M. L. van Beusichem (Ed.), *Plant nutrition – physiology and applications*, 313–316.

PLSO IPNC475

Plant uptake of cadmium as affected by variation in sorption parameters

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Key words: cadmium, crop quality, heavy metals, modelling, soil heterogeneity

Abstract

The effect of accumulation of cadmium in the topsoil on cadmium contents in crops is evaluated for field scale situations, using a model that links cadmium input, plant uptake, and leaching to cadmium accumulation in the rootzone. Measurements of pH and organic matter content, which regulate sorption behaviour to a large extent, show significant field-scale variability. Taking this heterogeneity into account, the probability that the cadmium concentration in part of the plants exceeds quality standards is compared with exceedance of the distribution average.

Introduction

Accumulation of heavy metals in an arable soil may cause acceptable heavy metal concentrations in plants to be exceeded. To assess the effect of elevated heavy metal contents in the topsoil, models can be used that describe the relevant processes involved. The process of heavy metal uptake is complex, because of the many interacting soil parameters that regulate availability of heavy metals to plant roots (Bingham *et al.*, 1983; Bjerre and Schierup, 1985; McBride *et al.*, 1981), next to the influence of the plant itself on its local root environment (Linehan *et al.*, 1985; Treeby *et al.*, 1989). For field scale predictions an additional complication arises, because natural soil systems are highly heterogeneous (Biggar and Nielsen, 1976; Jury *et al.*, 1987).

To investigate the impact of soil heterogeneity on model predictions of heavy metal concentration distributions over a field, a simplified physical description of the most important processes is used. The model includes a constant input rate of cadmium, equilibrium sorption of heavy metal onto the soil, and a relationship between heavy metal content of the soil and heavy uptake by plants. Stochastic theory is implemented in the model, to account for variability of parameters that are known to vary significantly throughout a field soil.

Taking cadmium uptake of barley as an example, the impact of variability of pH and organic matter content on crop quality is shown, comparing field-averaged cadmium concentration in plants with deterministic model predictions. The distribution of cadmium concentrations in all plants in the field is analyzed comparing percentiles of the frequency distribution of the plant uptake rate with official standards for crop quality.

Theory

The soil is considered to be homogeneous in vertical direction. The plough layer is assumed equivalent with rooting depth and the main processes in this soil compartment that regulate cadmium accumulation T [μmol.m^{-3}] in soil are cadmium input I [μmol.m^{-3}], leached amount J [μmol.m^{-3}] at the lower boundary of the system, and plant uptake of cadmium P [μmol.m^{-3}]:

$$\frac{dT}{dt} = \frac{dI}{dt} - \frac{dJ}{dt} - \frac{dP}{dt} = I_t - J_t - P_t . \qquad (1)$$

Solute flux J_t equals soil water flux v [$m.y^{-1}$] times solute concentration c [$\mu mol.m^{-3}$], with correction for soil compartment thickness L [m] and water content θ [$m^3.m^{-3}$] of the soil. For a high distribution ratio and assuming equilibrium Freundlich sorption, J_t can be approximated with:

$$J_t = \frac{v\theta c}{L} = \frac{v\theta}{L}\left[\frac{T}{\rho k_1}\right]^{1/n}, \tag{2}$$

in which ρ is the soil dry bulk density and k_1 and n are parameters that define the adsorption isotherm.

Soil chemical parameters as pH and organic matter content influence the shape of the adsorption isotherm. This is accounted for by Van der Zee and van Riemsdijk (1987) who included proton activity (H^+) mol.L^{-1}] and organic carbon content oc [$g.g^{-1}$.%] in the Freundlich equation:

$$k_1 = k_a oc(H^+)^{-1/2}, \tag{3}$$

in which k_a is the adjusted adsorption constant, excluding effects of oc and (H^+).

