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Characterization of Fe-Mn concretions from a Luvisol irrigated by mine water in a semi-arid agricultural area

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We studied Fe-Mn concretions from Cutanic Luvisol in the northern part of Namibia, where agricultural fields are irrigated with the drainage water from the Kombat Cu-Pb-Zn mine (pH 7, metal concentrations in ug/L: Fe 7, Mn 10, Zn 7, Cu 18). Concretions (0.5-2 cm in size) were mostly found towards the basis of the soil profile (BC horizon, depth 100-120 cm). Comparisons with the bulk chemical composition of the soil matrix indicated that Fe-Mn concretions were enriched with metals, metalloids and other trace elements (enrichment factor EFs varied in the range 1.3-6.4). Concentrations of the elements of interest in the Fe-Mn concretions were the following (mg/kg): As 23.1, Ba 3840, Cd 6.83, Cu 450, Pb 597, Zn 137. The X-ray diffraction analysis indicated that concretions were composed of quartz, goethite, hematite, illite/mica, lithiophorite (LiAl2Mn3O6(OH)6) and birnessite. The SEM observation confirmed that internal structure with concentric rings reflecting seasonal changes in redox conditions occurred within the concretions. Spot analyses and X-ray elemental maps performed using EDS spectrometry showed that concentrations of metalloids were rather low and slightly elevated Ba concentrations were only observed within the Mn-oxide zones. Selective extractions were used to understand the binding of trace elements onto individual target phases. Whereas Mn-oxide phases sequestered the majority of Cd (up to 98%), Ba, Pb and REEs (up to 78%), other metals such as Cu and Zn exhibited much lower values (47-65%) and were also significantly bound to Fe-oxides. The pH-static leaching test conducted in the pH range of 2-12 indicated that the majority of trace elements were mostly leached under acidic conditions with the exception of As, which was highly solubilized at pH 12 (up to 17%). Whereas Ba, Cd, Cu and Zn were significantly released under acidic conditions (up to 12%), the leaching of Pb was almost negligible over the entire pH range. Our results show that Fe-Mn concretions act as significant traps for trace metals in Luvisols irrigated with mine water. However, seasonal decrease of pH and changes in redox conditions may cause the dissolution of Fe-Mn concretions and subsequent release of contaminants into the soil system. This study was supported by a Czech Science Foundation project 15-07117S.