

## Acidification and metal mobilization: effects of land use changes on Cd mobility

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### Abstract

Due to the actual EC agricultural policy, arable land is transformed to forest. Termination of liming will lead to a decrease in soil pH and an increase in soil organic matter and Dissolved Organic Carbon concentration. Both field measurements and model predictions indicate that the decrease in soil pH from near neutral values to ca. 3 to 4 takes place within 40 to 60 years after forestation. As a result of this, Cd solution concentrations increase with a factor 2 to 6 and leaching losses and/or plant uptake are expected to increase accordingly.

### 1. INTRODUCTION

In several countries of the European Community, arable land is abandoned in an attempt to reduce arable crop production. Up to 30% of the actual arable land (approx. 8.5 million hectares) is estimated to be converted to non-agricultural purposes due to technical improvements and large scale agriculture. One of the options available is the creation of forests. These forests could both act as a sink for atmospheric CO<sub>2</sub> and be used for recreational purposes in densely populated areas like the Netherlands. However, the creation of forests on a large scale will also affect the chemical conditions in the soil. Since the majority of the areas that are to be converted to forest have been used for agricultural purposes for almost a century, changes in the trace metal status of these soils have occurred. As a result of manure application and fertilizer treatment, the total Cd and Cu content has increased compared to forest soils (van Driel and Smilde, 1990). The mobility of these (potentially) harmful metals was limited, however, due to the regular application of lime. In general the soil pH has been maintained at near neutral or slightly acid values

(5 to 6). In this pH range the solubility of most metals is limited due to strong sorption processes onto several solid soil components like clay particles, Fe- and Al-(hydr)oxides and organic matter (McBride, 1989). In case of termination of liming, however, the soil pH will decrease with time. Apart from natural acidification, the elevated input of acidifying components from the atmosphere accelerates the acidification, especially in soils with a low buffering capacity. In general the decrease of soil pH will cause an increase in the mobility of most metals due to desorption from the soil surface (Harter, 1982). It would therefore be preferable to convert only those areas which contain soils with a low degree of contamination and a high buffering capacity. Unfortunately, these well buffered, non-contaminated soils (e.g. the calcareous clay soils in the northern parts of the Netherlands) are highly productive and in general only the marginally productive soils will be transformed to forest. In the Netherlands these areas consist of poorly buffered sandy soils with a low clay content and sometimes elevated concentrations of metals like Cu and Cd due to the application of pig manure and/or phosphate fertilizers. Apart from soil pH also the organic matter chemistry will change. Due to the increased input of organic matter (e.g. leaf litter, tree needles, branches, roots etc.) an organic horizon will develop. This will affect metal mobility in two ways. First, the increase in soil organic matter could lead to an increase in the CEC of the soil and metals can be bound to the organic matter. Secondly, the increase in soil organic matter also leads to an increase in the production of soluble organic colloids (Dissolved Organic Carbon - DOC). Especially the mobility of metals like Cu and Pb, which form stable aqueous complexes with organic ligands, could increase as a result of the elevated DOC levels. In column studies the mobility of Cu was enhanced in the presence of DOC, compared to a system without DOC although not all types of DOC studied showed similar results. (Oden et al., 1993). In order to estimate the mobility of trace metals in case of a conversion of arable land to forest it is therefore important to know the rate of soil acidification and the effect of an increase in the soil organic matter content.

It is the purpose of this paper to show how soil acidification combined with a change in the organic matter chemistry affects the mobility of Cd after conversion of arable land to forest. Field data combined with model calculations are presented which show the consequences of land use changes for trace metal mobility .

## **2. MATERIALS AND METHODS**

The field study and model calculations presented here, have been carried out independently. The field study is an integral part of a national study concerning the mobility of trace metals in both arable and forest soils and the effect of soil parameters like pH and DOC on metal solution concentrations. The model calculations form part of a study referring to the response of soils to acidification.

