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Assessing Cr sources and biogeochemical processes influencing its bioavailability thanks to Cr isotopic signature

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In this study, we focus on the mining area of Sukinda Valley (Orissa, India) which comprises of ~98% of India's chromium ore reserve. We aimed at determining both the Cr sources and the biogeochemical processes enhancing or limiting its mobility along the valley through an isotopic study. The mining activity produces huge amounts of tailings that are non economically viable materials stored in the air. They are characterized by 80 and 15wt% of hematite and chromite respectively and are globally enriched in light Cr (δ^{53}Cr = -0.47 +/-0.04 ‰).

Downstream the mines, paddy soils were found to be enriched in iron oxides and chromium oxides, with up to 5.1wt% of Cr and up to 0.013% of exchangeable Cr(VI). The pounds, rivers and underground waters revealed an increasing gradient of dissolved Cr concentration from the upstream to the downstream of the valley: below 4 µg/L for the geochemical background and up to 1.6 mg/L in the mining area. The Cr(VI) represents up to 25%, 22% and 14% of total dissolved chromium in rivers, ponds and underground waters, respectively, in the most impacted area. From the weathering of tailings to Cr transported by surface waters, the relative proportion of $Cr(VI)/Cr_{Total}$ has a sixtyfold increase. The geochemical background is a surface water with Cr(III) enriched in heavy isotopes, 1.65+/-0.03‰. Moving towards the impacted area, $Cr(VI)/Cr_{Total}$ increases while the surface water is depleted in heavy isotopes (0.99+/-0.05‰ (n=8)), relatively to the background. In the most impacted area, δ^{53}Cr displays average values of 1.04±0.04 (n=12), 1.75±0.02 (n=5) and 1.24±0.04‰ (n=17) in rivers, ponds and underground waters, respectively. In surface and underground waters used to irriguate the paddy soils, Cr is mainly under its trivalent form. These waters are depleted in heavy isotopes compared to the geochemical background. The ponds which mostly contain trivalent Cr are enriched in heavy isotopes compared to the background. Cr adsorption onto suspended particulate matter or Cr(VI) reduction by Fe can explain Cr(III) enriched in heavy isotopes.