Determining the Effect of pH on Iron Oxidation Kinetics in Aquatic Environments: Exploring a Fundamental Chemical Reaction To Grasp the Significant Ecosystem Implications of Iron Bioavailability

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S Supporting Information

ABSTRACT: Understanding the controls of the oxidation rate of iron (Fe) in oxygenated aquatic systems is fundamental for students of the Earth and Environmental Sciences as it defines the bioavailability of Fe, a trace metal essential for life. The laboratory experiment presented here was successfully developed and used during a third-year undergraduate lab course at Imperial College London for several years. It employs ultraviolet−visible (UV−vis) spectroscopy calibrated externally with 0 to 50 μM Fe^{2+} standards created in a 492 μM ferrozine and 0.43 M acetate matrix. The students conducted the oxidation experiments in stirred batch reactors at equilibrium with atmospheric oxygen. The solution contained 40.5 μM initial Fe^{2+} concentration and a 5.1 mM imidazole buffer. The pH was adjusted to values between 7.22 and 7.77. The students observed a pseudo-first-order reaction with respect to Fe^{2+} concentration. Plotting the logarithms of the apparent rate constants (k') at different pH values leads to a gradient of 2.2 $\pm$ 0.2 min^{-1} pH^{-1}, indicating a second-order reaction with respect to OH^- concentration, in agreement with published literature. The oxidation reaction occurred rapidly (tens of seconds to tens of minutes) indicating that in oxygenated aquatic systems, Fe^{3+} will be the dominant oxidation state, significantly reducing the bioavailability of Fe. The simple laboratory experiment presented here allows the students to learn about kinetic parameters for a fundamental chemical reaction. It allows the students to explore the significant implications this has for aquatic ecosystems.

KEYWORDS: *Upper-Division Undergraduate, Environmental Chemistry, Geochemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Communication/Writing, Aqueous Solution Chemistry, Rate Law, Oxidation/Reduction*
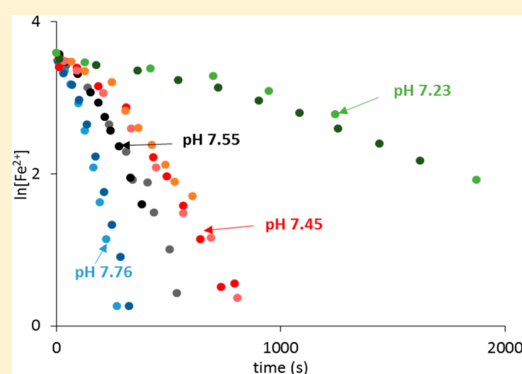
■ INTRODUCTION

Iron (Fe) is an essential trace element for life. It is required in the synthesis of molecules such as chlorophyll and in biological processes such as photosynthesis, electron transport, and metabolic functions.[1] In natural environments, Fe is dominated by its II (Fe^{2+}) and III (Fe^{3+}) oxidation states.[2] In oxygenated aquatic environments with circumneutral pH, Fe^{2+} is oxidized to Fe^{3+}, forming insoluble Fe hydroxide precipitates.[3] This leads to low Fe bioavailability, reducing biological activity in the environment. The rate at which Fe^{2+} oxidizes to Fe^{3+} depends on a variety of variables such as the concentrations of Fe, O_2, H_2O_2, and HCO_3^-; pH; temperature; and ionic strength. For instance, $Fe(OH)_2$ is oxidized at a faster rate when bicarbonate concentration increases or medium ionic strength decreases.[3,4] Understanding Fe oxidation kinetics is extremely important as it enables us to determine the half-life of Fe^{2+} in aquatic systems and in turn estimate the fraction of Fe available for consumption by biota.[5]

The laboratory study presented here allows students to develop a fundamental understanding of redox reactions and kinetic rate laws and puts this into the context of real-life environmental problems. This builds upon previous laboratory studies published in the *Journal of Chemical Education* that explore fundamental chemical processes that are key to global environmental problems.[6−8] Alongside developing basic laboratory skills (e.g., pipetting, making solutions, etc.), Earth and Environmental Science students learn how to use an important analytical technique used in geochemistry and environmental chemistry laboratories: ultraviolet−visible (UV−vis) spectroscopy. The students learn how to carry out an external calibration and calculate relevant statistical parameters. The degree to which students achieve the above

experimental goals is evaluated in the form of a laboratory report and student feedback.

