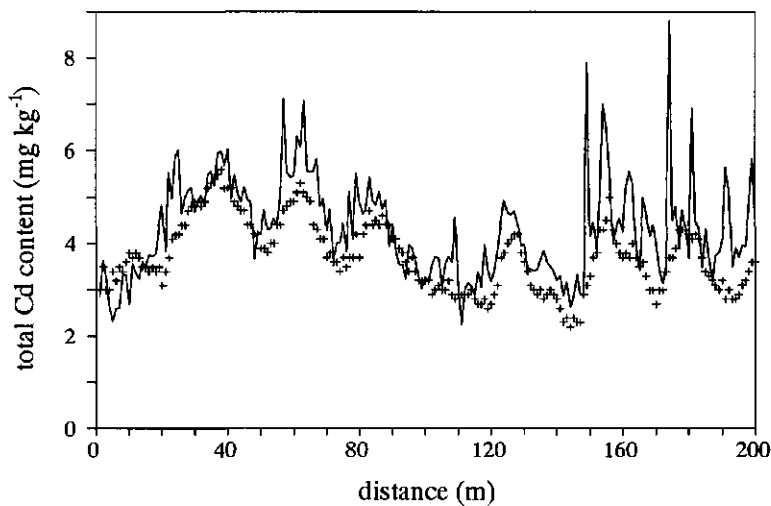


Fig. 4. Measured (points) and predicted (line) Cd contents of a field soil along a transect.

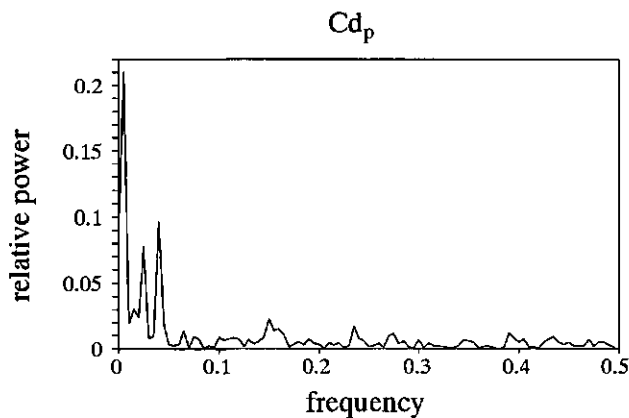


Fig. 5. Power spectrum of the predicted total Cd content, Cd_p ($mg\ kg^{-1}$).

Apparently, pH and organic C content are the main factors that regulate Cd sorption in this soil. Therefore, variability of pH and *oc* is the main factor that invokes variability of the total Cd content. The deviations of the prediction from the measured pattern may be induced by other factors that affect Cd sorption that are not included in the scaled sorption model.

Conclusions

An arable field has been shown to be heterogeneous in soil chemical parameters. The Cd content of this soil is correlated with pH and organic matter content, indicating a functional relationship between total Cd and soil chemical parameters. However, the spatial pattern of pH and organic matter contents along a transect differ considerably from the spatial pattern of total Cd content. Nevertheless, the scaled sorption model showed a remarkable good prediction of Cd contents in this soil.

It follows from the data that Cd_T poorly estimates Cd_s . This latter quantity is thought to indicate leaching potential as well as plant uptake potential. Usually only data on total heavy metal contents are present in soil contamination studies. Also information on the acidity and the organic matter content of the soil are of importance in judging the environmental impact of elevated Cd contents in agricultural soils.

Chapter 5
**Significance of Soil Chemical Heterogeneity for
Spatial Behavior of Cadmium in Field Soils**

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Significance of Soil Chemical Heterogeneity for Spatial Behavior of Cadmium in Field Soils

Abstract

To investigate the spatial behavior of Cd in an arable field and to analyze its dependency on pH and organic carbon content (*oc*), soil was sampled on a 0.5-ha field and analyzed for HNO₃-extractable cadmium and zinc contents (Cd_T and Zn_T respectively), soluble cadmium and zinc contents (Cd_s and Zn_s respectively), pH and *oc*. All parameters were spatially variable and anisotropic. Within the sampled area the measurements became independent of each other for *oc*, for Cd_T and Zn_T in the east-west direction, and for Cd_s in the north-south direction at distances of 5 to 20 m. For the other variables and directions, no range was observed. Similarity between anisotropy of HNO₃-extractable heavy metal contents and *oc*, as well as between soluble contents and pH, suggested a functional (spatial) relationship between these parameters. Because the field was anisotropic, the spatial structure of the parameters was different from the spatial structure obtained from transect analysis in the same field. Correlation between cadmium and zinc contents was high, both in soluble and in HNO₃-extractable form. No correlation was observed between HNO₃-extractable and soluble heavy metal contents. Soluble Cd and Zn were highly correlated with pH. A significant correlation was found between Cd_T and Zn_T, and pH, and between HNO₃-extractable contents and *oc*. Using a scaled sorption model, variability of pH and *oc* was explicitly accounted for when calculating Cd_s from HNO₃-extractable Cd contents. Predicted Cd concentrations in the soil solution correlated well ($r=0.87$) with measured Cd concentrations, whereas prediction when homogeneity of the sorption parameters is assumed yielded no significant correlation. Apparently, pH and organic matter content are the most important soil parameters that regulate Cd sorption in this soil.

Introduction

Major issues in environmental risk assessment of soil pollution are groundwater quality and yield and composition of crops. Leaching and plant uptake of a contaminant are highly dependent on the concentration of the contaminant in the soil liquid phase. This is the phase that can be transported to lower soil layers and from which plant roots extract water and nutrients. The concentration of a pollutant in the soil solution is therefore a better indicator of potentially adverse effects than its total content in the soil (De Haan *et al.*, 1987). This concentration in the soil solution is not only dependent on the total content, but also on soil chemical and mineralogical properties. Because this contribution focuses on Cd and Zn behavior at low concentrations in a soil of moderately low pH, only

sorption processes will be considered.

Besides soil chemistry, soil heterogeneity must be considered for field scale situations, because the concept of a homogeneous porous medium is not sufficient to describe actual behavior of water and solutes in the field (Brusseau and Rao, 1990). Due to spatial variability of soil parameters, different parameter values will be found for soil samples taken at different locations in a field. The effect of soil heterogeneity on solute behavior can be analyzed using simulation models that describe the relevant soil physical and soil chemical processes. Soil heterogeneity may be included using stochastic theory. When the field is considered as an ensemble of vertical homogeneous soil columns that differ only with respect to the soil parameter that is spatially variable, statistical homogeneity with random variability is assumed. By assigning a continuous probability distribution to this parameter, Monte Carlo simulation can be used to calculate the statistical properties of the model results (Van der Zee, 1988). More localized heterogeneity is considered by recognizing macropores and other preferential flow paths (White, 1985). Macropores may cause rapid infiltration and redistribution of water and solutes. Spatial variability of soil physical parameters has a pronounced effect on water and nonreactive solute transport (Bresler and Dagan, 1981, 1983; Amoozegar-Fard *et al.*, 1982). The coefficient of variation (CV) of the pore water velocity may be as large as 100% (Biggar and Nielsen, 1976). Field averaged concentration profiles in a heterogeneous soil are often different from the concentration profile calculated using the convection-dispersion equation with constant coefficients.

Although the impact of variability in soil physical parameters is important for the behavior of chemicals in soils, these reports are mainly dealing with (assumed) nonreactive contaminants. However, most contaminants are reactive as they interact with the soil solid phase and with other components in the soil solution. For phosphate and heavy metals spatial variability of the retention capacity may have an equally profound effect on field-averaged transport in soil as spatial variability of soil physical parameters (Van der Zee, 1988). Cadmium behavior is affected to the same extent by spatial variability of pH as by spatial variability of the pore water velocity (Boekhold and Van der Zee, 1991). Therefore, next to heterogeneity of soil physical properties, heterogeneity of soil chemical properties can be important for field scale behavior of most contaminants.

Field scale variability of soil physical parameters results in larger dispersivities (Butters and Jury, 1989). To adequately assess these larger dispersivities, the soil system studied should at least encompass the scale of variability of the

field (Schulin *et al.*, 1987). Therefore, the field scale variance can only be monitored completely when a sufficiently large site is sampled. Information with regard to the scale of sampling is needed to adequately estimate field scale variation of soil chemical parameters as they may differ from the scale relevant for flow. Information with regard to the scale of variability of the soil parameters can be obtained using geostatistical analysis. With the use of semivariograms the validity of the assumption of statistical homogeneity with random variability of the soil parameters, which is often used when soil heterogeneity is modelled, can be verified.

In this contribution field data of Cd and Zn contents, pH and organic carbon contents were analyzed to determine the magnitude of variability that can be expected for soil chemical parameters. The spatial structure was evaluated using geostatistical methods, in view of the commonly assumed stationarity of soil parameters when soil transport processes are modelled. The effect of variable soil chemical status on the Cd concentration in the soil solution was shown using a scaled sorption model.

Sorption Theory

Adsorption of cadmium at low concentrations that are environmentally relevant can be well described with the Freundlich adsorption isotherm (Christensen, 1984, Chardon, 1984):

$$q = kc^n \quad (1)$$

where q is the adsorbed amount of Cd (mg kg^{-1}), c is the Cd concentration in the soil solution (mg L^{-1}), and k and n are the Freundlich parameters. The sorption capacity of a soil is highly dependent on its chemical properties, especially pH (Christensen, 1989b, García-Miragaya and Page, 1978). The distribution coefficient, expressing the ratio of sorbed Cd to dissolved Cd at equilibrium, approximately doubled for each 0.5 unit increase in pH. Organic matter is known to adsorb considerable amounts of inorganic cations (Adriano, 1986), and is therefore a soil constituent that is important for cadmium sorption. Also the type of exchangeable cations present is an important factor that determines Cd sorption (García-Miragaya and Page, 1977). Other heavy metals and calcium have been found to compete with Cd for sorption sites (Chardon, 1984, Christensen, 1984, 1987).

The free divalent Cd ion is the most important species that interacts with the

soil solid phase. Cd present as stable complexes does not sorb onto soil nor dissociates when free or more weakly bound Cd is sorbed onto the soil (Neal and Sposito, 1986; Christensen, 1989a). Therefore, the presence of complexing agents influences the sorption equilibrium. Besides dissolved organic matter, Cl can form complexes with Cd. Chardon (1984) found that for different soil conditions and soil types the value of k varied by orders of magnitude, but that the value of n had a much smaller variation, and can be considered a constant for a particular soil type. Van der Zee and Van Riemsdijk (1987) derived a Cd sorption model that accounts explicitly for the effect of pH and organic matter content, expressed as the organic carbon content, on the sorption equilibrium:

$$q = k^* oc (H^+)^{-0.5} c^n \quad (2)$$

where H^+ is the proton activity in the soil solution (mol L^{-1}), and oc is the organic carbon content (g kg^{-1}). The scaled sorption parameter k^* now contains information of all other factors that regulate Cd sorption not explicitly accounted for in Eq. (2). When variability of these other parameters is small as compared with the spatial variability of pH and oc , k^* may be considered a field constant. The scaled sorption model, Eq. (2), is applied to the field data in order to check its validity and to quantify the influence of differences in oc and pH on field scale sorption of Cd.

Materials and Methods

Field sampling

The sampled field is located in the Kempen area in the south of the Netherlands and the north of Belgium. This area received large amounts of cadmium and zinc due to atmospheric deposition after emission of these heavy metals by zinc ore smelters during the past century. Soil is a Typic Haplaquod, a sandy soil with a humic upper layer of 0.25 to 0.30 m. At the time of sampling the groundwater level was at 1 m depth. The sampled field has been under cultivation for approximately 50 years.

Using a sampling grid of size 17×8 with 6 m node distance, with every point located at least 50 m away from the parcel boundaries, 136 soil samples were taken. Additionally, another 30 samples were randomly taken with a distance of 2 m from the nearest grid node, to analyse spatial variability on a scale < 6 m. Thus, a total of 166 soil samples were taken in approximately 0.5 ha.

All samples were mixed samples, composed of six individual auger samples from 0 to 0.20 m depth, which were taken regularly from a triangularly shaped mould with sides 0.5 m. In this way, average values were obtained for an area of 0.1 m². To obtain information on variability on the scale of the mould individual auger samples were collected separately at five locations. All samples were air dried and sieved to remove aggregates larger than 2 mm before chemical analysis.

Chemical analysis

Total extractable cadmium (Cd_T) and zinc (Zn_T) contents of the soil (mg kg⁻¹) were determined using nitric acid as an extractant. This method was preferred to a destruction of the soil, assuming that the quantity measured in nitric acid reflects the amount of cadmium that can potentially desorb (Houba *et al.*, 1988). Comparison with total contents measured after destruction of the soil indicated that more than 95% of the total content was extractable with HNO₃. All cadmium that does not dissolve in nitric acid is thought to be of negligible importance in the adsorption process. Five grams of soil were equilibrated with 50 mL 0.43 M HNO₃ solution for 2 h in an end-over-end shaker. After filtration the liquid phase was analyzed for Cd and Zn concentrations using flame atomic absorption spectroscopy (Instrumental Laboratory AA/AE spectrophotometer S11 with Smith Hieftje background correction). An air-acetylene flame was used at a wavelength of 228.8 nm for Cd and 213.9 nm for Zn.

In addition to the HNO₃-extraction, soil was extracted with 0.01 M CaCl₂. Cadmium concentrations after extraction with CaCl₂ reflected the soil-dependent differences in availability of Cd and Zn in pot experiments with different plant species, while methods using stronger extractants (stepwise acidification with HNO₃, extraction with NH₄Ac+EDTA) did not or were not satisfactory (Sauerbeck and Styperek, 1985). The amount of Cd and Zn extracted with 0.01 M CaCl₂ is thought to represent the soluble heavy metal content. To 3.5 g of soil, 35 mL CaCl₂ solution was added and shaken end-over-end for 20 h. The pH of the suspension was measured with a glass-calomel electrode. After centrifugation at 1000 × g Cd and Zn concentrations in the supernatant were determined with flame atomic absorption spectroscopy using scale expansion. The detection limit was ≈ 8 µg L⁻¹.

Organic-matter content of the soil was determined as the organically bound C content (oc) by oxidation of the organic matter with K₂Cr₂O₇ in a strong H₂SO₄ medium (Houba *et al.*, 1988).

For two soil samples that differed in pH and organic matter content, adsorption isotherms were determined using 0.01 M CaCl_2 as the background electrolyte. A Cd-concentration range of 0 to 0.3 mg L^{-1} was chosen, because these relatively low Cd concentrations are significant in the sampled field. Procedures were the same as for CaCl_2 -extraction of soil described above.

Geostatistical analysis

The spatial structure of the soil parameters can be analyzed by considering these parameters as regionalized variables (Matheron, 1971). Regionalized variables are spatially continuous, but the changes in these variables are too complex to describe with any practical deterministic function (Davis, 1986). Assuming statistical homogeneity of the data, the rate of change of a regionalized variable along a specific direction is given by the semivariance. Semivariance analysis requires that the intrinsic hypothesis holds for the data, that is that the mean and variance of increments ($z(x_i) - z(x_i + \mathbf{h})$) are stationary (Journel and Huijbregts, 1978). The semivariance is a measure of the degree of spatial dependence between samples:

$$\gamma(\mathbf{h}) = \sum_{i=1}^{N(\mathbf{h})} \frac{[z(x_i) - z(x_i + \mathbf{h})]^2}{2N(\mathbf{h})} \quad (3)$$

where $\gamma(\mathbf{h})$ is the semivariance and $N(\mathbf{h})$ is the number of data pairs $z(x_i)$, $z(x_i + \mathbf{h})$ separated by a distance vector \mathbf{h} . The semivariogram is thus estimated by averaging a series of parallel univariate slices (Philip and Watson, 1986). It is therefore a global method that does not reflect local deviations from the field average. As a rule of thumb at least 30 data pairs should be used to calculate $\gamma(\mathbf{h})$, and \mathbf{h} must be smaller or equal to half the maximum sampling distance (Journel and Huijbregts, 1978).

When the semivariance is calculated for different values of \mathbf{h} , the results can be plotted in a semivariogram, which is related for the one dimensional case to a correlogram by

$$\gamma(\mathbf{h}) = \sigma^2 \{1 - \rho(\mathbf{h})\} \quad (4)$$

where σ^2 is the variance and $\rho(\mathbf{h})$ the autocorrelation at lag \mathbf{h} . The autocorrelation is dependent on the variance, which must be finite. The semivariance is free of this restriction, and therefore preferred (Burgess and Webster, 1980). Since \mathbf{h} is a vector, the semivariogram depends both on the magnitude and the direction of \mathbf{h} . A regionalized variable is isotropic when the semivariance is independent of the direction of \mathbf{h} . When semivariograms calculated for different directions are

different, the parameter is anisotropic.

When the distance between sample points is zero, the value at each point is being compared with itself, and the semivariance for $\gamma(0)$ is zero. Sometimes non-zero values are obtained at $h=0$, this value is called the *nugget*. The presence of a nugget may indicate variability at separation distances smaller than the sampling distance and/or measurement errors. As the distance Δh is increased, the points being compared are less and less closely related to each other, resulting in larger values of $\gamma(h)$. When at some distance the points being compared are so far apart that they are not related to each other, the semivariance reaches a constant value. The semivariogram no longer increases, and a flat region develops, called the *sill*. The corresponding lag distance is called the *range*. The range gives an indication of the distance at which the parameter values become independent of each other. When the sampled area is smaller than the scale of variability of that parameter, the semivariogram does not reach a sill. When the semivariogram is independent of the separation distance between sampling points, the variable is truly random and does not exhibit a spatial structure.

Calculation of the semivariance for several lag distances yields a graph with a number of points (see, e.g., Figs. 1a-1f). Several models have been proposed to describe the relationship between the lag distance h and the semivariance continuously, e.g. linear, spherical, or exponential models (Davis, 1986). These models can be fitted to the calculated data points. A continuous description of the semivariogram is necessary when the technique of kriging is applied. With kriging, values of a variable at a certain point in space are estimated from known values in its neighborhood. The semivariogram provides the relative weight that can be assigned to a known value in estimating the value of the location of interest.

The use of model parameter values for nugget, sill, and range suggests that the fitted line gives a better estimation of the semivariance than the individual calculated points. But semivariograms do not describe intrinsic properties of the parameter in the field, it is a technique to represent the data which reveals differences in spatial structure between parameters and between different directions in the field. There is no a priori evidence that a proper identification of existing dependencies of neighboring points in space is given by a smooth curve. Furthermore, there is no a priori evidence that one model is more appropriate than another, each choice is more or less arbitrary. The fitting accuracy as may be quantified by the least sum of squares depends on the lag classes used and is therefore arbitrary as well. Models thus do not give more accurate or reliable values of nugget, sill, and range than a direct estimate from the experimental

semivariogram can give. Therefore, we preferred to estimate semivariogram characteristics directly from the experimental semivariogram.

Philip and Watson (1986) recognized the contradiction that with semivariogram analysis the spatial dependence of observations is calculated under the assumption of stationarity, which implies that the data are independent realizations of a random function. Moreover, if a theoretical function for the semivariogram is defined initially, and a simulated data set is generated, then the experimental semivariogram derived therefrom can be markedly different from the known parent function (Brooker, 1983). Although Philip and Watson (1986) concluded that the theory of regionalized variables has nothing to do with a scientific theory, calculation of the semivariance for different lag distances does provide information on the (field averaged) correlation length of that parameter, and directional semivariograms may indicate anisotropy of the data set. When the data are spatially dependent, the variance of the data set underestimates the field scale variance of the parameter. Semivariogram analysis may indicate the variance of independent measurements, which is important for stochastic modelling. Semivariogram analysis can be used to verify the assumptions of many transport models for solutes at the field scale, and therefore the applicability of these kind of models in real systems.

Results and Discussion

By calculating the mean and standard deviation of the field, it was assumed that the data are independent observations in a statistically homogeneous field with random, normally distributed variability. The standard deviation due to measurement errors (s_d) was calculated as the mean standard deviation of duplicate measurements. Table 1 summarizes the statistics for the 166 soil samples.

HNO₃-extractable heavy metal contents varied between 2.1 and 6.3 mg Cd kg⁻¹ and 121 and 315 mg Zn kg⁻¹. These values exceed the Dutch quality standards for cadmium and zinc which can be approximated as 0.5 mg Cd kg⁻¹ and 60 mg Zn kg⁻¹ for this soil type (Ministry of Housing, Physical Planning and Environment, 1987). Approximately 10% of the HNO₃-extractable heavy metal contents were extractable with 0.01 M CaCl₂. The average pH indicated that the soil is slightly acidic, and with an *oc* of 25 g kg⁻¹ the soil is moderately humose. All parameters are spatially variable, although 47% of the variability in *oc* and 32% of the variability in Cd_e is explained by measurement errors. Nevertheless,

the major part of the variability can be attributed to soil heterogeneity. It should be noted that pH is a logarithmic value of the proton activity in solution. Therefore, the variation in proton activity in the soil solution is much higher than the relatively low CV of pH suggests.

Table 1. Mean (\bar{x}), standard deviation (s), variance (s^2), coefficient of variation (CV), the proportion of the measurement error to the standard deviation ($s_d/s*100\%$), and minimum and maximum values of pH, organic carbon (oc), total extractable Cd (Cd_T) and Zn (Zn_T), and soluble Cd (Cd_s) and Zn (Zn_s). $N=166$.

	pH	oc g kg ⁻¹	Cd_T mg kg ⁻¹	Cd_s mg kg ⁻¹	Zn_T mg kg ⁻¹	Zn_s mg kg ⁻¹
\bar{x}	5.87	25.1	4.01	0.38	209	21
s	0.32	2.8	0.83	0.12	38	9.0
s^2	0.10	0.8	0.67	0.02	1465	80.8
CV	0.05	0.11	0.20	0.33	0.18	0.43
$s_d/s*100\%$	7	47	11	32	14	13
minimum	5.17	16.7	2.05	0.07	121	2.7
maximum	6.74	32.7	6.27	0.87	315	45.9

Normal and lognormal distributions were fitted to the frequency distribution of each parameter, because these types of frequency distributions are often assumed in stochastic modelling (Van der Zee, 1988). Table 2 summarizes the level of significance using the Kolmogorov-Smirnov test statistic (Press *et al.*, 1986). For Cd_s and in a lesser sense for Zn_T the data are not different from a normal distribution when a high degree of uncertainty (0.15-0.25) is permitted. The level of significance of all other fits was rather low, indicating that neither the normal nor the lognormal frequency distribution adequately described the frequency distribution of the measurements. However, when a distribution is needed for modelling purposes, a lognormal distribution is preferred over a normal distribution, because they are similar when the CV is relatively low. Moreover, a normal distribution may yield negative values, which is physically impossible (Van der Zee, 1988).

Table 2. Level of significance using the Kolmogorov-Smirnov test statistic for the six soil parameters when fitted to a normal or a lognormal frequency distribution.

Soil parameter	Level of significance	
	Normal distribution	Lognormal distribution
pH	0.20	0.30
<i>oc</i>	0.46	0.13
Cd _T	0.57	0.36
Cd _s	0.85	0.05
Zn _T	0.75	0.23
Zn _s	0.41	0.004

Before the data were used for geostatistical analysis they were normalized; that is, they were scaled such that the mean value equals zero and the standard deviation is one. Using normalized values, the structure of the different parameters can be compared independent of their absolute values. Figs. 1a to 1f give the semivariograms for the six soil parameters for the North-South (N-S) and the East-West (E-W) direction. When the field is isotropic with respect to a soil parameter, these two semivariograms coincide. The first point is calculated using only 30 data pairs, all others used between 70 to a maximum of 447 data pairs.

The semivariogram of pH (Fig. 1a) indicates that a nugget effect exists, which is supported by the variance measured within one mixed sample (Table 3). No sill is apparent in the N-S direction, and, therefore, no range. In the E-W direction a range of approximately 5 to 10 m can be seen, at a sill of around 60% of the total variance of the data set. Soil acidity is a structured parameter, samples close together are more alike than samples at larger distances, but samples within 0.1 m² are already variable at a level of approximately one fifth of the total variance within the sampled area. The semivariance in the N-S direction is lower than in the E-W direction when $h < 15$ m. So, the field is anisotropic for pH, observations in the N-S direction are more alike than in the E-W direction at equal separation distances.

