EXHIBIT 16

Evaluation of Flushing of a High-Selenium Backwater Channel in the Colorado River

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ABSTRACT: Concern has been raised that selenium contamination may be adversely affecting endangered fish in the upper Colorado River basin. The objective of the study was to determine if operation of a water control structure (opened in December 1996) that allowed the Colorado River to flow through a channel area at Walter Walker State Wildlife Area (WWSWA) would reduce selenium and other inorganic elements in water, sediment, aquatic invertebrates, and forage fish. Endangered Colorado pikeminnow were collected and muscle plug samples taken for selenium analysis. Selenium concentrations in filtered water were 21.0 μg/L in 1995, 23.5 μg/L in 1996, 2.1 μg/L in 1997, and 2.1 μg/L in 1998. Selenium concentrations in sediment cores and sediment traps were 8.5 μg/g in 1995, 8.2 μg/g in 1996, 4.8 μg/g in 1997, and 1.1 μg/g in 1998. Selenium concentrations in aquatic invertebrates were 27.4 μg/g in 1996, 15.5 μg/g in 1997, and 4.9 μg/g in 1998. Selenium concentrations in forage fish were 27.2 μg/g in 1996, 20.2 μg/g in 1997, and 8.6 μg/g in 1998. Selenium concentrations in muscle plugs of Colorado pikeminnow were 9.8 μg/g in 1995, 9.5 μg/g in 1996, 9.0 μg/g in 1997, and 10.3 μg/g in 1998. Although selenium concentrations in water, sediment, aquatic invertebrates, and forage fish decreased substantially after operation of the water control structure, a corresponding change in Colorado pikeminnow did not seem to occur. Selenium concentrations in muscle plugs decreased with increasing fish total length and weight, did not change between repeat sampling in the same year or recapture in subsequent years, and seemed to be most closely associated with the mean monthly river flow for the March–July period.
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Keywords: Colorado pikeminnow; selenium; endangered fish; flushing; Colorado River; trace elements; remediation

INTRODUCTION

Selenium contamination of the upper and lower Colorado River basins has been documented in water, sediment, and biota in studies by U.S. Department of the Interior agencies and academia (reviewed in Hamilton, 1998). Historic selenium contamination of the upper and lower Colorado River

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basins prior to the construction of main stem dams has been hypothesized to have contributed to the decline of native fish now federally listed as endangered (Hamilton, 1999). Earlier reports have suggested that endangered fish, especially razorback sucker, are being adversely affected by selenium contamination in the Green, Price, Yampa, and upper Colorado rivers (Hamilton, 1998; Stephens and Waddell, 1998; Hamilton et al., 2000).

The upper Colorado River provides critical habitats for four endangered fish species: Colorado pikeminnow (*Ptychocheilus lucius*), razorback sucker (*Xyrauchen texanus*), humpback chub (*Gila cypha*), and bonytail (*Gila elegans*) (USFWS, 1987, 1994). A combined approach for recovery of the four endangered fish in the upper Colorado River basin was undertaken in 1987 by the Upper Colorado River Endangered Fish Recovery Program (USFWS, 1987). The goal of the 15-year program was to reestablish self-sustaining populations of the four species while allowing continued water development.

In an effort to stabilize and enhance populations of endangered fishes in the upper Colorado River, the Floodplain Habitat Restoration Program within the Recovery Program has undertaken the task of restoring floodplain habitats for use by endangered fish larvae and adults. The proposed strategy for achieving these goals was to reconnect selected floodplain habitats to the main river channel in a manner that simulated historic hydrological conditions. An important component of this program was to select sites that after restoration would not pose contaminant problems to the fish, especially from selenium.

Adult Colorado pikeminnow are typically found in the deep fast-flowing waters of the Colorado River and in large pools of tributaries and are slow-growing and piscivorous (Moyle, 1976). Young Colorado pikeminnow less than 50 mm in total length frequent the quiet waters of the river's edge or shallow pools and feed mostly on cladocerans, copepods, and chironomid larvae (Moyle, 1976). By the 1970s Colorado pikeminnow had been extirpated from the Colorado River below Glen Canyon Dam (Moyle, 1976). The status and trends of the Colorado pikeminnow were reviewed by Osmundson and Burnham (1998), who estimated there were 598 Colorado pikeminnow in the upper Colorado River: 254 adults in the upper 98 km and 344 adults and subadults in the lower 181 km. They concluded that the abundance of Colorado pikeminnow was lower than that suggested in historical accounts. The current population was thought to have a constant adult survival rate, but recruitment was highly variable and could represent the most important demographic factor to population persistence in the upper Colorado River basin. High spring river flows were speculated to be an important precursor to successful reproduction of Colorado pikeminnow because of the importance of flow on maintaining cobble bars used for spawning, diluting pollutants, maintaining channel diversity and biological productivity, and reducing the number of nonnative fish in backwater nursery areas (Osmundson and Burnham, 1998).

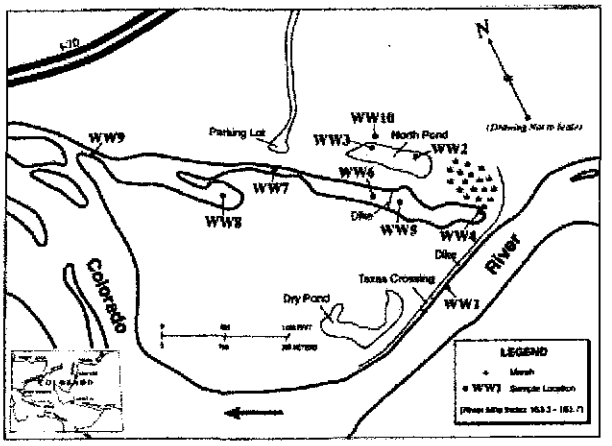

Fig. 1. Map of sampling stations during 1995–1996 at Walter Walker State Wildlife Area near Grand Junction, CO.

The study was conducted in the backwater channel of the Colorado River at Walter Walker State Wildlife Area (WWSWA) near Grand Junction, Colorado, which is highly contaminated with selenium (Butler and Osmundson, 2000; Hamilton et al., 2001a, 2001b). Numerous adult Colorado pikeminnow have been routinely found at WWSWA (Kidd, 1977; Valdez et al., 1982; Valdez and Wick, 1983; Archer et al., 1985; Osmundson and Kaeding, 1989; Mourning, 1995; Lloyd, 1996; Scheer, 1997). Recently, Colorado pikeminnow captured at WWSWA have been documented to have higher selenium concentrations in muscle plugs than have adults collected in other parts of the upper Colorado River basin (Butler and Osmundson, 2000; Osmundson et al., 2000). This backwater is also where razorback sucker had historically been observed (McAda, 1977; Kidd, 1977; Valdez et al., 1982; Osmundson and Kaeding, 1989).

The objective of this study was to determine if a water control structure that allowed flushing of a selenium-contaminated backwater with water having lower selenium than the backwater would reduce selenium concentrations in water, surficial sediment, aquatic invertebrates, forage fish, and Colorado pikeminnow.

MATERIALS AND METHODS

The study was conducted between May 1995 and September 1998 at WWSWA (Fig. 1), which is about a half kilometer southwest of the Grand Junction city limits.

Site Description

The sampling stations at WWSWA were designated WW1 through WW10 (Fig. 1). The backwater channel is in a bend

in the Colorado River that formerly was a gravel pit. A dike along the north side of the Colorado River prevents the river from flowing through the channel area. During spring runoff the river backs into the channel area at station WW9 and creates a backwater pool that in some years has extended the entire length of the channel to station WW4. In 1996 a water control structure was constructed in the dike near WW4 to provide flushing flows into the channel area from the Colorado River in order to reduce selenium concentrations in water, sediment, and biota. The water control structure was opened on December 5, 1996. The backwater channel receives an inflow of groundwater from the underlying cobble aquifer (Phillips, 1986). Elevated selenium concentrations in groundwater and surface seeps entering the channel area have been documented by Butler and Osmundson (2000).

North Pond is at WWSWA and is an isolated pond about 1 ha in size with a maximum depth of 1.5 m on a terrace about 2 m above the backwater channel. Water in North Pond was supplied primarily by groundwater discharge, which contained elevated selenium concentrations (Butler and Osmundson, 2000). The south side of North Pond had a dike and water overflow structure installed to maintain water levels, and overflow water entered the channel area. Water levels at North Pond were supplemented by inflow at WW10 from Independent Ranchman's Ditch. The channel area near WW6 received effluent from North Pond during periods between 1995 and 1997 when water from Independent Ranchman's Ditch was used to maintain water levels for a reproduction study with adult razorback sucker (Hamilton et al., 2001a, 2001b).

The sampling station at the outfall of the marsh was designated WW4 (Fig. 1) prior to construction and operation of the water control structure; it was designated WW4a after the installation and opening of the water control structure and was at the mixing zone of the water control structure and the marsh outfall (Fig. 2). A new station, WW4b, was established away from the mixing zone and nearer the marsh. Sampling station WW8 (Fig. 1), designated prior to the construction and operation of the water control structure, was designated WW8a after installation and opening of the control structure, and a new station, WW8b, was established (Fig. 2). Following operation of the water control structure, it became apparent that the water flow through the channel area was uniformly mixed. Consequently, the sampling of water quality characteristics was discontinued at WW5, WW7, and WW9 in 1997 and 1998.

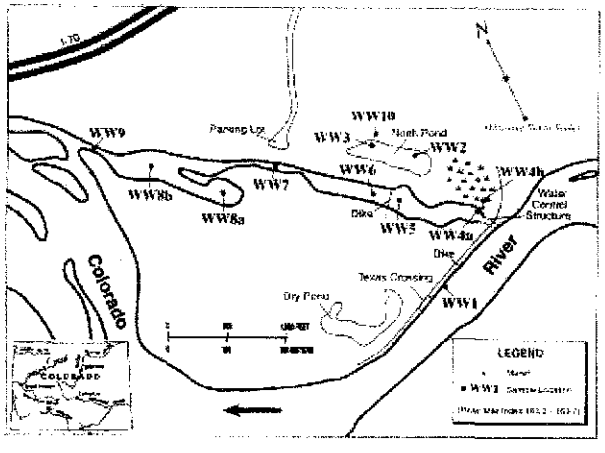

Fig. 2. Map of sampling stations during 1996–1998 at Walter Walker State Wildlife Area near Grand Junction, CO.

Fish and Aquatic Invertebrate Sampling

Fish were captured at various sites in the backwater channel by personnel of the Colorado River Fishery Project (CRFP), Grand Junction, Colorado. Details of fish collection and the resulting data are given in articles by Mourning (1995), Lloyd (1996), and Scheer (1997, 1998). Briefly, fish were collected by using fyke nets, using trammel nets, seining, using minnow traps, electrofishing, or a combination of two or more of these methods. Sampling was accomplished from April to late summer, when water levels dropped. Fish were identified by species and age classification and counted, and total length and weight were measured. Samples of forage fish were placed in Whirl-Pak bags, stored frozen at −20°C while awaiting analysis of total selenium and other inorganic elements, and shipped with dry ice when transported.

One razorback sucker was collected during 1995–1998, whereas numerous Colorado pikeminnow were collected each year. The razorback sucker, which was collected in 1995, did not have a passive integrated transponder (PIT) and was moved to the CRFP facility at Horsethief Canyon State Wildlife Area. For each Colorado pikeminnow collected, the PIT tag was determined, total length and weight were recorded, and a muscle plug sample for selenium analysis was taken from the dorsal area adjacent to the dorsal fin. If no PIT tag was found, a new one was implanted. Muscle plugs were collected using a 4- or 5-mm biopsy punch, placed in cryotubes, stored on ice in the field, stored in a freezer (−20°C) while awaiting analysis of selenium concentrations, and shipped with dry ice when transported.

