Modelling of cadmium fluxes on energy crop land

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Sammanfattning/Summary

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Abstract

The flux of cadmium on energy crop land is investigated. Three mechanisms are accounted for: uptake by plant, transport with water and sorption to soil. Sorption is described with Freundlich isotherms. The system is simulated mathematically in order to estimate the sensitivity and importance of different parameters on the cadmium flow and distribution.

The water flux through the soil and the uptake by plants are simulated with a hydrological model, SOIL. The simulated time period is two years. The hydrological model solves two equations, one to account for heat flow and one for water flow. The soil profile has a surface area of 1 m^2 and is divided into compartments of a chosen thickness. The flow of heat and water is calculated from one compartment to the next. Snow and frost are present during the winter months. Input is daily measurements on precipitation, air temperature, cloudiness and humidity, provided from a model database. The soil parameters (thermal and hydrological) are taken from a site close to the weather station. The parameters describing root distribution and evaporation due to crop are taken from measurements on energy crop (*Salix*). The resulting water flux, water content in the soil profile and the water uptake into roots, for each day and soil compartment, are used in the cadmium sorption simulation.

In the cadmium sorption simulation the flux and equilibrium chemistry of cadmium is calculated. It is assumed that cadmium is added at the top of the profile when the simulation starts. The cadmium is assumed to dissolve instantaneously in the water of the first soil compartment (of 10 cm:s thickness). It then sorbs partly to the soil according to the given isotherm. The rest of the cadmium dissolved in the water can follow the root water uptake and accumulate in a plant, go with the water flow further down in the soil, as well as stay with the water that still is in the compartment. This process is repeated for every soil compartment and day of the year.

It is shown that the amount of cadmium that accumulates in the plant, and the depth to which the applied cadmium reaches depends strongly on the constants in the sorption isotherm. With an application of 10 mg Cd/m^2 in the given range of Freundlich equations, the simulations gave a plant uptake of between 0 and 30 % of the applied cadmium in two years. In the simulated cases with low sorption coefficients (k_d=5 liter/kg), a small amount of the applied cadmium reached half a meter down in the soil after two years. Without sorption about 30% of the Cd had passed 1.5 m after two years. For k_d-values higher than 100 liter/kg almost all the cadmium is still in the first soil compartment after a simulation of two years. At higher concentrations, where cadmium sorption can be described by nonlinear isotherms, more cadmium is present in soil water and generally more bioavailable. The modelling of a nonlinear isotherm at an application of 100 mg Cd/m^2 gave 9% cadmium uptake after two years time. The same isotherm modelled with an application of 10 mg Cd/m^2 gave an uptake of about 1% of the applied cadmium.

1 Introduction

1.1 Energy production from biomass

Biomass as a fuel in industry and households, gives about 66 TWh of energy per year in Sweden. About 3/4 of this is used in industries. The figures are taken from a report on 'An environmentally sound energy system' (Ett miljöanpassat energisystem, 1989). According to the report a possible scenario for the year 2010 includes 30 TWh more energy produced from biomass. About 20 TWh of these would come from energy crop. The energy crop may be cultivated on land that was formerly used for farming.

Farmland has often been treated with commercial fertilizers or sewage sludge. These materials contain trace amounts of cadmium that sorb to the soil and accumulate. Fast growing *Salix* trees used as energy crop have been shown to have a high uptake of cadmium (Nilsson & Timm, 1983). When the trees are cut down to be burned this will mean that some of the cadmium is removed from the soils and dispersed.

1.2 Wood ashes

The ash content of wood is around one weightpercent (Nilsson & Timm, 1983). It consists of the inorganic materials that do not go off as gases when the wood is burnt. When the ash is spread or landfilled these elements can leach out with rain water and spread in the surroundings.

The high amount of sodium and potassium in the ash makes it interesting as fertilizing material. In the southern part of Sweden large amounts of calcium, sodium, potassium and magnesium has been leached out from the soil due to the decrease in pH caused by acid rain (Falkengren-Grerup et al, 1987). The wood ashes have a high content of these elements and a high pH (Nilsson & Timm, 1983). Using wood ash as fertilizer could be a way of recycling the elements back to the forest. Recycling the ashes could increase the sustainability of biomass energy. It could also be a substitute for the lime that is now spread in forests to compensate for acidification.

On the other hand, the ash contains different heavy metals that may have adverse effects on the environment. Field experiments have shown that crop that has been fertilized with wood ash (30 ton/hectare) contains up to six times the concentration of cadmium, compared to crop grown on reference fields (Bramryd, 1985). Also, if the salt content is released too quickly the environment may get a salt chock instead of just filling its supplies of ions. To avoid salt chock for the organisms it has been suggested that the ash should be granulated. This has been tried in field experiments and seems to work well (Lundkvist, 1990).

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1.3 Modelling

Material flows in soil can be very slow. To gain understanding of the processes that govern transport of metals such as cadmium, a combination of field experiments, laboratory experiments and theoretical modelling is needed.

To design a field experiment the number of chemical and hydrological parameters that could be measured are enormous. Also the time span before measurements show what has happened could range over several tens of years. With a mathematical model the influence of many of the parameters can be tested. Our understanding of the processes can often be formulated in equations.

1.4 Cadmium in the environment

Cadmium is a trace metal that is present in air, water and soil. The general human exposure to Cd originates primarily from the terrestrial environment and has in many parts of the world reached a level that is close to what could be considered critical (Christensen, 1989). During this century cadmium production, consumption and emissions to the atmospheric, aquatic and terrestrial environment have increased dramatically. Measurement on human tissue (liver, kidney) from 1897-1939 (year of death) found an average of 0.86 μg Cd/g in renal cortex. Comparing with modern autopsy material (1981) the concentration had increased by a factor of 47 (Drasch, 1983). Daily intake with food is estimated to 50 μg. About 5% of the Cd in what we eat is taken up in the body, while 40% of what we inhale is taken up (Laveskog et al, 1976). The biological half-life of Cd in man is estimated to several tens of years (Friberg et al, 1971). Cadmium resembles zinc in many ways. The two elements belong to group twelve in the periodic system. Cadmium is found in low concentrations wherever zinc is present. (Hägg, 1979). Intoxication of humans by cadmium has occurred both by oral intake and by inhaling (Friberg et al, 1971).

Table 1. Range of Cd concentration in different materials. From Christensen: Cd concentrations in Danish terrestrial environments and in wastes potentially applied to land.

Type of material	Range	Typical value
soils, ploughing layer	0.03-0.5 mg Cd/kg	0.21 mg Cd/kg
soils, 0.5-1.0 m	0.01-0.4 mg Cd/kg	0.09 mg Cd/kg
phosphatic fertilizers	1-20 mg Cd/kg	5 mg Cd/kg
sewage sludge	2-20 mg Cd/kg	7 mg Cd/kg
precipitation (dry & wet)	0.1-0.7 μg Cd/liter	0.3 μg Cd/liter

At environmentally pertinent Cd levels (unpolluted to moderately polluted areas, see Table 1), Cd-concentrations in soils is believed to be governed by sorption processes. In laboratory experiments, sorption of Cd onto soils is a fast process reaching equilibrium within an hour. The major factor governing Cd sorption is the pH of the soil solute system, increasing the sorption about three times per pH unit increase in the pH range 4 to 7 (Christensen, 1989). In a study on 63 Danish soils, Christensen found the linear k_d sorption coefficient to range between 15 and 2450 l/kg. The dominating cadmium species in the soil water is assumed to be Cd^{2+} (ibid). If Cd forms complexes with other constituents in the soil water, these Cd-complexes can have sorption isotherms that differ from the Cd^{2+} isotherm. Even if the Cd^{2+} isotherm would be the same the resulting Cd(total) isotherm can look different depending on the constituents of the soil water.

