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Selenium Diel Cycling and Sorption Kinetics

- Task 1. First-order controls on diel cycling of selenium
- Task 2. Kinetics of selenium sorption and implications for potential diel selenium cycles

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LIST OF ACRONYMS AND ABBREVIATIONS

DI water	Deionized water
FH	ferrihydrite
HEPES	2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (a buffer)
HFO	Hydrous ferric oxides
HG	Hydride generation
HG-ICP-OES	Hydride-generation Inductively Coupled Plasma – Optical Emission Spectroscopy (the coupled analytical method for analysis of Se(IV))
HX	Hydroxylamine hydrochloride
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
LOD	Limit of detection
MDL	Method detection limit
OSMRE	Office of Surface Mining Reclamation and Enforcement
R^2	Coefficient of regression
RSD	Relative standard deviation (standard deviation/mean reported as a percent)
RT	Room temperature
USEPA	United States Environmental Protection Agency
XRD	X-ray diffraction

LIST OF CHEMICAL SPECIES

Fe	Iron
Fe(II)	Ferrous iron including both dissolved and colloidal species. Measured on unfiltered water samples unless specified otherwise.
Fe(III)	Ferric iron including both dissolved and colloidal species. Measured on unfiltered water samples unless specified otherwise.
Fe(TOT)	Total dissolved including both dissolved and colloidal species for Fe(II) and Fe(III). Measured on unfiltered water samples unless specified otherwise.
HCl	Hydrochloric acid
KCl	Potassium chloride
KOH	Potassium hydroxide
Se	Selenium
Se(IV)	Dissolved selenite. This is a general reference to Se in the +IV state without indicating the specific chemical species (i.e., $\text{H}_2\text{Se}^{(\text{IV})}\text{O}_3$, $\text{HSe}^{(\text{IV})}\text{O}_3^-$, or $\text{Se}^{(\text{IV})}\text{O}_3^{2-}$) present.
Se(VI)	Dissolved selenate. This is a general reference to Se in the +VI state without indicating the specific chemical species (i.e. $\text{HSe}^{(\text{VI})}\text{O}_4^-$ or $\text{Se}^{(\text{VI})}\text{O}_4^{2-}$) present.
Se(TOT)	Total concentration of dissolved (unfiltered) selenium including both Se(IV) and Se(VI) oxidation states

UNITS OF MEASUREMENT

°C	degrees Celsius
cm	centimeter
g	grams
J/mol	Joules per mole
K	Kelvin
kJ/mol	kilojoules per mole
L	Liter
Lux	unit of light intensity
N	Normality (equivalents per liter of solution)
nm	nanometer
mg	milligrams
mg/L	milligrams per liter
mL	milliliter
mol/L or M	Molarity or moles per liter (moles of solute/liters of solution)
m ² g ⁻¹	square meters per gram
rpm	revolutions per minute
% (v/v)	volume-volume percentage (volume of one solution to the total volume of solution)
µg/L	micrograms per liter
µm	micrometer
µMol/m ² s	micromole per square meter second (unit of light intensity)

INTRODUCTION: PURPOSE OF STUDY

Selenium (Se) has a complex biogeochemical cycle driven by microbial-mediated reactions, multiple oxidation states, sorption-desorption reactions, and slow kinetics. Understanding this cycle is critical for predicting toxicity, bioavailability, natural distribution, mobility, and long-term storage of Se. However, many critical aspects of the biogeochemical cycle remain poorly understood. For example a study conducted on the Great Salt Lake (Dicataldo et al. 2011) found diel Se cycles in August but not in May or September. Short-term changes in Se concentration, combined with seasonal variability in cycles, may account for the inconsistent concentrations of Se reportedly measured at electrical plants and mining operations.

The overall goal of our research was to investigate the Se biogeochemical cycle with an emphasis on identifying first-order controls on the natural variability of Se concentrations. We hypothesized that Se cycles are closely linked to iron (Fe) cycles via selenite (Se(IV)) sorption onto Fe-oxide surfaces. To test this, we conducted Fe-Se coupled laboratory experiments in which we altered the factors that are well-established controls on Fe cycling.

This study focused on Se(IV) for these reasons:

- It is the first Se species to be oxidized from reduced mining-associated sources.
- It sorbs to solids more strongly than the more oxidized selenate (Se(VI)) and thus is more likely to cycle based on sorption interactions.
- Given the slow kinetics of Se(IV) oxidation to Se(VI), we did not anticipate significant species conversion during the diel cycles.

TASK 1. FIRST-ORDER CONTROLS ON DIEL CYCLING OF SELENIUM

1 SUMMARY OF TASK 1 DIEL STUDIES

The overall goal of our research was to investigate the Se biogeochemical cycle with an emphasis on identifying first-order controls on the natural variability of Se concentrations. We hypothesize that Se cycles are closely linked to iron cycles via selenite (Se(IV)) sorption onto the surfaces of hydrous ferric oxide (HFO).

Task 1 included two phases with six total planned activities; modifications and additions to the activities were discussed with Office of Surface Mining Reclamation and Enforcement (OSMRE) and reported in the quarterly reports. The initial tasks included assembly and evaluation of the experimental equipment and configuration, selection and installation of data loggers, and method validation for the Fe and Se(IV) determinations. We were able to alter temperature in the experiments but could not decouple the light cycles from the temperature cycles because the use of the light increased the temperature in the reaction vessels; therefore, to drive the cycles we used either (1) temperature only or (2) coupled temperature and light cycles.

Between July 2014 and April 2015 we completed a total of seven experimental cycles: two cycles for Fe only, two cycles for Se(IV) only, and three cycles that combined Se(IV) and Fe. Our results demonstrated that Se(IV) can cycle as a function of temperature in both light and dark conditions. The cycles were observed in both in the presence and absence of HFOs, although the cycles were more pronounced if HFOs were present. Solution pH was also a critical factor in the likelihood of Se(IV) cycles; this was attributed to the acid-base properties of Se(IV).

Overall, we demonstrated that Se(IV) cycles can exist under experimental conditions and thus may play a role in altering Se concentrations in the environment. The cycles were tied to temperature and pH but the complexity of those interactions are yet to be determined. Based on our data, the concentration of Se(IV) may change as much as +/- 40% from the mean concentration. Our study was conducted with higher Se(IV) concentrations than are typically found in nature to facilitate the analytical and experimental work, however the outcome suggests that Se concentrations in nature may vary with temperature and pH and that representative monitoring for Se should consider this possibility.

The details of the study follow: Table 1 is a summary of the planned and modified tasks, Section 2 summarizes the method testing and experimental design, Section 3 provides the results, and Section 4 is a discussion of the results. The full data set is provided in Appendix A.

Table 1. Summary of planned and completed activities for Task 1

No.	Planned	Modifications and Additions
1	Assemble and test the experimental equipment and instrumentation: reactor vessels and water-controlled temperature, data loggers for monitoring the experiments, HG-ICP-OES method for Se analysis; ferrihydrite preparation (Schwertmann and Cornell, 2007).	<ul style="list-style-type: none"> • Completed as planned. • Grinding and sieving steps added to ferrihydrite preparation.
2	Confirm that we can create Fe cycles using the drivers of temperature-controlled kinetics for Fe(II) oxidation and photo-reduction of Fe(III). We will test each driver independently so that the controlling factors are clear.	<ul style="list-style-type: none"> • Tests completed as planned. • Separating the light and temperature mechanisms proved challenging because having sufficient light to create photoreduction also affected temperature.
3	Once diel cycles for Fe have been established, we will conduct a parallel experiment – with the same configuration – but containing only Se(IV). We do not anticipate seeing cycles for the Se-only tests but will confirm this as a control.	<ul style="list-style-type: none"> • Tests completed as planned. • Quality control testing of glass vessels was added to ensure that hold-over contamination of the glassware was contributing to the Se concentration.
4	Create Fe cycles (using the more effective Fe cycle-driver from Phase 1) but with Se(IV) added to the reaction vessel. Given that we are testing if the Se(IV) is dissolved or sorbed to the Fe solids, we will use total Se as the monitor in the first set of combined experiments.	<ul style="list-style-type: none"> • Tests completed as planned but with coupled drivers. • All tests based on Se(IV) concentrations.
5	Replication of tests for statistical validation	<ul style="list-style-type: none"> • Tests completed as planned.
6	Conduct Fe-Se cycling tests under different conditions: (1) concentration of Se, (2) Se species used, or (3) incorporation of Se speciation analysis.	<ul style="list-style-type: none"> • Preliminary data obtained for these tasks. • A Se-reduction digestion method was developed and tested.

2 APPARATUS, MATERIALS, PROCEDURES, AND METHOD DEVELOPMENT

For this study we assembled an experimental apparatus so that test solutions could be subjected to changes in light and temperature while we continuously monitored and recorded the solution temperature and pH. Grab samples taken from each reaction vessel were analyzed for Fe species and Se(IV). This section details the apparatus, materials and procedures used along with several procedural tests that were completed.

2.1 Experimental apparatus

The experiments were conducted in 1-L jacketed reaction vessels that were actively stirred throughout the data collection (Figs. 1-2). A flow system was constructed to regulate temperature in four 1-liter water-jacketed vessels where the experiments were carried out. Containers with water at three different temperatures: ice water (ideally 0°C), room temperature (RT) water (21-23°C), and hot water (set to 35°C) were mixed to achieve the desired temperature.

We monitored temperature and pH in each reaction vessel using DrDAQ data logger systems (www.drdaq.com/datalogger.html). The data loggers from all reaction vessels were connected to a centralized computer via USBs. The data logger system, PicoLog Recorder and PicoLog Player software and computer, were dedicated to this project.

We controlled light using two 107 centimeter (cm) (42-inch) full-spectrum bulbs in a standard reflective fixture. The wavelength needed for iron photoreduction (ca. 450 nanometer (nm)) was produced by these bulbs. Light intensity could be adjusted by changing the height of the bulbs over the reaction vessels. We monitored light intensity with two systems. Continuous recordings for light and temperature were measured using Onset pendant loggers (www.onsetcomp.com/products/data-loggers/ua-002-64) that record total light in units of Lux and an AccuPAR Model LP-80 PAR/LAI ceptometer (www.decagon.com/index.php/products/canopy-atmosphere/light/) was used for spot measurements. The ceptometer measures in units of $\mu\text{Mol}/\text{m}^2\text{s}$; an empirical relationship between the two types of measurements allowed for data to be determined with either unit throughout the experiment.

2.1.1 Testing of light controls

Prior to beginning the cycle experiments, we tested the light controls and their placement relative to the reaction vessels. The intensity of the light on the vessels was tested by adjusting the height of the florescent light over the jacketed beakers and measuring the results using the HOBO Pendant loggers and the AccuPAR Model LP-80 PAR/LAI ceptometer. The light value was recorded by the AccuPAR, which was placed on top of the jacketed beakers.

Two HOBO Pendant loggers were used to record light intensity. One HOBO Pendant was submerged at the bottom of a water-jacketed beaker and the other logger floated at the top of another water-jacketed beaker. The light was hung at its lowest position above the beakers. The floating HOBO Pendant recorded values that ranged from 3617 Lux to 4306 Lux (approximately the variability of the logger). The submerged HOBO Pendant recorded values that ranged from 3445 Lux to 3961 Lux.

In all cases, the light intensity could be readily altered by changing the height of the light above the vessels. Slightly higher light intensity was measured in the pendant floating on top of the water-filled reaction vessel than the submerged pendant in a comparable vessel. During the diel experiments, the light intensity in the location of the submerged HOBO Pendant is expected to change once the solid is added. The empirical relationship between the two means of measuring light was consistent and can be used for approximating between the two methods of measurement (Fig. 3).

During light cycle experiments (Cycles 1 and 2), the light was placed at 10 cm above the reaction vessels. When the light was turned on, it heated the vessel solutions and therefore, the effects of light and temperature could not be separated. During Cycle 4 (a temperature cycle experiment with the light on), the light was placed 10 cm above the reaction vessels. The average light intensity values decreased over the course of the study (Lux data: Cycle 1: 4119, Cycle 2: 3759, Cycle 4: 3563); however, all of these values are within the expected range for a cloudy day. For Cycles 5 and 7 (temperature cycle experiments with the light on), the light was placed further away from the reaction vessels, because no Fe was present in the solutions for photoreduction. The average light intensity was 1346 Lux for Cycle 5 and 110 Lux for Cycle 7.

2.2 Preparation of hydrous ferric oxide (HFO) solids

Two-line ferrihydrite is a Fe(III) hydroxide ferric oxide (HFO) mineral with a large surface area (>200 m² g⁻¹) and a high affinity for Se(IV) sorption (Parida et al., 1997; Zhao et al., 1994). Sorption studies have shown that ferrihydrite is the best HFO for Se sorption under oxic and acidic conditions (Das et al.,

2013). Therefore, 2-line ferrihydrite was chosen as the sorption material and source of Fe and solids in the diel cycle experiments. We precipitated ferrihydrite (2-line ferrihydrite; protoferrihydrite) by rapid hydrolysis of a Fe(III) solution using the method developed by Schwertmann and Cornell (2007). First, 40 grams (g) iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) solution was dissolved in 500 milliliters (mL) of deionized water (DI) water (Fig. 4). Then, we added three hundred milliliters of 1 normal (N) potassium hydroxide (KOH) into the Fe(III) solution with constant vigorous stirring. We closely monitored the suspension pH to ensure values did not exceed a pH of 8, preventing the conversion of ferrihydrite into goethite or hematite. If the pH was lower than 7 after adding 300 mL of KOH, then KOH was added drop wise until it reached a value between 7 and 8 (the pH range in which ferrihydrite will precipitate). After five minutes of vigorous stirring, we then poured the slurry of ferrihydrite precipitate into 50 mL syringes and let them settle for 30 minutes, allowing the solid to separate from the solution. After separation, we immediately injected the precipitate into dialysis tubing where it was rinsed (by submersion) for 3 days with deionized (DI) water (Fig. 4); the liquid remained in the syringe. The purpose of rinsing the solid in dialysis membrane tubing was to eliminate the formation of potassium nitrate salts within the solid. After separation, we injected the precipitate into dialysis tubing where it was rinsed (by submersion) for 3 days with deionized (DI) water (Fig. 4). The dialyzed solids were air dried for 3 days in a porcelain crucible. X-ray diffraction (XRD) analysis confirmed that the solid phase created was 2-line ferrihydrite (see Appendix B).

Once the synthesized ferrihydrite was dry, it was ground into a fine powder with a mortar and pestle to pass through a 125- μm sieve (Fig. 5). A uniform particle size was needed to ensure that the mineral surface area was consistent in all vessels for Se(IV) sorption. The solid was then stored in a glass container until used.

2.3 Data collection and sample analysis

Grab samples were collected from the reaction vessels at regular intervals in each experiment. We analyzed the samples for Se(IV), reduced iron (Fe(II)), and total iron (Fe(TOT)) as described below.

2.3.1 Iron determination with ferrozine

The concentrations of Fe species were determined by the ferrozine method; ferrozine is a reagent which forms a purple-colored complex when it reacts with Fe(II) (Stookey, 1970). The intensity of the color depends on the Fe(II) concentration and was determined colorimetrically at a wavelength of 562 nm using a Hach, Inc. DR2800 Portable Spectrophotometer.

The ferrozine solution was buffered using a HEPES buffer (0.05 mol/L) and the pH was adjusted to 7 using NaOH. Fresh ferrozine solution was prepared within 24-hours before the start of each experimental cycle. Fe(II) analyses were conducted by adding 0.5 mL of unfiltered sample to 3 mL of ferrozine solution in a 4-mL vial. The vial was shaken, allowed to react for 2 minutes, and then the absorption was measured on the spectrophotometer. A calibration curve was constructed using the same sample-solution ratio with known concentrations of Fe(II) ranging from 0 to 10 mg/L.

Fe(TOT) samples were detected using the ferrozine method by reducing all Fe(III) to Fe(II) using 0.5N hydroxylamine hydrochloride (HX) as a reducing agent. For Fe(TOT), 0.5 mL of unfiltered sample was added to 1.5 mL of HX and 1.5 mL of ferrozine. A separate calibration curve was constructed for Fe(TOT). Fe(III) concentrations were calculated by subtracting Fe(II) concentrations from Fe(TOT) concentrations.

The method detection limit (MDL) for the ferrozine method for Fe(II) and Fe(III) was calculated using the EPA strategy. A total of 7 samples containing 0.04 mg/L of Fe(II) and 7 samples containing 0.04 mg/L of Fe(TOT) were analyzed. We determined the resulting MDL to be 0.02 mg/L.

To determine if the ferrozine was reacting with only the dissolved Fe(II) or if colloidal/particulate Fe was reacting, we completed a series of experiments in which both Fe(II) and Fe(TOT) analyses were performed on unfiltered and filtered samples. We used disposable 0.45-micrometer (μm) syringe filters for this test.

Six reaction vessels were prepared with the same background matrix used in the diel studies but with different concentrations of solid Fe added to each vessel (Table 2, Fig. 6). Water in two of the vessels was noticeably more turbid (vessels 1 and 6, Fig. 6). These were the two solutions prepared in regular beakers instead of jacketed reaction vessels and the solids seemed to be better mixed in these two due to a stronger response from the stir plate. Aliquots were taken from each vessel in replicates of 6; the average concentration and relative standard deviation (RSD) (relative standard deviation = $100 \times \text{mean standard deviation}$) are shown in Table 2.

In all cases, the concentrations of Fe(II) and Fe(TOT) were higher for the unfiltered sample than in the filtered sample (Fig. 7). The most likely explanation for this distinction is that some Fe is present as particles and colloids in the solutions.

This set of samples indicated that filtering does make a difference for both of the Fe(II) and Fe(TOT) analyses; however, it is also possible that colloidal Fe is also present in the filtered samples. Fe colloids are known to exist in the nanoparticle size range (Waychunas et al. 2005) and therefore this style of filtration is unlikely to remove them all. We did not use a more rigorous approach to filtering (e.g., tangential ultrafiltration) because the rigorous filtration may have caused difficulties with Fe and Se oxidation states given the long times necessary to complete the filtration. **Therefore, given that a more rigorous filtration process would create a new bias in the dataset, we decided to use unfiltered samples throughout this study.**

Table 2. Comparison of unfiltered and filtered samples for iron analysis

Vessel	Solid added (mg)	Fe(II) Analysis				Fe(TOT) Analysis			
		Unfiltered (mg/L)	RSD (%)	Filtered (mg/L)	RSD (%)	Unfiltered (mg/L)	RSD (%)	Filtered (mg/L)	RSD (%)
1	100	0.252	4.5%	0.146	6.0%	0.759	1.6%	0.644	1.8%
2	200	0.204	8.0%	0.130	4.4%	0.525	3.1%	0.447	2.6%
3	300	0.232	2.4%	0.155	15%	0.597	0.0%	0.487	1.2%
4	400	0.268	3.9%	0.162	3.5%	0.640	0.0%	0.468	2.3%
5	500	0.232	2.4%	0.151	4.8%	0.398	6.5%	0.272	2.1%
6	600	0.507	<1%	0.160	<1%	0.602	1.2%	0.194	3.7%

Fe(II) is ferrous iron only; Fe(TOT) includes both ferrous and ferric iron; mg/L = milligram/liter; % = percent; RSD = Relative standard deviation (standard deviation/mean reported as a percent)

In the experiments conducted in this study, unfiltered water samples were used therefore it is likely that the Fe concentrations reported include both colloidal and dissolved Fe species. Therefore, Fe(II) should be interpreted as both dissolved and colloidal Fe(II); Fe(TOT) should be interpreted to include the dissolved and colloidal species of both Fe(II) and Fe(III). The impacts of colloidal and dissolved Fe species on the diel cycles are discussed with the data results from those cycles.

2.3.2 Selenium determination

We completed the Se(IV) analysis using a coupled HG-ICP-OES system. Details of that method and procedure follow. We also tested a digestion procedure to convert Se(VI) into Se(IV) so that we could evaluate any conversion between the two different Se oxidation states; the development of the procedure and the implications for our experiments are also discussed in this section.

2.3.2.1 Selenite by HG-ICP-OES

Se(IV) was determined using thin-film hydride generation (HG, Marathon Scientific, Ontario, CA) coupled to ICP-OES analysis (Perkin Elmer Optima DV2100 ICP-OES) using the method developed by Huang (2010). This method measures only the Se(IV) concentration because only the Se(IV) reacts to form a hydride.

Six calibration standards of 5 µg/L, 10 µg/L, 50 µg/L, 100 µg/L, 150 µg/L, and 200 µg/L Se(IV) were prepared with a reference stock Se(IV) solution of 1000 µg/L in 10% (v/v) 6M HCl. The reference stock was prepared using the Spex CertiPrep 1000 mg/L Se(IV) ICP-OES standard. The blank was 10% (v/v) 6M HCl and DI water. Instrument stability was evaluated before each sample run by taking three replicate readings of a blank and each Se(IV) standard. We accepted results at relative standard deviation (RSD) values of less than 3%.

The MDL for Se(IV) was determined from the regression analyses for five different calibration curves using the Data Analysis ToolPak in Microsoft Excel. This method calculates the limit of detection (LOD), which is the same as the MDL for a single analyte. Specifically, the regression output for the upper 95% confidence interval of the intercept was equal to the LOD. Following the method of Konieczka and Namiesnik (2009), the LOD can also be calculated for five individual calibration curves as follows:

$$\text{LOD} = \frac{3 \times \text{SE(I)}}{S}$$

Where SE(I) is the standard error of the intercept and S is the slope of the calibration curve generated as the best-fit line of the standard solution data. The resulting LOD value of this equation is equivalent to the regression analysis LOD result in Microsoft Excel. To get the final MDL, we averaged the LOD results for all five calibration curves. The average MDL for Se(IV) was 5 µg/L.