Aquatic invertebrates were collected from stations in the channel using modified light traps (Espinosa and Clark, 1972) and sediment grab samplers. Light traps were set overnight and the trapped zooplankton and other aquatic invertebrates were collected the following morning. At each sampling station the contents of all the light traps were combined and concentrated by filtering the samples through the basket of a 153-μm plankton net. The combined samples were then backwashed into a 3.8-L plastic jar filled with site water, covered, and transported to the laboratory in coolers. In the laboratory the samples were filtered to remove water,

placed in Whirl-Pak bags, stored frozen at −20°C while awaiting analysis of total selenium and other inorganic elements, and shipped with dry ice when transported.

Benthic grab samples were collected in plastic jars and transported in coolers to the laboratory for separation of benthic invertebrates. Sediment samples were washed through a set of sieves and the invertebrates extracted from the debris using stainless-steel or plastic forceps.

Some sediment samples were shipped with wet ice packs to the Yankton Field Research Station (FRS) for separation of benthic invertebrates. Composite samples of invertebrates were placed in Whirl-Pak bags, stored frozen at −20°C while awaiting analysis of total selenium and other inorganic elements, and shipped with dry ice when transported.

Water and Sediment Sampling

From May 1995 to September 1998 selected water-quality characteristics were measured *in situ* on an irregular basis at the sampling stations in the channel area. In addition, water was collected on a regular basis at sample stations and analyzed for general water quality characteristics in a mobile laboratory housed at the CRFP facility. Water quality characteristics measured *in situ* at each station included pH, conductivity, and salinity. Water quality characteristics in unfiltered water samples measured in the mobile laboratory included pH, conductivity, hardness, calcium, magnesium, alkalinity, and chloride. Two subsamples of each sample taken to the mobile laboratory were collected in polyethylene bottles. One sample was used for ammonia analysis and was acidified to a pH of less than 2 with concentrated sulfuric acid. The other sample was used for nitrate, nitrite, sulfate, total suspended solids, volatile solids, and fixed solids analyses and was stored in a refrigerator at 4°C. These subsamples were then shipped in a cooler with wet ice packs by overnight express to the Yankton FRS for analysis. All water-quality characteristics were measured according to standard methods (APHA et al., 1995), except for the nitrogenous chemicals and chloride. Ammonia, nitrate, and nitrite were measured using ion-selective electrodes according to the procedures for low-concentration measurements of the electrode manufacturer (Orion, 1990, 1991; ATI Orion, 1994). Chloride was measured using the mercuric nitrate titration method (Hach Company, 1992, 1997).

Subsamples of water collected for water-quality analyses from sample stations were taken for analyses of selenium and inorganic elements. Filtered and unfiltered water was collected for selenium analysis. The water was filtered through a 0.4-μm polycarbonate filter using a Geotech filtration unit, and 200 mL of the filtered water was acidified with 2 mL of ultrapure HCl and stored frozen until the analysis of dissolved selenium concentrations. Two hundred milliliters of the unfiltered water was acidified with 2 mL of ultrapure HCl and stored frozen until the analysis of total selenium concentrations. Samples for analysis of inorganic elements were filtered as described above, acidified with 2 mL of ultrapure HNO_3, and stored frozen.

Samples of bottom sediment (hereafter referred to as sediment) were collected between May 1995 and September 1998 for analysis of selenium concentrations. Between 1995 and mid-1996, sediment was collected by a petit ponar grab sampler, placed in a large plastic pan and thoroughly mixed, and then large pieces of debris (plants, twigs, rocks, etc.) were removed. Subsamples of the homogenized sediment were collected in polyethylene bottles and stored in a freezer until analysis. One sample was analyzed for total selenium concentration, and a second sample was analyzed for concentrations of inorganic elements. A second portion of each sample collected between October 1995 and April 1996 was analyzed for total and inorganic carbon and for total, volatile, and fixed solids, and a third portion was examined for sediment particle size.

Samples for carbon analysis were oven dried overnight at 105°C in a Fisher Isotemp oven. Dried samples were homogenized and ground in a CRC Micro-mill (Pequannock, NJ). Subsamples of about 30 mg each were wrapped in aluminum foil and bagged in Whirl-Pak bags. The subsamples were sent to the Columbia Environmental Research Center (CERC), Columbia, Missouri, for analysis of total and inorganic carbon; organic carbon was determined by subtraction. The carbon analyses were accomplished with a Coulometrics Carbon model 5020 analyzer (Joliet, IL).

Total, volatile, and fixed solids measurements were determined by standard methods (APHA et al., 1995). Briefly, subsamples were weighed in an aluminum drying pan and air-dried prior to oven drying and muffle furnace ignition. Total solids were measured by drying the sediment overnight in a Fisher Isotemp oven (St. Louis, MO) at 105°C. Constant weights were determined by weight loss of less than 4% or 50 mg, whichever was less. Fixed and volatile solids measurements were determined by ignition at 550°C for 60 min in a Thermolyne model FA1730 muffle furnace (Dubuque, IA) and then allowed to cool overnight in the furnace before weighing.

Sediment particle size was determined by standard methods (ASTM, 1993). Samples were air-dried on fiberglass trays for 3–6 days, and large aggregates of dried sediment were crushed with a mortar and rubber-covered pestle. The dried sediment was sieved to remove particles greater than 2.0 mm in size. Dried sediment samples were weighed and then stored at 4°C until analysis. Each sample was analyzed in duplicate. Hydrometer analyses were conducted according to standard methods in 1-L sedimentation cylinders or graduated cylinders using ASTM model 152H hydrometers (ASTM, 1990). Briefly, sediment subsamples were dispersed overnight in a 40 g/L sodium hexametaphosphate solution. A Hamilton Beach Scovill mechanical stirrer

(Washington, NC) and a cup with baffles were utilized to further disperse the sample before hydrometer analysis. The results were plotted on graph paper, and the percentage for the particle size of interest was interpolated from the graph. Particle sizes were classified according to the U.S. Geological Survey (USGS) classification scheme, which is based on the Wentworth-grade scale: clay, <0.004 mm; silt, 0.004–0.062 mm; and sand, 0.063–2.0 mm (Guy, 1969).

From late 1996 through 1998 sediment sampling was done by coring and with traps. Sediment core samples were collected by pushing a 30-cm long, 7.6-cm-diameter polyvinyl chloride plastic (PVC) pipe (previously cut in half lengthwise) into the sediment using an apparatus that prevented the sides from splitting open as the pipe was forced into the sediment. The apparatus had a removable cap that was placed on top of the pipe to hold the halves together. The removable cap had a small hole in it through which overlying water escaped from the pipe as it was inserted into the sediment. After pipe insertion a rubber stopper was placed in the cap hole to create a vacuum in the pipe during removal of the pipe from the sediment so as to maintain the integrity of the sample during the removal process. After removal, the top and bottom pipe ends were capped. The cores were immediately frozen to maintain the longitudinal integrity of the sample and were shipped frozen. Three subsamples of each sediment core were collected by removing the end caps, splitting the pipe sides, removing the frozen sediment core, and cutting 1-cm sections from the top, middle (≈15 cm deep), and bottom (≈30 cm deep) of each core sample. Any frozen overlaying water was discarded. These 1-cm sections were analyzed for total selenium concentrations.

Sediment traps consisted of 22.9-cm long, 15.3-cm-diameter PVC pipes that were capped at one end. The capped end was pushed into the sediment and left to passively collect sediment over a period of time. Sediment traps were capped prior to removal from the sediment, placed in an upright position in a cooler for transport, and stored and shipped frozen. Any frozen overlying water was discarded. When sufficient sediment was available from a sediment trap, the sediment was cut into upper and lower portions for analysis of selenium concentrations.

Inorganic Element Analyses

Most samples collected for selenium analysis were analyzed at the Yankton FRS using a Perkin–Elmer model 3300 atomic absorption spectrophotometer equipped with a model MHS-10 hydride generator (AA-HG) (Norwalk, CT). The spectrophotometer was standardized with National Institute of Standards and Technology (NIST) standard reference material 3149 (water).

Water samples were digested using a persulfate digestion technique, and total selenium was determined by a modification of the method of Presser and Barnes (1984). Some samples were analyzed at the Environmental Trace Substances Laboratory (ETSL), University of Missouri, Rolla, Missouri. Similar equipment and procedures were used at ETSL in analyses, except that analysis of selenium concentrations was based on the U.S. Environmental Protection Agency (EPA) method 7000 (USEPA, 1983). Quality assurance/quality control measures included determination of the limit of detection, use of procedural blanks for background equivalent concentration, percent relative standard deviation of triplicate sample preparation and analysis, recovery of elements from reference material, and recovery of digested-spiked sample solutions and analysis-spiked samples.

For water, the mean limit of detection (LOD) was 1.0 μg/L at both analysis labs [standard error (*SE*) 0.1, $n = 37$]. The procedure blanks had background concentrations less than the LOD, which indicated no contamination from reagents or sample handling. The mean percent relative standard deviation (triplicate sample preparation and analysis) was 6.1% (*SE* 1.8, $n = 36$), which indicated consistent sample handling during preparation, digestion, and analysis. Recovery of selenium from NIST reference material 1643c water, NIST reference material 1643d, and Environmental Resources Associates 9969TM reference water was within the CERC's recommended ranges, indicating the digestion and analysis procedure accurately measured selenium concentrations. The mean percent recovery of digested-spiked sample solutions was 99% (*SE* 1, $n = 37$), indicating the digestion procedure did not alter the amount of spiked selenium in the sample, that is, it suggested no loss of selenium in water samples during the digestion procedure. Mean selenium recovery of analysis-spiked samples analyzed for matrix suppression or enhancement was 100% (*SE* 1, $n = 32$), which indicated no interference from other water components.

All sediment, aquatic invertebrate, and fish samples were prepared for analyses of selenium concentrations by first lyophilizing the sample to a constant dry weight using a Virtis Vacu-Freezer (Gardiner, NY). Fish samples were then homogenized with a food processor. Animal tissue, fish food, and sediment samples were digested using a combination nitric acid wet digestion and magnesium nitrate dry ash technique (Pettersson et al., 1986). The dry ash procedure was accomplished in a Thermolyne model FA1730 muffle furnace. Total selenium was determined by a modification of the method of Presser and Barnes (1984). Quality assurance/quality control measures were the same as for the water analyses, and the results are summarized in Table I.

Analyses of inorganic elements in water, aquatic invertebrates, and forage fish samples were performed by inductively coupled plasma spectroscopy (ICP) at the Environmental Trace Substances Research Center (University of Missouri), Rolla, Missouri. The list of elements and the LOD are given in Table II. For water, the pro-

TABLE I. Mean (standard error in parentheses and number of samples in brackets) quality assurance and quality control measures for selenium analysis of sediment, aquatic invertebrates, and forage fish

Measure	Matrix		
	Sediment	Aquatic Invertebrates	Fish
Limit of detection (μg/g)	0.16	0.16	0.4
	(0.04)	(0.05)	(0.7)
	[10]	[8]	[45]
RSD (%)[a]	9.0	3.4	7.6
	(3.5)	(1.3)	(1.2)
	[10]	[8]	[4]
Reference material	0.41[b]	1.30[c]	1.20[c]
	(0.01)	(0.03)	(0)
	[8]	[7]	[2]
	1.04[d]	5.20[e]	5.20[e]
	(0.16)	(0.06)	(0.06)
	[2]	[4]	[4]
Digested spikes[f]	102	98	84
	(2)	(3)	(2)
	[18]	[13]	[4]
Analysis spikes[g]	102	108	—
	(3)	(2)	
	[8]	[5]	

[a] RSD: Percent relative standard deviation for duplicate or triplicate preparation and analysis.