#### *Field data - trace metals*

To study the role of total metal content, soil pH and DOC on Cd, Zn and Cu solubility in Dutch soils, 30 sites have been investigated which represent the majority of Dutch soils and land use types. Both arable soils (pasture, crop production and fruit tree stands) and forested sites were included in the study. Soil samples have been collected at 10-cm depth intervals from 0 to 80 cm. Soil solution samples were obtained by centrifugation of 100 cm<sup>3</sup> field-moist samples in a centrifuge applying a rotational force of 20·10<sup>3</sup> N·kg<sup>-1</sup>. In the centrifuge tube the solution samples were expelled through a non-acid MN680M filter with a nominal pore diameter of 6µm. In this way more 'natural' soil solution samples were obtained compared to extraction with specific extractants (e.g. 0.01M CaCl<sub>2</sub>). Soil solution analyses included pH (ORION combination electrode model 91-02), total dissolved carbon and inorganic carbon (Shimadzu TOC-500 Total Organic Carbon Analyzer) and trace metal analysis. Cd was measured on a Graphite Furnace Atomic Absorption Spectrophotometer (Perkin Elmer model 5100) using standard addition methods and Zeeman background correction. Total metal content was determined using a hot-acid extraction as described by Del Castillo et al. (1993). Total organic matter content, CEC and soil pH were determined according to standard methods (Page et al., 1987).

#### *Field data - pH/DOC change with time*

To study the effect of forestation of arable land on soil pH and Dissolved Organic Carbon dynamics with time, 8 forests have been investigated. All forests have been planted on limed arable soils and vary in age from 1 to 70 years. On the terrain managed by the Dutch Forest Service (Staatsbosbeheer) in Jipsing Boertange (province of Groningen, the Netherlands) soil solution samples have been collected from the 0 to 30 cm soil layer. Extraction of the solution was obtained by centrifugation as described previously.

#### *Modelling approach*

In order to describe the effect of acidification, as a result of land use changes, on the Cd solubility a Cd sorption model (Bril, 1993) was linked to a soil acidification model (de Vries, 1994). The calculation of the Cd solution concentration is based on the assumption that, with a decrease in soil pH the adsorption of Cd decreases. Therefore, we used the calculated change in soil pH with time to calculate the Cd adsorption coefficient (described below). With this coefficient the solution concentration of Cd as a function of time was calculated and compared with the measured Cd solution concentration in existing field sites throughout the Netherlands.

#### *Cd adsorption model*

In the model applied, the change in the dissolved Cd concentration was described based on the Freundlich adsorption isotherm:

$$Cd_{ac} = KCd_{ad} \cdot [Cd]^n \quad (1)$$

$Cd_{ac}$  : sorbed Cd content ( $mg \cdot kg^{-1}$ )

$KCd_{ad}$  : adsorption constant for Cd ( $m^3 \cdot kg^{-1}$ )

$[Cd]$  : dissolved Cd concentration

$n$  : empirical constant, depending on soil type

The Cd adsorption constant was related to several soil parameters according to:

$$\log(KCd_{ad}) = -6.15 + 1.00 \cdot \log(CEC) - 0.24 \cdot \log(lut) + 0.50 \cdot pH - 0.41 \cdot \log[Ca] \quad (2)$$

$lut$ : clay content (%)

$[Ca]$ : dissolved Ca concentration ( $mol \cdot L^{-1}$ )

The values in equation 2 are based on data from Chardon (1984) and Christensen (1989); from these data also the value for  $n$  was estimated at 0.82. Based on the modelled change in soil pH and Ca solution concentration, the change in the adsorption constant for Cd can be calculated. Assuming that the sorbed Cd content does not change with time:

$$Cd_{ac}(t_p) = Cd_{ac}(t_0) \quad (3)$$

$t_p$ : time period  $p$  after start of acidification

$t_0$ : time zero, start of acidification

Equation 1 can be rewritten as:

$$KCd_{ad}(t_p) \cdot [Cd]^n(t_p) = KCd_{ad}(t_0) \cdot [Cd]^n(t_0) \quad (4)$$

From this the change in the dissolved Cd concentration at a given time  $p$  after forestation,  $[Cd](t_p)$ , was calculated according to:

$$\frac{[Cd](t_p)}{[Cd](t_0)} = \left( \frac{KCd_{ad}(t_0)}{KCd_{ad}(t_p)} \right)^{1/n} \quad (5)$$

#### *Soil acidification model*

The two main parameters needed to calculate the dissolved Cd concentration are soil pH and dissolved Ca concentration. The soil acidification model applied in the pH calculation is based on the "critical load" concept (see de Vries, 1994 for more detail). In those cases where the critical load is exceeded (in this approach the maximum input of acidifying components that can be buffered by a specified soil by weathering and N retention), the base saturation of the soil decreases which is related to a decrease in soil pH.