The mechanisms by which plants take up Cd seems to be unknown. A dissertation by Eriksson (1990a) shows that plant uptake of Cd is to a great extent related to the solubility of Cd in soil water. The experimental crops were ryegrass and rapeseed in pot experiments and oats and winter wheat in field investigations. The amount of Cd taken up varied for the same crop under different soil conditions (mainly pH and organic content differed). The field investigations also showed difference in uptake between varieties of the crops. The importance of considering not only soil conditions but also plant species and varieties when evaluating the risk for increased Cd levels in food crops is stressed.

Pot experiments show a linear relationship between Cd concentration in soil water and Cd content in pot experiments amended with ash from municipal refuse incinerators. The ash contained 1-477 ppm Cd dry weight. The uptake is believed to be promoted by chloride complexation of the metal owing to the high chloride content of the ashes, around 10%, increasing Cd mobility in the soil (Bache and Lisk, 1990).

1.5 Cadmium chemistry

Cd can form complexes with for example Cl^-, SO_4^{2-}, CO_3^{2-} and OH^- (Rai et al, 1987). Precipitates such as $CdCO_3$ (s) and $Cd(OH)_2$ (s) can form at high pH-levels. Under anaerobic conditions CdS could form. The complexes and precipitates formed depend of the composition of the soil water. It may therefore be of interest what other elements, except for Cd, the wood ash will add to the soil. In this study we assume that Cd is dissolved as Cd^{2+}.

Xu et al (1989) have shown in experiments that fulvic acids have a pronounced effect on Cd sorption to aluminium sites. For low pH the sorption increases and for high pH it decreases. Fulvic acids are present in soils and could possibly cause the Cd to be dissolved in the soil water even at high pH-levels where it should be expected to form precipitates with carbonates or hydroxides.

Competition with other divalent cations for sorption sites can be of importance for how much Cd is sorbed to the soil. Christensen (1989) investigated competition with zinc and with calcium. He concluded that Zn solute concentrations above 100 mg Zn/liter could significantly reduce Cd distribution coefficients, which implies that it can be important at contaminated sites and landfills. Ca present in the soil water is found to compete effectively with Cd for sorption sites in the soil. An increase in Ca concentration from 10^{-3} to 10^{-2} M (and accounting for change in ionic strength) was found to reduce the Cd sorption capacity of the sandy loam approximately by one third (ibid).

1.6 Aim of present study

The aim of the study is:

* To develop a model for Cd-transport in soil systems.

* To use this model in order to evaluate which factors are the most important ones in determining the transport.

This study is basically a sensitivity analysis of which mechanisms are important for the flow of cadmium in the soil/plant-system, where cadmium is assumed to be transported with water. Different parameters that govern sorption characteristics and water flow are varied in simulations and the resulting distribution of cadmium is investigated.

2 Materials and methods

This work is divided into two parts:

Part one: Simulation of water flow in the unsaturated zone of a farmland where *Salix* grows. This gives the water content in the soil, water flow and the root water uptake needed for part two, for each day. These figures vary from day to day, depending on for example temperature and precipitation pattern. To estimate how this variability influence the Cd distribution over the year, the mean values of these variables are also calculated and used in part two.

Part two: Simulation of what happens to cadmium applied to the land. We assume that cadmium is dissolved in the first soil compartment of 10 cm depth and that the following processes take place:

* it sorbs to the soil, according to the sorption isotherm. For a nonlinear isotherm this quantity is calculated by iteration.

* what is then left in solution follows the water, which can flow to the next soil compartment, be taken up by roots or stay in the same soil compartment.

The calculation is repeated for each day and each soil compartment containing Cd. It gives the concentration of Cd in soil water, the amount sorbed to soil , the amount of cadmium taken up by the roots and the depth to which cadmium has reached.

The simulations are done assuming that a certain amount of Cd is applied to the first compartment on the first day. The amount is arbitrarily chosen as an illustrative quantity, to be able to see the distribution of Cd, it is however based on figures on the amounts of ash that are planned to be spread and measurements of the cadmium content of wood ashes, taken from literature.The amount 10 mg Cd/m^2 is taken as a likely magnitude of the amount of Cd that will be applied to the soil with wood ash, based on figures from Bramryd (1985). The wood ash contained about 20 µg Cd/g. In these experiments 30 000 kg ashes/ha were applied, giving a total of 60 mg Cd/m^2 and considerable amounts of Cd in the crops. Eriksson (1990b) suggests an amount of 2000-3000 kg of ash/ha (about 6 mg Cd/m^2), that would approximately compensate for the metals withdrawn by trees. He also gives the figure of 300 g Cd/ha, (equivalent to 30 mg Cd/m^2) in a Swedish forest soil, half a meter down in the soil.

Experiments have to be made to see what quantities are likely to come out of the ash. We assume the cadmium is dissolved and can sorb on the soil in the first compartment. The sorption is assumed to be reversible. The equilibrium concentration for cadmium in soil water is calculated. This concentration determines (together with the water flow) the amount of Cd transported to the next compartment and the amount of Cd taken up by roots.

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Cadmium is applied once, at the top of the soil profile to simulate the application of wood ash. In reality there will of course always be cadmium present in the soil already. In the simulations we disregard this, since we are interested in where the applied cadmium is going. If the sorption can be described as linear, the amount of cadmium present will not affect the distribution in the soil/plant system (expressed as the percentage of the applied cadmium at a given time and a given place).

Different questions are posed: How is the behavior of cadmium affected by

1) the 'strength' (k) of the sorption

2) the shape (n) of the sorption isotherm

3) the variability of the water flow, as compared to a mean value on water flux and root water uptake

4) other hydraulic parameters, such as the precipitation pattern and the hydraulic conductivity of the soil

2.1 Water in an unsaturated soil profile

The water movement in a soil profile is calculated by the simulation program SOIL (Jansson, 1990).

The soil is regarded as a one-dimensional profile divided into several soil compartments. For simplicity these soil compartments will be refered to as boxes. Each box is assigned parameters, eg porosity and saturated conductivity, that govern the hydraulic and thermal properties of a chosen soil type. The water flow between two adjacent compartments is calculated with a finite difference approximation:

$$q_{i,i+1} = 2 \cdot K(\theta_{i,i+1})_{i,i+1} \cdot (\psi_i - \psi_{i+1})/(\Delta z_i + \Delta z_{i+1}) \qquad [1]$$

where i indicates the compartment number, q is the water flow between two compartments, $K(\theta)$ is the hydraulic conductivity, θ is the water content, ψ is the hydraulic potential and Δz is layer thickness. To obtain the water flow through the profile, this equation is solved together with a mass balance equation, which yields an equation known as Richards equation (de Marsily, 1986, Nielsen et al, 1986).

