

Project 4

Measurement of Selenium Flux – Amendment No. 1

Conduct Flux Chamber Measurements

CH2M HILL TASK ORDER NO. 5. University of Utah
SUBCONTRACT WITH:
PRINCIPAL INVESTIGATORS: Dr. William Johnson/University of Utah
CONTRACT VALUE: \$44,475
SCHEDULE: May 1, 2007 through November 30, 2007 (elapsed time: 7 months)

Introduction

This proposal concerns direct measurement of volatile selenium flux from the Great Salt Lake. We propose to make monthly measurements from April through September 2007 at two locations in the South Arm in order to examine seasonal trends, and to provide in-season replication of results for a range of values. The resulting fluxes will be used to confirm or refine flux estimates made based on measured volatile selenium concentrations and literature-based values for mass transfer. The literature-based mass transfer coefficients indicate that volatilization is the dominant permanent selenium removal mechanism from the Great Salt Lake. Estimated times necessary to directly measure volatile selenium flux indicate that the measurement is feasible using a commercially available flux hood combined with cryo-trapping-ICP-MS analyses.

The soon-to-end project concerning measurement of volatile selenium flux resulted in the successful development of analytical capability to measure dissolved volatile selenium to concentrations in the picomolar range. The dissolved volatile selenium concentrations measured at 12 locations and several depths in the South Arm of the Great Salt Lake yield an average volatile selenium concentration of 0.7 ng/L. This average represents conditions with different wind speeds and different temperatures. A more detailed report concerning these variations will be provided this spring.

Table 1 shows the expected maximum volatile selenium fluxes from the GSL, using the average volatile selenium concentration equal to 0.7 ng/L. These estimations were performed using models that were developed for fresh and sea waters. These models are based on wind velocity, water temperature, viscosity, diffusivity, and concentrations in water and air of the volatile species. The viscosity, diffusivity, and estimated concentration in air (Henry's constant) each were corrected for the salinity of the Great Salt Lake, which is 3-5 times saltier than the ocean. These corrections were made using established methods.

TABLE 1. ESTIMATED FLUX OF VOLATILE SELENIUM COMPOUNDS FROM THE GSL

T °C	Wind velocity								
	1 MPH (0.45 m/s)			5 MPH (2.2 m/s)			25 MPH (11.2 m/s)		
	k_w cm/h	Flux ng/m ² h	Flux Kg/yr	k_w cm/h	Flux ng/m ² h	Flux kg/yr	k_w cm/h	Flux ng/m ² h	Flux kg/yr
2	1.03	7.18	115.8	1.58	11.08	178.8	16.07	112.50	1815.4
6	1.15	8.02	129.5	1.77	12.38	199.8	17.96	125.72	2028.8
10	1.28	8.96	144.6	1.98	13.83	223.1	20.06	140.40	2265.6
17	1.54	10.77	173.8	2.38	16.63	268.3	24.12	168.84	2724.5
25	1.86	12.99	210	2.86	20.05	323.6	29.09	203.61	3286

The estimated selenium removal from the Great Salt Lake via volatilization ranges from 115 kg/yr (low temperature-low wind conditions) to 3,286 kg/yr (high temperature-high wind conditions) indicating that volatilization may be the dominant permanent removal mechanism from the Great Salt Lake. The estimated loss rate via permanent sedimentation is approximately **203** kg/yr based on a combination of recently measured selenium concentrations in lake sediment cores and sedimentation rates estimated from ²¹⁰Pb profiles. The loss rate via brine shrimp harvest is 26 kg/yr (Marden, 2006).

The estimated flux of selenium from the Great Salt Lake points toward volatilization as the predominant permanent removal mechanism. However, it is important to understand the assumptions built into these flux estimations. From Tessier, et al (2003) the following expression was modified to calculate the selenium flux from the Great Salt Lake:

$$\text{Flux density} = ak_w \left(C_{\text{water}}^{\text{VSe}} - \frac{C_{\text{air}}^{\text{VSe}}}{K'_{H_{\text{GSL}}}} \right) \text{ (mol/m}^2\text{yr)}$$

where: a is a unit correction factor (= 0.24); K_w is the transfer velocity in the air-water interface (cm/h); $C_{\text{water}}^{\text{VSe}}$ is the concentration of volatile selenium in water (mol/m³); $C_{\text{air}}^{\text{VSe}}$ is the concentration of volatile selenium in air (mol/m³); $K'_{H_{\text{GSL}}}$ is the dimensionless Henry's constant corrected for temperature and salinity.