2.3.2.2 Sample digestions to convert selenate to selenite

We developed a microwave-based method to convert Se(VI) to Se(IV) so that the combined species could be determined by HG-ICP-OES. We developed this method in a high ionic strength solution consistent with that used in the diel experiments but without the inclusion of solid or dissolved Fe. Additional method development will be required to incorporate Fe into this procedure. To do this, we created a series of solutions with known concentrations of Se(VI) and subjected the solutions to a microwave-

assisted digestion using HCl to reduce the Se oxidation state (Fig. 8). To determine the most effective method, we conducted 12 sets of trials in which we modified the following parameters for digestion: (1) power (400 to 1600 Watts); (2) digestion time (30 to 60 minutes); and (3) HCl concentration (4.8 to 8 mol/L, Appendix C). We conducted the digestions on a CEM MARSXpress™ 230/60 microwave (Matthews, NC).

To test the method, solutions of known concentration of Se(VI) were prepared, digested to reduce the Se(VI) to Se(IV), and then analyzed on the HG-ICP-OES. The success of the conversion is calculated as the percent recovery; in the early tests, the percent recovery ranged from 0-97%. However, when higher concentrations of acid were used, the percent recovery increased indicating that all of the Se(VI) had been converted to Se(IV) (Table 3 summary, Appendix C for full data).

Table 3. Percent recovery for conversion of Se(VI) to Se(IV)

Acid Conc. (mol/L)	Average % recovery for triplicate
6.0	112
6.5	112
7.0	112
7.5	107
8.0	107

Percent (%) recovery calculated as the ratio of the measured to the known concentration, reported as a percent; these values are averages of triplicate tests. For the results of the preliminary tests, see Appendix C.

Our final Se(VI)-reduction digestion procedure incorporates the following parameters:

- The method was tested using Se(VI) solutions of a known concentration.
- The standard solutions were prepared for digestion using 1 mL of a Se(VI) standard with a known concentration, 4 mL of deionized water, and 0.5 mL of 6 mol/L trace-metal grade HCl. This mixture is the same as that used for sample preservation.
- The digestion aliquot was then combined with 12M trace-metal grade HCl to a final HCl concentration of 7M.
- Samples were digested in a MARSXpress™ 230/60 microwave at 1600 Watts power, a 5 minute ramp time to 95°C, and 60 minutes at full temperature. Four vessels were digested at one time using this procedure.

2.3.2.3 Conversion of selenite to selenate in experiments

We tested the digestion method on 20 samples from the Se-only Cycle 7 experiment to determine if any Se species conversion was taking place during the experiment. For this test, we followed the final method outlined above using a total HCl concentration of 7 mol/L.

We conducted these analyses to determine if Se(IV) was converting to Se(VI) during the course of the laboratory experiment. This is critical because we assume that the loss of Se(IV) in solution is due to sorption; if we are losing significant amounts of Se(IV) to conversion to Se(VI), then the assumption regarding sorptive-loss is incorrect.

Given that total selenium (Se(TOT)) is the sum of the Se(IV) and Se(VI) species, a small percent difference between Se(IV) and Se(TOT) indicates that most of the Se is remaining in the Se(IV) oxidation state and little conversion has taken place. For the 20 samples analyzed, we found a percent difference ranging from 1 and 17%; all but three of the values were less than 10% and the average percent difference was 9% (Table 4). To confirm that this percent difference was not purely due to analytical variation, we analyzed four of the samples in triplicates for both Se(IV) and Se(VI). The analytical variation, measured as a RSD, was less than 3.5%. For some of the Se(IV)-Se(TOT) pairs, this variability could account for the difference in the two Se concentrations.

Overall, we conclude from this analysis that there was little species conversion from Se(IV) to Se(VI) taking place over the course of the laboratory experiments. If some does occur, it is generally negligible relative to the sorptive loss of Se(IV).

2.4 Additional quality control tests

Several additional tests were completed to evaluate the data quality; these included a test to determine the amount of evaporation that takes place during the experiments and tests to evaluate the interaction of the Se(IV) with the glass reaction vessels.

Table 4. Comparison of Se(IV) and Se(TOT) concentrations for paired samples from the Cycle 7 Se-only experiment illustrating the Se(IV) is the dominant species in the experiment and that little conversion occurred from Se(IV) to Se(VI)

Vessel	Sample number	Se(IV)				Se(TOT)				% difference between Se(IV) and Se(TOT)
		n	Se(IV) (µg/L)	Stdev (µg/L)	RSD	n	Se(TOT) (µg/L)	Stdev (µg/L)	RSD	
V3	0	3	364	3.26	0.89%	3	334	0.60	0.18%	8.72
V3	2	1	383			1	325			16.2
V3	4	1	372			1	339			9.26
V3	8	3	354	1.18	0.33%	3	314	5.14	1.64%	11.8
V3	12	1	377			1	330			13.3
V3	14	1	383			1	351			8.67
V1	0	3	347	7.22	2.08%	3	339	10.9	3.22%	2.40
V1	2	1	370			1	335			9.94
V1	4	1	364			1	338			7.37
V1	8	3	344	7.68	2.23%	3	338	1.54	0.46%	1.97
V1	12	1	374			1	340			9.52
V1	14	1	388			1	355			8.99
Average % difference										9.01

n indicates the number of samples; Stdev (standard deviations) and RSD (standard deviation/mean) reported for triplicate samples. Percent difference = (difference)/(average). None of the samples contained iron. The pH of these samples ranged from 2.80 to 2.95.

2.4.1 Evaporation tests

In previous experiments, the measured concentrations of Se(IV) exceeded the input concentrations in some cases. A likely reason for this is that water evaporated from the vessels during the experiment. All of the experiments have been completed in uncovered vessels to maximize any input from the lights (and to be consistent for the dark experiments). To evaluate this possibility, we analyzed samples from several vessels for potassium (K); the concentration of potassium is known at the beginning of the experiments and it should be conserved throughout. Therefore, any increase in the potassium concentration from the beginning to the end of an experiment can be attributed to evaporation.

Each vessel initially contained 0.1 mol/L of KCl (equal to 3908 mg/L K). Four vessels were prepared with the KCl and 300 µg/L Se(IV) and stirred for 2.3 days. Samples were collected at elapsed times of 0 days, 2 days, and 2.3 days (Table 5).

Table 5. Results of potassium analyses for determining evaporation from vessels

Vessel No	Elapsed time (days)	K (mg/L)	Change from background (%)
1	0	3579	0.87%
	2.03	3645	2.73%
	2.33	3753	5.78%
2	0	3577	0.82%
	2.03	3678	3.66%
	2.33	3856	8.68%
3	0	3679	3.69%
	2.03	3646	2.76%
	2.33	3766	6.14%
4	0	3561	0.37%
	2.03	3727	5.05%
	2.33	3883	9.44%

In all cases, the potassium concentration increased over the 2.3 day experiment indicating that the solutions were evaporating from the vessels. The numbers suggest that up to a 10% increase in Se concentration may be accounted for due to evaporation. However, this would only affect the absolute Se concentrations; diel cycles present as relative changes in concentration.

2.4.1.1 Selenium Se(IV) loss from sorption to glass

To determine if Se was being lost to sorption to the glass vessels, Se-only (no Fe) blanks were tested as part of the sorption study. In those tests, up to 15% of the Se(IV) was lost in the blanks. This may be due to either sorption to the glass vessels or conversion to Se(VI) in the experiment. While this introduces some error in the process, was considerably less than the loss in the Fe-containing experiments.

2.4.1.2 Selenium Se(IV) desorption from glass

To evaluate the possibility that the glass vessels were releasing Se into solution, we conducted dissolution experiments for glassware cleaned in the same way as the vessels used in the study.

- A solution of 300 µg/L Se(IV) was placed in two vessels and allowed to stir for two days.
- One vessel was washed with Sparkleen detergent and the other with an acid detergent.

- The vessels were filled with a solution that matched the studies to date (1 L of deionized water, adjusted to pH 3 using HCl, 7.45 g of KCl added); and allowed to equilibrate for 24 hours.
- Samples were collected for Se(IV) and Se(TOT) at elapsed times of 4 hours, 6 hours, and 24 hours.

None of the samples collected contained detectable Se(IV) at the MDL of 5 µg/L.

3 RESULTS OF CYCLING EXPERIMENTS

We conducted a series of experiments (cycles) in which light, temperature, and chemical concentrations were varied in the reaction vessels (**Table 6**). The cycles are numbered [chronologically but discussed according to their composition \(Fe-only, Se-only, and Se-Fe combined\)](#). The results are illustrated on [Figures 9 through 18](#).

Table 6. Summary of diel experiments. Cycles are numbered chronologically.

Cycle No	Start date	2-line ferrihydrite (mg)	Se(IV) (µg/L)	Light	Approx. Temp. Range	Total test time (hours)
Fe-only cycles						
1	7/22/14	500	0	Cycle	21-23 °C	22
2	10/17/14	500	0	Cycle	23-26 °C	30
Se-only cycles						
5	1/29/15	0	300	On	10-35 °C	3.5
7	4/26/15	0	300	On	5-35 °C	7
Combined Se-Fe cycles						
3	10/25/14	500	3000 ^a	Off	10-35 °C	10
4	12/9/14	500	0	On	0-35 °C	10
		500	300			
6	2/28/15	500	0	Off	0-35 °C	7
		500	300	Off		

^aA higher concentration of Se(IV) was unintentionally added to the reaction vessels.

3.1 Iron-only experiments

Cycles 1 and 2 experiments (**Table 6**) contained Fe but no Se; we conducted these experiments primarily to test the apparatus and procedures. Our primary goals were to confirm that we could control the temperatures in the reaction vessels and that we could create cycles for Fe. Cycle 1 was a preliminary test to determine which solid – ferrihydrite or FeCl_3 – was a better starting material for the experiments (Fig. 9). Although FeCl_3 is more soluble and generated more Fe in solution, insufficient HFO solids were present or formed to create sorption surfaces for the Se experiments. Therefore, we used the HFO solids for the remaining experiments. This experiment also indicated that changes in light controlled the temperature. When the light was on, it created sufficient heat so that the temperatures in the reaction vessels increased even if the water temperatures for the reaction vessels were held constant. After discussing this issue with OSMRE, we decided that future experiments would be in either light or dark conditions rather than changing both the temperature and light conditions in a single experiment.

During Cycle 2, the Fe(TOT) concentration decreased and the Fe(II) concentration increased when the lights were turned off and temperature decreased (Fig. 10). The increase of Fe(II) during the dark indicated that photoreduction is not occurring sufficiently to control the net change in Fe(II) concentrations. An alternative driver for Fe cycling, which is in agreement with the pattern observed in Cycle 2, is that Fe(II) concentrations are higher in colder temperatures because the rate of the oxidation from Fe(II) to Fe(III) is slower at lower temperatures.

Although the concentrations of Fe(II) and Fe(TOT) varied slightly between vessels, the relative change (reported as the percent change from the mean) was relatively constant, especially for Fe(II). The vessel with the greatest change in Fe(TOT) was number 3, which also had a different pH pattern from the other vessels.

Both Fe-only experiments illustrated that Fe cycles could be generated from the produced ferrihydrite and that the Fe speciation cycles were linked to temperature change.

3.2 Se-only experiments

Cycle 5 and 7 experiments (Figs. 11, 12) included Se but no Fe. The purpose of these cycles was to determine if Se cycled in the absence of Fe and if Se was being lost to the glassware. Because there was no evidence that Se speciation and sorption respond directly to light, both experiments were completed with the lights on.

Cycle 5 was short (<4 hours) and included only a partial temperature cycle (Fig. 11) and no clear Se cycle was observed. The concentration of Se(IV) in the vessels ranged between 195 and 371 $\mu\text{g/L}$. The initial concentration of Se(IV) in all vessels was 300 $\mu\text{g/L}$ with an estimated uncertainty of -20, +50 $\mu\text{g/L}$ (based on solution preparation uncertainty and possible evaporative loss).

The Se(IV) concentrations varied with a consistent pattern in Cycle 7 (Fig. 12) but with a small magnitude. In general, the Se(IV) concentrations changed linearly with temperature (Fig. 13). The magnitude of the change was minimal: the Se(IV) concentrations varied between 95 and 106% of the mean concentrations. The actual concentrations are likely biased high relative to the initial concentrations but the trends with temperature were consistent for all four vessels in this cycle. The cycles in the Se(IV) concentration indicated that some of the Se(IV) is likely to be interacting and sorbing to the glass reaction vessels. However, the magnitude is small when compared to similar cycles produced when Se(IV) is allowed to sorb to HFO.

Sample digestion and analysis for Se(TOT) was completed for multiple samples in Cycle 7. The Se(IV) and Se(TOT) generally agreed within 10% indicating that little to no oxidation of Se(IV) to Se(VI) occurred during this cycle.

3.3 Fe-Se combined experiments

Three cycles were completed that included both Se(IV) and HFO: Cycles 3 and 6 were conducted in the dark and Cycle 4 was conducted in the light (Figs. 14 and 17). The mean concentrations of Se(IV) and pH data are provided for the three cycles on Table 7 along with data from Cycle 7 which included Se(IV) but no HFO.

Cycles in Se(IV) concentrations were observed under both light and dark conditions. [The vessels with a highest maximum pH values are the same vessels in which Se\(IV\) did not cycle, supporting the likelihood that the pH is critical in the presence and absence of cycles.](#)

The mean concentrations of Se(IV) in the Se-Fe cycles were less than measured in the Se-only cycles (Cycle 7). This suggests that although some Se may be sorbing to the glass of the reaction vessels, the loss of dissolved Se(IV) due to sorption was considerably larger.

Table 7. Comparison of Fe-Se cycles with Se-only cycles illustrating that more Se(IV) is lost in the experiments containing HFO (Cycles 3, 4, and 6) than in the experiments without HFO (Cycle 7)

Cycle Number	Vessel	Dark or Light	Se cycle	Initial Se(IV) (µg/L)	Mean Se(IV) (µg/L)	% of Se(IV) lost	Maximum pH	Minimum pH	Mean pH	Se(IV) % Range ^b
3	V1	Dark	Yes	3000	233	92	2.99	2.96	2.97	73
3	V2	Dark	Yes	3000	306	90	3.00	2.96	2.98	48
3	V3	Dark	Yes	3000	293	90	3.18	3.16	3.17	39
3	V4	Dark	Yes	3000	233	92	2.97	2.92	2.94	50
6	V3	Dark	Yes	300	43.2	86	3.16	3.03	3.08	88
6	V4	Dark	No	300	39.4	87	3.43	3.30	3.34	77
4	V3	Light	No	300	12.1	96	3.35	2.98	3.20	43
4	V4	Light	Yes	300	48	84	2.98	2.66	2.74	103
7 (no HFO)	V1	Light	Yes	300	361	~0	2.88	2.80	2.83	9.9
7 (no HFO)	V2	Light	Yes	300	360	~0	2.87	2.85	2.86	9.6
7 (no HFO)	V3	Light	Yes	300	370	~0	2.95	2.85	2.88	9.9
7 (no HFO)	V4	Light	Yes	300	383	~0	2.91	2.79	2.82	9.5

HFO = Hydrous iron oxides; The “% of Se(IV) lost” is the difference between the initial and mean concentrations, divided by the initial concentration; a loss of “~0” indicates that no Se(IV) was lost within the error of the measurement; The “Se(IV) % range” is the difference in the maximum and min values for the % of mean concentration and is provided as a means for comparing the magnitude of the cycle.

The magnitude of the cycles was considerably greater in the vessels containing both Se(IV) and Fe than in comparable Se(IV)-only vessels. The “Se(IV) % Range” (Table 7) reports the difference in the maximum and minimum Se(IV) concentrations measured in an individual cycle, but reported as a percent value normalized to the mean concentration. In the Se(IV)-only vessels in Cycle 7, this value was less than 10%; in the Se-Fe vessels this value ranged from 39-88% indicating that greater cycling of Se(IV) concentrations occurred in the vessels that contained Fe in addition to the Se(IV).

The Se(IV) concentrations from Cycle 3 were graphed relative to temperature to evaluate the dependence of the Se(IV) and to estimate the enthalpies of sorption (Fig. 15). The Se(IV) concentrations increased with temperature (that is, sorption decreased with temperature) although the graphs indicate some hysteresis between the sorption and desorption process. For calculation of the enthalpy, we used the data from the maximum Se(IV) concentration until the end of the experiment because these data represent net sorption onto the solid. Following the method of Gammons et al. (2005), we calculated conditional enthalpies of adsorption, ΔH_{abs} , from the data using the Clausius-Clayperon equation; when the inverse of

temperature is plotted versus the log concentration, the enthalpy can be determined from the slope of the line as follows:

$$\log C = \frac{\Delta H_{ads}}{2.303R} \left(\frac{1}{T} \right) + b$$

where ΔH_{abs} is the conditional adsorption enthalpy (J/mol), R is the ideal gas constant, and C is the dissolved metal concentrations at each temperature (in Kelvin). The conditional enthalpies were calculated for individual vessels and separately for when the temperature was rising or falling (Fig. 14) and are reported for datasets with R^2 values greater than 0.8 (Table 8).

Table 8. Conditional enthalpies of sorption for the shaded data on Fig. 18

Vessel	R^2	slope	Enthalpy (kJ/mol K)
V1	0.850	-1008	-19.31
V2	0.915	-855	-16.37
V3	0.483	-473	Not
V4	0.251	-244	calculated

We have not yet found reported conditional enthalpies of sorption for Se onto Fe compounds. Estimated enthalpies reported for cationic trace metals range from 30 to 145 kJ/mol K (Parker et al. 2008, Quinn et al. 2007, Vesper and Smilley 2010). Anions like Se have been known to sorb out of phase with cations; that is, when the temperature decreases the cation concentrations increase and the anion concentrations decrease (Nimick et al. 2003). The negative sign on the enthalpies calculated for Se are because the Se concentrations decrease when the temperature decreases – consistent with Nimick et al.’s (2003) findings for arsenic. It should be noted that these conditional enthalpies of sorption assume that all loss of Se(IV) was due to sorption onto the HFO; any loss of Se(IV) due to oxidation to Se(VI) or to glassware would not be accounted for in this estimate.

4 DISCUSSION OF DIEL CYCLING EXPERIMENTS

This study was undertaken to better understand if diel cycles of Se(IV) can exist in nature and, if so, what are the critical drivers for those cycles. The initial hypothesis was that Se(IV) cycles exist and are coupled to the cycling of Fe species. To evaluate these hypotheses, the following questions were considered.

1. Can diel cycles of Se(IV) be created in the laboratory?

We were able to create cycles of Se(IV) in the laboratory under both light and dark conditions using changes in temperature as a driving force (Figs. 14 and 16). **In some cycles, the change in concentration was as much as +/- 40% of the mean concentration.**

2. Are the diel cycles of Se(IV) linked to sorption onto HFO?

Se(IV) is known to sorb to HFO so it seems a likely driver for the Se(IV) cycles. Larger Se(IV) cycles were observed in the presence of HFO than when only Se(IV) was present (Figs. 12, 14 and 16); the conditional enthalpies of sorption estimated from Cycle 3 were negative as would be expected for an anion.

3. Are diel cycles of Se(IV) linked to the cycling of Fe species?

Se(IV) cycles were observed even in the absence of Fe-species cycling. All of the experiments were conducted with an excess of HFO.

4. What factors other than light and temperature are important in the cycling of Se(IV)?

The pH of the solution is critical to Se cycling because both Se(IV) and Se(VI) anions protonate and form acids at lower pHs according to the following reactions for the dissociation of Se(IV) (Reactions 1 and 2) and Se(VI) (Reaction 3):



The distribution of the species can be illustrated graphically as a function of pH (Fig. 19). Because the different Se species sorb differently, the pH must be considered as critical factor influencing Se cycling.

5. Does a change in the Se(IV) oxidation state affect cycling?

For the Se-only experiments, both Se(IV) and Se(TOT) were determined and found to be within 10% of each other, indicating that no conversion of the Se(IV) species took place during those experiments. Although the Se(TOT) data support the lack of Se(IV) oxidation, it is possible that oxidation may occur in the presence of Fe. That is, it is possible that the oxidation of Se from Se(IV)

to Se(VI) can be coupled to the reduction of Fe from Fe(III) to Fe(II). The likelihood of that reaction taking place is a function of pH because of the change in the protonation of the Se(IV) species.



Where Reaction 4 occurs between pH 1.66 and 2.62 and Reaction 5 occurs at pHs from 2.62 to 8.32 (respectively Zone A and B on Fig. 19). Given the Gibbs Free Energy of Reaction (ΔG_R) for the approximate concentrations of Se and Fe in the experiments, Reaction 4 is unlikely to occur (that is, $\Delta G_R > 0$). The thermodynamics of Reaction 5 are favorable at pHs greater than approximately 3.5 when the estimated ΔG_R is negative. Although the thermodynamic calculations are only estimates of what could happen, they suggest that oxidation of Se(IV) to Se(VI) in the presence of Fe(III) is more likely to occur at pHs at or above about 3.5.

This factor may also explain why stronger Se(IV) diel cycles were observed at lower (<pH 3) pH values (Table 6). As the pH approaches 3.5, the loss of dissolved Se(IV) is likely to be a combination of sorption onto the HFO and conversion to an oxidized Se species. This also suggests that the diel cycling of Se(IV) is highly dependent on pH.

5 CONCLUSIONS

In this study we conducted a series of laboratory experiments designed to determine if Se is likely to cycle over diurnal conditions in nature. To do so, we tested solutions of Fe, solutions of Se, and mixtures of Fe and Se under changing light and temperature conditions to generate Se concentration changes that could occur. Our hypothesis was that the Se cycles would be linked to sorption of Se(IV) onto HFO.

Overall, our results demonstrated that Se(IV) can cycle as a function of temperature in both light and dark conditions. The cycles were observed both in the presence and absence of HFOs, although the cycles were more pronounced if HFOs are present. The pH of the solution was also a critical factor in the likelihood of Se(IV) cycles and cycles were observed most consistently at pHs less than or equal to 3.

Our data illustrate that Se(IV) cycles can exist under experimental conditions. The cycles are tied to temperature and pH but the complexity of the interactions is yet to be determined. The data suggest that cycles may also exist in the environment. Based on our data, the concentration of Se(IV) may change as

much as +/- 40% from the mean concentration. Our study was conducted with higher Se(IV) concentrations than typically found in nature to facilitate the analytical and experimental work, however the outcome suggests that Se concentrations in nature may vary with temperature and pH and that representative monitoring for Se should consider this possibility.