The evaporation is calculated empirically with Penman-Monteiths equation (Monteith & Unsworth, 1990). It is a sum of three terms: soil surface evaporation, transpiration through the plant and evaporation of the interception on the surfaces of the plant. The root water uptake is assumed to be the actual transpiration, which is calculated from each layer where there is a root distribution.

Frost, that occurs when temperatures go below the freezing point, affects the heat distribution in the profile and creates a potential gradient. Snow is accounted for in two extra 'water supplies', one with the amount of unfrozen water and the other with total water equivalent in the snow. Snow melt is calculated as a function of radiation and snow age.

As input, the model uses precipitation, cloudiness, temperature, wind and humidity. The different routines are connected to each other in a way indicated in Figure 1. The precipitation goes down into the soil. It can also be intercepted on the leaves of the crop, stored as snow or, if the soil is already saturated, become surface runoff.

Figure 1. The structure of the SOIL model (Picture from Jansson, 1991). The picture shows the water flow (heat flow is not shown). Every box contains a known amount of water. The arrows signify water flow. In the soil profile the boxes can be assigned different root parameters and permeability.
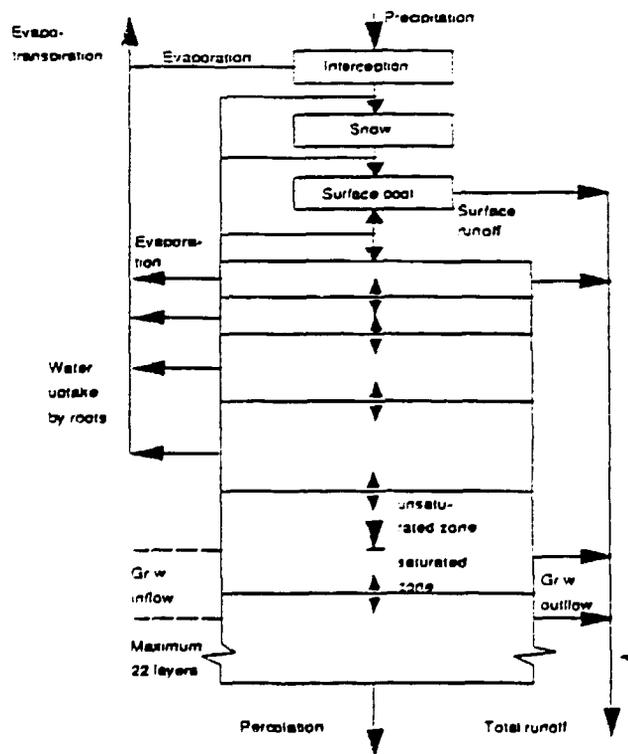
2.2 The reference profile

The simulations were done with a 1.5 meter deep profile, with an area of 1m². The measured hydraulic soil parameters, such as saturated conductivity, porosity, pore size distribution etc, were taken from an experimental site at Lanna in Västergötland. In the model the soil characteristics are described by a water retention curve (tension versus water content) and an unsaturated conductivity function (conductivity as function of water content) which are estimated from measurements on the hydraulic parameters. The soil was characterized as having a topsoil (the plow layer, about 30 cm thick) consisting of 37% clay, 9% sand and 7% organic material, and a subsoil with 58% clay, 3% sand and 3% organic material (see appendix for more details on model parameters). The first five compartments have a depth of 10 cm each, the two following are 25 cm and the last is 50 cm (see Figure 2). The evaporation parameters are chosen with the energy crop *Salix* in mind. Some were taken from measurements on *Salix* (Persson, 1991). The root distribution was discussed with Rosa Andersson, Ultuna. The roots in the simulation start to grow in April and stop growing in September. They reach 130 cm down and are exponentially decreasing (see Figure 3).

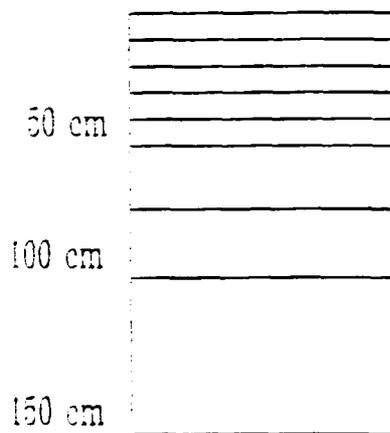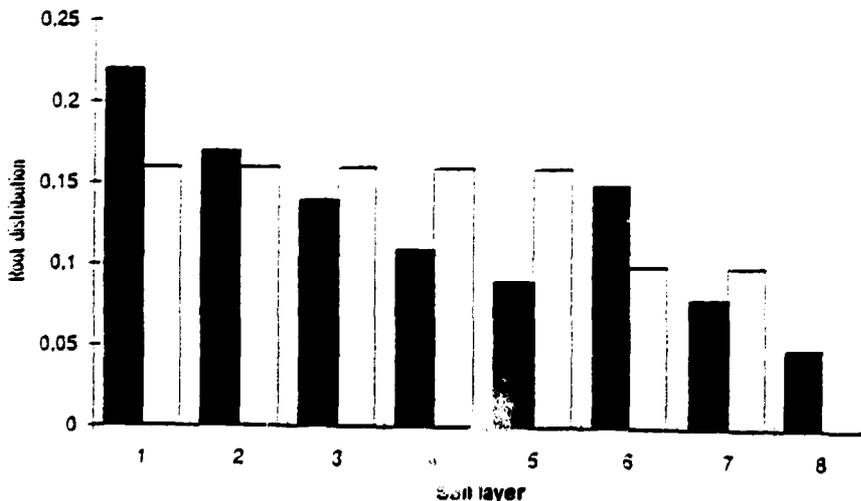Figure 2. The soil profile.

50 cm

100 cm

150 cm

Figure 3. The root distribution in the soil layers. The black staples show the exponentially decreasing root distribution. The soil layers are of different sizes, which is why the distribution per layer does not follow an exponential curve. The white staples show a different root distribution, used to evaluate the importance of changes in the assumed distribution.

The root water uptake, the water content of the soil and the water flux values, for each day and each compartment of the profile over a time period of two years, were calculated in the hydrological simulation of the water transport in the soil profile (see Figure 4a, 4b and 4c). This was used as input to the cadmium flow and sorption modelling. The mean value over the year of the root water uptake and the flux were calculated and used for comparison.

