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ANALYSIS OF IRON AND CALCIUM IN A GEOTHERMAL SYSTEM OUTFLOW STREAM

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ABSTRACT. A newly constructed building with an open-loop geothermal system outflow stream on campus provides a powerful context for student driven experimentation in an environmental chemistry course. In less than a year of operation, the rocks toward the frontend of the stream have already begun to turn orange (rusty) which has become a point of curiosity among the students. As a result, iron and calcium concentrations were monitored by atomic absorption spectroscopy along the stream in order to study the metal deposition process. The iron oxide deposition on the rocks in the stream, in-stream iron and calcium concentrations, and temperature were analyzed along the stream. As expected, the in-stream iron and calcium concentrations decreased down the stream, with a particularly larger drop in concentration following a small decorative waterfall. The concentration of iron oxide deposited on the rocks also decreased down the stream at a similar rate to the in-stream dissolved iron decline, strongly suggesting that the deposition on the rocks is the primary mode of iron removal. At less than a year in operation, the iron and calcium concentrations begin declining immediately upon entering the stream, indicating that the frontend of the stream has not yet become saturated. The environmental chemistry course plans to repeat these studies in subsequent years to monitor if/when the frontend becomes saturated and the deposition process begins moving farther downstream.

Keywords: Geothermal, AAS, Stream, Deposition, Iron

INTRODUCTION

Taylor University recently completed (Fall, 2012) the construction of a new science building (the Euler Science Complex), which employs many sustainable features including wind turbines, solar panels, and a geothermal cooling system. Geothermal heating/cooling systems are generally considered energy efficient and environmentally friendly design strategies in new construction (L'Ecuyer et al. 1993). In fact, it is estimated that more than half a million homes in the United States now use geothermal systems (DTE Energy 2013). Open-loop geothermal systems use relatively constant temperature ground (well) water to absorb heat from the building during the summer and to input heat to the building during the winter. After the heat exchange process, the warmed (summer) or cooled (winter) well water is released to the environment as surface water. The geothermal discharge will differ from natural surface water in temperature and high mineral content. Open-loop designs often incorporate intentionally designed streams to provide time and opportunity for the mineral rich ground water used in the system to be naturally softened before significantly impacting the chemistry of nearby surface water bodies. A significant rise in mineral content or change in lake temperature can alter the balance within a native ecosystem (USGS 2012). Rocky streambeds can be used to encourage temperature acclimation and mineral deposition before reaching a surface water body. The Spring, 2013 Environmental Chemistry class (CHE330/530) chose to evaluate the mineral deposition within this newly created geothermal outflow streambed as a way of learning several analytical laboratory methods in a meaningful context that might also be beneficial to the University.

One of the first things students noticed while looking at the streambed and brainstorming experiments to be performed was the obvious rust color on the rocks. Clearly the rocks near the beginning of the stream were being coated by iron oxide, and yet the geothermal system had only been operating for six months. The color became lighter farther from the start of the stream, and by approximately 100 meters the rocks no longer appeared to be discolored. As in a typical water treatment facility iron is

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primary precipitated as iron oxide through a process of aeration (Droste 2008). This reaction is encouraged in the streambed design by using rocks and even small, esthetic waterfalls. The class decided to monitor this successful deposition of iron by analyzing the stream iron concentration and extractions of iron oxide deposits from the surface of rocks by atomic absorption spectroscopy (AAS; Lee et al. 2007; Sidhu et al. 1981). Whether or not there exists a saturation limit for iron oxide on the rocks became a principle question the students were interested in exploring.

In addition to monitoring the iron deposition, students were eager to measure the calcium concentration in the stream, knowing that calcium is the principle hardness ion. Unless the stream was unusually acidic, calcium should primarily precipitate as an insoluble carbonate or bicarbonate, both white solids. Upon initial visual inspection these white precipitates were not observed on the rocks like the iron oxide, which led students to predict that either it is precipitating in the soil or not precipitating at all. Again, students decided to use AAS to monitor stream calcium concentration and extractions of calcium deposition from rock surfaces.

Students also elected to monitor temperature and conductivity to complete the study. Temperature is one of the primary variables of concerns for open loop geothermal systems. If there is not sufficient time and distance for the stream to reach typical surface water temperatures before reaching a meaningful surface water body, there is potential for a gradual increase in temperature for the water body in the warm summer months and a gradual decrease in temperature for the water body in the cold winter months. Additionally, conductivity was monitored to investigate any trends among total dissolved ions in the stream.

