

Prepared in collaboration with the U.S. Fish and Wildlife Service

Determination of Selenium in Fish from Designated Critical Habitat of the Gunnison River, Colorado, Summer 2011

Open-File Report 2012–1235

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By Thomas W. May and Michael J. Walther

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U.S. Department of the Interior
U.S. Geological Survey

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Contents

Abstract.....	1
Introduction.....	1
Methods.....	1
Field Collection and Preservation	1
Sampling History	1
Lyophilization	1
Instrumental Analysis.....	2
Results	2
Quality-Control Results	2
References Cited.....	4

Tables

1. Concentrations of selenium in fish muscle plugs collected from fish inhabiting the Gunnison River in Western Colorado, summer 2011.....3
2. Selenium recoveries from a reference tissue material analyzed with fish muscle plug samples.....4

Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
millimeter (mm)	0.03937	inch (in.)
	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)
milligram (mg)	0.000035	ounce, avoirdupois (oz)
microgram (μg)	0.00000035	ounce, avoirdupois (oz)

Temperature in degrees Celsius ($^{\circ}\text{C}$) may be converted to degrees Fahrenheit ($^{\circ}\text{F}$) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Concentrations of chemical constituents in solid materials are given in micrograms per gram ($\mu\text{g/g}$) dry weight.

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Abstract

This report presents results for the summer 2011 sampling of muscle plugs from common carps (*Cyprinus Linnaeus*), roundtail chub (*Gila robusta*), and bonytail chub (*Gila elegans*) 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 \pm standard deviation) in micrograms per gram dry weight for each species were as follows: common carp: 8.5 to 35, 13 ± 7.8 ; roundtail chub: 5.5 to 11.2, 7.3 ± 1.6 ; bonytail chub: 0.8 to 8.6, 3.9 ± 4.2 . Selenium concentrations in muscle plugs from 4 out of 15 roundtail chub, all 15 common carp, and 2 out of 5 bonytail chub 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 (ug/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 (*Xyrisuchen 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, roundtail chub, and bonytail chub collected during the summer of 2011 from a lower stretch of designated critical habitat in the Gunnison River between Escalante and the Colorado River confluence.

Methods

Field Collection and Preservation

Muscle plug samples were taken with a biopsy punch from live specimens of common carp, roundtail chub, and bonytail chub collected from the Gunnison River between Escalante (river mile 44.1) and the Colorado confluence (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 in August of 2011. 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 August 31, 2011, and contained 17 common carp muscle plugs, 15 roundtail chub muscle plugs, and 5 bonytail chub muscle plugs. The samples were assigned USGS batch number 1941 and USGS sample identification numbers 55406 to 55442. Selenium was to be determined in all samples by instrumental neutron activation analysis (INAA).

Lyophilization

All sample preparation before INAA was conducted by USGS at the Columbia Environmental Research Center in Columbia, Missouri in collaboration with the University of

2 Determination of Selenium in Fish from Designated Critical Habitat of the Gunnison River, Colorado, Summer 2011

Missouri Research Reactor (MURR). The entire plug was transferred from its original cryotube container into a 1.5 mL polyethylene vial provided by MURR staff. Vials were pre-cleaned 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 milli Torr was reached, the drying cycle commenced. All muscle plug samples were lyophilized to constant weight, and dried weights ranged from 20.8 to 60.1 milligrams (mg) and averaged 41.4 mg. Lyophilization greatly reduces the oxygen-19 radioisotope (¹⁹O) 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: ⁷⁶Se(n,γ)^{77m}Se and ^{77m}Se→^{77m}Se+γ 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 x 10¹³ neutrons x centimeter⁻² x second⁻¹ and 2 x 10¹² 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 quickly

opened 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. 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 for each species were as follows: common carp: 8.5 to 35, 13 ± 7.8; roundtail chub: 5.5 to 11.2, 7.3 ± 1.6; bonytail chub: 0.8 to 8.6, 3.9 ± 4.2. Selenium concentrations in muscle plugs from 4 out of 15 roundtail chub, all 15 common carp, and 2 out of 5 bonytail chub exceeded the 8 µg/g 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*=4) averaged 1.14 and ranged from 1.13 to 1.17 with an SD of 0.021 µg/g (table 2). Compared with the certified selenium concentration, these results expressed a selenium recovery of 104 percent with a percent relative standard deviation of 1.8.