■ OVERVIEW OF THE EXPERIMENT

This laboratory experiment has been designed for third-year undergraduate students studying Earth and Environmental Sciences. The experiment shown here explores the effect of changing pH on the rate of Fe^{2+} oxidation, and other influencing factors such as bicarbonate concentration, ionic strength, and temperature can be added if course time allows. Before the laboratory experiment, the students complete a risk assessment form to ensure that they acquaint themselves with the experimental procedure and associated safety hazards. The experiment is carried out in groups of two or three students and lasts approximately 6 h, comprising 3 h of experimental work and 3 h of data analysis. During this time, each group performs the kinetic experiment at two or three different pH values with a given type of natural water (i.e., bottled mineral water). To test the rate law, a different pH value should be assigned to each group, and all the data should be shared among the groups at the end of the laboratory course. The day after the experiment, the students submit an initial laboratory report, including a presentation of the methods used and the results of their experiments, on which they receive feedback from the instructor. The students write a final report using all the data collected by the different student groups. The report consists of deeper analysis and interpretation of the data and relates the data to the current scientific literature.

■ EXPERIMENTAL PROCEDURE

Chemical Reagents

All chemicals used were of analytical grade, and solutions were prepared in deionized 18.2 MΩ water. The deionized water was used as the water sample. The students prepared a 1 M imidazole buffer solution adjusted to pH 6.0. Then, 2.5 mL of the imidazole buffer solution was added to the water sample (493.5 mL total volume) leading to a final concentration of 5.1 mM. This was added to the water sample to buffer the pH. Imidazole was selected as the buffer because it does not complex with Fe^{2+} and does not affect the oxidation reaction. The students prepared a 0.5 M NaOH solution to adjust the pH to the desired value, and a 0.02 M Fe^{2+} stock solution, which was added to the water sample. The 0.03 M ferrozine solution complexes with Fe^{2+} and stops the oxidation reaction. A 2.6 M acetate buffer solution was prepared to keep the pH of the UV−vis sample solution constant.

Calibration of the UV−Vis Spectrometer

The volumes of acetate, imidazole, and Fe solutions required to create the calibration standards are provided in Table 1 in the student handout (Supporting Information). A 500 μM Fe^{2+} standard solution was created from the 0.02 M Fe^{2+} stock solution. The 500 μM Fe^{2+} standard solution was diluted to prepare 0.5, 1, 5, 25, and 50 μM Fe^{2+} standards. These standards were used to calibrate the UV−vis spectrometer. The solutions have fixed ferrozine (492 μM) and acetate (0.43 M) concentrations. A blank solution that contained 492 μM ferrozine and 0.43 M acetate but no Fe^{2+} was used to subtract the absorbance of the reagents (calibration blank). The calibration solutions were analyzed with the UV−vis spectrometer, and the change in absorbance versus the concentration of Fe^{2+} was plotted. The Fe^{2+} ferrozine complex absorbance maximum is at a wavelength of 562 nm; however, a

spectrum across a wider wavelength was collected so the students could visually see the peak. The LINEST function was used in Microsoft Excel to return the gradient, intercept, and associated standard errors.[9] From this, the Fe^{2+} concentrations of the samples collected from the water could be calculated using eq 1, where A, c, and m are the absorbance, the y-intercept, and the gradient, respectively.

$$[Fe^{2+}] = \frac{A - c}{m} \tag{1}$$

Experiment

All procedure details are given in the student handout (Supporting Information). Ten 15 mL test tubes were prepared with 0.1 mL of 0.03 M ferrozine and 1 mL of 2.6 M acetate buffer and shaken. These samples were matrix-matched to the calibration standards. Then, 2.5 mL of the 1 M imidazole buffer solution was added to the 490 mL water sample. The water sample was mixed with a magnetic stirrer to maintain a homogeneous solution. The pH of the water sample was adjusted to the pH of interest with 0.5 M NaOH. The recommended pH range is pH 7.2 to 7.9, as this allows for reasonable time intervals between sample collections. The water was purged with air for 10 min to equilibrate the O_2 concentration with that of the atmosphere.

