

Aqueous Geochemistry and Environmental Fate of Perchlorate

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Natural perchlorate has been recently measured in ground waters from 2 to 4 nanomolal (nm) (0.2 to 0.4 ppb) in northern New Mexico. Liquid chromatography-mass spectrometry/mass spectrometry (EPA SW846 method 8321A), with an instrument detection limit of 0.6 nm (0.06 ppb), was used during this investigation. Perchlorate consists of three-double and one-single covalent bonds between chlorine and oxygen, making this highly soluble oxyanion very stable and nonreactive in aqueous environments. Perchlorate does not adsorb onto inorganic surfaces, including hydrous ferric oxide, smectite, and manganese oxide, characterized by net-negative surface charges under circumneutral pH conditions (6.5 to 9.0). Physical processes including mixing and dispersion control the distribution of perchlorate in ground water. The overall reduction of perchlorate to chloride is given by the following half reaction: $\text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- = \text{Cl}^- + 4\text{H}_2\text{O}$, with an E° of 1.39 volts (V) and an Eh of 0.98 V at a pH of 7.0. This reaction has relevance to natural systems such as wetlands and other microbially-active environments with plentiful and diverse electron donors. Perchlorate is reduced to intermediate compounds (chlorate [Cl(V)] and chlorite [Cl(III)]) and eventually to chloride in anaerobic environments by serving as a terminal electron acceptor during oxidation of acetate and other forms of reactive organic carbon.

Dr. Patrick Longmire is an aqueous geochemist at Los Alamos National Laboratory specializing in the fate and transport of radionuclides and inorganic contaminants in ground-water systems. Patrick has been investigating the use of permeable reactive barrier technology to remediate ground water contaminated with perchlorate, nitrate, metals, and radionuclides. Dr. Longmire has 30 years of experience in the field of aqueous environmental geochemistry. Patrick has been teaching short courses on ground water geochemistry for NGWA since 1986.

Dale Counce is an analytical chemist with Los Alamos National Laboratory. Dale specializes in inorganic analyses including ion chromatography, inductively coupled plasma mass spectrometry, and inductively coupled plasma optical emission spectroscopy. Dale has 27 years experience in analytical chemistry.

Michael Dale is a hydrogeologist with the New Mexico Environment Department. Michael conducts hydrogeochemical investigations including measuring naturally-occurring perchlorate and delineating ground-water flow paths using isotopic and chemical tracers. Michael has 13 years experience in the fields of hydrochemistry and hydrogeology.