[b] National Research Council of Canada (NRCC) reference material BCSS-1 [marine sediment; 0.43 ± 0.06 (standard deviation; SD) μg/g].

[c] NRCC reference material DORM-2 [dogfish muscle tissue; 1.40 ± 0.09 (SD) μg/g].

[d] National Bureau of Standards reference material Buffalo River sediment (no certified concentration).

[e] NRCC reference material DOLT-1 [dogfish liver; 6.06 ± 0.49 (SD) μg/g].

[f] Percent recovery of selenium from samples spiked with selenium at the beginning of preparation for sample analysis.

[g] Percent recovery of selenium from digested samples spiked with selenium after sample preparation but before instrument analysis.

cedure blank had background equivalent concentrations less than the LOD for all elements except boron, iron, and magnesium in one blank and aluminum, copper, lead, magnesium, and strontium in a second blank. The mean percent relative standard deviation (duplicate sample preparation and analysis) was 1.7% (n = 3); the mean spike recovery was 103% (n = 3); and the recovery of trace elements in Environmental Resources Associates reference water ERA9969TM (n = 3) was within recommended ranges except for aluminum in two analyses. For aquatic invertebrates, the procedure blank had background equivalent concentrations less than the LOD for all elements except for arsenic and boron, the mean percent relative standard deviation (duplicate sample preparation and analysis) was 7.2% (n = 1), the mean spike recovery was 97% (n = 1), and the recovery of trace elements in National Research Council of Canada (NRCC) reference material DORM2 (dogfish muscle, n = 1) was within recommended ranges except for arsenic, cadmium, and lead. For forage fish, the procedure blank (n = 2) had background equivalent concentrations less than the LOD for all elements except zinc in one sample, the mean percent relative standard deviation (duplicate sample preparation and analysis) was 6.2% (n = 2), the mean spike recovery was 96% (n = 2), and the recovery of trace elements in NRCC reference material DOLT2 (dogfish liver, n = 2) was within recommended ranges except for arsenic, cadmium, manganese, and zinc in one sample and iron in a second sample.

Muscle plugs from Colorado pikeminnow were analyzed for selenium concentrations by neutron activation. Muscle plugs were prepared for analysis at CERC, and neutron activation analysis was performed at the University of Missouri Research Reactor (MURR), Columbia, Missouri. All sample preparation prior to neutron activation analyses as well as the neutron activation method were described in Waddell and May (1995). Samples were transported to MURR for determination of radionuclide ^{77m}Se (McKown and Morris, 1978). Selenium standards and quality control samples were analyzed in the same manner as animal tissues. National Institute of Standards and Technology 1577 (bovine liver) standard reference material was analyzed by MURR as a quality control check on accuracy and precision. The recovery of selenium was within the NIST recommended range, and the percent relative standard deviation of multiple analyses was

TABLE II. Limit of detection of elements measured by inductively coupled argon plasma spectroscopy in water (μg/L), aquatic invertebrates (μg/g dry weight), and forage fish (μg/g dry weight)

Element	Matrix		
	Water	Aquatic Invertebrates	Fish
Aluminum	40	4	2
Arsenic	20	5	2
Boron	4	0.4	0.5
Barium	0.6	0.1	0.06
Beryllium	0.1	0.1	0.06
Cadmium	2	0.4	0.2
Chromium	6	1	1
Copper	1	0.4	0.3
Iron	4	0.8	0.5
Lead	20	3	2
Magnesium	1	0.1	0.5
Manganese	1	0.2	0.1
Molybdenum	4	0.8	0.5
Nickel	4	0.9	0.6
Strontium	0.2	0.04	0.04
Vanadium	3	0.4	0.2
Zinc	5	0.2	0.09

TABLE III. Mean (range in parentheses and number of samples in brackets) *in situ* water quality measures at several stations in the channel at Walter Walker State Wildlife Area

Year and Measure	Station								
	WW1	WW4	WW4b	WW5	WW6	WW7	WW8	WW8b	WW9
1995									
pH	8.2 (7.3–9.3) [31]	7.8 (7.3–8.6) [30]	NS[a]	8.1 (7.5–8.9) [30]	8.1 (7.4–8.6) [30]	8.0 (7.0–9.1) [30]	8.1 (7.1–9.0) [28]	NS	8.0 (7.0–9.2) [30]
Conductivity (μmhos/cm)	630 (270–1040) [31]	6160 (380–11 120) [30]	NS	4990 (340–11 070) [30]	4470 (310–10 430) [30]	4500 (280–10 290) [30]	3860 (270–7600) [28]	NS	2960 (270–7890) [30]
Salinity (‰)	0.6 (0.5–1.0) [11]	4.4 (1.0–8.0) [25]	NS	3.9 (1.0–7.0) [24]	3.6 (0.5–6.0) [22]	4.3 (3.0–6.0) [19]	3.4 (1.0–5.0) [19]	NS	3.1 (1.0–4.5) [16]
1996									
pH	8.3 (7.2–10.3) [41]	8.2 (8.0–8.6) [4]	7.8 (7.0–8.9) [41]	8.1 (7.5–8.5) [28]	8.1 (7.5–8.6) [41]	8.1 (7.3–9.0) [27]	8.1 (7.5–8.7) [31]	8.1 (7.4–8.6) [12]	8.3 (7.3–9.3) [27]
Conductivity (μmhos/cm)	790 (280–1110) [41]	4310 (1160–11 610) [4]	8810 (1190–13 650) [41]	6770 (820–9830) [28]	4950 (830–8460) [41]	5190 (340–8660) [28]	5670 (1000–9040) [32]	4730 (1010–7340) [12]	3680 (340–9210) [28]
Salinity (‰)	0.7 (0.5–1.5) [30]	2.8 (1.0–7.0) [4]	7.5 (2.4–16.2) [41]	4.2 (1.0–6.0) [28]	3.3 (1.0–5.5) [41]	3.9 (0.5–6.0) [25]	3.8 (1.0–6.5) [32]	3.1 (0.5–4.5) [12]	2.7 (0.5–8.5) [26]
1997									
pH	7.9 (6.8–8.8) [26]	8.0 (7.2–8.7) [26]	7.8 (7.3–8.6) [25]	NS	8.2 (7.5–8.9) [26]	NS	8.0 (6.7–8.9) [19]	8.0 (7.2–8.8) [26]	NS
Conductivity (μmhos/cm)	680 (270–1030) [28]	1120 (280–2760) [28]	7600 (330–14 120) [28]	NS	730 (270–1080) [28]	NS	880 (350–1400) [21]	820 (270–1640) [28]	NS
Salinity (‰)	0.8 (0.5–1.0) [16]	1.1 (0.5–3.0) [17]	6.3 (0.5–9.0) [22]	NS	0.7 (0.5–1.0) [17]	NS	0.9 (0.5–1.0) [15]	0.8 (0.5–1.0) [17]	NS
1998									
pH	8.6 (8.2–9.2) [8]	8.6 (8.3–8.9) [8]	8.3 (7.7–8.6) [8]	NS	8.4 (8.2–9.0) [7]	NS	8.3 (7.6–9.2) [7]	8.7 (7.9–9.3) [8]	NS
Conductivity (μmhos/cm)	710 (380–920) [8]	780 (370–920) [8]	2620 (970–5800) [8]	NS	790 (490–1020) [8]	NS	960 (560–1150) [7]	1030 (500–1810) [8]	NS
Salinity (‰)	<1.0 — [8]	<1.0 — [8]	2.1 (1.0–4.5) [5]	NS	<1.0 — [8]	NS	2.0 — [1]	1.0 (1.0–1.0) [2]	NS

[a] NS: Not sampled.

TABLE IV. Mean (range in parentheses and number of samples in brackets) water quality in the laboratory of samples from several stations in the channel at Walter Walker State Wildlife Area

Year and Measure	Station								
	WW1	WW4	WW4b	WW5	WW6	WW7	WW8	WW8b	WW9
1995									
pH	8.0 (7.4–8.4) [8]	7.8 (7.5–8.2) [8]	NS[a]	8.1 (7.8–8.8) [8]	8.0 (7.8–8.2) [8]	7.9 (7.7–8.1) [8]	8.1 (7.9–8.4) [8]	NS	8.0 (7.8–8.2) [8]
Conductivity (μmhos/cm)	640 (270–930) [8]	7170 (410–11 120) [8]	NS	6030 (340–11 070) [8]	5560 (350–10 430) [8]	5160 (280–10 290) [8]	3940 (270–7570) [8]	NS	2650 (270–5710) [8]
Hardness (mg/L as $CaCO_3$)	226 (104–342) [8]	2280 (130–3680) [8]	NS	1680 (124–3160) [8]	1580 (109–2960) [8]	1420 (106–2900) [8]	1060 (104–2140) [8]	NS	780 (106–1940) [8]
Calcium (mg/L)	61 (31–94) [8]	293 (36–448) [8]	NS	198 (34–308) [8]	184 (32–272) [8]	170 (31–272) [8]	144 (32–264) [8]	NS	116 (32–244) [8]
Magnesium (mg/L)	18 (7–27) [8]	376 (10–622) [8]	NS	289 (9–608) [8]	272 (7–554) [8]	242 (7–540) [8]	171 (6–360) [8]	NS	119 (6–323) [8]
Alkalinity (mg/L as $CaCO_3$)	124 (81–164) [8]	405 (90–616) [8]	NS	261 (86–396) [8]	264 (80–369) [8]	257 (80–385) [8]	217 (80–361) [8]	NS	184 (80–323) [8]
Chloride (mg/L)	46 (12–76) [8]	710 (19–1150) [8]	NS	583 (18–1200) [8]	556 (14–1120) [8]	501 (13–1140) [8]	354 (13–700) [8]	NS	242 (12–630) [8]
Sulfate (mg/L)	153 (49–264) [8]	3620 (68–5900) [8]	NS	2510 (64–5880) [8]	2680 51–5280) [8]	2490 (51–5240) [8]	1600 (52–3700) [8]	NS	1190 (52–3450) [8]
Nitrate (mg/L-N)	0.7 (0.2–2.5) [5]	15.2 (1.5–37) [5]	NS	1.6 (<0.1–2.2) [5]	1.6 (<0.1–2.5) [5]	1.6 (0.1–3.3) [5]	1.3 (<0.1–2.4) [5]	NS	0.82 (0.2–2.7) [5]
Nitrite (mg/L-N)	0.01 (<0.01–0.01) [3]	0.15 (0.06–0.26) [3]	NS	0.10 (<0.01–0.15) [3]	0.09 (<0.01–0.10) [3]	0.10 (0.03–0.22) [3]	0.06 (0.01–0.10) [3]	NS	0.04 (<0.01–0.06) [3]
Total suspended solids (mg/L)	136 (11–540) [8]	24 (10–56) [8]	NS	47 (8–108) [8]	95 (47–227) [8]	89 (31–173) [8]	82 (7–201) [8]	NS	90 (24–238) [8]
Volatile solids (mg/L)	4.4 (1.2–11) [5]	5.7 (2.0–18) [5]	NS	9.3 (1.4–20) [5]	16 (7–24) [5]	14 (5.4–23) [5]	9.2 (1.7–16) [5]	NS	8.1 (3–14) [5]
Fixed solids (mg/L)	44 (9.3–116) [5]	21 (9.6–39) [5]	NS	49 (6.9–88) [5]	101 (39–204) [5]	77 (25–155) [5]	44 (5.6–75) [5]	NS	44 (21–95) [5]

