Brownlee Reservoir Mercury TMDL
Fish Tissue Study

Results and Field Summary

June 2006

Prepared by Hawk Stone

Contents

1. Distribution List

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2. Summary of Activities

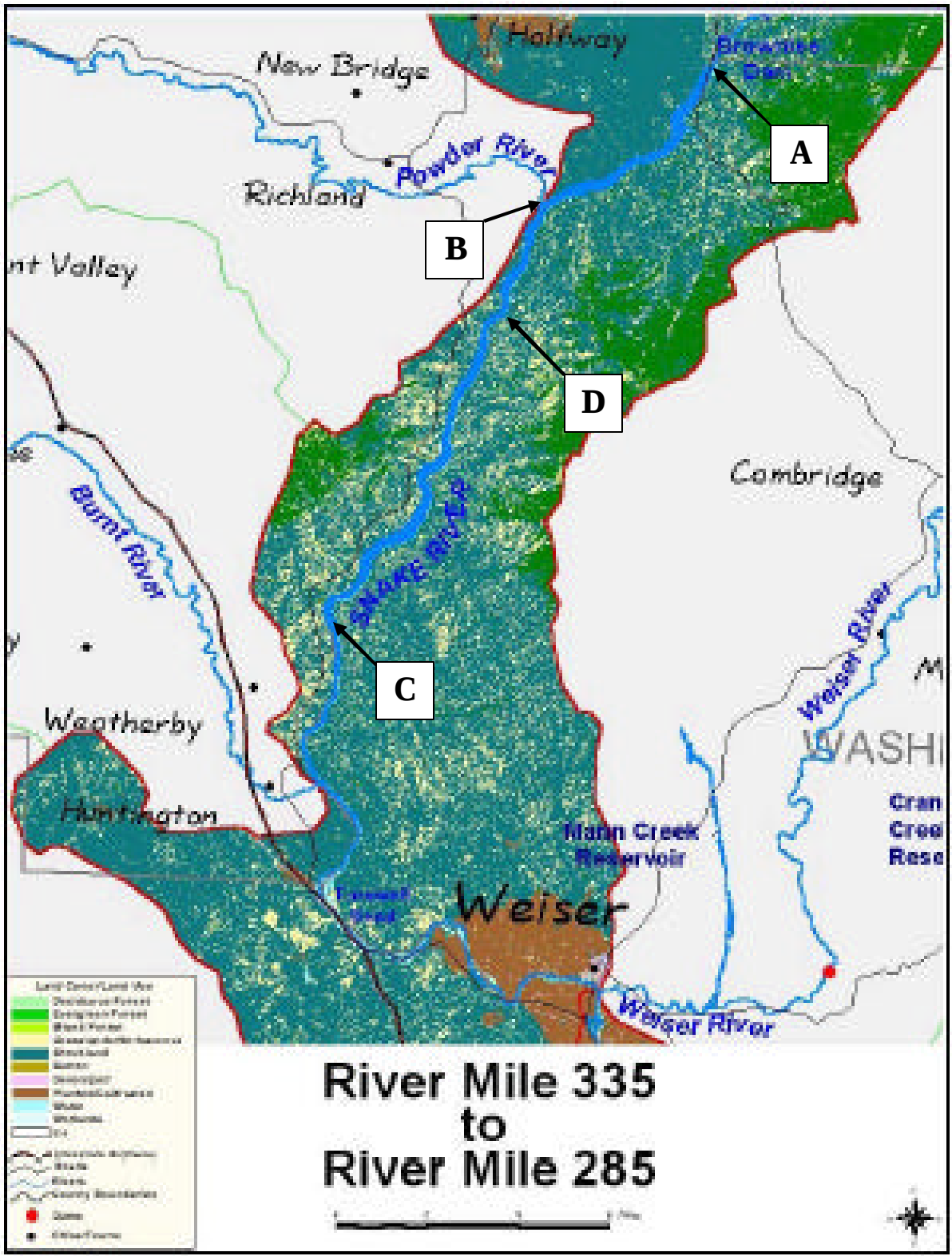
In April 2006, DEQ conducted an investigation into the occurrence of mercury in fish tissue in Brownlee Reservoir. For a detailed description of the monitoring protocol, please see the Quality Assurance Project Plan.

