Appendix C. Data Quality-Control Results[1]

Low-level selenium contamination (0.03 µg/L) in ambient blank samples exposed within the autosampler was detected in 1 of 21 ambient blank sample exposures. This low level of potential contamination does not affect the presentation or interpretation of the environmental data.

Variability in matched replicate samples collected by either the automated sampler, grab samples from a single point in the stream channel, or equal-width increment (EWI) samples was evaluated by comparing the relative sample deviation (RSD), also known as the coefficient of variability, and is defined as the standard deviation of all replicates values, divided by the average, expressed as a percentage. For selenium, 20 matched sets of automatically collected, grab, and EWI samples were evaluated. Of these, 90 percent of the RSD comparisons were 8.3 percent or less, and the median RSD was 2.5 percent, indicating low sampling and laboratory variability. One sample group (September 5, 2006) had much higher variability with an RSD of 94 percent (*table C1*). For trace elements, arsenic variability also was low, with a median RSD of 3.7 percent. The variability of cadmium and copper analyses was much higher, with RSDs of 53 and 22 percent, respectively, which is likely a consequence of the low concentrations of most results for cadmium and copper, which approached their analytical limits of quantification (*table C1*).

For the vast majority of the selenium samples, the similar results between grab samples and automatically collected samples indicate that the sampler pumping system did not significantly affect samples. Likewise, the similarity between most grab and EWI-collected samples suggests that the automatic sampler represented dissolved selenium in the stream cross section well.

Comparisons of Laboratory Results with Most Probable Values from Standard Reference Samples

Underlying the variability in the comparisons among the field sampling methods is the intrinsic measurement uncertainty of the laboratory analyses. Here, we consider the measurement uncertainty of the laboratory analyses by evaluating the accuracy and bias of selenium results obtained for blind, standard reference samples. Over the period of this study, 2001–12, the USGS National Water Quality Laboratory analyzed 1,608 blind standard reference samples (filtered river water samples that had been spiked with selenium and other inorganics). These results were matched with the most probable values (MPVs) obtained from round-robin sampling (*fig. C1*). The round-robin MPVs are considered here to represent "true" concentrations. Calculating the percent recovery of the laboratory samples reflects the inherent measurement uncertainty and any tendencies toward a positive or negative bias in the data (fig. C2). Most results showed a tight scatter of the laboratory values around the most probable values, without obvious influences of concentration. Several results in 2007–12 showed an unacceptable low bias, however, none of the environmental selenium samples from the Blackfoot River analyzed near those times showed unusually low values.

[1] *Appendix C to*: Mebane, C.A., G.C. Mladenka, L. Van Every, M.L. Williams, and M.A. Hardy. 2014. Selenium in the upper Blackfoot River watershed, southeastern Idaho, 2001-2012, with an appendix on selenium speciation analytical methods, by Garbarino, J. R.. U.S. Geological Survey Scientific Investigations Report 2014-5203. 34 p., *http://dx.doi.org/10.3133/sir20145203*.

Table C1. Matched quality-control sample results collected from replicate automated pump sampler "Auto", grab samples, and equal width increment (EWI) samples.

[As, arsenic; Cd, cadmium; Cu, copper; Se, selenium; µg/L, microgram per liter; <, less than]

