Brownlee Reservoir Mercury TMDL
Water Column Study

Results and Field Summary

March 2008

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Contents

1. Summary of Activities

From May through November 2007, the Department of Environmental Quality (DEQ) conducted an investigation into mercury in the water column of Brownlee Reservoir. The goal of this project was to measure the average mercury concentration to within 1 nanogram per liter (ng/L) with 95% confidence. The study was not designed to investigate reservoir dynamics or pollutant distribution, just the average, reservoir-wide mercury concentration.

The states of Oregon and Washington, neither of which has a fish-tissue based water quality criterion, use a chronic aquatic life water column value of 12 ng/L. The Columbia River is Idaho's downstream receiving water, so one of the goals of this study was to determine whether Idaho is meeting Oregon and Washington standards.

A new sampling design was used that was able to accurately represent the average mercury concentration throughout the entire reservoir. The new design was intended to simplify the monitoring method, while at the same time providing more representative data at considerably less expense. It used a type of multi-increment, stratified random sampling design.

The sample space (reservoir) was conceptually divided up into several equal-volume segments, and a randomly-located sample increment was taken from each segment using a Kemmerer sampler and a boat. The increments were composited into three-gallon jugs using a system of tubes that rendered user-contamination unlikely.

A "clean-room" was constructed at the DEQ laboratory to provide an isolated workspace intended to minimize sample contamination. Here, the jugs were sub-sampled for laboratory analysis. The clean room was also used to acid-wash all the equipment before each sampling run.

Many elements of EPA Protocol 1669 were used, including gloves, Tyvek suits, and the division of labor into "clean hands" and "dirty hands" tasks. For a detailed description of the monitoring protocol, please see the Project Plan on the DEQ website..

Sampling occurred approximately once per month, and were conducted by Hawk Stone, with help from Crystal Woolf, Fairlee Frey, Jacob Nelson, Craig Shepard, and Pete Wagner.

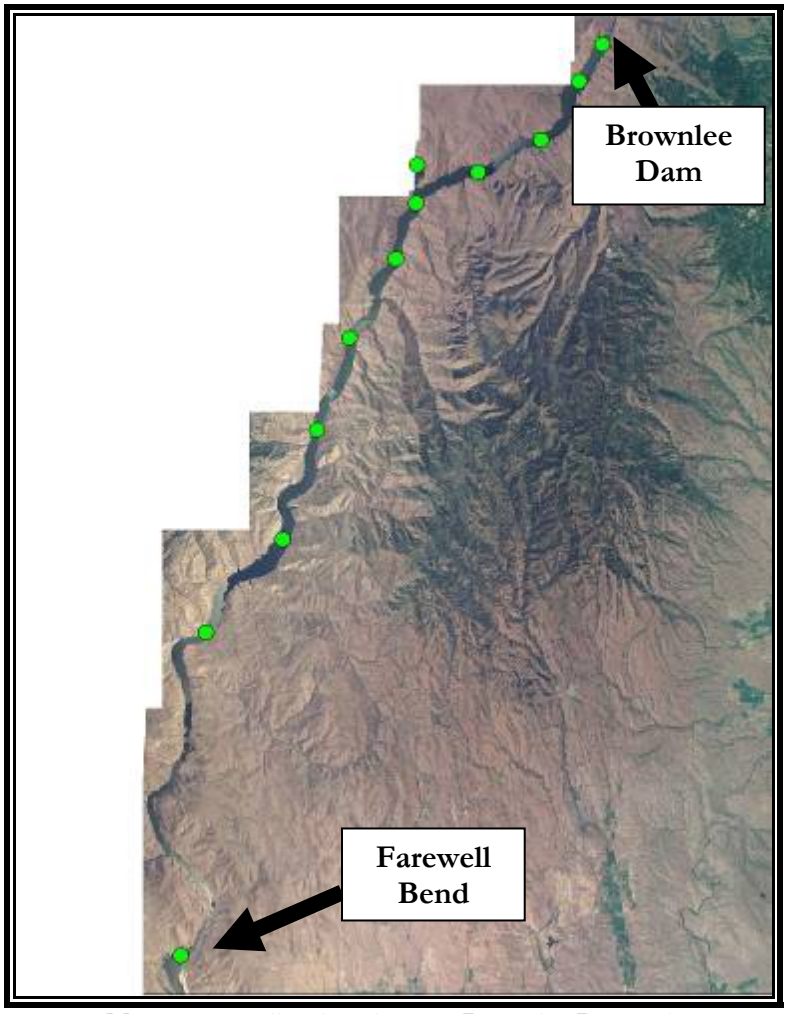
A vigorous quality assurance sampling regime was used. The entire sampling process was repeated in triplicate, and various blank samples were taken. These determine whether the equipment and/or method have contaminated the sample and caused a false positive result. Blank samples were