The semivariogram of *oc* (Fig. 1b) looks quite different from that of pH. Although a sill is reached at a range between 5 to 10 m in the E-W direction, as with pH, for the N-S direction the range is ≈ 20 m, and the corresponding sill is considerable higher than in the E-W direction. The data become independent of

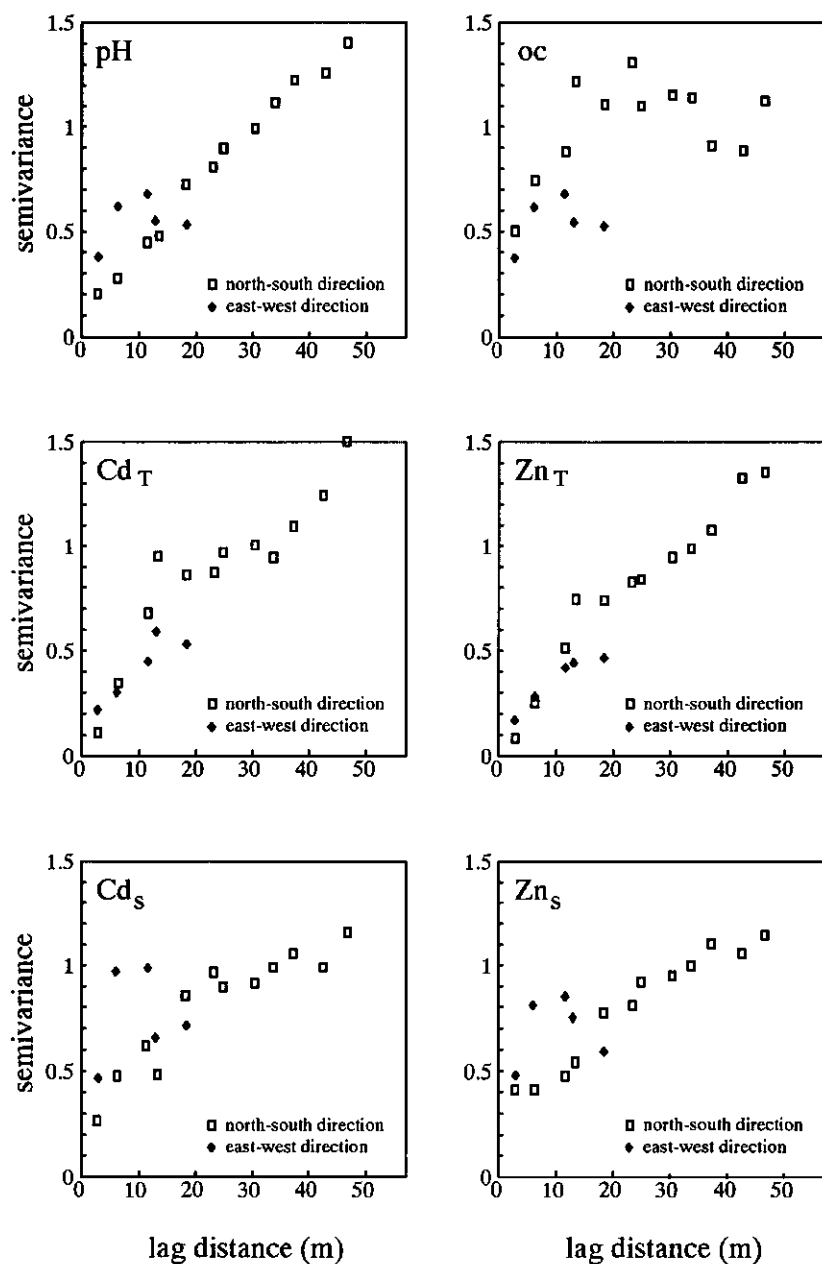


Fig. 1. Directional semivariograms for scaled values of pH, organic carbon, *oc*, total extractable Cd (Cd_T), total extractable Zn (Zn_T), soluble Cd (Cd_s), and soluble Zn (Zn_s).

each other at a sampling distance of 5 to 10 m for the E-W direction, and a distance of 20 m for the N-S direction. Supported by the variance measured within a mixed sample (Table 3), the nugget effect is large; samples within 0.1 m² show already a variation of one third of the total variation within the sampled area. The field is anisotropic with respect to *oc*, since observations in the E-W direction are more alike than in the N-S direction. This is in contrast with the directional effect observed for pH.

Table 3. Standardized variance (relative to the mean and variance within one mixed sample) of pH, organic carbon (*oc*), total extractable Cd (*Cd_T*) and Zn (*Zn_T*), and soluble Cd (*Cd_s*) and Zn (*Zn_s*) within one mixed sample for the five locations where the individual auger samples were analyzed.

Sample no.	pH	<i>oc</i>	<i>Cd_T</i>	<i>Cd_s</i>	<i>Zn_T</i>	<i>Zn_s</i>
10	0.31	0.21	0.03	0.34	0.04	0.36
45	0.51	0.20	0.06	0.71	0.02	0.54
70	0.20	0.54	0.01	0.11	0.01	0.07
95	2.16	1.00	0.14	1.40	0.16	1.41
120	0.20	0.35	0.07	0.35	0.12	0.50

The semivariograms of *Cd_T* (Fig. 1c) and *Zn_T* (Fig. 1d) are similar in that the nugget is negligibly small, which is supported by the variance within one mixed sample (Table 3). Therefore, at locations near to each other, HNO₃-extractable heavy metal contents are similar in magnitude. Although the semivariance at lag distances < 10 m is similar in magnitude in both directions, in the E-W- direction a sill seems to develop, although this is supported by one point of the semivariogram only. In general, a directional effect similar to the one observed for *oc* is present.

The spatial structures of *Cd_s* (Fig. 1e) and *Zn_s* (Fig. 1f) are characterized by a relatively large nugget of $\approx 40\%$ of the total variance of the data set. The value of the nugget is supported by Table 3. A range can be observed for the N-S direction at 20- to 25-m lag distance for *Cd_s*. No obvious sill for *Zn_s* can be recognized. At lag distances < 15 m the semivariance in the E-W direction is larger than in the N-S direction. At larger distances the semivariance is similar in magnitude in both directions. The directional effect as observed for pH also shows in the semivariograms of *Cd_s* and *Zn_s*.

All soil parameters are spatially structured and anisotropic. The anisotropy of the HNO_3 -extractable heavy metal contents is similar to the anisotropy of oc , but different from the anisotropy of pH, although Cd_T and Zn_T are better correlated with pH than with oc (Table 4). This may indicate that spatial patterns of oc in the field regulate spatial patterns of HNO_3 -extractable heavy metal contents to a larger extent than spatial patterns of pH. It may be reasoned from these results that whereas oc can be considered as a measure of the *potential* total sorption capacity of the soil, pH regulates the *actual* sorption equilibrium. This may also explain the similarity in anisotropy between soluble heavy metal contents and pH. Although evidence of causality must come from other sources and the above posed hypothesis stems from semivariogram analysis which is subject to criticism (Philip and Watson, 1986), it suggests that further investigations regarding the influence of spatial patterns of soil chemical parameters on the spatial behavior of reactive contaminants may improve the understanding of field scale behavior of contaminants.

The spatial structure as depicted in Figs. 1a to 1f is different from the spatial structure of pH, oc , Cd_s and Cd_T as calculated for the same field along a transect in the N-S direction, as reported by Boekhold *et al.* (1991). In semivariogram analysis, differences between sample locations are averaged between all possible pairs. Because the semivariogram for the N-S direction is the average result of the entire sampled area, the directional variogram for the N-S direction cannot be compared with the autocorrelation function calculated for one sequence of data points. This difference between transect analysis and grid analysis for the same field implies that extrapolation of transect information to the two dimensional case is not valid when the field is heterogeneous. For the water infiltration rate Vieira *et al.* (1981) observed a similar difference between autocorrelograms for individual rows and the semivariogram for the whole data set.

The correlation length of soil properties is likely to vary from one area to another (Peck, 1983). The sampled field showed a spatial structure for Cd_T and Zn_T , whereas Wopereis *et al.* (1988) found no spatial structure for heavy metals in a 1-ha forested plot. The scale of variability as observed in our field does not differ from the scale observed for soil hydraulic properties as reported by Bresler (1989) in an arable field of similar size. The correlation lengths are within the limits given for soil physical parameters by Peck (1983). Further evidence is needed on the correlation scale of soil chemical parameters to determine the normal range of values of correlation lengths for soil properties and significant differences in ranges between soil properties.

Table 4. Correlation matrix of pH, organic carbon (*oc*), total extractable Cd (Cd_T) and Zn (Zn_T), and soluble Cd (Cd_s) and Zn (Zn_s), $N=166$.

	pH	<i>oc</i>	Cd_T	Cd_s	Zn_T	Zn_s
pH	1					
<i>oc</i>	0.05	1				
Cd_T	0.47*	0.37*	1			
Cd_s	-0.83*	-0.05	-0.11	1		
Zn_T	0.56*	0.39*	0.90*	-0.28	1	
Zn_s	-0.90*	0.02	-0.23	0.85*	-0.31	1

* significant at $p < 0.0001$

Linear correlation of the soil parameters revealed that pH is highly correlated with Cd_s and Zn_s (Table 4). The negative sign indicates that at lower pH more cadmium and zinc is in solution. No significant correlation was found between soluble contents and *oc*. Moreover, although HNO_3 -extractable heavy metal contents were better correlated with pH, correlation with *oc* was also significant. Correlation between the soluble and HNO_3 -extractable heavy metal contents was not significant, indicating that HNO_3 -extractable contents are not indicative of possible adverse effects of soil pollution in terms of mobility and bioavailability. Nevertheless, they are related by the sorption equation. Since pH and *oc* are not correlated with each other, an improvement of the relation between HNO_3 -extractable and soluble Cd contents may be expected when pH and *oc* effects are taken into account.

In the following we restrict ourselves to analysis of Cd, because a sorption equation has been derived for Cd that accounts explicitly for pH and *oc*. Next to pH and *oc*, zinc is also known to be an important factor for adsorption of cadmium (Chardon, 1984, Christensen, 1987). In our field the Zn/Cd ratio is 50 on average. However, because cadmium and zinc are highly correlated both in HNO_3 -extractable and soluble contents, Zn is not an independent variable, and therefore no improvement of the sorption relation of cadmium can be expected when possible effects of Zn are included in the sorption equation.

In an earlier analysis of this field, using data along a transect (Boekhold *et al.*, 1990), cadmium accumulation in this field could be related to local soil chemical circumstances, expressed as pH and *oc*. A major part of the variability in Cd_T could be explained by variation in pH. Variability in Cd_T could be further

reduced by accounting for variability in oc . In this contribution, attention is focussed on Cd_s because this parameter gives a better indication of cadmium mobility and bioavailability than Cd_T .

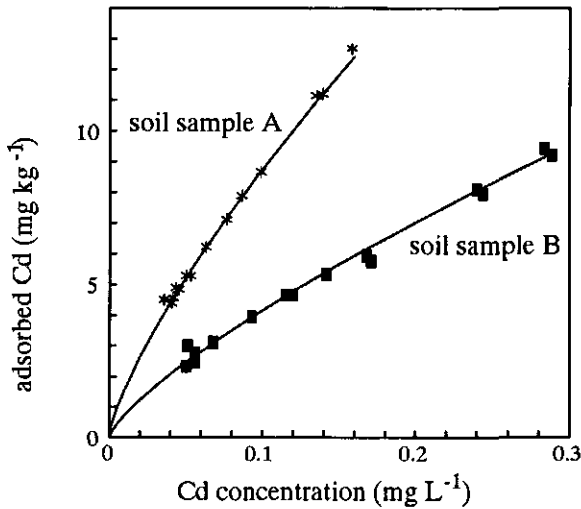


Fig. 2. Measured and fitted adsorption isotherms for two soil samples that differed in pH and organic matter content.

Sorption coefficients for the scaled sorption model, Eq. (2), were estimated using adsorption isotherms determined in 0.01 M CaCl₂ as a background electrolyte for two soil samples that differed in pH and oc . Values for k and n from Eq. (1) were determined by fitting the Freundlich sorption equation to adsorption data by nonlinear regression. In Fig. 2 the two adsorption isotherms are shown, and Table 5 summarizes the adsorption parameters for the two soil samples.

Table 5. Values of pH and oc , and the Freundlich adsorption coefficients k , k^* and n with their standard error of prediction, of two soil samples in the field that differed in sorption capacity.

	soil sample A	soil sample B
pH	5.6	5.2
oc	3.0	2.5
k	49 ± 2	24 ± 1
k^*	0.026 ± 0.001	0.024 ± 0.001
n	0.75 ± 0.02	0.77 ± 0.01

They have different values for k , whereas the value of n is of similar magnitude. When k is scaled according to the scaled sorption model, the parameter k^* now becomes approximately the same for the two soil samples. The average values of k^* (0.025) and n (0.76) are used to predict the distribution of Cd_s in the field from HNO_3 -extractable Cd content (Cd_T), pH and organic carbon content, known for every sample point, thus assuming that k^* and n are field constants. This is done using an iterative solution scheme (bisection method, Press *et al.*, 1986) for the sorption equation which is in the form

$$(q =) Cd_T - Cd_s = k^* oc (H^+)^{-0.5} \left(\frac{Cd_s}{10} \right)^n \quad (5)$$

where the factor 10 is the solution-soil ratio, necessary to change from Cd_s , expressed in $mg\ kg^{-1}$, to c , expressed in $mg\ L^{-1}$.

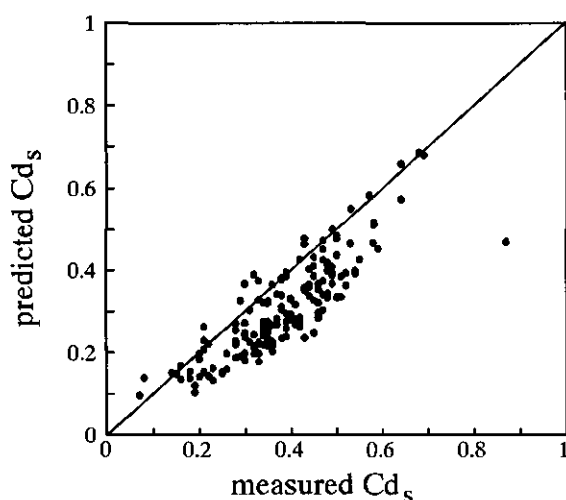


Fig. 3. Measured values of soluble Cd (Cd_s) vs. predicted values of Cd_s using Eq. (5).

Fig. 3 shows the predicted values of the soluble Cd content for each location, compared with the measured content. For prediction of Cd_s only Cd_T , pH, oc , and the scaled sorption parameters k^* and n are used. They are in good agreement with the independently measured Cd_s . The correlation coefficient between measured and predicted values of Cd_s in Fig. 3 is 0.87. When a constant value for k is used to predict Cd_s , using Eq. (1), no significant correlation exists between predicted and measured values. The model systematically underestimates Cd_s . A regression line with intercept zero and a slope of one is obtained when k^* is

set to 0.021. This value does not fall within the 0.95 confidence interval of k^* (Table 5). Apparently, k^* is biased, which is well possible since k^* is determined independently, using two soil samples only. This may be too low a number for accurate estimation of k^* in this heterogeneous field. Although oc and pH are not the only processes responsible for Cd sorption, and other factors may be assumed to be random variables as well, accounting for pH and oc highly reduced the variability in predicted Cd_s values. The estimated proportion of the variance of Cd_s that can be explained by Eq. (5) is 0.75. Apparently, pH and oc are the most important factors that regulate cadmium sorption in this soil. Although absolute values are somewhat underestimated in this independent prediction, variability in c is highly reduced when variability in pH and oc is accounted for.

Conclusions

In the sampled field, where diffuse source atmospheric deposition of Cd and Zn is the source of contamination, Cd and Zn contents are spatially variable. The maximum HNO_3 -extractable Cd and Zn contents observed are three times as high as the minimum values, and soluble contents can differ by a factor of 15. Neither a normal nor a lognormal frequency distribution could be fitted to the data with a level of significance > 0.85 . When for modelling purposes a frequency distribution is needed, however, a lognormal distribution is preferred over a normal distribution because they are similar when the CV is relatively low and a lognormal distribution cannot yield negative values.

Nitric acid extractable heavy metal contents and soluble heavy metal contents are structured parameters, but with different characteristics. No range was observed for the HNO_3 -extractable contents; the soluble Cd content had a correlation length of 20 to 25 m in the N-S direction only. The field was anisotropic for all measured parameters, with similar anisotropy for pH , Cd_s , and Zn_s , and, in the opposite direction, similar anisotropy of oc , Cd_T , and Zn_T . This may indicate a spatial relationship between soil chemical parameters and Cd and Zn behavior in this soil. However, evidence of causality cannot be derived from the observed correlation. Measured small scale variability supported the nugget effect that showed in the semivariograms for all six parameters. The spatial structure as derived from this two-dimensional sampling scheme differed from the spatial structure of a transect in the same field because the field is heterogeneous.

Variability of Cd and Zn contents is related to soil chemical variability, expressed through pH and *oc* content, according to the scaled sorption model. Although pH and *oc* are not the only parameters that determine Cd sorption, their spatial variability accounted for most of the spatial variability in Cd and Zn contents. The magnitude of variability of pH and *oc* was not as large as can be observed for soil physical parameters, but the impact on the field scale behavior of Cd and Zn is profound.

Soluble and HNO₃-extractable heavy metal contents were not correlated. Nitric acid extractable heavy metal contents therefore did not give a good indication of soluble heavy metal contents. Because soluble heavy metal contents better reflect mobility and bioavailability, the effect of pH and *oc* should be accounted for when environmental risks associated with soil pollution of Cd are assessed on the basis of HNO₃-extractable heavy metal contents. For our sandy soil the scaled sorption model gives a good indication of this effect.

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Chapter 6
**Evaluation of Kriging Variance to Estimate
Pollution Boundaries in Soil**

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Evaluation of Kriging Variance to Estimate Pollution Boundaries in Soil

Abstract

Evaluation of environmental risks of soil pollution involves estimation of the spatial distribution of the pollutant. In view of remedial action of polluted sites, pollution boundaries need to be estimated accurately. The ability of kriging variance to quantify prediction uncertainty of kriged interpolations was examined by cross validation of predicted cadmium contents in an acid sandy soil with their known, measured values. Normalized deviations of predictions from the true value were subjected to three statistical tests of significance: the Student's *t* test, the χ^2 test, and the binomial test. These tests indicated the accuracy of predictions. The original sampling density of 330 samples ha^{-1} could be reduced by 50% while maintaining the accuracy of kriged interpolations. Due to anisotropy, a higher sampling density in the east-west direction of the field was needed for reliable predictions. Kriging variance was used to predict the area that may exceed a threshold level of 5 mg Cd kg^{-1} with 0.95 probability. The area that exceeded the threshold level using a reduced data set was larger than predicted using the full data set, because kriging variance is higher for a lower sampling density. When this area needs remedial action, the reduction of research effort by minimizing the sampling density may well lead to an overall increase in sanitation costs.

Introduction

The spatial distribution of pollutants in soil is not uniform, due to (temporal and spatial) variability of deposition patterns. In case of a diffuse source, deposition may be homogeneous, but then soil heterogeneity may induce variations in the degree of pollution. Evaluation of potential environmental risks of soil pollution involves, among others, estimation of the spatial distribution of the pollutant. When certain levels of contamination exceed standards for good soil quality, remedial action may be necessary. Underestimation of the contaminated soil volume will lead incomplete clean-up, because then, after sanitation, some areas are still polluted and need additional treatment. Overestimation of the contaminated soil volume leads to sanitation of clean soil, which is a waste of time and money.

To determine the soil volume that needs to be sanitized, a number of spatially distributed soil samples may be analyzed on their degree of pollution. In general, more soil samples give more information, with which pollution boundaries can

be better assessed. Analysis of more samples also imply higher costs. In the ideal case, a certain number of soil samples is sufficient to define pollution boundaries with a predetermined precision.

Information obtained by soil data on the degree of pollution can be translated from point observations to estimates for the whole site by some kind of spatial interpolation. Several methods of spatial interpolation exist, e.g. simple linear interpolation, moving averages, trend surface analysis and spline interpolation (Davis, 1986), weighted moving averages using inverse distances squared functions (Van Kuilenburg *et al.*, 1982), and kriging (Matheron, 1971).

Kriging has advantages over the other methods of spatial interpolation. Kriging predicts not only the value of a parameter at an unvisited location, but also the variance of this prediction. These predictions are based on the spatial structure of the parameter as derived from the data set. This spatial structure (e.g. correlation) is estimated by the semivariogram. A disadvantage of kriging is that the predictions are based on the semivariogram function that cannot be derived optimally from the calculated semivariances. Semivariograms that were constructed by several researchers from the same data set were markedly different (Englund, 1990). This is inherent to the method, since a number of arbitrary choices need to be made by the user regarding size of lag classes and the appropriate semivariogram model.

Kriging variance is dependent on the configuration of the data points and on the semivariogram. The measured values themselves are considered to be true values. In general, this is not the case, since e.g. measurement errors induce uncertainty in the measured parameter values. This may explain why kriging variance underestimated the real uncertainty of predictions (Laslett *et al.*, 1987; Bregt *et al.*, 1991). In these cases, it cannot be used to identify pollution boundaries accurately.

In this contribution, we used a data set on Cd contents in a field soil with a sampling density of 330 samples ha⁻¹. Next to this original sampling scheme, reduced data sets were derived according to several hypothetical sampling procedures. Three statistical tests of significance were applied to kriged predictions at known locations (cross validation), to evaluate kriging variance as a measure of prediction uncertainty for the reduced data sets. For data sets that passed these tests, the effect of reduced sampling density on the size of the area that exceeds a certain threshold level of contamination is illustrated.

Geostatistical Theory

The kriging method of interpolation predicts values for any coordinate position within the domain considered without bias and with minimum variance (Matheron, 1971). A kriged value is found by attributing weights, λ_i , to its neighbouring data points which are known, measured values. The correlation structure of the data, given by the semivariogram function, is used to obtain the weights, λ_i .

The degree of autocorrelation between adjacent points in space separated by a distance vector h can be expressed as the semivariance, $\gamma(h)$:

$$\gamma(h) = \frac{\sum_{i=1}^{n(h)} [z(x_i) - z(x_i + h)]^2}{2n(h)}$$

where $n(h)$ is the number of data pairs $z(x_i)$, $z(x_i + h)$ separated by a distance vector h . As a rule of thumb at least 30 data pairs should be used to calculate $\gamma(h)$, and h must be less than half the maximum distance between two sampled points (Journel and Huijbregts, 1978). Usually $\gamma(h)$ is averaged over several distances forming a distance class. Semivariance analysis requires that the intrinsic hypothesis holds for the data, i.e. the mean and variance of increments $(z(x_i) - z(x_i + h))$ are stationary (Journel and Huijbregts, 1978).

For an idealized semivariogram, $\gamma(h)$ becomes zero for infinitesimal small values of h . In practice the semivariance often intercepts the y-axis at values larger than zero when h approaches zero. This so-called nugget effect may arise when variability of the measured parameter is relatively large at a scale smaller than the minimum sampling distance used. It may also arise due to measurement errors. As h becomes larger, the correlation between two data points decreases and as a result, the value of the semivariance increases. The value of h at which the semivariance approaches a maximum is called the range. The corresponding value of the semivariance is the sill.

Once the raw semivariogram has been obtained, it can be fitted to a semivariogram model. This model describes the calculated semivariances continuously, and must be definite positive. It serves as a basis to estimate the kriging weights, λ_i , used to predict values at unvisited locations, $\hat{z}(x_0)$:

$$\hat{z}(x_0) = \sum_{i=1}^n \lambda_i z(x_i)$$

The weights λ_i are chosen so that they sum to 1, thereby ensuring that the prediction is unbiased and minimizes the variance. The latter condition is obtained when

$$\sum_{j=1}^n \lambda_j \gamma(x_i, x_j) + \psi = \gamma(x_i, x_0) \quad \forall i$$

where ψ is the Lagrangian multiplier associated with the minimization.

The prediction variance of $z(x_0)$, or kriging variance is given by

$$\sigma_K^2 = 2 \sum_{i=1}^n \lambda_i \gamma(x_i, x_0) - \sum_{i=1}^n \sum_{j=1}^n \lambda_i \lambda_j \gamma(x_i, x_j) = \sum_{i=1}^n \lambda_i \gamma(x_i, x_0) + \psi$$

and the kriging standard deviation (KSD_i) is $\sqrt{\sigma_K^2}$.

In view of remedial action of contaminated soil, average values over areas rather than point values are of interest (Burgess and Webster, 1980; Gilbert and Simpson, 1985). When predictions are made for an area or block, V , that is larger than the support of the individual observations, the kriging variance σ_B^2 is:

$$\sigma_B^2 = \sum_{i=1}^n \lambda_i \gamma(x_i, V) + \psi_B - \gamma(V, V)$$

Here, $\gamma(x_i, V)$ is the average semivariance between the observation points and block V , $\gamma(V, V)$ is the within-block variance, and ψ_B is the Lagrangian multiplier. For more details see Journel and Huijbregts (1978).

Cross Validation

To examine kriging variance as a reliable measure of uncertainty of kriged predictions, known values, $z(x_i)$, can be compared with predicted values $\hat{z}(x_i)$ and its associated KSD_i . If we assume that the errors of prediction are normally distributed around the true value, the confidence interval around $\hat{z}(x_i)$ can be defined as:

$$z(x_i) \in [\{\hat{z}(x_i) - t_{\alpha,r} \cdot KSD_i\}, \{\hat{z}(x_i) + t_{\alpha,r} \cdot KSD_i\}] \quad (1)$$

where t is the Student's t -value at α level of significance with $r = (n-1)$ degrees of freedom. For large n , the probability that the true, measured value at x_i is within one KSD_i above or below the predicted value is 68%, and the probability is 95% that the true value lies within two KSD_i 's. The hypothesis of normality implies that observations are independent. Since the kriged predictions are

explicitly based on spatial dependence of observations, they are obviously not independent. In the following we assume that the effect of dependence of observations is small, and leads to negligible errors in the statistical procedures.