Date	Sample type	As	Cd	Cu	Se	Se. un-filtered	As	Cd	Cu	Se
		Concentrations (µg/L)					Relative Sample Deviation (percent)			
15-Apr-2004	Auto	0.7	<0.04	0.9	3.3		7.9		6.7	0.0
15-Apr-2004	Grab	0.8	<0.04	0.9	3.3					
15-Apr-2004	EWI	0.7	<0.04	0.8	3.3					
22-Jul-2004	Auto	0.9	0.06	0.5	1.2		0.0		11.7	7.4
22-Jul-2004	Grab	0.9	<0.04	0.4	1					
22-Jul-2004	Grab	0.9	<0.04	0.4	1.1					
22-Jul-2004	EWI	0.9	<0.04	0.4	1.1					
6-May-2005	Auto	1.0	0.04	0.6	7.1		5.1		8.9	2.5
6-May-2005	Grab	0.9	<0.04	0.6	7.2					
6-May-2005	Grab	1.0	<0.04	0.7	7.4					
6-May-2005	EWI	1.0	<0.04	0.7	7.5					
16-Aug-2005	Auto	0.6	0.06	0.4	1.2		0.00	78.5	27.2	4.6
16-Aug-2005	Grab	0.6	0.09	0.3	1.2					
16-Aug-2005	Grab	0.6	0.07	0.2	1.3					
16-Aug-2005	EWI	0.6	0.26	0.3	1.3					
19-Apr-2006	Auto	0.69	0.42	0.7	6.6		2.3	83.0	28.8	5.2
19-Apr-2006	Grab	0.71	0.10	0.7	7.4					
19-Apr-2006	Grab	0.71	0.10	0.8	7.3					
19-Apr-2006	Auto	0.73	0.13	1.2	6.9					
5-Sep-2006	Auto	0.47	0.16	1.3	3.1		6.90	84.56	100	94
5-Sep-2006	Grab	0.49	0.07	0.4	1.3					
5-Sep-2006	Grab	0.52	0.03	0.2	0.4					
5-Sep-2006	Auto	0.55	0.03	0.2	0.5					
2-May-2007	Auto	0.12	0.11	1.2	8.2		43.7	12.9	34.8	0.71
2-May-2007	Grab	0.16	0.14	1.6	8.2					
2-May-2007	Grab	0.33	0.15	2.7	8.1					
2-May-2007	EWI	0.25	0.13	1.8	8.1					
23-Aug-2007	Auto	0.54	0.03	1.1	0.87		4.1		60.1	3.8
23-Aug-2007	Grab	0.59	<0.04	0.39	0.9					
23-Aug-2007	Grab	0.59	<0.04	0.35	0.93					
23-Aug-2007	EWI	0.57	0.02	0.49	0.95					
13-May-2008	Auto	0.67	0.30	1.2	5.1		3.4	73.5	17.5	2.6
13-May-2008	Grab	0.64	0.08	0.98	4.9					
13-May-2008	Grab	0.65	0.05	1.2	5					
13-May-2008	EWI	0.69	0.19	1.5	5.2					
18-Sep-2008	Auto	0.5	0.03	<1.0	1.4		2.3	52.7	15.2	3.8

Date	Sample type	As	Cd	Cu	Se	Se. un-filtered	As	Cd	Cu	Se
		Concentrations (µg/L)					Relative Sample Deviation (percent)			
18-Sep-2008	Grab	0.5	0.07	1.2	1.3					
18-Sep-2008	Grab	0.52	0.04	1.3	1.3					
18-Sep-2008	EWI	0.52	0.10	1.6	1.3					
20-Apr-2009	Auto		0.02		1.5			22		3.7
20-Apr-2009	Grab		0.03		1.6					
20-Apr-2009	Grab		0.02		1.5					
20-Apr-2009	EWI		0.02		1.6					
10-Aug-2009	Auto		0.07		1.9			54.1		0.00
10-Aug-2009	Grab		0.02		1.9					
10-Aug-2009	Grab		0.01		1.9					
10-Aug-2009	EWI		0.07		1.9					
30-Apr-2010	Auto		0.09		5.0			74.9		1.9
30-Apr-2010	Grab		0.12		5.2					
30-Apr-2010	Grab		0.11		5.2					
30-Apr-2010	EWI		0.36		5.2					
16-Sep-2010	Auto		0.04		1.6			93.5		0.00
16-Sep-2010	Grab		0.05		1.6					
16-Sep-2010	Grab		0.05		1.6					
16-Sep-2010	EWI		0.21		1.6					
5-May-2011	Auto		0.10		5.2			25.53		0.95
5-May-2011	Grab		0.06		5.3					
5-May-2011	Grab		0.06		5.3					
5-May-2011	EWI		0.08		5.3					
23-May-2011	Auto		0.13		8.1			22.57		3.45
23-May-2011	Grab		0.14		8.3					
23-May-2011	Grab		0.13		7.8					
23-May-2011	EWI		0.08		7.7					
21-Sep-2011	Auto		0.04		2.5			17.32		2.02
21-Sep-2011	Grab		0.03		2.5					
21-Sep-2011	Grab		0.03		2.5					
21-Sep-2011	EWI		<0.02		2.4					
17-Apr-2012	Auto		<0.016		2.6					16.5
17-Apr-2012	Grab		<0.016		3.8					
17-Apr-2012	Grab		<0.016		3.7					
17-Apr-2012	EWI		<0.016		3.7					
10-Jul-2012	Auto		<0.016		2.6					2.19
10-Jul-2012	Grab		<.016		2.6					
10-Jul-2012	Grab		<.016		2.7					
10-Jul-2012	Grab					2.3				

Date	Sample type	As	Cd	Cu	Se	Se. un-filtered	As	Cd	Cu	Se
		Concentrations (µg/L)					Relative Sample Deviation (percent)			
24-Jul-2012	Grab				2.4					
24-Jul-2012	Grab					2.36				
20-Sep-2012	Grab					2.27				
20-Sep-2012	Auto		0.061		2.7			38.4		2.2
20-Sep-2012	Grab		0.028		2.6					
20-Sep-2012	EWI		0.041		2.6					
Maximum							**44**	**93**	**100**	**94**
90 percent-tile							**11**	**84**	**64**	**8.3**
75 percent-tile							**6.5**	**77**	**33**	**4.0**
Median							**3.7**	**53**	**22**	**2.5**
n comparisons							***10***	***15***	***10***	***20***