METHODS

The newly opened geothermal outflow stream on campus provides a rich and meaningful context for student laboratory exploration. The students' goals of measuring stream water iron and calcium concentration, deposited minerals on rocks, and stream water temperature and conductivity exposed them to the use of a state-of-the-art atomic absorption spectrometer, chemical extraction methods, and portable handheld data collection devices, respectively. Upon initial inspection of the stream, the rust colored coating on the rocks in the streambed faded away by about 100m from the stream source. Wanting to increase the level of student ownership of the project, this critical section of the stream was divided into fourteen sampling sites, one for each student in the class. Sampling sites were marked with flags throughout the study and for future follow-up work, at 6m intervals starting at the source. The would-be site at 24m is within a small culvert under a sidewalk and was not included as a sample site.

Stream iron and calcium monitoring by AAS.—Stream dissolved iron and calcium concentrations were analyzed using an iCE 3000 Series AAS (Thermo Scientific) equipped with an ASX-520 autosampler (CETAC). Three 300mL samples were collected at each sampling location. Samples were collected at 6 meter increments from 0 to 90m. 10mL of each sample were transferred into autosampler tubes for analysis. The instrument was calibrated using stock 1000ppm standard iron and calcium solutions from Sigma-Aldrich. 0.1 mg/L, 1.0 mg/L, 5.0 mg/L, 10.0 mg/L, and 30.0 mg/L calibration standards of iron and of calcium were prepared for quantitation.

Rock surface deposition extraction.—Average sized rocks, approximately the size of a baseball, were collected from the middle of the streambed at each of the 14 sample sites. In every case the top surface of the rocks were at least slightly discolored with the iron oxide. A 2cm by 2cm square was drawn with a Sharpie marker on the surface of the rock from where the surface mineral deposition would be extracted. Cotton swabs soaked in 0.1 M HCl were used to clean the marked 4cm^2 sampling area.(Lee et al. 2007; Sidhu et al. 1981) In most cases several cotton swabs were needed for each rock. The used cotton swabs were placed in a beaker containing 50mL of 0.1 M HCl to dissolve the extracted minerals from the swabs. During this step, the solutions turn a typical yellow color indicating the presence of iron. The extract solutions were then transferred to autosampler tubes for analysis of iron and calcium. The determined extract concentrations (mg/L) are multiplied by the extract volume (0.05L) and divided by the sampling surface area (4cm^2) to produce a surface deposition concentration value in terms of mass of mineral per cm^2.

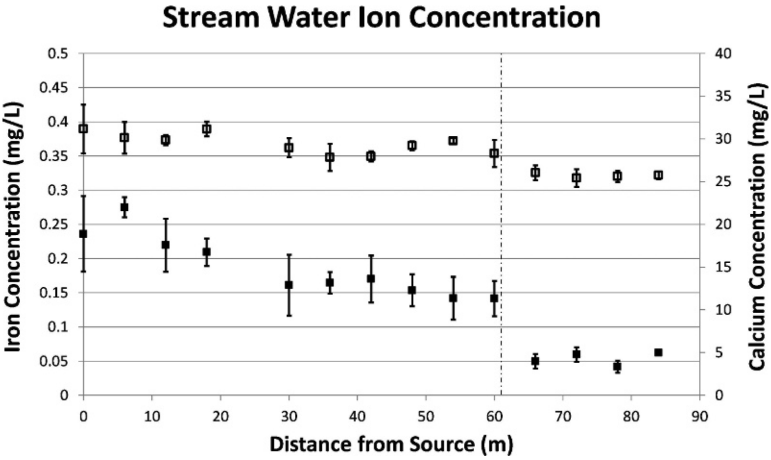

Figure 1.—In-stream dissolved iron (left axis, ■) and calcium (right axis, □) are shown versus distance from the stream source. Significant decreases in ion concentration occur following a small waterfall (61m) indicated with a dashed vertical line.

In-stream measurements of temperature and conductivity.—Temperature and conductivity measurements were made using respective probes for an Xplorer portable/handheld data collection device from Pasco Scientific. The temperature and conductivity measurements were recorded at each of the 14 sampling sites on five different days. The air temperature on each day was also recorded.