6 CITED REFERENCES

- Das, S., Hendry, M.J. and Essilfie-Dughan, J., 2013. Adsorption of Selenate onto Ferrihydrite, Goethite, and Lepidocrocite Under Neutral pH Conditions. *App Geochem*, 28, 185-193.
- Gammons, C.H., Wood, S.A., Pedrozo, F.L., Varekamp, J.C., Nelson, B.J., Shope, C.L., Baffico, G., 2005. Hydrogeochemistry and rare earth element behavior in a volcanically acidified watershed in Patagonia, Argentina. *Chem Geol* 222, 249-267.
- Konieczka, P., Namiesnik, J., 2009. Quality Assurance and Quality Control in the Analytical Chemical Laboratory. CRC Press, Boca Raton, FL, p. 146-147. (Chapter 7 - Method Validation)
- Machesky, M., 1990. Chapter 22. Influence of temperature on ion adsorption by hydrous metal oxides, in: Melchior, D.C., Bassett, R.L. (Eds.), *Chemical Modeling of Aqueous Systems II*. American Chemical Society, Washington DC, pp. 282-292.
- Nimick, D.A., Gammons, C.H., Cleasby, T.E., Madison, J.P., Skaar, D., Brick, C.M., 2003. Diel cycles in dissolved metal concentrations in streams: Occurrence and possible causes. *Water Resour. Res.* 39, 1247-1264.
- Parida, K.M., Gorai, B., Das, N.N., Rao, S.B., 1997. Studies on Ferric Oxide Hydroxides: III. Adsorption of Selenite (SeO_3^{2-}) on Different Forms of Iron Oxyhydroxides. *J Colloid Interface Sci*, 185(2), 355-362.
- Parker, S.R., Gammons, C.H., Pedrozo, F.L., Wood, S.A., 2008. Diel changes in metal concentrations in a geogenically acidic river: Rio Agrio, Argentina. *Journal of Volcanology and Geothermal Research* 178, 213-223.
- Quinn, K.A., Byrne, R.H., Schijf, J., 2007. Sorption of yttrium and rare earth elements by amorphous ferric hydroxide: Influence of temperature. *Environ. Sci. Tech.* 41, 541-546.
- Schwertmann, U., Cornell, R.M., 2007. *Iron Oxides in the Laboratory: Preparation and Characterization*. Wiley-VCH Verlag GmbH.
- Stookey, L.L., 1970. Ferrozine - A new spectrophotometric reagent for iron. *Anal. Chem.* 42, 779-781.
- Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters*. Third Edition. John Wiley & Sons, New York.
- Vesper, D.J., Smalley, M.J., 2010. The distribution and diel cycling of trace and rare earth elements in a coal mine drainage treatment wetland, Lambert Run, West Virginia. *Appl Geochem* 25, 795-808
- Waychunas, G.A., Kim, C.S., Banfield, J.F., 2005. Nanoparticulate iron oxide minerals in soils and sediments: unique properties and contaminant scavenging mechanisms. *J Nanopart Res* 7, 409-433.
- Zhao, J., Huggins, F.E., Feng, Z. and Huffman, G.P., 1994. Ferrihydrite: Surface Structure and its Effects on Phase Transformation. *Clays Clay Min*, 42(6), 737-746.

TASK 2. KINETICS OF SELENIUM SORPTION AND IMPLICATIONS FOR POTENTIAL DIEL SELENIUM CYCLES

1 SUMMARY OF TASK 2

The overall goal of Task 2 was to determine if the apparent sorption of Se to Fe(III)-oxides in the presence of light is the net effect of Se(IV) sorption (removal) and dissolution (release) from Fe(III)oxide photoreductive dissolution. The Task 2 experiments were intended to provide the kinetic data necessary to support the Task 1 results.

We conducted four sets of sorption experiments with 0 to 300 µg/L Se(IV); two sets were completed in the light and two sets were completed in the dark. Overall the sorption of Se onto HFO was not consistent between the datasets. However, the tests did demonstrate that more Se(IV) was removed from solution in the presence of HFO than without. The lack of repeatable results from the isotherms limits the additional work related to the kinetics of sorption.

The details of the study follow: Table 9 is a summary of the planned and modified tasks, Section 2 summarizes the method testing and experimental design, Section 3 provides the results, and Section 4 is a discussion of the results.

Table 9. Summary of planned and completed activities for Task 2

No.	Planned	Modifications and Additions
1	Assemble and test experimental equipment and instrumentation	<ul style="list-style-type: none"> Completed as planned. Grinding and sieving steps added to ferrihydrite preparation.
2	Construct Se(IV) sorption isotherms in fully lit conditions and completely dark conditions. Conduct corresponding dissolution experiments.	<ul style="list-style-type: none"> Two sets of experiments were conducted under light conditions and two sets of experiments were conducted in the dark
3	Se sorption/Fe dissolution kinetic experiments	<ul style="list-style-type: none"> These experiments were not conducted because of lack of strong isotherm results in Part 2.

2 MATERIALS AND EXPERIMENTAL PROCEDURES

A total of four sorption experiments (two each in Set A and Set B) were completed and sorption isotherms calculated for each of them. Each set included 12 vials (40 mL, glass) that were prepared individually; consistent parameters are listed on Table 10. Concentrations of Se(IV) ranged from 0 to 300 $\mu\text{g/L}$.

Table 10. Summary of method for sorption tests

2-line ferrihydrite added to each tube	0.05 g
Solid KCl added to tube	0.298 g
HCl added to tube	3 drops of 10 % acid solution
pH after HCl is added	~ 3.0
Speed	~42 rpm

The samples were shaken on a Rugged Rotator shaker. To ensure equilibrium was reached, pH was measured in each vial every 24 hours until it stabilized. Upon pH stabilization, the vials were allowed to settle for 30 minutes and then a 5-mL aliquot was collected from each vial for Se(IV) analysis and fixed with 0.5 mL of 6 N HCl. All samples were analyzed on the HG-ICP-OES for Se(IV) within 24 hours of their collection.

We conducted the experiments concurrently in pairs of light and dark. The test samples exposed to light were placed 15 cm (6 in) from the light source. The “dark” samples were shielded from light using a heavy-mil plastic designed to block light. Test samples containing HFO but no Se(IV) were included to check on blank contamination; test samples with 300 $\mu\text{g/L}$ Se(IV) but no HFO were included to check on sorption to the container or species conversion.

3 RESULTS AND DISCUSSION OF SORPTION EXPERIMENTS

The initial concentrations of Se(IV) decreased in solution during the sorption experiments with a percent loss between 68% and 91% (Table 11, Appendix D). “Blank” samples containing Se(IV) and no HFO were included in the experiment and loss less than 10% of the initial 300 $\mu\text{g/L}$ of Se(IV) indicating that the greater percent loss was due to the presence of HFO.

Table 11. Summary of results for sorption experiments under both light and dark conditions. *Note that far less Se(IV) is removed from solution in the control tubes with no solid HFO.*

Set	Initial Se(IV) (ug/L)	Initial HFO (g)	n	Dark Experiments		Light Experiments		Comments
				Mean Se(IV) (µg/L)	Mean % loss	Mean Se(IV) (µg/L)	Mean % loss	
Set A	0	0.5	2	<5	---	<5	---	HFO blank
	100	0.5	3	0.21*	99.8	11.1	88.9	
	150	0.5	3	2.60*	98.3	15.9	89.4	
	200	0.5	3	6.66	96.7	53.8	73.1	
	250	0.5	3	8.00	96.8	55.3	77.9	
Set B	150	0.5	3	46.3	69.1	27.5	81.7	
	200	0.5	3	40.8	79.6	63.6	68.2	
	250	0.5	3	43.3	82.7	60.6	75.8	
	300	0.5	3	50.1	83.3	26.0	91.3	
	300	0	3	271	9.54	271	9.58	Se(IV) blank

*Indicates concentrations measured but below MDL of 5 µg/L. [The complete dataset is provided in Appendix D.](#)

When the data are plotted in isotherm format there is minimal overlap between the datasets (Figure 20) and different slopes are obtained for the linear regression fits to the individual datasets. For the Set A data, the coefficients of regression (R^2) values for the linear regression were 0.96 for the experiments conducted in the dark and 0.68 for the experiments conducted in the light. For the Set B data, the R^2 values were 0.16 for the dark experiments and 0.12 for the light experiments. When all of the data are combined, the R^2 was less than 0.03.

There are several possible reasons for the lack of consistency between datasets. First, the temperature was not tightly controlled during the experiments due to room fluctuations and heat generated by the lights; we know from the diel experiments that Se(IV) sorption is dependent on temperature. Unfortunately complete temperature data were not collected during the experiments so this potential error cannot be quantified.

Another possible reason for the inconsistency is that some of the dissolved Se(IV) loss may be due to oxidation to Se(VI) rather than to sorption. As discussed for the diel experiments, the Se(IV) oxidation may be coupled to Fe(III) reduction at pH ca. 3.5. The equilibrated solutions in the sorption experiments had pHs that ranged from 2.88 to 3.32.

A third possible reason for the inconsistency is that some of the Se(IV) may be sorbing to the glass surfaces of the test tubes. To evaluate this possibility we included six quality control samples that contained 300 µg/L Se(IV) but no solid HFO. The loss of Se(IV) in those samples ranged from essentially zero (within the range of measurement) to 15% (Appendix D) with an average value of 9.6% (Table 11). This indicates that some removal of dissolved Se(IV) can be attributed to sorption onto the glass but it is small relative to the removal in the presence of HFO (60-98% removal, Appendix D).

4 CONCLUSIONS

The sorption experiments resulted in inconsistent results for the generation of sorption isotherms therefore sorption coefficients were not calculated for the datasets. However, the data clearly showed that Se(IV) was more strongly sorbed in the presence of HFO than without HFO thereby confirming that the use of glass vials did not impact the outcome of the study.

FIGURES

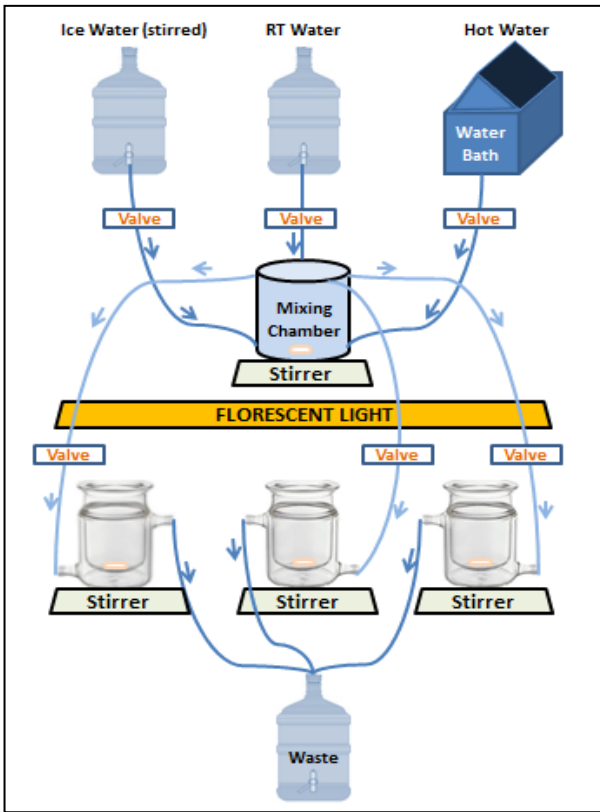


Fig. 1. Schematic of experimental layout. Blue arrows indicate water flow direction.

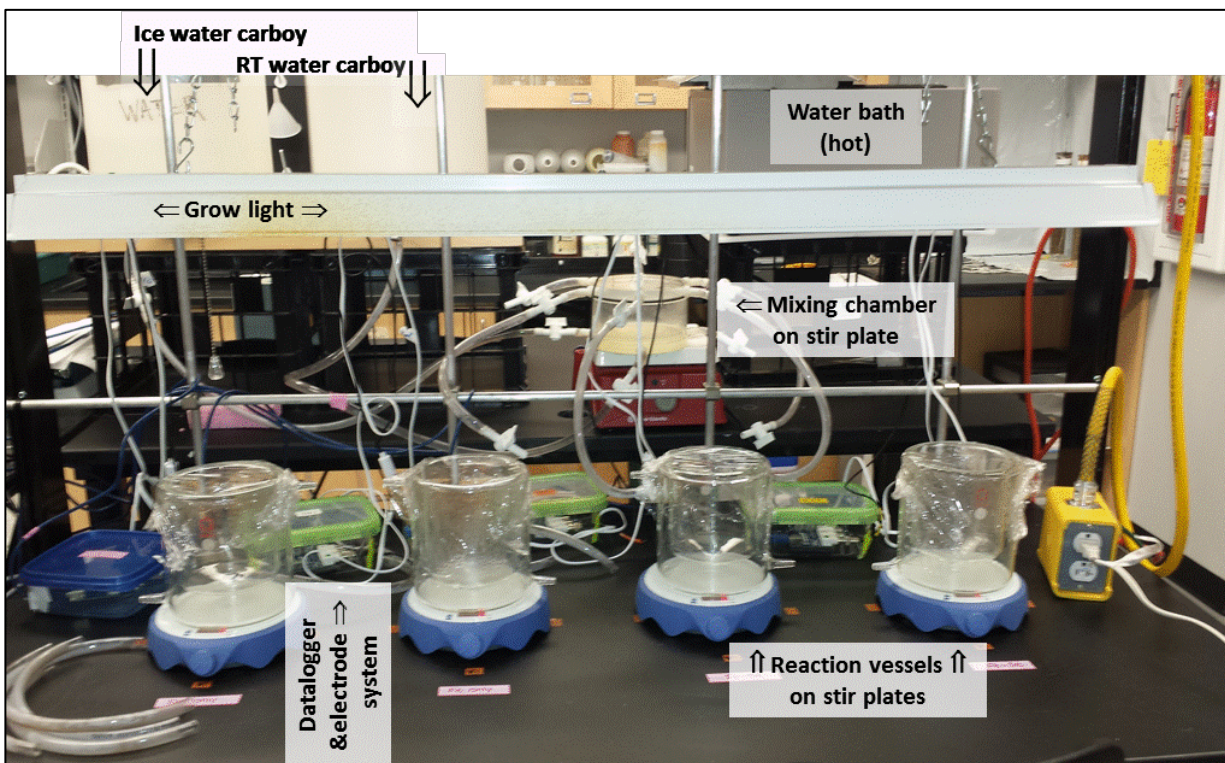


Fig. 2. Layout of experimental apparatus in the laboratory.

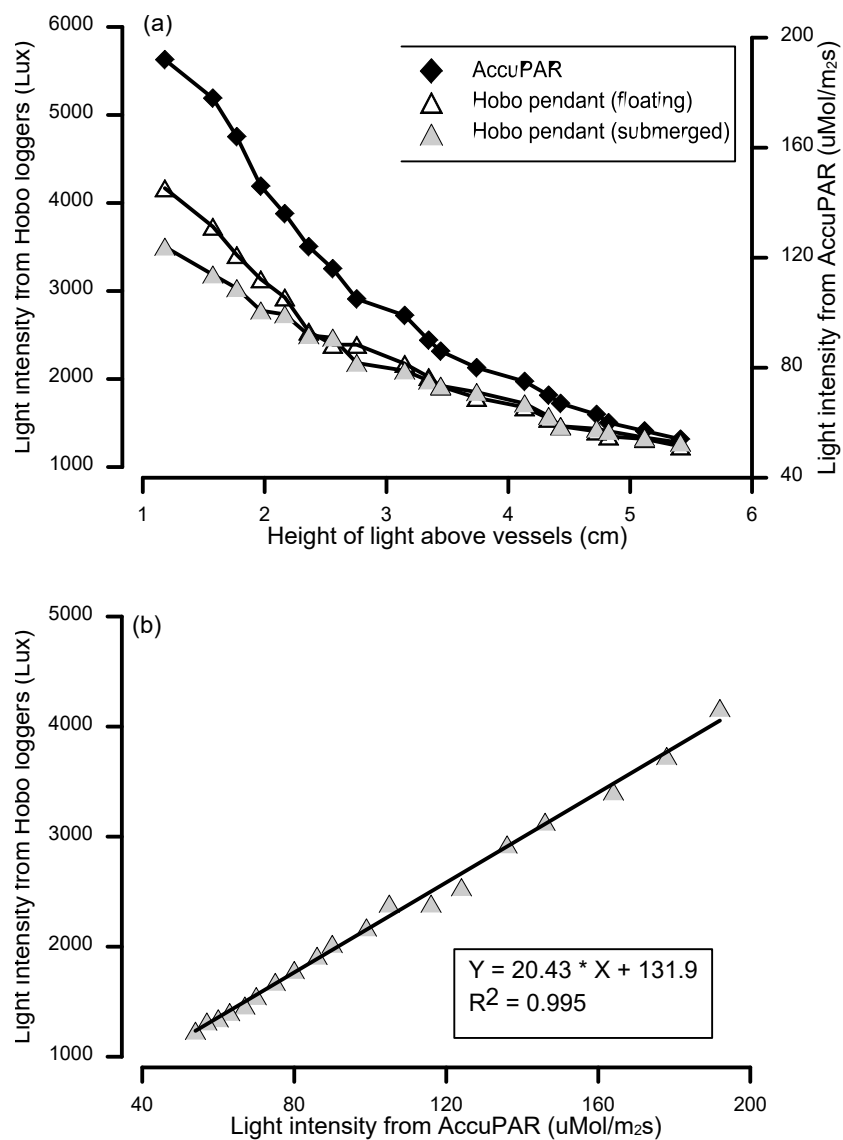


Fig. 3. (a) Light intensity measurements for HOBO pendant data loggers and AccuPAR meter for different heights of the light above the reaction vessels. (b) Empirical relationship between the results of the floating pendant and the AccuPAR meter.

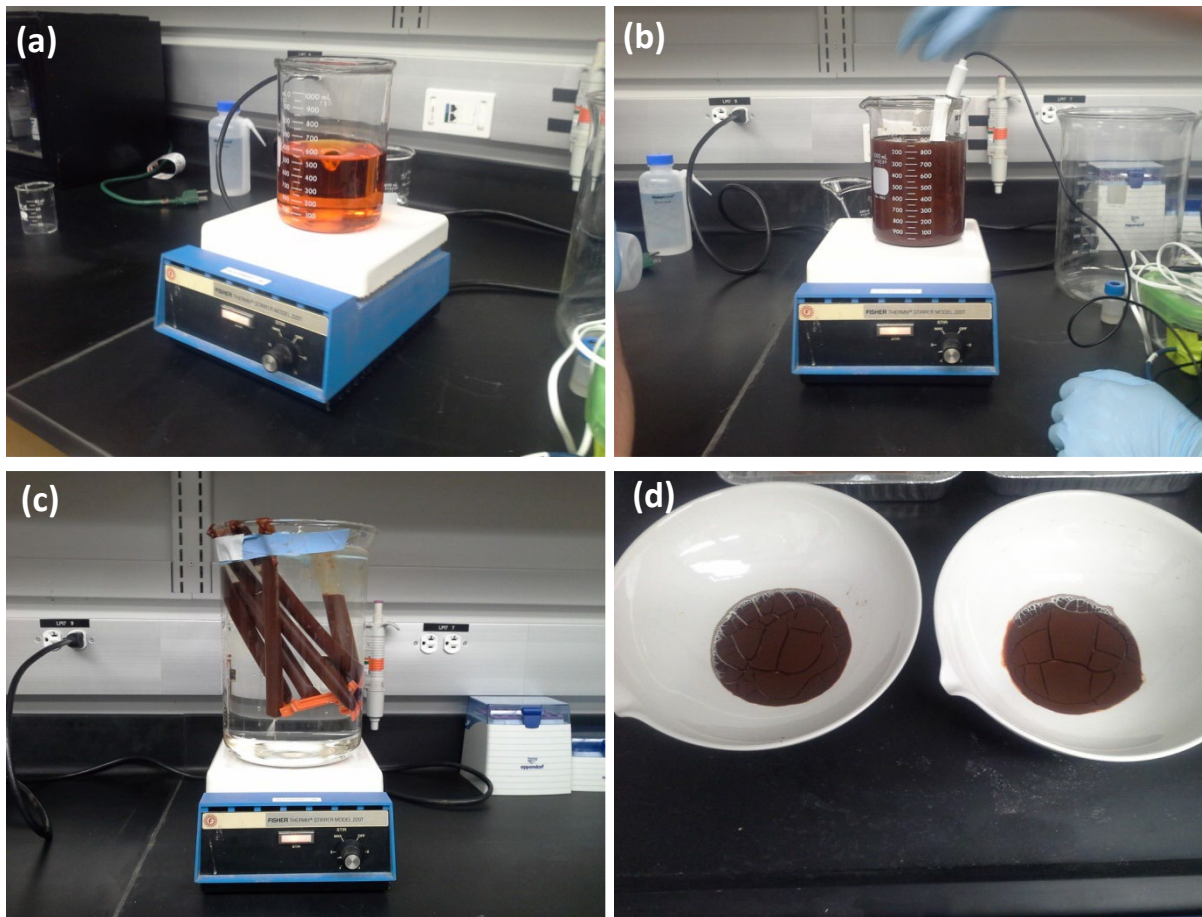


Fig. 4. Production of the hydrous ferric oxide (HFO) 2-line ferrihydrite: (a) solution of $\text{Fe}(\text{NO}_3)_3$, (b) mixing during reaction for aqueous ferrihydrite, (c) dialysis rinsing, (d) air drying. The procedure follows the method detailed in Schwertmann and Cornell (2007).



Fig. 5. Sieves used to ensure the ferrihydrite is uniform in size. The smallest sieve only allowed particles less than 125- μm to pass through. Those particles were used in the subsequent experiments.