Table 1. Concentrations of selenium in fish muscle plugs collected from fish inhabiting the Gunnison River in Western Colorado, summer 2011.

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

USGS ID	Field ID	Fish common name	Collection date	Percent moisture	Selenium (µg/g)
55406	GIICCP1	Common carp	08/19/11	72.5	10.2
55407	GIICCP2	Common carp	08/18/11	79.3	12.2
55408	GIICCP3	Common carp	08/18/11	78.5	8.50
55409	GIICCP4	Common carp	08/18/11	79.4	10.2
55410	GIICCP5	Common carp	08/17/11	77.9	10.6
55411	GIICCP6	Common carp	08/19/11	77.5	10.0
55412	GIICCP7	Common carp	08/19/11	79.0	10.9
55413	GIICCP8	Common carp	08/19/11	70.7	8.45
55414	GIICCP9	Common carp	08/17/11	78.0	9.74
55415	GIICCP10	Common carp	08/17/11	82.3	32.2
55416	GIICCP11	Common carp	08/18/11	76.4	10.5
55417	GIICCP12	Common carp	08/19/11	76.7	10.9
55418	GIICCP13	Common carp	08/19/11	77.4	11.6
55419	GIICCP14	Common carp	08/19/11	72.0	9.67
55420	GIICCP15	Common carp	08/18/11	79.7	11.0
55421	GU-BTMP3	Bonytail	08/23/11	72.3	0.81
55422	GU-BTMP3B	Bonytail	08/23/11	74.4	0.89
55423	GII-RTC1	Roundtail chubs	08/17/11	79.4	5.62
55424	GII-RTC2	Roundtail chubs	08/18/11	80.0	6.17
55425	GII-RTC3	Roundtail chubs	08/17/11	80.4	7.06
55426	GII-RTC4	Roundtail chubs	08/19/11	80.7	8.47
55427	GII-RTC5	Roundtail chubs	08/17/11	79.3	5.59
55428	GII-RTC6	Roundtail chubs	08/19/11	80.0	8.94
55429	GII-RTC7	Roundtail chubs	08/19/11	79.8	7.86
55430	GII-RTC8	Roundtail chubs	08/19/11	80.0	8.78
55431	GII-RTC9	Roundtail chubs	08/19/11	79.9	7.80
55432	GII-RTC10	Roundtail chubs	08/19/11	79.5	7.75
55433	GII-RTC11	Roundtail chubs	08/18/11	80.7	5.50
55434	GII-RTC12	Roundtail chubs	08/19/11	80.7	11.2
55435	GII-RTC13	Roundtail chubs	08/18/11	80.7	6.85
55436	GII-RTC14	Roundtail chubs	08/17/11	79.7	5.45
55437	GII-RTC15	Roundtail chubs	08/18/11	81.5	7.02
55438	GU-BTMP1	Bonytail	06/09/11	80.5	8.34
55439	GU-BTMP2	Bonytail	08/19/11	72.4	0.81
55440	GIICCP13B	Common carp	08/18/11	77.7	11.1
55441	GIICCP10B	Common carp	08/17/11	81.8	35.1
55442	GU-BTMP4	Bonytail	08/29/11	79.0	8.58

4 Determination of Selenium in Fish from Designated Critical Habitat of the Gunnison River, Colorado, Summer 2011

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; --, 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-11	NIST 1577 ^b	1.1 ± 0.1	1.15	1.14	0.021	1.8
BL-Z-12	NIST 1577 ^b	1.1 ± 0.1	1.13	--	--	--
BL-Z-15	NIST 1577 ^b	1.1 ± 0.1	1.17	--	--	--
BL-Z-16	NIST 1577 ^b	1.1 ± 0.1	1.13	--	--	--

^aCalculated as $SD \div \text{mean} \times 100$.

^bSRM 1577: bovine liver.

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