Figure 4. 4a) An example of the water flux at a depth of 10 cm, [mm/day] , simulated over two years, 1984 to 1985. The water flux is defined positive downwards, so negative values indicate that the flow direction is upwards. From the reference profile.
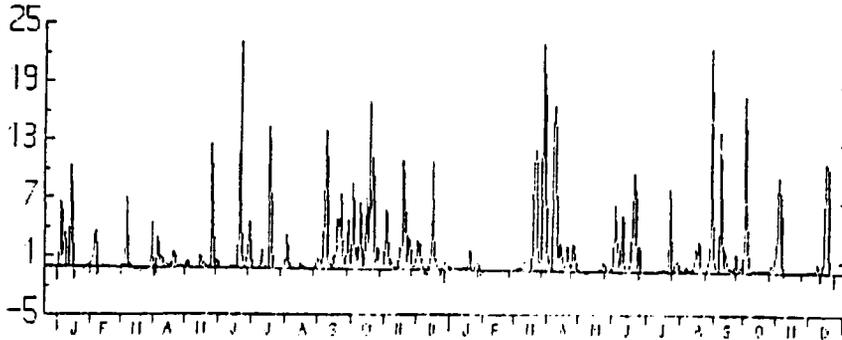
4b) Simulated root water uptake from the first soil compartment. From the reference profile. [mm/day]
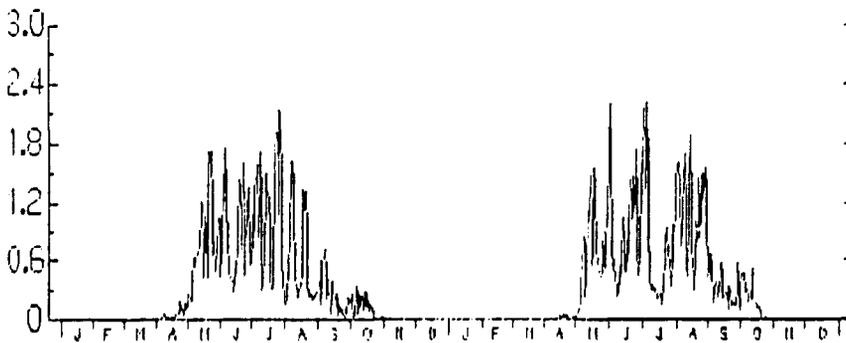
4c) Simulated water content in the first soil compartment. From the reference profile. [mm]
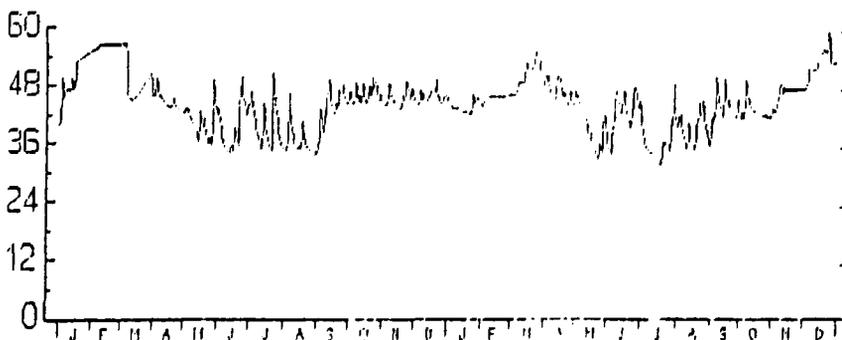
2.3 Sorption: Freundlich's isotherm

The term sorption refers to the uptake and storage by soil of solute species originally present in soil water. It can include several processes such as adsorption, absorption and ion-exchange. No assumption about the type of sorptive mechanism is done. Plotting the concentration in soil, as a function of the concentration in soil water, at a given temperature gives a sorption isotherm. This curve can be described by different equations. Over small concentration ranges the curve can be approximated with a straight line, a linear isotherm. For larger ranges the curve often bends off. Two common ways of describing it mathematically are the Freundlich and the Langmuir equations. We have chosen the Freundlich isotherm because many experiments indicate that cadmium sorption can be described by it (Travis & Etnier, 1981). The Freundlich isotherm is defined by the nonlinear relationship:

$$S = k \cdot C^n \qquad\qquad [2]$$

where k and n are experimentally determined constants (See Figure 5). C is the concentration in solution, mg/liter, and S is the concentration in the soil, mg/kg. The isotherm is empirical.

Figure 5. Freundlich isotherms for different n and k values.
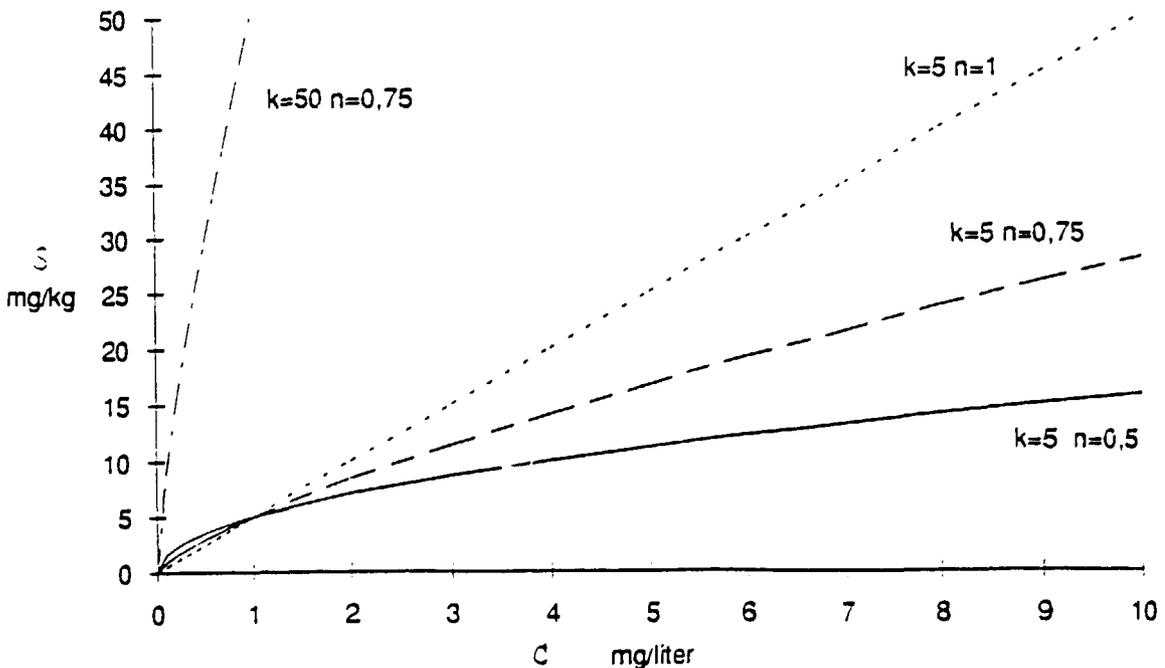
For a linear isotherm, n=1, the slope of the sorption isotherm is constant at all concentrations. In nature one would expect a number of sorption sites to be available for the metal, but with different affinities. With a limited number of available sorption sites there would be a maximum amount of ions that could sorb to the soil. That situation, where cadmium sorbs easier in low concentrations than in high concentrations, can be modelled with a Freundlich isotherm where n<1. No physical units can be attributed to k and n (except when n=1), but for an experimental purpose this method can be well suited. Many studies have confirmed that Cd-sorption follow this type of curve (Travis & Etnier, 1981). For a limited concentration range the curve can often be approximated with a linear isotherm. In a study by Chardon on Cd sorption to a number of Dutch soils (de Haan et al, 1987), the parameter k varied between 0.01 to 4.2 and n varied between 0.7 and 0.9. In an investigation of 63 Danish soils, Christensen observed k_d -values ranging between 15 and 2450 liter/kg for a linear isotherm: $S=k_d C$ (Christensen, 1989). We will use the notation k_d for the linear case, (the d stands for distribution coefficient). The unit of k_d is liter/kg. Observe that k and k_d are not strictly comparable, as k is linked to the value of n.

