

SEASONAL AND SPATIAL VARIATION OF HEAVY METAL SOLUBILITIES IN A FALLOW, ACIDIC LOAMY SAND SOIL

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ABSTRACT. Wide variations in heavy metal concentrations in top- and subsoil solutions were detected throughout the season in individual soil sections. Topsoil variation was explained by the combined action of soil solution pH and DOC; in the subsoil the changes were also correlated with the soil solution [Mn] and the soil iron status. No direct correlation between metals in the soil solution and the soil particles was observed. This may have implications if standards are set based on a constant distribution coefficient.

1. Introduction

The potential toxicity of heavy metals in the environment depends on their concentration in the soil and soil solution. The processes that affect heavy metal solubility may also influence heavy metal leaching in soils. The main purpose of the present study was to explain the observed soil solution [Cd] and [Zn] variations in subsoil sections from historically pig-manured acidic loamy-sand plots.

2. Methods

The plots (all tile drained at a depth of 1 m, the approximate winter ground-water table; having a moderate, a high, or no pig-manure history) were kept fallow, and received one single dose of cattle manure during the study period. Soil cores were taken bi-monthly down to 80 cm. The cores were divided into 10-cm sections. The soil solution was monitored before and after this event. From these sections soil solution samples were obtained by centrifugation at $20 \times 10^3 \text{ N kg}^{-1}$ and collection of the expelled water. In the soil solution pH, EC, DOC, major cations and anions, heavy metals, iron and manganese were measured. Soil characteristics were also determined. Extractable soil iron was measured in extracts obtained by gentle overhead shaking for 2 hours in the dark at 20 °C of a) 2.5 g air-dry soil with 50 ml 0.2 M ammonium oxalate/oxalic acid buffer (pH 3), or b) 1 g soil with 100 ml 0.1 M hydroxyl amine.HCl in 0.01 M HNO_3 (pH 2).

To explain the field variation in concentration of heavy metals in the soil solution two modeling approaches were applied: a) thermodynamic (for topsoil sections; Hesterberg et al., 199x), and b) statistical: multiple linear regression analysis (MLRA), using the stepwise variable selection mode of the programme Statgraphics® version

4.0 (for topsoil sections: Del Castilho et al., 199x, for subsoil sections: this paper).

3. Results

Soil solution [Cd] and [Zn], [DOC], and pH in topsoil sections are presented by Del Castilho et al. (199x). Here, and in Hesterberg et al. (199x) it was shown that the observed variation in metal concentration was too wide to be explained by variation in the total heavy metal levels of the soil. MLRA, and thermodynamic modelling of the data indicated that pH and DOC were the master variables.

However, the thermodynamic model concepts derived for the upper part of the soil failed to describe the metal behavior adequately for subsoil sections. MLRA of these data showed that the soil iron extractability (hydroxyl amine.HCl) and soil solution manganese were valuable additional parameters, explaining [Cd] and [Zn] to a large extent (eq 1). The r^2 values varied between 0.64 and 0.76. The coefficients for [Cd] were: $b = 0.005$; $c = 0.5$; $d = 0.2$; $e = 0.005$. For [Zn] they were 100 times higher.

$$[\text{Cd}], \text{ or } [\text{Zn}] = a + b \cdot [\text{DOC}] - c \cdot \text{pH} + d \cdot [\text{Mn}] + e \cdot \{\text{FeNH}_2\text{OH}\} \quad (1)$$

A positive correlation with [DOC] may either be caused by (dissolved/colloidal state) complexation, or by reductive dissolution of iron(manganese)(hydr)oxyde solid phases. The negative correlation with pH may be explained by proton/heavy metal exchange reactions. The meaning of both last 2 sections of the right-hand side of eq 1: - the more Fe is dissolved with hydroxylamine, and the more dissolved Mn is found in the soil solution, the more Cd and Zn is found in the soil solution -, is less clear. Acidic hydroxylamine extraction is mainly used for the reductive dissolution of trace metals occluded in manganese oxides (Beckett, 1989). It is tempting to conclude that elevated [DOC] levels promote dissolution of soil Mn and heavy metals by reduction of oxygen (gas) and nitrate, followed by Mn(IV), and Fe(III) to lower valency states. Thermodynamically, DOC cannot even exist in the presence of these oxidizing substances.

4. Conclusions

Dissolved [Cd] and [Zn] show solution pH-, and [DOC]-mediated fluctuations; for subsoil sections in addition dissolved [Mn] and the soil iron status seem to be important parameters to describe heavy metal behavior. The DOC effects in the sub soil may be explained by the change in redox conditions.

5. References

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