Plant uptake P_t can also be expressed as a function of T, although total content of heavy metals generally does not reflect bioavailability. However, literature shows little quantitative information on the relationship between c and P_t. Mathematical relationships between T and P_t of the type:

$$P_t = k_2 T^m \tag{4}$$

are proposed by Kuboi *et al.* (1986) and will be used instead.

We assume a constant cadmium input rate:

$$I_t = I_0 . \tag{5}$$

Substitution of eq. (2) and (4) in eq. (1) yields a differential equation in terms of T:

$$\frac{dT}{dt} = I_0 - k_2 T^m - \frac{v\theta}{L}\left[\frac{1}{\rho k_1}\right]^{1/n} T^{1/n} . \tag{6}$$

For some values of m and n this equation can be solved analytically. For our example a numerical solution is obtained.

Variability of soil parameters is included in this deterministic model using stochastic theory. Model predictions are then based on the assumption that an ensemble of measured parameter values on different locations in a field are representative for the underlying distribution at each location (ergodicity). The distribution of the variable soil parameters is represented by a probability density function (PDF), instead of single values. This implies that model predictions are also represented by PDF's. The parameters that describe the PDF are dependent on the sensitivity of the model to the variable soil parameter. Van der Zee and van Riemsdijk (1987) assumed a lognormal PDF for proton activity and organic carbon content:

$$f_y = [y s_x \sqrt{2\pi}]^{-1} \exp\left\{-0.5\left[\frac{x - m_x}{s_x}\right]^2\right\}, \tag{7}$$

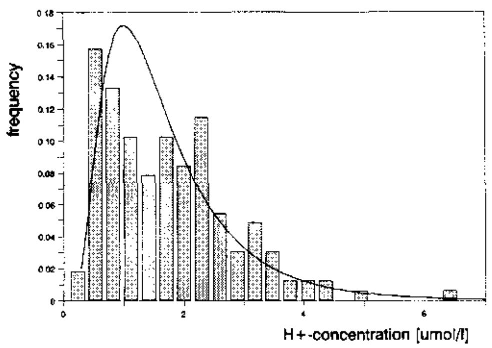
where y is (H^+) or oc, and x is ln y. m_x is the mean of the (normal) distribution of x and s_x the standard deviation of x. f_y is denoted $\Lambda(m_x, s_x^2)$.

The distribution of P_t can be characterized using percentiles of the distribution: The value where i% of the distribution is smaller or equal to, is the i-th percentile.

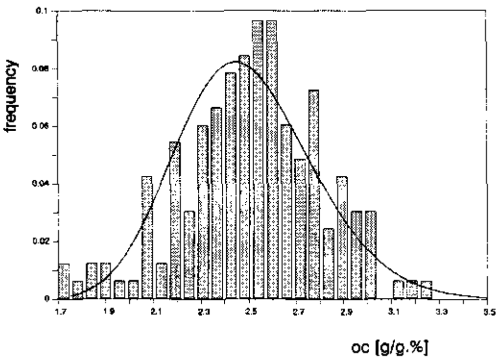
Results and discussion

Model calculations are done for a sandy soil in De Kempen region in the south of the Netherlands, that contains elevated average cadmium and zinc concentrations (4 mg/kg and 200 mg/kg respectively). A Cd/Zn ratio of 0.01 is assumed, for which parameter values for the adsorption isotherm are given by Chardon (1984). Soil samples were taken on a grid of size 17 × 8, with gridpoint distance 6 m. Measured values of (H^+) and oc showed a lognormal distribution (Fig. 1).

The plant uptake parameter m is chosen to be 1 in agreement with Kuboi *et al.* (1986), who found an average of m = 0.999 for 34 different plant species. Van Luit (1984) derived a value for k_2. Annual cadmium input I_0 consists of estimated Cd-input due to atmospheric deposition and phosphate fertilization of the soil (Ferdinandus, 1987). It is assumed that initially there is no cadmium present in the soil. Table 1 sum-



(a)



(b)

Fig. 1. Measured (bars) and fitted (line) frequency distribution for H^+-concentration (**1a**) and organic carbon content (**1b**).

marizes the parameter values used during simulation.

