TRACE PERCHLORATE IN GROUND WATER, NORTHERN RIO GRANDE BASIN, NEW MEXICO

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Perchlorate (ClO₄) is a naturally occurring and manmade anion that is mobile in ground water. If ingested, the contaminant can block the thyroid gland from taking up iodine (Plummer et al., 2006). Perchlorate in ground water from anthropogenic and natural sources has been discussed by previous authors (Rajagopalan et al., 2006; Jackson et al., 2005; Dasgupta et al., 2005). Naturally occurring ClO_4^{-} in ground water is ubiquitous in central New Mexico as shown by a recent study by Plummer et al. (2006). Plummer et al. (2006) showed that Pleistocene and Holocene age ground waters in the Middle Rio Grande Basin (MRGB) contain ClO₄⁻ from a natural source at concentrations ranging from 0.12 to 1.8 µg/L. Results were presented on the relationships between ClO₄⁻ concentration and other anions with respect to evapotranspiration (ET) and age. Plummer et al. (2006) concluded that (1) the source of ClO₄⁻ in MRGB ground water may be from an atmospheric (bulk deposition) origin, (2) that concentration may be dependent on ET and not age, and (3) that processes in the soil may deplete ClO_4 prior to recharge. With respect to ET, Plummer et al. (2006) suggest that higher levels of ClO₄⁻ in ground water may be associated with recharge areas with ET factors approaching 40 and/or where longterm accumulations of atmospheric salts in dry soil are suddenly leached.

The U.S. Environmental Protection Agency has yet to set a Federal drinking-water standard; however, they have established a human reference dose (estimated) that is equivalent to a

drinking-water maximum contaminant level of 24.5 μ g/L. Several states have set their own standards or public health goals. For example, California's public health goal is 6 μ g/L, meaning that ingestion of levels exceeding 6 μ g/L would pose a significant risk to human health.

In the Los Alamos area, CIO_4^- contamination is present in the shallow and intermediate aquifers, and in the regional drinking-water aquifer. The primary source of CIO_4^- is from the release of untreated and treated industrial liquid waste at the Los Alamos National Laboratory (the Laboratory) beginning in the mid 1940s. Monitoring for CIO_4^- in ground water at the Laboratory began in 2000. Concentrations range from non-detect at <0.03 to 280 µg/L. To date, the highest level of CIO_4^- in the drinking-water aquifer is 7 µg/L. Discerning the level at which CIO_4^- is natural versus anthropogenic is important with respect to detection monitoring, well-head protection, site investigations, remedial actions, and assessing human health and ecological risks and setting drinking-water standards.

The New Mexico Environment Department and the Laboratory undertook a four-year (2003 – 2006) project to determine background concentrations of naturally occurring ClO_4^- in the ground waters present in the Los Alamos and Taos areas of the Northern Rio Grande Basin, New Mexico. Additional objectives for this work included determining: (a) the spatial distribution of background ClO_4^- within a given aquifer with respect to the geochemical evolution along flow paths and ground-water age, (b) variability of ClO_4^- concentration within the ground-water system as a whole; (c) correlations between ClO_4^- concentration and concentrations of other ions such as chloride and stable-isotope ($\delta^{18}O$ and deuterium) composition; and (d) the presence or absence of ClO_4^- in local precipitation.

Completion of this project involved the collection, analysis, and interpretation of 153 groundwater and 13 precipitation samples. Of the 153 ground-water samples, 128 were derived from samples collected in the Los Alamos area. Samples were analyzed for low-level ClO₄⁻ using the liquid chromatography-mass spectrometry/mass spectrometry and ion chromatography-mass spectrometry/mass spectrometry methods, with detection limits ranging from 0.05 to 0.0088 µg/L. Complimentary analyses included major ions, trace elements, radiocarbon measured on the dissolved inorganic component for average-age determination, tritium and the noble gases helium-3, helium-4, and neon-22 for apparent-age determination, the stable isotopes of carbon, hydrogen and δ^{18} O, and the field parameters pH, temperature, specific conductance, and dissolved oxygen. A large portion of these data and their interpretation were presented and discussed in a recent publication by Longmire et al., (in press).

In the Los Alamos area, 11 wells and 25 springs were sampled (Fig. 1) for low-level ClO_4^- . Precipitation samples were collected from three stations at varying elevations. Ground-water stations were selected based on several criteria including age and the presence or absence and concentration of conservative chemicals such as chloride and tritium.