The goal of this project was to use state-of-the-art collection and analysis techniques to ascertain the mean fish tissue concentration of methyl mercury (MeHg) in smallmouth bass in Brownlee Reservoir. The study was conducted in partnership with the Idaho Department of Fish and Game, who were collecting bass and crappie for a population study. Fish collection occurred on the 17th and 19th April.

Fish were captured using one or more electrofishing boats, then transferred into a metal live-well. They were then moved into a large workup bucket in a separate boat, where they were killed and sealed in sample bags by Hawk Stone. Approximately eleven smallmouth bass were collected at each of four distinct sampling locations. In addition, several bottom-feeding fish were collected at each location.

A mercury-free 'clean-room' was constructed at the DEQ laboratory. Here, fish were filleted and ground to a pulp by Richard Lee. Fish fillets from each site were combined, resulting in one composite sample per site. All bottom-feeding fish were composited into a single sample. Several quality assurance samples were prepared, including blanks and a duplicate.

3. Map of Sample Sites



Map taken from Snake River Hells Canyon TMDL

4. Results

Site ID	Description	Latitude	Longitude	Mercury (mg/kg fish tissue)
A	Opposite Woodhead Park	44º 48' 23.4"	116º 55' 23.0"	0.467
B	Mouth of Powder River	44º 45' 3.0"	117º 2' 54.5"	0.652
C	near Rock Creek	44º 29' 14.9"	117º 13' 3.5"	0.634
D	upstream of Sturgill Creek	44º 39' 39.9"	117º 6' 2.1"	0.777
E	bottom-feeders from sites A-D	various	various	0.289
K	Duplicate of site A	44º 48' 23.4"	116º 55' 23.0"	0.471
X	Trip Blank	n/a	n/a	<0.001
Y	Field Blank at site A	44º 48' 23.4"	116º 55' 23.0"	<0.001
Z1	Sample Processing Blank (Day 1)	n/a	n/a	<0.001
Z2	Sample Processing Blank (Day 2)	n/a	n/a	<0.001

Idaho water quality standard = 0.3 mg/kg

Individual fish information can be found in the appendix (section 9).

5. Deviations from Protocol

As with any field activity, some deviations from the planned monitoring protocols occurred. As required by the Quality Assurance Project Plan, all deviations are summarized here:

Collection

- Site A: the fish for this site were collected at night, between 10pm and 2am.
- Site B: the electrofishing boat motor was run for a few minutes during fish measuring/bagging stage.
- Site D: no face mask was worn during fish measuring on the boat.
- Site E: this site was an 'extra' site, added at the last minute. Several bottom feeding fish (catfish, suckers and carp) from each of the other sampling locations were composited. A total of 13 fish were collected, between 9 and 24 inches in length. The goal of this extra site was to see whether sediment-dwelling fish had high levels of mercury. These fish generally occupy a lower trophic level than smallmouth bass, and do not bioaccumulate mercury to the same degree. Therefore, it was expected that the levels of mercury would be much lower than in bass. If their mercury level were comparable to the bass, then it could point to the sediments as a possible source of mercury. Because of the different species and size, the results are not directly comparable to sites A-D.
- Site E: the large size of these fish necessitated using only a portion of each fillet. The catfish were very difficult to kill, and incurred several blunt-force trauma lesions during euthanasia.
- General: loose ice was used instead of 'blue' ice packs. It was kept separate from fish tissue by a layer of plastic sheeting.

Processing

- Site A: the blender motor started smoking and then burned out. It was immediately replaced, using the same (covered) glass pitcher. The partially liquidized fish fillets were kept

covered, and smoke was not observed to enter the pitcher. A short while later, the second motor also burned out. A third motor began smoking, so compositing was stopped for this sample. The final product was mostly liquidized, but there were a few small chunks of flesh in the sample. Sample processing blank Z1 was run in the first blender.

- Site K: a new, heavy-duty commercial-grade food processor was purchased to grind the fish. It was sterilized in the standard way, with detergent followed by dilute HCl, and then rinsed with distilled water. It stopped running within a few minutes. The sample was judged to have been adequately homogenized. A new food processor was purchased, which operated trouble-free for the rest of the study
- Site Z2: this was an extra quality assurance blank sample added to ensure that the new blender purchased for fish analysis was mercury free
- Site E: The largest fish had a portion of their fillet used, instead of the whole fillet. Typically, one fillet was cut in two, and half was kept for archiving, and half was processed. This was easier than cutting two fillets from these fish.
- General: the final fish samples were not frozen, because they were delivered to the analyzing laboratory within twenty four hours of collection. They were immediately frozen upon arrival at the laboratory.
- General: no dry ice was used because of short shelf life. Regular cubed ice was used instead, and was kept separate from the sample containers by a plastic sheet.
- General: the weight of each fish was recorded
- General: on several occasions, bass spines pierced the sample bags. No meltwater was noticed in any bags.