Correction of values for salinity and temperature was performed as follows (Guo et al 2000; Schwarzenbach et al, 2003), where K_{DMS}^s is the salinity constant for dimethyl sulfide:

$$K'_{H_{\text{GSL}}} = 0.0248 \exp(0.0418 \cdot T) \cdot 10^{K_{\text{DMS}}^s [\text{salt}]_{\text{cor}}}$$

Dimethyl sulfide was determined to have a similar chemical behavior to dimethyl selenide (Amouroux 1995), allowing use of the salinity constant for dimethyl sulfide to correct the dimensionless Henry's constant for dimethyl selenide.

To calculate the air-water transfer velocity, an approximation used in the Hudson Bay by Clark et al (1995), corrected via the Schmidt number from Schwarzenbach et al (2003), is:

$$k_w = \left(\frac{Sc}{600} \right)^{-0.5} (2 + 0.24u_{10}^2)$$

$$Sc_{DMS}^{sea\ water} = 2674.0 - 147.12T + 3.726T^2 - 0.038T^3$$

where Sc is the Schmidt number of dimethyl sulfide (as a function of temperature) (Saltzman et al, 1993); and u_{10} is the wind velocity measured 10 m over the surface of the lake.

The estimated flux measurements therefore assume the following: 1) that negligible volatile selenium concentrations occur in the vapor phase immediately above the water surface; 2) that the air-water transfer velocity expression developed for Hudson Bay applies to the Great Salt Lake; 3) that temperature and salinity corrections for the air-water transfer velocity and the Henry's constant reasonably capture actual influences on these parameters.

The estimated flux measurements suggest the dominance of volatilization for permanent selenium removal from the Great Salt Lake; however, significant assumptions are built into the flux estimates, indicating a need to directly measure volatile selenium flux via a floating flux chamber. The feasibility of direct measurement of volatile selenium flux is described below.

Flux Chamber

Fortunately, a floating flux chamber is commercially available that will stand up to the rigors presented by the Great Salt Lake. The AC'SCENT Flux Hood is shown below with specifications.



Specifications:

Diameter: 16 in (40 cm)

Area: 0.13 m²

Stainless steel

Includes:

SS chain, 50-ft rope & inner tube (could be Teflon)

Requires:

Pump (sweet air supply) and flow regulator

Recommended to use with a vacuum chamber.

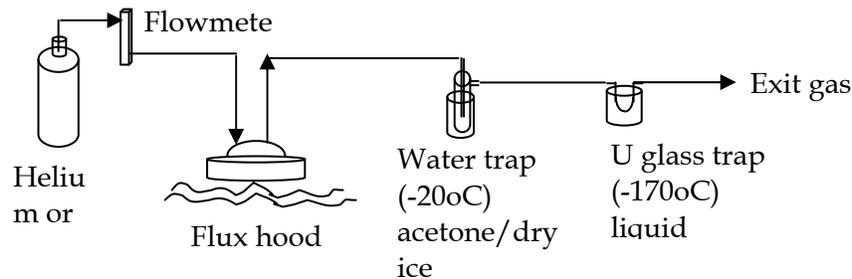
Extra:

Extra fitting on hood for adding a thermocouple probe

The sweep rate in the flux chamber will be set to match environmental conditions. The volatile selenium swept from the flux chamber will be cryo-focused onto a trap as

performed for the volatile selenium measurements. However, the sweep times used for flux measurements are expected to be much longer (4-8 hours) than those used for the volatile selenium measurements (15 minutes). The trapped volatile selenium will be digested with nitric acid 2% and made up to a volume of 10 mL prior to analysis via inductively couple plasma mass spectrometry (ICP-MS).

The total cost for the flux hood and ancillary equipment is approximately \$5000, including the flux hood itself, vacuum chamber and pump for sweep and sampling, and temperature controller for the cryo-focusing trap. The system lay-out is shown below:



Collection Time

Fortunately, equipment is commercially available to perform the flux measurement; however, the equipment is not designed to be deployed independent of operators. Hence, the expected times necessary to measure flux must be demonstrated to be less than approximately 8 hours. To estimate the on-lake collection time for measurement of actual flux, we can use the estimated flux in $\text{ng}/\text{m}^2\text{h}$ calculated above. The mass of volatile selenium that can be collected per hour is estimated from the lake-vapor interfacial area in the flux hood (0.13 m^2).

Determination of the expected sweep time for flux measurements depends on expected background signals. The background concentration of volatile selenium obtained (during measurement in the concentrated solution) during volatile selenium measurements (using 7 liters of pure water, sparged for 15 minutes) is $116 \text{ ng Se}/\text{L}$. Using the background level, and assuming that this background would not increase with increased sparging time, the minimum concentration needed for the flux measurement can be set to five times above this background ($= 580 \text{ ngSe}/\text{L}$).