Statistical Tests of Significance

Since we have only one observation at each location in the field, Eq. (1) cannot be used. The hypothesis that KSD_i is a good estimator of the prediction uncertainty cannot be tested. However, when several observations are cross validated, their normalized deviations from the true value should be standard normal distributed with mean zero and standard deviation one:

$$\frac{z(x_i) - \hat{z}(x_i)}{KSD_i} \in N(0,1) \quad \forall i$$

When the distribution is not Gaussian, the KSD_i 's are not a reliable measure of prediction uncertainty. To test the accuracy of KSD_i to estimate prediction uncertainty, three statistical tests of significance were used. The Student's t test is used to examine the hypothesis of zero mean for the distribution, the χ^2 test verifies for a variance of one, and the binomial test can be used to indicate extreme values in the distribution.

Student's t Test

To analyse the hypothesis that the expectation of $\{(z(x_i) - \hat{z}(x_i))/KSD_i\}$, or y , estimated by

$$E\{y\} = \frac{1}{n} \cdot \sum_{i=1}^n y_i$$

equals zero, the Student's t test can be used. With the Student's t test the null-hypothesis $H_0: \mu_0 = 0$ is tested against the alternative hypothesis $H_1: \mu_0 \neq 0$.

The t test statistic equals

$$t_r = \frac{\bar{y} - \mu_0}{s\sqrt{1/n}}$$

and the confidence interval around y for H_0 is

$$\frac{-t_{(1-\alpha);n-1} \cdot s}{\sqrt{n}} < \bar{y} < \frac{t_{(1-\alpha);n-1} \cdot s}{\sqrt{n}}$$

where s is the estimator of the standard deviation of y .

χ^2 Test

The hypothesis that the variance of y , estimated by

$$\sigma_y^2 = \frac{1}{n-1} \cdot \sum_{i=1}^n (y_i - \mu_0)^2$$

equals one, was analyzed using the χ^2 test. The null hypothesis $H_0: \sigma^2 = 1$ is tested against the alternative hypothesis $H_1: \sigma^2 \neq 1$.

The χ^2 test statistic equals

$$\chi_{n-1}^2 = \frac{(n-1)s^2}{\sigma_0^2}$$

where s^2 is the estimator of the variance of y . The confidence interval around s^2 for H_0 is

$$\frac{\chi_{\alpha,n-1}^2}{n-1} < s^2 < \frac{\chi_{(1-\alpha),n-1}^2}{n-1}$$

The value of the test statistic will be within the critical area when the variance of y is larger or smaller than one. This happens when KSD_i is too large or too small, but also when $\hat{z}(x_i)$ is biased.

Binomial Test

With a $(1-\alpha)$ confidence interval of a frequency distribution, random sampling of this distribution should give a probability of $(1-\alpha)$ that the sampled value lies inside the confidence interval, and a probability of α that it is not. Therefore, samples from a frequency distribution with a predefined confidence interval follows a binomial distribution. The (binomial) probability that $\underline{k} \leq k$ is

$$P[\underline{k} \leq k] = \sum_{i=0}^k \binom{n}{i} \cdot p^i \cdot (1-p)^{n-i} \quad (2)$$

where k is the expected number of y -values that lie within the confidence interval, \bar{k} is the actual number of y -values in the confidence interval, p is probability, and n is the number of cross validated data. The null hypothesis $H_0: p = 1 - \alpha$ is tested against $H_1: p < 1 - \alpha$. The value of k that belongs to a certain value of α can be calculated with Eq. (2). When the number of cross validated sample locations that lie within the $(1 - \alpha)$ confidence interval of the standard normal distribution is smaller than k , the null hypothesis is rejected.

Description of the Data Set

A total of 164 soil samples from 0 to 0.20 m depth were taken from an acid sandy soil with a humic upper layer of 0.25 to 0.30 m that is polluted with Cd and Zn. The area is contaminated as a result of atmospheric deposition of Cd and Zn due to the presence of a zinc smelter nearby. Due to the diffuse nature of the source, deposition can be regarded as homogeneous. Observed spatial variability of Cd and Zn contents can be explained by spatial variability of sorption parameters in the field (Boekhold and Van der Zee, 1992).

Using a grid of 8×17 with a grid node distance of 6 m, an area of approximately 0.5 ha was sampled. In addition to these 136 soil samples, 28 samples were taken at random, located at a distance of 2 m to the nearest grid node. This resulted in a total sampling density of approximately 330 samples ha^{-1} . The total extractable Cd content of the soil, Cd_T , was measured in all soil samples. For details of sampling and chemical analysis see Boekhold and Van der Zee (1992).

With reduced data sets, we simulated a less intensive sampling strategy. In sampling strategy A, increasingly more data in the east-west (E-W) direction were omitted, while the sampling density in the north-south (N-S) direction was maintained. Systematic sampling was sustained as much as possible. Reduced data sets contained 116, 88, 72, 56, or 48 data points, equalling sampling densities of approximately 230, 175, 145, 110, and 95 samples ha^{-1} respectively. Strategy B followed the opposite methodology, leading to data sets with 116, 88, 76, 72, 60, 53, and 44 data points, equivalent to sampling densities of approximately 230, 175, 150, 145, 120, 105, and 90 samples ha^{-1} .

To illustrate the reduction procedure, Figure 1 shows the sample locations of the full data set, and of two reduced data sets. Omitted data points were used for cross validation. A complete evaluation of the effect of reduced sampling density

on prediction accuracy would require analysis of all possible combinations of cross validated data points from the full data set. But since we did these calculations for illustrative purposes, we chose to analyse one reduction strategy only.

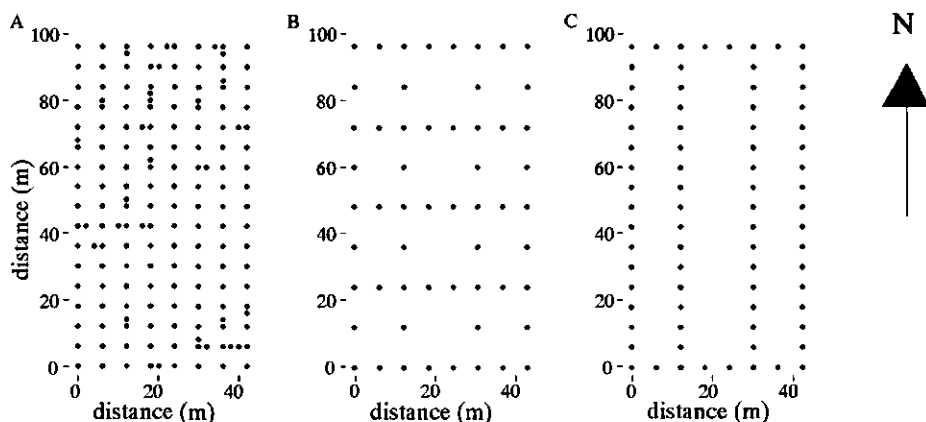


Fig. 1. Sampling strategies used, A: sampling density is 330 ha⁻¹, B: 110 ha⁻¹, and C: 150 ha⁻¹.

For each data set a semivariogram model was fitted to calculated semivariances at specific lag distances, assuming isotropy of the data set. This assumption is known to be incorrect, because anisotropy was observed for the full data set (Boekhold and Van der Zee, 1992). Nevertheless, assuming isotropy reduces the effort considerably, without interfering with the objective of this study. Specific boundaries and confidence bands are affected by anisotropy, but cross validation and the effect of reduced sampling density on pollution boundaries can be illustrated by assuming isotropy as well.

With the continuous semivariograms, Cd_T was predicted by block kriging for blocks of 2 by 2 m at the locations that were initially omitted from the data set. Using the *KSD* of these predictions, the frequency distribution of the normalized values according to Eq. (1) was tested on its normality by the Student's *t* test, the χ^2 test, and the binomial test.

Results and Discussion

Semivariograms for sampling strategy A were similar, whereas for strategy B they show more differences (Table 1).

This indicates that local variability in the E-W direction is similar to the global variability of the field as estimated by the semivariogram. In the N-S direction, however, local heterogeneity is different from the global heterogeneity, leading to different semivariograms when data in the N-S direction are omitted from the data set. This confirms the anisotropy as observed by Boekhold and Van der Zee (1992).

Table 1. Semivariogram model characteristics for the reduced data sets of sampling strategy A and B.

sampling density (samples ha ⁻¹)	model	nugget	sill	range (m)
strategy A				
230	spherical	0	0.49	18
175	spherical	0	0.45	18
145	spherical	0	0.47	18
110	exponential	0	0.65	35
95	spherical	0	0.46	14
strategy B				
230	spherical	0	0.49	18
175	spherical	0	0.49	18
150	exponential	0	0.95	75
145	spherical	0	0.52	17
120	exponential	0	0.65	40
105	exponential	0	0.87	45
90	exponential	0	0.65	30

Cross validation of predicted values for Cd_T with measured values showed that the null hypotheses of the three statistical tests of significance were not rejected for reduced data sets that followed strategy A, up to one-third of the original size of the data set (Table 2). This indicates that means as well as variances of kriged Cd_T were not different from observed values with 0.95 confidence. The binomial test gave no evidence of skewness. With sampling strategy B reduction of the data set to 50% may already lead to unreliable predictions of Cd_T (Table 3). This difference is due to anisotropy of the data set.

Table 2. Test results for sampling strategy A, n_x is number of data points used for cross validation, and $\alpha = 0.05$.

sampling density (samples ha ⁻¹)	n_x	binomial	χ^2	Student's t
230	48	critical area: [0, 43] test statistic: 47 null hypothesis: do not reject	[0, 30.0] \cup [67.8, ∞) 43.3 do not reject	($-\infty$, -2.014] \cup [2.014, ∞) 0.426 do not reject
175	76	critical area: [0, 69] test statistic: 75 null hypothesis: do not reject	[0, 53.0] \cup [101, ∞) 91.1 do not reject	($-\infty$, -1.995] \cup [1.995, ∞) -0.441 do not reject
145	92	critical area: [0, 84] test statistic: 91 null hypothesis: do not reject	[0, 67.4] \cup [119, ∞) 98.4 do not reject	($-\infty$, -1.990] \cup [1.990, ∞) 0.504 do not reject
110	108	critical area: [0, 99] test statistic: 108 null hypothesis: do not reject	[0, 80.3] \cup [138, ∞) 84.6 do not reject	($-\infty$, -1.984] \cup [1.984, ∞) 0.711 do not reject
95	116	critical area: [0, 106] test statistic: 114 null hypothesis: do not reject	[0, 87.2] \cup [147, ∞) 101 do not reject	($-\infty$, -1.982] \cup [1.982, ∞) 2.09 REJECT

Table 3. Test results for sampling strategy B, n_x is number of data points used for cross validation, and $\alpha = 0.05$.

sampling density (samples ha ⁻¹)	n_x	binomial	χ^2	Student's t
230	48	critical area: test statistic: null hypothesis: [0,43] 48 do not reject	{0,30.0] \cup [67.8, ∞) 29.7 do not reject	$(-\infty, -2.014] \cup [2.014, \infty)$ -0.777 do not reject
175	76	critical area: test statistic: null hypothesis: [0,69] 76 do not reject	{0,53.0] \cup [101, ∞) 55.8 do not reject	$(-\infty, -1.995] \cup [1.995, \infty)$ -0.569 do not reject
150	88	critical area: test statistic: null hypothesis: [0,80] 84 do not reject	{0,63.1] \cup [115, ∞) 117 REJECT	$(-\infty, -1.991] \cup [1.991, \infty)$ -2.601 REJECT
145	92	critical area: test statistic: null hypothesis: [0,84] 91 do not reject	{0,67.4] \cup [119, ∞) 76.6 do not reject	$(-\infty, -1.990] \cup [1.990, \infty)$ -1.521 do not reject
120	104	critical area: test statistic: null hypothesis: [0,95] 96 do not reject	{0,77.3] \cup [133.7, ∞) 170 REJECT	$(-\infty, -1.986] \cup [1.986, \infty)$ -1.059 do not reject
105	111	critical area: test statistic: null hypothesis: [0,101] 110 do not reject	{0,82.9] \cup [141, ∞) 70.3 REJECT	$(-\infty, -1.983] \cup [1.983, \infty)$ -2.353 REJECT
90	120	critical area: test statistic: null hypothesis: [0,110] 119 do not reject	{0,90.7] \cup [151, ∞) 83.2 REJECT	$(-\infty, -1.980] \cup [1.980, \infty)$ -1.970 do not reject

Anisotropy implies that when local and global variability are different, local predictions using a global method of variability may not give accurate results. The assumption of statistical homogeneity of the data is not valid. Since anisotropy is something usually not known *a priori* when a sampling scheme is developed, a sampling density less than approximately 160 samples ha^{-1} is not recommended for this field. In practice, this high sampling density is seldomly realised, since it requires major investments in the early stage of the sanitation project. However, when it considerably reduces the soil volume that needs sanitation, and thus the costs of remedial action, the initial expenses may be rewarding altogether.

Although many reduced data sets yielded reliable predictions at unvisited locations, the associated KSD_i 's were larger than for predictions using the full data set. This increase in KSD induces more uncertainty in the predictions. When the area of soil in which values of Cd_T exceed a certain threshold level, and thus needs sanitation, not only the area where kriged predictions exceed this value must be considered, but also the area for which the right sided $(1 - \alpha)$ confidence limit of the predictions exceeds the threshold level.

To illustrate the effect of sampling density on the size of the area that needs sanitation, Fig. 2a shows the area that exceeds 5 mg Cd kg^{-1} (the current 'B-value' from the Dutch soil sanitation program) with 0.95 confidence, calculated using the full data set of 330 samples ha^{-1} . Although only 15% of the kriged predictions exceeds the B-value, an additional 15% exceeds this value when the right sided 0.95 confidence limit is considered. When a reduced data set of 110 samples ha^{-1} according to sampling strategy A is used to interpolate with kriging (Fig. 1b), an area of 42% must be considered for remedial action with 0.95 confidence (Fig. 2b). A reduction of the sampling density by one third leads to an increase in the predicted area that needs to be sanitized by 12%.

A reduced data set of 150 samples ha^{-1} according to sampling strategy B led to an area of 45% that exceeded the B-value with 0.95 confidence (Fig. 2c). It is obvious that although reduction of sampling density yielded reliable predictions of Cd_T (Table 2), the area that exceeds the threshold level of 5 mg Cd kg^{-1} increased. Saving money in the first stage of the investigation by reducing the sampling density will lead to increased expenses in the final stage of soil redevelopment in this example.

The analysis described above was done for an area that was polluted by Cd due to diffuse source atmospheric deposition. The spatial variability of Cd contents in this agricultural field was relatively small. The assumption of statistical homogeneity of the data, and the assumption that spatial dependence of

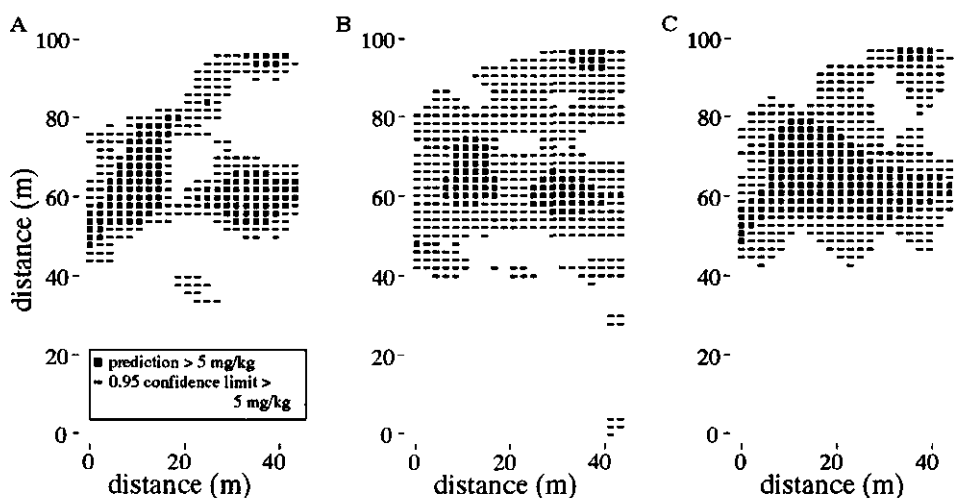


Fig. 2. Predicted area that exceeds a threshold level of 5 mg Cd kg^{-1} .

the observations can be described globally by the semivariogram function, seems warranted. Kriging is then an adequate tool to interpolate between sampled locations.

Even for this relatively homogeneously contaminated field, the area that is designated as contaminated is very sensitive to sampling density. It can be expected that for sites that show more spatial variability, the amount of samples needed for reliable predictions must be increased considerably. When predictions are reliable, the effect of sampling density on the $(1-\alpha)$ confidence interval of predictions will be larger as well. The balance between costs of sampling and chemical analysis on the one hand, and remediation costs and costs of leaving contaminated sites untreated on the other hand, determine the optimal redevelopment strategy of a contaminated site. Although a low sampling density may yield good and reliable predictions at unvisited locations, its profit may not outweigh the increased costs of sanitation of a larger area, and environmental risks of leaving contaminated sites uncleaned.

Conclusions

Three statistical tests of significance were used to test the ability of kriging variance to quantify prediction uncertainty at unvisited locations. Spatial inter-

polations of Cd contents in soil using block kriging were of good quality when approximately 160 samples ha^{-1} were included in spatial analysis.

However, the relatively large value of the kriging variance of the predictions resulted in a larger area that exceeds a threshold level of 5 mg Cd kg^{-1} than predicted with the full data set with a sampling density of 330 samples ha^{-1} . Therefore, decreasing the research effort by reducing the sampling density is not recommended in this case, because then the area that exceeds the threshold level of 5 mg Cd kg^{-1} with 0.95 confidence increased considerably. When this threshold level marks the border line between 'clean' and 'polluted' soil, the sanitation budget will increase in the final stage of remedial action at the site.

For sites that show more spatial variability, the amount of samples needed for reliable predictions must be even larger than calculated for this field. The effect of sampling density on the $(1-\alpha)$ confidence interval of predictions will be larger as well. The optimal redevelopment strategy of a contaminated site must be determined from the balance between costs of sampling and chemical analysis on the one hand, and costs of sanitation together with environmental considerations regarding the risk of leaving contaminated soil untreated on the other hand.

Chapter 7
**Long Term Effects of Soil Heterogeneity on
Cadmium Behaviour in Soil**

Co-author: Sjoerd E.A.T.M. Van der Zee

Long Term Effects of Soil Heterogeneity on Cadmium Behaviour in Soil

Abstract

A deterministic model for long term behaviour of contaminants in the rootzone is developed that includes sorption, leaching, and plant uptake. The model is applied to cadmium accumulation in a sandy soil and uptake of cadmium by barley. Sensitivity analysis showed that the sensitivity of the leaching rate to changes in soil chemical and soil physical parameters decreases as a function of time, and becomes zero when steady state is reached. In contrast, accumulation of cadmium in soil and the plant uptake rate of barley are increasingly sensitive to soil chemical and soil physical parameters as time proceeds. To analyse cadmium behaviour in a field that is heterogeneous with respect to soil physical properties, the interstitial flow velocity was assumed to be a random, lognormally distributed variate. Using Monte Carlo simulation, the average plant uptake rate appeared to be much higher in the stochastic analysis than in the deterministic approach. Steady state is reached after a very long period of time. For a lognormally-distributed proton activity, causing heterogeneity with respect to the sorption capacity of the soil, the model predicted similar deviations from the deterministic approach. It is concluded that reference values for ground water and crop quality are exceeded earlier in a heterogeneous field than in a homogeneous soil profile. Moreover, when average values suggest an acceptable situation, variability of the leaching rate and the plant uptake rate can still cause exceedance of reference values in part of the field. Therefore, it is reasoned that environmental quality standards should take soil heterogeneity into account.

Introduction

During the past decades soil contamination has motivated studies on the behaviour of chemicals in soil. Because soil can immobilize chemicals such as pollutants by sorption or precipitation, soil acts as a natural filter for these compounds. However, soil has a finite capacity for retaining chemicals. Exceedance of this capacity may have adverse consequences for the environment, expressed as increased mobility and bioavailability in the soil system.

The capacity of soil to immobilize pollutants depends on both soil and pollutant properties. To understand the effect of soil chemistry on transport of water and solutes a large number of studies were done for one dimensional flow through homogeneous columns (Van Genuchten and Wierenga, 1976; 1977; Bolt, 1982). One of the main problems appeared to be soil heterogeneity.

Aggregated soil was considered by Van Genuchten and Dalton (1986) and Rasmuson (1986), Van Genuchten *et al.* (1984) studied macropores, and Barry and Parker (1987) examined layered soils.

More recently the effect of soil spatial variability in the horizontal plane on flow and transport has been dealt with explicitly. Variability of flow was studied by Nielsen *et al.* (1973), Biggar and Nielsen (1976) and Warrick *et al.* (1971). Flow velocity appeared to be often lognormally distributed and this variability could be dealt with using the scaling theory of similar media. Using this approach to describe variability of flow Dagan and Bresler (1979) and Bresler and Dagan (1981; 1983) studied the effect of variability on non-reactive solute transport. These studies indicated that field-averaged non-sigmoid fronts may develop, of which the shape generally depends much more on horizontal variability than on pore scale dispersion. Reactive solute transport was considered by Van der Zee and Van Riemsdijk (1986) and De Haan *et al.* (1987). They found that spatial variability of sorption parameters had an equally profound effect on field averaged transport as variability of flow and that modeling with averaged properties will underestimate the time for first breakthrough. Loague *et al.* (1989) characterized the uncertainty for estimated regional retardation factors (RFs) for pesticides due to data uncertainty. Considerable uncertainty exists in the predicted RF-values used to screen and rank pesticides. The greatest contribution to this uncertainty was by the regional estimates of the organic matter content of the soil. Boekhold *et al.* (1990) showed that spatial variability of Cd contents in an arable field could be explained by spatial variability of pH and organic matter content.

A different approach advocated by Jury (1982) is the transfer function concept. According to this concept processes in soil are generally too complex for deterministic modeling, but transport may be described effectively assuming a distributed residence time in the soil system of interest. The compatibility of this concept with deterministic models based on the Convection-Dispersion Equation (CDE) was shown by Sposito *et al.* (1986), and the ability to describe field data was demonstrated by White *et al.* (1984).

Whereas the large effect of flow and sorption variability on field-averaged transport has been given much attention, the effect on plant uptake has remained relatively unexplored. Nevertheless, since flow and sorption are related to availability to plants, the effects of spatial variability on crop quality may be expected to be significant.

In this contribution we present a simple root zone balance model applicable for heavy metals. With this model the transient accumulation of contaminants in soil and its long term effects on plant uptake and leaching may be evaluated. After giving a sensitivity analysis for a reference situation that is realistic for cadmium the effects of a spatially-variable flow velocity as well as a spatially-variable sorption capacity are made explicit.

Theory

Balance equation

The behaviour of contaminants in soil may be evaluated using the conservation equation for solute transport:

$$\rho \frac{\partial s}{\partial t} + \theta \frac{\partial c}{\partial t} = \theta D \frac{\partial^2 c}{\partial z^2} - \theta v \frac{\partial c}{\partial z} + \Phi \quad (1)$$

where ρ is the soil dry bulk density (kg m^{-3}), s is the adsorbed amount ($\mu\text{mol kg}^{-1}$), t is time (yr), θ is the volumetric water content of the soil ($\text{m}^3 \text{m}^{-3}$), c is the solute concentration ($\mu\text{mol m}^{-3}$), D is the diffusion-dispersion coefficient ($\text{m}^2 \text{yr}^{-1}$), v is the interstitial water flow velocity (m yr^{-1}), z is soil depth (m), and Φ is a production term. In practice, soils in agricultural use are ploughed. When the plough layer, reaching from $z = 0$ to $z = L$, is assumed equivalent with the root zone and sorption is negligible below $z = L$, solute that leaches beyond depth L may enter ground water. For a perfectly mixed plough layer, which may be assumed when long term processes are studied in an annually ploughed field, and neglecting dispersion at $z = L$ (Van der Zee and Van Riemsdijk, 1987) eq. 1 can be rewritten as:

$$\rho \frac{\partial s}{\partial t} + \theta \frac{\partial c}{\partial t} = \frac{\theta v}{L} [c(0, t) - c(L, t)] + \Phi \quad (2)$$

The first term on the right hand side is equivalent to the leaching rate, dI/dt , at the lower boundary of the system, and the second term equals the input rate, dI/dt , at the soil surface. Uptake of a contaminant by plant roots, P , can be accounted for using the production term of eq. 2 ($\Phi = dP/dt$). The left hand side of eq. 2 can be regarded as the change in total content of the contaminant, T ($= \theta c + \rho s$), as a function of time. Thus a balance equation develops that expresses the difference in inflow and outflow of a chemical within the system:

$$\frac{dT}{dt} = \frac{dI}{dt} - \frac{dJ}{dt} - \frac{dP}{dt} = I_i - J_i - P_i \quad (3)$$

For a contaminant that adsorbs according to the Freundlich sorption equation given by

$$s = k_1 c^n \quad (4)$$

where k_1 and n are constants, the total content, T , can be expressed as

$$T = \theta c + \rho k_1 c^n \quad (5)$$

when equilibrium conditions prevail. Other sorption equations can be incorporated in the model as well. Writing eq. 5 as $T = f(c)$, then

$$c = f^{-1}(T) \quad (6)$$

Assuming that the distribution ratio, r_d , defined by

$$r_d = \frac{\rho s}{\theta c} = \frac{1}{\theta} \rho k_1 c^{n-1} \quad (7)$$

is large, which is reasonable for cadmium (Christensen, 1984), eq. 6 may be approximated by:

$$c = \left[\frac{T}{(\rho k_1)} \right]^{1/n} \quad (8)$$

The leaching rate, J_i , can be expressed in terms of total content, T , using eq. 8:

$$\frac{dJ}{dt} = \frac{\theta v}{L} \left[\frac{T}{\rho k_1} \right]^{1/n} \quad (9)$$

To solve eq. 3 it is convenient to express plant uptake also in terms of T , although the availability of heavy metals to plants does not only depend on the total heavy metal content of the soil but also upon a variety of soil and plant factors (Bjerre and Schierup, 1985). Relationships of the type

$$\frac{dP}{dt} = k_2 T^m \quad (10)$$

were proposed by Kuboi *et al.* (1986) and are used in our analysis. Contaminant input, I_i , is considered to be constant in time ($I_i = I_0$) which is reasonable for long term diffuse source soil contamination.

