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Determination of Selenium in Fish from Designated Critical Habitat in the Gunnison River, Colorado, March through October, 2012

Open-File Report 2013–1104

U.S. Department of the Interior
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Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
milliTorr (mTorr)	1,000	Torr
	Volume	
liter (L)	33.82	ounce, fluid (fl. oz)
milliliter (mL)	0.034	ounce, fluid (fl. oz)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kiloelectron volt (keV)	1,000	electron volt (eV)
milligram (mg)	0.000035	ounce, avoirdupois (oz)
microgram (µg)	0.000000035	ounce, avoirdupois (oz)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8×°C)+32.$$

Concentrations of chemical constituents in solid materials are given in micrograms per gram (µg/g) dry weight.

Concentrations of chemical constituents in liquids are given in micrograms per liter (µg/L).

Determination of Selenium in Fish from Designated Critical Habitat in the Gunnison River, Colorado, March through October, 2012

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Abstract

This report presents results for the summer 2012 sampling of muscle plugs from common carp (*Cyprinus carpio*), bonytail chub (*Gila elegans*), Colorado pikeminnow (*Ptychocheilus lucius*), and razorback suckers (*Xyrauchen texanus*) inhabiting critical habitat in the Gunnison River in western Colorado. Total selenium in fish muscle plugs was determined by instrumental neutron activation analysis. Total selenium concentrations (range and mean ± standard deviation) in micrograms per gram dry weight were 6.0 to 10.7, 8.8 ± 1.3 for common carp; 2.9 to 8.7, 5.6 ± 2.4 for Colorado pikeminnow; and 1.4 to 7.3, 3.4 ± 2.7 for razorback sucker. The selenium concentration for one bonytail chub sample was 0.8 micrograms per gram dry weight. Selenium concentrations in muscle plugs from 1 Colorado pikeminnow and 12 common carp exceeded the 8 micrograms per gram dry weight toxicity guideline for selenium in fish muscle tissue.

Introduction

Irrigation drainage from large irrigation projects in the Uncompahgre and Grand Valley in western Colorado has resulted in selenium (Se) loading into the Uncompahgre, Gunnison and Colorado Rivers that exceeds the 5 micrograms per liter (µg/L) aquatic life protection standard established in 1977 by the Colorado Water Quality Commission (Colorado Department of Public Health and Environment, 2007). Within this area, the lower Gunnison River and the Colorado River are designated critical habitat for the endangered Colorado pikeminnow (*Ptychocheilus lucius*), razorback sucker (*Xyrauchen texanus*), and bonytail chub (*Gila elegans*). There is concern that high selenium concentrations in water, sediment, and biota collected from these rivers also are adversely affecting these endangered fish species (Hamilton, 1998). In collaboration with the Colorado River Recovery Program, the U.S. Fish and Wildlife Service (USFWS) monitors endangered fish populations in the lower Gunnison River as well as selenium concentrations in fish through the use of non-lethal muscle plug biopsies (Osmundson and others, 2000). The USFWS has sought collaboration from the U.S. Geological Survey (USGS) for the determination of selenium in muscle plug samples. This report includes results for the analysis of selenium in muscle plugs of common carp (*Cyprinus carpio*), Colorado pikeminnow, razorback suckers, and bonytail chub collected in spring through early fall of 2012 from a lower stretch of designated critical habitat in the Gunnison River between Delta and Grand Junction in western Colorado.

Methods

Field Collection and Preservation

Muscle plug samples were taken with a biopsy punch from live specimens of common carp, Colorado pikeminnow, razorback suckers, and bonytail chub collected from the Gunnison River between Delta (river mile 44.1) and the Grand Junction (river mile 0.7). Samples were placed in cryotubes, enclosed in a Whirl-Pak® bag, and frozen on dry ice. All samples were collected by USFWS personnel from March through October of 2012. Samples were stored in a freezer until shipment to the USGS.