The critical deposition level (critical load) has been defined as:

$$S_{td} + N_{td}(\text{crit}) = BC_{td} + BC_{we} - BC_{gu} + N_{gu} + N_{im} + N_{de}(\text{crit}) + Ac_{le}(\text{crit}) \quad (6)$$

S, N:	Sulfur and Nitrogen	le:	leached
BC:	Base Cation	td:	total deposition
Ac:	Acidity	im:	net immobilization
gu:	growth uptake	crit:	critical level
we:	weathering		

All pools are expressed in  $\text{mol}_c \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$

The assumptions in this approach and their justifications (e.g. total nitrification, no nitrogen- and sulfur fixation) are given by de Vries (1994). The critical amount of acidity leached from the soil ( $Ac_{le}(\text{crit})$ ) is based on the critical concentration of acid components in the soil solution multiplied by the net precipitation surplus. Assuming that the acidity has to stay constant at values encountered at near neutral pH, a pH of 5 was used to calculate the critical leaching of acidity. This has been defined as:

$$[\text{Ac}] = [\text{H}] + [\text{Al}_i] - [\text{HCO}_3] \quad (7)$$

where  $[\text{Al}_i]$  is dissolved inorganic Aluminum ( $\text{mol}_c \cdot \text{m}^{-3}$ )

The change in the soil base saturation has been calculated as the difference between the actual deposition and the critical deposition according to:

$$frB_{ac}(t_p) = frB_{ac}(t_0) - \sum_{t=t_0}^{t=t_p} [(S_{td} + N_{td})(\text{act}) - (S_{td} + N_{td})(\text{crit})] / (\rho \cdot D \cdot CEC \cdot 10) \quad (8)$$

$frB_{ac}$ :	base saturation	$D$ :	thickness of soil layer
$\rho$ :	soil bulk density	$CEC$ :	Cation exchange capacity

In the calculations the initial values are based on 1990 ( $t_0$ ) and calculations are made for 2000, 2010 and 2050. If the critical load is not exceeded, the base saturation will remain constant and the acidic input will be compensated completely by net cation release and net N retention (cf Eq. 6) resulting from weathering and denitrification processes. If the acid input exceeds the critical load, the base saturation and pH will drop according to an empirical relationship determined by Bloom and Grigal (1985):

$$\text{pH} = 4.96 + 0.80 \cdot \log ( frB_{ac} / (1 - frB_{ac}) ) \quad (9)$$

The change in the dissolved Ca concentration was calculated from the the charge balance equation:

$$[\text{Ca}] = [\text{SO}_4] + [\text{NO}_3] + [\text{HCO}_3] + [\text{Cl}] - [\text{H}] - [\text{Al}] - \Sigma\{\text{Mg, K, Na}\} \quad (10)$$

Concentrations of  $\text{SO}_4$ ,  $\text{NO}_3$ , Cl and base cations were based on their deposition, uptake (for N and base cations) and weathering (base cations). Dissolved concentrations of both Al and  $\text{HCO}_3$  were derived from equilibrium calculations (cf Eq. 11 and 12)

$$[\text{HCO}_3] = K_{\text{CO}_2} \cdot p\text{CO}_2 / [\text{H}] \quad (11)$$

The dissolved Al solution concentration was calculated from the equilibrium with amorphous Al-hydroxide according to:

$$[\text{Al}_i] = K_{\text{Al-ox}} \cdot [\text{H}]^3 \quad (12)$$

#### *Data requirements for the model*

Based on the actual deposition levels for S and N, estimates are made for the total deposition until 2050. In the scenario applied here, a constant input of acidifying components has been assumed using the 1990 input levels. For the Netherlands, data for the actual deposition were available for 1985 and 1994 on a 10 x 10 km grid basis. The values for 1990 have been calculated using a linear interpolation program. The actual base saturation has been calculated for the upper 40 cm of the soil. Both CEC and bulk density have been estimated using transfer functions based on the organic matter and clay content (Breeuwsma et al., 1986; Hoekstra and Poelman, 1982):

$$\text{CEC} = 15 \cdot \text{OM} + 5 \cdot \text{lut} \quad (13)$$

OM: Organic Matter content (%)

lut: clay content (%)

$$\rho = \frac{1000}{b_0 + b_1 \cdot \text{OM} + b_2 \cdot \text{lut}} \quad (14)$$

$b_i$ : empirical constants

Organic matter and clay content were also used to calculate the adsorption constant for Cd (cf Eq. 2).