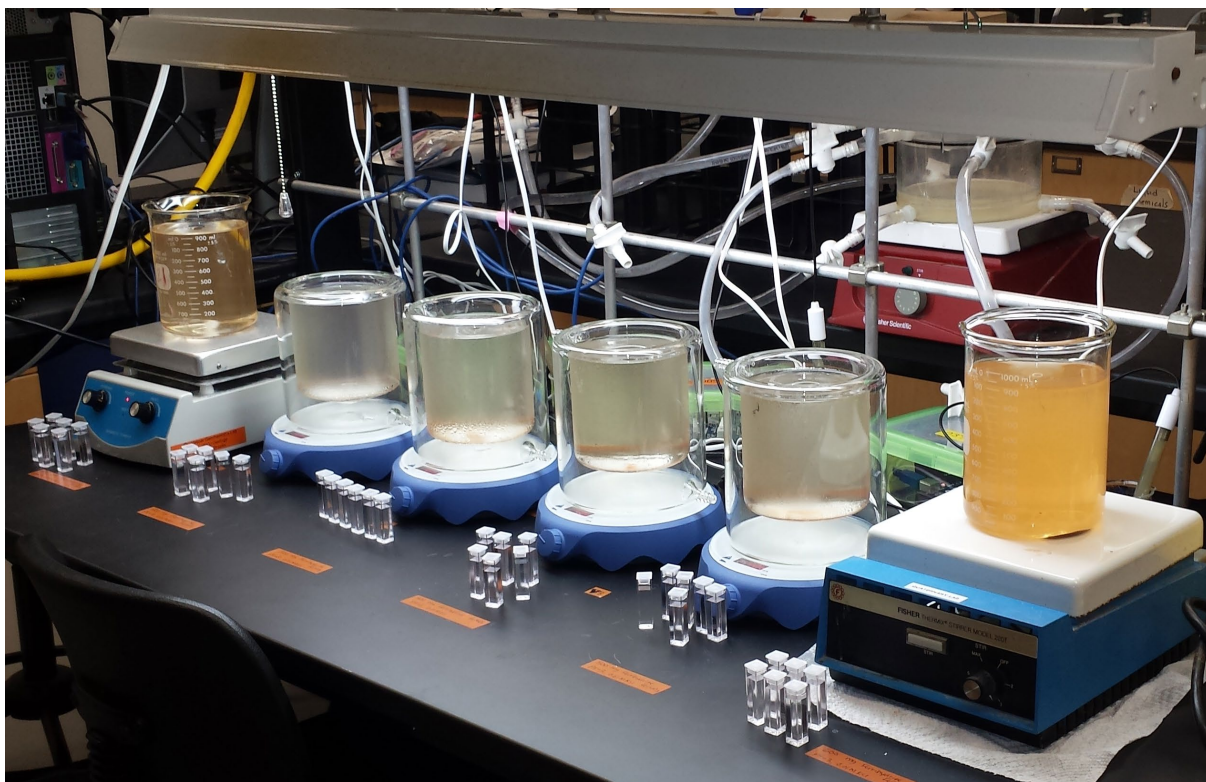


Fig. 6. Photograph of the Fe colloid experiment. Vessels were numbered V1 to V6 from left to right. V1 and V6 are standard 1000 mL beakers; the other four are jacketed reaction vessels.

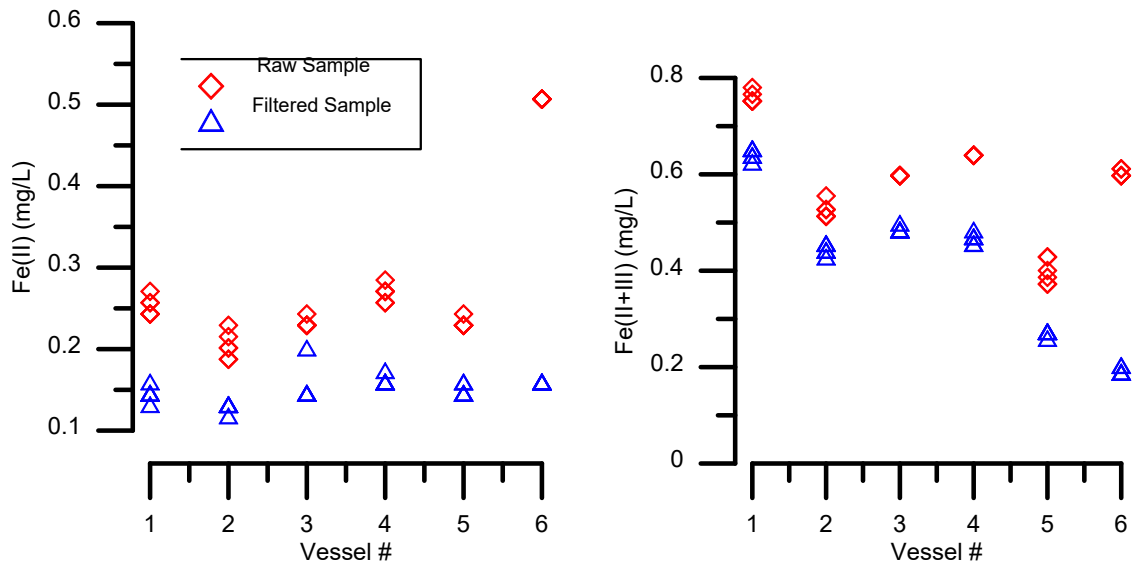


Fig. 7. Results of the Fe colloid experiment comparing raw and filtered samples analyzed for Fe(II) and Fe(TOT). "Raw" indicates that these samples were unfiltered. The filtered samples were passed through a disposable 0.45- μm filter.

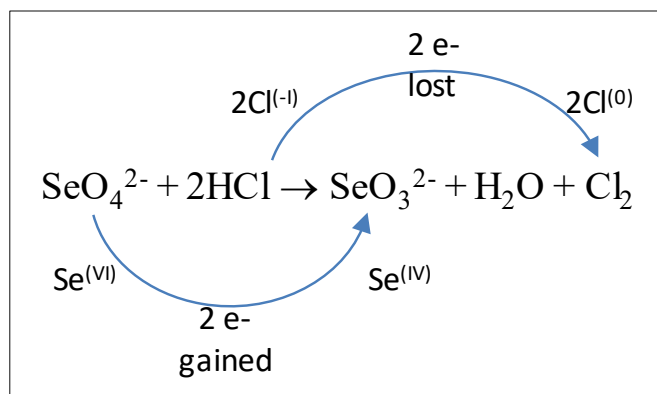


Fig. 8. Summary of reaction employed for digestion of Se sample to convert Se(VI) to Se(IV). The reduction of Se(IV) is coupled to the oxidation of chlorine. The transfer of electrons (e-) is indicated by the arrows.

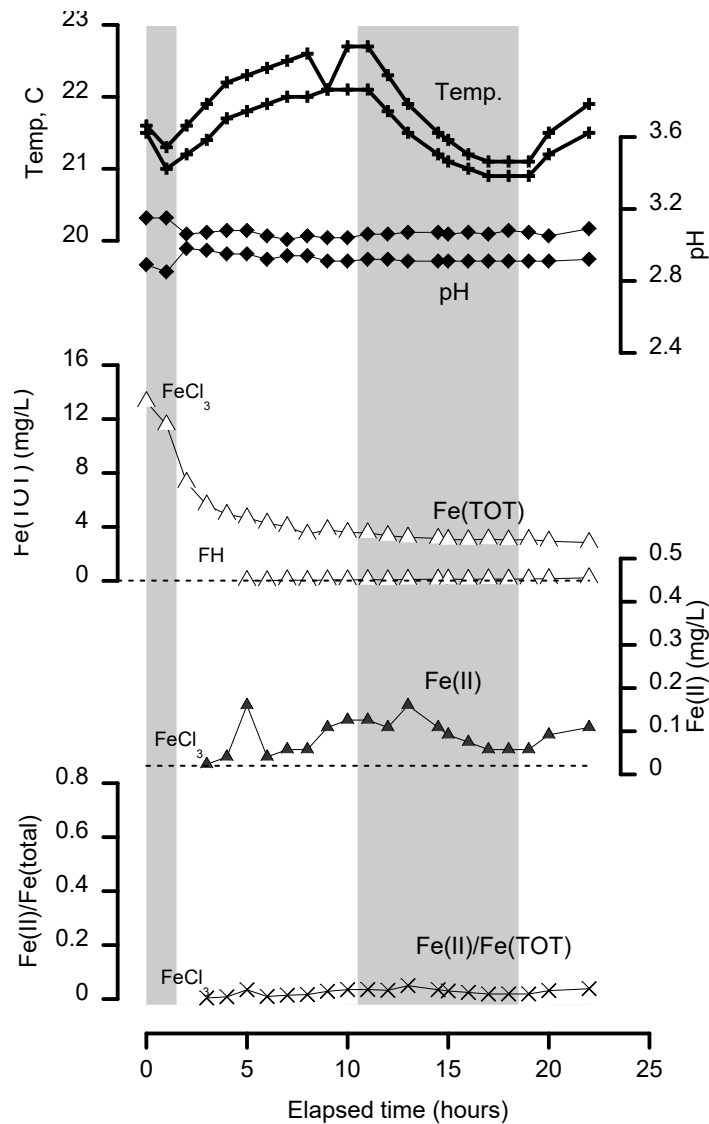


Fig. 9. Results of diel Cycle 1 for vessels containing ferrihydrite (FH) and FeCl₃ solutions. Gray shaded areas indicate when the light is turned off; dashed horizontal line illustrates the method detection limits (MDLs) for Fe(TOT) and Fe(II). There are no lines for Fe(II) and the Fe ratio for the FH vessel because the Fe concentrations were below detection. **Temp = temperature.**

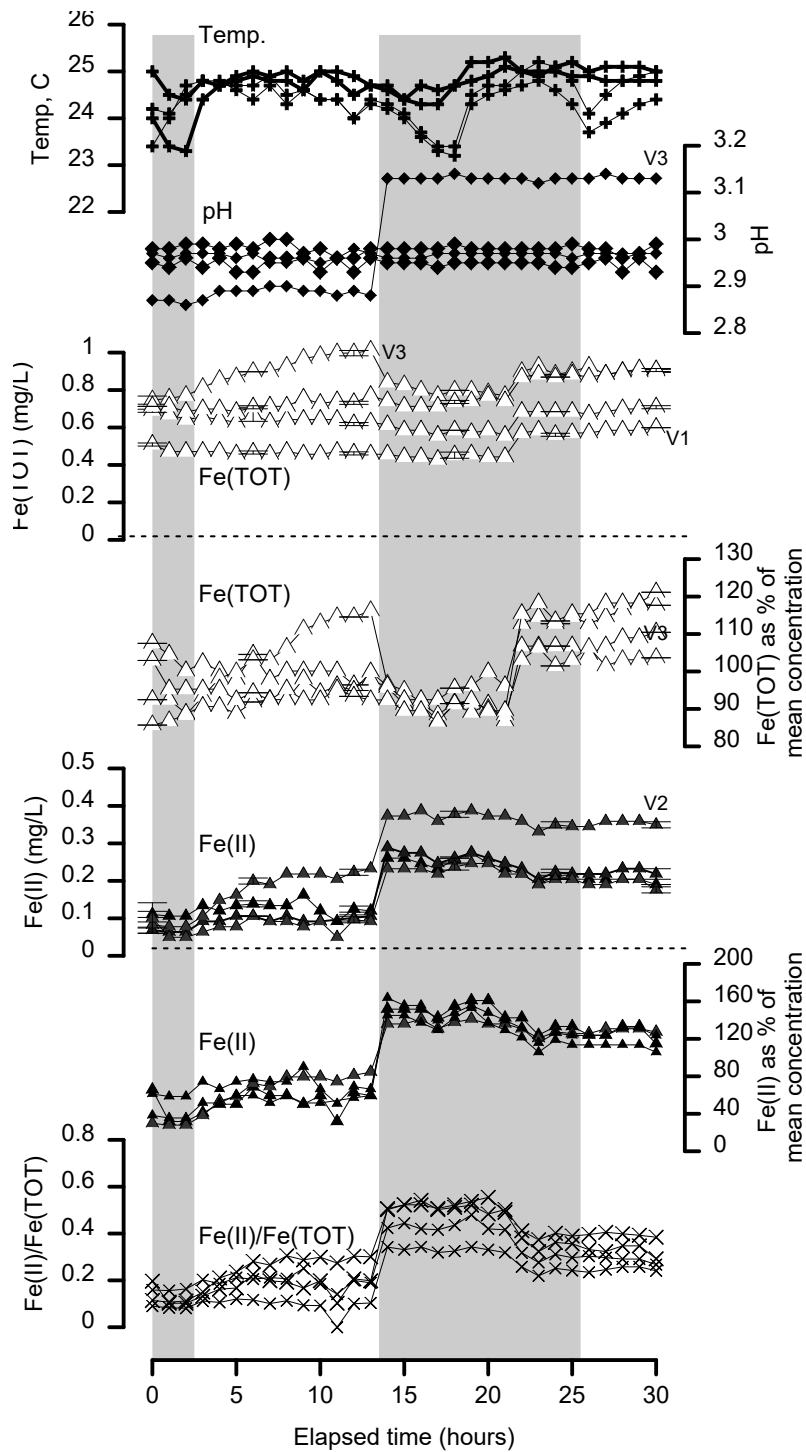


Fig. 10. Results for the Cycle 2 30-hour cycle. Shaded areas indicate when the light was off. Error bars are for the standard deviations of replicate samples. Fe concentrations are for dissolved species; Fe(TOT) is the sum of the Fe(II) and Fe(III) species. Temp = temperature; the V's indicate vessel numbers.

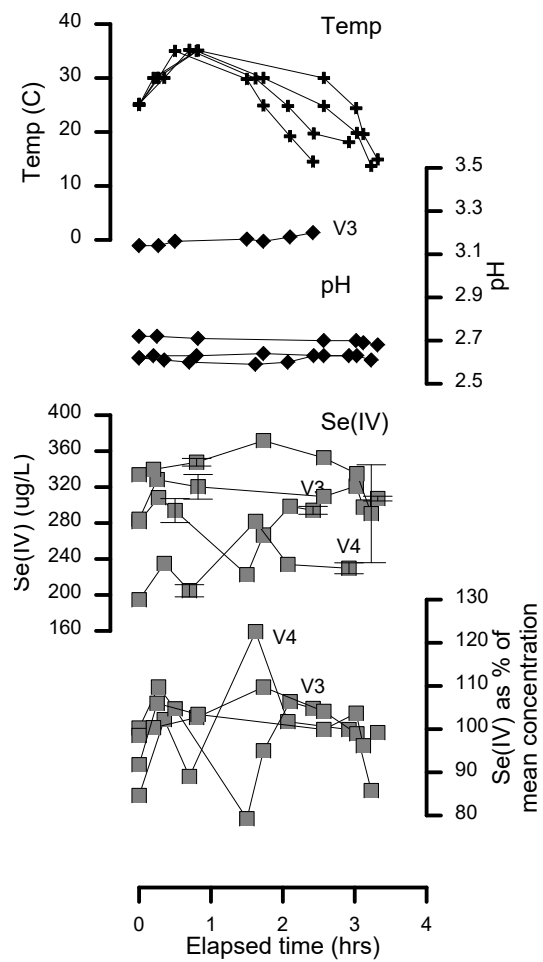


Fig. 11. Results for the Se(IV)-only Cycle 5. The experiment was completed with the lights on. Error bars are for the standard deviations of replicate samples. Temp = temperature; the V's indicate vessel numbers.

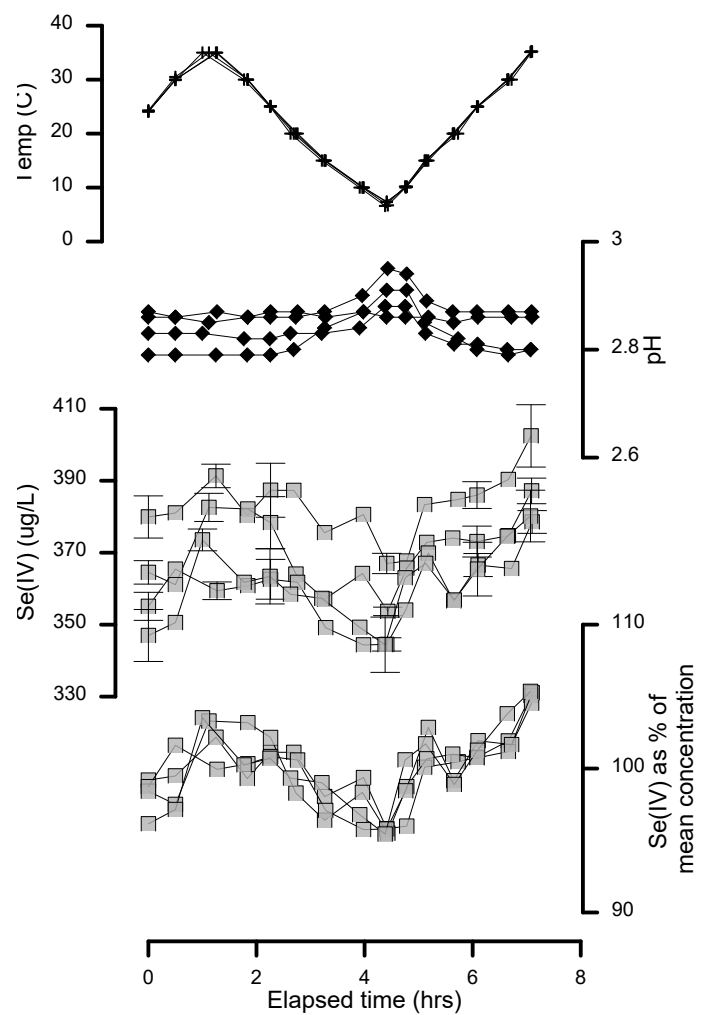


Fig. 12. Results for the Se(IV)-only Cycle 7. The experiment was completed with the lights on. Error bars are for the standard deviations of replicate samples. Temp = temperature.

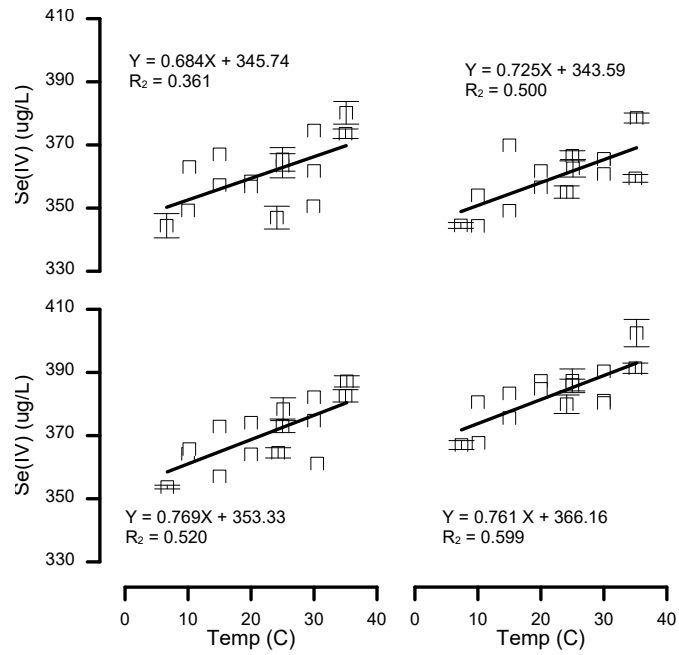


Fig. 13. Relationships between temperature and Se(IV), Cycle 7. Error bars are for the standard deviations of replicate samples. Temp = temperature.

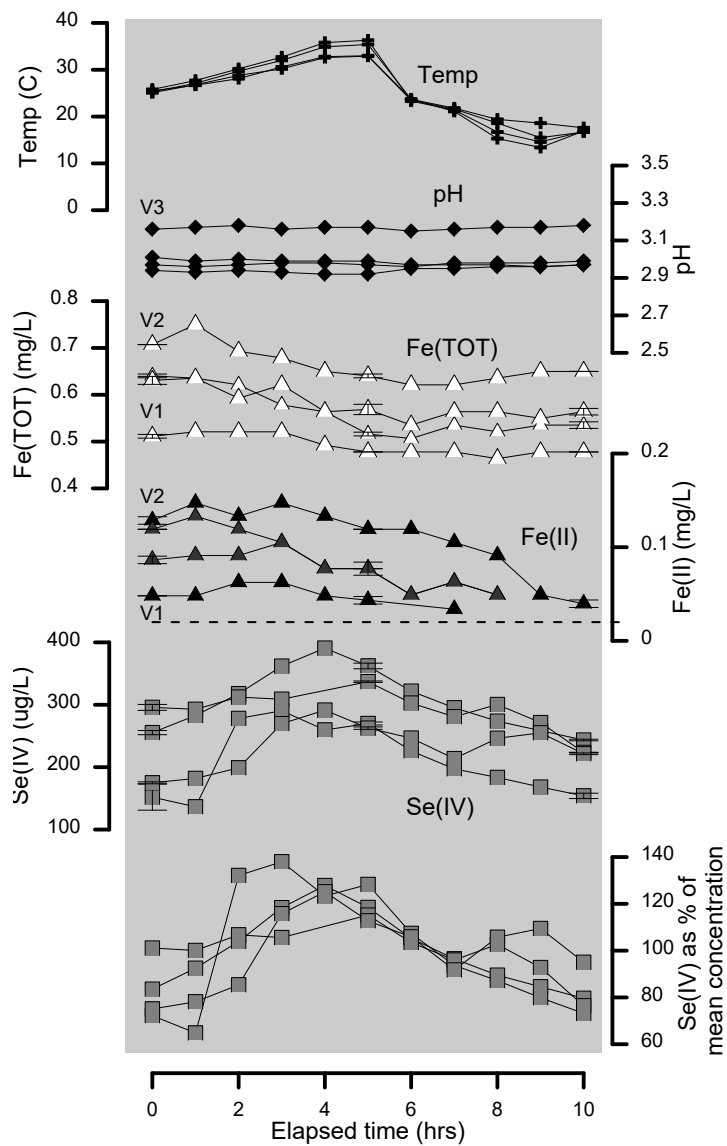


Fig. 14. Results for the Cycle 3 10-hour test conducted in the dark. Error bars are the standard deviations for replicate samples (n=3). Fe concentrations are for dissolved species; Total Fe is the sum of the Fe(II) and Fe(III) species.