The percent recoveries were evaluated for bias trends over time through locally weighted (LOESS) regression (Cleveland and Devlin, 1988) and the nonparametric Mann-Kendall test for trends in time-series data. These evaluations suggest a slight but persistent and increasing low bias to the results. For the entire period corresponding with the Blackfoot River sampling, the median percent recovery of selenium from the MPV of the blind standard reference samples was 96 percent, with 90 percent of the recoveries (5th to 95th percentiles) falling between 73 and 115 percent of the MPVs. Year-to-year, the LOESS regression suggests a slight high bias in 2001 with a median percent recovery of 102 percent, but thereafter a tendency toward slight low biases. By 2012, the median percent recovery had decreased to about 93 percent of the MPV (*fig. C2*).

The implications of these evaluations are that over the range of selenium concentrations tested through the standard reference samples (~0.7–8 µg/L), the inherent measurement uncertainty of any given reported laboratory selenium value had about a 90th percentile probability of being within a range of about 15 percent greater than or 27 percent less than the "true" selenium concentration. From about 2003 through 2012, laboratory analyses of filtered selenium tended to have a slight low bias, ranging from—10 to -1 percent.

Idaho Department of Environmental Quality Quality-Control Data

In the two to three equipment blanks sampled each year by IDEQ from 2004 through 2012, no selenium was detected in any sample, with the detection limit ranging from 1 to 3 µg/L. Variability in the IDEQ data was examined through a similar statistic as the RSD, except that for duplicate samples, instead of using the standard deviation, the absolute value of the percent difference between the two samples defines the relative percent difference (RPD). The median RPD of the IDEQ samples was 11 percent, ranging from 0 to 59 percent (*table C2*).

The annual IDEQ southeastern Idaho selenium monitoring project includes sampling sites outside of the Blackfoot River watershed study area (Idaho Department of Environmental Quality, 2007). All duplicate quality control samples analyzed as part of the southeastern Idaho selenium monitoring project were included in the comparisons in table C2, regardless of whether they were collected within the Blackfoot River watershed.

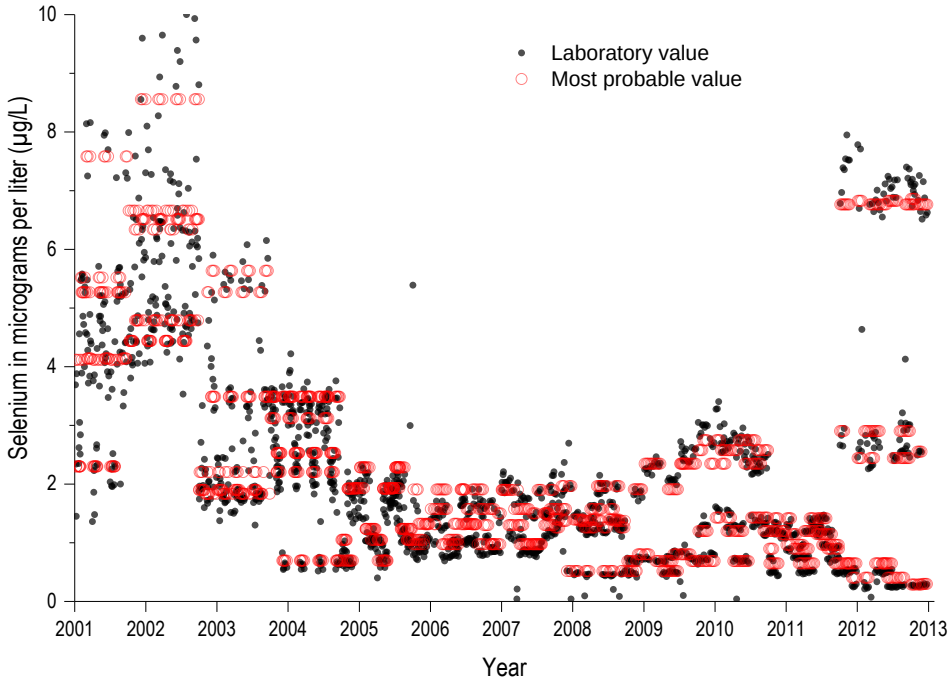

Figure C1. Quality-control results of dissolved selenium values measured by the USGS National Water Quality Laboratory compared with the most probable values of spiked filtered river water samples.