### 3. RESULTS

#### 3.1 Field data

In figure 1, the changes in soil pH and DOC concentration with time are shown. After termination of liming, the soil pH decreased to 3.5 - 4 within 3 to 4 decades, indicating a rapid acidification of the topsoil due to a lack of buffering capacity in these sandy soils.

Despite the lower soil pH, the DOC concentration increased with time. It has been shown by Bergkvist, 1987) that under field conditions, metals like Cu and Pb are mobilized in the presence of DOC. The increase from an initial DOC concentration of 5 - 10 mg·L<sup>-1</sup> to 50 mg·L<sup>-1</sup> within 40 years could therefore be of significance for the mobility of those metals which form stable aqueous complexes with DOC. Results for Cu (not presented here) indeed showed that solution concentrations increase with increasing DOC concentrations (Römken and Salomons, 1993). However, the increase of the total organic matter content also increases the capacity of the soil to retain metals from solution and the net effect of the change in the organic matter chemistry (net release or retention of metals) thus remains unclear until now.

However, the solubility of metals like Cd and Zn is mainly controlled by pH and the acidification due to the land use changes will lead to a significant increase in the dissolved Cd concentrations. In figure 2 the results from the screening of 30 sites in the Netherlands are shown. It appeared that the solubility of Cd was controlled mostly by soil pH and, to a much lesser extent, by DOC. Despite the large range in the dissolved Cd concentration at a given pH, there is a significant increase with a decrease in soil pH. Especially below pH 5, dissolved Cd concentrations increase rapidly due to pH dependent desorption from the soil surface. Similar results were obtained for Zn (not shown here).

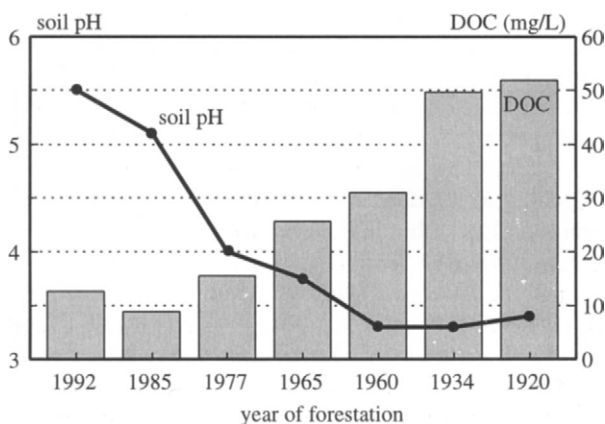


Figure 1. Change in soil pH and DOC concentration due to forestation of arable land (0 - 30 cm soil layer).

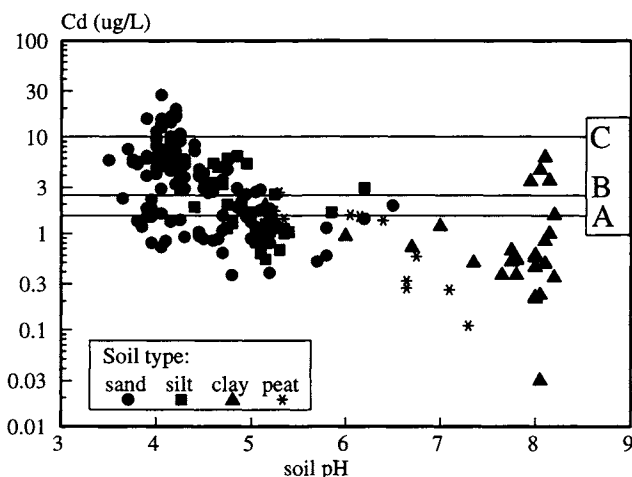


Figure 2. Relation between pH and dissolved Cd concentrations in arable soils and forest soils (0 - 80 cm; A, B, and C refer to Dutch Reference Values, see fig. 3 and text)