The estimated sampling time needed to measure Se volatilization flux under these conditions would therefore be:

$$t(h) = \left(\frac{5 \times \text{background ngSe}_{bkgd}}{L} \right) \left(\frac{L h}{\text{estimated flux ngSe}} \right)$$

Table 2 presents the estimated sweep times for flux measurements for three wind velocities and three temperatures. The vast majority of sweep times are less than 8 hours, permitting the measurement of volatile selenium fluxes via the commercially available equipment.

TABLE 2. TIME REQUIRED FOR AIR SAMPLING (SAMPLING WON'T BE PERFORMED AT 25 MPH).

T °C	Wind velocity								
	1 MPH (0.45 m/s)			5 MPH (2.2 m/s)			25 MPH (11.2 m/s)		
	Flux ng/m ² h	[Se] ng/L/h	Time sampling (h)	Flux ng/m ² h	[Se] ng/L/h	Time samplin g (h)	Flux ng/m ² h	[Se] ng/L/h	Time sampling (h)
2	7.18	66.8	8.7	11.08	103.1	5.6	112.50	1046.6	0.6
10	8.96	83.3	7.0	13.83	128.6	4.5	140.40	1306.1	0.4
25	12.99	120.9	4.8	20.05	186.5	3.1	203.61	1894.1	0.3

Extra Requirements

Because the sweep times are large (several hours), special precautions are required to avoid clogging the cryo-focusing trap with condensed nitrogen or oxygen. This concern can be met by careful control of the trap temperature via a commercially available temperature regulator. The temperature that was estimated to be safe to avoid those condensations is 160°C ± 10°C.

The electronic equipment and parts required are:

- temperature controller
- temperature probe
- heater
- power adapter to 12V battery
- battery
- plastic hermetic box to keep the electronic sensible connections from being exposed to the saline water.

Expected prices for a commercially available temperature controller range from \$2000 to \$3000, including the heating system and temperature probe.

It will be necessary to have an extra set of traps, dewars and Teflon tubing, to purge and trap collected water samples at the same location. The cost for it would be around \$250.

Project Objective

The objective of this project is to verify the above estimates for selenium removal from the Great Salt Lake via volatilization by direct measurement. It is expected that the measured values will differ from the estimates, but that these measured values will demonstrate the same trend as the theoretical measurements, allowing them to serve as corrections for the estimated volatile selenium flux from the Great Salt Lake.

Activities

1. Prior to executing work, Data Quality Objectives (DQOs) will be prepared and reviewed by the Great Salt Lake (GSL) Science Panel, Utah Division of Environmental Quality, technical advisors, and GSL Steering Committee. DQOs should address how this

experiment will address DQOs for Project 4. Principal investigators will participate in study team meetings and conference calls on an as-needed basis.

2. Prepare Standard Operating Procedures defining sampling and analytical protocol to be followed. The SOPs should be forwarded for review via defined communication lines.
3. Air samples will be collected at two sites in the GSL: One at the north part of the South Arm and one at the south. Since the equipment should be deployed for several hours, it is convenient to attach it during the collection time to a buoy. Hence, the locations will be at sites 3510 and 2267 in the South Arm. Air samples will be collected monthly April through September 2007 (6 months).
4. This experiment will only address selenium flux and is not intended to address other potential contaminants, i.e., mercury.
5. All work will follow UDWQ's Quality Assurance Plan protocol. Air samples will be processed with all analytical work to be completed at the University of Utah laboratory. All associated costs are included in project budget.

Deliverables

1. Data Quality Objectives (see example from Project 4)
2. Standard Operating Procedures (see examples from Project 4)
3. Preliminary report summarizing results from sampling in April and how field measurements affect selenium flux estimates previously reported in final report for Project 4. The objective of this report is to provide an update that the Science Panel can use during evaluation of the Project 4 report this summer. Preliminary report will be completed by 05/31/2007.
4. Progress updates in the form of data graphs and statistical summaries will be provided to UDWQ or designee as requested. Data requests cannot exceed 2 requests for study period. Any questions or results that could materially impact conclusions included in the Project 4 final report will be reported right away via defined communication lines.
5. Final report on estimate of selenium flux to atmosphere. Report will include seasonal maps showing areas of potential selenium vapor flux in open water of GSL and estimated annual selenium loss to the atmosphere from this process. Report will document activities, methods, assumptions, data, recommendations, and conclusions completed as part of this task (completed by 11/30/2007).

References

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