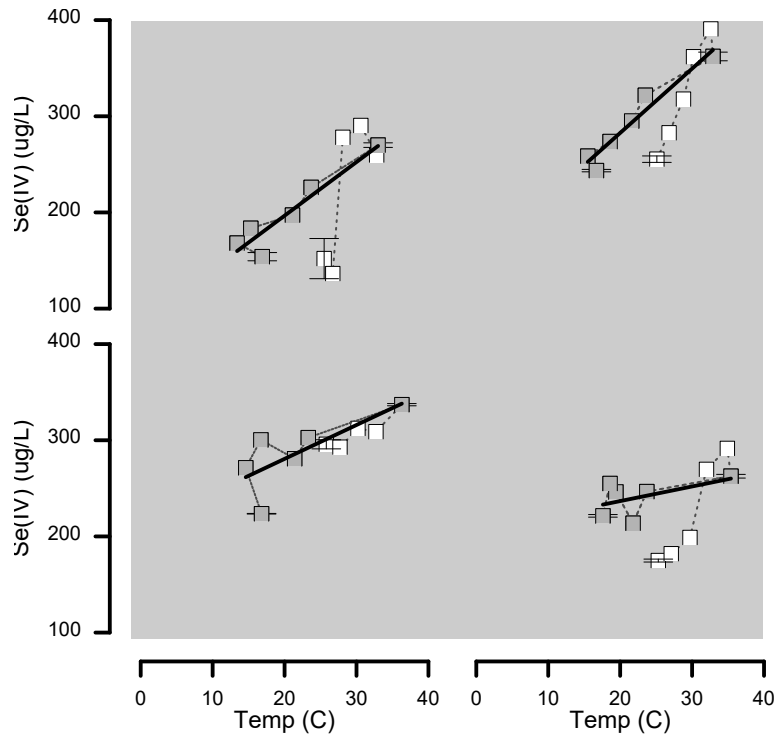


Fig. 15. Relationships between temperature and Se(IV), Cycle 3. Thick lines are regressions for shaded symbols; dashed lines are for order of samples. The solid squares indicate when the temperature is increasing and the open boxes indicate when the temperature is decreasing. These data were obtained in the dark.

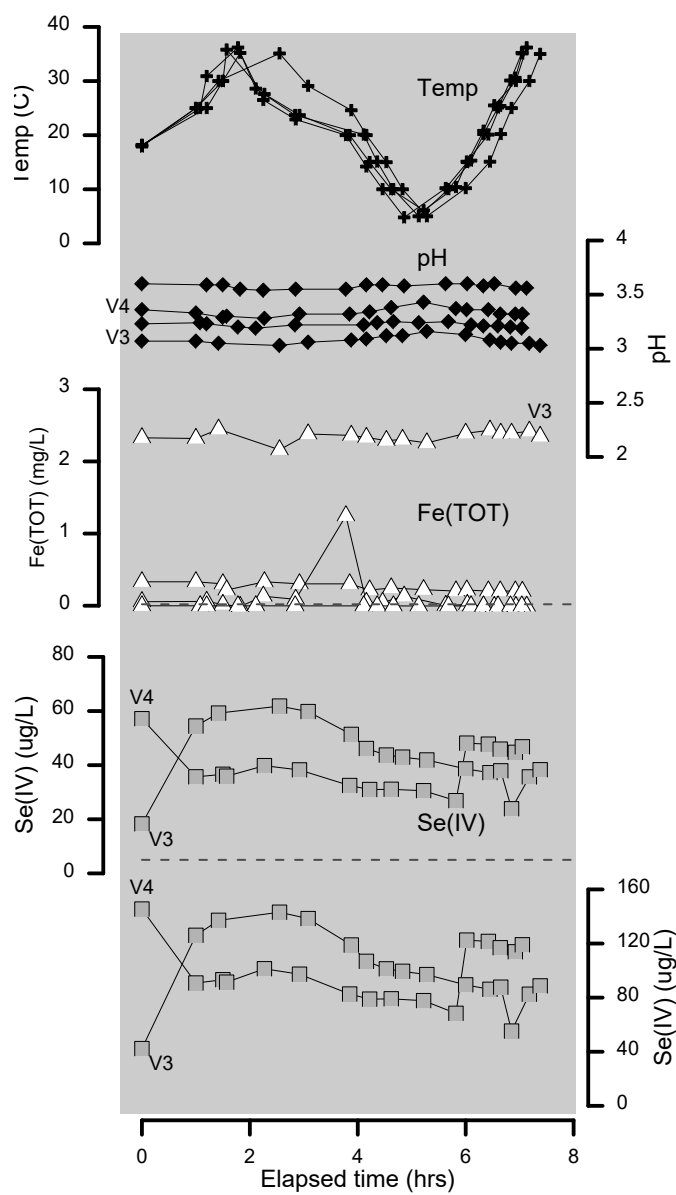


Fig. 16. Results for the Cycle 6, conducted in the dark. Fe concentrations are for dissolved (unfiltered) species; Total Fe is the sum of the Fe(II) and Fe(III) species. Temp = temperature.

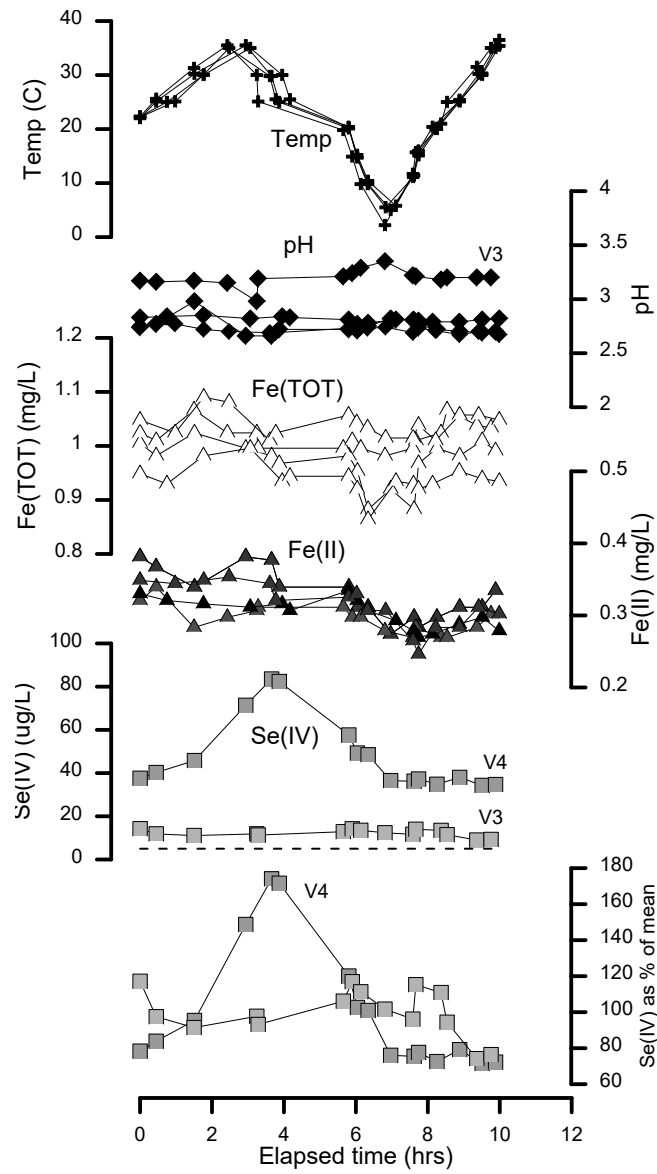


Fig. 17. Results for the Cycle 4, conducted in the light. Fe concentrations are for dissolved (unfiltered) species; Total Fe is the sum of the Fe(II) and Fe(III) species. Temp = temperature; the V's indicate vessel numbers. The dashed line for Se(IV) indicates the method detection limit (MDL).

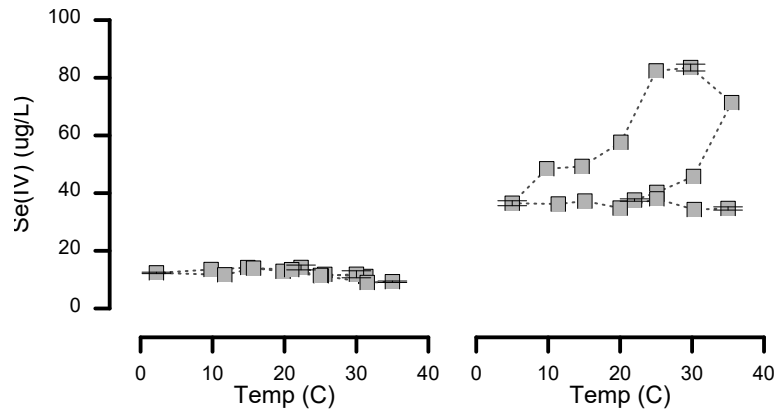


Fig. 18. Relationships between temperature and Se(IV), Cycle 4. The dashed lines indicate the order the samples were collected. Temp. = temperature.

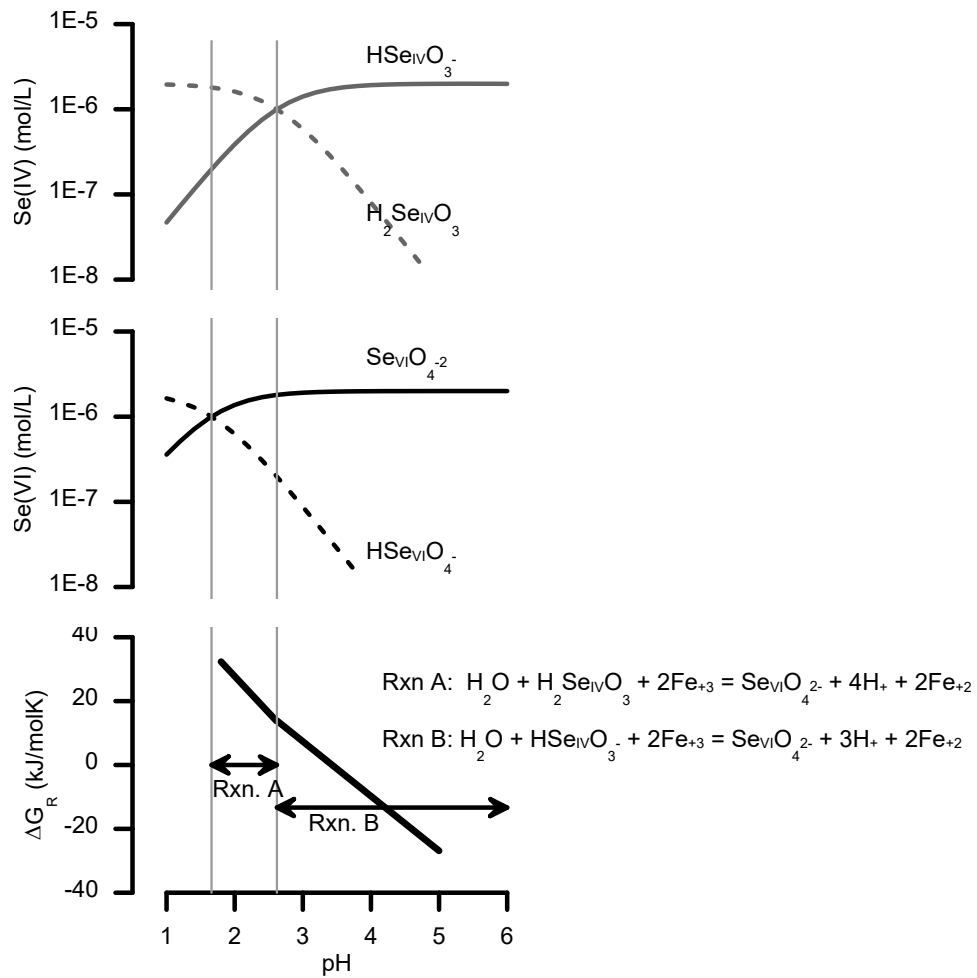


Fig. 19. Calculated using thermodynamic data from Stumm & Morgan (1996), assuming $[\text{Se(IV)}] = [\text{Se(VI)}] = 3.8 \times 10^{-6}$ mol/L and $[\text{Fe(II)}] = [\text{Fe(III)}] = 9 \times 10^{-6}$ mol/L, and that activity coefficients = 1. **Rxn = reaction.**

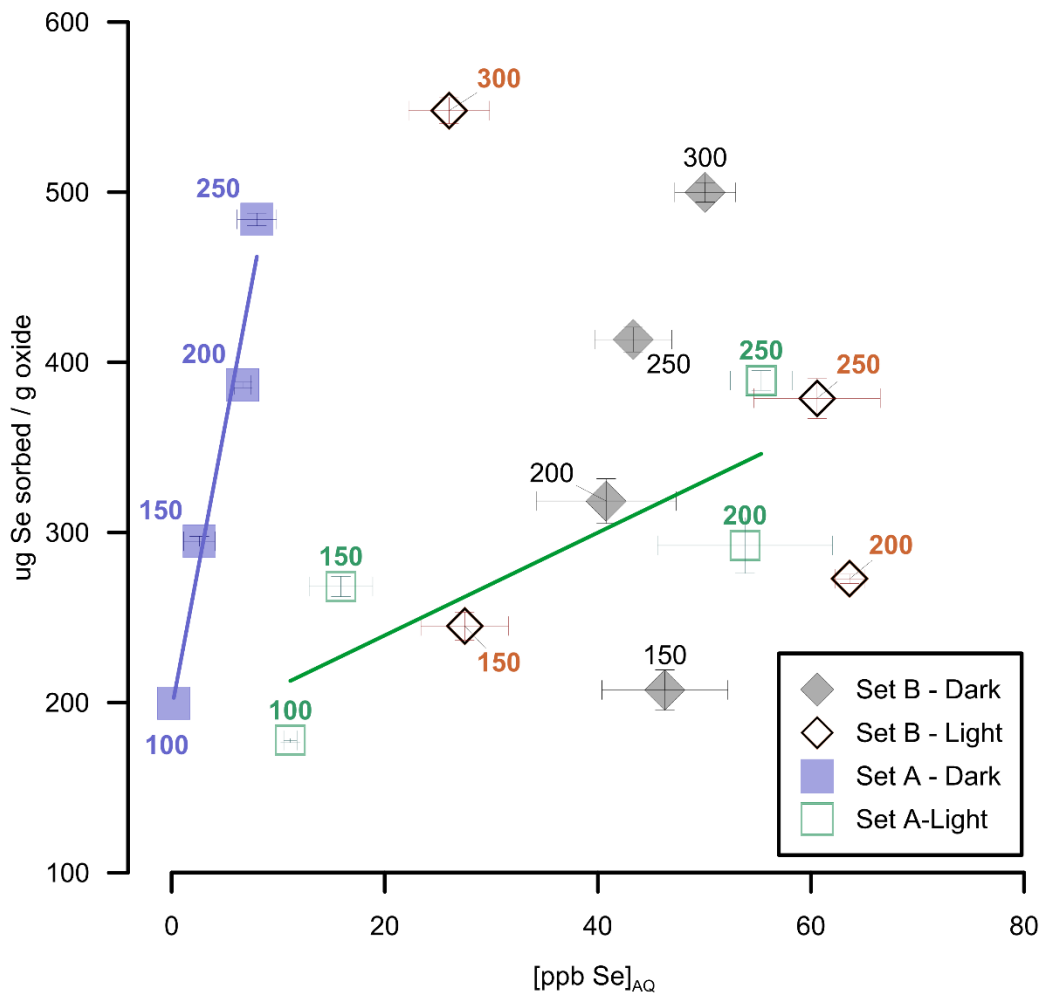


Fig. 20. Data from the sorption experiments plotted in isotherm format. Coefficients of determination (R^2) values for the linear regressions for the four data sets were 0.16 (Set B dark – line not shown), 0.12 (Set B light – line not shown), and 0.96 (Set A dark) and 0.68 (Set A light). The numbers by the symbols provide the initial concentrations. Error bars are based on the standard deviations of the replicate samples of the same initial Se(IV) concentration. The full dataset is provided in Appendix D and is summarized on Table 11.

APPENDICES

APPENDIX A. DATA TABLES FOR DIEL EXPERIMENTS

Table A-1. Data for Cycle 1 (7-22-14)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Light intensity (Lux)	Fe ^{II} (mg/L)	Fe(total) (mg/L)
Vessel 1	1	V1 - 1	0	21.5	3.15	off	0	<0.02	<0.02
	2	V1 - 2	1	21.0	3.15	off	0	<0.02	<0.02
	3	V1 - 3	2	21.2	3.06	on	3961	<0.02	<0.02
	4	V1 - 4	3	21.4	3.07	on	4133	<0.02	<0.02
	5	V1 - 5	4	21.7	3.08	on	4478	<0.02	<0.02
	6	V1 - 6	5	21.8	3.08	on	4306	<0.02	0.023
	7	V1 - 7	6	21.9	3.05	on	3961	<0.02	<0.02
	8	V1 - 8	7	22.0	3.03	on	4650	<0.02	0.075
	9	V1 - 9	8	22.0	3.05	on	4133	<0.02	0.023
	10	V1 - 10	9	22.1	3.04	on	4306	<0.02	0.075
	11	V1 - 11	10	22.1	3.04	on	4478	<0.02	0.075
	12	V1 - 12	11	22.1	3.06	on	3961	<0.02	0.092
	13	V1 - 13	12	21.8	3.06	off	0	<0.02	0.075
	14	V1 - 14	13	21.5	3.07	off	0	<0.02	0.109
	15	V1 - 15	14	21.2	3.07	off	0	<0.02	0.126
	16	V1 - 16	15	21.1	3.06	off	0	<0.02	0.126
	17	V1 - 17	16	21.0	3.07	off	0	<0.02	0.109
	18	V1 - 18	17	20.9	3.06	off	0	<0.02	0.143
	19	V1 - 19	18	20.9	3.08	off	0	<0.02	0.126
	20	V1 - 20	19	20.9	3.07	off	0	<0.02	0.143
	21	V1 - 21	20	21.2	3.05	on	4133	<0.02	0.160
	22	V1 - 22	21	21.5	3.09	on	4133	<0.02	0.228

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Concentrations with "<" indicate the analyte was not present above the detection limit

Table A-2. Data for Cycle 2 (10-17-14)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH ⁺	Light (on/off)	Light intensity (Lux)	Fe ^{II} (mg/L)	Fe(total) (mg/L)
Vessel I	1	V1 - 1a	0	25.0	2.98	off	0	0.077	0.513
	2	V1 - 1b	0	25.0	2.98	off	0	0.147	0.499
	3	V1 - 1c	0	25.0	2.98	off	0	0.077	0.513
	4	V1 - 2	1	24.5	2.98	off	0	0.048	0.471
	5	V1 - 3	2	24.4	2.99	off	0	0.048	0.471
	6	V1 - 4	3	24.8	2.99	on	3703	0.063	0.471
	7	V1 - 5	4	24.7	2.98	on	3961	0.077	0.471
	8	V1 - 6	5	24.9	2.99	on	3961	0.077	0.457
	9	V1 - 7a	6	25.0	2.98	on	3617	0.105	0.471
	10	V1 - 7b	6	25.0	2.98	on	3617	0.105	0.457
	11	V1 - 7c	6	25.0	2.98	on	3617	0.105	0.471
	12	V1 - 8	7	24.9	3.00	on	3789	0.091	0.457
	13	V1 - 9	8	25.0	3.00	on	3961	0.091	0.471
	14	V1 - 10	9	24.8	2.97	on	3703	0.077	0.457
	15	V1 - 11	10	25.0	2.98	on	3875	0.091	0.457
	16	V1 - 12	11	25.0	2.96	on	3875	0.048	0.471
	17	V1 - 13a	12	24.9	2.96	on	3875	0.091	0.457
	18	V1 - 13b	12	24.9	2.96	on	3875	0.091	0.471
	19	V1 - 13c	12	24.9	2.96	on	3875	0.105	0.457
	20	V1 - 14	13	24.7	2.98	on	3961	0.091	0.457
	21	V1 - 15	14	24.6	2.98	on	3617	0.231	0.457
	22	V1 - 16	15	24.4	2.98	off	0	0.231	0.442
	23	V1 - 17	16	24.3	2.98	off	0	0.231	0.442
	24	V1 - 18	17	24.3	2.98	off	0	0.217	0.428
	25	V1 - 19a	18	24.7	2.99	off	0	0.231	0.471
	26	V1 - 19b	18	24.7	2.99	off	0	0.245	0.442
	27	V1 - 19c	18	24.7	2.99	off	0	0.231	0.442
	28	V1 - 20	19	24.8	2.98	off	0	0.245	0.457
	29	V1 - 21	20	24.9	2.98	off	0	0.245	0.442
	30	V1 - 22	21	25.1	2.98	off	0	0.217	0.442
	31	V1 - 23	22	25.0	2.98	off	0	0.217	0.570
	32	V1 - 24	23	25.0	2.98	off	0	0.189	0.584
	33	V1 - 25a	24	25.0	2.98	off	0	0.203	0.556
	34	V1 - 25b	24	25.0	2.98	off	0	0.203	0.570
	35	V1 - 25c	24	25.0	2.98	off	0	0.203	0.556
	36	V1 - 26	25	24.9	2.99	off	0	0.203	0.570
	37	V1 - 27	26	24.9	2.98	off	0	0.189	0.570
	38	V1 - 28	27	24.8	2.98	on	3617	0.189	0.584
	39	V1 - 29	28	24.8	2.96	on	3402	0.203	0.584
	40	V1 - 30	29	24.8	2.97	on	3531	0.203	0.584
	41	V1 - 31a	30	24.8	2.99	on	3703	0.175	0.599
	42	V1 - 31b	30	24.8	2.99	on	3703	0.175	0.599
	43	V1 - 31c	30	24.8	2.99	on	3703	0.189	0.599

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Concentrations with "<" indicate the analyte was not present above the detection limit