Analysis

- The Idaho State Laboratory used EPA Method 200.8, not 7473:
    1. An aliquot of the sample is accurately weighed or measured.
    2. Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization and ionization.
    3. The ions are extracted from the plasma through a differentially pumped vacuum interface.
    4. The ions are separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer.
    5. The ions transmitted through the quadrupole are detected by an electron multiplier or Faraday detector and the ion information processed by a data handling system.

6. Audit

As specified in the Quality Assurance Project Plan, an audit of the clean-room laboratory was conducted, by Scott Pitzer. His observations are below, with a response to each in italics.

1. Written copy of the QAPP not on hand for personnel to refer too.
   A condensed summary of processing instructions was taped to the wall instead.

2. Large fish not double bagged as per section (B2.2 – Handling Fish) of the QAPP.
   It was not anticipated that such large fish would be collected. They were exclusively bottom feeders in group E, and were too large for our sample bags. They were wrapped in plastic sheets instead.

3. Loose ice not double bagged in coolers to prevent escape of meltwater as per section (B2.2 – Handling Fish) of the QAPP.
   Ice was separated from the fish samples by a layer of plastic sheeting. No meltwater was observed to have contacted the samples.

4. Only 1 trip blank, 1 field blank and 1 processing blank collected. Section (B5 – Quality Control) states these will accompany samples at all times. QAPP not entirely clear on this subject, but seems to indicate that 1 each of these blanks should be for each cooler/sample site for a total of 5 each.
   The QAPP is unclear. It was intended that only one of each of these blank samples be collected, not one per cooler.

5. Hawk Stone stated they had burned up 3 blenders while processing fish yesterday and they will finish the project today. No procedure in the QAPP to address burning up a blender while processing fish in the clean room.
   Burning up three blenders was not anticipated. The fillets were very lean, and so formed a sticky ball with a clay-like consistency. In hindsight, a more powerful food processor was needed.

   a. Will this contaminate the fish and the clean room?
      The fish were kept covered in the in the same glass pitcher. The fan was running, so any smoke would have been removed fairly quickly. The sample processing blanks (Z1 & Z2) show there was no contamination.

   b. Should fish processing stop, cover/seal/secure all samples and allow room to ventilate, etc?
      There was no protocol to address this situation, and so it was decided to proceed, but to take an extra sample processing blank (Z2) for the new blender.

7. Quality Assurance

All quality assurance measures were met:

- Representativeness: data are quoted at 95% confidence, with a maximum error of ±0.05ppm.
- Completeness: 57 fish at five sites were collected, representing 114% of the planned collection.
- Precision: duplicate samples were with 1% of each other.

TRIP BLANK, X: This accompanied the samples at all times, and was not opened except for final total mercury analysis at the analyzing laboratory.
FIELD BLANK, Y: This accompanied the samples at all times. On the boat, it was thrown overboard, 'caught' with a net, hit with the stun stick, and packaged and placed in the appropriate sample cooler. It remained unopened, and was packaged and shipped with the other samples.
PROCESSING BLANKS, Z1 & Z2: These accompanied the samples at all times. They remained unopened until it was time for processing in the clean room, at which time they were treated as separate sites. Z1 was used on the first day of sampling, and Z2 was used on the second day, when a new blender had to be purchased.
On each occasion, the Z sample was opened, a clean laboratory bench cover was be placed over the opening, and the bottle was shaken. Next, a sterile scalpel was stirred in the water, which was then

poured into the sterilized blender. The water was be blended for one minute, and then poured back into the bottle, which was then packaged and sent for total mercury analysis.

All blank samples contained less than <0.001 mg/kg mercury (the laboratory reporting limit), indicating that mercury was not introduced at any time throughout the sampling process.

DUPLICATE SAMPLE, K:
Precision was calculated from a duplicate sample of site A. The relative percent difference (RPD) between the samples was 0.85%, well below the 20% criterion specified in the project plan.