To model the cadmium concentration in a soil with a nonlinear isotherm, no explicit solution can be made. Instead we have to iterate gradually until we find a concentration that satisfy two equations, with given accuracy. The Freundlich isotherm, [2], gives one equation and the mass balance, [3], gives the other equation. (The mass balance states that the sum of Cd in solution and the Cd sorbed to the soil should equal the total amount of Cd.)

$$S_i \cdot \rho \cdot V_{i,soil} + C_i \cdot V_{i,water} = \text{Total Cd in compartment} \qquad [3]$$

where ρ is soil density and V is volume.

$V_{i,soil} = 1m \cdot 1m \cdot$ (thickness of layer i, in mm)

$V_{i,water} =$ calculated by the hydrological model, the amount of water in layer i (in mm)

2.4 Cadmium uptake by roots

We assume that cadmium is taken up passively, following the water that is taken up into the roots. The root water uptake is expressed as amount of water, in mm/day. To get the amount of Cd that follows with the water, we take the Cd-concentration in the soil water, C, times the root water uptake, r, :

$C \cdot r = \text{Cd uptake in roots} \qquad [mg/dm^3] \cdot [mm/day] = [mg/day \text{ and } m^2]$

3 Results

The results from the simulations are shown as functions of k and n in the sorption isotherms, and of different flow patterns.

1) The 'strength' (k) of the sorption

An example of the effect of sorption can be seen in Figure 6 and 7. In a simulation with no sorption (k=0) all the Cd will be dissolved in the soil water (Figure 6a). By the end of the year we find that more than 70 % of the applied Cd has been taken up with the roots (Figure 6b). The rest is transported with the water out of the soil profile. In this simulation about 30% of the cadmium had passed down to the bottom of the soil profile. The water flux has a mean value that lies around 1 mm/day (the flux from one soil compartment to another). If there are larger pores in the soil, water can move faster. (Higher flux is a question we will investigate under point 4.)
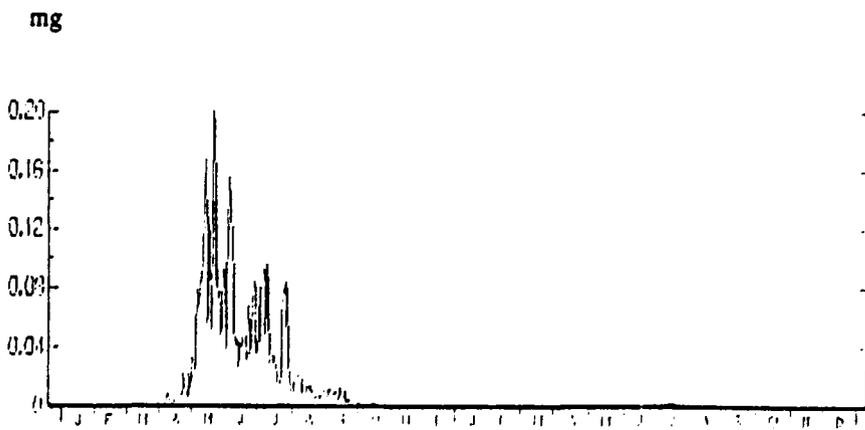
Figure 6. Simulation with k=0.

6a) The amount of Cd (in mg) dissolved in the water in the first compartment.

Cd (in mg)
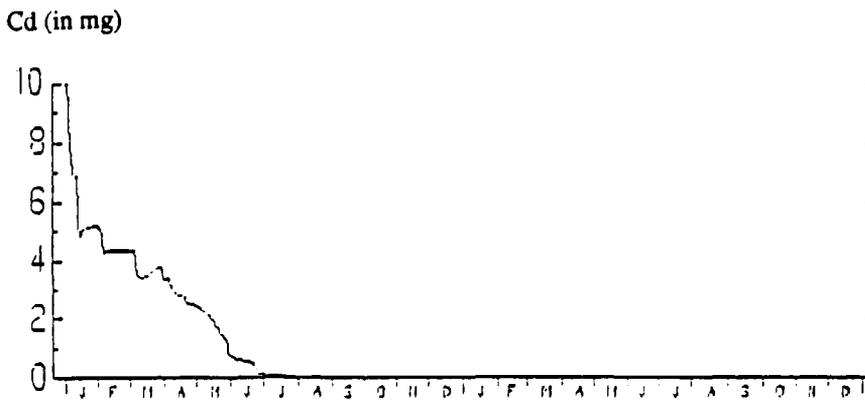
6b) The amount of Cd that accumulates in the plant over time.

mg
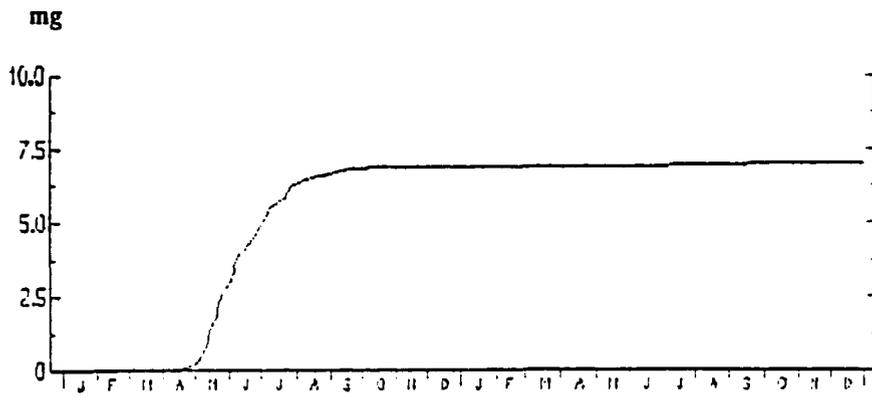
**6c) The amount of Cd that is transported with the root water uptake per day.**

mg

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As soon as sorption is present, a smaller amount of the Cd is dissolved in water. In the case of k=5 and n=1, (Figure 7) only about 10 % of the Cd is present in the water. The rest sorbs to the soil matrix in the beginning of the year. As Cd is lost from the soil water (by root uptake or transport) the soil matrix release Cd according to the isotherm. The amount of Cd in solution is thus almost constant over the year. In this simulation only 20% of the Cd will have gone into the plant by the end of the first year and 30% after two years.
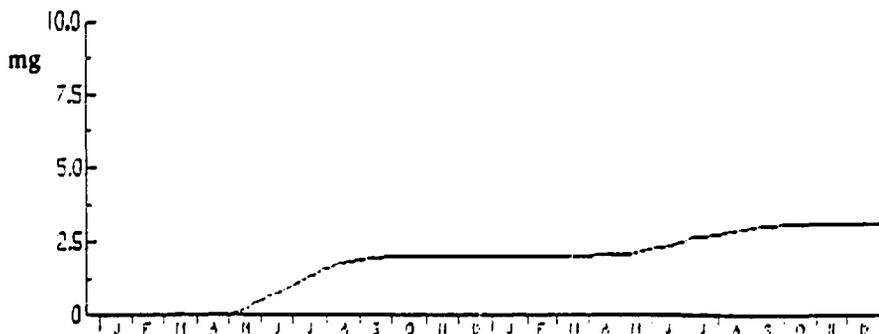
Figure 7. Simulation with k=5, n=1. 7a) The amount of Cd (in mg) dissolved in the water of the first compartment.