RESULTS AND DISCUSSION

Stream iron and calcium monitoring by AAS.—The average of the triplicate samples for dissolved iron and calcium by AAS show a decrease in concentration with distance from the stream source as seen in Figure 1 ($\text{Iron}_{(aq)}$: linear $R^2 = 0.954$, with a total drop in concentration of −0.19mg/L which is much greater than the linear regression standard deviation of 0.014mg/L; $\text{Calcium}_{(aq)}$: linear $R^2 = 0.954$, with a total drop in concentration of −4.78mg/L which is much greater than the linear regression standard deviation of 0.70mg/L). Interestingly, iron and calcium share the same pattern of decrease in concentration. The set of iron and calcium concentration data pass the paired t-test after setting the expected mean difference equal to the difference between the observed mean values for all sites ($p = 0.721$; t-calc. = 0.37, t-crit. = 2.23). It is important to notice that although the iron concentration is significantly less than calcium, by 90m the iron concentration has decreased by approximately 85%. Calcium, which is much higher in concentration, has only decreased by approximately 16%. Despite the nearly complete depletion of iron, the small decrease in calcium concentration corresponds to a much larger total amount of calcium deposition than iron. Also, it is interesting to note the significant decrease in stream concentrations of both ions following the 60m sample. At approximately 61m, the stream has a small 1m aesthetic waterfall which may be contributing to oxidative deposition through aeration.

Rock surface deposition extraction.—The concentration of iron on the rock surfaces decreases with distance from the stream source until approaching an apparent minimum at around 66m and is displayed in Figure 2 (linear $R^2 = 0.963$, with a total drop in concentration of −1.66mg/L which is much greater than the linear regression standard deviation of 0.10mg/L). The surface iron concentration decreases by approximately 85% and at a very similar rate to the decline in dissolved iron concentration. The change in concentration for the two sets of iron data (deposition and dissolved) pass the paired t-test after setting the expected mean difference equal to the difference between the observed mean values for all sites ($p = 0.9999$; t-calc. = 3.3×10^{-5}, t-crit. = 2.2). There is a slight rise in iron deposition following the waterfall, which may be a result of increased aeration. One of our primary questions regarding the rock deposition is if there is a saturation point at which no more iron will collect on the rocks. Because the concentration at the 2nd site is

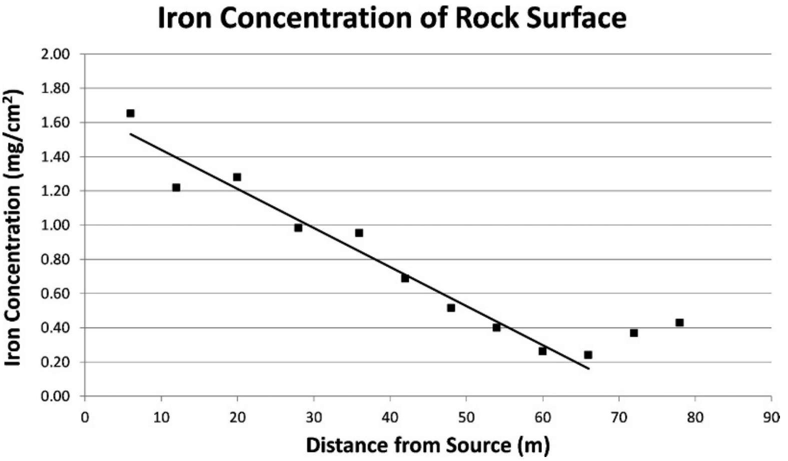

Figure 2.—A three point running average of the rock surface iron deposition concentration is shown versus the distance from the stream source. The deposition concentration decreases somewhat linearly ($R^2 = 0.963$) until reaching a minimum at 66m. The rate of decay (slope = -0.023 mg/cm^2 per m) will be compared to that observed in subsequent years.

significantly lower than that at the 1st site (drop in concentration from 1st to 2nd = -0.433mg/L which is much greater than the linear regression standard deviation of 0.10mg/L), the data reveals an immediate decline in deposition from the source suggesting that such a saturation has not occurred, yet. This type of study may be repeated in subsequent years, to specifically monitor the potential saturation at the beginning of the stream. If saturation occurs, it is expected that this deposition range will begin migrating downstream.