We subdivided the ground-water system at Los Alamos into four distinct (but connected) zones of occurrence. The first zone (zone 1) is perched within the Sierra de Los Valles and the mountain front area near the Pajarito fault zone. The second zone (zone 2) is found within saturated canyon-bottom alluvium, forming alluvial aquifers. The third zone (zone 3) represents perched lenses of saturation at intermediate depths beneath canyon-bottom alluvial aquifers. The

fourth zone (zone 4) is the regional drinking-water aquifer. For this study, the first, third, and fourth zones were evaluated for background ClO_4^- .

Generally, non-impacted ground water in the Los Alamos area is a mixed Ca/Na-Mg-HCO₃-SO₄ type, with varying amounts of Ca, Na, and HCO₃. Chloride and SO₄ concentrations for all zones vary between 1 and 7 mg/L and 1 and 35 mg/L, respectively. Ground-water age varies from modern (younger than 1943) in the mountain-block area to sub-modern (older than 1943) in the deep regional aquifer. Zone 1 discharges at varying elevations from Tschicoma Formation dacites and upper Bandelier Tuff units (Longmire et al., in press). The springs are perennial with discharge rates varying from about 380 to less than one liter per minute. Ground-water age is predominantly modern for the springs; however two stations are of mixed age (older and younger than 1943). Zone 3 ground water is perched between 40 - 250 meters below land surface (bls) as thin lenses of saturation in Bandelier Tuff, Puye fangolmerate, and Cerros del Rio basalt. Ground-water flow is from the west to the east-to-southeast. Ground-water age is mixed and submodern. Only one well and one spring exhibit background conditions for the intermediate perched zone 3. Zone 4 contains ground water that is mixed (contaminated) and sub-modern (non-contaminated) in age, and found at depths ranging from approximately 200 to 400 meters bls within the Puye Formation (Pliocene age sands and gravels), Tschicoma Formation (Pliocene age dacites), Cerros del Rio basalt (Pliocene age), older basalt flows (Miocene age), and the Santa Fe Group (Miocene sands and gravels). Zone 4 terminates at the Rio Grande as springs within White Rock Canyon and may intersect the Rio Grande.

Statistical analyses were performed on analytical data collected from zones 1, 3, and 4. For zone 1, 13 stations were sampled with a total of 24 results. Mean plus one-standard deviation (1σ) and median concentrations for ClO₄⁻ in zone 1 were 0.282(± 0.065) and 0.280 µg/L, respectively. Six analytical results were obtained from two stations for zone 3. Mean plus (1σ) and median concentrations for ClO₄⁻ in zone 3 were 0.289(± 0.124) and 0.317 µg/L, respectively. For zone 4, the regional drinking-water aquifer, 10 wells and 12 springs were sampled that provided 98 analytical results. Mean plus (1 σ) and median concentrations for ClO₄⁻ were 0.281(±0.063) and 0.276 μ g/L, respectively, in zone 4. The mean plus (1 σ) and median for all samples collected in the Los Alamos area were 0.282 ± 0.067 and $0.280 \,\mu\text{g/L}$, respectively. The upper tolerance level (mean plus 2σ) for ClO₄ in this data set is 0.416 µg/L, meaning that any sample result exceeding this concentration of ClO₄ would be considered impacted by an anthropogenic source. Minimal variability between the mean, median, and 1σ occurs between the three zones, suggesting that age and/or water-rock interactions along the flow paths have little impact on concentration. No correlations were observed with respect to ClO₄⁻ concentration and other hydrochemical constituents such as chloride, δ^{18} O or total dissolved solids.

Thirteen precipitation samples were collected and analyzed for ClO_4^- . Eight were from snow events and five from summer monsoon events. Of the 13 samples collected, only two contained detectable ClO_4^- . These two samples, collected during monsoon events, contained ClO_4^- at 0.021 and 0.0099 µg/L with a detection limit of 0.0012 µg/L. Both results were qualified due to blank contamination at a concentration of 0.0039 µg/L. We suspect dust particles mixing with the sample introduced the ClO_4^- into the water sampled by surface desorption and/or dissolution of ClO_4^- from the dust.

These data suggest that natural ClO_4^- in the Los Alamos ground-water system originated postprecipitation and during recharge, and that evapotranspiration during recharge may be the mechanism for concentrating ClO_4^- .