prepared using deionized water provided by the Idaho State Laboratory. The following table explains each type of blank sample, and which part of the process it was designed to test.

Type	Method	Tested Element
Subsample Blank	Run through the churn splitter.	Churn splitter
Trip Blank	Kept in sample bottles. Not opened in the field.	Bottles and transport
Method and Equipment Blank	Run through sampling equipment in the field.	Equipment, Atmospheric exposure and method
Equipment Blank	Run though sampling equipment in the clean room.	Equipment and method

2. Sample Site Locations

The boat used for sampling was launched from Farewell Bend State Park in Oregon and travelled the length of Brownlee Reservoir and back for each run. Sampling runs typically took about 10 hours, including travel time. Sample site locations are shown below.



Mercury sampling locations on Brownlee Reservoir

3. Results

A) **Average mercury concentrations**. The precision of the triplicate results prove that the survey truly represents the water and successfully samples through the heterogeneity in the reservoir.

Date	Replicate Mercury Concentration (ng/L)*			Average Mercury Concentration (ng/L)
	A	B	C	
05/15/07	5	3	3	**3.7**
06/07/07	3	3	2	**2.7**
07/02/07	8	4.7†	4.6†	**5.8**
08/05/07	6	4	7	**5.7**
09/04/07	7	9	8	**8.0**
10/11/07	3	3	7	**4.3**
11/20/07	2	3	6	**3.7**
Reservoir Average	**4.9**	**4.2**	**5.4**	**4.8 ± 1.3**

* The practical quantification limit is 5ng/L. Results below this value are provided by the laboratory as estimates only. The method detection limit is 1.5ng/L.
† Significant figures are as reported by the laboratory

B) **Subsample Replicates**. One jug was poured into the churn splitter, and three fractions were removed. This was to ensure that the churn splitter was operating properly.

Date	Details	Hg Concentration (ng/L)
05/15/07	Replicate C from table above	**3**
05/15/07	Subsample replicate	**3**
05/15/07	Subsample replicate	**3**

C) **Blank Samples**. These ensure that the survey method does not cause false positive results.

Date	Details	Hg Concentration (ng/L)
05/15/07	Subsample Blank	**<1**
06/07/07	Subsample Blank	**<1**
07/02/07	Subsample Blank	**<1**
08/05/07	Subsample Blank	**<1**
09/04/07	Subsample Blank	**<1**
10/11/07	Subsample Blank	**<1**
05/15/07	Trip Blank	**<1**
06/07/07	Trip Blank	**<1**

07/02/07	Trip Blank	**<1**
08/05/07	Trip Blank	**<1**
09/04/07	Trip Blank	**2**
10/11/07	Trip Blank	**1**
05/15/07	Method & equipment blank (field)	**3**
06/07/07	Method & equipment blank (field)	**6**
07/02/07	Method & equipment blank (field)	**103**††
08/05/07	Method & equipment blank (field)	**27**
09/04/07	Method & equipment blank (field)	**29**
10/11/07	Method & equipment blank (field)	**7**
11/20/07	Method & equipment blank (field)	**10**
10/11/07	Equipment Blank (clean room)	**4**
11/20/07	Equipment Blank (clean room)	**<1**
11/20/07	Rubber Stopper Blank (clean room)	**<1**

†† See discussion below

4. Deviations from Original Protocol

Changes from the original monitoring plan are as follows:

- Originally, 22 triplicate sample increments were to be collected from the length of the reservoir. This number was chosen based upon the variance observed in the DEQ's Salmon Falls Reservoir study. For 22 triplicates, 66 collections would have been required, which was tiring and time-consuming. After the first two sampling runs, a new variance was calculated based upon the variability among triplicate samples taken during the first two runs. As provided for in the monitoring plan, it was decided to reduce the number of sample increments to 12, entailing 36 draws of water from the reservoir during each sampling event.