1996									
pH	8.1	7.7	7.5	7.9	7.9	7.8	8.1	8.0	8.0
	(7.8–8.3)	(7.4–8.1)	—	(7.6–8.2)	(7.7–8.2)	(7.4–8.2)	(7.7–8.8)	(7.8–8.4)	(7.8–8.3)
	[12]	[12]	[1]	[8]	[12]	[8]	[9]	[4]	[8]
Conductivity	800	7930	11630	6380	4540	4750	5940	4790	3330
(μmhos/cm)	(280–1090)	(1190–12780)	—	(820–9450)	(830–8460)	(340–7390)	(1230–8330)	(1060–6190)	(340–9210)
	[12]	[12]	[1]	[8]	[12]	[8]	[9]	[4]	[8]
Hardness	259	2390	3350	1760	1220	1370	1570	1260	1050
(mg/L as $CaCO_3$)	(98–370)	(368–4180)	—	(250–2660)	(240–2160)	(120–2440)	(336–2240)	(326–1700)	(120–2520)
	[12]	[12]	[1]	[8]	[12]	[8]	[9]	[4]	[8]
Calcium (mg/L)	70	295	416	222	158	175	189	154	141
	(32–101)	(72–508)	—	(54–336)	(37–264)	(34–312)	(84–264)	(82–206)	(35–276)
	[12]	[12]	[1]	[8]	[12]	[8]	[9]	[4]	[8]
Magnesium (mg/L)	20	401	562	293	202	227	266	213	169
	(4–29)	(46–707)	—	(28–442)	(27–377)	(9–404)	(31–384)	(29–288)	(8–445)
	[12]	[12]	[1]	[8]	[12]	[8]	[9]	[4]	[8]
Alkalinity (mg/L as	129	404	580	310	264	286	264	233	189
$CaCO_3$)	(81–157)	(147–637)	—	(115–431)	(112–372)	(84–445)	(154–347)	(151–296)	(84–339)
	[12]	[12]	[1]	[8]	[12]	[8]	[9]	[4]	[8]
Chloride (mg/L)	75	792	1020	586	417	450	530	451	326
	(16–106)	(91–1420)	—	(58–850)	(54–710)	(18–760)	(117–720)	(115–578)	(18–858)
	[12]	[12]	[1]	[8]	[12]	[8]	[9]	[4]	[8]
Sulfate (mg/L)	184	3810	5500	2750	1960	2260	2760	2180	1650
	(42–294)	(439–6890)	—	(272–4000)	(229–3570)	(65–4080)	(274–4120)	(258–2840)	(63–4430)
	[12]	[12]	[1]	[8]	[12]	[8]	[9]	[4]	[8]
Nitrate (mg/L-N)	0.5	10.9	13.9	6.1	1.2	2.3	1.8	0.4	0.8
	(0.2–0.7)	(0.1–38)	—	(<0.1–15)	(<0.1–4.3)	(0.1–9.2)	(0.1–5.9)	(0.1–0.6)	(<0.1–2.8)
	[11]	[11]	[1]	[8]	[11]	[7]	[9]	[4]	[7]
Nitrite (mg/L-N)	0.01	0.15	0.16	0.12	0.05	0.14	0.09	0.03	0.06
	(<0.01–0.02)	(0.02–0.38)	—	(<0.01–0.25)	(<0.01–0.16)	(<0.01–0.46)	(<0.01–0.20)	(0.01–0.05)	(<0.01–0.16)
	[12]	[12]	[1]	[8]	[12]	[8]	[9]	[4]	[8]
Total suspended	72	26	10	71	50	82	42	52	81
solids (mg/L)	(9–283)	(12–47)	—	(33–149)	(7–108)	(32–144)	(8–82)	(19–120)	(11–162)
	[11]	[11]	[1]	[7]	[11]	[7]	[9]	[4]	[7]
Volatile solids	17	6.5	1.5	14	9.5	15	10	8	14
(mg/L)	(1–129)	(2.8–13)	—	(5.6–40)	(0.9–21)	(6–31)	(1.3–33)	(2.0–16)	(1.9–33)
	[11]	[11]	[1]	[7]	[11]	[7]	[9]	[4]	[7]
Fixed solids (mg/L)	55	20	9	57	41	67	32	44	67
	(1–256)	(9.2–40)	—	(22–109)	(6–96)	(17–125)	(6.7–64)	(17–103)	(9.6–129)
	[11]	[11]	[1]	[7]	[11]	[7]	[9]	[4]	[7]
1997									
pH	8.2	8.1	8.0	NS	8.1	NS	8.1	8.1	NS
	(7.7–8.5)	(7.7–8.4)	(7.6–8.7)		(7.8–8.4)		(7.6–8.4)	(7.8–8.3)	
	[12]	[12]	[12]		[12]		[11]	[12]	

TABLE IV. (Continued)

Year and Measure	Station								
	WW1	WW4	WW4b	WW5	WW6	WW7	WW8	WW8b	WW9
1997									
Conductivity (μmhos/cm)	680 (310–920) [12]	920 (300–2040) [12]	6460 (390–11240) [12]	NS	700 (320–930) [12]	NS	780 (350–1120) [11]	768 (330–1120) [12]	NS
Hardness (mg/L as $CaCO_3$)	236 (116–322) [12]	278 (130–446) [12]	1920 (130–3710) [12]	NS	250 (124–326) [12]	NS	264 (130–324) [11]	259 (118–350) [12]	NS
Calcium (mg/L)	64 (34–87) [12]	70 (38–98) [12]	226 (39–468) [12]	NS	67 (37–89) [12]	NS	69 (44–88) [11]	68 (34–90) [12]	NS
Magnesium (mg/L)	18 (6–25) [12]	25 (8–49) [12]	330 (8–630) [12]	NS	20 (6–30) [12]	NS	22 (5–30) [11]	22 (7–36) [12]	NS
Alkalinity (mg/L as $CaCO_3$)	124 (80–150) [12]	136 (95–167) [12]	335 (93–588) [12]	NS	131 (94–154) [12]	NS	137 (92–159) [11]	134 (84–163) [12]	NS
Chloride (mg/L)	64 (17–100) [12]	78 (18–155) [12]	633 (18–1120) [12]	NS	68 (16–108) [12]	NS	73 (16–110) [11]	70 (16–110) [12]	NS
Sulfate (mg/L)	156 (56–255) [12]	218 (68–412) [12]	3230 (70–6450) [12]	NS	174 (63–252) [12]	NS	194 (62–269) [11]	195 (57–315) [12]	NS
Nitrate (mg/L-N)	0.4 (0.2–0.6) [11]	0.6 (0.1–1.2) [11]	11.4 (<0.1–37) [11]	NS	0.4 (<0.1–0.7) [11]	NS	0.4 (0.2–0.7) [10]	0.4 (0.2–0.7) [11]	NS
Nitrite (mg/L-N)	0.01 (<0.01–0.02) [11]	0.02 (<0.01–0.02) [11]	0.08 (<0.01–0.18) [11]	NS	0.01 (<0.01–0.02) [11]	NS	0.01 (<0.01–0.02) [10]	0.02 (<0.01–0.02) [11]	NS
Total suspended solids (mg/L)	140 (24–457) [12]	119 (20–363) [12]	50 (6–167) [12]	NS	78 (9–212) [12]	NS	84 (14–176) [11]	96 (8–303) [12]	NS
Volatile solids (mg/L)	12 (2.8–30) [12]	11 (2.4–29) [12]	9.4 (1.2–23) [12]	NS	8.2 (1.1–20) [12]	NS	9.4 (1.8–16) [11]	9.1 (1.0–20) [12]	NS
Fixed solids (mg/L)	128 (21–427) [12]	109 (17–337) [12]	41 (4.2–149) [12]	NS	70 (7.5–192) [12]	NS	74 (12–160) [11]	87 (7.4–283) [12]	NS

1998								
pH	8.3 (8.1–8.6) [8]	8.3 (8.1–8.4) [8]	8.1 (7.6–8.4) [8]	NS	8.2 (8.1–8.4) [8]	NS	8.0 (7.7–8.3) [7]	8.2 (8.0–8.8) [8]	NS
Conductivity (μmhos/cm)	710 (380–920) [8]	780 (370–920) [8]	2620 (970–5800) [8]	NS	790 (490–1020) [8]	NS	960 (560–1150) [7]	1030 (500–1810) [8]	NS
Hardness (mg/L as $CaCO_3$)	266 (192–376) [7]	275 (196–378) [7]	649 (322–1550) [7]	NS	280 (194–388) [7]	NS	304 (224–372) [6]	366 (210–564) [7]	NS
Calcium (mg/L)	72 (52–104) [7]	74 (56–104) [7]	110 (67–216) [7]	NS	75 (58–106) [7]	NS	77 (63–94) [6]	85 (60–125) [7]	NS
Magnesium (mg/L)	21 (15–28) [7]	22 (14–29) [7]	91 (32–245) [7]	NS	23 (12–30) [7]	NS	27 (16–34) [6]	37 (15–66) [7]	NS
Alkalinity (mg/L as $CaCO_3$)	139 (114–176) [7]	142 (124–165) [7]	199 (137–312) [7]	NS	145 (124–169) [7]	NS	140 (127–152) [6]	151 (128–176) [7]	NS
Chloride (mg/L)	75 (42–100) [7]	82 (42–120) [7]	181 (82–468) [7]	NS	81 (41–110) [7]	NS	95 (52–115) [6]	104 (44–173) [7]	NS
Sulfate (mg/L)	195 (109–364) [8]	210 (112–351) [8]	832 (278–2200) [8]	NS	208 (114–345) [8]	NS	272 (168–406) [7]	327 (46–641) [8]	NS
Nitrate (mg/L-N)	0.4 (0.4–0.6) [6]	0.5 (0.3–0.7) [6]	3.2 (<0.1–14) [6]	NS	0.4 (0.3–0.6) [6]	NS	0.4 (<0.1–0.7) [5]	0.5 (0.2–0.9) [6]	NS
Nitrite (mg/L-N)	0.02 (<0.01–0.02) [8]	0.01 (<0.01–0.01) [7]	0.04 (<0.01–0.09) [8]	NS	0.01 (<0.01–0.01) [8]	NS	— (<0.01) [7]	0.02 (<0.01–0.02) [8]	NS
Total suspended solids (mg/L)	230 (12–917) [8]	222 (26–790) [8]	92 (20–182) [8]	NS	112 (19–362) [8]	NS	133 (10–329) [7]	247 (52–928) [8]	NS
Volatile solids (mg/L)	19 (1.4–73) [8]	18 (2.8–63) [8]	13 (3.6–35) [8]	NS	9.8 (2.0–31) [8]	NS	27 (4.2–75) [7]	12 (5.5–38) [8]	NS
Fixed solids (mg/L)	211 (10–844) [8]	204 (23–727) [8]	80 (17–163) [8]	NS	103 (17–331) [8]	NS	135 (39–280) [6]	76 (47–114) [8]	NS

[a] NS: Not sampled.

4.2% during one analysis ($n = 11$) and 6.5% during another ($n = 5$). Selenium values in micrograms were obtained by direct comparison of peak areas obtained for the samples to the average peak areas obtained for a set of standards. The limit of detection was 0.015 μg/g. Duplicate muscle plugs from the same fish were not taken, so no other quality assurance measures were evaluated.

Statistics

Data were analyzed with the Statistical Analysis System Institute, Inc., statistical application (SAS, 2002). Analysis of variance testing was done to compare the variation in water, sediment, aquatic invertebrates, and forage fish (logarithmically transformed values) residues among sites. When significant differences ($p \leq 0.05$) were observed, means were compared by the Bonferroni (Dunn) multiple means comparison test (Snedecor and Cochran, 1967). In cases in which measured selenium concentrations in water [27 data points out of 337 (8%)] were below the LOD, one-half of the LOD value was used in correlation analysis (Kushner, 1976; USEPA, 1996).