After 10 min, 1 mL of the 0.02 M Fe^{2+} stock solution was added to the water sample ($[Fe^{2+}]$ = 40.5 μM) to initiate the Fe^{2+} oxidation reaction. A 5 mL sample was taken immediately and added to one of the test tubes containing the ferrozine complexant and acetate buffer. The time was noted when the 5 mL sample was added to the test tube as the oxidation reaction ends when Fe^{2+} complexes with ferrozine. Samples (5 mL) were collected over time and added to the test tubes. The students visually observed a decrease in the purple color in the test tubes at later sampling times due to the reduction of the Fe^{2+} ferrozine complexes, reflecting a reduction in Fe^{2+} concentration. After the experiment, the samples were analyzed for absorbance using the UV−vis spectrometer, and the concentration of Fe^{2+} was calculated using eq 1.

■ HAZARDS

Personal protective equipment must be worn by the students at all times in the laboratory. This includes the use of laboratory coats, closed-toed shoes, long trousers/pants, safety goggles, and gloves. The students should be aware of the safety data sheets (SDS) and associated information about the health hazards, safety hazards, and handling precautions for all chemicals used. All hazards were discussed with the students before starting the experiment.

The imidazole buffer solution is irritating to the eyes and skin and may cause harm to unborn children. Sodium hydroxide, sulfuric acid, and acetic acid are corrosive and cause severe skin burns and eye damage. Acetic acid is flammable. Concentrated solutions of sulfuric acid and acetic acid should be handled inside a fume hood under supervision of the instructor. Ferrozine is irritating to the eyes, respiratory system, and skin.

■ RESULTS AND DISCUSSION

Calibration Curve and Statistical Analysis

Students produced a five point calibration curve with 0.5, 1, 5, 25, and 50 μM Fe^{2+} standards, creating a linear plot of absorbance, A, versus Fe^{2+} concentration. An example

calibration curve is shown in Figure 1 with the corresponding Fe^{2+} concentration and absorbance data provided in Table 1.
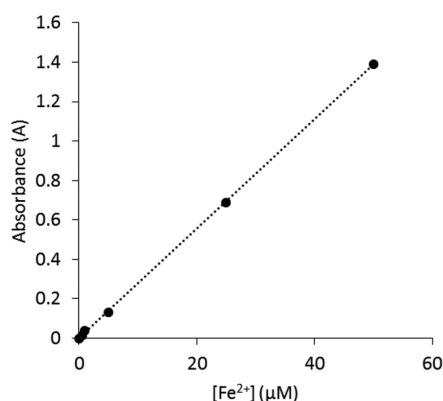
Figure 1. Example calibration curve for the UV–vis spectrometer. The linear equation obtained was used to convert sample absorbance to Fe^{2+} concentration. The equation is $A = (0.0277 \pm 0.0002) \times [Fe^{2+}] + (0.0007 \pm 0.0035)$. The standard error in the y-value is 0.007. This error is too small to be seen as error bars.

Table 1. Student-Obtained Results for the Fe^{2+} Oxidation Reaction in Deionized Water

pH	k' (s^{-1})^a	log k'^{a}
7.23	$(8.3 \pm 0.5) \times 10^{-4}$	-3.08 ± 0.03
7.23 (2)^b	$(8 \pm 1) \times 10^{-4}$	-3.08 ± 0.06
7.41	$(3.2 \pm 0.3) \times 10^{-3}$	-2.50 ± 0.04
7.45	$(4.4 \pm 0.3) \times 10^{-3}$	-2.36 ± 0.03
7.45 (2)^b	$(4.1 \pm 0.3) \times 10^{-3}$	-2.39 ± 0.03
7.55	$(5.3 \pm 0.3) \times 10^{-3}$	-2.28 ± 0.03
7.61	$(5.5 \pm 0.4) \times 10^{-3}$	-2.26 ± 0.03
7.70	$(1.01 \pm 0.06) \times 10^{-2}$	-2.00 ± 0.03
7.76	$(1.28 \pm 0.08) \times 10^{-2}$	-1.89 ± 0.03

^{a}The apparent rate constant (k') results and log k' results and their associated standard errors stem from the data presented in Figure 2. ^{b}The "(2)" represents a repeat experiment at a given pH value.