The high dissolved Cd concentrations at pH 8 were found in a tree stand treated repeatedly with a pesticide containing Cd. The range of dissolved Cd concentrations at a given pH is due to the fact that in this plot all samples are shown; both forest soils with low Cd content ( $Cd_{tot} < 0.1 \text{ mg}\cdot\text{kg}^{-1}$ ) and arable soils containing elevated amounts of Cd ( $Cd_{tot} \geq 0.5 \text{ mg}\cdot\text{kg}^{-1}$ ). However, the highest dissolved Cd concentrations were found in forest soils ( $Cd_{aq}$  ranged between 6 and  $24 \mu\text{g}\cdot\text{L}^{-1}$ ) despite their very low Cd content (sometimes less than  $0.05 \text{ mg}\cdot\text{kg}^{-1}$ ). The total metal content in arable soils was higher compared to forest soils due to application of fertilizers, manure and lime. Dissolved Cd concentrations however, were usually very low due to the near neutral soil pH (5.5 - 7.5). In figure 3, the dissolved Cd concentrations are compared to the Dutch soil quality standards for the soil solution and the upper ground water (Stoop and Rennen, 1990). These standards are divided in three classes: A-, B-, and C-value. Concentrations below the A-value are considered 'multi-functional': the site can be used without any restriction. If the dissolved Cd concentration exceeds the B-value, further research is necessary and values above the C-level require treatment (sanitation).

For Cd (and similar results were obtained for Zn), more than 70% of all samples in forest soils exceeded the B-value and 15% even exceeded the C-value. For arable soils only 20% of all samples exceeded the B-value (Figure 3). In arable soils more than 90% of these values were found in the topsoil and are directly related to the application of Cd to the soil. In forest soils, however, a large part of the high dissolved Cd concentrations were encountered in the deeper soil



horizons (between 50 and 80 cm) which reflects the poor binding capacity of the soil due to a low soil pH combined with a low organic matter and clay content.

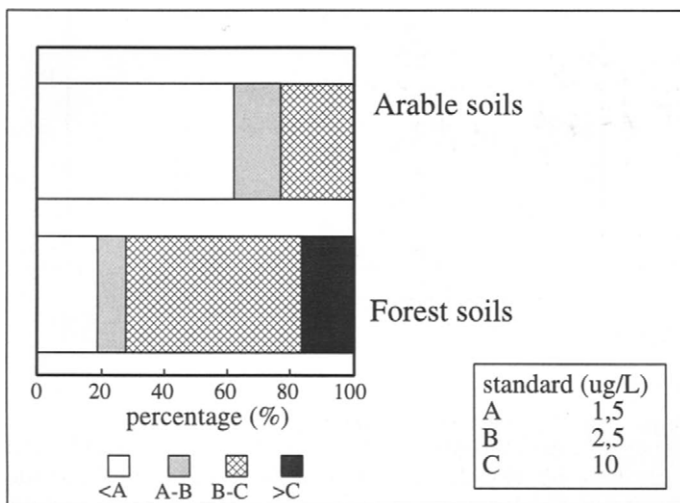


Figure 3. Exceedances of soil quality standards for dissolved Cd concentrations in Dutch arable soils and forest soils.

### 3.2 Model results and comparison with field data

#### *Soil acidification*

The model results indicate that termination of liming leads to a significant acidification of the topsoil within 40 years as is shown in figure 4. This graph shows the cumulative frequency distribution of the predicted pH values in clayey and sandy soils for the 4 time periods (1990, 2000, 2010, 2050). In all simulations, the deposition level exceeded the critical level, which resulted in a significant reduction of the base saturation and soil pH. The predicted decrease in the sandy soil from 5 to 3 - 3.5 was in reasonable agreement with the measured pH in the old forest stands. The difference between the measured and calculated pH is partly due to the fact that the model takes into account the 0 - 40 cm layer, whereas the measured values stand for the 0 - 30cm layer. The predicted decrease in soil pH in clay soils is larger compared to forest soils during the first few decades. This is partly due to the stronger relationship between soil pH and base saturation in the 'high' pH range (5 - 7). For clay soils, the initial base saturation was set at 100% compared to 50% in the sandy soils. Consequently the base saturation in forest soil diminishes whereas the base saturation in clay soil remains higher than 50%.