Substituting eqs. 9 and 10 in eq. 3, a differential equation develops in terms of total content T :

$$\frac{dT}{dt} = A - BT^m - CT^{1/n} \quad (11a)$$

in which

$$A = \frac{dI}{dt} = I_0 \quad (11b)$$

$$B = k_2 \quad (11c)$$

$$C = \frac{v\theta}{L} \left(\frac{1}{\rho k_1} \right)^{1/n} \quad (11d)$$

Table 1 gives five possible analytical solutions for different values of n and m , where a linear sorption equation is assumed when n equals 1, while a Freundlich type sorption equation is represented by $n = 1/2$. Parameter m may be equal to $1/2$, thus representing a convex plant uptake relationship. With $m = 1$, linear plant uptake is assumed, and $n = 2$ expresses a concave plant uptake relation. Note that eqs. 1.1, 1.4, and 1.5 are mathematically the same (Table 1). In practice the Freundlich power, n , may not be equal to 0.5 or 1. Then an analytical solution may not be available, and the solution of eq. 11 may be approximated numerically using the 4th order Runge-Kutta method (Press *et al.*, 1986).

Sensitivity analysis

Sensitivity is the change in one factor, y , due to a change in another factor, x , and implies a quotient of two differentials (McCuen, 1973). For continuous systems with time invariant parameters the relative sensitivity function, U , for the system $y = f(y, x, t)$ can be defined:

$$U_y(x) = \frac{\partial y(x, t)}{\partial x} \frac{x}{y(x, t)} = \frac{\partial \ln y(x, t)}{\partial \ln x} \quad (12)$$

To compare the sensitivity of the system to changes in all parameters involved, the relative sensitivity of parameter y to parameter x , $U_y(x)$, can be used since $U_y(x)$ is invariant to the magnitude of x . Values of $U_y(x)$ ranging from -1 to 1 indicate attenuation of x in y , values smaller than -1 or larger than 1 imply that variations in x are amplified in y . Negative values of $U_y(x)$ indicate a decrease in y when x increases.

With the equations presented in Table 1 the relative sensitivity functions for each parameter A , B , and C can be derived analytically. In the following we restrict ourselves to (1.1) which can be thought of as representative for solute transport with Freundlich type sorption and a linear plant uptake relationship, which is most appropriate for cadmium (Chardon, 1984, Van Luit, 1984).

Table 1. Analytical solutions of the balance equation (eq. 11a) for positive values of A , positive $(B + C)$ in eqs. 1.2 and 1.3, negative B and C in eqs. 1.1, 1.4 and 1.5, and $T = 0$ when $t = 0$.

m	n	Balance equation	Total content T	T $t \rightarrow \infty$
(1.1)	1	$\frac{dT}{dt} = A + BT + CT^2$	$\frac{(B + \sqrt{\Delta})(B - \sqrt{\Delta})(e^{\sqrt{\Delta}t} - 1)}{2C[B + \sqrt{\Delta} - (B - \sqrt{\Delta})e^{\sqrt{\Delta}t}]}$ with $\Delta = B^2 - 4AC$	$\frac{B + \sqrt{\Delta}}{-2C}$
(1.2)	2	$\frac{dT}{dt} = A - (B + C)T^2$	$\frac{\sqrt{A}(e^{\frac{2\sqrt{A}}{\sqrt{B+C}}t} - 1)}{\sqrt{(B + C)}(e^{\frac{2\sqrt{A}}{\sqrt{B+C}}t} + 1)}$	$\frac{\sqrt{A}}{\sqrt{B + C}}$
(1.3)	1	$\frac{dT}{dt} = A - (B + C)T$	$\frac{A - e^{-(B+C)t}}{(B + C)}$	$\frac{A}{B + C}$
(1.4)	2	$\frac{dT}{dt} = A + BT^2 + CT$	$\frac{(C + \sqrt{\Delta})(C - \sqrt{\Delta})(e^{\sqrt{\Delta}t} - 1)}{2B[C + \sqrt{\Delta} - (C - \sqrt{\Delta})e^{\sqrt{\Delta}t}]}$ with $\Delta = C^2 - 4AB$	$\frac{C + \sqrt{\Delta}}{-2B}$
(1.5)	1/2	$\frac{dT}{dt} = A + B\sqrt{T} + C(\sqrt{T})^2$	$\left\{ \frac{(B + \sqrt{\Delta})(B - \sqrt{\Delta})(e^{\sqrt{\Delta}t} - 1)}{2C[B + \sqrt{\Delta} - (B - \sqrt{\Delta})e^{\sqrt{\Delta}t}]} \right\}^2$ with $\Delta = B^2 - 4AC$	$\left\{ \frac{B + \sqrt{\Delta}}{-2C} \right\}^2$

Table 2. Sensitivity functions for total content $U_T(x)$ for each parameter $x = A, B$ or C , for eq. 1.1, and $\Delta = B^2 - 4AC$.

	x	$U_T(x)$	$\lim_{t \rightarrow \infty} U_T(x)$
(2.1)	A	$1 - \frac{2AC}{\sqrt{\Delta}} \left\{ \frac{1 + 2\sqrt{\Delta}te^{\sqrt{\Delta}t} - e^{2\sqrt{\Delta}t}}{(\sqrt{\Delta} - B)e^{2\sqrt{\Delta}t} + 2Be^{\sqrt{\Delta}t} - \sqrt{\Delta} - B} \right\}$	$1 + \frac{2AC}{\Delta - B\sqrt{\Delta}}$
(2.2)	B	$\frac{2B^2\sqrt{\Delta}te^{\sqrt{\Delta}t} - 2B\sqrt{\Delta}e^{\sqrt{\Delta}t} + B\sqrt{\Delta} + B^2 + B\sqrt{\Delta}e^{2\sqrt{\Delta}t} - B^2e^{2\sqrt{\Delta}t}}{(\sqrt{\Delta}e^{\sqrt{\Delta}t} - \sqrt{\Delta})(B + \sqrt{\Delta} - Be^{\sqrt{\Delta}t} + \sqrt{\Delta}e^{\sqrt{\Delta}t})}$	$-1 - \frac{4AC}{\Delta - B\sqrt{\Delta}}$
(2.3)	C	$\frac{-2AC}{\sqrt{\Delta}} \left\{ \frac{1 + 2\sqrt{\Delta}te^{\sqrt{\Delta}t} - e^{2\sqrt{\Delta}t}}{(\sqrt{\Delta} - B)e^{2\sqrt{\Delta}t} + 2Be^{\sqrt{\Delta}t} - \sqrt{\Delta} - B} \right\}$	$\frac{2AC}{\Delta - B\sqrt{\Delta}}$

Table 2 summarizes the relative sensitivity functions $U_T(x)$ for eq. 1.1, with $x = A, B$, or C . Table 3 gives $U_P(x)$ and $U_J(x)$, henceforth denoted as $U_P(x)$ and $U_J(x)$ respectively, which are for A, B and C simple derivatives of $U_T(x)$. For eqs. 1.2 and 1.3 the sensitivity functions can be found in the appendix.

Table 3. Sensitivity functions for the plant uptake rate $U_P(x)$, the leaching rate $U_J(x)$, and the input rate $U_I(x)$ for eq. 1.1.

	x	$U_J(x)$ leaching rate	$U_P(x)$ plant uptake rate	$U_I(x)$ input rate
(3.1)	A	$2U_T(A)$	$U_T(A)$	1
(3.2)	B	$2U_T(B)$	$U_T(B) + 1$	0
(3.3)	C	$2U_T(C) + 1$	$U_T(C)$	0

Soil heterogeneity

When we consider a field we may expect that certain variables vary as a function of horizontal position. To evaluate the field averaged response to cadmium deposition it is necessary to appropriately homogenize the variable local response. This may be done by considering the field as an ensemble of N parallel, non-interacting soil columns that differ only with respect to variables x_i , $i = 1, \dots, N$. Using stochastic theory, the variables x_i do not have fixed values, but are represented by probability density functions (PDFs). Measurements of soil properties are then one random realization of the stochastic process. An ensemble of measured values at different locations in the field is assumed to be representative for the PDF at each location (hypothesis of ergodicity) when the process is stationary.

The statistics of the PDF may be estimated using moment theory. Stochastic variables are underscored. The k -th raw moment, μ_k , of variable \underline{x} is defined as:

$$\mu_k = E \{ \underline{x}^k \} = \int_{-\infty}^{\infty} x^k f_x dx \quad (13)$$

in which f_x is the PDF of \underline{x} . By definition $\mu_0 = 1$. The k -th central moment, μ_k , of \underline{x} is:

$$\mu_k = E \{ (\underline{x} - E \{ \underline{x} \})^k \} = \int_{-\infty}^{\infty} (x - \mu_1)^k f_x dx \quad (14)$$

The expectation value of \underline{x} equals μ_1' which is the mean of the distribution, henceforth denoted as μ . The estimator of μ is m_x . The second central moment equals the variance of \underline{x} , denoted as σ^2 , estimated with s_x^2 . The coefficient of variation, CV (s_x/m_x), expresses the relative degree of variability.

Soil parameters like water conductivity or interstitial flow velocity were found to be approximately normally or lognormally distributed (Nielsen *et al.*, 1973, Russo and Bresler, 1981). The PDF for a lognormally distributed variable y is

$$f_y = [y\sigma_x\sqrt{2\pi}]^{-1} \exp\left\{-0.5\left[\frac{\underline{x} - \mu_x}{\sigma_x}\right]^2\right\} \quad (15)$$

with $\underline{x} = \ln y$, denoted as $y = \Lambda(\mu_x, \sigma_x^2)$.

Whereas normal distributions are symmetrical about the mean, a lognormal distribution is positively skewed. The lognormal distribution has multiplicative reproductive properties (Aitchison and Brown, 1966). If y is lognormally distributed, then

$$cy^b = \Lambda(a + b\mu_x, b^2\sigma_x^2) \quad (16)$$

where b and c are constants, and $c = e^a$. This simple reproductive property can be used to calculate the PDF of model output parameters from the mean and variance of the PDF of input parameters.

Model predictions are based on a large number of simulations using sample values drawn from the PDF of the spatially variable property (Monte Carlo simulation). These results can be used to calculate the mean, standard deviation, and frequency distribution for selected times.

Model Parameters

Because model sensitivity is highly dependent on the relative magnitude of all parameters involved it is important to use realistic parameter values. The model developed here is illustrated with cadmium accumulation in soil and uptake of cadmium by barley. Parameter values for a reference case were estimated from literature data.

The behaviour of cadmium in different Dutch soils was studied by Chardon (1984). He found that sorption can be adequately described with the Freundlich equation (eq. 6), which confirms results of Christensen (1984). The power n appeared to be reasonably constant for 12 different soils and different experimental conditions. However, the value of k_1 varied considerably. Part of this

variation could be explained deterministically by differences in pH between the experiments. Van der Zee and Van Riemsdijk (1987) derived a Freundlich sorption equation that accounts explicitly for differences of both pH and organic carbon content of the soil:

$$k_1 = k_a oc (H^+)^{-0.5} \quad (17)$$

We used eq. 17 to evaluate the effect of soil chemical variability on cadmium behaviour in an arable soil with parameter values obtained by Chardon (1984) for a sandy soil, assuming pH was spatially variable.

Table 4. Parameter values used in calculations.

k_a	adjusted Freundlich parameter ($\mu\text{mol}^{1-n} \text{ L}^n \text{ kg}^{-1}$)	analytical:	0.13
		numerical:	0.22
k_2	uptake rate constant for cadmium by barley (yr^{-1})		1.25×10^{-4}
n	Freundlich exponent (-)	analytical:	0.5
		numerical:	0.83
oc	organic carbon content ($\text{g g}^{-1} \%$)		2
pH	pH		5
v	interstitial flow velocity (m yr^{-1})		1
I_0	input rate of cadmium ($\text{g ha}^{-1} \text{ yr}^{-1}$)		50
L	plough layer thickness (m)		0.3
Y	yield of barley grains ($\text{kg m}^{-2} \text{ yr}^{-1}$)		0.5
ρ	soil bulk density (kg m^{-3})		1400

Plant uptake of cadmium was studied by Busch (1984), Kuboi *et al.* (1986) and Van Luit (1984). For different soils and crops they found a linear relationship between P and T . Van Luit (1984) provided a value for the plant uptake constant, k_2 , for barley grown on a sandy soil. To transform P to P_b , a value for the annual barley yield, Y ($\text{kg ha}^{-1} \text{ yr}^{-1}$), is obtained from De Jonge (1981).

Cadmium deposition was estimated from Davidson (1980) who summarized deposition rates for both rural and industrial areas. Rates up to $50 \text{ g Cd ha}^{-1} \text{ yr}^{-1}$ were observed in areas with combined industrial and agricultural activity. The flow velocity is based on the average Dutch rainfall surplus and an average soil water content of $0.3 \text{ m}^3 \text{ m}^{-3}$. Parameter values that were used in model calculations are given in Table 4.

Results and Discussion

A first impression of the model is obtained by considering the development of different rates as a function of time. This can be done analytically and yields results of Fig. 1. Initially the accumulation rate equals the input rate as most cadmium entering the soil is adsorbed. Under continuous input of cadmium the accumulation rate decreases, which is practically balanced by an increase in cadmium leaching out of the plough layer. At steady state the accumulation rate is zero.

Uptake of cadmium by plants comprises only a small fraction of the total amount of cadmium involved. Therefore, when the model is at steady state, almost all cadmium that enters the soil is leached. At steady state ($t \rightarrow \infty$) model behaviour may be evaluated with the analytical solution (eq. 1.1). Total accumulation in the rootzone, T , reaches 4900 mg m^{-3} , which equals with 3.5 mg kg^{-1} . Consequently, $J_t = 16 \text{ mg m}^{-3} \text{ yr}^{-1}$, corresponding with a cadmium concentration of $16 \text{ } \mu\text{g L}^{-1}$ in the steady state water flux, and $P_t = 0.6 \text{ mg m}^{-3} \text{ yr}^{-1}$, resulting in 0.36 mg kg^{-1} fresh weight.

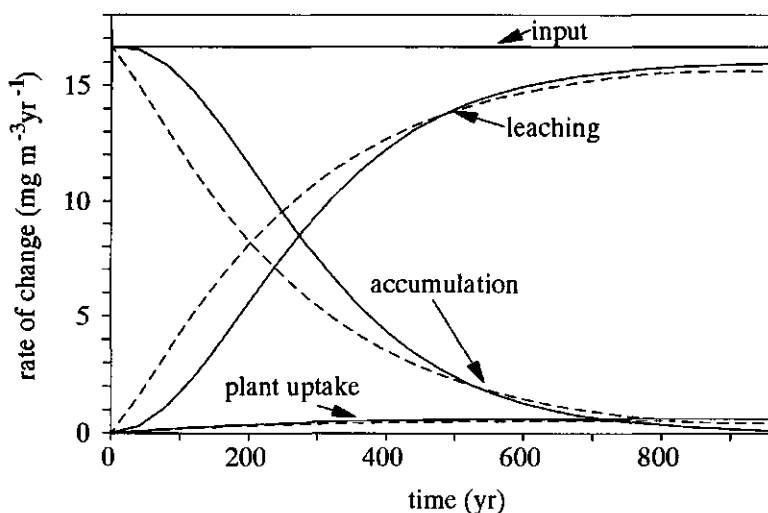


Fig. 1. Cadmium balance as a function of time for a sandy soil and uptake by barley. Solid lines: analytical solution; dashed lines: numerical solution of the balance equation.

For $n = 0.83$ (Table 4) the numerical solution of eq. 11 is used to simulate cadmium behaviour, and is also shown in Fig. 1. The differences between both solutions are significant and strictly due to the difference between the values of the sorption parameters.

The official Dutch reference values for good soil quality (Table 5) are exceeded in our example. This indicates that a situation where agriculture is practised in the vicinity of industrial activity will become unacceptable in view of environmental protection.

Table 5. Official Dutch reference values for cadmium in a sandy soil, groundwater, and cereals.

		corresponds with
in soil:	$0.45^a \text{ mg kg}^{-1} \text{ dry weight}$	T is 630 mg m^{-3}
in groundwater:	$1.5^a \text{ } \mu\text{g L}^{-1} \text{ water}$	J_i is $1.5 \text{ mg m}^{-3} \text{ yr}^{-1}$
in cereals:	$0.15^b \text{ mg kg}^{-1} \text{ fresh weight}$	P_i is $0.25 \text{ mg m}^{-3} \text{ yr}^{-1}$

a: Ministry of Housing, Physical Planning and Environment (1987)

b: Bleys (1987)

In practice we may expect the governing sorption parameters to vary with soil type and composition, while uptake parameters are dependent on crop and cultivar (Page *et al.*, 1981; Adriano, 1986). Moreover, the magnitude of cadmium deposition may vary with distance from the emission source. To evaluate which of these factors affect the response of the system and to what extent, the sensitivity functions derived for the analytical solution of the balance equation (Table 2 and 3) were used.

Fig. 2 shows the relative sensitivity U of model output parameters to changes in A , representing the cadmium input rate. Total content, T , and the plant uptake rate, P_i , are equally sensitive which follows from eq. 3.1. Since the sensitivity is larger than one for a broad range of values of A , implying a more than proportional increase in total content and plant uptake rate when the cadmium input rate becomes higher, it is evident that the magnitude of I_0 should be deduced from accurate data on cadmium loads of the soil. Especially for short term application of the model this is of prime importance.

Model sensitivity to changes in parameter B , which equals the plant uptake parameter k_2 , is almost constant as a function of time because plant uptake forms only a minor part of the cadmium balance in our example. $U_T(B)$ is approximately zero (eq. 2.2) and from eq. 3.2 it follows that in that case also $U_{J_i}(B)$ is close to

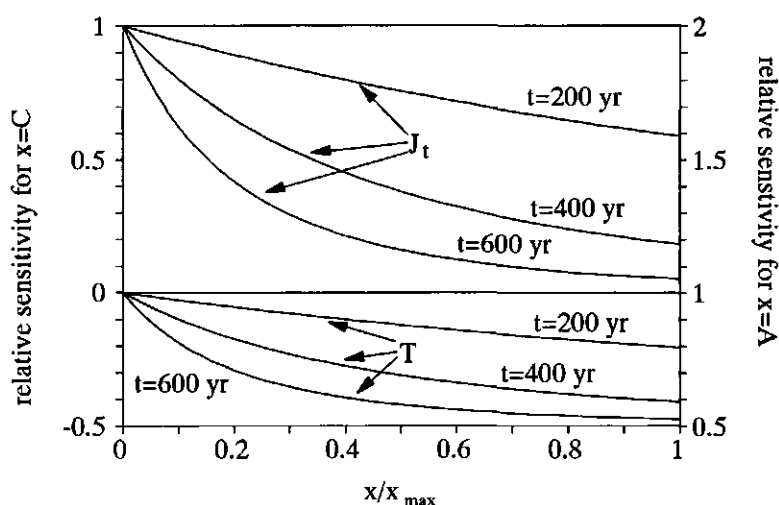


Fig. 2. Sensitivity of total cadmium content, T , and the leaching rate, J_t , for parameter $x = A$ (eq. 2.1 and 3.1 respectively), or $x = C$ (eq. 2.3 and 3.3 respectively) as a function of the relative value of x for three times, where x_{\max} equals twice the value of A and C obtained with the parameter values of Table 4.

zero. Logically $U_p(B)$ is close to unity (eq. 3.2). P_t is sensitive to variations in B , which implies that correct estimation of parameter k_2 is necessary for reliable predictions of crop quality from data on total cadmium contents of the soil.

Model parameter C lumps sorption and soil physical parameters and reflects solute mobility. As with parameter A , P_t and T are sensitive to changes in C to an equal extent. Sensitivity of the leaching rate to variations in parameter C is initially unity, but approaches zero at model equilibrium (Fig. 2). Low values of C , corresponding with high pH, high organic matter content, and a low flow velocity, result in higher sensitivity of the leaching rate as compared with high values of C . Total content and thus also the plant uptake rate display the opposite trend. Sensitivity increases as a function of time and as a function of C , being zero at $t = 0$ and when $C = 0$, and changing towards a value of -0.5 at infinite time and for large values of C . The negative sign of the sensitivity here indicates an increase in T (and P_t) when C decreases. Although variations of C are attenuated in T and P_t , because U is smaller than 1, variation of T may still be significant when variation of C is profound.

When ground water quality is of prime importance accurate knowledge of input rates and sorption parameters is necessary for reliable predictions of the

leaching rate. Soil-plant relationships do not give additional information in our example, because sensitivity of the leaching rate to changes in plant uptake parameters is very small. However, when crop quality is an important environmental factor that needs to be considered, the rate at which plants extract contaminants from soil is crucial. Additionally the value of parameter C becomes increasingly important in time, especially for low values that correspond with high accumulation rates. Although the input rate of cadmium is not as important for plant uptake as for leaching, this parameter still needs to be carefully estimated for reliable predictions of crop quality. When the effects of soil contamination on soil ecosystems are to be considered, total cadmium content of the soil can serve as an indicator. Here the input rate is especially important for short term analyses, and sorption and flow conditions become increasingly influential as long term effects are considered. As with ground water quality, plant uptake parameters can be disregarded for our example when attention is focussed on accumulation.

To analyze cadmium behaviour in a field stochastic analysis was done with the numerical approximation of eq. 11a using parameter values of Table 4 and a lognormally distributed water flow velocity with $m_v = 1 \text{ m yr}^{-1}$ and $s_v = 1 \text{ m yr}^{-1}$, which corresponds with $CV_v = 1$.

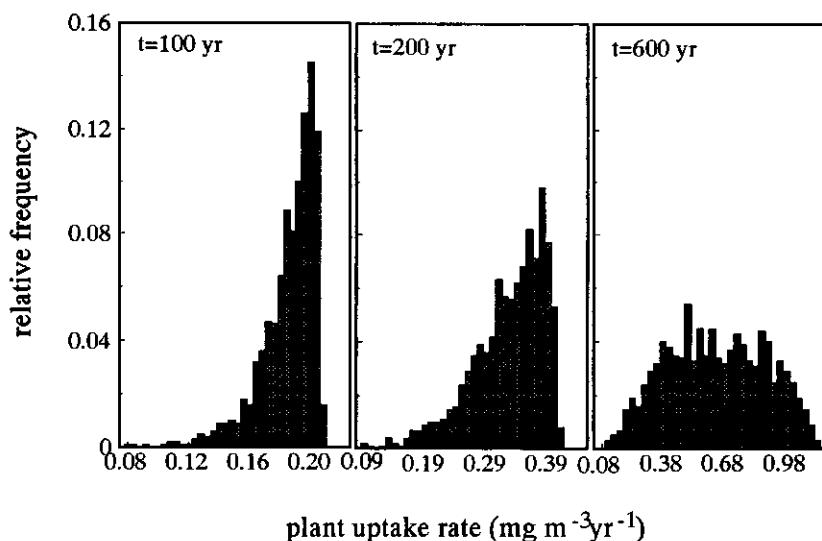


Fig. 3. Frequency distribution of the plant uptake rate, P_p , for $t = 100, 200$, and 600 yr. Note the different horizontal scales.

From sensitivity analysis we know that \underline{P}_c is insensitive to \underline{v} initially ($t = 0$) and becomes increasingly sensitive as a function of time. This is visualized in Fig. 3, where the width of each successive frequency distribution increases as a function of time. Also the shape of the distribution is time dependent, changing from an asymmetric peaked distribution with a tail extending out to smaller values towards a symmetric distribution, followed by a transformation into an asymmetric distribution with a tail oriented towards more positive values.

Using the barley yield, Y , cadmium contents of barley can be calculated from P_r . At $t = 140$ yr, m_p equals the reference value for crop quality of $0.15 \text{ mg Cd kg}^{-1}$ fresh weight (Table 5). But at this moment part the distribution exceeds this standard due to variability in the plant uptake rate. Because of the relatively low value of CV_p at this moment, exceedance of the reference value is not likely to occur much earlier.

