Effects of land use changes on organic matter dynamics and trace metal solubility in soils
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1998

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Download date: 05-08-2024
SUMMARY AND CONCLUSIONS

Conversion of agricultural land to forest or pasture has a profound impact on soil chemical conditions. Major changes include effects on soil pH, soil organic matter (SOM) content and dissolved organic carbon (DOC). First, the observed pH, SOM, and DOC dynamics as well as the consequences of those changes will be summarized followed by a synopsis of the impact of these changes on trace metal solubility and speciation in the soil solution. Finally, the various model approaches that were applied will be discussed in the light of their usefulness, validity and predictive capacity.

Acidification

Soil acidification has been a research topic since the 1980’s following the growing awareness of adverse effects on soil (micro-)organisms, plants and ground- and surface water quality. Termination of liming in combination with afforestation can also result in a significant acidification in soils with a limited buffering capacity. In the Netherlands, most areas that were, or are going to be, converted from agriculture to forest have sandy soils with a low clay content. Data from forests of variable age presented in Chapter 8 show that soil pH in these soils is predominantly buffered by the exchangeable Ca pool and, after depletion of the amount of adsorbed Ca, soil pH rapidly decreases until it reaches values between 3.5 and 4.5. For the soils studied here, roughly 10 to 15 years is needed to deplete the Ca-buffer after which time soil pH decreases to approx. 4 within the next two decades. Maintenance of the base cation supply (especially Ca and Mg), therefore, seems to be the most effective way to avoid extreme soil acidification. Whether or not this should be accomplished by application of lime remains questionable since Ca has a profound impact on the type of plant species that will grow.

SOM dynamics

SOM contributes significantly to the CEC of sandy soils and an increase in the SOM content, therefore, leads to a higher metal-binding capacity. Results from the forest screening (Table 3 in Chapter 8) and the study of SOM dynamics after conversion of maize land to pasture (Chapters 3 and 4) show that SOM increases following the transformation of arable land to forest or pasture. The transition from arable land to pasture resulted in a rapid recovery of SOM. Within 10 years, SOM in the topsoil quantitatively ‘recovered’ from the depletion that had occurred during maize cropping. After afforestation, however, SOM decreased during the first few years as a result of a continued microbial mineralization of SOM initially present in the topsoil. Only after 15 to 20 years, continuous litter-fall and conversion of litter to SOM, resulted in a detectable increase in the SOM content in the mineral soil. This indicates that the type of landuse has a profound impact on both the quantitative and qualitative ‘recovery’ of SOM. Pasture installation leads to a relatively fast recovery due to input from organic material from
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roots whereas litter from trees contributes much less to the SOM content of the mineral horizon during the first 5 to 10 years.

Two effects should be taken into account, though, that will mitigate the beneficial effect of SOM on the metal binding capacity of SOM. As a result of the protonation, the net negative SOM-surface charge decreases upon acidification which results in a lower effective CEC and a lower potential of SOM to bind trace metals.

Not only the net binding capacity of SOM decreases with pH, also the chemical composition of SOM will change upon acidification of the soils. Microbial decomposition processes also depend on soil pH because bacterial activity usually decreases with pH which will retard the conversion of litter to stable SOM upon acidification.

DOC dynamics: impact of Ca on DOC 'speciation'

Copper solubility and speciation strongly depends, among others, on the presence of DOC. Between pH 5 to 7, copper solubility in arable soils is enhanced by DOC, as was shown in Chapter 2. Also the Cu$^{2+}$ activity is controlled largely by DOC; in the presence of DOC, the free ionic Cu$^{2+}$ activity is several orders of magnitude lower than the total dissolved Cu concentration. Even below pH 4, more than 95% of the total dissolved Cu concentration remained bound to DOC (Chapter 7). As a result of the preferential binding of Cu to DOC, Cu mobility can be greatly enhanced by DOC and processes that control the solubility of DOC, therefore, also control Cu solubility.

Both solubility and molecular size distribution of DOC depend not only on pH but also on the calcium concentration in solution (Chapter 5). As a result of flocculation of Ca-humates at pH 6, DOC, and Cu that was initially attached to it, were removed from solution at Ca concentrations that occur in agricultural soils (approx. 100 mg L$^{-1}$). HPSEC revealed that the part of DOC that was removed by flocculation, primarily contained the high molecular size fraction (HMW), which appeared roughly equal to humic acids. Both the flocculated HMW-fraction and the low molecular size fraction (LMW) that remained soluble at elevated Ca concentrations in solution (roughly equivalent to the fulvic acid fraction) contained Cu bound to dissociated surface groups.

