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OPEN-LOOP GEOTHERMAL DISCHARGE STREAM DESIGN AFFECTS THE PRECIPITATION OF CALCIUM

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ABSTRACT. Open-loop geothermal outflows have the potential for altering the chemical composition of local freshwater bodies by infusing them with spent ground water from geothermal heating/cooling systems (geothermal systems). A recently installed geothermal system and outflow on the campus of Taylor University has been investigated as a model for understanding the importance of certain stream design features in the removal of hardness ions. It has been previously reported that aerating streambed features preferentially removed iron but had little impact on the removal of dissolved calcium. This study describes the evaluation of dissolved calcium concentrations along the entirety of the stream (540 m from the geothermal system discharge to a nearby lake) by analyzing stream samples using atomic absorption spectroscopy. A slight gradual decrease in calcium concentration was observed along the 19 sampling sites with the exception of a 30% decrease between sites 12 and 13, the location of a large settling basin. When a lake-fed pool/fountain, designed to supplement the stream flow was turned on, only a 7% decrease in calcium concentration was observed. It was determined that while rapid moving water through rocky environments maximized the precipitation of iron; soil beds, slow moving water, and settling basins tended to maximize the precipitation of calcium. Additionally, a stream design that incorporates supplemental fresh water being added to the stream, often used for aesthetic reasons, caused a greater mobility of calcium ions and dramatically decreased its precipitation.

Keywords: Geothermal, stream design, calcium, deposition, atomic absorption spectroscopy

INTRODUCTION

In fall of 2012, Taylor University finished the construction of a new science building complete with many sustainable features. The features included wind turbines, solar panels, a heliostat, and an open-loop geothermal heating and cooling system, resulting in a Gold LEED (Leadership in Energy and Environmental Design) building certification. An outflow, which winds through campus to a nearby lake, was created to receive the discharge water from the geothermal system. Through numerous student projects and lab activities, the Department of Chemistry and Biochemistry has been studying the chemistry of Taylor Lake for years. Consequently, the recent construction has created a prime opportunity to study the impact of the stream design on the chemistry of the outflow and the lake.

Geothermal systems come in many forms and are one of the most widely used "green" heating and cooling systems (Spitler 2005). In the United States, it is estimated that 50,000 systems are installed annually in homes, schools, and commercial buildings (Curtis et al. 2005). These systems offer clear environmental and economic benefits. Geothermal heating and cooling systems have higher initial costs than conventional systems but lower operating costs due to their efficiency (Self et al. 2013). If properly maintained, most systems retain their efficiency for 25 to 30 years (Bloomquist 2000). These systems produce half of the CO_2 emissions of conventional systems and therefore are expected to help cut global CO_2 emissions by over 6% (Curtis et al. 2005; Chua et al. 2010).

Several geothermal heating and cooling system designs have been created; each catering to a different geographical region with their varying soil and rock type as well as water availability and composition (Curtis et al. 2005). A geothermal system that uses ground or surface water to absorb and reject heat from the building and then discharge the used water either back into the ground or out to surface is considered an open-

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loop system. A system in which the heat exchange occurs when building system water is circulated through pipes buried in the ground or submerged in surface water is considered a closed-loop system. It is recommended that for small systems, such as the one featured here, discharge be released to surrounding surface water (Rafferty 2003).

The calcium concentration within surface water bodies, typically less than 15 mg/L (Chapman 1996), is primary affected by substrate rock type, and their fluctuations can be due to changes in flow rates, litter fall (Webster & Patten 1979), and changes in turbidity – which facilitates nucleation (Mercer et al. 2005). When calcium levels are so high that intervention is required, typically in industrial wastewater situations, approaches utilizing cation exchange, chemical precipitation, and bioreactors have been employed (Hammes et al. 2003a, b; Nomanbhay & Palanisamy 2005). However, for geothermal outflows with only moderately elevated hardness levels, a carefully designed geothermal discharge stream may allow the discharge to naturally soften before it reaches its endpoint. If the stream design features do not effectively soften the discharge, then the remaining mineral content could cause a disruption in the ecosystem receiving it. Rocky streambeds, waterfalls, and high flow rates, among other features, encourage mineral deposition along the stream bottom through aeration. Previous investigation of the discharge outflow (Griffiths et al. 2013) demonstrated this to be true for iron. Atomic absorption spectroscopy (AAS) measurements along the first 90 m of the stream showed dramatic decrease in iron concentration that correlated strongly to the location of a rocky streambed and a small waterfall – both oxygenating features. However, the study found only a 16% gradual decrease in dissolved calcium concentration over that same distance suggesting that aeration does not significantly facilitate the precipitation of calcium. It is, therefore, believed that any decrease in calcium concentration occurs anaerobically, through precipitation with anions which are insoluble with calcium (e.g., carbonate or bicarbonate) found along the streambed. This paper outlines a study of the entire length of the stream, 540 m, in the hopes of finding a stream feature that preferentially facilitates a decrease in calcium concentrations more readily. Additionally, a new design feature was added to the stream between the earlier study and the present one that needed to be investigated. A fresh water lake-fed pool was connected 30 m above the source of the geothermal discharge to supplement the stream flow.