At model equilibrium ($t \rightarrow \infty$) an approximately lognormal distribution has developed for \underline{T} and \underline{P}_c . The properties of this distribution cannot be deduced from input characteristics, since the balance equation is solved numerically. The structure of the solution can be understood though when we assume that plant uptake is negligible in the cadmium balance, which is reasonable for the example parameter values used. The balance equation then reduces to

$$\frac{dT}{dt} = A - CT^{1/n} \quad (23)$$

For t approaching infinity, $dT/dt = 0$, and eq. 23 can be solved and rewritten in terms of the original variables:

$$\underline{T} = \left[\frac{A}{C} \right]^n = \left[\frac{I_0 L}{\theta} \right]^n \rho k_1 \underline{v}^{-n} \quad (24)$$

For a homogeneous soil this results in $T = 4500 \text{ mg m}^{-3}$. In case the soil water flux is spatially variable, \underline{T} becomes a stochastic variable, whose characteristics can be deduced from the statistics of \underline{v} using eq. 16. This results in $\underline{T} = \Lambda(8.70, 0.691^2)$, corresponding with $m_T = 7600 \text{ mg m}^{-3}$ and $s_T = 6000 \text{ mg m}^{-3}$. Comparing this with the deterministic behaviour of the model we see that the average total cadmium content is considerably higher than the value obtained for a homogeneous field. Not only m_T , but also s_T is large, yielding a $CV_T = 0.79$.

It is evident that information on soil quality solely based on average values obscures actual field conditions as they are predicted for our example. Soil heterogeneity not only causes higher average accumulation of cadmium as compared with predicted cadmium contents for the corresponding homogeneous

case, but also implies variability in output parameters to such an extent, that average values alone do not contain enough information for a proper quality assessment.

The leaching rate J_L shows a different response to variation in ν , due to the non-linearity of sorption. CV_{J_L} equals CV_ν at $t = 0$, which follows from the linear relationship between ν and J_L . Sensitivity analysis showed a decrease in sensitivity as a function of time. This is reflected in Fig. 4. The width of the frequency distribution decreases as a function of time, and the shape of the distribution shifts from a lognormal distribution towards a symmetric distribution, then transforming into a negatively skewed and highly peaked distribution. The leaching rate will eventually reach an almost constant value, equal to the input rate minus plant uptake. From J_L the cadmium concentration in the leachate can be calculated. At $t = 40$ yr, the average cadmium concentration in the mean water flux equals the reference value for ground water quality of $1.5 \mu\text{g L}^{-1}$, while at that moment a large percentage of the distribution exceeds this value, due to large values of CV_{J_L} at that moment. Because of the large CV a significant exceedance of the reference value may be expected before this time as well. This indicates that large areas within a field may have too high leaching rates that may not be detected when only the average behaviour of cadmium is considered.

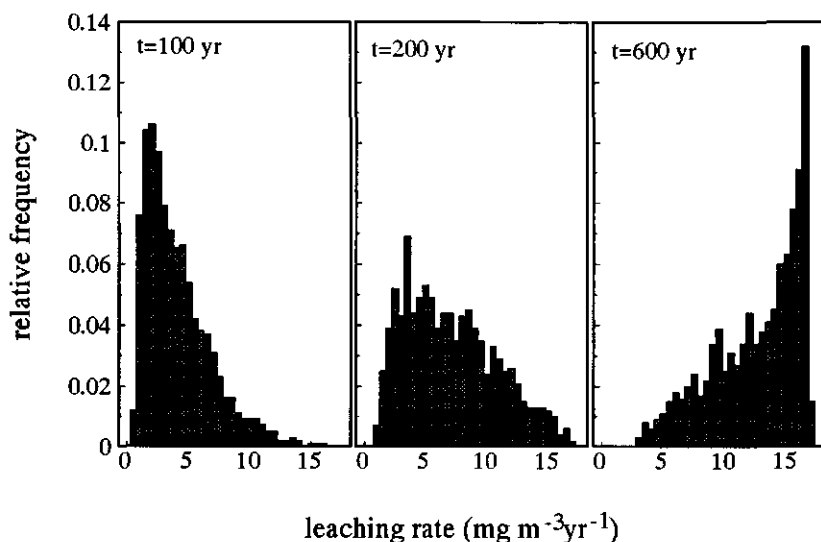


Fig. 4. Frequency distribution of the leaching rate, J_L , for $t = 100$, 200, and 600 yr.

Therefore predictions of ground water quality would benefit from reliable information on heterogeneity of soil parameters that influence leaching of reactive contaminants.

Until now we have only focussed on the effects of variable soil physical parameters, represented by a lognormally distributed flow velocity. But not only parameters that regulate solute flow may show variation in a field, also parameters that influence the sorption equilibrium may vary in the horizontal plane. Simulation of cadmium behaviour in a field that is heterogeneous with respect to soil chemical parameters may be done for a lognormally distributed proton activity and the parameter values of Table 4. With $m_{H^+} = 10^{-5} \text{ mol L}^{-1}$ and $s_{H^+} = 10^{-5} \text{ mol L}^{-1}$ a CV_{H^+} of 1 is assumed. Such variability of soil acidity can be observed in an arable field (Boekhold *et al.*, 1991), and a frequency distribution for H^+ is obtained with realistic values in the whole range of values. Although absolute values are somewhat different, the overall behaviour of the model for random H^+ is similar to model behaviour for random v (Fig. 5). Variability in soil chemical parameters as well as variability in soil physical parameters results in random output parameters, with a significant coefficient of variation and an average cadmium behaviour that is considerably different from an equivalent homogeneous field.

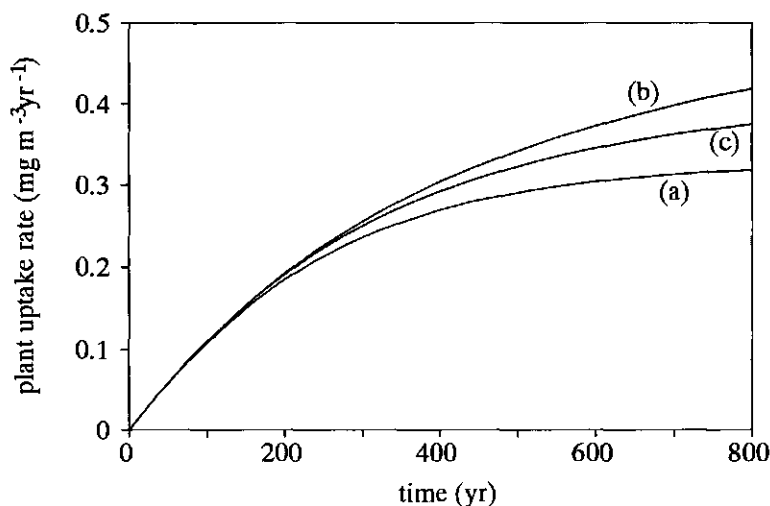


Fig. 5. Development of the average plant uptake rate, P_p , as a function of time for a homogeneous field (a), an a field that is heterogeneous with respect to soil physical (b) or soil chemical (c) parameters.

Summary and Conclusions

A balance equation was developed to study the long term behaviour of contaminants in the ploughed rootzone of a soil in agricultural use. For diffuse source deposition of cadmium onto a sandy soil, accumulation, leaching, and uptake of cadmium by barley were simulated. Initially all cadmium that enters the soil is adsorbed. The accumulation rate gradually decreases in favour of an increase in leaching rate. At steady state the accumulation rate reduces to zero and almost all cadmium that penetrates the soil surface is leached out of the rootzone. Uptake of cadmium by barley appeared to be very small relative to the annual cadmium load of the soil. In our example official Dutch reference values for good soil, ground water, and crop quality are exceeded. This indicates that in the case of continuing cadmium deposition at a rate that is commonly observed in areas close to industrial activity, adverse effects on environmental quality may be expected.

The response of the model to variations in input parameters was analyzed using analytical solutions of the sensitivity function. The leaching rate appeared to be very sensitive to the cadmium input rate and to flow and sorption parameters. In our example the plant uptake rate is too small to have significant effects on the predicted leaching rate. In contrast, crop quality predictions are sensitive to the plant uptake rate parameter. Moreover, the plant uptake rate is increasingly sensitive to flow and sorption parameters as a function of time. Total cadmium content of the soil may be of interest in studies on the functioning of soil ecosystems. For prediction of cadmium accumulation the input rate is of paramount importance for short term analyses. However, if long term effects are also considered the total cadmium content becomes sensitive to variation in flow and sorption parameters as well.

The effect of soil heterogeneity on model predictions was studied using stochastic theory. Calculated average values were considerably higher than deterministic analysis predicted, when the soil water flux was represented by a lognormal frequency distribution with a CV_p of 1. Moreover, variability of soil hydraulic properties also induced partial exceedance of reference values for soil, ground water, and crop quality before the field average has reached these values. Prediction of ground water and crop quality may gain from this kind of information, because not only the average behaviour of contaminants is estimated, but also extreme events are considered.

Simulation of cadmium behaviour in a field that is heterogeneous with respect to soil chemical properties yielded similar results as for a field that is heterogeneous in soil hydraulic properties. So, both soil chemical and soil physical heterogeneity affected predicted cadmium behaviour considerably.

At the moment environmental quality standards are usually expressed in terms of a single value that may not be exceeded. However, because of the highly heterogeneous nature of most field soils even on a scale of meters (Boekhold *et al.*, 1991), it may be more appropriate to express soil, ground water, and crop quality in probabilistic terms, i.e. expressing quality standards as the probability that the standard will be exceeded. Scenarios for soil management in contamination problems may give a better understanding of the actual situation when soil heterogeneity is accounted for explicitly.

Appendix

Table A1. Sensitivity functions for total content $U_T(x)$ for each parameter $x=A, B$ or C , for eq. 1.2

x	$U_T(x)$	$\lim_{t \rightarrow \infty} U_T(x)$
A	$\frac{1}{2} + \frac{2\sqrt{A}\sqrt{B+C}te^{2\sqrt{A}\sqrt{B+C}t}}{e^{4\sqrt{A}\sqrt{B+C}t} - 1}$	$\frac{1}{2}$
$B+C$	$-\frac{1}{2} + \frac{2\sqrt{A}\sqrt{B+C}te^{2\sqrt{A}\sqrt{B+C}t}}{e^{4\sqrt{A}\sqrt{B+C}t} - 1}$	$-\frac{1}{2}$

Table A2. Sensitivity functions for total content $U_T(x)$ for each parameter $x=A, B$ or C , for eq. 1.3

x	$U_T(x)$	$\lim_{t \rightarrow \infty} U_T(x)$
A	$\frac{A}{A - e^{-(B+C)t}}$	1
$B+C$	$\frac{(B+C)te^{-(B+C)t}}{A - e^{-(B+C)t}} - 1$	-1

Table A3. Sensitivity functions for the plant uptake rate $U_P(x)$, leaching rate $U_f(x)$ and the input rate $U_I(x)$

x	$U_f(x)$ leaching rate	$U_P(x)$ plant uptake rate	$U_I(x)$ input rate
for (1.2)			
A	$2U_T(A)$	$2U_T(A)$	1
$B+C$	$2U_T(B+C) + (B+C)/C$	$2U_T(B+C) + (B+C)/B$	0
for (1.3)			
A	$U_T(A)$	$U_T(A)$	1
$B+C$	$U_T(B+C) + (B+C)/C$	$U_T(B+C) + (B+C)/B$	0

Chapter 8
**Field Scale Variability of Cadmium and Zinc in
Soil and Barley**

Co-author: Sjoerd E.A.T.M. Van der Zee

Field Scale Variability of Cadmium and Zinc in Soil and Barley

Abstract

CaCl₂-extractable soil Cd and Zn contents have been suggested as a measure of bioavailability. To investigate the ability of this measure to reflect spatial patterns of Cd and Zn concentrations in barley (*Hordeum vulgare* L.) in an arable field, plant and soil samples were taken from a 0.5 ha area sandy soil contaminated with Cd and Zn. Cd and Zn contents in barley and yield were spatially variable. Yield was low, which may have been caused by Zn toxicity or atrazine turnover. For Cd, CaCl₂-extractable soil contents explained only 17% of the variation in Cd contents in grain, and for Zn no significant correlation was observed. Nevertheless, surface plots of CaCl₂-extractable soil contents and contents of barley grain illustrated their corresponding spatial patterns. Despite the poor linear correlation between CaCl₂-extractable soil-Cd and grain-Cd, a stochastic model for long term behaviour of Cd in field soils predicted observed variability in Cd contents of barley grain well from spatial variability of soil pH and organic matter content. The probabilistic model predicted behaviour of Cd in terms of probability, and was more appropriate than the deterministic approach.

Introduction

Leaching and plant uptake of contaminants such as heavy metals are environmental risks associated with soil pollution. Plant uptake of heavy metals from soil may lead to either yield reduction or to an unacceptable quality in view of human and/or animal health. Whereas total heavy metal contents of soil are essential to assess the extent of soil pollution, they do not give insight into the significance of the observed contamination in terms of groundwater and crop quality. Both leaching and plant uptake are controlled by the heavy metal concentration in the soil solution. This is the phase that is transported to lower soil layers and from which plants extract water and nutrients.

Methods of soil extraction have been developed that are assumed to reflect heavy metal mobility and bioavailability. Significant correlations between extractable soil Cd, using different extractants and procedures, and tissue concentrations of plants grown under greenhouse conditions have been reported (Street *et al.*, 1977; Bjerre and Schierup, 1985; Filipinski and Kuntze, 1990, Smilde *et al.*, 1992). Extraction with a neutral salt solution seemed to be the most

promising with respect to correlation with plant tissue concentrations (Sauerbeck and Styperek, 1985). Whereas NaNO_3 extracted little Cd from neutral soils, the amounts of Cd in a CaCl_2 -extract were considerably higher, reflected soil properties well, and were proportional to plant Cd concentrations. Because already 1 or 2 mg Cd kg^{-1} in certain soils may be critical, the most important advantage of CaCl_2 seems that it extracts sufficiently large fractions even at these low contamination levels.

The heavy metal concentration in solution is primarily regulated by pH. Concentrations of Cd in the soil solution are larger at lower pH. Extraction of soil with CaCl_2 reflected this dependency on pH (Boekhold and Van der Zee, 1992). However, this increased solubility cannot be directly considered as an increase in bioavailability. During vegetative growth absorption of Cd by plants is enhanced with increasing pH. Therefore, the extent to which Cd uptake increases with decreasing pH in soil will be less than expected based solely on concentrations in the soil solution (Hatch *et al.*, 1988). The same tendency can be expected for other competing cations, e.g. Zn.

Whereas in pot experiments significant correlations are found between extractable Cd and Cd in plant tissue, under natural growth conditions it will be more difficult to relate plant uptake to soil factors. Contrary to pot experiments, the soil volume associated with individual plants is difficult to assess in field soils, because soil roots may extend to distances far away from the stem, and roots respond on local soil conditions in their uptake and growth pattern (De Willigen and Van Noordwijk, 1987)). Eriksson (1990) reported that the content of CaCl_2 -extractable Cd explained 42% of the variation in Cd contents of oat grain in samples taken at several locations throughout Sweden, whereas no significant correlation was found with total Cd contents of the soil.

A problem with field soils is that they are heterogeneous with respect to flow parameters (Biggar and Nielsen, 1976), soil chemical parameters (Van der Zee, 1988) and crop yield (Bresler, 1989). Since local soil chemical conditions determine the Cd concentration in the soil solution, which may be thought of as an indicator for bioavailability, Cd contents of plants in the field are expected to be variable as well. By acknowledging spatial variability, it may be possible to estimate the variability in Cd concentrations in the plant from the inherent variability of soil parameters. Risks of exceedance of threshold levels for heavy metals in plants may then be better expressed in terms of probability instead of fixed values.

The purpose of this investigation was to study spatial differences in Cd and Zn contents in barley and soil, and to survey possible similarities in spatial

behaviour of Cd and Zn in soil, and Cd and Zn in barley. Linear correlation as well as kriged contour plots were used to compare field scale trends of these parameters. By using a model that describes long term effects of diffuse source atmospheric deposition of Cd onto a heterogeneous soil, the ability to predict field scale variability of cadmium contents of barley from field scale variability of soil chemical parameters was discussed.

Materials and Methods

Field Sampling

The sampled field is located in the 'Kempen', a region in the south of the Netherlands and the north of Belgium. The area is contaminated with Zn and Cd due to atmospheric deposition after emission by zinc ore smelters in the region. The field is privately owned and has been under cultivation for more than 50 years. Soil sampling and analysis was described by Boekhold and van der Zee (1992), only relevant aspects are summarized here.

An area of 0.5 ha sandy soil (Typic Haplaquod) was sampled, at least 50 m from the field boundaries. Soil samples were taken from a sampling grid of size 17×8, with 6 m grid node distance. Another 30 samples were randomly selected at a distance of 2 m from the nearest grid node to analyse spatial variability at a scale smaller than 6 m. In addition to these 166 soil samples, full-grown and ripened barley samples were taken, according to a sampling scheme as depicted in Figure 1. A total of 80 grain samples and 64 straw samples were analyzed.

Soil samples were mixed samples of 6 individual 0.20 m auger samples from an area of 0.1 m². This sampling scheme was chosen because it provides average data for a soil volume believed to be more representative in view of root system development than individual auger samples. All soil samples were analyzed on total extractable Cd and Zn content (Cd_T and Zn_T respectively) by extraction with 0.43 M HNO₃ for 2 hours at a solid:solution ratio of 1:10. Soluble Cd and Zn contents (Cd_s and Zn_s respectively) were defined as the amount of Cd and Zn extracted with 0.01 M CaCl₂-solution at a solid:solution ratio of 1:10 for 20 hours. In the latter soil suspension pH was measured. After centrifugation at 1000 g, Cd and Zn contents in the extracts were measured in the supernatant with an Atomic Absorption Spectrophotometer (Instrumental Laboratory AA/AE spectrophotometer S11 with Smith Hieftje background correction). An air-acetylene flame was used at a wavelength of 228.8 nm for Cd and 213.9 nm

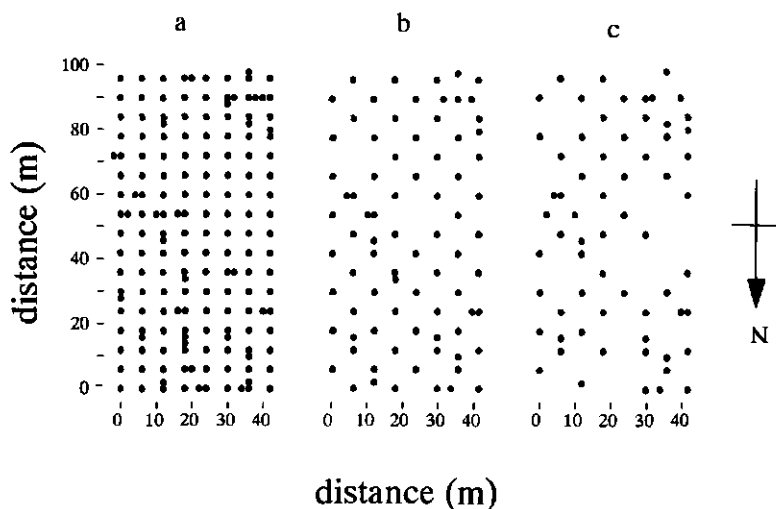


Fig. 1. Sampling grid used for soil and plant sampling.

for Zn (Walinga *et al.*, 1989). Organic matter content was determined as the organically bound carbon content according to Kurmies (Houba *et al.*, 1988), hereafter referred to as *oc*.

At maturity, all plants rooting within a circle pvc tube with a diameter of 0.7 m were cut off 10 cm above the soil and dried at 70° C for 3 days. After measuring total dry weight, grain was separated from straw, and grain was weighed. Ground grain and straw samples were digested with a mixture of HNO₃, HClO₄, and H₂SO₄ in a volume ratio of 40:4:1. After filtration, the Cd and Zn contents of the destruates (Cd_g and Zn_g respectively) were measured with AAS. In each destruction series standardized samples with known Cd and Zn contents and blanks were included.

Kriging

The kriging method of interpolation estimates values for any coordinate position within the domain considered without bias and with minimum variance (Matheron, 1971). A kriged or estimated value is found by attributing weights, λ_i , to neighbouring measured values. The correlation structure of the data, comprised in the semivariogram function, is used to obtain the weights λ_i .

The degree of autocorrelation between adjacent points in space separated by a distance vector **h** can be expressed as the semivariance, $\gamma(\mathbf{h})$:

$$\gamma(\mathbf{h}) = \frac{\sum_{i=1}^{N(\mathbf{h})} [z(x_i) - z(x_i + \mathbf{h})]^2}{2N(\mathbf{h})} \quad (1)$$

where $N(\mathbf{h})$ is the number of data pairs $z(x_i)$, $z(x_i + \mathbf{h})$ separated by a distance vector \mathbf{h} . Usually $\gamma(\mathbf{h})$ is averaged over several distances forming a distance class. Semivariance analysis requires that the intrinsic hypothesis holds for the data, i.e. the mean and variance of increments $(z(x_i) - z(x_i + \mathbf{h}))$ are stationary (Journel and Huijbregts, 1978).

Once semivariances are obtained for several distance classes, they can be fitted to one of the available semivariogram models. These models describe the calculated semivariances continuously, and must be definite positive. They serve as a basis to estimate the kriging weights, λ_i , used to estimate values at unvisited locations ($\hat{z}(x_0)$):

$$\hat{z}(x_0) = \sum_{i=1}^N \lambda_i z(x_i) \quad (2)$$

The weights λ_i are chosen such that they sum to 1, thereby ensuring that the estimate is unbiased and minimizes the variance. The latter condition is obtained when

$$\sum_{j=1}^N \lambda_j \gamma(x_i, x_j) + \psi = \gamma(x_i, x_0) \quad \forall i \quad (3)$$

where $\gamma(x_i, x_j)$ is the semivariance over the distance \mathbf{h} between the data points x_i and x_j , and $\gamma(x_i, x_0)$ is the semivariance belonging to the data point x_i and the unknown point x_0 . The Lagrange parameter ψ is associated with the minimisation process.

When estimates are made for an area or block, V , that is larger than the support of the individual observations, kriged estimates for the block are weighted averages of neighbouring observations. The semivariances between the x_i 's and x_0 (in center of block) of Eq. (3) are then replaced by the average semivariances between the x_i 's and all points in block V . For more details see Journel and Huijbregts (1978).

Prediction of Long-Term Behaviour of Cd in Field Soils

We developed a model for evaluating long-term effects of Cd deposition onto a field soil (Boekhold and Van der Zee, 1991). The model consists of a material balance for Cd in the root zone of an arable field as a function of time:

$$\frac{dT}{dt} = \frac{dI}{dt} - \frac{dP}{dt} - \frac{dJ}{dt} \quad (4)$$

where T is total Cd content in the soil ($\mu\text{mol m}^{-3}$), t is time (yr), I is input of Cd ($\mu\text{mol m}^{-3}$), P is plant uptake of Cd ($\mu\text{mol m}^{-3}$), and J is leaching of Cd ($\mu\text{mol m}^{-3}$).

Input of Cd at the soil surface is assumed to be uniform for the entire field, and constant in time ($dI/dt = I_0$). This is an assumption that applies well to the sampled field, as contamination was due to diffuse source atmospheric deposition during almost a century. The soil is considered to be perfectly mixed vertically, e.g. due to ploughing of the root zone. Plant uptake was modelled as a linear function of the total accumulated amount of Cd in soil ($dP/dt = k_2 T$). As was discussed in the introduction, a relationship with c is more plausible, but literature provided no parameter values for a Cd uptake model for barley. Van Luit (1984) analyzed Cd uptake by barley from soil from the Kempen area, and provided a value for parameter k_2 .

The leaching flux depends on the Cd concentration in the soil solution and the soil water flow velocity:

$$\frac{dJ}{dt} = \frac{\theta v c}{L} \quad (5)$$

where θ is the volumetric water content of the soil ($\text{m}^3 \text{m}^{-3}$), v is the interstitial water flow velocity (m yr^{-1}), c is the Cd concentration in solution ($\mu\text{mol m}^{-3}$), and L is the rooting depth (m). Sorption of Cd determines the equilibrium Cd concentration in solution, as described by a nonlinear Freundlich sorption isotherm:

$$q = k_1 c^n \quad (6)$$

in which q is the adsorbed amount (mg kg^{-1}), k_1 is the Freundlich adsorption parameter, and n is the Freundlich exponent, where $0 < n \leq 1$. Sorption equilibrium is dependent on the soil pH and organic carbon content (oc) of the soil. Boekhold and Van der Zee (1992) found that implementation of empirical factors in Eq. (6) improved predictions of Cd behaviour for this soil considerably:

$$q = k^* oc (H^+)^{-0.5} c^n \quad (7)$$

Here, k^* is the scaled Freundlich adsorption constant, and (H^+) is the proton activity in solution (mol L^{-1}). Since $T = \rho q + \theta c$, where ρ is soil bulk density (kg m^{-3}), c can be expressed in terms of T . When the adsorbed amount is large as compared to the concentration in solution, the following nonlinear differential equation develops as a function of T :

$$\frac{dT}{dt} = I_0 - k_2 T - \frac{\theta v}{L} \left(\frac{1}{\rho k^*_{oc} (H^*)^{-0.5}} \right)^{1/n} T^{1/n} \quad (8)$$

Eq. (8) was solved analytically for $n=0.5$ and $n=1$ (Boekhold and Van der Zee, 1991); numerical techniques must be used for other values of n .