The amount of copper bound to both HMW- and LMW components appeared to be a function of the total soil copper content (Chapter 5). This is not surprising because a large part of Cu added to sandy soils is probably bound to SOM, which is the source of DOC in soils.

Afforestation of arable land, therefore, induces the following changes in DOC dynamics:

- Changes in the DOC concentration; the increase in the total organic matter content leads to higher DOC levels. The data presented in Chapter 8 show that DOC levels in the A horizon reach values of 50 mg L$^{-1}$.
- Changes in the composition of DOC that result from (1) a lower soil pH, (2) a lower Ca concentration, and (3) a higher Al concentration (below pH 4.5). These processes will have an opposite effect. The decrease in the Ca solution concentration due to termination of
The beneficial effect of the net negative effective CEC and a chemical composition of mineral processes also which will retard the content of the mineral nutrient.

The presence of DOC, as was shown in the presence of DOC, the total dissolved Cu concentration of Cu to DOC, Cu solubility of DOC, pH but also on the solubility of Ca-humates at pH from solution at Ca and pH revealed that the flocculated HMWDOC appeared to be a because a large part of DOC in soils.

DOC dynamics:

Water content leads to DOC levels in the A horizon. (1) A lower Ca concentration leads to termination of liming enhances the solubility of HMW-DOC. The simultaneous decrease in soil pH, however, in combination with an elevated dissolved Al concentration will suppress the solubility of (HMW-) DOC.

It is hypothesized that DOC that is generated at low pH after afforestation will be dominated by LMW components. Due to the hydrophilic nature of LMW components, its potential mobility will be relatively high compared to that of HMW components. Apart from chemical changes in the topsoil, DOC-enhanced transport of Cu also depends on changes in soil conditions that are imposed on DOC during vertical displacement. Although this was not specifically addressed in this study, model calculations presented in Chapter 6 suggest that the contribution of HMW-components decreases with depth. This is most likely due to preferential adsorption or flocculation of HMW-DOC.

**Effects of land use changes on trace metal solubility and speciation: modeling approaches**

In this thesis, several ‘modeling’ approaches have been presented. A relatively simple Kd-concept (Chapter 2), was able to describe Cd, Zn, and, to a lesser extent Cu, solubility in a range of soils fairly well (R² ranges from 0.49 for Cu to 0.83 for Zn). This approach enables us to estimate the Kd and is based on a limited number of soil parameters (CEC and pH) which facilitates its application. Especially under field conditions, the use of equations that require limited input data, is preferred to more advanced mechanistic models because it cannot be expected that the required input parameters can be obtained on the desired scale (in time and space).

It appears that the solubility of Cd and Zn is mainly controlled by pH dependent adsorption onto clay and organic matter. Due to the impact of DOC on the solubility of Cu, the correlation between measured and predicted Kd values was substantially less for Cu than for Cd or Zn. Results from the Kd-model indicated that afforestation leads to an increase in the Cd and Zn concentration with a factor 5 for Cd to 13 for Zn. The model that was described in Chapter 5 and used to simulate field data from artificially contaminated soils in Chapter 6, illustrates the role of DOC with respect to Cu solubility. In soils where Cu is adsorbed mainly on soil organic matter, i.e. in sandy soils, (changes in) the solution concentration of Cu can be attributed almost entirely to (changes in) the solution concentration and ‘speciation’ of DOC. Hence, parameters that control the solubility of DOC, (e.g. Ca and pH) also indirectly control Cu solubility. This was illustrated quite nicely by data and model calculations that were presented in Chapter 6. The increase in the base cation concentration in solution, that resulted from lime application, reduced both the DOC solution concentration and the dissolved Cu concentration quite drastically.

Apart from the impact on Cu solubility, DOC also controls Cu speciation in solution. Results presented in Chapter 7 indicate that even under moderately acid conditions, the majority of Cu remains bound to DOC. Nevertheless, high Cu activities (pCu < 8) were measured in samples that contained DOC from Cu-contaminated soils. Titration data revealed that potentially toxic Cu²⁺ levels can be reached below pH 5. The model used to describe Cu and Ca binding to
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DOC proved effective although Ca binding was predicted less accurately as a result of the lower binding affinity of Ca for DOC. It can be concluded that a two-pK model is able to describe Cu binding to DOC quite well in the pH range from 3 to 7.