8. Conclusion / Evaluation

Mean reservoir-wide concentration of methylmercury in smallmouth bass fillets is 0.633mg/kg, more than double the Idaho water quality standard of 0.3mg/kg. The mercury concentration was highest at Sturgill Creek, and lowest near the dam. Bottom feeding fish had a highly elevated mercury concentration of 0.289mg/kg.

Based upon the high degree of variability between sample sites, it may be necessary to analyze individual fish fillets from each site. If necessary, this will be addressed in another project plan.

Quality assurance samples indicate that contamination was not introduced at any stage of the monitoring or processing efforts.

Aside from some problems with the blenders, the entire project went smoothly, and predominantly followed the monitoring plan.

Special thanks to Art Butts and Jeff Dillon of the Idaho Department of Fish and Game, and Richard Lee and Scott Pitzer of DEQ.

9. Appendix – Individual Fish Information

Fish ID	Species	Length	Fish Weight (g)
A1	SMALLMOUTH BASS	12-15"	375
A2	SMALLMOUTH BASS	12-15"	362
A3	SMALLMOUTH BASS	12-15"	403
A4	SMALLMOUTH BASS	12-15"	649
A5	SMALLMOUTH BASS	12-15"	384
A6	SMALLMOUTH BASS	12-15"	407
A7	SMALLMOUTH BASS	12-15"	393
A8	SMALLMOUTH BASS	12-15"	468
A9	SMALLMOUTH BASS	12-15"	466
A10	SMALLMOUTH BASS	12-15"	677
A11	SMALLMOUTH BASS	12-15"	500
A12	SMALLMOUTH BASS	12-15"	519
B1	SMALLMOUTH BASS	12-15"	470
B2	SMALLMOUTH BASS	12-15"	453
B3	SMALLMOUTH BASS	12-15"	495
B4	SMALLMOUTH BASS	12-15"	456
B5	SMALLMOUTH BASS	12-15"	382
B6	SMALLMOUTH BASS	12-15"	605
B7	SMALLMOUTH BASS	12-15"	537
B8	SMALLMOUTH BASS	12-15"	498
B9	SMALLMOUTH BASS	12-15"	624
B10	SMALLMOUTH BASS	12-15"	605
B11	SMALLMOUTH BASS	12-15"	500
C1	SMALLMOUTH BASS	16"	687
C2	SMALLMOUTH BASS	12-15"	681
C3	SMALLMOUTH BASS	12-15"	509
C4	SMALLMOUTH BASS	12-15"	482
C5	SMALLMOUTH BASS	12-15"	509
C6	SMALLMOUTH BASS	12-15"	420
C7	SMALLMOUTH BASS	12-15"	478
C8	SMALLMOUTH BASS	12-15"	674
C9	SMALLMOUTH BASS	12-15"	426
D1	SMALLMOUTH BASS	12-15"	542
D2	SMALLMOUTH BASS	12-15"	678
D3	SMALLMOUTH BASS	12-15"	375
D4	SMALLMOUTH BASS	12-15"	507

D5	SMALLMOUTH BASS	12-15"	321
D6	SMALLMOUTH BASS	12-15"	619
D7	SMALLMOUTH BASS	12-15"	576
D8	SMALLMOUTH BASS	12-15"	563
D9	SMALLMOUTH BASS	12-15"	563
D10	SMALLMOUTH BASS	12-15"	623
D11	SMALLMOUTH BASS	12-15"	355
D12	SMALLMOUTH BASS	12-15"	398
E1 (B)	CARP	18"	1575
E2 (B)	CARP	18"	1324
E3 (B)	LARGESCALE SUCKER	20"	1373
E4 (C)	FLATHEAD CATFISH	12-15"	321
E5 (C)	FLATHEAD CATFISH	12-15"	288
E6 (C)	FLATHEAD CATFISH	12-15"	234
E7 (C)	FLATHEAD CATFISH	12-15"	148
E8 (D)	CHANNEL CATFISH	12-15"	210
E9 (D)	CHANNEL CATFISH	12-15"	252
E10 (D AREA)	BRIDGELIP SUCKER	unknown	too large for scales
E11 (D AREA)	CHANNEL CATFISH	24"	too large for scales
E12 (D AREA)	BRIDGELIP SUCKER	18"	too large for scales
E13 (D AREA)	CHANNEL CATFISH	unknown	1163