Sampling History

The muscle plug samples collected by USFWS personnel were received in one shipment by the Environmental Chemistry Branch Inorganic Section (henceforth referred to as "the laboratory") of the USGS shortly after collection on December 4, 2012, and contained 16 common carp muscle plugs, 5 razorback sucker muscle plugs, 1 bonytail chub muscle plug, and 4 Colorado pikeminnow muscle plugs. The samples were assigned USGS batch number 2073 and USGS sample identification numbers 57506 to 57531. Selenium was to be determined in all samples by instrumental neutron activation analysis (INAA).

Lyophilization

All sample preparation before INAA was performed by USGS at the Columbia Environmental Research Center in Columbia, Missouri in collaboration with the University of Missouri Research Reactor (MURR). The entire plug was transferred from its original cryotube container into a 1.5 milliliter (mL) polyethylene vial provided by MURR staff. Vials were precleaned by stepwise washing with acetone, nitric acid, and deionized water. Each sample was positioned and pressed flat against the vial bottom with a cleaned glass rod. All vials were left open and placed in the tray chamber of a Virtis Genesis 35EL lyophilizer in "shelf" control and frozen to -75 degrees Celsius (°C). Once a condenser temperature of –70° C and vacuum of 300 milliTorr was reached, the drying cycle commenced. All muscle plug samples were lyophilized to constant weight, and dried weights ranged from 17 to 57 milligrams (mg) and averaged 43 mg. Lyophilization greatly reduces the oxygen-19 radioisotope (^{19}O) from water in the irradiated sample, and markedly enhances measurement precision. Upon recording of final sample weight, an expandable, cleaned polyethylene plug was inserted into the vial against which the vial lid was compressed shut. All samples were transported to MURR for the determination of selenium.

Instrumental Analysis

Standards in the range of 0.01 to 5 micrograms (µg) selenium were prepared by pipetting the appropriate quantities from a series of selenium stock solutions dried onto filter pulp paper which was comparable in geometric configuration to that of the samples. The pulp paper was then placed in the bottom of the polyethylene vials. A National Institutes of Standards and Technology (NIST) lyophilized Standard Reference Material (SRM) 1577 Bovine Liver also was run as a MURR internal quality control sample. All standards and samples were analyzed for selenium by way of ^{77m}Se using the following nuclear reaction: $^{76}Se(n,\gamma)^{77m}Se$ and $^{77m}Se \rightarrow {}^{77m}Se+\gamma$ and measuring the 161.9 kiloelectron volt (keV) gamma-ray. Each standard or sample was placed in the top-center position of a shuttle rabbit and irradiated for 5.00 seconds in the Row I position using the pneumatic-tube irradiation facility at MURR. This position has thermal and epithermal neutron flux densities of 8×10^{13} neutrons x centimeter^{-2} x second^{-1} and 2×10^{12} neutrons x centimeter^{-2} x second^{-1}. The pneumatic transfer facility used has a delivery time to the counting station of about 4 seconds. The returned shuttle rabbit was opened quickly and the sample vial transferred to a special holder that positions the small polyethylene vial on the face of the detector. All samples were analyzed using a 5-second irradiation, 15-second decay, and 25-second real-time count using a high resolution gamma-ray spectrometer. The gamma-ray spectrometer included a Tennelec 244 amplifier coupled to a Nuclear Data 599 loss-free counting module and a Nuclear Data 581 ADC (analog-to-digital converter). Data acquisition and peak extraction were done using a VAX station 3100, model 38 with Canberra/ND applications software. The 161.9keV gamma-ray from the decay of ^{77m}Se was used to determine selenium concentrations by standard comparison (Spate and others, 1994; Baskett and others, 2001).

