Evaluation of Perchlorate Sources in a Southern California Aquifer Using Four Different Isotopic Measurements

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Background/Objectives. Perchlorate (ClO_4^-) in groundwater has several potential sources including synthetic ClO_4^- derived from military, aerospace and industrial products, and natural ClO_4^- that was either imported in the past with nitrate fertilizers from the Atacama Desert (Chile) or accumulated locally from atmospheric deposition (indigenous). The objective of this study was to test the use of four different isotopic ratio measurements to distinguish sources of ClO_4^- in groundwater in a complex subbasin of southern California. All three of these major ClO_4^- source categories could potentially contribute to local groundwater ClO_4^-.

Approach/Activities. The area of study included groundwater plumes having ClO_4^- concentrations as high as 1,150 µg/L from known military/industrial sources, and wider areas of groundwater outside of the plumes where ClO_4^- was detected at lower levels sometimes exceeding the state's maximum contaminant level for drinking water of 6 µg/L, but where no synthetic source was known. Groundwater was collected from 33 different wells or well depth intervals using ion exchange columns to trap adequate quantities for isotopic analysis. Perchlorate was then purified and analyzed for chlorine and oxygen stable isotope ratios ($d^{37}Cl$, $d^{18}O$, $d^{17}O$) and radioactive chlorine-36 (^{36}Cl) isotopic abundance. Other geochemical, isotopic, and hydrogeologic parameters also were characterized.

Results/Lessons Learned. Stable and radioactive isotope data indicate that ClO_4^- from all three principal sources (synthetic, Atacama nitrate fertilizer, and indigenous natural) was present in the aquifer. Data from sampled wells within the contours of the two mapped ClO_4^- plumes were consistent with a dominantly synthetic ClO_4^- source. In wells downgradient from the synthetic plumes and in the subbasin to the southwest, data indicate that Atacama fertilizer was the dominant source of groundwater ClO_4^-. This is consistent with historical land use records, showing that this was a largely agricultural area growing crops, such as citrus, that once depended upon Atacama nitrate fertilizer for high productivity. The ^{36}Cl and $d^{18}O$ data indicate that all wells also contained a low concentration of indigenous natural ClO_4^-. This source was most evident in wells having the lowest ClO_4^- concentrations (< 1 µg/L), which is consistent with the occurrence of ClO_4^- as a low-level background constituent throughout the arisd southwestern US. Overall, the ClO_4^- isotope data permitted discrimination of synthetic and Atacama fertilizer sources in wells with concentrations greater than 1 µg/L, and provided an important regional perspective on anthropogenic and natural ClO_4^- in groundwater.