Soil spatial variability in the horizontal plane may be included in this balance model by considering a field as an ensemble of parallel vertical non-interacting homogeneous soil units. These units are all the same, except for the spatially variable soil parameters. These parameters are considered to be random variables, characterized by a probability density function (PDF) instead of a fixed value. This implies that output parameters are characterized by a PDF as well. Because of the nonlinearity of Eq. (8), these latter PDFs cannot be inferred directly from the input-PDF. By assuming statistical homogeneity and ergodicity of the field, the effect of random soil parameters may be evaluated using Monte Carlo simulation. Then, many values are drawn from the PDF of the random parameter, and each value is used to calculate Cd accumulation with Eq. (8). With this model it can be assessed to what extent a certain degree of variability of model input parameters results in variability of predictions.

Results and Discussion

The average yield and Cd and Zn contents of barley are summarized in Table 1, together with their standard deviation, and the standard deviation of duplicate measurements. All parameters are spatially variable, since the standard deviation due to measurement errors was always considerably smaller than the standard deviation in the field. The data were not systematically biased, as evidenced from parallel analysis of standardized samples (not depicted).

The Cd content of barley grain is above the Dutch quality standard for cereals (0.15 mg kg^{-1}). For Zn no such standard exists. Average total yield is low as compared with the average yield of barley grain in the Netherlands, which equals approximately 5000 kg ha^{-1} (Bosch, 1985)). Moreover, variability of yield is considerable, with a coefficient of variation (CV) of 50%. The level and variability of yield could not be explained by (spatial differences in) nutrient (N and P) availability (data not presented).

Table 1. Mean (\bar{x}), standard deviation (SD), average standard deviation of duplicate measurements (SD_d), coefficient of variation (CV), minimum, and maximum values of yield of barley grain (Y_g) and straw (Y_{st}), Cd content of grain (Cd_g) and straw (Cd_{st}), and Zn content of grain (Zn_g) and straw (Zn_{st}). Values for soil are from Boekhold and Van der Zee (1992).

	\bar{x}	SD	SD_d	CV
Grains (N=80):				
Y_g (kg ha ⁻¹)	1370	680	-	0.50
Cd_g (mg kg ⁻¹)	0.33	0.07	0.012	0.21
Zn_g (mg kg ⁻¹)	95	12	1.3	0.12
Straw (N=64):				
Y_{st} (kg ha ⁻¹)	1760	710	-	0.40
Cd_{st} (mg kg ⁻¹)	1.35	0.36	0.07	0.27
Zn_{st} (mg kg ⁻¹)	271	52	9.9	0.19
Soil (N=166):				
Cd_T (mg kg ⁻¹)	4.0	0.83	0.09	0.20
Cd_s (mg kg ⁻¹)	0.38	0.12	0.04	0.33
Zn_T (mg kg ⁻¹)	209	38	5	0.18
Zn_s (mg kg ⁻¹)	21	9.0	1.2	0.43

Barley growth may have been stressed by several factors that are operative in a uncontrolled, contaminated field site. Growth may have been repressed by Zn toxicity. Zn concentrations in barley grains and yield were significantly negatively correlated (Table 2). Davis *et al.* (1978) found an upper critical toxicity range of 160-320 mg Zn kg⁻¹ in barley tissue at the five-leaf stage. Since we measured an average of 95 mg kg⁻¹ for Zn_g and 271 mg kg⁻¹ for Zn_{st} , the phytotoxic concentration for Zn may have been exceeded. For Cd, Davis *et al.* (1978) found a toxicity range of 14-16 mg kg⁻¹ in tissue. This is a factor 10 higher than the concentrations measured in our field (Table 1), hence Cd-toxicity is not plausible.

Table 2. Correlation matrix soil and plant data (N=59).

	pH	oc	Cd _T	Cd _s	Zn _T	Zn _s	Cd _g	Zn _g	Y _g	Cd _{st}	Zn _{st}	Y _{st}
pH	1											
oc	-	1										
Cd _T	.44**	-	1									
Cd _s	-.86**	-	-	1								
Zn _T	.59**	-	.90**	-.30*	1							
Zn _s	-.91**	-	-	.93**	-.30*	1						
Cd _g	-.33*	-	-	.41**	-.28*	.32*	1					
Zn _g	-	-.28*	-.58**	-	-.55**	-	.45**	1				
Y _g	-	.37**	.26*	-	-	-	-.41**	-.61**	1			
Cd _{st}	-	-	-	-	-	.26*	-	-	-	1		
Zn _{st}	-	-	-	-	-	-	-	-	-	.68**	1	
Y _{st}	-	.53**	-	-	-	-	-.36**	-.40**	.73**	-	-	1

-: not significant ($p > 0.05$)

*: $p \leq 0.05$

** : $p \leq 0.01$

Another factor that may have caused growth stress are residues of atrazine, used in the year preceding barley growth for pest management in corn. Such adverse effects of atrazine are often encountered in the year following corn production. We considered analysis of these field data on soil Cd and Zn behaviour and Cd and Zn contents of barley relevant, even though barley growth may have matured under considerable stress. Causal relationships cannot be deduced from these data, but the ability of soil measures to reveal Cd and Zn concentrations in plants under typical growth conditions can be examined.

Table 2 gives the correlation matrix of soil and plant parameters for the 59 locations for which all data were available. Correlation between soil parameters was discussed by Boekhold and Van der Zee (1992), and will not be repeated here. In general, correlation between soil and plant parameters was poor. Total Cd contents of the soil were not correlated with Cd concentrations in barley grains and straw. CaCl_2 -extractable Cd contents of the soil were significantly correlated with Cd concentrations in barley grains, but explained only 17% of the variation of Cd_g . Negative correlation between total Zn contents in soil and Zn concentration in barley grain indicated that total Zn contents of the soil were not indicative for Zn concentrations in grains. No significant correlation was found between Zn_s and Zn concentrations in barley grain and straw. This poor correlation is in contrast with literature cited earlier, which suggests that Cd_s and Zn_s are representative indicators for bioavailability of Cd and Zn.

Table 3. Semivariogram model parameters.

variable	Cd_g	Zn_g	Cd_s	Zn_s
semivariogram				
model	exponential	exponential	exponential	exponential
nugget	0	20	0.003	15
sill	0.005	115	0.014	75
range (m)	20	40	40	40

In pot experiments soil is homogenized, and roots are confined to a fixed and known soil volume and composition. In field soils, roots may develop in a non-regular manner because of soil heterogeneity. Moreover, due to differences in availability of nutrients at the scale of individual plants, root density and activity for one plant may be highly variable as well (De Willigen and Van

Noordwijk, 1987). Although a sampling strategy was developed in an attempt to handle this problem by analyzing a mixed soil sample composed of 6 individual auger samples of 20 cm depth from an area of 0.1 m^2 , the poor correlation between soil and plant parameters may be due to the difficulty to define the representative soil volume used by the plants in field situations. Local variability of root density and root activity, and variability of yield may have caused this lack of correlation as well. Variability of yield made any inference on plant uptake mechanisms speculative.

Despite the poor linear correlation, which compares point values of soil parameters with point values of plant parameters, a more global approach by comparing spatial patterns may be more appropriate in a field situation.

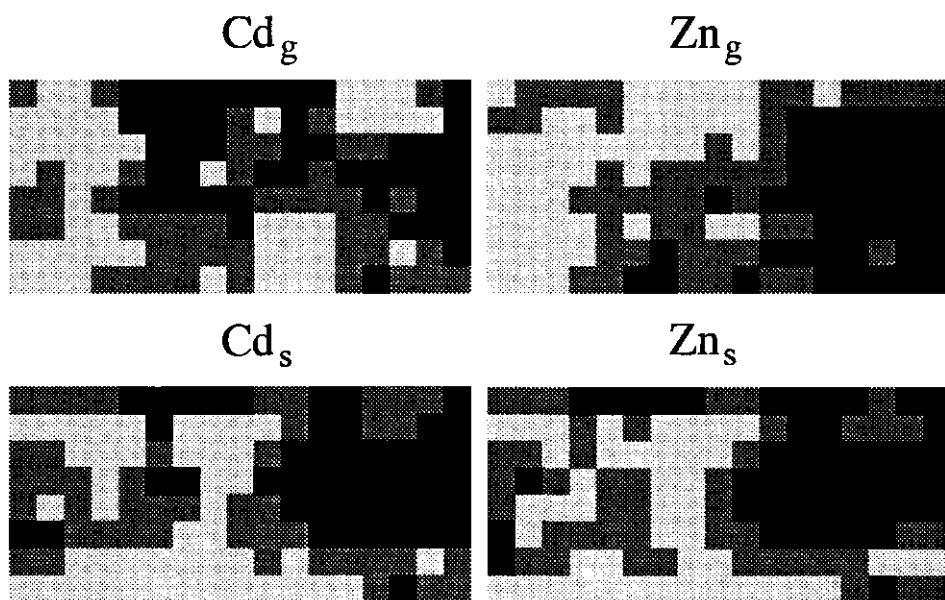


Fig. 2. Surface plots of CaCl_2 -extractable soil Cd and Zn contents and Cd and Zn contents in barley grains.

Block kriging on $6 \times 6 \text{ m}$ blocks with the estimated semivariogram models (Table 3) yielded plots of the average Cd and Zn contents over the blocks within the field covered by the sampling grid. In Figure 2 surface plots of Cd_s and Cd_g , and Zn_s and Zn_g show that although correlation between soil and plant parameters was poor, CaCl_2 -extractable soil contents indicated spatial patterns of concentrations in plants. High levels of Cd are found in the center top and right part of

the respective plots, whereas low levels are found in the left and bottom part. For Zn, concentrations in the left part of the plot are low for both Zn_s and Zn_g , and high in the right part of the plot. Field scale trends of $CaCl_2$ -extractable Cd and Zn contents of soil were comparable to field scale trends of Cd and Zn concentrations in barley grains.

Linear correlation between Cd_s and Cd_g was poor. Erroneous assumptions on local homogeneity of soil, root density, and root activity may have caused this poor correlation. When local errors are not systematic, a stochastic analysis without an explicit relation between variates and space may be more appropriate for field scale analysis of soil processes. The data presented above are well suited to evaluate the ability of the model of Boekhold and Van der Zee (1991) to predict spatial variability of Cd contents in barley grain from spatial variability of soil parameters.

Table 4. Parameter values used for model calculations.

k_2	Cd uptake rate constant for barley (yr^{-1})	1.25×10^{-4}
k^*	adjusted Freundlich parameter ($mg^{1-n} L^n kg^{-1}$)	0.025
n	Freundlich exponent (-)	0.76
ν	interstitial water flow velocity ($m yr^{-1}$)	1
(H^+)	proton activity in solution ($mol L^{-1}$)	$\bar{x} = 1.74 \times 10^{-6}$ SD = 1.46×10^{-6}
I	Cadmium input at the soil surface ($g ha^{-1} yr^{-1}$)	200
L	rooting depth/ploughing depth (m)	0.2
oc	organic carbon content ($mg kg^{-1}$)	$\bar{x} = 25.1$ SD = 2.9
ρ	soil bulk density ($kg m^{-3}$)	1400

Input data for the model are chosen such that they are applicable to the sampled field (Table 4). The soil water flux was not measured, but estimated by the average Dutch annual rainfall surplus. Since pH and oc varied spatially in the sampled field, they were considered to be random variables. The measured frequency distributions of H^+ and oc were fitted to a lognormal frequency distribution with no correlation between the two variates (Table 2). Soil bulk density was estimated from the average bulk density in sandy soils. The Freundlich sorption parameters were determined from measured sorption isotherms for two soil samples from the field, after correction for pH and oc (Boekhold and Van der Zee, 1992).

No data were available of Cd input at the soil surface. Estimation of Cd input was done by dividing the Cd enrichment of the soil, as compared with the natural background concentration for Cd in sandy soils, by the estimated years of Cd emission by the Zn smelters in the region. Since the highest Cd content in the field was measured as 6.27 mg kg^{-1} in a soil sample of 0-0.2 m depth, the deposition rate must have been at least $200 \text{ g ha}^{-1} \text{ yr}^{-1}$ for 80 years. This is a conservative estimate, since no Cd losses from the soil (e.g. leaching and/or removal by harvesting) are accounted for.

Model calculations are done for 70, 80, 90, and 100 years. Comparison of predicted values (Table 5) and measured values in the field (Table 1) shows that averaged predicted values for Cd_T after 80 years correspond best with averaged measured Cd_T in the Kempen field. Coefficient of variation, however, is higher in reality than predicted by the model. Standard deviation of Cd_g is predicted well by the model, but because average values are slightly overestimated, the CV is underestimated.

Table 5. Calculated mean (\bar{x}), standard deviation (SD) and coefficient of variation (CV) for total Cd content (Cd_T) and Cd content of barley grains (Cd_g) for four times.

time (yr)	Cd_T mg kg^{-1} soil			Cd_g mg kg^{-1} grain		
	m	SD	CV	m	SD	CV
70	3.8	0.44	0.12	0.40	0.05	0.12
80	4.1	0.55	0.13	0.43	0.06	0.13
90	4.4	0.66	0.15	0.47	0.07	0.15
100	4.7	0.76	0.16	0.50	0.08	0.16

Comparison of predicted and measured frequency distributions of Cd_g (Figure 3 and 4) shows that the range of predicted values corresponds well with the range of measured values. The model predicted Cd concentrations in barley independently from the field observations of Cd_g . Exact agreement between model calculations and field data is not achieved nor expected. The model is a simplified description of the soil system, and parameter values for the model are only rough estimates. Nevertheless, this simple balance model describing long term behaviour of Cd in an arable field does yield relevant predictions when compared

with field measurements. General behaviour of Cd in an arable field is predicted fairly well in terms of Cd accumulation and Cd-concentrations in barley, using a probabilistic model.

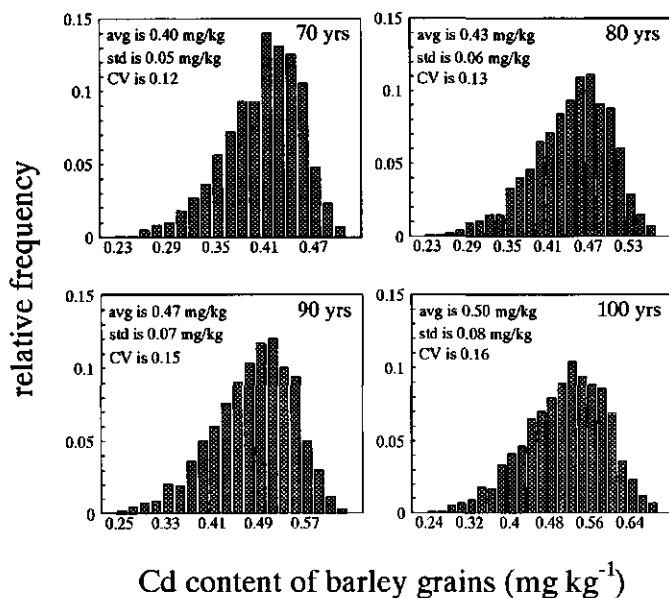


Fig. 3. Predicted frequency distribution of Cd content in barley grains, Cd_p, for four times.

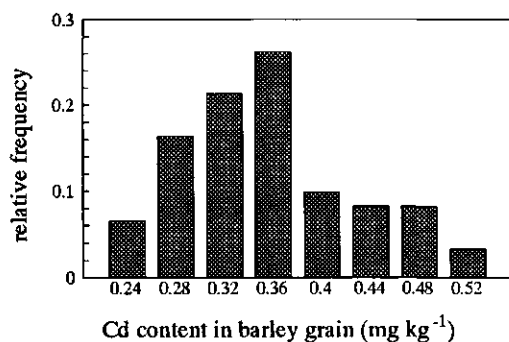


Fig. 4. Measured frequency distribution of Cd contents in barley grains.

Conclusions

In an arable field contaminated with Cd and Zn, soil and barley samples were taken from about 0.5 ha. Cd and Zn contents in barley grain were spatially variable. Cd contents were above the Dutch quality standard for cereals. Yield was low, and variability of yield was large. This could not be explained by differences in nutrient availability in the field, but may have been caused by Zn toxicity. The possible effect of atrazine residues, used in the previous year for pest management in corn, was acknowledged. Because stress from atrazine is regularly encountered in the year following corn production, we considered assessment of the relationships between soil Cd and Cd in barley under these growth conditions relevant.

Cd and Zn concentrations in barley grain were poorly correlated with CaCl_2 -extractable Cd and Zn contents of the soil. This disappointing result (in view of literature findings) may be due to erroneous assumptions regarding the soil volume the plants actually used to extract their water and solutes from. Differences in root density and root activity at the scale of individual plants, and variability of yield may have caused this lack of correlation as well. Although linear correlation was poor, surface plots of Cd_s and Cd_g showed large scale resemblances in spatial patterns. Areas of high Cd and Zn concentrations in a CaCl_2 -extract of soil showed high Cd and Zn concentrations in barley as well. This promising result may inspire further exploration of the merits of CaCl_2 -extractable Cd and Zn contents of soil as an indicator for bioavailability.

Although a direct correlative relationship between Cd_s and Cd_g was not found, a stochastic model for long-term behaviour of Cd in field soils was able to describe observed variability in Cd contents of barley grain from spatial variability of soil pH and organic matter content. These soil chemical parameters determine Cd behaviour in soil to a large extent. The range in values predicted by the model was comparable with the observed range of Cd concentrations in barley grains.

Because barley is mixed while harvested, spatial variability of Cd concentrations in grain are averaged in the final product. However, for crops where this is not the case, spatial variability may lead to partial exceedance of threshold levels for Cd concentrations in edible parts. Although spatial correlation between soil Cd and plant Cd was difficult to interpret in our sampled field, the stochastic approach predicted observed variability of Cd concentrations in barley grain from spatial variability of soil chemical parameters reasonably well. The model is developed for Cd and is applied to one field situation only. Nevertheless, results

indicate that a stochastic approach may give important information for reliable risk assessment of Cd contamination of soils in terms of probability. At the field scale a direct approach using spatial dependence of soil and plant processes was less appropriate for prediction of Cd concentrations in barley.

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Chapter 9

Epilogue

Epilogue

The findings reported in this thesis are relevant for different areas of research and soil protection policy. In this closing chapter, I use the main conclusions to elaborate on aspects of soil quality standards, bioavailability, heterogeneity and scale, and scenario studies.

Main Conclusions

1. In a 0.01 M CaCl_2 -extract of soil, Cd sorption is reduced by 80% as compared to sorption in an equivalent NaCl -electrolyte due to competition between Cd and Ca. Half of the Cd^{2+} ions in solution is complexed by Cl^- , which reduces Cd sorption by 50% as compared with sorption in an equivalent NO_3^- -electrolyte (Chapter 2).
2. The effect of soil pH on Cd sorption is substantial, and can be explained by assuming that Cd and protons sorb onto the same sorption sites (Chapter 2).
3. At the scale of soil column transport studies, nonequilibrium conditions need to be taken into account (Chapter 3).
4. At the field scale behaviour of Cd is spatially variable. Spatial patterns of total Cd contents, CaCl_2 -extractable Cd contents, soil pH and organic matter content were all very different from each other (Chapter 4 and 5).
5. The extended Freundlich equation explained field scale behaviour of Cd. Soil pH and organic matter content of the soil were the most important soil factors that controlled field scale variability of Cd sorption (Chapter 3, 4 and 5).
6. Spatial variability implied that a large number of soil samples was necessary to delineate pollution boundaries. The technique of kriging reduced estimation uncertainty of interpolated values when sampling density was increased (Chapter 6).
7. Spatial variability of soil water flow velocity as well as soil pH caused model predictions of the impact of long-term Cd deposition onto agricultural soils to deviate from predictions in equivalent homogeneous soils (Chapter 7).
8. Spatial variability of CaCl_2 -extractable Cd contents in a field soil reflected spatial variability of Cd contents in barley grains to some degree. Linear correlation was poor, but spatial patterns were comparable. The model for long-term effects of Cd deposition predicted spatial variability of both Cd contents of the soil and Cd concentrations of barley grains reasonably well (Chapter 8).

Soil Quality Standards

From the work described in this thesis, it follows that in acid sandy soils pH is the most important soil parameter that controls the distribution of Cd over the soil solid and liquid phase. As was pointed out in the first chapter, C-values for heavy metals in soils have been proposed that are supposed to indicate the possibility of unacceptable risk for men and the environment. These C-values are scaled for clay content and organic matter content. This scaling suggests that effects of soil properties on exposure of humans and ecosystems is accounted for. The latter assumption is disputable, because soil pH is not (yet) included.

The effect of pH appeared to be large, and should be implemented in quality standards that indicate acceptable concentrations based on (eco)toxicology. With the presented extended Freundlich equation it is possible to account for pH effects on Cd sorption in acid sandy soils.

Bioavailability Indicators

The chemical characterization of sorption in 0.01 M CaCl₂ needs to be extended to other soil types, and other heavy metals, when it is to be used for bioavailability assessment of heavy metals in soil. Moreover, analytical aspects like the applied ionic strength and the solid-solution ratio need further justification. Ionic composition and strength not only determine the amount extracted, but also influence the accuracy of chemical analysis. Too high ionic strengths may give disturbances of AAS measurements. Too low ionic strengths may not extract enough heavy metal to enable reliable chemical analysis. Because suspension pH is influenced by the solid-solution ratio, results obtained from different solid-solution ratios cannot be compared directly.

Optimal conditions for soil extraction in view of environmental risks of soil pollution are now discussed within several national standardization organizations in Europe. The International Standardization Organization is currently working on standardization of soil extraction methods for heavy metals in soil. The Community Bureau of Reference of the EC recently accepted methodologies for sequential extraction of sediments for heavy metal analysis. Methods for soil are in development (V.J.G. Houba, personal communication). After standardization of analytical techniques, observations from different laboratories can be compared, and relationships between concentrations measured in the extract and concentrations in different plant species or soil organisms may evolve from it.

However, analytical data production always needs a continuous quality check, as is illustrated by the results of the International Plant and Soil Analytical Exchange Programmes (e.g. Houba *et al.*, 1989).

Besides the chemical aspects mentioned above, the applicability of soil extractants as bioavailability indicators depends on biological factors as well. Until now, lack of knowledge on plant uptake mechanisms seriously hampers interpretation of soil extraction data of heavy metals in terms of plant concentrations. Soil and plant parameters that determine crop growth and plant vitality may not be optimal in field soils (Chapter 8). Furthermore, spatial variability of these parameters restricted the interpretation of the field data. More research at the field scale is definitely recommended.

The impact of soil contamination on the functioning of soil ecosystems is still a poorly developed area of research. Next to the problem of defining what an ecosystem is, and how individual organisms cooperate for its functioning, it is not well defined which concentrations the different organisms are exposed to. A complication regarding animals is that they are mobile. Therefore, it is difficult to ascertain the effective exposure during their lifetime. To reveal the complexities of soil in all its aspects, I agree with Nielsen *et al.* (1986) that the development of a unified approach that includes all relevant physical, chemical, and biological processes operative in the unsaturated zone is a challenge (Nielsen *et al.*, 1986).

Soil Heterogeneity and the Scale Problem

The scale problem has been emphasized before in hydrology and flow in porous media (for example Dagan, 1989). The importance of soil chemical heterogeneity for reactive solute transport in soil has been illustrated by modelling results of Van der Zee (1988) and Destouni (1991). The experimental and modelling results that I present in this thesis regarding accumulation, leaching, and plant uptake of cadmium show the importance of heterogeneity again, although from a somewhat different perspective. In Chapter 3, I studied sorption of Cd at different scales of observation. By going from one scale to the other, the formulation of the higher scale models gained from knowledge obtained from the lower scale studies, for instance the influence of soil pH on Cd sorption (Chapter 2).

Chemical heterogeneity of field soils implies that when total contents in the field are constant, concentrations in solution are spatially variable. Consequently, risks of soil contamination are different for different locations in the contami-

nated area, although these locations are equally enriched with contaminants. On the other hand, when the concentration in solution is approximately constant, locations with different total contents exhibit the same environmental risks. The consequences for risk assessment and development of soil quality standards is obvious, and I refer to the first paragraph of this chapter for suggestions regarding soil quality standards for Cd that account for the effect of sorption chemistry.

Correlation between Soil Parameters

The extended Freundlich equation uses both pH and organic matter content to explain Cd behaviour in field soils. This indicates that more than one soil parameter determines spatial behaviour of Cd sorption. In the sampled field these soil chemical parameters were not correlated. In case these parameters are correlated, different behaviour can be expected, as is illustrated by the following example.