METHODS

Description of the geothermal discharge stream.—The stream is 540 m long and runs downhill from an elevation of about 284 m at its source to an elevation of about 271 m where it enters Taylor Lake (Fig. 1). This gradient supports fast flowing water along the majority of the stream. The streambed is narrow from its source to the lake, never widening more than 2 m except for in several settling basins. Before reaching the lake, the water travels through four settling basins where the flow is slowed. The basins, located at 90 m, 330 m, 390 m, and 420 m from the source, have approximate diameters of 5 m, 10 m, 25 m, and 30 m respectively. Upstream from the first settling basin, the streambed is composed of mostly rocks, but downstream from the basin the streambed becomes mostly soil, sediment, and plant matter. Additionally, the stream flow is supplemented by fresh water pumped from the lake to a small pool (and fountain) just above the geothermal discharge. When ambient temperatures are nearer the desired building temperature and the geothermal discharge is consequently less, the flow from this lake-fed pool, located 30 m above the source of the geothermal outflow, is turned on allowing fresh lake water to mix with the outflow water to supplement the stream flow. Under more extreme temperature conditions, and when the geothermal discharge is consequently higher, the lake-fed pool flow is sometimes off.

Sampling.—Samples were collected in a similar fashion as in the previous study (Griffiths et al. 2013). Each of the sample sites was marked with a flag, photographed, and denoted on a map of the stream so that they could be revisited. At each site, 300 mL samples were collected in triplicate. Sample sites spanned the length of the stream from 0 to 540 m from the source, in 30 m increments. As to not disturb the streambed and skew results, the samples were collected initially from the sampling site farthest downstream, near the lake, and then upstream toward the source. This sampling procedure was followed once while the lake-fed pool flow was off and once again while it was on. Samples were preserved with dilute hydrochloric acid (0.1 M) to

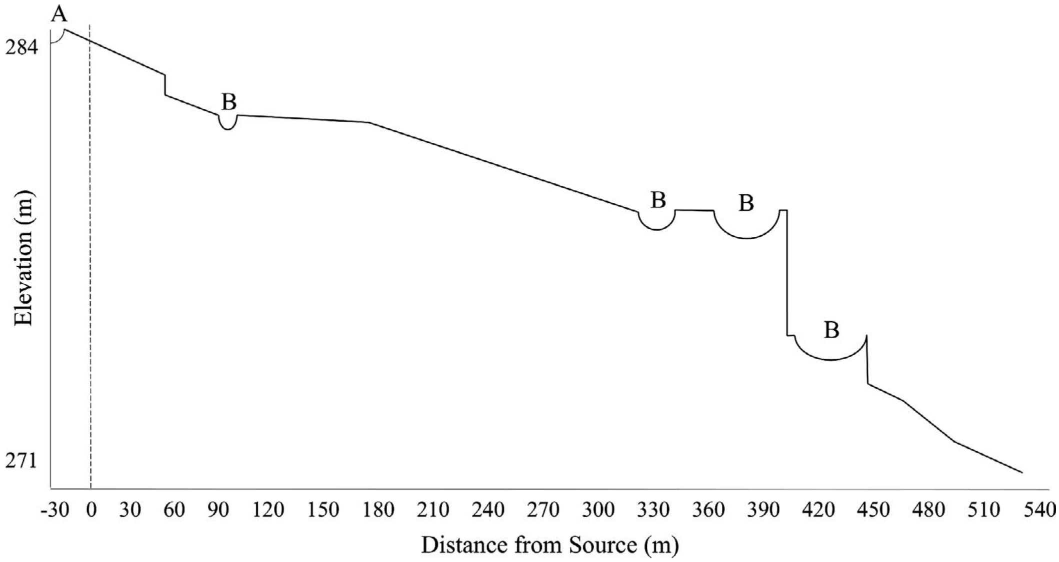

Figure 1.—Elevation change from geothermal discharge source (dashed line) to lake. The lake-fed pool location (A) at -30 m above the source and settling basins (B) at 90 m, 330 m, 390 m, and 420 m are also shown.

minimize precipitation and to avoid the potential interference during analysis (also added to standards) (EPA method 215.1) (Chapman 1996).

