Surface Water Quality Implications of Valles Caldera Geothermal Fluids on Jemez Watershed: A Holistic Hydrogeochemical Investigation

A Final Report for the New Mexico Water Resources Research Institute 2018-2019 Student Water Research Grant Program

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Problem and Objectives

The Jemez River (JR) (Figure 1), a major tributary of the Rio Grande, is in north-central New Mexico within the Jemez Mountains, which houses the active, world-class, high-temperature (\leq 300 °C), liquid-dominated Valles Caldera geothermal system (VC) (Goff & Grigsby, 1982). Highly mineralized geothermal systems usually have a significant hydrologic and environmental footprint. Subsurface processes, such as mixing with magmatically influenced fluids and water-rock interactions at elevated temperatures, enrich ascending and laterally-flowing geothermal waters with major and trace elements (Bau, 1991; Hedenquist & Lowenstern, 1994; Henley & Ellis, 1983; Kaasalainen & Stefánsson, 2012). The potential introduction

of dissolved trace elements into the JR poses societal and environmental concerns, as many local stakeholders use the water resource for various domestic, irrigational, and recreational uses. Particularly, a primary use of the JR is to house coldwater aquatic life, through which metals could bioaccumulate, which adds importance to drinking water standards.



Figure 1: Map of study area, with outline of Jemez River and tributaries and reported sampling and survey sites.

We focus on the northern portion of the JR, spanning a reach from the East Fork JR to the town of San Ysidro (Figure 1). Previous work has examined major-solute contributions from two outflow expressions of the VC, Soda Dam Springs and Jemez Hot Springs, and two major tributaries, Rio San Antonio and Rio Guadalupe (Purtymun et al., 1974; Sherson et al., 2009; Trainer, 1978). There is generally a net \sim 500-ppm increase from below Soda Dam to the end of the study segment. Here, we investigate the dissolved trace element load of the JR. This study aims to (1) recognize the sources of significant loading and (2) determine whether these substances remain in or become removed from solution.

Methodology

During low-discharge conditions (~15 cfs) on August 25^{th} 2018, water samples have been collected from important junctions and inflows along the JR, namely at East Fork Jemez, Rio San Antonio (SA), La Cueva, Battleship Rock, Hummingbird (HBRD), Soda Dam (SD), Jemez Springs (JS), Rio Guadalupe (GUAD), and San Ysidro bridge (SY). The discharge of the JR is estimated from a United States Geological Survey stream gauging station (unit #08324000) below the confluence at GUAD (USGS, 2019).

Total alkalinity (expressed as HCO_3) was measured via potentiometric acid-neutralization titration (Dickson, 1981; Gran, 1952). Major cation and anion chemistries were analyzed via Inductively Coupled Plasma (ICP) – Optical Emission Spectroscopy and Ion Chromatography, respectively. Trace metals will be determined via ICP-Mass Spectrometry. All analytical work was done at the Analytical Geochemistry Laboratory, University of New Mexico. Additionally, spatial profiles of pH, dissolved oxygen, temperature, oxidation-reduction potential, and turbidity were sampled with regular 1-km spacing and finer (50-m) resolution along sites with complete aqueous chemistry.

Results & Discussion

Major-ion chemistry from 2018 reflects patterns observed in sampling campaigns from the preceding decade (Figure 2) (Crossey et al., in prep.; Jochems et al. 2010). Except for GUAD, there is an increase in solute concentrations at each inflow. The greatest contributions are usually at SD, where diffuse thermal seeps have been identified (Goff et al., 1981), and the flow path through SY, along which groundwaters are dissolving carbonates and evaporites (Goff et al., 1981; McGibbon et al., 2018; Trainer et al., 2000). Levels of total dissolved solids began to exceed the EPA primary drinking water standard at JR below SD. This salinization is maintained throughout the rest of the JR study reach. Hence, major-solute chemistry is defined by conservative behavior, since changes in downstream concentrations only occur when mixing with inflowing waters of different geochemical compositions.



Figure 2: A downstream plot of major-solute chemistry with marked inflows (gray dashed) and the EPA Maximum Contaminant Level (MCL) for total dissolved solids (red solid). The datum is where the East Fork Jemez joins with Rio San Antonio to form the JR.

The distribution of measured trace element concentrations is shown by Figure 3. Notably, two metals, Fe and Mn, exceed secondary drinking water standards that relate to minor properties like odor, taste, and color. There is a violation of primary drinking water standards, which pertain to health concerns, in As. Except for Al, Mo, and V, the thermal springs exhibit the highest concentrations for the trace elements. These observed concentration ranges and abundances are dependent on processes that control movement of these trace metals downstream.

