



Copper and lead isotopic and metallic pollution record in soils from the Kombat mining area, Namibia

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Copper (Cu) and lead (Pb) concentration, isotopic composition ($^{206}\text{Pb}/^{207}\text{Pb}$, $^{65}\text{Cu}/^{63}\text{Cu}$) and speciation were studied in soils from the Kombat mining area. The Cu and Pb concentrations in the studied soils ranged between 21 mg/kg – 757 mg/kg, and 19 mg/kg – 815 mg/kg respectively. In the sequential extractions, the largest part of soil Cu appeared in the residual and reducible fractions and Pb was predominantly bound in reducible and residual fractions and was more mobile compared to Cu. Copper and Pb concentration are higher in soils close to the slime deposit. Concentration of both metals increased with increasing soil depth in irrigated and cultivated soils. In soils not contaminated by dust eroded from the slime deposit, Cu and Pb contents are not dependent on the soil depth. The Pb isotopic signatures ($^{206}\text{Pb}/^{207}\text{Pb}$) ranged between 1.15 – 1.21 in soils from the Kombat area. In most of soil samples, surface horizons exhibited lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, which originates from the slime dust pollution ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.15$) compared to deeper soil horizons, with lithogenic Pb signatures ($^{206}\text{Pb}/^{207}\text{Pb} > 1.2$). Isotopic composition of Cu differs on contaminated and uncontaminated sites and cultivated and non-cultivated sites. The $\delta^{65}\text{Cu}$ in the studied soil horizon ranged between -0.373 ‰ and 0.561 ‰ . The most pronounced variations occurred in contaminated non cultivated and non-irrigated soils (0.529 ‰). The contaminated top horizons are enriched in isotopically heavier Cu (tailing materials), and $\delta^{65}\text{Cu}$ decreased with depth. Irrigated (cultivated) and contaminated soils exhibited heavier Cu in the surface horizons (originated from tailing dust $\delta^{65}\text{Cu} = 0.260$), decrease of $\delta^{65}\text{Cu}$ in Bt horizons (biological uptake of light isotope by crop, and their incorporation in this horizons) and increase of $\delta^{65}\text{Cu}$ in Bc horizons. The Bc horizons of cultivated and irrigated Phaeozems are enriched in Mn nodules (0.2 – 1.5 cm diameter, prevailing Mn phase pyrochroite $\text{Mn}(\text{OH})_2$) which contain 400 mg/kg of Cu. Manganese nodules containing horizons are enriched in isotopically heavier Cu ($\delta^{65}\text{Cu} = 0.378\text{ ‰}$). Similar $\delta^{65}\text{Cu}$ patterns were found in soils without manganese nodules, but with higher secondary iron and aluminium hydroxides, which may bind Cu on their surfaces. Fractionation of Cu isotopes (enrichment in ^{65}Cu) in soil formation processes are attributed to preferential adsorption of heavier isotopes on secondary soil components.