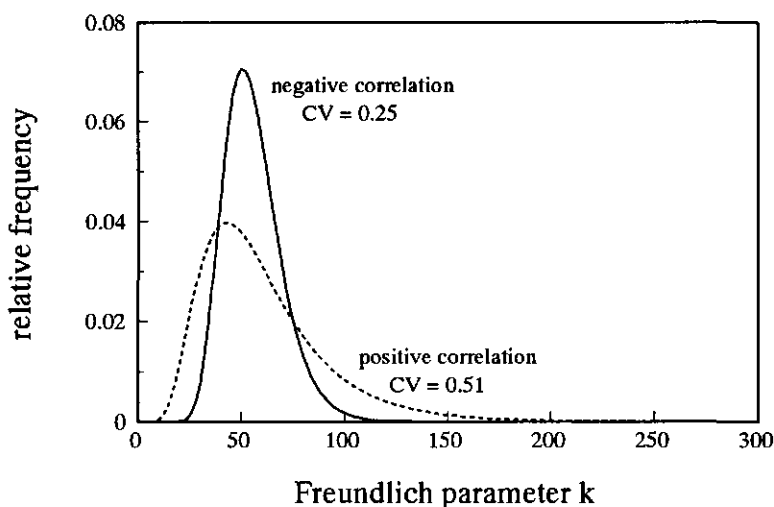


Fig. 1. Frequency distribution of the Freundlich parameter k when pH and oc are positively or negatively correlated.

The effect of correlation between pH and organic matter content can be clarified by calculating parameter k from the Freundlich equation, assuming either complete positive or complete negative correlation. Parameter k from the Freundlich equation is calculated by

$$k = k^* oc (H^+)^{-0.5}$$

using parameter values from Table 1 of Chapter 3. Values of pH were transformed to values of proton activity, and fitted to a lognormal frequency distribution. Values of oc were fitted to a lognormal distribution as well.

When pH and oc are positively correlated, high values of oc coincide with high values of pH, resulting in relatively strong adsorption of Cd. The same applies to low values, resulting in relatively weak adsorption. Negative correlation smooths these extreme events, and consequently, variability is much lower in this case (Fig. 1). The average value of k is approximately the same, but the standard deviation is twice as high. This simple exercise shows that besides soil heterogeneity, also spatial correlation between soil parameters that are relevant to the process studied, deserves further attention.

Spatial Structure and Modelling

Spatial variability was approximately random for CaCl_2 extractable Cd contents in the Kempen field, but structured for total Cd contents with a correlation length of approximately 10-15 m (Chapter 4 and 5). This means that different spatial structures were found for parameters of one contaminant in one field. The existence of spatial structure is of relevance for sampling strategies (see next paragraph) and for modelling.

Modelling field scale behaviour of solutes in heterogeneous soils was done in Chapter 7 using stochastic theory. The field soil was considered as an ensemble of N parallel, non-interacting soil columns that differ only with respect to x_i , $i=1, \dots, N$. In reality, individual soil columns are not independent, they will show lateral interaction with each other. Structured spatial variability will then respond differently to interactions than random spatial variability, as will be illustrated by the next one-dimensional case. Taking parameter oc from Fig. 1 as an example, I used the lognormal frequency distribution to draw 1000 random values. This data sequence is unstructured. Extreme high structure is simulated by sorting of the data set. Then, values near to each other are very similar. Both sets of sample values were subjected to a simple kind of lateral interaction. By averaging each two neighbouring values, 999 new values resulted, which may be seen as the outcome of some interaction model. These resulting values were averaged, and the standard deviation was calculated (Table 1).

Table 1. Statistics of frequency distribution of αc for random data, results of interaction, and results after sorting. \bar{x} is average, s is standard deviation, CV is coefficient of variation.

	original data	results of interaction	results after sorting
\bar{x}	2.51	2.50	2.51
s	0.29	0.20	0.29
CV	0.12	0.08	0.12

Comparison of the coefficient of variation (CV) of the results of interaction of random data shows that interactions reduced spatial variability with one third. Interactions between soil columns after sorting of the data sequence resulted in unaltered variability as compared to the original data set. This shows that modelling results of lateral interactions in heterogeneous field soils are affected by spatial structure of the variable soil parameters. This example illustrates the relevance of spatial correlation for modelling, although the model that was applied was highly simplified.

To predict field scale behaviour reliably, extremely complex physically based models can be developed which take full account of the spatial variability of various parameters. Another approach may be the derivation of field scale models in which the global effects of spatially variable properties is parameterized in some way (Dooge, 1986). The first approach requires extremely sophisticated models and expensive computers to be successful. The latter approach requires the discovery of new process laws at the field scale that represent more than mere data fitting. This is an appealing, but daunting research task.

Spatial Structure and Sampling Strategy

As was already pointed out, sampling strategies in spatially variable field soils may improve when spatial correlation scales of soil parameters are acknowledged. Little is known about spatial structure and correlation scales of soil parameters in field soils. In case similarities exist between certain soil types or between certain soil parameters, this information can be used in future studies. When no rules apply to the scale problem, no *a priori* estimates of spatial structure

are available for future studies. When the latter would be the outcome of an inventory on spatial variability of soils, soil parameters and correlation scales, a high sampling density is necessary for every new situation.

The relevance of spatial structure for sampling becomes obvious when different correlation scales are considered, for sake of simplicity in one dimension (Fig. 2). When the correlation scale of a soil parameter is large as compared to the scale of the contaminated area, the soil parameter is a field constant with some white noise (a). Another extreme is when the correlation scale is very small are compared to the scale of the contaminated area. The soil parameter can then be seen as a random variable, values are independent of location in the field. They vary, but in a irregular manner (b). At intermediate correlation scales, spatial variability is structured. Values measured at one location are to some extent representative for a larger domain surrounding it (c).

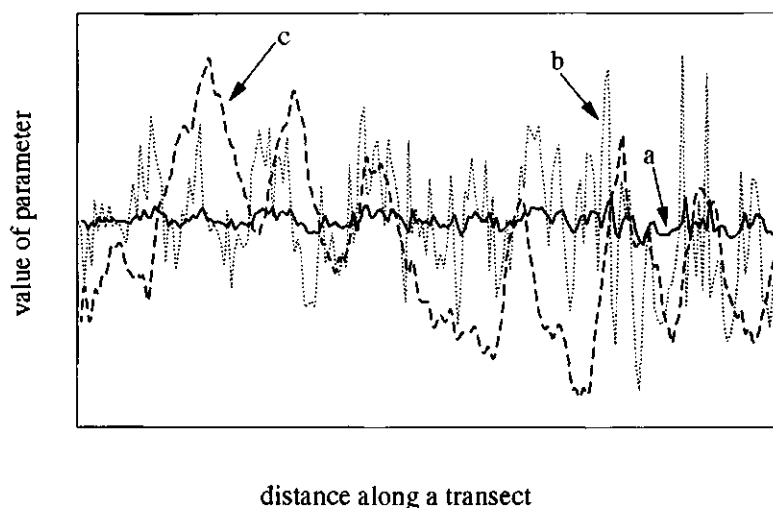


Fig. 2. Three spatial signals that differ in correlation scale, a) white noise, b) random, and c) spatially structured.

Theoretically, one soil sample is sufficient to characterize the field average value when the correlation scale is relatively large (a). Random variables require a statistically justifiable approach. This involves a large amount of samples (b). At the intermediate scale (c), the number of soil samples necessary to characterize soil spatial variability can significantly be reduced, as compared to the sampling density required for random variables. This advantage of spatial structure should be used for development of effective sampling strategies.

Chapter 6 demonstrated that a high sampling density was needed to obtain reliable estimates of Cd contents at unvisited locations in the Kempen field. Increasing the sampling density improved the accuracy of the predicted boundaries. This accuracy determines the soil volume that needs sanitation in remedial action projects. For an area that is cylindrically shaped, a quadratic relationship exists between the radius of the cylinder and its volume. Uncertainties in the size of the radius of a contaminated soil cylinder are then magnified quadratically in the uncertainty of the associated soil volume that needs treatment. This introduces a risk of cleaning uncontaminated soil, or leaving contaminated soil untreated. Both risks must be avoided.

High sampling densities can minimise these kinds of risks, which would improve the remedial action plan. It implies, however, that major investments in the beginning of the sanitation project are necessary. In many cases, costs associated with soil sampling and chemical analysis are much lower than costs of soil sanitation. Hence, increasing the effort in the first stage of the investigation may be worthwhile in those cases.

Scenario Studies

In 1990 the Foundation for Ecodevelopment of the Dutch Ministry of Housing, Physical Planning, and Environment initiated a project with the intriguing name of 'Chemical Time Bombs' (CTBs). In this paragraph I introduce Cd and Zn pollution of the Kempen area as a so-called chemical time bomb, and show how the findings reported in this thesis can be used in the context of the project.

The CTB project focuses on long term problems of nonlinear and time delayed effects of pollution due to the accumulation of chemicals (Stigliani *et al.*, 1991). The concept of CTBs refers to the fact that soils and sediments have the capacity to store and immobilize chemicals in sinks. These chemicals can be mobilized when the storage reservoir of the soil is overloaded and the system starts to leak, or when factors that influence the storage capacity of soils and sediments change. Such changes may be land use changes, erosion, or acidification. A consequence may be increased bioavailability of the previously immobilized chemicals. This may cause sudden and often unexpected adverse effects on the environment.

In this context, the recent report of the Dutch Scientific Committee for Governmental Policy (WRR, 1992) is of special relevance. They forecasted that

in the near future at least 40% of the European agricultural soils will be abandoned, using different scenarios of socio-economic development. The Kempen area is mentioned explicitly in this context.

This expected change in land use in the Kempen, from agricultural to non-agricultural use, implies changes in soil management that may be important for heavy metal retention. Land used for agriculture is usually limed to maintain a soil pH of about 5-6 which is favourable for crop production. Abandonment of agricultural land may lead to a decrease of the soil pH when liming of the soil is stopped. The impact of pH changes on Cd mobility in the Kempen area can be illustrated using the extended Freundlich equation. An example of such an exercise is given below.

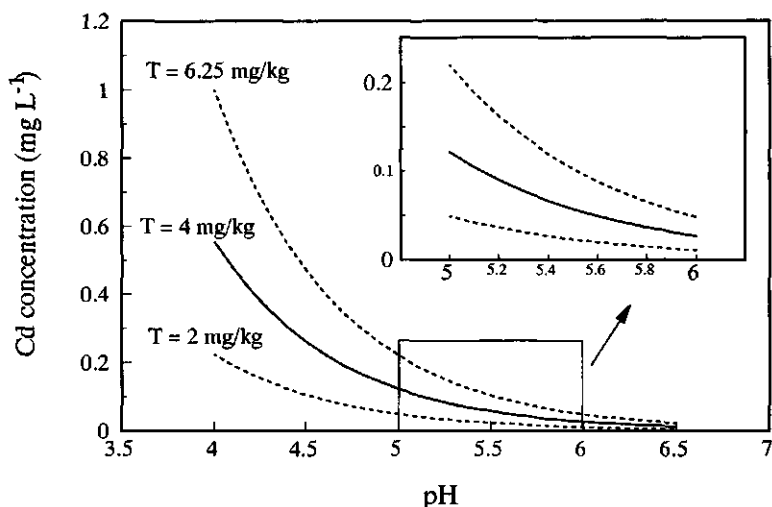


Fig. 3. Dependence of Cd concentration in the soil solution on pH for three values of the total Cd content.

By assuming that the retention capacity of the soil for Cd is large, and thus that the distribution coefficient is large, the concentration in solution is very small as compared to the adsorbed amount. Then, the extended Freundlich equation reduces to:

$$T = k^* oc (H^+)^{-0.5} c^n$$

where T is the total Cd content of the soil (mg kg^{-1}). Parameter values of this model are given in Table 1 of Chapter 3. For the sampled field in the Kempen, the average total Cd content was 4 mg Cd kg^{-1} , and measured minimum and maximum values were 2.0 and 6.25 mg kg^{-1} respectively. Fig. 3 gives the dependency of the Cd concentration in solution on soil pH for these three values of total Cd content.

As was already shown, the Cd concentration in the soil solution is very sensitive to pH. For instance, a decrease of pH in the sampled field from an average of 5.9 to an average of 5.0, results in an increase in the Cd concentration in solution from $30 \mu\text{g L}^{-1}$ to $120 \mu\text{g L}^{-1}$, when the total Cd content is 4 mg kg^{-1} . This is an increase by a factor of 4.

A decrease of soil pH in the Kempen has serious consequences for Cd mobility and bioavailability. It will result in mobilization of retained heavy metals, not only of cadmium but of zinc as well. The example as given above illustrates the possible effects of changes in land use in the Kempen area, despite the simplifying assumptions that were made. The effect of pH on Cd mobility and availability is irrefutable. Even though more sophisticated models need to be developed and applied to this specific situation, the approach may serve as a tool for decision making with regard to future land use of the Kempen.

Chapter 10

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Summary

Summary

The impact of discharging chemicals into the environment remained unnoticed for a long time because of the capacity of the environment to store chemicals without direct occurrence of adverse effects. Of the three environmental compartments soil, water, and air, storage in soils is the most effective. However, the capacity of soils to immobilize chemicals is finite, and overloading of this buffering capacity may lead to harmful environmental effects caused by increased mobility and bioavailability in the soil system. Furthermore, events that reduce the storage capacity of soils may result in the release of previously stored chemicals. Knowledge of the behaviour of contaminants in soils is necessary to prevent adverse effects of soil pollution to occur and may inspire society to take adequate measures that reduce inputs to acceptable levels. Cadmium is a very zootoxic heavy metal, and its dissemination is an important environmental issue. This thesis is intended to add to the understanding of Cd behaviour in soils.

Within the framework of the Dutch soil protection policy, quantification of exposure of man and the environment to contaminants in soil is now in development. Interpretation of the impact of Cd contents in soil can only be achieved when contents can be translated to exposure. Although many soil factors are known to influence retention mechanisms of chemicals in soils, little is known about quantitative relationships, which is necessary to come to a relevant system of soil quality standards.

In acid sandy soils, retention of Cd is primarily controlled by sorption. In this thesis, the macroscopic approach is used to describe Cd sorption in acid sandy field soils. The Freundlich equation describes Cd sorption well in the environmentally relevant concentration range, but its parameter values are only valid for the system in which they were derived. The applicability of the Freundlich equation was expanded by Van der Zee and Van Riemsdijk (1987), who derived an extended Freundlich equation that includes the effect of soil pH and organic matter content on Cd sorption. This extended Freundlich equation was subject to further study in this thesis.

When soils are considered, different scales of observation can be distinguished, ranging from the molecular scale to the global scale. The relevance of field scale heterogeneity for water and solute transport has been addressed before, and may be important for accumulation, bioavailability and leaching behaviour

of Cd as well. The main objective of this thesis was to develop and test methodologies with which environmental risks of cadmium pollution of field soils can be evaluated.

Although total heavy metal contents are often used to express the degree of contamination, they are of little value to judge biological effects. A method to determine the mobile and bioavailable fraction of the total Cd content may be soil extraction with 0.01 M CaCl_2 . Cadmium concentrations in CaCl_2 -extracts of soil correlated well with Cd concentrations in plants grown on that soil, which makes this method a promising one. However, causal relationships between Cd concentrations in a CaCl_2 -extract of soil and Cd concentrations in plants are not available (yet). The development of causal relationships may gain from knowledge of the chemical behaviour of Cd in a CaCl_2 -extract of soil.

To obtain insight into the effect of electrolyte composition and pH on Cd sorption, adsorption isotherms of Cd were determined for an acid sandy soil in 0.01 M CaCl_2 at different values of pH ranging from 3.8 to 4.9. To study the effect of competition between cadmium and calcium for sorption sites, Ca was replaced by Na and Cd sorption isotherms were determined for otherwise equivalent conditions. The same was done to study cadmium complexation by chloride, by replacing Cl with NO_3 . To exclude both effects of competition and complexation, Cd sorption experiments in a NaNO_3 -electrolyte were included as well. Sorption was linear in the applied concentrations range of 0-1 $\mu\text{mol Cd L}^{-1}$. In the Cl-electrolytes, approximately 50% of the Cd in solution was complexed with Cl. Competition between Ca and Cd reduced Cd sorption by 80% in the Ca-electrolytes as compared to the Na-electrolytes. These effects of electrolyte composition on Cd concentrations in a 0.01 M CaCl_2 -extract of soil must be kept in mind when this soil measure is used for bioavailability assessment.

Sorption of Cd was highly sensitive to pH as each 0.5 unit increase in pH resulted in twice as much sorption of Cd. To account for this pH effect in sorption models, a mechanistic model was developed by assuming that a two-site Langmuir sorption isotherm for protons described the proton titration curve of the soil, and that Cd and protons sorb onto the same reactive sites. From these assumptions, a mechanistic factor was derived that accounts for the effect of pH on linear Cd sorption. This factor showed a similar response to changes in pH as the empirical square root relationship with the proton activity of the extended Freundlich equation. This similarity may explain the successful application of the extended Freundlich equation in this and previous studies.

To study the ability of the Freundlich model to describe Cd sorption at another scale of observation, Cd sorption was examined during transport in soil. A transport model was developed for Cd in soil including Freundlich sorption, and breakthrough curves of Cd were determined for two different Cd concentrations. Predictions of solute breakthrough were made that were in good agreement with measurements, using sorption parameter values that were derived independently from batch adsorption experiments. However, this was only true when the same background electrolyte concentration and composition was used in both batch and transport experiments, and when the impact of sorption kinetics on solute breakthrough was included in the transport model.

For field scale analysis of Cd behaviour, soil samples were taken along a transect in an arable field in the Kempen. The Kempen is an area in the South of the Netherlands and the North of Belgium that is contaminated with Cd and Zn due to the presence of zinc smelters in this area. The transect consisted of 200 soil samples with 1 m sampling distance. Statistical and spectral analysis of the transect data showed that spatial variability of total Cd contents, CaCl_2 -extractable Cd contents, soil pH and organic matter contents was distinct and different for all four soil parameters. No substantial correlation was found between total and CaCl_2 -extractable Cd contents. This implied that total contents are not indicative of environmental risks of soil pollution with Cd in terms of mobility and bioavailability. Application of the extended Freundlich equation to the transect data was remarkably successful. Spatial variability of soil pH and organic matter content explained a large proportion of the heterogeneity of Cd contents. Apparently, Cd behaviour in this soil is primarily controlled by soil pH and organic matter content.

To analyze spatial behaviour of Cd in multiple directions in the field, a two-dimensional grid sampling scheme was used as well. Soil was sampled in the Kempen field using a grid size of 17×8 , with 6 m grid node distance. An additional 30 sample locations were distributed randomly at a distance of 2 m from the nearest grid node, to analyze spatial variability at a scale < 6 m. Total cadmium and zinc contents (Cd_T and Zn_T respectively), CaCl_2 -extractable Cd and Zn contents (Cd_s and Zn_s respectively), pH and organic matter content were measured in all soil samples. Spatial variability was analyzed using semivariograms.

All parameters were anisotropic, i.e. spatial patterns were different for different directions in the field. This illustrated the limitations of the one-dimensional approach with respect to field scale analysis. Values of organic matter content, of total Cd and Zn contents in the East-West direction, and of

CaCl₂-extractable Cd contents in the North-South direction showed spatial dependence within distances of 5-20 m. For these soil parameters, values at locations within this range were rather similar, beyond this range they are different. For the other soil parameters and directions no such range was observed. CaCl₂-extractable Cd and Zn contents were highly correlated with soil pH. Total Cd and Zn contents were significantly correlated with both soil pH and organic matter content. These correlations, together with observed similarities between anisotropy of total heavy metal contents and organic matter content on the one hand, and between CaCl₂-extractable heavy metal contents and pH on the other hand, suggested a functional (spatial) relationship between these parameters.

As opposed to the transect data that were used to predict total Cd contents, the grid data were used to predict CaCl₂-extractable Cd contents because these values are of relevance for risk assessment of soil pollution with Cd. The extended Freundlich equation was again used for this purpose. Predicted values of CaCl₂-extractable Cd contents correlated well ($r=0.87$) with measured contents, whereas prediction based on the assumption of homogeneity of sorption yielded no significant correlation. As was observed for the transect data, the extended Freundlich equation gave a good quantitative approximation of the dependency of Cd sorption on soil pH and organic matter content. Field scale heterogeneity of Cd sorption in an acid sandy soil was substantial. In spite of relatively homogeneous deposition patterns, total Cd contents in a 0.5 ha area ranged from 2 mg Cd kg⁻¹ to more than 6 mg Cd kg⁻¹.

Spatial variability implies that at some locations the risks of Cd pollution in terms of mobility and bioavailability are higher than at other locations. So, evaluation of environmental risks of Cd pollution involves estimation of the spatial distribution of the pollutant. This was done for total Cd contents in the Kempen field. The spatial interpolation technique of kriging provides not only estimates at unvisited locations, but also the standard deviation of these estimates, and was used to delineate pollution boundaries.

The accuracy of kriged interpolations was examined by cross validation of predicted Cd contents of soil with their known, measured values. The original sampling density of 330 samples ha⁻¹ could be reduced by 50% while maintaining the accuracy of kriged interpolations. Predicted variance of the estimates was used to assess the size of the area that may exceed a threshold level of 5 mg Cd kg⁻¹ with 0.95 probability. This area increased in size when the data set was reduced, because kriging variance increases at lower sampling densities. Estimation of the area where Cd contents exceed a certain threshold value with a certain accuracy is necessary for effective clean-up of contaminated sites. When

this area needs remedial action, the reduction of research effort by minimizing the sampling density may well lead to an overall increase in sanitation costs because it leads to an increase of the area that exceeds the threshold level.

Risk assessment of soil pollution not only involves analysis of sites that are already polluted, but also analysis of the capacity of field soils to withstand negative effects of long-term additions of contaminants, for instance due to atmospheric deposition. To meet with this purpose, a deterministic model for long term behaviour of Cd in the root zone of an acid sandy soil was developed that includes sorption, leaching, and plant uptake by barley. Sensitivity analysis of the model gave insight into the response of model output to changes in values of soil chemical and soil physical parameters used for input. Sensitivity of the leaching rate decreases as a function of time, and becomes zero when steady state is reached. In contrast, accumulation of Cd in soil and the plant uptake rate of barley are increasingly sensitive as time proceeds.

To simulate Cd behaviour in a field that is heterogeneous with respect to the soil water flow velocity, this parameter was assumed to be a random, lognormally distributed variate. Using Monte Carlo simulation, the average plant uptake rate appeared to be much higher in the stochastic case than in the deterministic approach. For a lognormally distributed proton activity, causing heterogeneity with respect to the sorption capacity of the soil, the model predicted similar deviations from the deterministic approach. From these model predictions, it can be concluded that threshold values for Cd concentrations in groundwater and crops are exceeded earlier in a heterogeneous field than in a homogeneous soil profile. Moreover, when average values suggest an acceptable situation, variability of the leaching rate and the plant uptake rate can still cause exceedance of quality standards in part of the field. This demonstrates the importance of soil heterogeneity for environmental impact assessment of soil contamination.

To analyze the capability of this model to predict field scale variability of Cd concentrations in plants, barley (*Hordeum vulgare* L.) was sampled in the Kempen field at the same locations where the soil samples were taken. This enabled investigation of Cd concentrations in CaCl_2 -extracts of soil as plant availability indicators as well. Cd and Zn contents in barley and yield were spatially variable. Yield was low, which may have been caused by Zn toxicity or atrazine turnover. For Cd, CaCl_2 -extractable soil contents explained only 17% of the variation in Cd concentrations in grain, and for Zn no significant correlation was observed. So, although high correlations were found in greenhouse experiments, field scale application was less successful. Surface plots of CaCl_2 -extractable Cd contents of soil and Cd contents in barley grain illustrated

their corresponding spatial patterns. Apparently, a more general point of view did reflect spatial patterns of Cd concentrations in barley grains from CaCl_2 -extractable Cd contents. The stochastic model for long term behaviour of Cd in field soils predicted observed variability in Cd contents of barley grain well from spatial variability of soil pH and organic matter content. The probabilistic model predicted behaviour of Cd in terms of probability, and was more appropriate than the deterministic approach.

The main conclusions that evolved from this thesis were used to elaborate on aspects of different areas of research. With regard to governmental soil quality standards it is argued that the proposed C-values that indicate risks of exposure of organisms to contaminants in soil should take the effect of soil pH into account. With the presented extended Freundlich equation it is possible to quantify this effect for acid sandy soils.

Soil heterogeneity and the scale problem are relevant to the field scale analysis of Cd sorption. Simple calculations illustrate the importance of spatially correlated soil parameters, as well as spatial structure. These aspects of soil heterogeneity need further attention. Before Cd concentrations in a 0.01 M CaCl_2 -extract of soil can be used in risk assessment of soil pollution, chemical characterization of sorption needs to be extended to other soil types and other heavy metals. Several national and international standardization organizations are currently working on this.

Scenario studies may gain from the knowledge of Cd behaviour in acid sandy soils as described in this thesis. As an example, the Kempen area is analysed with respect to possible effects of changes in future land use in this area. Cadmium and zinc that are now safely stored in the soil profile may be mobilized by soil acidification after abandoning of agricultural land. This should give rise to concern about future land use in the Kempen area.