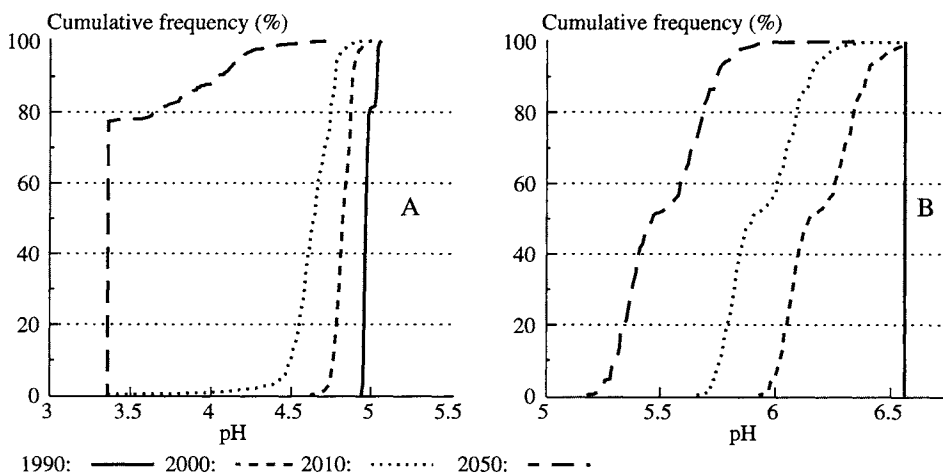


Figure 4. Simulated frequency distributions of soil pH in sandy soils (A) and clay soils (B)

#### *Cd release*

Due to the decrease in soil pH, also the adsorption-constant for Cd decreases (equation 2) as is illustrated in table 1. According to equation 1 this leads to higher dissolved Cd concentrations. In figure 5 the cumulative distribution of the relative increase in the dissolved Cd concentration is shown. In clay soils, the relative increase is even larger compared to sandy soils, but the absolute concentration will be lower due to the higher adsorption-constants in clay soils as is illustrated in table 1.

Table 1

Adsorption constants for Cd in soil ( $\text{m}^3 \cdot \text{kg}^{-1}$ )

	clay	sand
1990	2.10 <sup>1</sup>	0.19
2000	1.30	0.17
2010	0.95	0.13
2050	0.60	0.08

<sup>1</sup>: these values represent the median value for both soil types

In case of a pH drop from 5.5 to 3.5, dissolved Cd concentrations are expected to increase with a factor 2 to 6. This was also observed for sandy soils under field conditions where Cd solution concentrations were found to increase from 2 - 5  $\mu\text{g} \cdot \text{L}^{-1}$  to 10 - 15  $\mu\text{g} \cdot \text{L}^{-1}$  with a decrease in soil pH from 5.5 to 4.

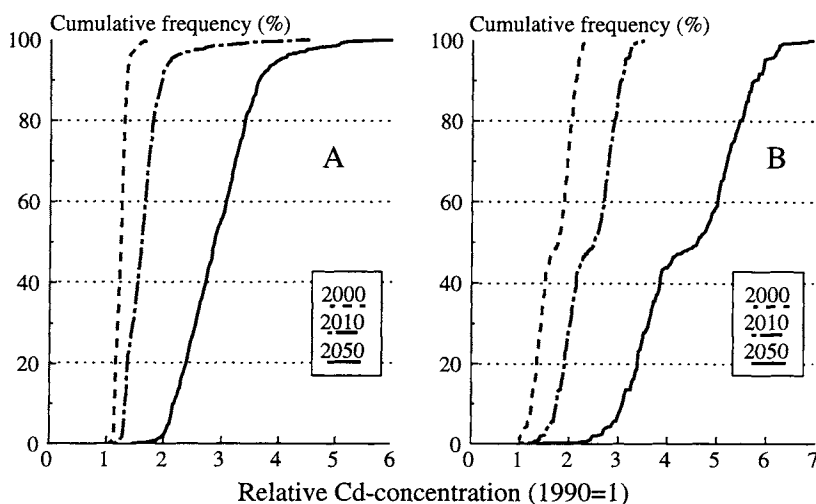


Figure 5. Simulated frequency distributions of the relative Cd concentration in sandy soils (A) and clay (B) soils.

