Elevated concentrations of zinc in soils developed from Jurassic limestones: Changes in zinc speciation during soil formation.

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Some soils of the Jura mountain range in Switzerland were reported to contain high concentrations of zinc (Zn) and cadmium (Cd), often exceeding the Swiss soil protection guideline values. Recent studies suggested that the trace metal enrichments are related to the underlying parent rocks, consisting of oolitic carbonates of middle to late Jurassic age (Baize and Sterckman, 2001; Benitez Vasquez, 1999). Little is known about the relative metal accumulation and metal speciation in relation to soil formation. Trace metals bound in minerals resistant to weathering may still be present in the soils, while metals released during weathering and soil formation may have formed new species, for example, metals adsorbed to soil surfaces or metals incorporated into newly formed mineral phases. The chemical speciation of trace metals in soils has important implications for their bioavailability, mobility, and potential toxicity to organisms. The objectives of our work are to determine the speciation of Zn in the parent carbonate rocks and in corresponding soils.

The speciation of Zn in three soils and their corresponding parent rocks was investigated by sequential selective extraction (SSE) and X-ray absorption fine structure (XAFS) spectroscopy. The first site, Gurnigel, is located close to the pass of “la Vue des Alpes” (Neuchâtel Canton). The parent rock consists of oolitic limestone of late Bajocian age. The second site, Schleifenberg, is situated near Liestal (Basel Canton) on early Bajocian oolitic limestone. The third site, Dornach, is located 1 km south of the village Dornach (Basel Canton). The geology at the site is dominated by oolitic micritic limestone of late Oxfordian age, covered by a thin loess deposit.

Total contents of Zn in soil and rock samples were determined by X-ray fluorescence (XRF) analysis. Soil samples were characterized by SSE using the procedure of Zeien and Brümmer (1989), yielding seven Zn fractions. In the following, the extractant solutions and the soil-to-solution ratios (SSR) used are given, along with a hypothetical interpretation of possible metal species. (F1): 1M NH$_4$NO$_3$, SSR 25 (readily soluble and exchangeable Zn); (F2): 1M NH$_4$-acetate, pH 6.0 (specifically adsorbed, CaCO$_3$ bound, and other weakly bound Zn species); (F3): 0.1 M NH$_2$OH–HCl plus 1M NH$_4$-acetate, pH 6.0 (Zn bound to Mn oxides); (F4): 0.025M NH$_4$ EDTA, pH 4.6 (Zn bound to organic substances); (F5): 0.2M NH$_4$-oxalate, pH 3.25 (Zn bound to amorphous and poorly crystalline Fe oxides); (F6): 0.2M NH$_4$-oxalate, pH 3.25 in boiling water (Zn bound to crystalline Fe oxides); and (F7): residual fraction calculated from the difference between total Zn (XRF) and sum of Zn extracted in F1 to F6.

Information about the spatial distribution of Zn and other elements and the coordination chemistry of Zn in the soil and rock samples was obtained by advanced synchrotron X-ray techniques. Bulk XAFS spectra of powdered samples were collected at the Zn K-edge (9659 eV). In addition, polished thin sections were investigated by synchrotron -XRF and -XAFS spectroscopy, respectively. XAFS spectra were analyzed by linear combination fitting based on an extensive set of reference spectra of known Zn species.

The total concentrations of Zn in soil and rock samples from the three sites are reported in Table 1. All three soils had total Zn concentrations in excess of the Swiss guideline value (>150 mg kg$^{-1}$). The soils were clearly enriched in Zn relative to the respective parent rocks. First XAFS spectroscopic results indicate that Zn in the limestones from Schleifenberg and Gurnigel was present mainly as Zn-substituted goethite. A small fraction of Zn in both rocks was found to be bound in sphalerite (ZnS). These results were confirmed by extraction of the powdered rocks with 1M NH$_4$-acetate solution (pH 6), which suggested that most of the Zn was bound in non-carbonaceous components, which were not...
extractable with NH₄-acetate (Table 1). In contrast, XAFS results and extraction with NH₄-acetate showed that almost all Zn in the Dornach limestone was contained as a substitute for Ca in the calcite structure.

Table 1: Total and NH₄-acetate extractable Zn in rock and soil samples.

<table>
<thead>
<tr>
<th>Site</th>
<th>Rock total Zn [mg kg⁻¹]</th>
<th>Soil extractable Zn * [% of total]</th>
<th>Soil total Zn [mg kg⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gurnigel</td>
<td>43</td>
<td>43</td>
<td>864</td>
</tr>
<tr>
<td>Schleifenberg</td>
<td>92</td>
<td>23</td>
<td>237</td>
</tr>
<tr>
<td>Dornach</td>
<td>207</td>
<td>100</td>
<td>476</td>
</tr>
</tbody>
</table>

* Zn bound in carbonate minerals, extracted with 1M NH₄-Acetate at pH 6.

The Gurnigel soil contained considerable amounts of Zn-bearing goethite, stemming from the parent rock, and smaller amounts of newly formed Zn species identified as Zn sorbed to birnessite and Zn bound in the octahedral interlayer sheets of Al-hydroxy interlayered minerals (HIM). These results suggest that Zn in goethite is very stable during pedogenesis. The speciation of Zn in Schleifenberg soil was similar, with Zn-goethite and Zn-HIM representing the major fractions. Sphalerite was also found in minor quantity. For both soils, the results of SSE confirmed that Zn was associated mainly with iron oxides (F5 and F6 containing 45% of total Zn at Schleifenberg and 50% at Gurnigel) and the residual mineral fraction (F7 containing 37% and 36% of total Zn, respectively).

Bulk XAFS analysis of the Dornach soil suggested that Zn was primarily bound in octahedral interlayer sheets of HIM. This was supported by the SSE results, showing that the largest fraction of Zn was bound in the residual mineral fraction (F7 equal to 74% of total Zn).

In summary, our results obtained so far show that the Zn-substituted goethite occurring in limestones is very stable during pedogenesis, while Zn bound in carbonates is released and subsequently incorporated into newly formed mineral species in the soil. Sphalerite partly dissolves during pedogenesis, but can still be found in the soils. One major newly formed Zn species was identified as Zn bound in octahedral sheets of hydroxy-interlayered minerals.

REFERENCES