The 12 of 16 analyzed trace elements reflect the salinization pattern of major solutes and mostly behave conservatively downstream (Figure 4). These elements can be grouped according to their inherent chemical properties. The alkali (Li, Rb, and Cs) and alkali earth



Figure 3: A dot plot of trace element distributions with EPA MCLs.

metals (Ba and Sr) are cations with low ionic potential, and, thus, are weakly electrostatically attracted to anions like O_2^- (Railsback, 2003). This weak bonding potential enables relatively good solubility. The rest of the elements (Fe, Ni, Co, V, U, Pb, and Cu) consists of cations with intermediate potential, which have a greater likelihood of coordinating with S and O groups and may be potentially incorporated into major oxides and hydroxides, aluminosilicates, sulfides, and carbonates (Railsback, 2003). This second group of conservatively behaving elements may also exist under variable oxidation states, some of which are insoluble forms (Brookins, 1988).

The latter quarter (As, Mo, Al, and Mn) of the trace element suite consists of metals that show unique non-conservative behavior. For example, exclusive non-conservative behavior of As is marked by the river section between this area of greatest loading and the town of Jemez Springs (Figure 5). The concentration of As is expected to increase slightly or remain relatively constant since the JS inflow is more enriched relative to the last JR point. Instead,



Figure 4: A downstream plot of trace elements that behave like TDS or major solutes, with marked inflows.

about 60% of introduced As at SD is removed from solution. This removal may correspond with signals found along the same JR section. There are global minima for pH and Eh, which may signify a shift to relatively reducing conditions. Furthermore, turbidity peaks at its highest levels twice. Turbid waters are often associated to the elevated presence of particulate matter, which may function as adsorbents of heavy metals. Hence, the drastic changes in physiochemical conditions (pH and Eh) may be enhancing scavenging of As introduced by SD to the JR by potentially abundant charged solid surfaces (turbidity).

Future Work

This preliminary effort showed that most of the significant increases in trace element concentrations in the JR is attributed to the inflowing thermal waters at SD and JS. Moreover, 75% of trace elements remain in solution and is not naturally attenuated downstream. However, further characterization of the whole suite is necessary in providing a better overview.



Figure 5: Subplots of arsenic downstream profile and spatial surveys of physiochemical parameters. The term, $\Delta \mu M_{inflow-river}$, is the difference in concentration between an inflow and the preceding river sample.

Future work, in the form of an eventual M.Sc. thesis and a journal article, will incorporate these tasks to present a more complete discussion:

- Discussion of geothermal origins of trace elements (i.e., relation of VC hydrothermal outflow plume to lithology along different SD and JS flow paths)
- Speciation modeling to better understand elemental behavior and potential transformations (via complexation)
- Relation of physiochemical signals to analogous hydrogeochemical processes

Budget

Item #	Item Description	Expenditures (\$)
1	Lab Analyses and Supplies (for major and trace elements)	3355.57
2	Salary (1 month)	1700.00
3	Conferences and Travel	944.43

Table 1: Tabulated expenditures of awarded \$6000 grant. As of May 15th, the remaining balance is \$0.

Notes:

- Salary comparable to monthly stipend under current assistantship contract (\$1760 for 86.67 hours/month) w/ fringe benefits.
- 3. For travel costs for upcoming Geological Society of America 2018 Annual Meeting, November 2018: Registration (\$135) + Abstract Fee (\$50) + Total for Albuquerque-Indianapolis Flight & Claimed Meals & Incidentals for 3 days of conference (\$600.62) + 2 Posters printed (\$79.405/poster)

Presentations

- New Mexico Academy of Science 2017 Research Symposium, November 2017 [poster]
- "Minute Madness", NM EPSCOR Year 5 All Hands Meeting, November 2017 [talk]
- New Mexico Geological Society Spring Meeting, April 2018 [poster]
- 70th Geological Society of America Rocky Mountain Section Meeting, May 2018 [poster
- Geological Society of America 2018 Annual Meeting, November 2018 [talk & poster]
- University of New Mexico Shared Knowledge Conference, November 2018 [poster]
- New Mexico State Graduate Education Day, February 2019 [invited poster]

- University of New Mexico STEM Research Symposium, March 2019 [invited poster]
- University of Puget Sound Thompson Hall Science and Mathematics Seminar [invited talk]
- New Mexico Geological Society Spring Meeting, April 2019 [talk]

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