7b) The amount of Cd sorbed to the soil in the first compartment.
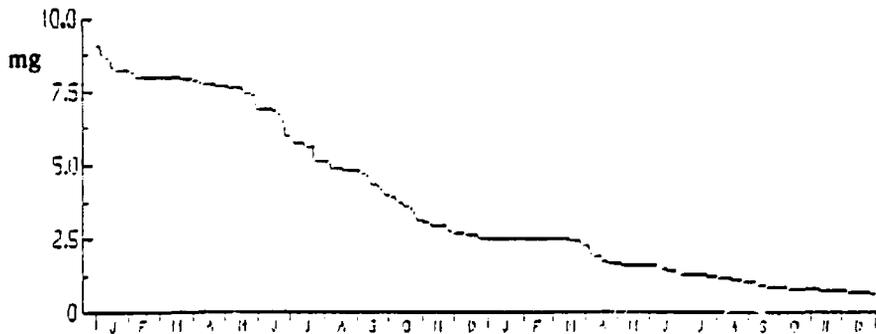
7c) The amount of Cd that accumulates in the plant over time.

2) The shape (n) of the sorption isotherm

A nonlinear isotherm implies more or less sorption in comparison to a linear isotherm depending on the concentration range (see Figure 8). If we compare a nonlinear isotherm with k=5 and n= 0.5 with a linear isotherm with k_d=5, as in Figure 8, we see that for soil water concentrations of C<1 mg/liter the nonlinear isotherm indicate more sorption than the linear, but less for C>1 mg/liter.

The isotherms are not directly comparable in this way. Depending on what concentration range we focus on, we can choose different linear isotherms as approximations of the nonlinear. Another choice for comparison could be (see Figure 8) the linear isotherm k_d=10, which follows the beginning of the slope of the nonlinear isotherm. With this comparison the nonlinear isotherm will give less sorption than the linear for nearly every soil solute concentration.

Figure 8. Comparison between the nonlinear isotherm defined by k=5, n=0.5, and two linear isotherms: k_d=5 and k_d=10. The arrow points at C=1 mg/liter, where the nonlinear isotherm starts sorbing less than the linear k_d=5. S is concentration in soil, C is concentration in water.
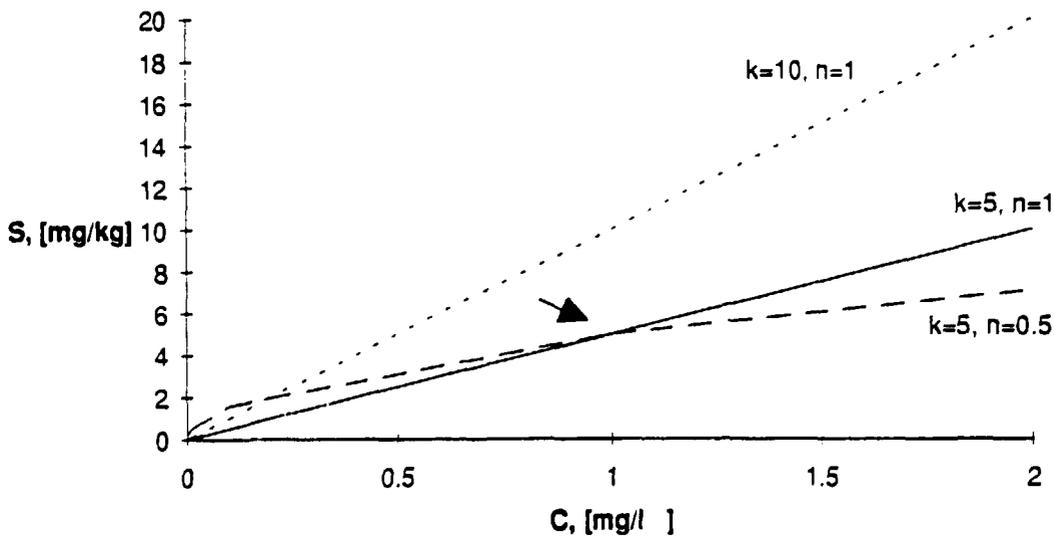

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Table 2 gives simulated root uptake of Cd with different isotherms and with different amounts of Cd applied to the soil. As long as the concentration is below 1 mg/liter the linear isotherm gives more Cd dissolved in soil water and consequently a higher root uptake. For higher concentrations we see the influence of the nonlinear isotherm.

Table 2. Simulated root uptake of Cd with different isotherms and with different amounts of Cd applied to the soil. The approximate concentration indicates the magnitude of Cd in soil water. The Cd root uptake is given in percent of applied Cd.

| k	n	Cd applied mg/m^2	Approx. Conc mg/liter	Cd root uptake
5	1	10	0.01	26%
5	0.5	10	$1 \cdot 10^{-3}$	2%
10	1	10	0.01	15%
5	1	100	0.1	26%
5	0.5	100	0.1	17%
5	1	1000	1	26%
5	0.5	1000	10	54%

3) The variability of the flow

To test the effect of the variability of water flux and root uptake, a simulation was done with both parameters held constant at their mean values, counted over a year. The flux for each compartment was set to the mean value from the simulation with variable parameters, around 1 mm/day, (see appendix) over the whole year. The root water uptake was set to its mean value counted from April to the end of August. Comparing Figure 6 with Figure 9 we see that the main features of the curves are the same. (The amount taken up by the roots is however somewhat lower in the constant value-simulation.)

Figure 9. Simulation with k=0, with constant water flux and constant root water uptake.