Table A-2 Continued. Data for Cycle 2 (10-17-14)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH ⁺	Light (on/off)	Light intensity (Lux)	Fe ^{II} (mg/L)	Fe(total) (mg/L)
Vessel 2	44	V2 - 1a	0	24.0	2.95	off	0	0.077	0.712
	45	V2 - 1b	0	24.0	2.95	off	0	0.077	0.712
	46	V2 - 1c	0	24.0	2.95	off	0	0.091	0.712
	47	V2 - 2	1	23.4	2.94	off	0	0.077	0.712
	48	V2 - 3	2	23.3	2.96	off	0	0.077	0.684
	49	V2 - 4	3	24.4	2.94	on	3703	0.105	0.698
	50	V2 - 5	4	24.7	2.96	on	3961	0.147	0.698
	51	V2 - 6	5	24.8	2.93	on	3961	0.161	0.684
	52	V2 - 7a	6	24.9	2.93	on	3617	0.203	0.698
	53	V2 - 7b	6	24.9	2.93	on	3617	0.189	0.712
	54	V2 - 7c	6	24.9	2.93	on	3617	0.203	0.712
	55	V2 - 8	7	24.8	2.96	on	3789	0.189	0.712
	56	V2 - 9	8	24.8	2.96	on	3961	0.217	0.712
	57	V2 - 10	9	24.6	2.96	on	3703	0.217	0.755
	58	V2 - 11	10	25.0	2.93	on	3875	0.217	0.726
	59	V2 - 12	11	24.8	2.96	on	3875	0.203	0.741
	60	V2 - 13a	12	24.5	2.93	on	3875	0.217	0.726
	61	V2 - 13b	12	24.5	2.93	on	3875	0.217	0.726
	62	V2 - 13c	12	24.5	2.93	on	3875	0.231	0.741
	63	V2 - 14	13	24.7	2.96	on	3961	0.231	0.769
	64	V2 - 15	14	24.7	2.95	on	3617	0.372	0.741
	65	V2 - 16	15	24.4	2.95	off	0	0.372	0.712
	66	V2 - 17	16	24.7	2.95	off	0	0.386	0.712
	67	V2 - 18	17	24.6	2.94	off	0	0.358	0.712
	68	V2 - 19a	18	24.7	2.95	off	0	0.372	0.741
	69	V2 - 19b	18	24.7	2.95	off	0	0.386	0.741
	70	V2 - 19c	18	24.7	2.95	off	0	0.372	0.726
	71	V2 - 20	19	25.2	2.95	off	0	0.386	0.741
	72	V2 - 21	20	25.2	2.95	off	0	0.372	0.769
	73	V2 - 22	21	25.3	2.95	off	0	0.372	0.741
	74	V2 - 23	22	25.0	2.95	off	0	0.358	0.868
	75	V2 - 24	23	24.9	2.95	off	0	0.330	0.883
	76	V2 - 25a	24	25.1	2.94	off	0	0.344	0.868
	77	V2 - 25b	24	25.1	2.94	off	0	0.344	0.868
	78	V2 - 25c	24	25.1	2.94	off	0	0.358	0.868
	79	V2 - 26	25	25.2	2.94	off	0	0.344	0.883
80	V2 - 27	26	25.0	2.95	off	0	0.344	0.868	
81	V2 - 28	27	25.1	2.96	on	3617	0.358	0.883	
82	V2 - 29	28	25.1	2.93	on	3402	0.358	0.897	
83	V2 - 30	29	25.1	2.96	on	3531	0.358	0.911	
84	V2 - 31a	30	25.0	2.93	on	3703	0.344	0.911	
85	V2 - 31b	30	25.0	2.93	on	3703	0.344	0.911	
86	V2 - 31c	30	25.0	2.93	on	3703	0.358	0.897	

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Concentrations with "<" indicate the analyte was not present above the detection limit

Table A-2 Continued. Data for Cycle 2 (10-17-14)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH ⁺	Light (on/off)	Light intensity (Lux)	Fe ^{II} (mg/L)	Fe(total) (mg/L)
Vessel 3	87	V3 - 1a	0	23.4	2.87	off	0	0.063	0.769
	88	V3 - 1b	0	23.4	2.87	off	0	0.077	0.726
	89	V3 - 1c	0	23.4	2.87	off	0	0.063	0.741
	90	V3 - 2	1	24.0	2.87	off	0	0.063	0.755
	91	V3 - 3	2	24.7	2.86	off	0	0.063	0.769
	92	V3 - 4	3	24.8	2.87	on	3703	0.091	0.812
	93	V3 - 5	4	24.8	2.89	on	3961	0.091	0.854
	94	V3 - 6	5	24.6	2.89	on	3961	0.105	0.868
	95	V3 - 7a	6	24.4	2.89	on	3617	0.105	0.897
	96	V3 - 7b	6	24.4	2.89	on	3617	0.105	0.897
	97	V3 - 7c	6	24.4	2.89	on	3617	0.105	0.897
	98	V3 - 8	7	24.7	2.90	on	3789	0.091	0.897
	99	V3 - 9	8	24.3	2.90	on	3961	0.105	0.925
	100	V3 - 10	9	24.6	2.89	on	3703	0.091	0.968
	101	V3 - 11	10	24.4	2.89	on	3875	0.091	0.982
	102	V3 - 12	11	24.4	2.88	on	3875	<0.02	0.996
	103	V3 - 13a	12	24.0	2.89	on	3875	0.091	0.996
	104	V3 - 13b	12	24.0	2.89	on	3875	0.105	1.011
	105	V3 - 13c	12	24.0	2.89	on	3875	0.105	0.982
	106	V3 - 14	13	24.4	2.88	on	3961	0.105	1.011
	107	V3 - 15	14	24.3	3.13	on	3617	0.288	0.840
	108	V3 - 16	15	24.1	3.13	off	0	0.274	0.826
	109	V3 - 17	16	23.7	3.13	off	0	0.274	0.797
	110	V3 - 18	17	23.4	3.13	off	0	0.245	0.769
	111	V3 - 19a	18	23.4	3.14	off	0	0.259	0.797
	112	V3 - 19b	18	23.4	3.14	off	0	0.259	0.797
	113	V3 - 19c	18	23.4	3.14	off	0	0.259	0.797
	114	V3 - 20	19	24.5	3.13	off	0	0.274	0.797
	115	V3 - 21	20	24.7	3.13	off	0	0.259	0.783
116	V3 - 22	21	24.7	3.13	off	0	0.245	0.769	
117	V3 - 23	22	25.0	3.13	off	0	0.231	0.897	
118	V3 - 24	23	25.2	3.12	off	0	0.203	0.925	
119	V3 - 25a	24	25.1	3.13	off	0	0.231	0.883	
120	V3 - 25b	24	25.1	3.13	off	0	0.217	0.883	
121	V3 - 25c	24	25.1	3.13	off	0	0.217	0.883	
122	V3 - 26	25	24.8	3.13	off	0	0.217	0.897	
123	V3 - 27	26	24.1	3.13	off	0	0.217	0.925	
124	V3 - 28	27	24.5	3.14	on	3617	0.217	0.883	
125	V3 - 29	28	24.8	3.13	on	3402	0.231	0.897	
126	V3 - 30	29	24.9	3.13	on	3531	0.231	0.897	
127	V3 - 31a	30	25.0	3.13	on	3703	0.217	0.897	
128	V3 - 31b	30	25.0	3.13	on	3703	0.231	0.897	
129	V3 - 31c	30	25.0	3.13	on	3703	0.203	0.911	

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Concentrations with "<" indicate the analyte was not present above the detection limit

Table A-2 Continued. Data for Cycle 2 (10-17-14)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH ⁺	Light (on/off)	Light intensity (Lux)	Fe ^{II} (mg/L)	Fe(total) (mg/L)
Vessel 4	130	V4 - 1a	0	24.2	2.97	off	0	0.119	0.698
	131	V4 - 1b	0	24.2	2.97	off	0	0.105	0.684
	132	V4 - 1c	0	24.2	2.97	off	0	0.105	0.684
	133	V4 - 2	1	24.1	2.96	off	0	0.105	0.670
	134	V4 - 3	2	24.5	2.97	off	0	0.105	0.641
	135	V4 - 4	3	24.8	2.97	on	3703	0.133	0.655
	136	V4 - 5	4	24.7	2.97	on	3961	0.119	0.641
	137	V4 - 6	5	24.7	2.96	on	3961	0.133	0.627
	138	V4 - 7a	6	24.7	2.97	on	3617	0.133	0.641
	139	V4 - 7b	6	24.7	2.97	on	3617	0.133	0.655
	140	V4 - 7c	6	24.7	2.97	on	3617	0.147	0.712
	141	V4 - 8	7	24.9	2.95	on	3789	0.133	0.627
	142	V4 - 9	8	24.5	2.95	on	3961	0.133	0.641
	143	V4 - 10	9	24.6	2.96	on	3703	0.161	0.641
	144	V4 - 11	10	24.4	2.95	on	3875	0.119	0.641
	145	V4 - 12	11	24.4	2.96	on	3875	0.091	0.641
	146	V4 - 13a	12	24.0	2.98	on	3875	0.133	0.613
	147	V4 - 13b	12	24.0	2.98	on	3875	0.119	0.613
	148	V4 - 13c	12	24.0	2.98	on	3875	0.119	0.627
	149	V4 - 14	13	24.3	2.97	on	3961	0.119	0.627
	150	V4 - 15	14	24.2	2.96	on	3617	0.259	0.613
	151	V4 - 16	15	24.0	2.96	off	0	0.259	0.584
	152	V4 - 17	16	23.6	2.96	off	0	0.245	0.584
	153	V4 - 18	17	23.3	2.97	off	0	0.231	0.556
	154	V4 - 19a	18	23.2	2.97	off	0	0.259	0.584
	155	V4 - 19b	18	23.2	2.97	off	0	0.259	0.584
	156	V4 - 19c	18	23.2	2.97	off	0	0.245	0.584
	157	V4 - 20	19	24.3	2.97	off	0	0.274	0.570
	158	V4 - 21	20	24.5	2.97	off	0	0.245	0.584
	159	V4 - 22	21	24.6	2.97	off	0	0.231	0.556
	160	V4 - 23	22	24.7	2.97	off	0	0.217	0.684
	161	V4 - 24	23	24.8	2.97	off	0	0.189	0.684
162	V4 - 25a	24	24.6	2.97	off	0	0.217	0.684	
163	V4 - 25b	24	24.6	2.97	off	0	0.203	0.684	
164	V4 - 25c	24	24.6	2.97	off	0	0.217	0.684	
165	V4 - 26	25	24.3	2.96	off	0	0.203	0.684	
166	V4 - 27	26	23.7	2.97	off	0	0.203	0.670	
167	V4 - 28	27	23.9	2.97	on	3617	0.203	0.684	
168	V4 - 29	28	24.1	2.97	on	3402	0.203	0.698	
169	V4 - 30	29	24.3	2.97	on	3531	0.203	0.698	
170	V4 - 31a	30	24.4	2.97	on	3703	0.189	0.698	
171	V4 - 31b	30	24.4	2.97	on	3703	0.189	0.712	
172	V4 - 31c	30	24.4	2.97	on	3703	0.189	0.712	

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Concentrations with "<" indicate the analyte was not present above the detection limit

Table A-3. Data for Cycle 3 (10-25-14)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Fe ^{II} (mg/L)	Fe(total) (mg/L)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 1	1	V1 - 1a	0	25.5	2.97	off	0.048	0.507	126	---
	2	V1 - 1b	0	25.5	2.97	off	0.048	0.507	130	---
	3	V1 - 1c	0	25.5	2.97	off	0.048	0.521	200	---
	4	V1 - 2	1	26.7	2.96	off	0.048	0.521	136	---
	5	V1 - 3	2	28.1	2.97	off	0.062	0.521	278	---
	6	V1 - 4	3	30.6	2.98	off	0.062	0.521	290	---
	7	V1 - 5	4	32.8	2.98	off	0.048	0.492	260	---
	8	V1 - 6a	5	33.0	2.97	off	0.034	0.478	265	---
	9	V1 - 6b	5	33.0	2.97	off	0.048	0.478	272	---
	10	V1 - 6c	5	33.0	2.97	off	0.048	0.478	274	---
	11	V1 - 7	6	23.7	2.96	off	<0.02	0.478	226	---
	12	V1 - 8	7	21.1	2.98	off	0.034	0.478	197	---
	13	V1 - 9	8	15.3	2.98	off	<0.02	0.464	184	---
	14	V1 - 10	9	13.4	2.98	off	<0.02	0.478	168	---
	15	V1 - 11a	10	16.9	2.99	off	<0.02	0.478	145	---
	16	V1 - 11b	10	16.9	2.99	off	<0.02	0.478	162	---
	17	V1 - 11c	10	16.9	2.99	off	<0.02	0.478	154	---
Vessel 2	18	V2 - 1a	0	25.1	3.01	off	0.133	0.707	250	1673
	19	V2 - 1b	0	25.1	3.01	off	0.133	0.707	263	1701
	20	V2 - 1c	0	25.1	3.01	off	0.119	0.707	254	---
	21	V2 - 2	1	26.8	2.99	off	0.147	0.750	283	---
	22	V2 - 3	2	28.8	3.00	off	0.133	0.693	318	---
	23	V2 - 4	3	30.2	2.99	off	0.147	0.679	362	---
	24	V2 - 5	4	32.6	2.99	off	0.133	0.650	391	---
	25	V2 - 6a	5	32.9	2.99	off	0.119	0.636	353	2882
	26	V2 - 6b	5	32.9	2.99	off	0.119	0.650	362	2738
	27	V2 - 6c	5	32.9	2.99	off	0.119	0.636	371	---
	28	V2 - 7	6	23.5	2.97	off	0.119	0.621	322	---
	29	V2 - 8	7	21.6	2.97	off	0.105	0.621	295	---
	30	V2 - 9	8	18.6	2.97	off	0.091	0.636	274	---
	31	V2 - 10	9	15.5	2.96	off	0.049	0.650	259	---
	32	V2 - 11a	10	16.7	2.97	off	0.049	0.650	244	1717
	33	V2 - 11b	10	16.7	2.97	off	0.035	0.650	241	1744
	34	V2 - 11c	10	16.7	2.97	off	0.035	0.650	246	---

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

Table A-3 Continued. Data for Cycle 3 (10-25-14)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Fe ^{II} (mg/L)	Fe(total) (mg/L)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 3	35	V3 - 1a	0	25.8	3.16	off	0.119	0.636	293	---
	36	V3 - 1b	0	25.8	3.16	off	0.119	0.650	306	---
	37	V3 - 1c	0	25.8	3.16	off	0.119	0.636	288	---
	38	V3 - 2	1	27.7	3.17	off	0.133	0.636	293	---
	39	V3 - 3	2	30.2	3.18	off	0.119	0.621	312	---
	40	V3 - 4	3	32.7	3.16	off	0.105	0.578	309	---
	41	V3 - 5	4	35.8	3.17	off	0.077	0.564	520	---
	42	V3 - 6a	5	36.3	3.17	off	0.077	0.521	335	---
	43	V3 - 6b	5	36.3	3.17	off	0.077	0.521	340	---
	44	V3 - 6c	5	36.3	3.17	off	0.077	0.507	336	---
	45	V3 - 7	6	23.3	3.15	off	0.049	0.507	303	---
	46	V3 - 8	7	21.4	3.16	off	0.063	0.535	281	---
	47	V3 - 9	8	16.7	3.17	off	0.049	0.521	300	---
	48	V3 - 10	9	14.6	3.17	off	<0.02	0.535	271	---
	49	V3 - 11a	10	16.8	3.18	off	<0.02	0.535	224	---
50	V3 - 11b	10	16.8	3.18	off	<0.02	0.550	223	---	
51	V3 - 11c	10	16.8	3.18	off	<0.02	0.521	---	---	
Vessel 4	52	V4 - 1a	0	25.3	2.94	off	0.091	0.621	176	---
	53	V4 - 1b	0	25.3	2.94	off	0.077	0.650	172	---
	54	V4 - 1c	0	25.3	2.94	off	0.091	0.621	177	---
	55	V4 - 2	1	27.1	2.93	off	0.091	0.636	182	---
	56	V4 - 3	2	29.7	2.94	off	0.091	0.593	199	---
	57	V4 - 4	3	32.0	2.93	off	0.105	0.621	270	---
	58	V4 - 5	4	34.9	2.92	off	0.077	0.564	292	---
	59	V4 - 6a	5	35.4	2.92	off	0.077	0.550	259	---
	60	V4 - 6b	5	35.4	2.92	off	0.091	0.593	262	---
	61	V4 - 6c	5	35.4	2.92	off	0.063	0.564	267	---
	62	V4 - 7	6	23.7	2.95	off	0.049	0.535	247	---
	63	V4 - 8	7	21.8	2.95	off	0.063	0.564	214	---
	64	V4 - 9	8	19.4	2.96	off	0.049	0.564	246	---
	65	V4 - 10	9	18.6	2.96	off	<0.02	0.550	255	---
	66	V4 - 11a	10	17.6	2.97	off	<0.02	0.578	221	---
	67	V4 - 11b	10	16.6	2.97	off	<0.02	0.550	219	---
	68	V4 - 11c	10	15.6	2.97	off	<0.02	0.564	224	---

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "----" indicates the sample was not analyzed.

Table A-4. Data for Cycle 4 (12-9-14)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Light Intensity (Lux)	Fe ^{II} (mg/L)	Fe(total) (mg/L)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel I	1	V1 - 1a	0.0	22.2	2.75	on	3617	0.339	1.038	---	---
	2	V1 - 1b	0.0	22.2	2.75	on	3617	0.353	1.067	---	---
	3	V1 - 1c	0.0	22.2	2.75	on	3617	0.353	1.038	---	---
	4	V1 - 2a	1.0	25.1	2.77	on	3789	0.339	1.024	---	---
	5	V1 - 2b	1.0	25.1	2.77	on	3789	0.353	1.024	---	---
	6	V1 - 2c	1.0	25.1	2.77	on	3789	0.339	1.024	---	---
	7	V1 - 3a	1.8	30.1	2.72	on	3445	0.353	1.095	---	---
	8	V1 - 3b	1.8	30.1	2.72	on	3445	0.353	1.095	---	---
	9	V1 - 3c	1.8	30.1	2.72	on	3445	0.339	1.081	---	---
	10	V1 - 4a	2.5	35.0	2.70	on	3617	0.353	1.095	---	---
	11	V1 - 4b	2.5	35.0	2.70	on	3617	0.353	1.095	---	---
	12	V1 - 4c	2.5	35.0	2.70	on	3617	0.353	1.052	---	---
	13	V1 - 5a	3.6	29.8	2.69	on	3703	0.339	1.024	---	---
	14	V1 - 5b	3.6	29.8	2.69	on	3703	0.353	0.967	---	---
	15	V1 - 5c	3.6	29.8	2.69	on	3703	0.339	1.038	---	---
	16	V1 - 6a	3.8	25.5	2.69	on	3358	0.325	1.010	---	---
	17	V1 - 6b	3.8	25.5	2.69	on	3358	0.311	1.024	---	---
	18	V1 - 6c	3.8	25.5	2.69	on	3358	0.325	1.038	---	---
	19	V1 - 7a	5.8	20.4	2.73	on	3703	0.325	1.081	---	---
	20	V1 - 7b	5.8	20.4	2.73	on	3703	0.339	1.024	---	---
	21	V1 - 7c	5.8	20.4	2.73	on	3703	0.311	1.067	---	---
	22	V1 - 8a	6.0	14.9	2.71	on	3703	0.311	1.067	---	---
	23	V1 - 8b	6.0	14.9	2.71	on	3703	0.353	1.024	---	---
	24	V1 - 8c	6.0	14.9	2.71	on	3703	0.325	1.038	---	---
	25	V1 - 9a	6.3	9.8	2.73	on	3531	0.297	1.038	---	---
	26	V1 - 9b	6.3	9.8	2.73	on	3531	0.311	1.010	---	---
	27	V1 - 9c	6.3	9.8	2.73	on	3531	0.311	1.052	---	---
	28	V1 - 10a	6.8	5.5	2.74	on	3617	0.311	1.024	---	---
	29	V1 - 10b	6.8	5.5	2.74	on	3617	0.311	0.996	---	---
	30	V1 - 10c	6.8	5.5	2.74	on	3617	0.297	1.024	---	---
	31	V1 - 11a	7.6	11.1	2.69	on	3703	0.269	1.010	---	---
	32	V1 - 11b	7.6	11.1	2.69	on	3703	0.255	1.024	---	---
	33	V1 - 11c	7.6	11.1	2.69	on	3703	0.269	1.010	---	---
	34	V1 - 12a	7.7	15.6	2.73	on	3531	0.269	1.024	---	---
	35	V1 - 12b	7.7	15.6	2.73	on	3531	0.227	1.038	---	---
	36	V1 - 12c	7.7	15.6	2.73	on	3531	0.241	1.052	---	---
	37	V1 - 13a	8.2	20.0	2.71	on	3445	0.283	0.996	---	---
	38	V1 - 13b	8.2	20.0	2.71	on	3445	0.269	1.024	---	---
	39	V1 - 13c	8.2	20.0	2.71	on	3445	0.297	1.010	---	---
	40	V1 - 14a	8.9	25.4	2.67	on	3445	0.283	1.081	---	---
	41	V1 - 14b	8.9	25.4	2.67	on	3445	0.283	1.052	---	---
	42	V1 - 14c	8.9	25.4	2.67	on	3445	0.283	1.038	---	---
	43	V1 - 15a	9.4	30.2	2.70	on	3445	0.325	1.067	---	---
	44	V1 - 15b	9.4	30.2	2.70	on	3445	0.297	1.038	---	---
	45	V1 - 15c	9.4	30.2	2.70	on	3445	0.311	1.067	---	---
	46	V1 - 16a	10.0	36.5	2.67	on	3358	0.297	1.010	---	---
	47	V1 - 16b	10.0	36.5	2.67	on	3358	0.297	1.067	---	---
	48	V1 - 16c	10.0	36.5	2.67	on	3358	0.311	1.067	---	---