The students used the least-squares regression technique to statistically analyze the quality of the calibration curve. Details on how to use this are given in textbooks.[9] The statistical outputs are presented in the caption of Figure 1. The error associated with the intercept is $\pm 3.54 \times 10^{-3}$, the error associated with the gradient is $\pm 1.55 \times 10^{-4}$, and the error associated with the measured y-value (absorbance) is $\pm 6.99 \times 10^{-3}$. The linearity of the calibration curve was analyzed by the students looking at the correlation coefficient (R^2). This is important to explore with the students as the calibration curve may become nonlinear at high concentrations, leading to a breakdown in the validity of eq 1. In the example calibration curve, R^2 is 0.9999 across the 0.5 to 50 μM Fe^{2+} range, indicating that eq 1 can be used to calculate the concentration of Fe^{2+} in the range of interest.

A midrange calibration standard (5 μM) was measured three times, providing an average absorbance of 0.132 ± 0.008 (error of one standard deviation). This allowed the students to calculate the precision of the instrument, which was 6%. The reproducibility, calculated by dividing the standard deviation by the average absorbance and multiplying by 100, was 18%.

Using the blank-corrected calibration curve, the students estimated the detection limit (DL) using eq 2, where S is the standard deviation of the lowest concentration standard measured n times ($n \geq 7$), and m is the gradient of the blank-corrected calibration curve.[9] As an example, using the standard deviation of the 0.5 μM standard measured for each calibration curve ($n = 3$) gives a detection limit of 0.854 μM.

$$DL = \frac{3S}{m} \tag{2}$$

Theoretical Description of the Pseudo-First-Order Law for Fe^{2+} Oxidation

Before starting the experiment, the teaching assistants discussed the theory behind rate laws with the students. The proposed oxidation reaction is presented in eq 3. The corresponding rate law for Fe^{2+} oxidation, present in eq 4, has been proposed on the basis of experimental data, where r is the reaction rate, t is time, and k is the rate constant.[3,10] Keeping the concentration of OH^- and P_{O_2} in excess reduces eq 4 to the pseudo-first-order rate law presented in eq 5, where k' is the apparent rate constant. The apparent rate constant is shown in eq 6.

$$Fe^{2+} + \frac{1}{4}O_2 + 2OH^- + \frac{1}{2}H_2O \rightarrow Fe(OH)_3(s) \tag{3}$$
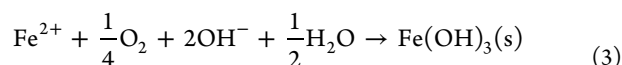
$$r = -\frac{d[Fe^{2+}]}{dt} = k[Fe^{2+}][OH^-]^2 P_{O_2} \tag{4}$$

$$r = -\frac{d[Fe^{2+}]}{dt} = k'[Fe^{2+}] \tag{5}$$

$$k' = k[OH^-]^2 P_{O_2} \tag{6}$$

Equation 4 shows that the rate in which the concentration of Fe^{2+} decreases is proportional to the remaining Fe^{2+} concentration multiplied by k'. Integration of eq 5 leads to eq 7. Equation 7 indicates that for a first-order reaction, the change in $\ln([Fe^{2+}])$ with time should decrease linearly with gradient $-k'$ when $\ln([Fe^{2+}])$ is plotted versus time (detailed derivation is provided in the Supporting Information).

$$\ln\left(\frac{[Fe^{2+}]_t}{[Fe^{2+}]_0}\right) = -k't \tag{7}$$

Experimental Exploration of the Pseudo-First-Order Law for Fe^{2+}

The pH dropped during all the experiments by an average of 0.04 pH units (maximum of 0.1 pH units). The students were encouraged to consider why the pH dropped. For example, it could be because of the formation of carbonic acid due to the influx of atmospheric CO_2 into the sample solution. The average pH over the course of experiment was taken for subsequent data analysis.