9a) The amount of Cd (in mg) dissolved in the water in compartment 1 to 4. Also shown are the same curves with a variable flow (same simulation as in figure 6)
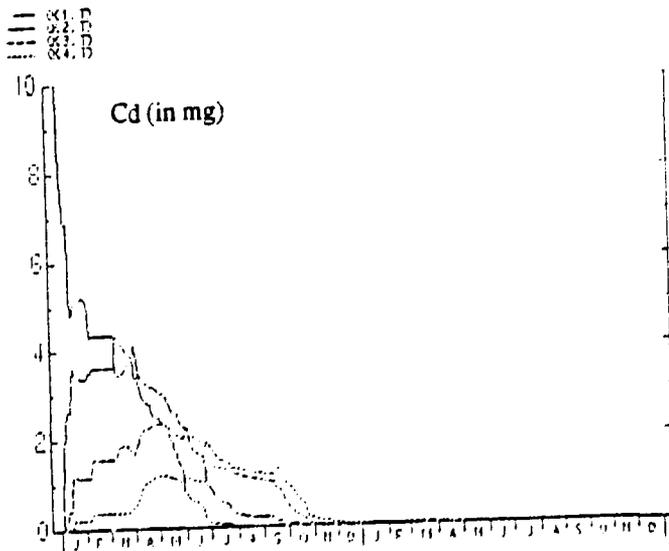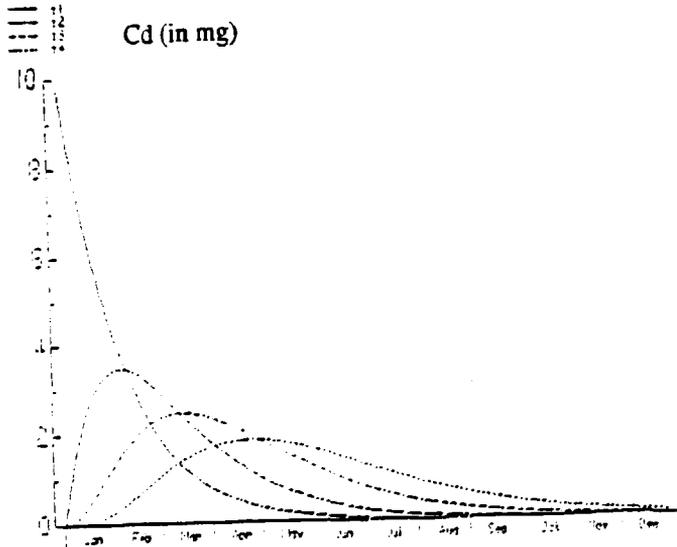
9b) The amount of Cd (in mg) that accumulates in the plant over a year.
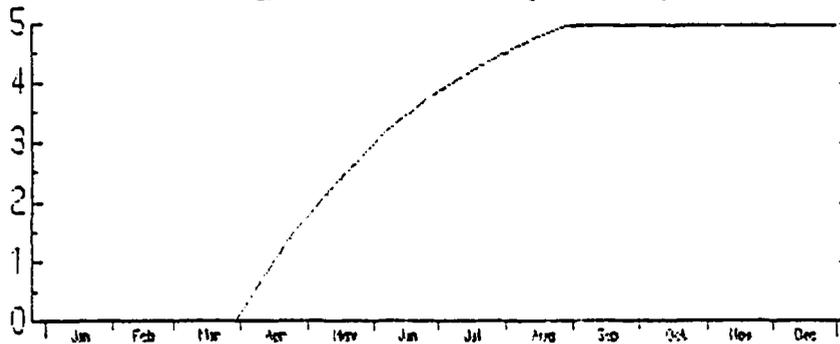
9c) The amount of Cd (in mg) that is transported with the root water uptake per day.
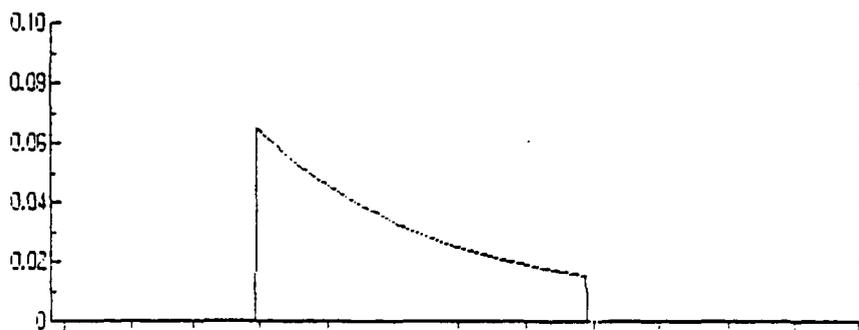
4) Other parameters affecting the water flow

The reference case represents a situation where the water flow from one compartment to another in the soil profile is around 1 mm/day. If we have larger pores in the soil the flow will be different and Cd transport through soil may be quicker. The SOIL model has a submodel that accounts for macropore flow. If the soil is saturated with water the hydraulic conductivity becomes larger and water is transported at a higher rate. Such a simulation was done, but the soil never reached saturation, so the results were the same as for the reference case. Another situation where more water will flow through the soil is when there is no vegetation growing on the soil. A simulation was done with no root water uptake. Another simulation was done to see effects on changes in the root distribution (figure 3). To check how dependent the model is on the chosen size of soil compartments, a simulation with twice as thick compartments was made. Some of the results from the different simulations are collected in Table 3.

As can be seen in Table 3, the sorption is of vital importance for how deep the Cd has migrated in the soil profile and how much is taken up by the roots. The figures in % indicate percentage of applied Cd. Of course these should be interpreted carefully (so that 1% means little, 50% a lot, and 100% much). For a linear isotherm the percentage is the same no matter how much Cd is applied. For the nonlinear isotherms this is not the case, as can be seen for k=5 and n=0.5.

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Table 3. Results from five different hydrological simulations

A The reference case. Values below 0.1% are given as zero.

Sorption isotherm	k=0	k=5, n=1	k=5, n=0.5	k=200, n=1	k=200, n=0.5
Root uptake after one year	70%	20%	0.5% (10mg) 5% (100mg)	0.7%	0%
Root uptake after two years	70%	30%	1.4% (10mg) 9% (100mg)	1.4%	0%
Conc. in first compartment when the Cd is applied	0.25 mg/l	0.02 mg/l	$0.6 \cdot 10^{-3}$ mg/l (10mg)	$0.6 \cdot 10^{-3}$ mg/l	$0.4 \cdot 10^{-3}$ mg/l (10mg)
Amount dissolved in soil water in the deepest box, after two years	27% (box 8)	0.3% (box 5)	0.3% (box 1)	0.4 % (box 1)	0 % (box 1)

B The reference case, with constant mean values of flow

Sorption isotherm	k=0	k=5, n=1	k=5, n=0.5	k=200, n=1
Root uptake after one year	49%	22%	0.7% (10mg)	0.7%
Amount dissolved in soil water in the deepest box, after one year	18% (box 8)	0.4%(box 4)	0.3% (box 1)	0.3% (box 1)

C The reference case, with double box size

Sorption isotherm	k=0	k=5, n=1	k=5, n=0.5	k=200, n=1
Root uptake after one year	60%	17%	0.3% (10mg)	0.6%
Root uptake after two years	62%	28%	0.6% (10mg)	1%
Amount dissolved in soil water in the deepest box, after two years	32% (box 8)	0.3% (box 4)	0.2% (box 1) (10 mg)	0.3% (box1)

D The reference case, with no root water uptake

Sorption isotherm	k=0	k=5, n=1	k=5, n=0.5	k=200, n=1
Amount dissolved in soil water in the deepest box, after two years	100% (box 8)	0.1% (box 8)	0.3% (box 1) (10mg)	0.4% (box 1)

E The reference case, with a new root distribution

Sorption isotherm	k=0	k=5, n=1	k=5, n=0.5	k=200, n=1
Root uptake after one year	70%	15%	0.5%	0.5%
Root uptake after two years	70%	26%	1%	1%
Amount dissolved in soil water in the deepest box, after two years	27% (box 8)	0.1% (box 6)	0.1% (box 1)	0.1% (box 1)

The box size has only a limited influence. Since it is assumed that all the Cd is dissolved in the first box, a doubling of a compartment decreases the initial concentration. However, only limited differences in the results can be seen. In the case of no sorption, Cd is transported further down in the profile. In the no sorption case the root uptake is smaller than for the reference case, probably because the Cd is transported away from the root zone more quickly. To have smaller compartments than the reference case, the time step of one day would have to be abandoned for smaller time steps. Otherwise the amount of water going in or out of a compartment can be larger than the compartment itself, resulting in mass balance errors with the Cd that should be left to equilibrate in the box.