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

Table A-4 Continued. Data for Cycle 4 (12-9-14)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Light Intensity (Lux)	Fe ^{II} (mg/L)	Fe(total) (mg/L)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 2	49	V2 - 1a	0.0	22.3	2.83	on	3617	0.325	0.939	---	---
	50	V2 - 1a	0.0	22.3	2.83	on	3617	0.325	0.953	---	---
	51	V2 - 1a	0.0	22.3	2.83	on	3617	0.339	0.953	---	---
	52	V2 - 2a	0.8	25.0	2.84	on	3789	0.311	0.939	---	---
	53	V2 - 2b	0.8	25.0	2.84	on	3789	0.325	0.925	---	---
	54	V2 - 2c	0.8	25.0	2.84	on	3789	0.325	0.925	---	---
	55	V2 - 3a	1.8	30.0	2.85	on	3445	0.311	0.967	---	---
	56	V2 - 3b	1.8	30.0	2.85	on	3445	0.311	0.996	---	---
	57	V2 - 3c	1.8	30.0	2.85	on	3445	0.325	0.982	---	---
	58	V2 - 4a	3.1	35.0	2.82	on	3617	0.297	0.996	---	---
	59	V2 - 4b	3.1	35.0	2.82	on	3617	0.311	1.010	---	---
	60	V2 - 4c	3.1	35.0	2.82	on	3617	0.325	0.982	---	---
	61	V2 - 5a	4.0	30.0	2.84	on	3703	0.311	0.939	---	---
	62	V2 - 5b	4.0	30.0	2.84	on	3703	0.311	0.939	---	---
	63	V2 - 5c	4.0	30.0	2.84	on	3703	0.325	0.925	---	---
	64	V2 - 6a	4.2	25.5	2.83	on	3358	0.311	0.939	---	---
	65	V2 - 6b	4.2	25.5	2.83	on	3358	0.311	0.953	---	---
	66	V2 - 6c	4.2	25.5	2.83	on	3358	0.297	0.939	---	---
	67	V2 - 7a	5.8	20.3	2.81	on	3703	0.339	0.953	---	---
	68	V2 - 7b	5.8	20.3	2.81	on	3703	0.325	0.953	---	---
	69	V2 - 7c	5.8	20.3	2.81	on	3703	0.339	0.925	---	---
	70	V2 - 8a	6.0	15.2	2.77	on	3703	0.325	0.911	---	---
	71	V2 - 8b	6.0	15.2	2.77	on	3703	0.311	0.925	---	---
	72	V2 - 8c	6.0	15.2	2.77	on	3703	0.325	0.925	---	---
	73	V2 - 9a	6.3	10.4	2.78	on	3531	0.325	0.882	---	---
	74	V2 - 9b	6.3	10.4	2.78	on	3531	0.297	0.840	---	---
	75	V2 - 9c	6.3	10.4	2.78	on	3531	0.297	0.868	---	---
	76	V2 - 10a	7.1	5.8	2.81	on	3617	0.297	0.925	---	---
	77	V2 - 10b	7.1	5.8	2.81	on	3617	0.283	0.911	---	---
	78	V2 - 10c	7.1	5.8	2.81	on	3617	0.297	0.967	---	---
	79	V2 - 11a	7.6	11.6	2.81	on	3703	0.297	0.939	---	---
	80	V2 - 11b	7.6	11.6	2.81	on	3703	0.269	0.925	---	---
	81	V2 - 11c	7.6	11.6	2.81	on	3703	0.269	0.925	---	---
	82	V2 - 12a	7.7	16.0	2.80	on	3531	0.255	0.939	---	---
	83	V2 - 12b	7.7	16.0	2.80	on	3531	0.269	0.911	---	---
	84	V2 - 12c	7.7	16.0	2.80	on	3531	0.283	0.911	---	---
85	V2 - 13a	8.1	20.4	2.79	on	3445	0.283	0.953	---	---	
86	V2 - 13b	8.1	20.4	2.79	on	3445	0.269	0.925	---	---	
87	V2 - 13c	8.1	20.4	2.79	on	3445	0.269	0.911	---	---	
88	V2 - 14a	8.9	25.2	2.79	on	3445	0.297	0.953	---	---	
89	V2 - 14b	8.9	25.2	2.79	on	3445	0.283	0.953	---	---	
90	V2 - 14c	8.9	25.2	2.79	on	3445	0.283	0.953	---	---	
91	V2 - 15a	9.5	30.0	2.81	on	3445	0.297	0.939	---	---	
92	V2 - 15b	9.5	30.0	2.81	on	3445	0.283	0.939	---	---	
93	V2 - 15c	9.5	30.0	2.81	on	3445	0.311	0.939	---	---	
94	V2 - 16a	10.0	35.4	2.82	on	3358	0.283	0.967	---	---	
95	V2 - 16b	10.0	35.4	2.82	on	3358	0.255	0.953	---	---	
96	V2 - 16c	10.0	35.4	2.82	on	3358	0.297	0.882	---	---	

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "----" indicates the sample was not analyzed.

Table A-4 Continued. Data for Cycle 4 (12-9-14)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Light Intensity (Lux)	Fe ^{II} (mg/L)	Fe(total) (mg/L)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 3	97	V3 - 1a	0.0	22.3	3.17	on	3617	0.311	1.024	15.6	85.1
	98	V3 - 1b	0.0	22.3	3.17	on	3617	0.325	1.024	14.7	---
	99	V3 - 1c	0.0	22.3	3.17	on	3617	0.325	1.024	12.4	---
	100	V3 - 2	0.5	25.6	3.16	on	3789	0.339	1.010	11.8	---
	101	V3 - 3	1.5	31.3	3.17	on	3445	0.283	1.067	11.1	---
	102	V3 - 4	2.4	35.5	3.15	on	3617	0.297	1.024	81.5	---
	103	V3 - 5a	3.3	30.0	2.98	on	3703	0.325	1.024	10.3	68.1
	104	V3 - 5b	3.3	30.0	2.98	on	3703	0.297	1.024	10.6	66.6
	105	V3 - 5c	3.3	30.0	2.98	on	3703	0.297	1.024	14.7	65.6
	106	V3 - 6	3.3	25.1	3.19	on	3358	0.311	0.996	11.3	---
	107	V3 - 7	5.7	19.8	3.21	on	3703	0.311	0.996	12.9	---
	108	V3 - 8	5.9	14.9	3.24	on	3703	0.297	1.010	14.2	---
	109	V3 - 9	6.1	9.8	3.29	on	3531	0.297	0.996	13.5	---
	110	V3 - 10a	6.8	2.2	3.35	on	3617	0.283	0.982	11.8	57.0
	111	V3 - 10b	6.8	2.2	3.35	on	3617	0.283	0.982	12.8	---
	112	V3 - 10c	6.8	2.2	3.35	on	3617	0.269	0.982	12.4	---
	113	V3 - 11	7.6	11.7	3.22	on	3703	0.269	0.996	11.7	---
	114	V3 - 12	7.7	15.7	3.21	on	3531	0.283	1.010	14.0	---
	115	V3 - 13	8.4	21.0	3.18	on	3445	0.269	1.024	13.5	---
	116	V3 - 14	8.5	25.0	3.20	on	3445	0.269	1.067	11.5	---
117	V3 - 15	9.4	31.5	3.20	on	3445	0.283	1.038	9.00	---	
118	V3 - 16a	9.8	35.0	3.20	on	3358	0.311	1.038	9.63	57.0	
119	V3 - 16b	9.8	35.0	3.20	on	3358	0.297	1.052	8.92	56.6	
120	V3 - 16c	9.8	35.0	3.20	on	3358	0.297	1.010	<5	57.9	

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "----" indicates the sample was not analyzed.

Table A-4 Continued. Data for Cycle 4 (12-9-14)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Light Intensity (Lux)	Fe ^{II} (mg/L)	Fe(total) (mg/L)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 4	121	V4 - 1a	0.0	22.0	2.74	on	3617	0.381	1.010	<5	218
	122	V4 - 1b	0.0	22.0	2.74	on	3617	0.381	1.010	38.2	---
	123	V4 - 1c	0.0	22.0	2.74	on	3617	0.381	0.996	37.0	---
	124	V4 - 2	0.5	25.1	2.77	on	3789	0.367	0.982	40.3	---
	125	V4 - 3	1.5	30.2	2.98	on	3445	0.339	1.024	45.8	---
	126	V4 - 4	2.9	35.5	2.66	on	3617	0.381	0.996	71.4	---
	127	V4 - 5a	3.7	29.8	2.66	on	3703	0.395	0.982	84.7	484
	128	V4 - 5b	3.7	29.8	2.66	on	3703	0.381	0.967	80.8	488
	129	V4 - 5c	3.7	29.8	2.66	on	3703	0.353	0.996	85.1	484
	130	V4 - 6	3.9	25.0	2.72	on	3358	0.339	0.967	82.4	---
	131	V4 - 7	5.8	20.1	2.72	on	3703	0.339	0.982	57.6	---
	132	V4 - 8	6.0	14.7	2.71	on	3703	0.311	0.953	49.3	---
	133	V4 - 9	6.3	9.8	2.75	on	3531	0.311	0.882	48.4	---
	134	V4 - 10a	7.0	5.0	2.82	on	3617	0.283	0.925	34.9	201
135	V4 - 10b	7.0	5.0	2.82	on	3617	0.283	0.939	36.3	---	
136	V4 - 10c	7.0	5.0	2.82	on	3617	0.255	0.897	38.3	---	
137	V4 - 11	7.6	11.4	2.80	on	3703	0.297	0.882	36.2	---	
138	V4 - 12	7.7	15.1	2.76	on	3531	0.283	0.967	37.3	---	
139	V4 - 13	8.3	20.0	2.72	on	3445	0.297	0.996	34.8	---	
140	V4 - 14	8.9	25.1	2.70	on	3445	0.311	0.982	38.0	---	
141	V4 - 15	9.5	30.3	2.69	on	3445	0.311	1.010	34.3	---	
142	V4 - 16a	9.9	35.0	2.70	on	3358	0.339	0.996	33.5	176	
143	V4 - 16b	9.9	35.0	2.70	on	3358	0.339	0.967	35.7	191	
144	V4 - 16c	9.9	35.0	2.70	on	3358	0.325	1.010	34.9	182	

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

Table A-5. Data for Cycle 5 (1-29-15)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Light Intensity (Lux)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 1	1	V1 - 1	0.0	25.0	2.72	on	1432	284	---
	2	V1 - 2	0.3	30.0	2.72	on	1437	328	---
	3	V1 - 3a	0.8	35.1	2.71	on	1335	333	---
	4	V1 - 3b	0.8	35.1	2.71	on	1335	306	---
	5	V1 - 3c	0.8	35.1	2.71	on	1335	321	---
	6	V1 - 4	2.6	30.0	2.70	on	1238	309	---
	7	V1 - 5	3.0	24.4	2.70	on	1243	321	---
	8	V1 - 6	3.1	19.6	2.69	on	1173	298	---
	9	V1 - 7a	3.3	14.9	2.68	on	1211	309	---
	10	V1 - 7b	3.3	14.9	2.68	on	1211	305	---
Vessel 2	11	V2 - 1	0.0	25.0	2.62	on	1432	334	---
	12	V2 - 2	0.2	30.0	2.63	on	1437	340	---
	13	V2 - 3a	0.8	35.0	2.63	on	1335	343	---
	14	V2 - 3b	0.8	35.0	2.63	on	1335	348	---
	15	V2 - 3c	0.8	35.0	2.63	on	1335	352	---
	16	V2 - 4	1.7	30.0	2.64	on	1238	372	---
	17	V2 - 5	2.6	24.8	2.63	on	1243	352	---
	18	V2 - 6	3.0	19.8	2.63	on	1173	335	---
	19	V2 - 7a	3.2	13.7	2.61	on	1211	329	---
	20	V2 - 7b	3.2	13.7	2.61	on	1211	252	---
Vessel 3	21	V3 - 1	0.0	25.0	3.14	on	1432	281	---
	22	V3 - 2	0.3	30.0	3.14	on	1437	308	---
	23	V3 - 3a	0.5	35.0	3.16	on	1335	309	---
	24	V3 - 3b	0.5	35.0	3.16	on	1335	285	---
	25	V3 - 3c	0.5	35.0	3.16	on	1335	288	---
	26	V3 - 4	1.5	29.8	3.17	on	1238	222	---
	27	V3 - 5	1.7	24.9	3.16	on	1243	267	---
	28	V3 - 6	2.1	19.2	3.18	on	1173	299	---
	29	V3 - 7a	2.4	14.5	3.20	on	1211	291	---
	30	V3 - 7b	2.4	14.5	3.20	on	1211	297	---
Vessel 4	31	V4 - 1	0.0	25.2	2.62	on	1432	195	---
	32	V4 - 2	0.4	30.0	2.61	on	1437	235	---
	33	V4 - 3a	0.7	35.2	2.60	on	1335	202	---
	34	V4 - 3b	0.7	35.2	2.60	on	1335	199	---
	35	V4 - 3c	0.7	35.2	2.60	on	1335	212	---
	36	V4 - 4	1.6	29.9	2.59	on	1238	282	---
	37	V4 - 5	2.1	24.8	2.60	on	1243	234	---
	38	V4 - 6	2.4	19.7	2.63	on	1173	---	---
	39	V4 - 7a	2.9	18.1	2.63	on	1211	225	---
	40	V4 - 7b	2.9	18.1	2.63	on	1211	234	---

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

Table A-6. Data for Cycle 6 (2-28-15)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Fe ^{II} (mg/L)	Fe(total) (mg/L)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 1	1	V1 - 1a	0.0	18.1	3.19	off	<0.02	0.346	---	---
	2	V1 - 1b	0.0	18.1	3.19	off	<0.02	0.317	---	---
	3	V1 - 1c	0.0	18.1	3.19	off	<0.02	0.332	---	---
	4	V1 - 2	1.1	25.0	3.20	off	<0.02	0.332	---	---
	5	V1 - 3	1.2	30.9	3.19	off	<0.02	0.303	---	---
	6	V1 - 4	1.8	36.2	3.16	off	<0.02	0.217	---	---
	7	V1 - 5a	2.1	28.6	3.15	off	<0.02	0.317	---	---
	8	V1 - 5b	2.1	28.6	3.15	off	<0.02	0.317	---	---
	9	V1 - 5c	2.1	28.6	3.15	off	<0.02	0.360	---	---
	10	V1 - 6	2.8	23.7	3.18	off	<0.02	0.303	---	---
	11	V1 - 7	4.1	20.1	3.18	off	<0.02	0.303	---	---
	12	V1 - 8	4.4	15.1	3.20	off	<0.02	0.217	---	---
	13	V1 - 9	4.7	10.0	3.21	off	<0.02	0.246	---	---
	14	V1 - 10a	5.1	5.0	3.20	off	<0.02	0.217	---	---
	15	V1 - 10b	5.1	5.0	3.20	off	<0.02	0.217	---	---
	16	V1 - 10c	5.1	5.0	3.20	off	<0.02	0.232	---	---
	17	V1 - 11	5.7	10.0	3.21	off	<0.02	0.203	---	---
	18	V1 - 12	6.1	15.3	3.18	off	<0.02	0.217	---	---
	19	V1 - 13	6.3	20.2	3.17	off	<0.02	0.203	---	---
	20	V1 - 14	6.6	25.1	3.17	off	<0.02	0.203	---	---
	21	V1 - 15	6.8	30.1	3.16	off	<0.02	0.203	---	---
	22	V1 - 16a	7.0	35.2	3.15	off	<0.02	0.189	---	---
	23	V1 - 16b	7.0	35.2	3.15	off	<0.02	0.203	---	---
	24	V1 - 16c	7.0	35.2	3.15	off	<0.02	0.203	---	---

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

Table A-6 Continued. Data for Cycle 6 (2-28-15)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Fe ^{II} (mg/L)	Fe(total) (mg/L)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 2	25	V2 - 1a	0.0	18.2	3.60	off	<0.02	0.046	---	---
	26	V2 - 1b	0.0	18.2	3.60	off	<0.02	0.060	---	---
	27	V2 - 1c	0.0	18.2	3.60	off	<0.02	0.060	---	---
	28	V2 - 2	1.2	25.0	3.59	off	<0.02	0.060	---	---
	29	V2 - 3	1.5	30.0	3.59	off	<0.02	<0.02	---	---
	30	V2 - 4	1.8	35.2	3.55	off	<0.02	<0.02	---	---
	31	V2 - 5a	2.3	26.5	3.54	off	<0.02	<0.02	---	---
	32	V2 - 5b	2.3	26.5	3.54	off	<0.02	0.117	---	---
	33	V2 - 5c	2.3	26.5	3.54	off	<0.02	0.146	---	---
	34	V2 - 6	2.9	22.9	3.55	off	<0.02	0.089	---	---
	35	V2 - 7	3.8	20.0	3.55	off	<0.02	1.246	---	---
	36	V2 - 8	4.2	14.2	3.59	off	<0.02	0.046	---	---
	37	V2 - 9	4.5	10.0	3.59	off	<0.02	0.046	---	---
	38	V2 - 10a	4.9	4.8	3.58	off	<0.02	0.060	---	---
	39	V2 - 10b	4.9	4.8	3.58	off	<0.02	0.260	---	---
	40	V2 - 10c	4.9	4.8	3.58	off	<0.02	0.074	---	---
	41	V2 - 11	5.6	10.2	3.60	off	<0.02	<0.02	---	---
	42	V2 - 12	6.0	15.0	3.60	off	<0.02	<0.02	---	---
43	V2 - 13	6.3	20.8	3.58	off	<0.02	<0.02	---	---	
44	V2 - 14	6.5	25.5	3.60	off	<0.02	<0.02	---	---	
45	V2 - 15	6.9	30.0	3.56	off	<0.02	<0.02	---	---	
46	V2 - 16a	7.1	36.2	3.56	off	<0.02	<0.02	---	---	
47	V2 - 16b	7.1	36.2	3.56	off	<0.02	<0.02	---	---	
48	V2 - 16c	7.1	36.2	3.56	off	<0.02	<0.02	---	---	

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

Table A-6 Continued. Data for Cycle 6 (2-28-15)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Fe ^{II} (mg/L)	Fe(total) (mg/L)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 3	49	V3 - 1a	0.0	17.9	3.07	off	<0.02	2.318	10.15	---
	50	V3 - 1b	0.0	17.9	3.07	off	<0.02	2.347	9.16	---
	51	V3 - 1c	0.0	17.9	3.07	off	<0.02	2.318	35.5	---
	52	V3 - 2	1.0	25.0	3.07	off	<0.02	2.318	54.5	23.11
	53	V3 - 3	1.4	30.0	3.05	off	<0.02	2.447	59.2	---
	54	V3 - 4	2.6	35.1	3.03	off	<0.02	2.161	61.8	35.58
	55	V3 - 5a	3.1	29.1	3.06	off	<0.02	2.318	60.3	---
	56	V3 - 5b	3.1	29.1	3.06	off	<0.02	2.389	60.0	---
	57	V3 - 5c	3.1	29.1	3.06	off	<0.02	2.432	59.1	---
	58	V3 - 6	3.9	24.6	3.08	off	<0.02	2.361	51.4	---
	59	V3 - 7	4.2	20.0	3.09	off	<0.02	2.332	46.1	---
	60	V3 - 8	4.5	15.0	3.12	off	<0.02	2.289	43.7	---
	61	V3 - 9	4.8	10.0	3.12	off	<0.02	2.304	43.0	---
	62	V3 - 10a	5.3	5.0	3.16	off	<0.02	2.247	43.1	8.38
	63	V3 - 10b	5.3	5.0	3.16	off	<0.02	2.247	42.0	---
	64	V3 - 10c	5.3	5.0	3.16	off	<0.02	2.275	40.6	---
	65	V3 - 11	6.0	10.2	3.13	off	<0.02	2.389	38.6	---
	66	V3 - 12	6.5	15.1	3.08	off	<0.02	2.432	37.2	---
	67	V3 - 13	6.7	20.2	3.06	off	<0.02	2.389	37.9	---
	68	V3 - 14	6.9	25.0	3.05	off	<0.02	2.389	23.9	---
	69	V3 - 15	7.2	30.0	3.05	off	<0.02	2.418	35.6	---
	70	V3 - 16a	7.4	35.0	3.03	off	<0.02	2.361	37.8	<5
	71	V3 - 16b	7.4	35.0	3.03	off	<0.02	2.289	37.3	---
	72	V3 - 16c	7.4	35.0	3.03	off	<0.02	2.389	39.8	---

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

Table A-6 Continued. Data for Cycle 6 (2-28-15)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Fe ^{II} (mg/L)	Fe(total) (mg/L)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 4	73	V4 - 1a	0.0	18.1	3.36	off	<0.02	0.346	57.2	---
	74	V4 - 1b	0.0	18.1	3.36	off	<0.02	0.317	54.5	---
	75	V4 - 1c	0.0	18.1	3.36	off	<0.02	0.332	59.8	---
	76	V4 - 2	1.0	25.0	3.33	off	<0.02	0.332	35.7	<5
	77	V4 - 3	1.5	30.0	3.29	off	<0.02	0.303	36.6	---
	78	V4 - 4	1.6	35.8	3.30	off	<0.02	0.217	35.9	<5
	79	V4 - 5a	2.3	27.6	3.28	off	<0.02	0.317	41.9	---
	80	V4 - 5b	2.3	27.6	3.28	off	<0.02	0.317	38.7	---
	81	V4 - 5c	2.3	27.6	3.28	off	<0.02	0.360	38.9	---
	82	V4 - 6	2.9	23.7	3.32	off	<0.02	0.303	38.2	---
	83	V4 - 7	3.9	20.0	3.32	off	<0.02	0.303	32.5	---
	84	V4 - 8	4.2	15.0	3.34	off	<0.02	0.217	31.0	---
	85	V4 - 9	4.6	10.0	3.38	off	<0.02	0.246	31.1	---
	86	V4 - 10a	5.2	6.1	3.43	off	<0.02	0.217	30.5	<5
	87	V4 - 10b	5.2	6.1	3.43	off	<0.02	0.217	30.5	---
	88	V4 - 10c	5.2	6.1	3.43	off	<0.02	0.232	30.7	---
	89	V4 - 11	5.8	10.4	3.37	off	<0.02	0.203	26.9	---
	90	V4 - 12	6.0	15.1	3.36	off	<0.02	0.217	48.1	---
	91	V4 - 13	6.4	20.1	3.36	off	<0.02	0.203	47.8	---
	92	V4 - 14	6.6	25.4	3.32	off	<0.02	0.203	45.9	---
93	V4 - 15	6.9	30.6	3.32	off	<0.02	0.203	44.7	---	
94	V4 - 16a	7.1	35.1	3.32	off	<0.02	0.189	45.5	25.7	
95	V4 - 16b	7.1	35.1	3.32	off	<0.02	0.203	47.8	---	
96	V4 - 16c	7.1	35.1	3.32	off	<0.02	0.203	47.1	---	

