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Mass balance of zinc redistribution during the pedogenesis of a soil developed on a natural geochemical anomaly

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Introduction

Pedogenetic processes that redistribute soil elements over time have been considerably investigated and clearly identified. Nevertheless, the quantification of their respective influences on element redistribution is still poorly known, while soil protection requires extensive knowledge of their long-time depending evolution. The quantitative redistribution of elements is of prime importance in polluted soils, since the long-term environmental hazards depend on their potential mobility and biodisponibility, thus speciation. Among the elements frequently encountered in polluted soils and exhibiting a well-established phytotoxic nature, zinc is of great concern. Nevertheless, pollutions are too recent to observe or even predict the long-term behavior of zinc in polluted soils.

An alternative approach is to study paleosoil developed on natural geochemical anomalies. Indeed, such paleosoils display zinc concentrations equivalent to those of polluted soils with the advantage to involve long pedological time of contact between the elements and the different soil phases. Our study aims at quantifying the long-term redistribution of zinc during the pedogenesis of a soil developed upon a natural geochemical anomaly. We first determined zinc speciation both in the parental material and in the solum, then quantified redistribution by mass balance calculations. This approach permits to estimate Zn outputs or inputs in the solum and to quantify its redistribution along the profile and among the different mineral phases.

Material and methods

The studied site is located on the northeastern sedimentary margin of Morvan Mountain (Burgundy, France). It lies on a Sinemurian aged limestone platform that underwent mineralization events during the Lias at the origin of its high contents in Zn, Fe and Mn notably. The soils developed upon this carbonated platform are rich in the <2 μm
particle-size fraction and exhibit numerous Fe-Mn concretions within the whole profile. The sampled solum exhibits the following horizonation from top to bottom: A, E, Bd (degraded B horizon), B_p (phosphate nodule bearing horizon), Bc (Fe-Mn concretion-rich horizon) and C-horizon developed in a water table, particularly rich in the <2 μm particle-size fraction. The A- to B_p-horizons derive from the autochthonous weathering of the Lotharingian aged limestone, the B_p-horizon being inherited from the phosphate nodule bearing bed at the base of this buildup, while the Bc- and C-horizons derive from the weathering of the Sinemurian aged limestone (Baize and Chrétien, 1994). Four main pedogenetic processes occurred in the solum during pedogenesis: decarbonatation, succession of oxidative and reductive conditions (past and present), eluviation and weathering (Baize and Chrétien, 1994). The mineralogy and the chemistry of the parental limestones and of the different particle-size fractions of each horizon of the solum were determined. Sequential extractions (adapted from Gupta and Aten, 1993; Hall et al., 1996; Benitez and Dubois, 1999), performed on bulk fractions, were particularly focused on the extraction of Zn bound to Fe and Mn-oxides. Mass balance calculations were performed using Ti and Zr as cross-references (Brimhall et al., 1991).

Results

Zinc distribution in the parental limestones

In both the Lotharingian and the Sinemurian aged limestones, Zn occurs at low concentration in the carbonated matrix probably in association with phyllosilicates (kaolinite and interstratified). The most important Zn concentrations are found in association (i) with both Fe and S (as a mix of pyrite and sphalerite) in spots included in the carbonated matrix of the Sinemurian aged limestones or (ii) with Fe (as goethite) in the phosphate nodules of the Lotharingian aged limestone.

Zinc distribution in the solum

Zinc concentration in the bulk fraction increases with depth, with a peak in the B_p-horizon and an abrupt increase in the C-horizon. The main Zn bearing particle-size fraction is the <20 μm one, especially the <2 μm one which consists, in decreasing order of contribution, of kaolinite, interstratified phyllosilicates, quartz, Fe- and Mn-oxides. Phosphate nodules (mainly apatite) and Fe-Mn concretions (mainly goethite, ferrihydrite and Mn-oxides including birnessite), are responsible for the important Zn fraction bound to the >500 μm particle-size fraction. In the phosphate nodules, Zn is associated with goethite grains scattered or amassed in the matrix, but is absent from the matrix. Sequential extractions show that Zn is essentially associated to amorphous and crystallized Fe-oxides (ferrihydrite and goethite) and to phyllosilicates (kaolinite and interstratified) along the whole profile. Nevertheless, the extremely high Zn concentration in the C-horizon is related to an abrupt increase of Zn contents in Mn- and amorphous Fe-oxides, Mn-oxides (including birnessite) displaying an extreme Zn enrichment.

Zinc mass balance calculations

Mass balance calculations show Zn losses in the A- to Bd-horizons and Zn accumulations, slight in the B_p- and Bc-horizons, but important in the C-horizon.
Conclusion

The pedogenesis, through eluviation, oxido-reduction and weathering, may have impoverished in Zn the top solum, with an almost disappearance of the most easily extractable phases containing zinc, which is now bound to stable phases. In the Bp- and Bc-horizons, Zn accumulation is small but important redistributions occurred, especially due to the alternation of oxidative and reductive conditions that permit the coprecipitation of Zn with goethite and ferrihydrite. Zinc is now partly accumulated in the C-horizon where Zn is bound to more easily extractable phases.

References