The simulation without root uptake, shows a faster flow of Cd for low values of the sorption coefficient. For stronger sorption this shows no effect, at least not on considered time scales.

The simulation with a root distribution that is slightly different from the reference case indicates that smaller changes in the assumed distribution might have some effect, although the values are close enough to be regarded equivalent.

4 Discussion

I. The model

Using a combination of laboratory isotherms (Christensen,1989) and a field experiment (Eriksson,1990a), we can check if the model gives a root uptake of a reasonable magnitude. The crops are wheat and oats, so the root uptake cannot be expected to be very similar to the model. *Salix* is expected to take up more water and consequently (according to our assumption on passive uptake) to take up more cadmium.

Two isotherms are chosen fromChristensen 1989 (page 211). One is linear, k_d=200 for loamy sand , pH 6, and the other is nonlinear with k=386 and n=0.8 (with our definition of n, being the inverted value of Christensens) sandy loam, pH 6.

With 10 mg/m^2 applied, the simulation gives a plant uptake of 70 µg Cd/m^2 for the linear isotherm for the first year, 140 µg/m^2 for the second and 5 µg/m^2 and 10 µg/m^2 respectively for the nonlinear isotherm.

To recalculate the simulated application of 10 mg/m^2 into mg/kg it is assumed that all the Cd is distributed in the upper 10 cm of the soil, giving a volume of 100 mm · m · m=100 dm^3. With an estimated density of 1.6 kg/dm^3, 160 kg of soil is obtained. Now 10 mg/160 kg equals 0.06 mg/kg .

In the field experiment the s... ontained between 0.23 - 0.39 mg Cd/kg (HNO_3-extracted) giving a plant uptake of between 9 - 24 $\mu g/m^2$ (see Table 4). The comparison thus gives: 5 and 70 $\mu g/m^2$ in simulated plant uptake as compared with 9 - 24 for the field experiment. The magr ...de appears reasonable.

Table 4. From Eriksson 1990a. Cadmium uptake in crops as measured in field experiments. Figures in parenthesis are standard deviations. Last column is a multiplication (done by us) of the two first columns and gives uptake in the same units as the simulation.

crop	Cd-grain	yield	Cd-HNO_3	pH	Cd plant uptake
	$\mu g/kg$	kg/ha	mg/kg		$\mu g/m^2$
oats	30.9(17.6)	2870	0.23	6.4(0.6)	9
wheat	53.1(26.5)	4550	0.27	6.6(0.6)	24
oats	41.5(23.5)	2820	0.38	5.8(0.8)	12
wheat	46.8(13.8)	4270	0.39	5.7(0.3)	20

II. Sensitivity analysis

1   The sorption is of major importance when calculating the distribution of cadmium in the soil-water-plant system.

2   The root uptake has some influence on the distribution of cadmium, especially at low sorption coefficients. The root distribution in itself does not seem to be a sensitive parameter in the simulation.

3   The water flow changes in these simulations did not affect the cadmium distribution to any large extent. Another way of investigating the influence of the water flow is to simulate cadmium flow in another type of soil. Simulations of cadmium flow in a forest soil are planned.

4   Since the sorption coefficient has such an impact on the result, it is of interest to determine it experimentally.

With the addition of wood ash to soil, elements such as K, Ca, Na and Mg will also be added. This study does not cover effects such as different sorption behavior linked to complexing and competing agents in the soil water. Both complexing and competing agents can make cadmium more soluble in soil water. The sorption in this study is also assumed to be described by one sorption isotherm in the whole soil profile, when in the field it can be expected to vary with the content of organic

material in different layers of the soil and with pH. In following studies we hope to cover these issues.

5 Conclusions

The model, with a separate flow modelling describing the water fluxes and an equilibrium sorption modelling, with a possibility to choose different Freundlich isotherms and a passive metal plant uptake, seems to work well. The variation of soil compartment sizes and slight changes in the root distribution gave small changes in the results, which is interpreted as a measure of the solution stability. The comparison between measured root uptake of Cd and the magnitude of the modelling results in the discussion is also an indication that the model can be an instrument to use in connection to field and laboratory studies.

The factor influencing cadmium transport most, according to these simulations, is the sorption isotherm. The degree to which Cd sorbs to soil decides how much will be available in the soil water, for plant uptake or transport through the soil to the ground water. Other studied factors such as root distribution and hydrological properties influences the result only to a limited degree. With an application of 10 mg Cd/m^2 in the given range of Freundlich isotherms, the simulations gave a plant uptake of between 0 and 30 % of the applied cadmium in two years.

In the simulated cases with low sorption coefficients (k_d=5 liter/kg), a small amount of the applied cadmium reached half a meter down in the soil after two years. Without sorption, about 30% of the Cd had passed 1.5 m after two years. For k_d-values higher than 100 liter/kg, almost all the cadmium is still in the first soil compartment (the uppermost 10 cm of the soil profile) after a simulation of two years.

At higher concentrations, where cadmium sorption can be described by nonlinear isotherms, cadmium is to a higher extent present in soil water and is generally more bioavailable. The modelling of a nonlinear isoterm at an application of 100 mg Cd/m^2 gave 9% cadmium uptake after two years time. The same isotherm modelled with an application of 10 mg Cd/m^2 gave an uptake of about 1% of the applied cadmium. If the sorption isotherm is nonlinear, Cd can sorb easily at lower concentrations, but in a longer perspective accumulate in the soil and sorb less as the concentration increases. Accumulated Cd can also be released if the pH of the soil decreases.

Experiments will give us more information on what sorption isotherm to expect with biomass ashes and a 'representative' field soil. If complexes are important they may cause the cadmium to move faster down into the soil. The charge of a particle moving through soil may affect its ability to sorb to the soil. Also, the sorptive behavior can be different from that seen in laboratory measurements because of for example the variability of soil water and temperature. The fate of cadmium in the field should be considered before a policy on how the ashes should be treated is established.

Acknowledgements

Table of notation

C   the concentration in solution, [mg/liter]

Δz soil layer thickness [mm]

i   indicates the number of a soil compartment

k   an experimentally determined constant in the Freundlich isotherm (Figure 5)

$K(\theta)$ the hydraulic conductivity, [length/time]

k_d the distribution constant, [liter/kg]

n   an experimentally determined constant in the Freundlich isotherm (Figure 5)

q   the water flow between two compartments, [mm/day]

r   the root water uptake, [mm/day]

S   the concentration in the soil, [mg/kg]

$V_{i,soil}$ the volume of soil in a soil compartment, [dm^3]

$V_{i,water}$ the volume of soil water in a soil compartment, [liter]

ρ soil density, [kg/dm^3]

θ the moisture content, [volume percent]

ψ the hydraulic potential, [Nm/area]

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