The students plotted $\ln([Fe^{2+}])$ versus time, and the results are presented in Figure 2. In all experiments, the observed rate of change in $\ln([Fe^{2+}])$ with time was less steep at the beginning of the time series. This could potentially be a stirring effect as Fe is mixed into the large sample volume. One may wish to instruct students to exclude initial data points from the determination of k'. However, for ease of data processing, the students used the entirety of each data series. Using this approach, the change in $\ln([Fe^{2+}])$ over time is approximately
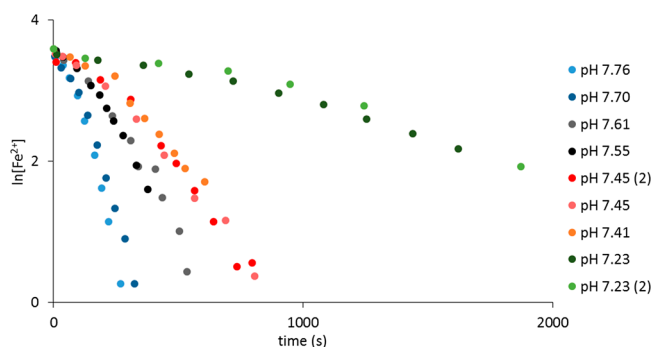
Figure 2. First-order dependence of Fe^{2+} concentration with time at different pH values for the oxidation reaction in deionized water. The data were collected during the 2017 course by three undergraduate student groups and a group of Ph.D. students new to the experiment. Each group was composed of two or three students. Group 1 collected the pH 7.23 (2) and 7.70 data. Group 2 collected the pH 7.45 (2) and 7.61 data. Group 3 collected the pH 7.41 and 7.55 data. The Ph.D. group collected the pH 7.23, 7.45, and 7.76 data. The "(2)" represents a repeat experiment at a given pH value. The figure is taken directly from a student report. The average standard error for all data points is $0.21 \pm 0.07 \ln([Fe^{2+}])$ units.

linear with the average correlation (R^2) across all experiments being 0.96 ± 0.02. The linear relationship indicates the oxidation reactions followed first-order kinetics, agreeing with the literature.[3,11]

The students determined the apparent rate constant, k', for the pseudo-first-order reaction by taking the gradient of the curve resulting from the $\ln([Fe^{2+}])$ versus time plot. The k' value and its logarithmic value ($\log k'$) for each of the experiments are presented in Table 1. The standard error of the gradient was determined using the least-squares linear regression function (LINEST), discussed above. This error is the uncertainty in k' for each experiment. The average error of k' across the experiments was 7%.

Experimental Exploration of the Quadratic Relationship of the Rate Constant with OH^- Concentration

Testing the oxidation rate at different pH values allows the students to investigate the sensitivity of the reaction rate to the concentration of OH^-. The students tested the oxidation kinetics with respect to OH^- concentration by plotting the logarithm of the apparent rate constant, k', from the collected experimental data against the pH, as shown in Figure 3. The error in $\log k'$ was evaluated with eq 8, where e_y is the absolute error in $\log k'$, and e_x/x is the relative error in k' (Table 1).[9] The students determined a gradient of 2.2 ± 0.2 min^{-1} OH^{-1} from their experimental results. These results had a strong linear correlation ($R^2 = 0.93$). Emmenegger et al.[3] found a slope of 1.7 ± 0.1 min^{-1} pH^{-1} above pH 7.3, which is an approximate second-order reaction. The data in this work show the trend continuing to pH 7.2 (pOH 6.8). Other studies have also found $\log k'-pH$ relationships of ~ 2 min^{-1} pH^{-1} in a variety of synthetic and natural waters.[4,12]

$$e_y = 0.424 \frac{e_x}{x} \tag{8}$$

Final Report

The students were encouraged to explore the experimental data set obtained by the entire class in depth in their final laboratory report. Several scientific questions are posed in the student handouts, attached in the Supporting Information, to
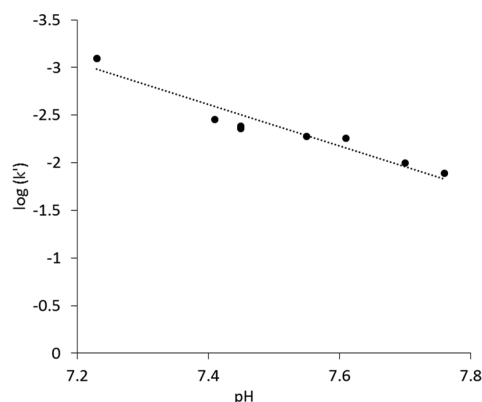
Figure 3. Second-order dependence of the oxidation rate on pH conducted in deionized water. The equation for the plot is $\log k' = (2.18 \pm 0.22) \times pH - (18.76 \pm 1.66)$. The standard error in y from the equation is ± 0.12. The average standard error in $\log k'$ of each data point is 0.03 ± 0.01.

provide a starting point for the students. Students typically address several of these questions in a separate discussion section in their final report. The level of knowledge of the students is assessed on the basis of the grading rubric presented in the teacher handout in the Supporting Information. This includes student understanding of key concepts and inclusion of relevant literature. One of the questions encourages deeper understanding of fundamental analytical chemistry and the errors of the experiment (calibration, pipetting, volumetric flask, etc.) by asking the students, "Where is the error?"