The stochastic model used the PDF's of Fig. 1 in Monte Carlo simulation. With (H^+) and oc negatively correlated, a lower buffer capacity for protons is assumed when the soil is lower in

Table 1. Parameter values used for calculations

I_0	$= 15.5\ [g.ha^{-1}.y^{-1}]$
ka	$= 6.91 \times 10^{-3}\ [\mu mol^{1-1/n}.l^{1/n}.kg^{-1}]$
k_2	$= 1.25 \times 10^{-4}\ [-]$
L	$= 0.3\ [m]$
m	$= 1\ [-]$
n	$= 0.6847\ [-]$
v	$= 0.83\ [m.y^{-1}]$
θ	$= 0.3\ [m^3.m^{-3}]$
ρ	$= 1400\ [kg.m^{-3}]$
oc	$: \Lambda(0.915, 0.117^2)$, $m_{oc} = 2.51$, $s_{oc} = 0.29\ [g/g.\%]$.
H^+	$: \Lambda(-13.45, 0.599^2)$, $m_{H^+} = 1.72 \times 10^{-6}$, $s_{H^+} = 1.13 \times 10^{-6}\ [mol.L^{-1}]$.

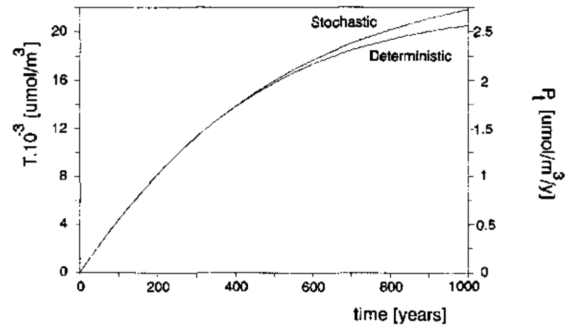


Fig. 2. Development of total content T and plant uptake P_t as a function of time for both the stochastic and the deterministic model.

organic matter. The mean values of these distributions are used as fixed numbers in the deterministic model.

Figure 2 gives T and P_t as a function of time, for both the deterministic (results as fixed numbers) and the stochastic (mean values of the PDF of T and P_t) model. The difference between both models is small, only after a long period of time the values diverge. Comparing P_t with the official Dutch standard for cadmium in grains (Bleys, 1987), which equals 0.15 mg Cd/kg fresh weight (equivalent with 2.22 $\mu mol.m^{-3}.y^{-1}$), the average plant uptake of cadmium is below the standard for approximately 610 years. Average behaviour of cadmium in the heterogeneous soil is very similar to cadmium behaviour in an equivalent homogeneous soil.

However, also extreme values for plant uptake are present in the PDF of P_t. Figure 3 shows percentiles of the distribution of P_t for the sto-

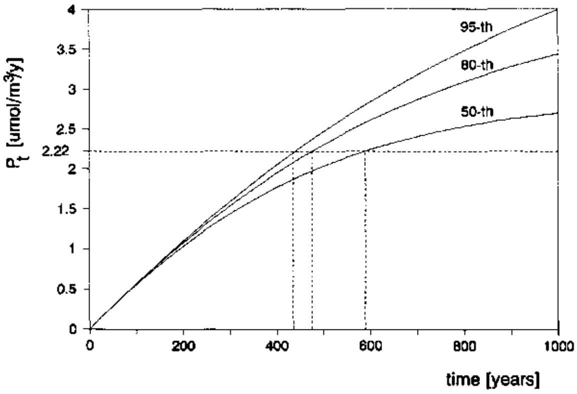


Fig. 3. Development of percentiles of P_t as a function of time when oc and (H^+) are negatively correlated.

chastic model. The 50-th percentile (the median of the distribution) exceeds the standard after 590 years. The difference between the mean value of P_t and the median indicates a non-symmetric frequency distribution. When the mean is smaller than the median, this implies a skewed distribution towards lower values. The 80-th percentile is at the standard after 480 years and after 440 years already 5% of the plants contains cadmium concentrations higher than the standard. So, when 95% of the harvest should remain below quality standards, exceedance of the standard occurs 170 years earlier than the deterministic model would predict.