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

Table A-7. Data for Cycle 7 (4-26-15)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Light Intensity (Lux)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 1	1	V1 - 1a	0.0	24.1	2.83	on	118	339	350
	2	V1 - 1b	0.0	24.1	2.83	on	118	351	329
	3	V1 - 1c	0.0	24.1	2.83	on	118	351	337
	4	V1 - 2	0.5	29.9	2.83	on	118	351	---
	5	V1 - 3a	1.0	35.0	2.83	on	113	371	335
	6	V1 - 3b	1.0	35.0	2.83	on	113	377	---
	7	V1 - 3c	1.0	35.0	2.83	on	113	374	---
	8	V1 - 4	1.8	30.0	2.82	on	113	362	---
	9	V1 - 5a	2.3	25.0	2.82	on	113	364	338
	10	V1 - 5b	2.3	25.0	2.82	on	113	371	---
	11	V1 - 5c	2.3	25.0	2.82	on	113	356	---
	12	V1 - 6	2.6	20.0	2.83	on	113	358	---
	13	V1 - 7	3.2	15.0	2.83	on	108	357	---
	14	V1 - 8	3.9	10.0	2.84	on	108	349	---
	15	V1 - 9a	4.4	6.6	2.88	on	108	353	338
	16	V1 - 9b	4.4	6.6	2.88	on	108	337	336
	17	V1 - 9c	4.4	6.6	2.88	on	108	344	339
	18	V1 - 10	4.8	10.2	2.88	on	108	363	---
	19	V1 - 11	5.1	15.0	2.83	on	108	367	---
	20	V1 - 12	5.7	20.0	2.81	on	102	357	---
	21	V1 - 13a	6.1	25.0	2.81	on	102	374	340
	22	V1 - 13b	6.1	25.0	2.81	on	102	360	---
	23	V1 - 13c	6.1	25.0	2.81	on	102	362	---
	24	V1 - 14	6.6	30.0	2.80	on	102	375	---
	25	V1 - 15a	7.1	35.1	2.80	on	118	388	355
	26	V1 - 15b	7.1	35.1	2.80	on	51	375	---
	27	V1 - 15c	7.1	35.1	2.80	on	118	377	---

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

Table A-7 Continued. Data for Cycle 7 (4-26-15)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Light Intensity (Lux)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 2	28	V2 - 1a	0.0	24.1	2.86	on	118	351	---
	29	V2 - 1b	0.0	24.1	2.86	on	118	356	---
	30	V2 - 1c	0.0	24.1	2.86	on	118	359	---
	31	V2 - 2	0.5	30.0	2.86	on	118	365	---
	32	V2 - 3a	1.3	35.0	2.87	on	113	359	---
	33	V2 - 3b	1.3	35.0	2.87	on	113	362	---
	34	V2 - 3c	1.3	35.0	2.87	on	113	357	---
	35	V2 - 4	1.8	30.0	2.86	on	113	361	---
	36	V2 - 5a	2.3	25.1	2.87	on	113	368	---
	37	V2 - 5b	2.3	25.1	2.87	on	113	357	---
	38	V2 - 5c	2.3	25.1	2.87	on	113	362	---
	39	V2 - 6	2.8	20.0	2.87	on	113	362	---
	40	V2 - 7	3.3	15.0	2.86	on	108	349	---
	41	V2 - 8	4.0	10.0	2.87	on	108	344	---
	42	V2 - 9a	4.4	7.3	2.86	on	108	344	---
	43	V2 - 9b	4.4	7.3	2.86	on	108	347	---
	44	V2 - 9c	4.4	7.3	2.86	on	108	343	---
	45	V2 - 10	4.8	10.0	2.86	on	108	354	---
	46	V2 - 11	5.2	15.0	2.86	on	108	370	---
	47	V2 - 12	5.7	20.0	2.85	on	102	357	---
	48	V2 - 13a	6.1	25.0	2.86	on	102	370	---
	49	V2 - 13b	6.1	25.0	2.86	on	102	364	---
	50	V2 - 13c	6.1	25.0	2.86	on	102	366	---
	51	V2 - 14	6.7	30.0	2.86	on	102	366	---
	52	V2 - 15a	7.1	35.2	2.86	on	118	382	---
	53	V2 - 15b	7.1	35.2	2.86	on	51	377	---
	54	V2 - 15c	7.1	35.2	2.86	on	118	376	---

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

Table A-7 Continued. Data for Cycle 7 (4-26-15)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Light Intensity (Lux)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 3	55	V3 - 1a	0.0	24.3	2.87	on	118	364	335
	56	V3 - 1b	0.0	24.3	2.87	on	118	362	334
	57	V3 - 1c	0.0	24.3	2.87	on	118	368	334
	58	V3 - 2	0.5	30.5	2.86	on	118	361	---
	59	V3 - 3a	1.1	35.0	2.85	on	113	383	339
	60	V3 - 3b	1.1	35.0	2.85	on	113	386	---
	61	V3 - 3c	1.1	35.0	2.85	on	113	379	---
	62	V3 - 4	1.8	30.0	2.86	on	113	382	---
	63	V3 - 5a	2.3	25.1	2.86	on	113	372	325
	64	V3 - 5b	2.3	25.1	2.86	on	113	377	---
	65	V3 - 5c	2.3	25.1	2.86	on	113	386	---
	66	V3 - 6	2.7	20.0	2.86	on	113	364	---
	67	V3 - 7	3.3	15.0	2.87	on	108	357	---
	68	V3 - 8	4.0	10.0	2.90	on	108	364	---
	69	V3 - 9a	4.4	6.7	2.95	on	108	355	318
	70	V3 - 9b	4.4	6.7	2.95	on	108	353	316
	71	V3 - 9c	4.4	6.7	2.95	on	108	353	308
	72	V3 - 10	4.8	10.2	2.94	on	108	366	---
	73	V3 - 11	5.2	15.0	2.89	on	108	373	---
	74	V3 - 12	5.6	20.0	2.87	on	102	374	---
	75	V3 - 13a	6.1	25.0	2.87	on	102	377	330
76	V3 - 13b	6.1	25.0	2.87	on	102	374	---	
77	V3 - 13c	6.1	25.0	2.87	on	102	368	---	
78	V3 - 14	6.7	30.0	2.87	on	102	375	---	
79	V3 - 15a	7.1	35.2	2.87	on	118	383	351	
80	V3 - 15b	7.1	35.2	2.87	on	51	390	---	
81	V3 - 15c	7.1	35.2	2.87	on	118	389	---	

Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

Table A-7 Continued. Data for Cycle 7 (4-26-15)

	Sample No.	Sample Name	Elapsed time (hr)	Temp. (°C)	pH	Light (on/off)	Light Intensity (Lux)	Se ^{IV} (µg/L)	Se(total) (µg/L)
Vessel 4	82	V4 - 1a	0.0	24.1	2.79	on	118	379	---
	83	V4 - 1b	0.0	24.1	2.79	on	118	386	---
	84	V4 - 1c	0.0	24.1	2.79	on	118	375	---
	85	V4 - 2	0.5	30.0	2.79	on	118	381	---
	86	V4 - 3a	1.3	35.0	2.79	on	113	394	---
	87	V4 - 3b	1.3	35.0	2.79	on	113	---	---
	88	V4 - 3c	1.3	35.0	2.79	on	113	389	---
	89	V4 - 4	1.8	30.0	2.79	on	113	380	---
	90	V4 - 5a	2.3	25.0	2.79	on	113	383	---
	91	V4 - 5b	2.3	25.0	2.79	on	113	383	---
	92	V4 - 5c	2.3	25.0	2.79	on	113	396	---
	93	V4 - 6	2.7	20.0	2.80	on	113	387	---
	94	V4 - 7	3.3	15.0	2.84	on	108	376	---
	95	V4 - 8	4.0	10.0	2.87	on	108	381	---
	96	V4 - 9a	4.4	7.4	2.91	on	108	370	---
	97	V4 - 9b	4.4	7.4	2.91	on	108	364	---
	98	V4 - 9c	4.4	7.4	2.91	on	108	368	---
	99	V4 - 10	4.8	10.1	2.91	on	108	368	---
100	V4 - 11	5.1	15.0	2.85	on	108	383	---	
101	V4 - 12	5.7	20.0	2.82	on	102	385	---	
102	V4 - 13a	6.1	25.0	2.80	on	102	382	---	
103	V4 - 13b	6.1	25.0	2.80	on	102	390	---	
104	V4 - 13c	6.1	25.0	2.80	on	102	386	---	
105	V4 - 14	6.7	30.0	2.79	on	102	390	---	
106	V4 - 15a	7.1	35.2	2.80	on	118	398	---	
107	V4 - 15b	7.1	35.2	2.80	on	51	413	---	
108	V4 - 15c	7.1	35.2	2.80	on	118	397	---	

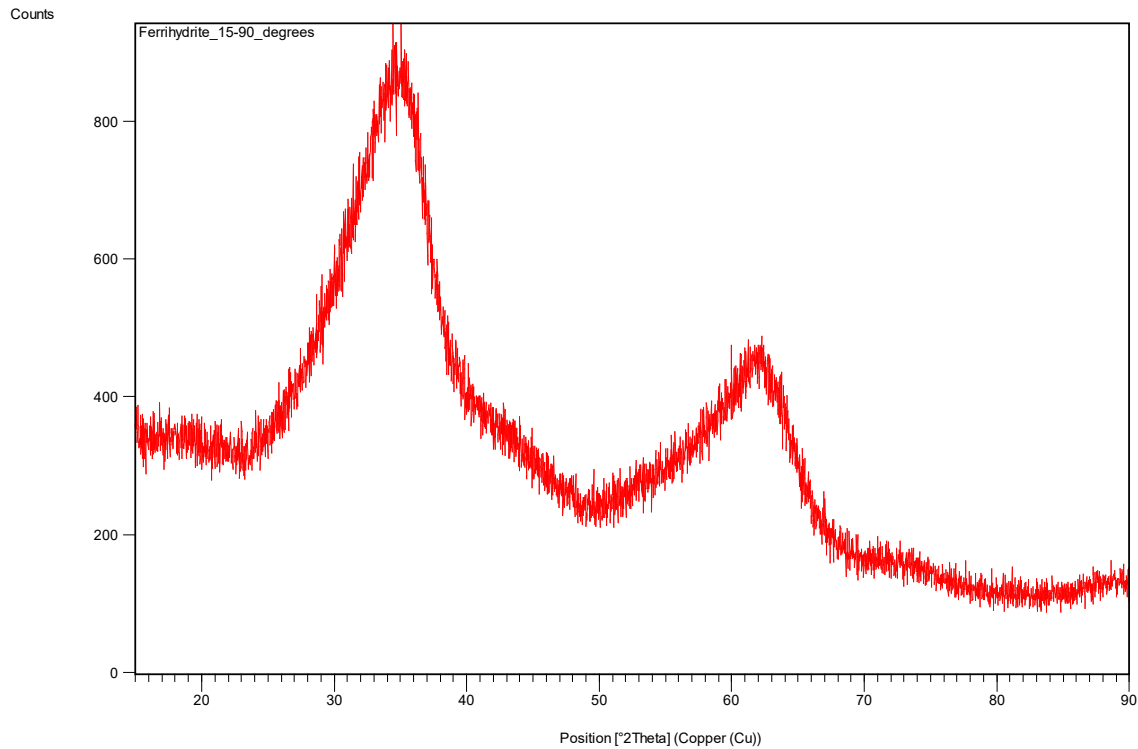
Notes: Temperature (Temp.) and pH measured using a DrDAQ PicoLog Recorder; Light intensity measured using a HOBO Pendant Light Logger; unfiltered samples for Fe(II) and Fe(total) measured using a HACH DR2800 Spectrophotometer and the ferrozine method; Se was analyzed using HG-ICP-OES; Concentrations with "<" indicate the analyte was not present above the detection limit; "---" indicates the sample was not analyzed.

APPENDIX B. X-RAY DIFFRACTION (XRD) DATA AND REPORT

Measurement Conditions:

Dataset Name	Ferrihydrite_15-90_degrees
File name	C:\X'Pert Data\EKH\Ferrihydrite_15-90_degrees.xrdml
Comment	Configuration=Bracket Flat Sample Stage, Owner=User-1, Creation date=11/26/2002 10:15:54 AM
	Goniometer=PW3050/60 (Theta/Theta); Minimum step size 2Theta:0.001; Minimum step size Omega:0.001
	Sample stage=PW3071/xx Bracket
	Diffractometer system=XPRT-PRO
	Measurement program=EKH_Ferrihydrite, Owner=User-1, Creation date=8/28/2014 1:50:38 PM
Measurement Date / Time	8/28/2014 1:53:24 PM
Operator	xrd
Raw Data Origin	XRD measurement (*.XRDML)
Scan Axis	Gonio
Start Position [°2Th.]	15.0000
End Position [°2Th.]	90.0000
Step Size [°2Th.]	0.0200
Scan Step Time [s]	30.0000
Scan Type	Pre-set time
Offset [°2Th.]	0.0000
Divergence Slit Type	Fixed
Divergence Slit Size [°]	0.9570
Specimen Length [mm]	10.00
Receiving Slit Size [mm]	3.0300
Measurement Temperature [°C]	25.00
Anode Material	Cu
K-Alpha1 [Å]	1.54060
K-Alpha2 [Å]	1.54443
K-Beta [Å]	1.39225
K-A2 / K-A1 Ratio	0.50000
Generator Settings	40 mA, 45 kV
Diffractometer Type	0000000013030095
Diffractometer Number	0
Goniometer Radius [mm]	240.00
Dist. Focus-Diverg. Slit [mm]	91.00
Incident Beam Monochromator	No
Spinning	No

Main Graphics, Analyze View:



Comments from the XRD technician:

Both samples showed patterns that would generally be considered amorphous. We did a wider range run on one of them - I've attached the report - and it matches pretty well to one of two high areas (they're not really peaks) of 2-line ferrihydrite. The second area is offset in the sample. The scan was a 24-hour scan so it's unlikely that peaks were there but not showing up as can sometimes happen. I can run a wider range scan on the sample labeled B1 if you would like and see if it matches the 2-line ferrihydrite spectrum better. Right now the scan I have for that is just up to 50 or 60 deg and it shows that same first high amorphous area.

APPENDIX C. DATASET FOR METHOD DEVELOPMENT OF Se(VI) TO Se(IV) DIGESTION

Trial No.	Test parameters for trial					Results of trials		
						Concentration (µg/L)		% Recovery
	HCl (mol/L)	Power (Watts)	Ramp time to 95°C (minutes)	Hold time at 95°C (minutes)	Total volume (mL)	Se(VI) Known	Se(IV) Measured	
1	4.8	400	5	60	8	50	7.68	15.4
						100	50.4	50.4
						200	154	77.4
						300	285	95.0
2	4.8	800	5	30	8	50	12.2	24.4
						100	31.7	31.7
						200	159	79.3
						300	292	97.2
3	6.0	400	5	30	8	50	4.55	9.10
						100	40.4	40.4
						200	119	59.6
						300	222	74.0
4	6.0	800	5	30	8	50	7.36	14.7
						100	40.7	40.7
						200	123	61.7
						300	238	79.3
5	4.8	1600	5	30	8	50	21.2	42.5
						100	63.4	63.4
						200	162	80.8
						300	278	92.6
6	4.8	1600	5	60	8	50	<5	<10
						100	<5	<5
						200	23.5	11.8
						300	124	41.3
7	4.8	1600	5	60	8	50	8.17	16.3
						100	51.7	51.7
						200	159	79.3
						300	263	87.8
8*	6.0	1600	5	60	9	100	130	116
						100	123	109
						100	125	111
9*	6.5	1600	5	60	9	100	124	110
						100	124	110
						100	129	115
10*	7.0	1600	5	60	9	100	127	113
						100	130	116
						100	121	107
11*	7.5	1600	5	60	9	100	118	105
						100	122	109
						100	120	107
12*	8.0	1600	5	60	9	100	119	105
						100	126	112
						100	119	105

Notes: HCl concentration is the final concentration in the digested samples (obtained by varying the volume of 12 mol/L HCl added); the total volume includes the combined prepared standard solution and the HCl; Se(IV) was measured using HG-ICP-OES; % Recovery = (measured concentration of Se)/(known concentration of Se) x100. A summary of trials 8 through 12 is provided on Table 3 in the text.

APPENDIX D. COMPLETE RESULTS FOR Se(IV) SORPTION STUDIES

Table D-1. Complete data from the sorption experiments							
Data Set	Test Tube #	Initial Se(IV) (µg/L)	HFO (g)	Light on/off	pH	Final Se(IV) (µg/L)	Se(IV) % Loss
1	1	0	0	off	nm	<5	---
1	2	0	0.5	off	nm	<5	---
1	3	100	0.5	off	nm	<5	>95
1	4	100	0.5	off	nm	<5	>95
1	5	100	0.5	off	nm	<5	>95
1	6	150	0.5	off	nm	<5	>96
1	7	150	0.5	off	nm	<5	>96
1	8	150	0.5	off	nm	5.97	96.0
1	9	200	0.5	off	nm	6.46	96.8
1	10	200	0.5	off	nm	8.35	95.8
1	11	200	0.5	off	nm	5.18	97.4
1	12	250	0.5	off	nm	12.2	95.1
1	13	250	0.5	off	nm	5.22	97.9
1	14	250	0.5	off	nm	6.58	97.4
1	1L	100	0.5	on	3.18	12.6	87.4
1	2L	100	0.5	on	3.19	10.5	89.5
1	3L	100	0.5	on	3.17	10.3	89.7
1	4L	150	0.5	on	3.02	21.7	85.5
1	5L	150	0.5	on	3.20	16.1	89.3
1	6L	150	0.5	on	3.07	9.82	93.5
1	7L	200	0.5	on	3.10	44.3	77.8
1	8L	200	0.5	on	2.93	44.3	77.8
1	9L	200	0.5	on	3.11	72.8	63.6
1	10L	250	0.5	on	3.01	61.8	75.3
1	11L	250	0.5	on	3.18	50.7	79.7
1	12L	250	0.5	on	3.04	53.4	78.6
1	13L	0	0	on	3.11	<5	---
1	14L	0	0.5	on	3.32	<5	---

The "Initial Se(IV)" is the known concentration added to the test tube for the experiment; HFO = hydrous ferric oxides; the "Final Se(IV)" is the measured concentration of Se(IV) in each test tube after the experiment is complete. "Fe(g)" are the grams of 2-line ferrihydrite added to each test tube. pH is measured at the end of the experiment (nm = not measured). The "Se(IV) % loss" is the percent of the initial Se(IV) that is lost during the experiment, expressed as a percentage; "----" indicates values that are not applicable, "<" indicates percent loss values based on the method detection limit of 5 µg/L.

Table D-1 Continued. Complete data from the sorption experiments

Data Set	Test Tube #	Initial Se(IV) (µg/L)	HFO (g)	Light on/off	pH	Final Se(IV) (µg/L)	Se(IV) % Loss
2	15D	150	0.5	off	3.16	59.9	60.1
2	16D	150	0.5	off	3.17	38.3	74.5
2	17D	150	0.5	off	3.26	40.8	72.8
2	18D	200	0.5	off	3.27	54.3	72.9
2	19D	200	0.5	off	3.16	28.0	86.0
2	20D	200	0.5	off	3.10	40.1	80.0
2	21D	250	0.5	off	3.24	51.3	79.5
2	22D	250	0.5	off	3.14	41.4	83.5
2	23D	250	0.5	off	3.14	37.3	85.1
2	24D	300	0.5	off	3.15	43.6	85.5
2	25D	300	0.5	off	3.04	52.2	82.6
2	26D	300	0.5	off	2.97	54.4	81.9
2	27D	300	none	off	2.88	255	14.9
2	28D	300	none	off	3.04	258	14.0
2	29D	300	none	off	3.00	301	negligible
2	15L	150	0.5	on	3.18	27.9	81.4
2	16L	150	0.5	on	3.27	19.1	87.3
2	17L	150	0.5	on	3.05	35.5	76.3
2	18L	200	0.5	on	3.16	62.0	69.0
2	19L	200	0.5	on	3.26	62.0	69.0
2	20L	200	0.5	on	3.20	66.8	66.6
2	21L	250	0.5	on	3.12	73.1	70.8
2	22L	250	0.5	on	3.31	59.2	76.3
2	23L	250	0.5	on	3.26	49.5	80.2
2	24L	300	0.5	on	3.15	34.7	88.4
2	25L	300	0.5	on	3.13	23.2	92.3
2	26L	300	0.5	on	3.07	20.3	93.2
2	27L	300	none	on	3.17	260	13.2
2	28L	300	none	on	3.26	262	12.8
2	29L	300	none	on	3.30	292	2.7

The "Initial Se(IV)" is the known concentration added to the test tube for the experiment; the "Final Se(IV)" is the measured concentration of Se(IV) in each test tube after the experiment is complete. "Fe(g)" are the grams of 2-line ferrihydrite added to each test tube. pH is measured at the end of the experiment (nm = not measured). The "Se(IV) % loss" is the percent of the initial Se(IV) that is lost during the experiment, expressed as a percentage; "---" indicates values that are not applicable, "<" indicates percent loss values based on the method detection limit of 5 µg/L.