Correlation analyses were used to test for relationships among water quality characteristics and inorganic element concentrations in water, sediment, aquatic invertebrates, and forage fish. The Spearman correlation (r_s) was used to determine the correlation of selenium concentration in sediment (assuming a nonnormal distribution of selenium in sediments; Peltz and Waddell, 1991; Stephens, 1996; Zhang and Moore, 1997) with selenium concentrations in aquatic invertebrates. Correlation analyses of the means with standard deviation and variance measures were conducted to determine if transformations were needed to meet the assumptions of normality and homogeneity of variance (M. Ellersieck, University of Missouri, Columbia, Missouri, personal communication).

Multiple regression analyses were used to test for relationships among sediment characteristics and selenium concentrations in sediment and among selenium concentrations in water, aquatic invertebrates, and forage fish. A Wilcoxon signed-rank test was used to determine if the recaptured Colorado pikeminnow at WWSWA showed significant differences in selenium concentrations in their muscle plugs sampled in different years.

The results of statistical tests were considered significant if the p value was less than or equal to 0.05.

RESULTS

Water Quality

Water quality characteristics varied over the years primarily by season. Station WW1 on the Colorado River tended to have high conductivity with low water flow, about 1000 μmhos/cm, and low conductivity with high water flow, about 300 μmhos/cm (Table III), which is typical for western rivers (written communication, J. Yahnke, U.S. Bureau of Reclamation).

Station WW4 was on the north side of the levee from WW1 at a site where a marsh was formed from groundwater discharge. Conductivity in this area varied seasonally, with low conductivity, about 1000–4000 μmhos/cm, from late May to early July 1995 and high conductivity, about 7000–12 000 μmhos/cm, in fall through spring. After the water control structure was opened, conductivity values at this station were slightly higher than those at WW1, except when the water flow through the structure was reduced, resulting in elevated conductivity in the channel. In contrast, station WW4b (which was started in December 1996 at the marsh outflow) had very elevated conductivity concentrations through most of 1997, similar to those at WW4 prior to the opening of the water control structure. After the control structure was opened, average conductivity at the marsh station decreased: 6160 μmhos/cm in 1995, 8810 μmhos/cm in 1996, 7600 μmhos/cm in 1997, and 2620 μmhos/cm in 1998 (Table IV). This change in conductivity was more evident in the maximum conductivity values at the marsh station: 11 120 μmhos/cm in 1995, 12 780 μmhos/cm in 1996, 14 120 μmhos/cm in 1997, and 5800 μmhos/cm in 1998.

Conductivity concentrations at other stations in the channel followed those at WW4, but at progressively lower concentrations with increasing distance from WW4. After the water control structure was opened, conductivity at all stations, except WW4b, was slightly higher than in the river, but substantially lower than before the structure opening (Table IV). Water quality characteristics of samples measured in the mobile laboratory, such as hardness and alkalinity, followed changes in conductivity measured on-site, which was lowest during runoff and highest during low-flow periods (Table IV). The years 1995 and 1997 seemed to be high-flow years, whereas 1996 and 1998 were average-flow years (Ugland et al., 1995; Crowfoot et al., 1996, 1997, 1998, 1999; Fig. 3).

Selenium and Other Elements in Water

There was a significant difference in selenium concentrations between filtered and unfiltered water at two stations, WW1 (Colorado River) and WW4b (marsh area), shown in Table V. In 1995, 1996, and 1997 the selenium concentration in filtered water samples at WW1 was consistently lower than in that in unfiltered water samples. At WW4b selenium in filtered water was lower than in unfiltered water in 1997. The higher level of selenium in unfiltered water was probably a result of selenium associated with particulate matter. At stations WW4, WW5, WW6, WW7, WW8, WW8b, and WW9 no difference in selenium concentrations between filtered and unfiltered water samples was found.

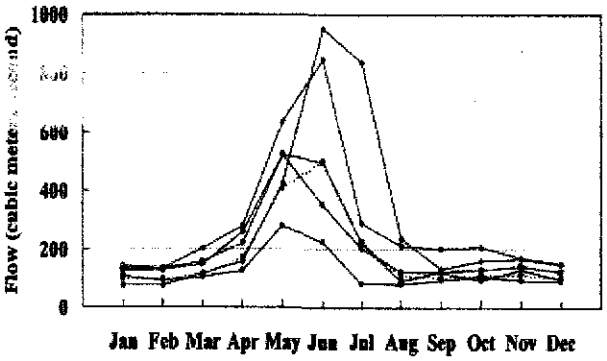

Fig. 3. Mean flow (cubic meters per second) in the Colorado River at the U.S. Geological Survey gauging station near the Colorado–Utah border during 1994–1998 (● 1994, ♦ 1995, ■ 1996, ◇ 1997, ○ 1998; ● with dashed line average for 1951–1998).

There were significant differences in selenium concentrations according to the year at WW4, WW6, and WW8 (Table V). Selenium concentrations in water at WW1 were consistent over the 4-year monitoring period, about 2.4–3.3 μg/L in unfiltered water. At WW4 selenium concentrations in water before the water control structure was in operation were 48–58 μg/L, whereas after operation of the control structure selenium concentrations dropped to 2.0–4.8 μg/L. Similar changes were observed at WW6 (9.2–15 μg/L before, 1.6–2.3 μg/L after) and WW8 (10–29 μg/L before, 1.7–3.0 μg/L after). During the time the water control structure was operating, water with elevated selenium concentrations entered the channel area from WW4b between December 1996 and September 1998 (84 μg/L in December 1996, 43 μg/L in 1997, and 11 μg/L in 1998).

Significant differences in selenium concentrations were also observed between stations (Table V). In 1995 WW4 had the highest selenium concentrations, and WW5, WW6, WW7, and WW8 had concentrations significantly higher than either WW1 or WW9. A similar pattern was observed in 1996, except that WW9 had elevated selenium concentrations, in part because of the high selenium concentrations at WW8. However, when the water control structure was operating, in 1997 and 1998, there were no interstation

TABLE V. Mean (range in parentheses and number of samples in brackets) selenium concentrations (μg/L) in filtered and unfiltered water at several stations in the channel at Walter Walker State Wildlife Area

Year and Measure	Station								
	WW1	WW4	WW4b	WW5	WW6	WW7	WW8	WW8b	WW9
1995									
Filtered	1.9a	55Ab	NS[a]	19ab	15Aab	22ab	10Aab	NS	6.3a
	(<1–3.3)	(<1–126)		(<1–80)	(<1–69)	(<1–70)	(<1–34)		(<1–21)
	[8]	[8]		[8]	[8]	[8]	[8]		[8]
Unfiltered	3.3	58	NS	11	9.2	16	16	NS	8.6
	—	—		—	—	—	—		—
	[1]	[1]		[1]	[1]	[1]	[1]		[1]
1996									
Filtered	1.7a	48Ab	84	24b	9.8Aab	24a	29Ab	3.0	11ab
	(<1–3.5)	(4.9–135)	—	(1.7–58)	(1.4–22)	(<1–71)	(3.1–53)	—	(<1–41)
	[7]	[6]	[1]	[6]	[6]	[6]	[4]	[1]	[6]
Unfiltered	2.5	49	82	25	10	16	16	3.0	13
	(1.3–3.0)	(5.2–138)	—	(3–59)	(2.6–22)	(<1–41)	(3.0–24)	—	(<1–37)
	[4]	[6]	[1]	[5]	[6]	[5]	[3]	[1]	[5]
1997									
Filtered	1.6a	2.9Ba	43b	NS	1.6Ba	NS	1.9Ba	2.0a	NS
	(<1–2.7)	(<1–6.0)	(<1–152)		(<1–3.0)		(<1–3.2)	(<1–3.4)	
	[12]	[12]	[12]		[12]		[11]	[12]	
Unfiltered	2.4	4.8	99	NS	2.3	NS	3.0	2.9	NS
	(<1–4.4)	(1.5–6.4)	(1.3–148)		(1.1–3.0)		(<1–4.8)	(1.0–4.2)	
	[5]	[5]	[5]		[5]		[5]	[5]	
1998									
Filtered	1.6a	2.0Ba	11b	NS	1.8Ba	NS	1.7Ba	2.9a	NS
	(<1–3.1)	(1.0–3.8)	(1.8–31)		(<1–3.7)		(<1–3.5)	(1.0–6.0)	
	[8]	[8]	[8]		[8]		[7]	[8]	
Unfiltered	NS	NS	NS	NS	NS	NS	NS	NS	NS

Uppercase letters within a column indicate significant differences between years ($p \leq 0.05$). Lowercase letters within a row indicate significant differences between locations ($p \leq 0.05$)

[a] NS: Not sampled.

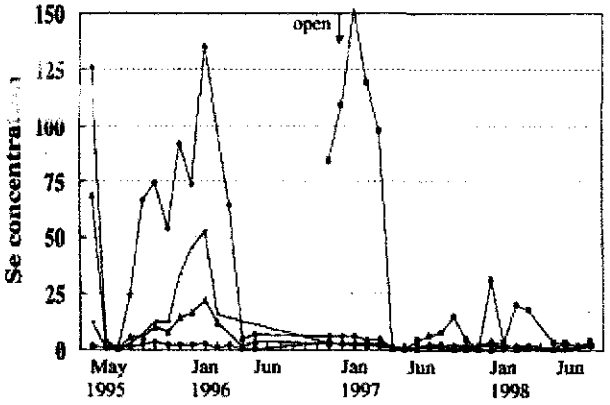

Fig. 4. Selenium concentrations (μg/L) in filtered water at various sampling stations at Walter Walker State Wildlife Area (● WW1, ♦ WW4, ■ WW4b, ▲ WW6, ■ WW8).

differences in selenium concentrations of the sampling stations within the channel, except for WW4b, which showed elevated selenium concentrations from selenium draining from the marsh area. Overall, selenium concentrations in filtered water decreased in the channel area after the control structure was operational (Fig. 4). Combining the selenium values for all but the WW1 and WW4b stations within the channel showed that the selenium concentrations in the filtered water samples by year were 21.0 μg/L in 1995 (n = 47), 23.5 μg/L in 1996 (n = 35), 2.1 μg/L in 1997 (n = 47), and 2.1 μg/L in 1998 (n = 31).

The most prominent entry point of selenium into the channel area was WW4b, where concentrations in water were substantially elevated in January 1998 (31 μg/L), March 1998 (20 μg/L), and April 1998 (18 μg/L). However, elevated levels of selenium also entered the channel at WW7 between October 1995 and April 1996 (Hamilton et al., 2003). Selenium concentrations at WW7 were some times 2–4 times higher than the those at the slightly upstream WW6 station. At WW8 in January and February 1997 and at WW8b in August and September 1998, selenium concentrations were higher than at WW6, suggesting there was selenium input from the WW7 area of the channel.

For inorganic elements in water, as measured by ICP, boron, chromium, iron, magnesium, manganese, molybdenum, strontium, and vanadium were found to be elevated at WW4b during the same periods when selenium was elevated (Hamilton et al., 2003). Selenium concentrations measured with the AA-HG in water were significantly correlated with eight elements measured by ICP: boron (r = 0.68, p = 0.0001), barium (r = −0.38, p = 0.01), chromium (r = 0.45, p = 0.002), magnesium (r = 0.74, p = 0.0001), manganese (r = 0.57, p = 0.0001), molybdenum (r = 0.77, p = 0.0001), strontium (r = 0.80, p = 0.0001), and vanadium (r = 0.76, p = 0.0001). There was a significant positive correlation between selenium in water with several water quality characteristics including, from highest to lowest correlation coefficient, nitrate (0.90), calcium (0.85), hardness (0.83), magnesium (0.81), sulfate (0.81), conductivity (0.79), chloride (0.79), alkalinity (0.77), and nitrite (0.57) (all p = 0.0001). These results showing significant correlation of selenium with other inorganic elements and water quality characteristics suggest that selenium concentrations increased with increasing water hardness and conductivity that was associated with irrigation-influenced groundwater discharge.