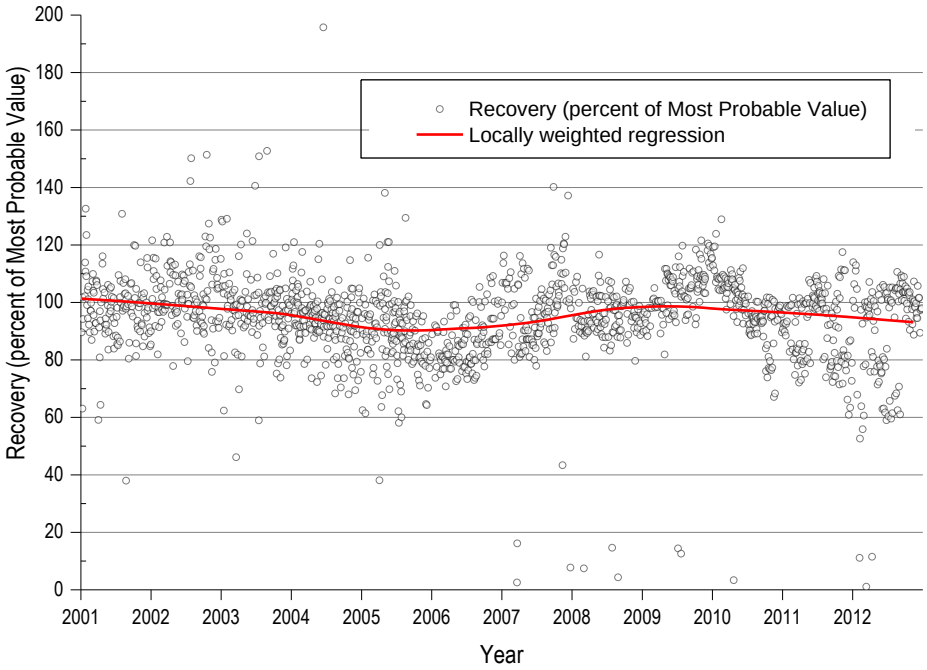

Figure C2. Accuracy and bias of selenium measurements made by the USGS National Water Quality Laboratory with blind standard reference samples (spiked river water samples), as percentages of most probable values.

Table C2. Quality control duplicate samples collected by Idaho Department of Environmental Quality, including samples collected for sites outside of the Blackfoot River watershed, southeastern Idaho.

[RPD, relative percent difference; µg Se/L, microgram selenium per liter, %, percent]

Site name	Sample pair (µg Se/L)		RPD (%)	Sample pair (µg Se/L)		RPD (%)	Sample pair (Se µg/L)		RPD (%)	Years sampled
Angus Creek	39	39	0	4	4	0				2005, 2007
Blackfoot River above Narrows	11	6	59	6	6	0	7	6	15	2005, 2006, 2007
Goodheart Creek below Champ Mine	33	38	14							2006
Sheep Creek Lanes Creek Road	2	2.3	14							2010
Spring Creek	46	39.4	15							([2])
East Mill Creek	860	870	1	625	677	8	282	256	10	2008, 2009, 2010
East Mill Creek	240	212	12							([3])
Other quality control samples collected from streams in southeastern Idaho outside of the Blackfoot River watershed										
Crow Creek at Hartman Ranch [1]	4	5	22	4	3	29				2006, 2007
Georgetown Creek below mine [1]	11	12	9	9.05	8.85	2	5.6	5.8	4	2008, 2009, 2010
Sage Creek at Crow Cr Road [1]	9	9	0	7.28	7.56	4	11.4	11.2	2	2008, 2009, 2010
Maximum RPD			**59**							
Median RPD			**11**							
n comparisons			***20***							

[1] Sites are outside the Blackfoot River watershed, but are included because they were sampled as part of the same southeastern Idaho selenium monitoring project. More information is available at Idaho Department of Environmental Quality (2007).

[2] Comparison in 2010 with duplicate samples analyzed by ACZ Laboratories, Steamboat Springs, Colorado, and Energy Laboratories, Billings, Montana.

[3] Comparison in 2012 with duplicate samples analyzed by SVL Laboratory, Kellogg, Idaho, and Bureau of Reclamation Soil and Water Laboratory, Boise, Idaho.

References Cited

Cleveland, W.S., and Devlin, S.J., 1988, Locally weighted regression: an approach to regression analysis by local fitting: Journal of the American Statistical Association, v. 83, no. 403, p. 596-610, also available at *http://dx.doi.org/10.1080/01621459.1988.10478639*

Idaho Department of Environmental Quality, 2007, Water Quality Sampling for Metals - Blackfoot River and Tributaries and Selected Bear and Salt River Tributaries (May 2007). 300 p, accessed September 2014, at https://*www.deq.idaho.gov/regional-offices-issues/pocatello/southeast-idaho-phosphate-mining/southeast-idaho-selenium-investigations.aspx*.