Samenvatting

Samenvatting

Menselijke activiteiten hebben geleid (en leiden nog steeds) tot de verspreiding van allerlei stoffen in het milieu. Het heeft vele jaren geduurd voordat de gevolgen hiervan zich openbaarden in de vorm van milieuverontreiniging. Dit heeft te maken met de mogelijkheid die het milieu heeft om stoffen op te nemen zonder dat nadelige effecten hiervan zich openbaren. In vergelijking tot die van water en lucht is de buffercapaciteit van de bodem in het algemeen gesproken het grootst. Maar ook voor de bodem is de buffercapaciteit niet oneindig en overbelasting kan leiden tot uitspoeling van stoffen naar het grondwater, of tot opname door gewassen die groeien op verontreinigde grond. Tevens kan de buffercapaciteit van de bodem verminderen door bijvoorbeeld verandering van bodemgebruik, waardoor vastgelegde stoffen kunnen worden gemobiliseerd. Om nadelige effecten van reeds bestaande bodemverontreiniging te voorkomen, is kennis over stofgedrag in de bodem noodzakelijk. Daarnaast kan deze kennis worden ingezet om de juiste maatregelen te nemen die verdere verspreiding van stoffen in het milieu voorkomen.

In het kader van het Nederlandse bodembeschermingsbeleid wordt onderzoek gedaan naar de blootstelling van mens en milieu aan verontreinigingen in de bodem. Het totaalgehalte van een verontreinigende stof kan namelijk niet direct worden vertaald naar blootstelling. Gelijke totaalgehalten kunnen in verschillende grondsoorten leiden tot verschillende blootstellingsniveaus. De specifieke eigenschappen van een bodem zijn namelijk mede bepalend voor het effect dat kan worden verwacht van een bepaald gehalte aan verontreinigingen. Bruikbare relaties die de afhankelijkheid tussen bodemeigenschappen en blootstelling beschrijven zijn slechts beperkt voorhanden. Dergelijke relaties zijn echter wel nodig om tot een goed bodembeschermingsbeleid te komen.

Het zware metaal cadmium is één van de stoffen die door zijn toxiciteit voor mens en dier aandacht krijgt in milieubeleid en milieuonderzoek. Dit proefschrift heeft tot doel meer duidelijkheid te verschaffen ten aanzien van het gedrag van cadmium in de bodem. Hierbij is vooral aandacht geschonken aan het sorptiegedrag van cadmium in de bodem, en de gevolgen van bodemheterogeniteit op veldschaal voor het ruimtelijke verspreidingspatroon van cadmium. Het is bekend dat vastlegging van cadmium in neutrale en zure zandgronden voornamelijk wordt gereguleerd door sorptie van cadmium aan bodemdeeltjes. In dit proefschrift wordt de Freundlichvergelijking (zie bijvoorbeeld Hoofdstuk 3, vergelijking (1)) gebruikt om sorptie van cadmium te beschrijven. Deze vergelijking geeft een eenvoudig verband tussen de hoeveelheid cadmium die

in de vloeistoffase aanwezig is, en de hoeveelheid cadmium die bij die concentratie is geadsorbeerd. Omdat parameterwaarden voor deze vergelijking slechts geldig zijn voor de gebruikte bodem en meetomstandigheden, zijn uitbreidingen van de Freundlichvergelijking ontwikkeld die de toepasbaarheid kunnen vergroten. Door Van der Zee en Van Riemsdijk (1987) is een dergelijke uitgebreide Freundlichvergelijking voorgesteld (Hoofdstuk 3, vgl. (2)). Deze vergelijking houdt rekening met het effect van de bodem-pH en het organische stofgehalte van de bodem op de adsorptie van cadmium.

Deze uitgebreide Freundlichvergelijking is in dit proefschrift gebruikt om cadmiumadsorptie te analyseren in bodemsystemen die verschillen in ruimtelijke dimensie. De bodem kan namelijk worden bestudeerd op verschillende niveaus, reikend van het niveau van individuele moleculen tot het niveau van bodemkundige eenheden. Op al deze niveaus wordt het bodemsysteem gekenmerkt door heterogeniteit. Heterogeniteit is het verschijnsel dat eigenschappen van de bodem verschillen op verschillende plekken binnen het beschouwde domein. Reeds eerder is aangetoond dat het bestaan van bodemheterogeniteit op perceelsniveau belangrijke consequenties kan hebben voor het transport van water en opgeloste stoffen door de bodem. Dit belang kan ook worden verwacht ten aanzien van het gedrag van cadmium in de bodem. Een belangrijke doelstelling van dit proefschrift was methoden te ontwikkelen en te testen die de milieuhygiënische risico's van bodemverontreiniging op perceelsniveau kunnen schatten.

Alhoewel totaalgehalten van stoffen in de bodem worden gebruikt om de mate van verontreiniging weer te geven, zijn deze totaalgehalten van weinig waarde bij de beoordeling van de milieuhygiënische risico's. De biologisch beschikbare en mobiele hoeveelheid aan zware metalen in de bodem kan wellicht beter worden geschat aan de hand van gehalten die kunnen worden geëxtraheerd met milde zoutoplossingen, zoals 0.01 M CaCl_2 . In de literatuur is beschreven dat cadmiumconcentraties in planten die groeiden op verontreinigde grond goed correleren met cadmiumconcentraties in een CaCl_2 -extract van die grond. Een verklaring voor deze goede correlaties is echter nog niet beschikbaar. Om een goede verklaring mogelijk te maken, kan kennis over het adsorptiegedrag van cadmium van dienst zijn.

Om hier inzicht in te verkrijgen zijn schudexperimenten uitgevoerd waarbij cadmiumoplossingen in evenwicht zijn gebracht met een zandgrond in een pH-bereik van 3.8 tot 4.9. Als achtergrondselectrolyet werd 0.01 M CaCl_2 gebruikt. Calcium beïnvloedt de adsorptie van cadmium omdat beide adsorberen aan dezelfde typen reactieve plaatsen aan het bodemoppervlak. Dit Ca-effect

werd bestudeerd door identieke experimenten uit te voeren met één verschil: in plaats van calcium werd natrium gebruikt. Bovendien werden experimenten uitgevoerd om het effect van complexering van cadmium door chloride te bestuderen. Hiertoe werd chloride vervangen door nitraat. Om effecten van zowel calciumcompetitie als chloridecomplexering zo veel mogelijk uit te schakelen, werden adsorptie-isothermen bepaald in NaNO_3 -oplossingen onder overigens gelijke omstandigheden.

De gemeten adsorptie-isothermen waren lineair in het concentratiebereik van $0\text{--}1\ \mu\text{mol L}^{-1}$. In de Cl-electrolieten was ongeveer 50% van de hoeveelheid cadmium in oplossing gecomplexeerd met chloride. Deze cadmiumcomplexen adsorbeerden niet of nauwelijks. Adsorptie van cadmium werd met 80% gereduceerd in de Ca-electrolieten, in vergelijking met de Na-electrolieten. Als extractie van de bodem met $0.01\ \text{M CaCl}_2$ wordt gebruikt om biologische beschikbaarheid en mobiliteit van cadmium in de bodem te karakteriseren moet rekening worden gehouden met de hier beschreven invloed van de samenstelling van de extractievloeistof.

De adsorptie van cadmium was erg gevoelig voor de pH. Elke stijging van de pH met 0.5 eenheid resulteerde in een twee keer zo sterke adsorptie van cadmium. Een wiskundige beschrijving van deze afhankelijkheid werd afgeleid door aan te nemen dat de titratiecurve van deze grond voor protonen kan worden beschreven met een zogeheten 'two-site Langmuir isotherm', en door aan te nemen dat cadmium en protonen aan dezelfde reactieve plaatsen van het bodemoppervlak adsorberen. Hieruit kon een factor worden afgeleid welke het effect van pH op de adsorptie van cadmium goed beschrijft. Deze factor bleek even gevoelig te zijn voor pH-veranderingen als de factor die pH-afhankelijkheid beschrijft in de uitgebreide Freundlichvergelijking. De mechanistische benadering zoals hier beschreven sluit dus goed aan bij de empirische Freundlichvergelijking. Dit zou een verklaring kunnen zijn voor de gebleken bruikbaarheid van de uitgebreide Freundlichvergelijking in deze en eerder gerapporteerde experimenten.

Alhoewel de uitgebreide Freundlichvergelijking bruikbaar is gebleken om adsorptie van cadmium te beschrijven in schudexperimenten, betekent dit nog niet dat deze vergelijking een goede beschrijving geeft van cadmiumadsorptie onder andere omstandigheden, bijvoorbeeld gedurende transport in de bodem. Met kolomexperimenten kan het gedrag van cadmium worden bestudeerd terwijl het in opgeloste vorm door de grondkolom beweegt. Hiermee worden de omstandigheden zoals die voorkomen in 'echte' bodems beter benaderd dan met schudexperimenten. Er zijn doorbraakcurven van cadmium in een grondkolom

bepaald voor twee cadmiumconcentraties. Een transportmodel is ontwikkeld en gebruikt om het geobserveerde transportgedrag te verklaren. In dit model is het sorptiegedrag van cadmium beschreven met de Freundlichvergelijking. Het model voorspelde de gemeten doorbraak goed, gebruikmakend van parameterwaarden die onafhankelijk waren bepaald met schudexperimenten. Dit ging echter alleen op als het achtergrondselectrolyet in deze onafhankelijke experimenten hetzelfde was als bij de bepaling van de doorbraakcurve. Bovendien moest in het model rekening worden gehouden met het effect van niet-evenwichtssorptie.

Hieruit blijkt dat de Freundlichvergelijking sorptie van cadmium goed beschrijft op het niveau van schudexperimenten en op het niveau van kolomexperimenten. Het blijft echter een vraag of de bruikbaarheid ook geldt op perceelsniveau. Om deze vraag te beantwoorden zijn bovengrondmonsters genomen in een landbouwperceel in de Kempen, een gebied in de provincie Noord-Brabant. Het plaatsje Budel in deze streek is bekend, omdat de activiteiten van zinkverwerkende bedrijven in dit gebied hebben geleid tot diffuus verspreide bodemverontreiniging.

Met de (zeer gewaardeerde) toestemming van de pachter van het perceel zijn 200 bovengrondmonsters van 0-20 cm diepte genomen langs een raai in het veld op 1 m afstand van elkaar. In deze monsters zijn het cadmium-totaalgehalte, het CaCl_2 -extraheerbare cadmiumgehalte, de pH en het organisch stofgehalte bepaald. De ruimtelijke variabiliteit van elk van deze parameters was aanzienlijk en voor alle vier verschillend. De cadmium-totaalgehalten en de CaCl_2 -extraheerbare gehalten waren niet significant gecorreleerd, wat aangeeft dat totaalgehalten niet indicatief zijn voor de milieuhygiënische risico's van bodemverontreiniging in termen van mobiliteit en biologische beschikbaarheid. De uitgebreide Freundlichvergelijking werd met succes toegepast op deze veldgegevens door totaalgehalten te voorspellen met gemeten waarden van pH, organisch stofgehalte, en CaCl_2 -extraheerbare Cd-gehalten. De ruimtelijke variabiliteit van pH en het organische stofgehalte verklaarde een groot gedeelte van de heterogeniteit van totaal-Cd-gehalten. Blijkbaar is het sorptiegedrag van cadmium in deze grond voornamelijk gereguleerd door de pH van de bodem en het gehalte aan organische stof.

Naast deze raabemonstering zijn ook monsters genomen volgens een twee-dimensionale bemonsteringsstrategie. Op deze wijze kon het gedrag van cadmium op perceelsniveau worden bestudeerd in meerdere richtingen tegelijkertijd. Van een oppervlak van ongeveer 0.5 ha zijn monsters van 0-20 cm diepte gestoken volgens een grid van 6 bij 6 m. Bovendien zijn 30 monsters

geselecteerd waarbij op 2 m afstand een extra bovengrondmonster is gestoken. Op deze wijze kon de ruimtelijke variabiliteit worden bestudeerd op afstanden kleiner dan 6 m. Alle monsters zijn geanalyseerd op cadmium- en zink-totaalgehalten, CaCl_2 -extraheerbare Cd- en Zn-gehalten, pH en organisch stofgehalte. Ruimtelijke variabiliteit is bestudeerd aan de hand van semivariogrammen, die aangeven hoe verschillend monsterpunten zijn die op een bepaalde afstand van elkaar liggen.

Alle bodemparameters vertoonden anisotropie, dat betekent dat ruimtelijke patronen verschilden voor verschillende richtingen in het veld. Dit laat zien dat de bruikbaarheid van ééndimensionale bemonsteringsschema's beperkt is. Sommige parameters vertoonden ruimtelijke afhankelijkheid. Dit betekent dat locaties die dicht bij elkaar in de buurt liggen overeenkomstige waarden hebben. De afstand waarover ruimtelijke afhankelijkheid werd gemeten bedroeg 5 tot 20 m. Berekening van de correlatie tussen de bodemparameters liet zien dat CaCl_2 -extraheerbare cadmium- en zinkgehalten significant gecorreleerd waren met de bodem-pH. Totaalgehalten waren gecorreleerd met zowel de pH als het organisch stofgehalte. Bovendien waren er duidelijke overeenkomsten in de anisotropie van enerzijds totaalgehalte en organisch stofgehalte, en van CaCl_2 -extraheerbare gehalte en pH anderzijds. Dit suggereert een functioneel verband tussen deze bodemparameters.

Daarom werden deze twee-dimensionale gegevens gebruikt om de CaCl_2 -extraheerbare cadmiumgehalten te voorspellen. Deze CaCl_2 -extraheerbare gehalten zijn relevanter voor risico-evaluatie van bodemverontreiniging dan totaalgehalten. Hiervoor werd wederom de uitgebreide Freundlichvergelijking gebruikt. De voorspelde waarden van het CaCl_2 -extraheerbare cadmiumgehalte in de bodem kwamen opmerkelijk goed overeen met de waargenomen gehalten (correlatie-coëfficiënt = 0.87). Zoals ook al voor de raaigegevens was gebleken, geeft de uitgebreide Freundlichvergelijking een goede kwantitatieve beschrijving van de afhankelijkheid van het adsorptiegedrag van cadmium voor pH en organisch stofgehalte.

De metingen laten zien dat de ruimtelijke variabiliteit van de bodem leidt tot variabiliteit van cadmiumgehalten. Ondanks de relatief homogene aanvoer van cadmium en zink aan het bodemoppervlak (als gevolg van diffuse atmosferische depositie), varieerde bijvoorbeeld het cadmium-totaalgehalte van circa 2 tot 6 mg kg^{-1} . Ruimtelijke variabiliteit betekent dat sommige locaties gevoeliger kunnen zijn dan andere locaties voor zowel uitspoeling van cadmium naar het grondwater als voor negatieve effecten van cadmium op biota. Voor een goede risico-evaluatie van bodemverontreiniging moet daarom ook het ruimtelijke

patroon van de verontreiniging wordt geschat. Een mogelijkheid om dit te doen wordt geboden door een ruimtelijke interpolatietechniek die kriging heet. Kriging levert niet alleen schattingen voor waarden van een parameter op niet-bezochte locaties, maar geeft eveneens de standaardafwijking van die schatting, en daarmee een maat voor de betrouwbaarheid. De mogelijkheden van kriging om verontreinigde locaties af te bakenen zijn onderzocht door gebruik te maken van de gegevens over de totaal cadmiumgehalten in het bemonsterde perceel in de Kempen. Het totaalgehalte is gekozen omdat deze een duidelijk ruimtelijke structuur kende. Door de aard van de variabiliteit van de CaCl_2 -extraheerbare cadmiumgehalten, leenden deze gegevens zich minder goed voor een dergelijke analyse van de (on)mogelijkheden van kriging.

Het bleek dat de originele bemonsteringsdichtheid van 330 monster ha^{-1} (achteraf) kon worden gehalveerd zonder dat dit de betrouwbaarheid van de schattingen van het cadmium-totaalgehalte beïnvloedde. De standaardafwijking van deze schattingen is gebruikt om het gebied te definiëren waar een (arbitraire) grenswaarde van 5 mg Cd kg^{-1} werd overschreden met een betrouwbaarheid van 0.95. Dit gebied werd 12% groter als de bemonsteringsdichtheid werd teruggebracht tot één-derde van de originele bemonsteringsdichtheid. Dit is een gevolg van het feit dat de standaardafwijking van de schattingen groter wordt naarmate minder monsterpunten worden gebruikt. Dit is een belangrijk feit in relatie tot bodemsaneringsoperaties. Als het gebied waar de grenswaarde wordt overschreden moet worden gesaneerd, dan kan het de moeite waard zijn om veel geld en moeite te investeren in bemonstering en chemische analyse van de grond, omdat dit de grootte van het te saneren gebied minimaliseert.

Risico-evaluatie van bodemverontreiniging vereist niet alleen onderzoek naar risico's van reeds verontreinigde grond, maar ook onderzoek naar risico's van langdurige atmosferische depositie van luchtverontreiniging op de bodem, zoals in veel geïndustrialiseerde gebieden plaatsvindt. Voor dit doel is een deterministisch simulatiemodel ontwikkeld, dat het effect van lange-termijn depositie van cadmium op een landbouwperceel voorspelt. Dit model beschrijft adsorptie, uitspoeling en opname van cadmium door gewassen bij een constante aanvoer aan het bodemoppervlak als functie van de tijd. Om de gevoeligheid van het model te kwantificeren voor onzekerheden in bodemfysische en bodemchemische parameters is een wiskundige gevoeligheidsanalyse uitgevoerd voor deze parameters. Hieruit bleek dat voor reële variaties van parameterwaarden de uitspoelingssnelheid van cadmium in de tijd steeds minder gevoelig is, en ongevoelig wordt als het model de evenwichtssituatie heeft bereikt. Accumulatie van cadmium in de bouwvoor en de opnamesnelheid van

cadmium door planten worden juist steeds gevoeliger in de tijd. Dit geeft aan dat het model gevoelig is voor heterogeniteit van invoerparameters.

Bodemheterogeniteit met betrekking tot een bodemfysische grootheid is gesimuleerd door aan te nemen dat de stroomsnelheid van water in de poriën in de bodem niet een constante is, maar een random, lognormaal verdeelde grootheid. Dit verandert het deterministische model in een stochastisch model. Door gebruik te maken van Monte Carlo simulatie bleek dat de gemiddelde waarde voor de opnamesnelheid van cadmium door het gewas hoger was dan wanneer men uitgaat van een vergelijkbare homogene bodem. Heterogeniteit met betrekking tot een bodemchemische grootheid is gesimuleerd door aan te nemen dat de protonactiviteit in de bodemoplossing een random, lognormaal verdeelde grootheid is. In dit geval werden analoge afwijkingen gevonden ten opzichte van de homogene benadering als voor bodemfysische heterogeniteit. Deze modelberekeningen laten zien dat grenswaarden voor cadmiumconcentraties in grondwater en gewassen eerder worden overschreden in een heterogeen perceel dan in een homogeen perceel. Bovendien houdt ruimtelijke variabiliteit in dat normen kunnen worden overschreden in een gedeelte van het veld wanneer dat gemiddeld gesproken niet het geval is. Daarom is bodemheterogeniteit belangrijk bij risico-evaluatie van langdurige depositie van luchtverontreiniging op de bodem.

Voorspellingen van dit stochastische model over accumulatie van cadmium in de bodem en opname van cadmium door gewassen kunnen worden getoetst aan gemeten ruimtelijke variabiliteit van cadmiumconcentraties in grond en gewas. Hiertoe is gerst (*Hordeum vulgare* L.) bemonsterd op het perceel in de Kempen, op dezelfde locaties als waar de bodemmonsters zijn genomen. Dit maakte het mogelijk om eveneens te onderzoeken of CaCl_2 -extraheerbare cadmiumgehalten van de grond een indicatie konden geven van ruimtelijke patronen van cadmiumconcentraties in gerstekorrels. Uit de metingen bleek dat zowel de cadmium en zinkconcentraties van gerst, alsmede de opbrengst ruimtelijk variabel waren. De opbrengst was relatief laag, wat veroorzaakt zou kunnen zijn door zinktoxiciteit of door gewasschade veroorzaakt door het bestrijdingsmiddel atrazine. Het CaCl_2 -extraheerbare cadmiumgehalte van de grond verklaarde slechts 17% van de variabiliteit van de Cd-concentraties in gerst, en voor zink werd geen significante correlatie gevonden. Deze teleurstellende resultaten geven aan, dat alhoewel potproeven met grond en gewassen veelbelovende resultaten te zien gaven, onder veldomstandigheden dergelijke relaties minder eenvoudig te leggen zijn. Naast een directe vergelijking van grond en gewas, zijn ook de ruimtelijke patronen van CaCl_2 -extraheerbare cadmium-

gehalten en cadmiumconcentraties in gerst vergeleken. Deze ruimtelijke patronen werden verkregen met geostatistische technieken, en bleken globaal gezien overeen te komen. Het stochastische model voor lange-termijn effecten van atmosferische depositie van cadmium op grond bleek variabiliteit van cadmiumconcentraties in gerst goed te voorspellen op basis van beredeneerde aannamen over cadmium aanvoer en ruimtelijke variabiliteit van de bodem-pH en het organisch stofgehalte. Dit model voorspelde het gedrag van cadmium in termen van kansen in plaats van enkelvoudige waarden en bleek beter in staat het gedrag van cadmium te voorspellen dan de deterministische benadering.

De belangrijkste conclusies die uit dit proefschrift naar voren komen zijn gebruikt om te illustreren wat ze kunnen betekenen voor verschillende onderzoeksdisciplines. Risico's van bodemverontreiniging met cadmium worden in sterke mate worden beïnvloed door de pH van de bodem. Grenswaarden voor gehalten in de bodem die aangeven dat een onacceptabel risico voor mens en milieu is bereikt, zouden dan ook rekening moeten houden met de bodem-pH. Met de uitgebreide Freundlichvergelijking is het mogelijk dit effect te kwantificeren voor neutrale en zure zandgronden. Voor andere gronden en andere zware metalen is nader onderzoek gewenst.

Bodemheterogeniteit is belangrijk gebleken voor de risicobeoordeling van bodemverontreiniging. Met behulp van eenvoudige berekeningen is aangetoond dat eventuele correlaties tussen bodemparameters de voorspellingen over het gedrag van cadmium in de bodem kunnen beïnvloeden. Bovendien speelt ruimtelijke structuur van variabele bodemparameters een belangrijke rol. Deze aspecten zouden meer aandacht moeten krijgen bij het ontwikkelen van modellen.

Risico-evaluatie gebaseerd op bodemextractie met CaCl_2 moet nader worden onderzocht op de bruikbaarheid voor andere zware metalen en andere gronden. Nationale en internationale organisaties die zich bezig houden met het standaardiseren van meetmethoden zijn momenteel bezig om bodemextractiemethoden te standaardiseren.

De resultaten zoals beschreven in dit proefschrift kunnen ook worden gebruikt bij zogenaamde scenariostudies. Scenariostudies proberen voorspellingen te doen voor de toekomst, op grond van aannames over toekomstige ontwikkelingen. Een voorbeeld van een dergelijke scenariostudie zou de invloed van veranderingen in het grondgebruik in de Kempen kunnen zijn. In een rapport van de Wetenschappelijke Raad voor het Regeringsbeleid (1992) wordt gesuggereerd dat in de toekomst sommige landbouwgebieden in Europa, waaronder de Kempen, uit productie zullen worden genomen. Omdat braak-

legging van landbouwgronden over het algemeen resulteert in een verlaging van de bodem-pH, kan op grond van de resultaten van dit proefschrift worden verwacht dat de huidige bodemverontreiniging met zware metalen in de Kempen problemen zal gaan opleveren in de toekomst.

Levensloop

Alexandra Eva Boekhold werd geboren op 29 mei 1963 te Oldenzaal als één van vier dochters van Eva Koetzier en Jacob Boekhold.

Van 1975 tot 1981 doorliep zij het atheneum-B op de Thorbecke Scholengemeenschap te Utrecht. In 1981 begon zij met haar studie aan de toenmalige Landbouwhogeschool te Wageningen in de studierichting Milieuhygiëne. Na het behalen van het kandidaatsdiploma in 1985 heeft zij een afstudeervak microbiologie gedaan bij het Instituut voor Cultuurtechniek en Waterhuishouding te Wageningen onder begeleiding van dr. Jan Hoeks en dr.ir. Maurice Huntjens. Het afstudeervak bodemhygiëne en -verontreiniging is uitgevoerd bij ir. Meindert Keizer. Van januari tot juli 1986 heeft zij een driemaands afstudeervak bodemnatuurkunde gecombineerd met drie maanden praktijktijd bij het Instituut voor Bodemvruchtbaarheid te Haren onder begeleiding van dr. ir. Pieter A.C. Raats. Van september tot december 1987 verbleef zij aan de University of Guelph, Canada, voor een praktijktijd bij Prof. dr. Pieter H. Groenevelt. In 1988 ontving zij haar getuigschrift.

Van april 1988 tot en met maart 1990 was zij werkzaam als toegevoegd onderzoeker bij de vakgroep Bodemkunde en Plantevoeding van de Landbouwuniversiteit Wageningen voor 2/10 weektaak. In opdracht van de Technische Commissie Bodembescherming verrichtte zij onderzoek naar de milieuhygiënische risico's van grondgebonden residuen van bestrijdingsmiddelen.

In dezelfde periode voor 8/10 weektaak, plus van april 1990 tot en met september 1992 voltijds, was zij werkzaam als Assistent in Opleiding bij dezelfde vakgroep. Het promotieonderzoek heeft geleid tot dit proefschrift.