Calcium deposition on the rocks was below the detection limit and considered negligible. In every case the extraction concentrations of calcium were below 0.1mg/L (the smallest prepared standard) and are therefore not reported. The dissolved calcium concentration was observed to decrease significantly, and it is therefore concluded that most of the calcium deposition must be occurring with/on the streambed soil.

In-stream measurements of temperature and conductivity.—Stream conductivities at all sites

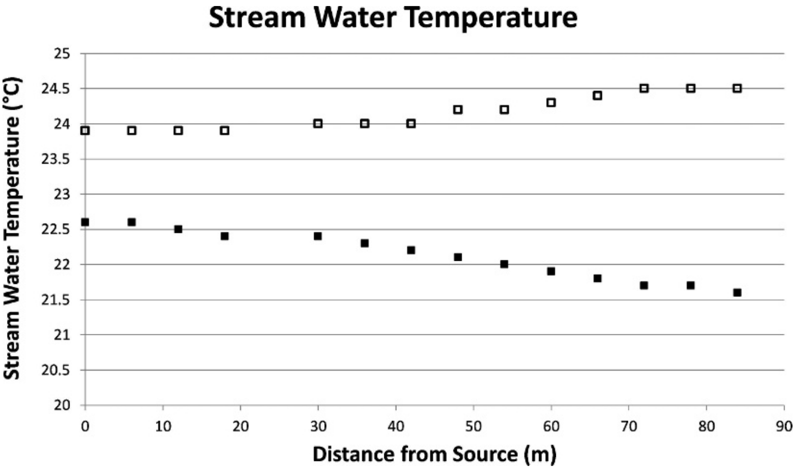

Figure 3.—The stream temperature versus distance from the source is shown. The warmest day, 23.0°C, is indicated with open squares, and the coolest day, 14.3°C, is indicated by the solid squares.

and on all days were in the range of 800–1000 µS but no discernible pattern of increase, decrease, or homeostasis could be determined. Plots of conductivity versus distance for source for each day of the five days, yielded least squares fit line with R^2 values ranging from 0.0063–0.862 and an average R^2 of 0.272. Temperature data from the warmest and coldest days are shown in Figure 3. On all five days, the temperatures at the outflow source were similar, ranging from 22.6 and 23.9°C and all within two standard deviations of the mean (22.26–24.24°C). However, on coolest day the temperature decreased gradually from the source (linear $R^2 = 0.977$, with a total $\Delta T = -1.0°C >>$ than the linear regression standard deviation = 0.06°C) and on warmest day the temperature increased gradually from the source (linear $R^2 = 0.913$, with a total $\Delta T = +0.6°C >>$ than the linear regression standard deviation = 0.07°C. Despite the fact that it is difficult to predict what stream temperatures ought to be, it can be generalized that in the warm spring/summer months (when this data was collected) the optimal scenario would be that the stream temperature is primarily governed by atmospheric temperature and not by the geothermal system (initial temperature at source). This small collection of data may suggest that the atmospheric conditions are capable of manipulating the stream water temperatures. Although there are challenges in accounting for variation in shade, flow rates, and surface area, future studies may include monitoring a natural stream nearby to provide statistical comparison with the geothermal stream and to determine if the geothermal stream temperatures eventually reach that of the natural stream.

LITERATURE CITED

Droste, R.L. 2008. Pp. 471–473, Theory and Practice of Water and Treatment. John Wiley & Sons, Inc. New York.

DTE Energy. 2013. Geothermal Systems. http://www.dteenergy.com/residentialCustomers/ products Programs/electric/geothermal.html.

L'Ecuyer, M., C. Zoi & J. Hoffman. 1993. Space Conditioning: The Next Frontier. EPA 430-R-93-004.

Lee, S.O., T. Tran, B.H. Jung, S.J. Kim & M.J. Kim. 2007. Dissolution of iron oxide using oxalic acid. Hydrometallurgy 87:91–99.

Sidhu, P.S., R.J. Gilkes, R.M. Cornell, A.M. Posner & J.P. Quirk. 1981. Dissolution of iron oxides and oxyhydroxides in hydrochloric and perchloric acids. Clays and Clay Minerals 29:269–276.

USGS. "Water Hardness and Alkalinity." USGS Office of Water Quality. http://water.usgs.gov/owq/hardness-alkalinity.html., 2012, Accessed May 1, 2013.

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