Analysis.—Dissolved calcium concentrations were evaluated using an iCE 3000 Series AAS (Thermo Scientific) equipped with an ASX-520 autosampler (CETAC) following the EPA method 215.1. Absorbance was monitored at 422.7 nm using an air/acetylene flame with a fuel flow rate of 1.4 L/min. One mL of HCl was added to samples to reduce precipitation prior to analysis. The addition of HCl also has the benefit of reducing the interference effects from phosphate and sulfate, the two most likely interferents for calcium in this study. For analysis, 10 mL of each sample was transferred to an autosampler tube and labeled based on its sample location. Calibration of the instrument was done using 1000 mg/L standard stock calcium solution from Fisher Scientific. Since calcium concentrations were in the 20 to 35 mg/L range in the past survey of the stream, 1 mg/L, 5 mg/L, 15 mg/L, 30 mg/L, and 40 mg/L standards were prepared for quantitation. Each triplicate sample was analyzed in triplicate to evaluate instrumental and sampling precision. Values reported in this paper are averages of all nine measurements corresponding to each location and each sampling event, so that one value and standard deviation is given to represent each site. The time intensive method of standard addition, which is capable of accommodating potential matrix effects resulting from the differences among sample solutions and standard solutions (Ito & Tsukada 2002), was not employed because of the large number of samples analyzed during this study. The addition of HCl should help to minimize matrix effects, but the concern should not be ignored. The data are presented as absolute concentrations, but may be more cautiously considered as relative values. It is the relative values and not the absolute values that are critical to the present investigation. The statistical analysis of the data was performed using the OriginPro 9.0 software package. Two-way ANOVA (analysis of variance) was performed to evaluate the statistical interactions between distance from outflow source and pool flow status (on or off).

RESULTS AND DISCUSSION

Previous investigation into the geothermal discharge outflow showed a dramatic decrease in iron concentration but only minimal decrease in calcium concentration along the initial aerating portion of the stream, 0–90 m (Griffiths et al. 2013). Consequently, the present study involved analyzing dissolved calcium concentration in

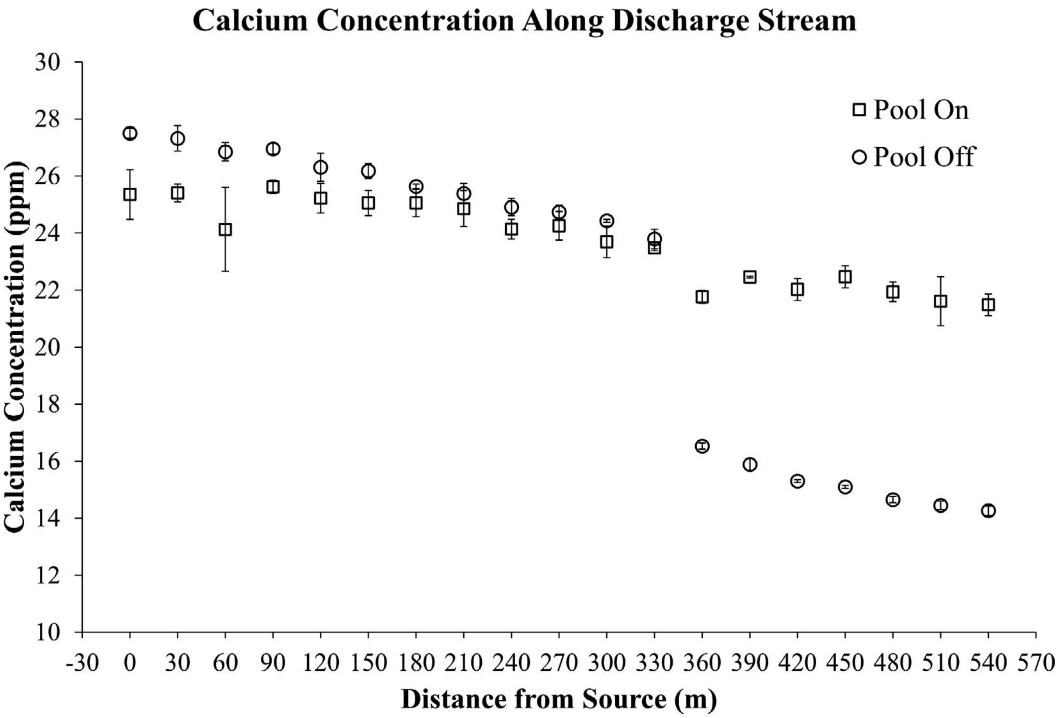

Figure 2.—Dissolved calcium concentration along the stream when the lake-fed pool flow was on (squares) and off (circles). Error bars represent the standard deviation among the nine analyses for each site. The relative standard deviation of the repeated measurements was determined to be approximately 0.1%. Therefore, the primary contribution to the sample site standard deviations (error bars) is due to the variation among samples.

samples collected along the entire stream, once while the lake-fed pool flow was on, and once while it was off. Prior to this study, other parameters that may influence the behavior of dissolved calcium had been investigated (unpublished) to a limited extent at a few locations and, although not directly applicable, the typical values observed provide a general description of the water system (pH ~7.1, temperature ~22.3° C, alkalinity ~16 mg/L $CaCO_3$ (EPA method 310.1), sulfate ~320 mg/L (EPA method 375.4), conductivity ~900 µS/cm (EPA method 120.1). An ANOVA test determined that, at the 0.05 level, the rate of the decrease in calcium concentration was statistically different between when the lake-fed pool flow was on and when it was off.

