CURRENT STATE-OF-THE-PRACTICE OF PERCHLORATE FORENSICS

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Introduction

Since the late 1950s, ammonium perchlorate (NH_4ClO_4) has been manufactured and used as a solid rocket engine fuel oxidizer; perchlorate salts are also contained in munitions, pyrotechnics (fireworks and road flares), and electroplating solutions. When dissolved in water NH_4ClO_4 disassociates into the ammonium (NH_4^+) cation and perchlorate (ClO_4^-) anion. Before 1997, ClO_4^- could not be readily detected in groundwater at concentrations below 100 micrograms per liter (µg/L). In that year, the California Department of Health Services developed an acceptable analytical method (now EPA Method 314.0) that lowered the detection limit to 4 µg/L. Subsequently, ClO_4^- contaminated groundwater was soon encountered in several western states and contamination also became apparent in Colorado River water. However, ClO_4^- has also been discovered to occur naturally in rock formations and groundwater. This has posed the question: can anthropogenic (human) sources be differentiated from geogenic (natural) sources? In the past two years, scientific progress in answering this question has been rapid and is discussed in the following article.

Perchlorate Characteristics

The ClO_4^- anion, containing a central chlorine (Cl) atom surrounded by four oxygen (O) atoms, is produced when highly soluble solid salts of ammonium, potassium, and sodium perchlorate dissolve in water. Perchlorate salt solubilities range to 220,000 parts per million (ppm) for NH_4ClO_4. Concentrated solution densities are greater than water, producing brines capable of sinking through the groundwater column. Once dissolved, ClO_4^- is extremely mobile and stable, requiring decades to naturally degrade. In groundwater, ClO_4^- is relatively unretarded moving by advection through porous, unconsolidated sediments.

Perchlorate Occurrences

Geogenic derived ClO_4^- salts have been documented in imported nitrate fertilizer from the Atacama Desert of Chile, caliche in alluvium, evaporate deposits, and kelp. Natural ClO_4^- of possible atmospheric origin has also been detected in eastern New Mexico and west Texas groundwater. A natural ClO_4^- occurrence has also been reported in southern California marine sedimentary rocks. The EPA has reported anthropogenic ClO_4^- releases in 35 different states, two territories, and Washington, D.C. As of mid October 2005, California had 38 documented releases from aerospace, explosive, flare, ordinance, and other facilities. Confirmed plumes occur in Rancho Cordova, Santa Clara Valley, Rialto-Colton area, San Gabriel Valley, Stringfellow Superfund site in Glen Avon, and other locations, primarily in southern California. In Nevada, two ClO_4^- groundwater plumes occur near Henderson, emerging in Las Vegas Wash, which drains to Lake Mead, the southern Colorado River and California aqueduct. In 2004, ClO_4^- concentrations at the drinking water intakes of Lake Havasu ranged from 4 to 6 µg/L. This ClO_4^- has impacted southern California agriculture (e.g., lettuce and milk).

Environmental Forensics

Because ClO_4^- moves at groundwater flow rates, it was once used as a tracer for associated volatile organic compounds and metal contaminants that are significantly more retarded. However, with the advent of ClO_4^- as a direct groundwater contaminant the search has been for newer forensic techniques that directly analyze the ClO_4^- anion's chlorine (^{35}Cl and ^{37}Cl) and oxygen (^{16}O, ^{17}O, and ^{18}O) isotopic ratios to fingerprint perchlorate plumes and potentially trace them back to their source. Chlorine-oxygen isotope forensics has now differentiated anthropogenic ClO_4^- from solid rocket fuel sources and geogenic ClO_4^- in Chilean nitrate

fertilizers and west Texas groundwater. Other forensic techniques (defined as ClO_4^- surrogates) include identification of metals and stable isotopes associated with ClO_4^- compounds used in manufactured products. For example, metals are commonly included in pyrotechnics to add color to the explosive display. These include antimony, chromium, copper, magnesium, mercury, nickel, strontium, titanium, uranium, zinc, and zirconium. Strontium isotopes could also potentially be used to define different ClO_4^- sources because strontium nitrate is often combined with ClO_4^- compounds in flares and pyrotechnics. Oxygen-deuterium isotopes in water and nitrogen-oxygen isotopes in dissolved nitrate may also be used to identify both water and nitrate sources and therefore may be useful ClO_4^- surrogates.

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