

Linking N cycle to contamination of groundwater by geogenic Cr(VI)

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Groundwater contamination by geogenic Cr(VI) has been documented in many ultramafic aquifers around the world. At the same time, nitrate (NO_3^-) exists in groundwater at elevated concentrations as a result of excessive application of fertilizers, animal manure and inappropriate sewage management. Some studies have implied that groundwater bodies of agricultural areas are more vulnerable to Cr(VI) contamination. Here, we examine the linkage between the two contaminants following two geochemical approaches: a) application of laboratory incubation experiments to assess the effect of nitrate in groundwater on Cr(VI) generation from ultramafic rocks, b) use of coupled nitrogen and oxygen isotopes of NO_3^- in groundwater to examine possible associations between NO_3^- sources and transformations, and Cr(VI) mobilization.

The first linkage arises from the fact that nitrate acts competitively to chromate anions, previously adsorbed onto solid surfaces. Leaching of Cr-bearing rocks with a neutral NO_3^- solution released environmentally relevant amounts of Cr(VI) from serpentinites and laterites (43 and 892 $\mu\text{g}/\text{kg}$, respectively). Values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in Cr(VI)-impacted groundwater (range 8-121 $\mu\text{g}/\text{L}$) showed that domestic sewage and nitrification of NH_4^+ -based fertilizers are responsible for the high NO_3^- concentrations in central Greece aquifers. We found a clear relationship between dissolved NO_3^- and Cr(VI) when residential waste cesspool is the source of NO_3^- in groundwater, possibly indicating an enhanced Cr(VI) generation or mobilization when sewage waste interferes with Cr-bearing ultramafic source material. When geochemical conditions favor the process of nitrification, Cr(VI) generation could be the result of its desorption by NO_3^- . Acidification caused during oxidation of NH_4^+ to NO_3^- also favors the mobilization of Cr(III) and its subsequent oxidation by natural oxidants. We suggest that human activities such as agriculture and inappropriate human waste disposal affect the geochemical occurrence of Cr(VI) in groundwater.