Selenium in Sediment

Selenium concentrations in various portions of sediment from the channel area were significantly different from each other (Table VI). Selenium concentrations in sediment cores collected from WW4 in August and November 1996 were elevated in the top (18–19.6 μg/g) and middle (11.3–16.3 μg/g) portions, whereas cores collected in April and September 1998 had concentrations of 0.6 μg/g or less. Uniformly elevated selenium concentrations in cores collected before operation of the control structure were also present at WW5, WW6, and WW7, whereas during the same period WW8 and WW9 showed elevated selenium in the top and middle portions of the cores.

At WW4 a sediment trap deployed between November 1996 and March 1997 had a selenium concentration of 17.2 μg/g at the bottom (before the control structure was opened) and 3.4 μg/g at the top (after the water structure had been open about 3 months). The sediment trap at WW6 contained insufficient sediment to analyze layers, but the sediment collected had intermediate selenium concentrations (4.4 μg/g) compared to concentrations in the top of the sediment core at WW6 before (5.4–6.1 μg/g) and after (0.5–1.9 μg/g) operation of the control structure. The sediment trap at WW8 contained uniform selenium concentrations in the two layers sampled (5.5–5.9 μg/g), which were similar to concentrations in sediment cores collected in 1996 before the control structure was operating (5.2–6.6 μg/g), but higher than concentrations in cores collected in 1998, after operation of the control structure (1.1–1.8 μg/g).

Freshly deposited sediment samples after the control structure operation showed buried high-selenium sediment at WW6, WW8, and WW8b (Table VI). Sediment cores collected at these stations in April and September 1998 generally had low selenium concentrations in the top of the cores and elevated selenium concentrations in the bottom portions.

Most sediment cores tended to have the highest percentages of volatile solids, total carbon, inorganic carbon, and organic carbon in the upper portions of the cores. Selenium concentrations in sediment were positively correlated (r) with volatile solids (r = 0.45, p = 0.01, n = 31), total carbon (r = 0.61, p = 0.0002, n = 31), inorganic carbon

($r = 0.50$, $p = 0.004$, $n = 31$), and organic carbon ($r = 0.55$, $p = 0.001$, $n = 31$) and were negatively correlated with total solids ($r = -0.42$, $p = 0.02$, $n = 31$) and fixed solids ($r = -0.45$, $p = 0.01$, $n = 31$). No significant correlation between selenium concentrations in sediment and sediment particle size was found. However, selenium concentrations in sediment were significantly correlated with selenium concentrations in filtered ($r = 0.69$, $p = 0.0001$, $n = 29$) and unfiltered ($r = 0.68$, $p = 0.004$, $n = 16$) water samples.

Overall, selenium concentration in sediment decreased substantially after the water control structure began operations. Combining all sediment selenium concentrations for the top layers of the various sediment types (cores and traps) and stations over a year showed that selenium concentrations decreased from 8.5 μg/g ($n = 12$) in 1995, to 8.2 μg/g ($n = 17$) in 1996, to 4.8 μg/g ($n = 4$) in 1997, to 1.1 μg/g ($n = 8$) in 1998. The selenium concentrations in 1995, 1996, and 1997 were not significantly different from each other, but all were significantly higher than the selenium concentration in 1998.

Selenium and Other Elements in Aquatic Invertebrates

Selenium concentrations in aquatic invertebrate samples from channel stations decreased after the water control structure was in operation (Table VII). In 1996 before the control structure was operating, the channel had very elevated selenium concentrations in aquatic invertebrates, ranging from 11 to 33 μg/g, whereas in 1998, after operation of the control structure the selenium concentrations ranged from 3 to 5.8 μg/g. For stations WW6 and WW8, where invertebrates were collected in 1996, 1997, and 1998, the decrease in selenium was readily apparent (Table VII). Although invertebrates were collected at WW8b and WW9 for only 2 years, a decrease in selenium concentrations was also apparent. WW7 was the only station at which selenium concentrations did not decrease.

Overall, combining selenium concentration values for all invertebrates and at all stations showed that the selenium concentration in invertebrates in the channel decreased from 27.4 μg/g ($n = 13$) in 1996, to 15.5 μg/g ($n = 9$) in 1997, to 4.9 μg/g ($n = 6$) in 1998. The selenium concentration in 1996 was significantly higher than those in 1997 and 1998, but the 1997 selenium concentration was not significantly higher than that in 1998.

In contrast to the results of previous studies, the selenium accumulation in chironomids was similar to that in zooplankton (Hamilton et al., 2003). The correlation of the selenium concentrations in aquatic invertebrates with those in filtered water was $r = 0.83$ ($p = 0.0001$, $n = 18$) and with those in unfiltered water was $r = 0.77$ ($p = 0.003$, $n = 12$). The Spearman correlation (r_s) between selenium concentrations in sediment and in aquatic invertebrates was $r_s = 0.81$ ($p = 0.0004$, $n = 14$).

The level of inorganic elements in aquatic invertebrates collected after operation of the water control structure seemed consistent among stations (Hamilton et al., 2003). Selenium concentrations in invertebrates were correlated with barium ($r = -0.89$, $p = 0.05$, $n = 5$) and zinc ($r = 0.89$, $p = 0.04$, $n = 5$).

Selenium and Other Elements in Forage Fish

Concentrations of selenium in forage fish were elevated prior to the water control structure being in operation and decreased after operation (Table VIII). Five species were collected both before and after operation: fathead minnow (*Pimephales promelas*), green sunfish (*Lepomis cyanellus*), white sucker (*Catostomus commersoni*), red shiner (*Cyprinella lutrensis*), and western mosquito fish (*Gambusia affinis*); killifish (*Fundulus* sp.) were collected only before operation; and sand shiner (*Notropis stramineus*), common carp (*Cyprinus carpio*), black crappie (*Pomoxis nigromaculatus*), and flannelmouth sucker (*Catostomus latipinnis*) were collected only after operation. The predominate species were fathead minnow and green sunfish.

There were several interesting occurrences in the forage fish collection. A fathead minnow regurgitated from a Colorado pikeminnow collected at WW8 in May 1996 had a selenium concentration of 40 μg/g. The selenium concentration was 8.9 μg/g in a composition sample of five male red shiner collected at WW6 in July 1998, whereas it was 12 μg/g selenium in a composition of five gravid females. Thirteen sets of fathead minnows were collected as 2–3 individual or composite samples over the 3-year period, and 12 sets of samples had consistent selenium concentrations (coefficient of variation between 0 and 25 in 12 sets and 48 in the 13th set), which demonstrated little variability in selenium concentrations within a site and on a collection date (Hamilton et al., 2003).

Selenium concentrations in forage fish were highest in 1996 and 1997 at WW4, where water with an elevated level of selenium entered the channel area from the marsh (Table VIII). Selenium in forage fish tended to decrease from WW4 to WW9, except for one sample collected in the WW6 area in 1996 (Table VIII). Within a station, selenium tended to decrease between 1996 and 1998, except for one sample at WW6 in 1996. Overall, combining the concentrations of all forage fish and at all stations by year showed that selenium concentrations decreased from 27.2 μg/g ($n = 24$) in 1996 to 20.2 μg/g ($n = 23$) in 1997 to 8.6 μg/g ($n = 21$) in 1998. The selenium concentration in forage fish in 1996 was not significantly different from that in 1997, but both were significantly higher than the concentration in forage fish in 1998.

Selenium in forage fish was positively correlated with selenium in filtered water samples ($r = 0.58$, $p = 0.02$, $n =$

TABLE VI. **Selenium concentrations (μg/g dry weight) in sediment collected from various stations in the channel at Walter Walker State Wildlife Area**

Station	Date	Day of Study	Sediment Type	Sediment Section	Selenium (μg/g)
WW1	04/25/96	358	Mixed[a]		0.4
WW4	05/04/95	1	Mixed		20.8
	10/18/95	168	Mixed		13.1
	04/25/96	358	Mixed		14.8
	08/23/96	478	Core	Top	18.0
				Middle	11.3
				Bottom	7.7
	11/19/96	566	Core	Top	19.6
				Middle	16.3
				Bottom	1.6
	11/13/96–03/12/97	560–679	Trap	Top	3.4
				Middle	3.8
				Bottom	17.2
WW4a	04/06/98	1062	Core	Top	0.4
				Middle	0.5
				Bottom	0.3
	09/09/98	1218	Core	Top	0.6
				Middle	0.5
				Bottom	0.5
WW5	05/04/95	1	Mixed		4.0
	10/18/95	168	Mixed		6.0
	04/25/96	358	Mixed		8.0
	08/23/96	478	Core	Top	8.1
				Middle	7.3
				Bottom	7.4
WW6	05/04/95	1	Mixed		4.8
	10/18/95	168	Mixed		5.5
	04/25/96	358	Mixed		7.2
	08/23/96	478	Core	Top	6.1
				Middle	8.1
				Bottom	2.7
	11/19/96	566	Core	Top	5.4
	11/19/96	566	Core	Middle	7.7
				Bottom	5.0
	11/21/96–03/12/97	568–679	Trap	Top	NS[b]
				Middle	NS
				Bottom	4.4
	04/06/98	1062	Core	Top	1.9
				Middle	3.9
				Bottom	18.0
	09/09/98	1218	Core	Top	0.5
				Middle	0.6
				Bottom	0.4
WW7	05/04/95	1	Mixed		17.8
	10/18/95	168	Mixed		14.5
	04/25/96	358	Mixed		15.7
	08/23/96	478	Core	Top	8.5
				Middle	9.2
				Bottom	13.7

TABLE VI. (*Continued*)

[illegible]	Date	Day of Study	Sediment Type	Sediment Section	*Selenium* (μg/g)
WW8	05/04/95	1	Mixed		5.6
	10/18/95	168	Mixed		4.4
	04/25/96	358	Mixed		4.4
	08/23/96	478	Core	Top	5.2
				Middle	1.7
				Bottom	1.1
	11/19/96	566	Core	Top	6.6
				Middle	9.4
				Bottom	0.9
	11/12/96–03/12/97	559–679	Trap	Top	5.9
				Middle	NS
				Bottom	5.5
	04/06/98	1062	Core	Top	1.8
				Middle	0.6
				Bottom	3.4
	09/09/98	1218	Core	Top	1.1
			Core	Middle	0.9
				Bottom	0.5
WW8b	11/19/96	566	Core	Top	6.8
				Middle	14.6
				Bottom	0.6
	11/12/96–03/12/97	559–679	Trap	Top	5.3
				Middle	5.8
				Bottom	5.8
	04/06/98	1062	Core	Top	1.4
				Middle	0.5
				Bottom	4.4
	09/09/98	1218	Core	Top	1.1
				Middle	2.2
				Bottom	6.9
WW9	05/04/95	1	Mixed		2.7
	10/18/95	168	Mixed		2.4
	04/25/96	358	Mixed		2.6
	08/23/96	478	Core	Top	1.7
				Middle	2.1
				Bottom	0.8

[a] Mixed; the sediment was thoroughly mixed before subsampling for chemical analysis.
[b] NS: Not sampled.

15) but not unfiltered water samples ($r = -0.21$, $p = 0.57$, $n = 10$). Selenium in forage fish was positively correlated with selenium in sediment ($r = 0.75$, $p = 0.003$, $n = 13$) but not in aquatic invertebrates ($r = 0.46$, $p = 0.10$, $n = 14$).