#### 4. DISCUSSION AND CONCLUSIONS

##### *Soil acidification and Cd release*

The results from both field measurements and model predictions indicate that the conversion of arable land to forest leads to major changes in the chemistry of the soil solution:

- i. After termination of liming, the pH of the soil decreases from near-neutral (5.5 - 6.5) to acid (4 - 4.5) within 30 to 40 years. Despite some assumptions made in the model (see below) the model predictions are in good agreement with the measured pH decrease in the field.
- ii. The pH decrease will lead to a significant increase in the dissolved Cd concentration. In both field and model results, dissolved Cd concentrations increased with a factor 2 to 6 with a decrease in soil pH. In mature natural forest soils, dissolved Cd concentrations are high compared to actual arable soils despite the much lower total metal content. This indicates that if soils with an elevated Cd total content (0.5 to 2 mg·kg<sup>-1</sup>) are converted to forest, dissolved Cd concentrations will even exceed the actual concentrations encountered in forests.

*Uncertainties and model improvements*

Despite the good agreement between field data and model predictions several assumptions have been made that deserve further attention:

- i.* The acid input was based on external deposition only. After forestation a strong internal acidification will occur due to a net mineralization and nitrification which is not compensated for by  $\text{NO}_3^-$  uptake. On a longer term, a net immobilization will occur due to the formation of an organic horizon.
- ii.* Interactions between the amounts of H and Al leached and the base saturation on one hand and the distribution between dissolved Cd and the adsorbed fraction on the other hand have not been included in the model. The cumulative amount of Cd mobilized in sandy soils during the simulation run, amounted up to 75% of the total Cd content in the soil. This decrease will probably affect the equilibrium between the solid phase and the dissolved Cd concentrations as well.
- iii.* The interaction between DOC and Cd has not been taken into account. Although the interaction between Cd and DOC is less strong compared to Cu or Pb, the increase in the DOC solution concentration (figure 1) could still affect the dissolved Cd concentration as well (see point 4) as plant uptake.
- iv.* One of the major uncertainties at the moment is the role of the vegetation. Due to acidification, Cd is released to the soil solution. However as a result of the forest development, a net increase in the plant uptake from the soil solution seems possible. This could mitigate the effect of the Cd mobilization and prevent any leaching to the ground water. However, due to the increase in the DOC concentration, the degree of Cd-complexation (in solution) also increases. Several studies showed that the uptake of organically complexed metals is strongly reduced compared to the uptake of the free metal (Kuiters and Mulder; 1993). Recent work done by Ernst showed that the uptake of metals by plants on a contaminated site decreased after a few years due to the increase in the organic matter content and the complexation of the metals in solution (Ernst, 1994). The role of organic matter is therefore two-fold: it increases the capacity of the soil to retain metals from solution (to the solid organic phase) but it simultaneously decreases the uptake by plants as a result of the formation of aqueous complexes.

*Future needs and integration of Acidification research with Trace Metal studies*

This study clearly shows that the combination of soil acidification research combined with trace metal monitoring studies can be used as a tool to predict the consequences of land use changes. At present several large-scale activities affecting both land use and management are being carried out. In the Netherlands this includes both forestation of arable land as well as the creation of wetlands along the main rivers. In order to assess the chemical consequences of these new management strategies it will be necessary to combine studies concerning both the macro-chemistry (e.g. Ca-Al chemistry in combination with soil pH as well as redox chemistry) and the micro-chemistry (behaviour of trace

elements and organic chemicals). In this context, the large experience gained in acidification and trace metal research (both in field/laboratory experiments and modelling studies) will be useful to couple various models developed in the different fields.

In case of forestation, especially the processes of acidification combined with the organic matter dynamics (development of an O<sub>h</sub> layer, increase in DOC content, Al - organic matter interactions) need further attention in order to assess future consequences of present activities in relation to soil quality and protection. With respect to land use changes in general, it can be concluded that there is still a lack of information concerning the dynamics of soil chemical processes on a time-frame of 10 to 100 years.

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