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Impact of Manganese-Inhibited Calcite Precipitation on Fluoride Mobilization in Groundwater

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Fluoride (F) contamination in groundwaters of low-to-middle income countries is a major water quality problem. Regular intake of F contaminated water can cause health problems like dental and skeletal fluorosis. In India, 24 states out of 30 are affected by F contamination. The origin of F in Indian groundwaters is mostly geogenic, caused by F-bearing minerals. Calcite and dolomite precipitation followed by fluorite dissolution is the major process controlling F mobilization in carbonated groundwaters. While F mobilization mechanism in such groundwaters is well known, the reasons for occurrence of lower levels of F in comparable aquifers with elevated manganese are poorly understood. Statistical analysis of published data on Indian groundwaters reveals that the probability of F being above drinking water limit (1.5 $mg.L^{-1}$) is higher when manganese (Mn) concentration is lower, and vice versa. Also, strong negative correlation was observed between F and Mn in some studies. The objective of this study was to systematically evaluate the possible effect of Mn on F mobilization. A series of batch experiments were carried out under approximate in-situ conditions. The first experiment was performed with an initial equimolar Ca and Mn (10 mM) with variable dissolved inorganic carbon (10 and 20 mM), in conditions supersaturated with respect to calcite and rhodochrosite in uncontaminated groundwater matrix. Control experiments were also performed in ultrapure water and synthetic groundwater matrices. Irrespective of background matrices, more Mn precipitated than Ca after 30 d (Figure 1). Another experiment was performed with equal initial supersaturation (saturation index = 1) levels with respect to both calcite and rhodochrosite, in UW and SGW matrices. Even at the lower level of initial Mn (0.023 mM), calcite precipitation was hindered in both matrices. Precipitation of calcite and rhodochrosite were confirmed through XRD and SEM-EDS analyses on solids collected from batch reactors. Rhodochrosite precipitation outcompeted calcite precipitation in short time scales. In Mn-rich aquifers, rhodochrosite precipitation could likely hinder calcite precipitation in the presence of elevated carbonate, which may in turn minimize fluorite dissolution. Inferences from this study could be used to explain F mobilization mechanisms in other aquifers and develop F mitigation techniques.

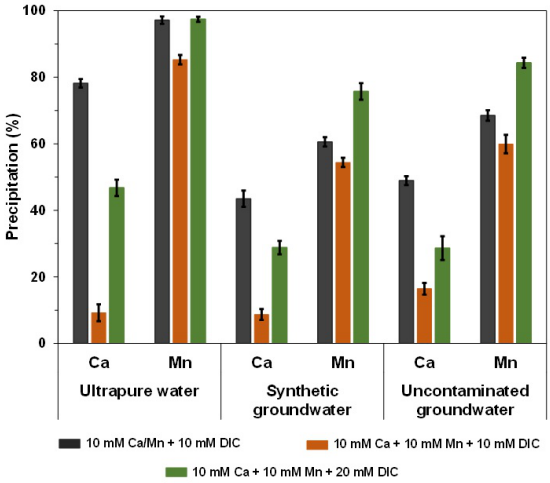

Figure 1. Relative precipitation of calcium and manganese obtained after 30 d of reaction in the batch reactors in presence of different background matrices.