Results

Total selenium concentrations [micrograms per gram dry weight, (µg/g)] in fish muscle plug samples collected from fish inhabiting the Gunnison River in western Colorado are listed in table 1. Total selenium concentrations [range and mean ± standard deviation (SD)] in µg/g dry weight were 6.0 to 10.7, 8.8 ± 1.3 for common carp; 2.9 to 8.7, 5.6 ± 2.4 for Colorado pikeminnow; and 1.4 to 7.3, 3.4 ± 2.7 for razorback sucker. The selenium concentration for 1 bonytail chub sample was 0.8 micrograms per gram dry weight. Selenium concentrations in muscle plugs from 1 Colorado pikeminnow and 12 common carp exceeded the 8 micrograms per gram dry weight toxicity guideline (Lemly, 2002) for selenium in fish muscle tissue.

Quality-Control Results

Concentrations (µg/g dry weight) of selenium in National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1577 Bovine Liver (n=3) averaged 1.13 and ranged from 1.11 to 1.14 with an SD of 0.017 µg/g (table 2). Compared with the certified selenium concentration (1.1 ± 0.1 µg/g), these results expressed selenium recoveries that were all within this certified range.

Table 1. Concentrations of selenium in fish muscle plugs collected from fish inhabiting the Gunnison River in western Colorado, March through October, 2012.

[USGS, United States Geological Survey; ID, identification; µg/g, micrograms per gram dry weight]

USGS ID	Field ID	Fish common name	Collection date (month/day/year	Percent moisture	Selenium (µg/g)
57506	GRZ5705	razorback sucker	10/01/12	80.8	1.53
57507	GRZ5E22	razorback sucker	10/01/12	77.3	1.35
57508	GRZDE84	razorback sucker	10/05/12	78.2	7.28
57509	GRZ61FD	razorback sucker	10/05/12	72.8	5.20
57510	GRZ9D7B	razorback sucker	10/04/12	78.7	1.40
57511	GPMCE69	colorado pikeminnow	10/04/12	78.2	5.08
57512	GPMCE69B	colorado pikeminnow	07/31/12	66.2	2.93
57513	GPM5DEF	colorado pikeminnow	07/18/12	83.7	8.68
57514	GPMD35C	colorado pikeminnow	07/18/12	76.4	5.68
57515	PS-E826	bonytail	03/13/12	69.7	0.77
57516	12GRCMP1	common carp	08/27/12	76.2	8.49
57517	12GRCMP2	common carp	08/27/12	76.6	9.76
57518	12GRCMP3	common carp	08/28/12	79.8	8.04
57519	12GRCMP4	common carp	08/29/12	72.2	8.47
57520	12GRCMP5	common carp	08/29/12	75.7	6.03
57521	12GRCMP6	common carp	08/29/12	75.9	9.49
57522	12GRCMP7	common carp	08/30/12	71.9	9.39
57523	12GRCMP8	common carp	08/30/12	77.9	10.45
57524	12GRCMP9	common carp	08/30/12	78.9	6.87
57525	12GRCMP10	common carp	08/30/12	78.6	9.15
57526	12GRCMP11	common carp	08/31/12	74.3	7.64
57527	12GRCMP12	common carp	10/05/12	75.6	10.1
57528	12GRCMP13	common carp	10/03/12	77.7	10.7
57529	12GRCMP14	common carp	10/03/12	78.2	9.67
57530	12GRCMP3B	common carp	08/28/12	76.4	7.40
57531	12GRCMP7B	common carp	08/30/12	85.3	8.66

Table 2. Selenium recoveries from a reference tissue material analyzed with fish muscle plug samples.

[MURR, University of Missouri Research Reactor; QC, quality control; ID, identification; µg/g, microgram per gram dry weight; SD, standard deviation; RSD, relative standard deviation; NIST, National Institute of Standards and Technology; ±, plus or minus; na, not applicable]

MURR QC ID	Reference material	Certified range (µg/g)	Selenium (µg/g)	Mean (µg/g)	SD (µg/g)	Percent RSD[a]
BL-Z-66	NIST 1577[b]	1.1 ± 0.1	1.14	1.13	0.017	1.5
BL-Z-67	na	na	1.11	na	na	na
BL-Z-68	na	na	1.14	na	na	na

[a]Calculated as standard deviation divided by mean times 100.

[b]Standard Reference Material 1577: Bovine liver.

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