For crop like barley, where all grains are mixed during the harvest, extreme high cadmium concentrations in some of the grains are averaged out. For crops that are consumed as separate entities, the extremes in the distribution of P_t are important. The deterministic approach does not give an adequate indication of crop quality in the latter cases.

Conclusions

The difference between deterministic modeling and stochastic modeling is small for the example used here, when the field averaged cadmium concentration in plants is considered. Extremes in the frequency distribution of cadmium concentration in plants cause the 95-th percentile of the distribution to reach the quality standard for cadmium in plants much earlier than the average cadmium concentration in plants. When pH and organic carbon content show profound variability, soil heterogeneity should be taken into account explicitly in models that predict crop quality. When accurate data are available that describe the variability of those parameters the model is sensitive for, stochastic modeling can serve as a first screening tool for risk assessment of elevated concentrations of heavy metals in the topsoil of an agricultural land.

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M. L. van Beusichem (Ed.), *Plant nutrition – physiology and applications*, 317–322.
 PLSO IPNC300

Interactive effects of cadmium, copper, manganese, nickel, and zinc on root growth of wheat (*Triticum aestivum*) in solution culture

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Key words: cadmium, copper, heavy metals, manganese, metal interactions, nickel, root growth, *Triticum aestivum* L., zinc

Abstract

The interactive effects of cadmium (Cd), copper (Cu), manganese (Mn), nickel (Ni), and zinc (Zn) on growth of *Triticum aestivum* L. in solution culture were evaluated using conventional analysis of variance (ANOVA) of both root weight data and a root weight index (RWI) designed to identify antagonistic, synergistic, and multiplicative interactions. In all trials, Ni (0 to 60 μM) served as the primary metal stress, producing near complete inhibition of root growth at 60 μM. A single concentration of either Cd, Cu, Mn, or Zn provided a secondary stress which further reduced root growth in all but the highest Ni treatments. Analysis of variance of root weight data indicated significant Ni × Cd, Ni × Mn, and Ni × Zn interactions. Such interactions, however, may not have been indicative of biological interactions. When relative root growth was expressed as root weight above the empirical growth minimum (the RWI), only the Ni × Mn interaction was significant, indicating an antagonistic interaction (growth was greater than predicted by the multiplicative model). Differences in interpretation of root weight data and the derived RWI suggest caution is needed when using primary growth data to detect possible interactions between phytotoxic metals.

Introduction

In recent years, a number of authors have documented responses of plants to combinations of metals in soils or growth solutions, but a clear understanding of potential interactions between phytotoxic metals has yet to appear. While differences in the chemistry of various metals and the biology of various plant species might be expected to lead to observed differences in interactive effects, Taylor (1989) suggested that our view of multiple metal stress may be clouded by continuing inconsistency in definitions of, and techniques used to differentiate between, additive, multiplicative, antagonistic, and synergistic effects. To illustrate this point, Taylor (1989) examined the phytotoxic effects of Ni and aluminium (Al) on *Triticum aestivum*. In this study, conventional ANOVA of root weight data indicated a significant Ni × Al interaction which could be interpreted as antagonistic, since growth was greater than predicted by the additive model. However, when data were interpreted in light of the full dose response relationship for Ni, the data were adequately represented by a multiplicative model. While it may be presumptuous to suggest that differences in analytical methods or terminology could account for the lack of a unified view of metal-metal interactions, such inconsistencies could nonetheless be hindering our understanding of multiple metal stress. The objectives of this study were (i) to document the effects of Cd, Cu, Mn, and Zn on the response of *Triticum aestivum* to varying concentrations of Ni in solution culture, and (ii) to examine the nature of potential metal-metal