The Ks-approach was further ‘extended’ in Chapter 8 to describe Cu adsorption in various soils. In combination with the solution speciation model described in Chapter 7, the model was able to predict the measured copper concentrations in solution in a large field experiment quite well although the fit was better for samples from the topsoil than for samples from the lower soil horizons. The model was calibrated using data from the topsoil (0 – 30 cm) and the discrepancy between measured data and model estimates from various soil horizons probably reflects changes that occur with depth (e.g., binding affinity of DOC and SOM, availability of Cu).

Although the model calculation shown in Chapter 8 includes a considerable part of the work presented in this thesis, it still serves merely as an illustration of a hypothetical case. The results show that in a soil with a total Cu content between 50 and 200 mg kg⁻¹, high Cu solution concentrations and activities can occur which could lead to elevated leaching losses and/or uptake by soil organisms.

Land use changes and metal mobility in soils: what do we (still...) need to know?

The results presented in this thesis indicate that afforestation or pasture installation induce important changes in soil acidity and organic carbon content (both quantity and quality) that affect metal mobility and speciation. However, this research was (necessarily) limited to several chemical processes and effects of land use changes on soil organisms and plants are not being considered. Organisms probably will experience ‘stress’ that results from changes in metal speciation and SOM dynamics. On the other hand, plants and soil (micro-)organisms can actively change soil conditions (e.g., excretion of organic ligands and mineralization of SOM) which may have an important effect on metal solubility or speciation. Only if the (complex) relationships between the activity of soil organisms, the presence of metals in soils, plant growth and parameters like soil pH and SOM are included in research projects we can predict the consequences of land use changes for the various compartments mentioned here. The study of various processes and models that are presented here can be of help to elucidate the chemical consequences of land use changes.

Apart from the magnitude of the changes (e.g., the change in soil pH from 6 to 4), especially the dynamics of these changes are highly relevant. Gradual acidification allows for adaptation of organisms to changes imposed on them and they may be able to develop resistance towards increasing levels of dissolved metals. After all, mature forests and their microbial populations are able to thrive quite well on extremely acid soils with elevated Al and trace metal concentrations.

The results from the forest screening that were presented in Chapter 8 indicate that soil pH remains buffered between 5 and 6 as long as the exchangeable Ca pool is not depleted. In the system studied here, a rapid decline in soil pH was observed upon depletion of the Ca pool. The difference in the recovery of the SOM content between forests and pasture indicates that the dynamics of these changes are indeed slow. A major factor is that the organisms we did not study in this research cannot secrete a proton and hence, we are only looking at part of the process. There are probably other processes and mechanisms that we are not aware of.

These processes are related to the ultimate fate of metals in soil and are denoted as environmental processes. It has been hypothesized that plants and soil (micro-)organisms are involved in the processes related to the fate of metals in soils.

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as a result of the uptake of metals, the model was able to predict adsorption in various plant species. The field experiment quite accurately predicted adsorption losses and/or uptake for metal concentrations that were not being used in the model. The results indicate that soil pH depletion in the Ca pool. Evidence of the dynamic nature of soil chemical processes is controlled by both chemical factors (e.g., base saturation) as well as biological factors (type of vegetation).

A major flaw of the model described in Chapter 8 as well as many other models, is the fact that we cannot yet model DOC dynamics and composition. DOC appears to be one of the key parameters with respect to metal solubility, bioavailability and transport. Although many of the processes that control DOC solubility have been studied (including chapters in this thesis), we are not able to yet fully understand the various interactions between SOM, soil organisms, and DOC in solution.

These facts (impact of soil micro-organisms, vegetation, soil type, rate of soil chemical processes, interaction between processes) imply that it will remain difficult to answer the ultimate question: What will happen if (slightly) contaminated land is transformed to forest, pasture, wetland? This thesis shows, as it should, a few answers to some (details) of questions related to land use changes and it would be too easy to end with: More research should be done......

It has become clear, however, that reliable answers can be obtained from integrated research only, where biological, physical and chemical aspects related to land use changes are combined. And, although well-defined laboratory studies remain important for insight in various mechanisms, field research remains equally important and valuable.