Lake-fed pool flow off.—When the outflow stream carries only geothermal discharge (i.e., without dilution by lake water) the calcium concentration decreased by about 48% from source to lake. The data from the sample sites along the stream were grouped into two segments (Fig. 2). These segments extended from the source (0 m) to 330 m and from 360 m to 540 m. In both segments, there was an obvious decrease in calcium concentration as the distance from the outflow source increased (Segment 1: linear $R^2 = 0.985$, with a total drop in concentration of -3.71 mg/L; Segment 2: linear $R^2 = 0.952$, with a total drop in concentration of -2.27 mg/L). The two segments are divided by a 7.26 mg/L decrease in calcium concentration (30%) between 330 m and 360 m along the stream. This transitional region of the stream (330 m to 360 m) corresponds to the location of a settling basin (Fig. 1) that, consequently, is suspected to aid in the deposition of calcium to the stream bed. Given this rapid decrease in calcium concentration, it is not surprising that the population means of Segment 1 and Segment 2 were significantly different at a 0.05 level according to an ANOVA test.

Lake-fed pool flow on.—When the pool flow was turned on, lake water is added to the discharge stream, presumably resulting in higher flow rates and dilution of dissolved ions. The calcium concentration in the lake and pool were determined to be similar, ~13 mg/L, and notably lower than at the discharge source, ~25 mg/L. At the discharge source the dissolved calcium concentration was lower than the "pool flow off" value by 2.15 mg/L, presumably as a result of dilution (Fig. 2). Although the population means of the two segments (0 m – 330 m and 360 m – 540 m) were still determined to be significantly different at a 0.05 level, the dramatic drop in concentration between the two segments of the stream, as noted when the pool was on, did not exist (Fig. 2). For pool-on data, there was a clear decrease in calcium concentration as the distance from the stream source increased (linear $R^2 = 0.859$), but only a total drop in concentration of -3.86 mg/L. When the lake-fed pool flow was on, calcium concentration decreased by only 15% from source to outflow. Additionally, a two-way ANOVA analysis found a strong statistical interaction between the sample site location and the pool flow status. In other words, whether the pool was on or off had a significant impact on calcium concentration. Consequently, despite the potential dilution caused by the surface water being added to the stream (seen early in the stream), the calcium concentration was dramatically higher in the water flowing into the lake when the lake-fed pool is on (Fig. 2).

In summary, the decrease in calcium concentration likely occurs through precipitation as insoluble salts with anions within the water or streambed rather than through oxidation. This may be a slower process. When the lake-fed pool flow was on, calcium concentration decreases by only 15% between the source and the lake. However, when the lake-fed pool flow was off, calcium concentration decreases by 48% between the source and the lake. The addition of the lake-fed pool water to the stream causes an increase in flow rate. The higher flow rate leaves less time for the precipitation process to occur in the settling basins. This explanation accounts for the difference in percent calcium concentration decrease when the lake-fed pool flow was on as opposed to when it is off. In addition, when the pool flow is off, 98% of the decrease in dissolved calcium occurs beyond 90 m where the streambed design changes dramatically, suggesting that stream design features occurring later in the stream dissipate calcium more effectively.

The design of this stream is important for lessening the impact that high mineral content geothermal discharge has on the downstream lake ecosystem. It must contain features that naturally soften the water on its way to the lake. In this study, settling basins may the design feature that dissipate calcium concentrations from the stream, just as the rocky streambed and small waterfall did for iron in the previous study. Interestingly, the strategies that ought to be employed to remove two of the most abundant hardness ions are somewhat opposed to one another. Consequently, the ideal stream design must be long enough to incorporate both an aerating environment for iron and a settling environment for calcium.

Unfortunately, with the present data it is impossible to determine if the rapid decrease in calcium concentration within the third settling basin is primarily driven by the chemistry of the basin sediment through cation-exchange or precipitation or driven by the low flowrate within the basin. The geothermal outflow design generates a variable flow within the stream throughout the day and between days, as a function of the difference between ambient and building temperatures, which make it difficult to exhaustively study all sites within the same sampling conditions. However, now that the key location has been identified, a subsequent comprehensive analysis of this third settling basin can be performed at various flowrates.

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