Most inorganic elements in forage fish decreased between 1996 and 1998 (Hamilton et al., 2003). Combining all stations within a year, four elements had greater than twofold decreases between 1996 and 1998: aluminum (5.8 times lower), iron (3.7 times lower), manganese (2.0 times lower), and vanadium (2.3 times lower), whereas little change (less than twofold differences) was noted for arsenic, barium, beryllium, boron, cadmium, chromium, copper, magnesium, molybdenum, nickel, strontium, and zinc. Lead was the only inorganic element in forage fish to show a twofold increase between 1996 and 1998. In contrast, selenium in forage fish had a fourfold reduction between 1996 and 1998.

Combining the figures reported from all stations over a year showed that zinc, but none of the other 16 elements, was significantly and negatively correlated with selenium concentrations in forage fish ($r = -0.41$, $p = 0.04$, $n = 26$). This low correlation value resulted in part from the small, less-than-twofold change in zinc concentrations between 1996 and 1998.

Selenium in Colorado Pikeminnow

Mean selenium concentrations in muscle plugs of Colorado pikeminnow collected from WWSWA were 9.8 μg/g (n =

TABLE VII. Mean (range in parentheses and number of samples in brackets) selenium concentrations (μg/g dry weight) in aquatic invertebrates collected from various stations in the channel at Walker Walter State Wildlife Area

	Station							
Year	WW4	WW4a	WW5	WW6	WW7	WW8	WW8b	WW9
1996	45.2	NS[a]	38.1	33.0	23.6	21.2	14.9	17.7
	(37.7–52.8)		—	(29.2–36.8)	(13.8–33.3)	(15.2–24.4)	—	(11.2–24.2)
	[2]		[1]	[2]	[2]	[3]	[1]	[2]
1997	NS	NS	NS	11.4	55.0	18.4	6.6	7.4
				(7.6–15.2)	—	(7.9–28.8)	(3.1–10.0)	—
				[2]	[1]	[2]	[2]	[1]
1998	NS	3.0	NS	4.6	NS	5.8	NS	NS
		—		(4.5–4.7)		(4.0–8.5)		
		[1]		[2]		[3]		

[a] NS: Not sampled.

49) in 1995, 9.5 μg/g (n = 40) in 1996, 9.0 μg/g (n = 54) in 1997, and 10.3 μg/g (n = 3) in 1998 (Table IX). No significant differences in selenium concentrations were found in muscle plugs collected between 1995 and 1998; however, in those collected in 1995, 1996, and 1997, but not 1998, the selenium concentrations were significantly less than the 16.1 μg/g (n = 17) concentration the muscle plugs of Colorado pikeminnow collected from WWSWA in 1994 prior to the current study (Osmundson et al., 2000).

Several Colorado pikeminnow were captured repeatedly during the 1994–1998 period (Table X). For repeatedly captured fish, selenium in muscle plugs of fish captured in 1994 was significantly different than in those captured in 1995, 1996, and 1997, but selenium levels in the latter 3 years were not different from each other. As for the other measurements taken, above, 1994 seemed to be an unusual year, with low flows in the river and elevated selenium residues in muscle plugs of Colorado pikeminnow.

Using the yearly mean values for 1995–1998 showed selenium concentrations in muscle plugs were not significantly correlated with selenium concentrations in water (r = −0.02, p = 0.98, n = 4), sediment (r = −0.42, p = 0.58, n = 4), aquatic invertebrates (r = −0.58, p = 0.60, n = 3), or forage fish (r = −0.73, p = 0.27, n = 4).

Selenium concentrations in muscle plugs of Colorado pikeminnow for 1994–1998 were significantly and negatively correlated with mean monthly river flow in May (r = −0.87, p = 0.05), but not in June (r = −0.69, p = 0.20) or in July (r = −0.45, p = 0.45). The correlation between muscle plug selenium concentrations and the average river flow during the May–July period was r = −0.74 (p = 0.16); for the April–July period it was r = −0.79 (p = 0.11), and for the March–July period it was r = −0.85 (p = 0.07).

Selenium concentrations in muscle plugs seemed to decrease with increasing fish weight (Fig. 5) and fish total length (Fig. 6). Combining data for 1994–1998 showed that muscle plug selenium in fish from WWSWA was significantly correlated with fish weight (r = −0.34, p < 0.0001, n = 157) and fish total length (r = −0.37, p < 0.0001, n = 162). Similar correlations were found for muscle plugs collected in 1995, 1996, and 1997, with 1996 having the

TABLE VIII. Mean (range in parentheses and number of samples in brackets) selenium concentrations (μg/g dry weight) in forage fish collected from various stations in the channel at Walker Walter State Wildlife Area

	Station							
Year	WW4	WW4a	WW5	WW6	WW7	WW8	WW8b	WW9
1996	51	NS[a]	31.5	4.8	25.3	22.9	15.0	14.0
	(29–66)		(30–33)	—	(17–32)	(11–40)	(13–19)	—
	[4]		[4]	[1]	[3]	[8]	[3]	[1]
1997	22.9	NS	NS	21.5	NS	18.1	16.7	NS
	(10–35)			(16–29)		(5.1–39)	(10–21)	
	[7]			[6]		[7]	[3]	
1998	NS	6.1	NS	11.6	6.2	9.8	6.1	6.4
		—		(5.6–20)	(5.9–6.6)	(5.7–19)	(5.1–8.0)	(2.8–13)
		[1]		[4]	[2]	[8]	[3]	[3]

[a] NS: Not sampled.

TABLE IX. Mean (range in parentheses and number of samples in brackets) selenium concentrations (μg/g dry weight) in muscle plugs from Colorado pikeminnow caught in various segments (RM: river mile) of the upper Colorado River near Grand Junction, CO

	Year				
Segment	1994[a]	1995[a]	1996[a]	1997	1998
RM <158	5.3 (4.4–6.2) [2]	NS[b]	5.4 (3.7–7.4) [15]	NS	NS
RM 158–162	4.4 (—) [1]	6.4 (5.2–7.7) [3]	NS	NS	NS
RM 163 (WWSWA)	16.6 (4.4–30.7) [16]	9.4 (4.1–22.0) [45]	9.4 (4.4–21.5) [35]	9.0 (3.0–20.0) [54]	10.3 (7.6–12.0) [3]
RM 164–170	8.5 (4.1) [6]	NS	NS	NS	NS
RM >170	5.4 (3.2–10.0) [13]	4.9 (3.6–5.7) [17]	NS	NS	NS

[a] Data from Osmundson et al. (2000).
[b] NS: Not sampled.

highest correlations ($r = -0.46$, $p = 0.003$, $n = 49$) for both fish weight and total length.

DISCUSSION

Water Quality

Concentrations of cations and anions in water in the channel area, as characterized by conductivity, were dominated by groundwater recharge during periods of low stream flow and by river flow during high-stream-flow periods. Prior to operation of the water control structure, elevated water quality characteristics were probably a result of the inflow of groundwater from the underlying cobble aquifer (Phillips, 1986). Water in the cobble aquifer sampled as part of the National Irrigation Water Quality Program (NIWQP) in 1992 at a location about 5.5 km north of WWSWA had conductivity concentrations of 4370–5720 μmhos/cm, as well as elevated calcium (480–540 mg/L), sulfate (2500–3400 mg/L), and chloride (240–280 mg/L) (Butler et al., 1994).

Although the characteristics in water from the channel area in the present study demonstrated a reduced groundwater influence (e.g., reduced conductivity) between January 1997 and June 1998 because of river influences from the operation of the water control structure, water quality characteristics were still elevated in groundwater adjacent and up gradient of the channel area. Water quality measurements in 1997 and 1998 in wells in the cobble aquifer close to North Pond and the marsh area at WWSWA demonstrated elevated characteristics: conductivity 10 200–18 700 μmhos/cm, calcium (370–540 mg/L), sulfate (5000–7600 mg/L), and chloride (900–3300 mg/L) (Butler and Osmundson, 2000). The water quality characteristics measured by Butler and Osmundson (2000) were similar to those measured in the present study and demonstrated that the channel area was receiving groundwater with elevated cations and anions probably derived from up-gradient irrigated areas.

Water from the cobble aquifer comes to the surface in a marsh area adjacent to WW4b, which during the present study had selenium concentrations of 82–152 μg/L. The WWSWA channel and North Pond have been identified by the USGS as discharge areas for high-selenium groundwater (Butler and Osmundson, 2000).

Based on the above discussion, if groundwater were to become the dominant water recharge mechanism of the WWSWA backwater, the water quality characteristics along with the selenium concentrations would most likely return to conditions prior to operation of the water control structure.

Selenium and Other Elements in Water

The similarity of selenium concentrations in filtered and unfiltered water samples in most samples from the present study was consistent with findings from the previous study (Hamilton et al., 2001a, 2001b), investigations of flowing water systems at Kesterson Reservoir, California (Fujii, 1988; Moore et al., 1990), and seven riverine sites associated with irrigation drainage in the San Joaquin Valley of California (Saiki et al., 1993).

The difference in selenium concentrations between filtered and unfiltered water samples at WW1 in 1995–1997 and WW4a in 1997 probably resulted from the selenium

TABLE X. Selenium concentrations (μg/g dry weight) in muscle plugs from Colorado pikeminnow captured at Walter Walker State Wildlife Area (some data from Osmundson et al., 2000)

	1994			1995			1996			1997			1998		
PIT Tag Number	Date	Fish Wt (g)	Se (μg/g)	Date	Fish Wt (g)	Se (μg/g)	Date	Fish Wt (g)	Se (μg/g)	Date	Fish Wt (g)	Se (μg/g)	Date	Fish Wt (g)	Se (μg/g)
1F41340666	5/24	2048	4.4	5/4	3545	4.1									
7F7D170B16[a]	6/13	7936	4.4	6/13	6500	5.1									
1F41200E65	5/24	2950	6.4	8/4	3500	8.3	5/14	3400	8.0						
7F7D16184E	5/24	1890	20.4	5/25	2025	15.0									
7F7D141911[b]	6/14	980	17.8	7/10	1150	15.0	5/13	1225	17.2	5/7	1200	18.0			
1F4041312F[c]	5/24	1110	7.1	7/25	1900	5.8									
7F7D0F3B28	5/24	1840	13.7	7/10	2450	6.5									
7F7D133C6F	5/24	1260	29.1	5/4	1818	19.0				4/22	2350	19.0			
7F7B135115	5/24	1706	30.7	6/5	1725	22.0	5/21	1950	21.5	4/22	1600	19.0			
7F7B176531	5/24	1897	16.6	5/4	2545	10.0				5/16	2100	10.0			
7F7F366E7F	5/24	1663	25.9	7/10	2200	18.0									
1F43600B33	5/27	—	5.3				5/22	—	5.5						
7F7D1D3317	5/20	—	6.8				5/13	3900	5.1						
7F7D170D4F	6/15	—	9.8				5/14	2050	7.2						
7F7D173405	5/24	2240	12.5				5/14	2150	9.5	5/30	2300	8.8			
7F7D1A3460	5/24	2210	29.6				5/22	2800	17.7	5/8	2100	18.0			
1F404A1542	5/24	—	15.6							5/15	1250	13.0			
1F41353A31	5/24	—	7.4							6/17	1750	8.3			
1F401A7710				6/15	3000	6.4	6/6	2550	6.2						
1F73276562				7/25	1250	8.8	5/7	—	5.9						
1F732C2D15				8/4	4100	7.0	6/6	4050	5.2						
7F7D073002				6/13	4750	5.6	6/6	4950	5.6						
7F7D073E2E				5/25	1500	6.3	5/16	—	5.4						
7F7D1E3127				6/12	1950	5.3	6/6	2250	5.8						
7F7D22513D				6/12	2000	15.0	5/13	1988	12.5						
7F7F362E6D				6/1	1700	18.0	5/21	1850	18.1						
7F7D152D61				5/25	1775	20.0	5/23	1850	20.4	5/7	1800	20.0			
1F40312B45				5/25	1200	8.8	6/6	1200	13.3	4/22	2200	11.0			
1F74342C0D				5/25	1300	11.0	6/6	1350	13.8	4/22	1150	13.0			
7F7B135346				7/10	1375	11.0				4/22	1550	10.0			
7F7D072F30				5/25	1150	14.0				5/8	1300	11.0			
7F7D1A323D				5/4	4609	8.6				5/30	5500	7.6			
1F46515A70							5/13	3450	5.7	5/16	3800	6.2			
1F53235813							5/13	1120	6.0	4/22	2300	9.4			
1F5B261A46							6/6	2150	7.1	6/18	2000	7.0			
1F6B1F6C6B							6/6	4050	5.4	6/17	3856	6.5			
7F7B1A6215							6/4	—	5.7	5/30	4000	5.0			
1F416A7B3B							5/13	1200	14.1	4/22	1050	13.0	6/16	752	12.0
1F462E7C71							5/22	1700	13.5	5/16	1400	12.0	6/16	1390	11.2

[a] Fish captured at RM 130.1 in 1994.
[b] Fish captured at RM 169.5 in 1994.
[c] Fish captured at RM 163.9 in 1994.

that was associated with particulate matter. Fujii (1988) and Moore et al. (1990) reported that unfiltered water samples (reported as total selenium) had higher selenium concentrations than filtered samples (reported as dissolved selenium). Adams (1976) reported similar findings and attributed the higher total selenium concentrations than dissolved selenium concentrations to the sorption of selenium onto suspended solids and the selenium contained in plankton.