- Often, during sampling, the wind would blow and cause the boat to drift. This meant the Kemmerer sampler did not drop vertically, but at an angle proportional to the velocity of the boat. For the deeper samples, this angle could sometimes be as much as 45°.

- On three occasions, the GPS was not used. Landmarks for each site had been previously memorized and described, and so we are confident that the boat was positioned in the right place. Regardless, because this is a stratified *random* design, a slight change in the stratification boundaries is not critical to the final result.

- On one occasion, the uppermost segment of the reservoir was not sampled because it was too shallow.

- On another occasion, the lowermost segment of the reservoir was not sampled because of mechanical problems with the boat, and the resulting need to return to shore quickly.

- Following some unexpectedly high results for the field blank sample, extra blank samples were taken.

- Contracting difficulties precluded an inter-laboratory comparison.

5. Discussion

The results show that the average mercury concentration in Brownlee Reservoir during summer and fall is 4.8 ± 1.0 ng/L. Most of the triplicate sample averages were within this range, indicating that the method successfully represents the reservoir volume.

Calculation of this mercury concentration is complicated by the number of results below the practical quantification limit (56%). With one exception, every sampling trip included at least one result of less than 5ng, making it difficult to extrapolate precise averages from the data. Estimated values were provided by the lab, and these have been used in all calculations.

The wind-caused angle of the Kemmerer sampler might cause the results to underrepresent the lower depths of the reservoir. In future studies, this could be solved by adding weight to the sampler.

The subsampler (churn splitter) was shown to cause no measurable contribution of mercury. Although Teflon churn splitters are available (at a cost of more than $3000), a regular churn ($430) was used in this case. The churn splitter triplicate subsample results were identical (each was 3ng/L), indicating that the churn was accurately subsampling each 3 gallon jug of water.

The bottles and transport were shown not to contribute mercury, and the clean-room equipment blanks show that the Kemmerer sampler, tubing, and sample jugs also did not contribute mercury above the detection limit.

The highest levels of mercury concentration were found in the field equipment and method blank samples. Perplexingly, these levels were not approached in the actual samples, indicating that the high values may be an artifact of the blank sampling procedure. The field blank was handled in the same way as the actual samples, with the following minor differences:

1) The blank sample was the first sample collected, and so may have picked up traces of mercury left by the acid-washing process. If the small quantity of blank water (250ml) rinsed the remaining acid, it could show a very high concentration of mercury. The October and November equipment-only (clean room) blanks were collected to test this hypothesis. The blank was collected in the clean room *before* the method blank. If acid-wash residues were causing the contamination, it would be expected that the first sample collected would have the highest readings. Instead, the first sample came back as non-detect, while a concentration of 7ng/L was detected in the field blank.

2) The blank samples were intentionally shaken in the increment jug, whereas the true samples were not. This would bring the water into contact with the rubber stopper, a possible contributor of mercury. A follow-up test was conducted to determine whether this was the case: blank water was poured all over the rubber cap, directly into a sample bottle. The results indicated that the stoppers do not contribute mercury.

3) The blank sample was a smaller volume (250ml) than the actual sample increments (2000ml). This would increase the effect of contributions from air deposition, boat exhaust or other contamination. There was not opportunity to test the equipment using a large volume of blank sample.

Even though there was a problem with this blank sample, the actual field samples did not appear to be contaminated (56% of the sample results were below the reporting limit). For this reason, the conclusions are still considered to be valid.

6. Conclusion

Mercury levels in the water of Brownlee Reservoir average 4.8 ng/L during the summer and fall, meeting Oregon's and Washington's chronic aquatic life water column total mercury criterion of 12 ng/L. Mercury levels average 4.8ng/L during the summer and fall.

Aside from the perplexing contamination in some of the blank samples, the study met its objectives and successfully illustrated a new method for collecting water samples from lakes or reservoirs.