The key outcome of the experiment is explored by posing the question: "What effects have you observed upon changing the pH, i.e., changing $[OH^-]$?" This was discussed in greater detail in the section Experimental Exploration of the Quadratic Relationship of the Rate Constant with OH^- Concentration. The results from the experiments can be related to natural aquatic systems by indicating that in increasingly alkaline waters, the oxidation rate increases significantly, as shown in Figure 2 and Table 1. The students are encouraged to explore the literature and consider the molecular level mechanism that leads to the oxidation reaction, and why increasing the OH^- concentration increases the oxidation rate. The mechanism is an outer sphere reaction between the Fe atom and O_2 (the two reactants remain separate species during the reaction).[13] Hydroxyl ligands add electrodensity to the Fe when forming Fe hydroxide species. This makes it easier for an electron to be transferred from Fe^{2+} to the O_2. Hydroxyl ions also help stabilize higher oxidation states.[13]

The students consider the scientific literature in their final reports by comparing their results to those of Emmenegger et al.[3] and other, more recent studies using search engines such as Web of Science, Scopus, Google Scholar, and more. This encourages the students to think about the difference in results between a simple laboratory experiment in controlled conditions compared with natural aquatic systems where multiple different components can affect the reaction rate, including the concentrations of Fe, O_2, H_2O_2, and HCO_3^-; temperature; and ionic strength.[3,4]

Further investigation of the environmental context is encouraged by asking the students: "How much Fe^{2+} will be present in aquatic systems, and what is the significance of this?" This highlights to the students that in natural, oxygenated

aquatic systems containing typical pH values (i.e., surface conditions), Fe^{2+} rapidly oxidizes to insoluble Fe^{3+} hydroxide precipitates, which significantly reduces the bioavailability of Fe.[3] It allows students to explore the novel solutions plants, bacteria, and fungi have developed over millions of years to increase the bioavailability of Fe, such as the release of low molecular weight organic molecules such as siderophores to dissolve Fe^{3+} hydroxide.[14]

Lecturer Discussion and Thoughts

This experiment has been successfully run and continuously developed at Imperial College London for six years now, and it forms part of the Environmental Geochemistry laboratory course that undergraduate students of Earth Science and Engineering take in their third year. We have presented three units of that course in this *Journal*.[15−17] The laboratory course builds upon a classroom lecture given in year 2 where the students learn the basics of environmental chemistry and use the textbooks of Stumm and Morgan[10] and of Eby[18] as accompanying literature for referencing. The exercise discussed here was originally designed by the group of Professor Laura Sigg at ETH Zurich and, on the basis of the experiments described by Stumm and Lee,[11] was adapted and developed to our laboratory class successfully. The experiment takes up 6 h: 3 h for the experimental work (conducted in the morning) and 3 h for data processing and analysis. The report is written at the end of the entire lab course.

Our experience is that this unit is a favorite for the students as it integrates many aspects of environmental chemistry, including analytical chemistry, data analysis, kinetics, trace element cycling, and water quality. Analysis of student performance using the grading rubric in the teacher handout attached in the Supporting Information shows that on average over 2 years, 7 out of 10 students performed, on average, at level 3 across all aspects assessed (i.e., experiment, data processing, and final report). The student feedback for the module via the Imperial College London Student On Line Evaluation (SOLE) system ranked the course over a 5 year period consistently in the top, with an overall rate for good/very good of over 85/100.

CONCLUSION

The students have learned about fundamental chemical processes relevant to environmental processes by carrying out simple laboratory experiments. Students learned about pseudo-first-order reactions and tested a proposed rate law. The students also learned how these fundamental processes play an important role in the environment, in terms of the bioavailability of Fe^{2+} in aquatic systems, and they learned about the differences between simple, well controlled laboratory conditions and complex, real systems. Analytical aspects such as how to use analytical equipment (UV−vis spectrometer) were also taught. The students learned how to externally calibrate analytical equipment, and how to do statistical analysis. These are fundamental techniques that environmental scientists and geochemists need to understand.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.8b01036.

> Student handout (PDF, DOCX)
> Grading rubric (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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