The selenium concentrations in water in the channel area were reduced substantially by operation of the water control structure. This reduction was a result of the low-selenium river water passing through the control structure and channel, which was also documented by Butler and Osmundson (2000), who measured selenium concentrations from <1 to 3 μg/L. Only two samples of river water had elevated selenium concentrations, an August 1997 sample that

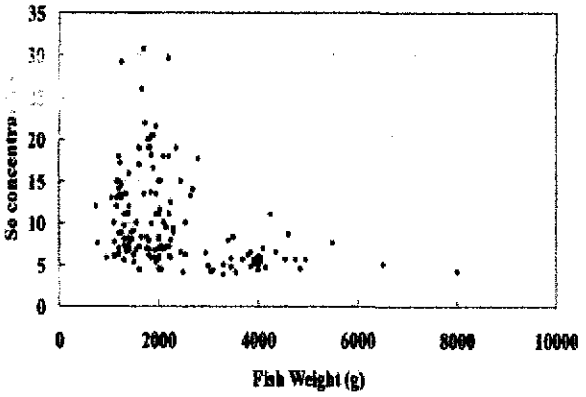

Fig. 5. Selenium concentrations (μg/g) in muscle plugs versus fish weight (g) of Colorado pikeminnow collected during 1994–1998 at Walter Walker State Wildlife Area (n = 157).

showed a concentration of 8 μg/L and a September 1997 sample whose concentration was 5 μg/L (Butler and Osmundson, 2000).

Water with an elevated selenium concentration entered the channel area at WW4 before and at WW4b after operation of the control structure had begun: 55 μg/L in 1995, 48 μg/L in 1996, 43 μg/L in 1997, and 11 μg/L in 1998. Butler and Osmundson (2000) also reported elevated selenium in water in samples from the marsh area in February 1998 (41–47 μg/L). Groundwater in one well up-gradient of the marsh contained a selenium concentration of 120–200 μg/L in 1997–1998, whereas a second, close well contained 4–7 μg/L, which illustrated the variability of groundwater sources in the cobble aquifer.

Selenium concentrations more elevated in water from stations WW7, WW8, and WW8b than from the upstream station WW6 was observed in the present study, suggesting groundwater input of selenium downstream of WW6. Butler and Osmundson (2000) demonstrated this groundwater input in sampling conducted in 1997–1998: selenium in groundwater from a well near our station WW6 was between <1 and 4 μg/L, whereas selenium in groundwater near our station WW7 was 22–190 μg/L.

Selenium concentrations in water observed in the present study at various stations in the lower WWSWA channel (WW6–WW9, 6–30 μg/L) prior to operation of the water control structure were typical of other surface waters in the Grand and Uncompahgre valleys that are affected by irrigation activity. Selenium concentrations were 4–7 μg/L (median 5 μg/L, n = 11) in the Colorado River at the Colorado–Utah state line, 5–7 μg/L (median 6 μg/L, n = 11) in the Gunnison River at Whitewater, and 8–25 μg/L (median 14 μg/L, n = 20) in the Uncompahgre River (Butler et al., 1994). Butler et al. (1996) and Butler and Osmundson (2000) also reported elevated selenium concentrations in areas influenced by irrigation activities. Selenium concentrations in water from the WWSWA channel area, in addition to most waters in the irrigation influenced areas of the Colorado, Gunnison, and Uncompahgre rivers, were elevated compared to uncontaminated aquatic ecosystems, which typically have <1 μg/L (Maier and Knight, 1994).

The significantly elevated concentrations of inorganic elements in water in the present study at WW4b (boron, chromium, iron, magnesium, manganese, molybdenum, strontium, and vanadium) were similar to those observed at North Pond in two previous studies (Hamilton et al., 2001a, 2001b). In the present study selenium concentrations in channel water were significantly correlated with eight elements—boron, barium, chromium, magnesium, manganese, molybdenum, strontium, and vanadium—whereas in the 1996 reproduction study selenium concentrations were significantly correlated with nine elements—boron, calcium, potassium, lithium, magnesium, molybdenum, sodium, phosphorus, and strontium (Hamilton et al., 2001a), and in the 1997 reproduction study, barium was the only element significantly correlated with selenium in water (Hamilton et al., 2001b). Finger et al. (1994) also reported a strong relationship (r^2 = 0.80) among selenium, boron, cobalt, copper, lithium, and strontium. This correlation probably depends in part on the composition of the geologic material being leached by irrigation activities, that is, elevated elements in soil generally will leach out in proportion to their concentration in soil, depending on the adsorption coefficients. The relationship between geologic sources of selenium and their movement and potential consequences was reviewed by Presser and Ohlendorf (1987), Presser et al. (1994), and Presser and Piper (1998). Wright (1999) reported that application of nitrogen fertilizers mobilized selenium from seleniferous Cretaceous shales such as those found in western Colorado.

The significant positive correlations between selenium concentrations in water and water quality characteristics found in the present study were similar to those found in

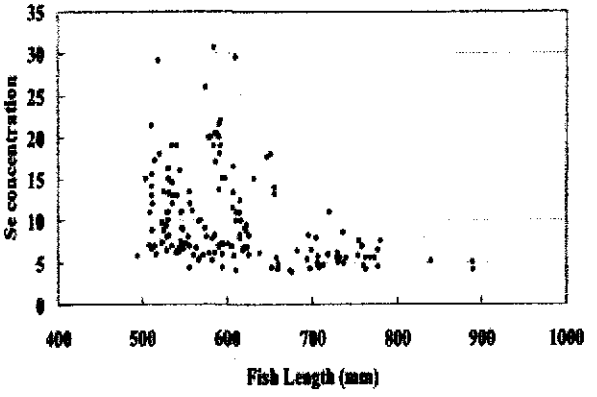

Fig. 6. Selenium concentrations (μg/g) in muscle plugs versus fish total length (mm) of Colorado pikeminnow collected during 1994–1998 at Walter Walker State Wildlife Area (n = 163).

two previous studies at North Pond. In the 1996 study calcium, chloride, conductivity, hardness, magnesium, nitrate, nitrite, and sulfate were correlated with waterborne selenium (Hamilton et al., 2001a), and in the 1997 study chloride and conductivity were correlated with waterborne selenium (Hamilton et al., 2001b).

Selenium in Sediment

The change in collection methods of sediments from 1995 to early 1996 and from mid-1996 to 1998 is an important consideration in the interpretation of selenium concentrations in the sediment samples. The early samples were thoroughly mixed, which resulted in a homogeneous distribution of selenium, whereas in cored samples, the depth distribution of selenium was maintained. Selenium concentrations in the top portions of cored samples are readily available to biota such as benthic invertebrates and bottom-dwelling fish and thus are more easily incorporated into the food web than is selenium disposed in deeper sediment.

Operation of the water control structure substantially reduced selenium concentrations in sediment in the WWSWA channel. Both sediment cores and sediment traps demonstrated that high-selenium sediment was buried by deposition of low-selenium sediment carried or moved by river flow through the control structure. Maintenance of low-selenium sediments probably would depend on continued low-selenium sediment deposit because groundwater recharge by high-selenium water could cause re-elevation of selenium concentrations in sediment. For example, selenium concentrations in sediment in North Pond at WW3 in May 1995 were elevated at 50.6 μg/g, in October 1995 they were reduced to 8.2 μg/g, and in April 1996 they were re-elevated to 46.1 μg/g (Hamilton et al., 2001a). Although selenium concentration in sediment can be variable (Peltz and Waddell, 1991; Stephens, 1996; Zhang and Moore, 1997), the decrease observed in October 1995 was thought to be a result of the deposition of fresh, low-selenium sediment from WW10. Water from WW10 was irrigation supply water from Independent Ranchman's Ditch and was used to maintain water levels in North Pond during two razorback sucker reproduction studies. An increase in sediment selenium concentrations seemed to occur at Adobe Creek (Grand Valley, CO) in two previous studies: 0.79 μg/g in May 1995, 0.95 μg/g in October 1995, 1.11 μg/g in April 1996, 1.21 μg/g in October 1996, and 2.52 μg/g in April 1997 (Hamilton et al., 2001a, 2001b).

Several investigators have proposed sediment guidelines. Stephens et al. (1997) proposed a "no effect concentration" of <2 μg/g for effects of selenium on fish and wildlife, a "level of concern" of 4 μg/g, and a toxic threshold guideline value of >4 μg/g. Lemly (1995) proposed a no-hazard concentration of <1 μg/g, a minimal hazard concentration of 1–2 μg/g, a low-hazard concentration of 2–3 μg/g, a moderate hazard concentration of 3–4 μg/g, and a high-hazard concentration of >4 μg/g. Presser et al. (1994) reported the upper limit of the expected baseline range for selenium concentrations in soils of the western United States was 1.4 μg/g. In contrast, Moore et al. (1990) used 0.5 μg/g as a reasonable selenium concentration in sediment to represent the threshold between uncontaminated, background conditions and environments with elevated selenium concentrations in sediment. Neither Lemly (1993a, 1996) nor Maier and Knight (1994) proposed a toxic threshold for selenium concentrations in sediment, but Lemly (2002) recommended 2 μg/g as a sediment toxicity threshold. The national background concentration of selenium in sediment is <1 μg/g (Maier and Knight, 1994).

Accumulation of selenium in the top layer of sediment is generally the result of deposition of dead organic material from the water column and incorporation in the detrital food chain (Holland, 1979; Cumbie, 1984; Weres et al., 1989; Kiffney and Knight, 1990; Oremland et al., 1990; Bender et al., 1991; Graham et al., 1992; Stephens, 1996). Graham et al. (1992) reported that in a pond study, selenium rapidly disappeared from the water column and correspondingly increased in sediments and biota, especially periphtyton. One component of the sediment is the detrital layer, which is partly composed of bacteria. Bender et al. (1991) reported selenium was rapidly removed from the water column by bacteria and cyanobacteria and incorporated into a detrital-like mat composed of anaerobically processed grass clippings. In their experiment, the initial selenium concentration of 40 mg/L dropped to an undetectable level in water after 27 days of microbial activity.

Prior to operation of the control structure, selenium concentrations in the top layer of sediment in the WWSWA channel at all stations except WW9 were above the toxic threshold of Stephens et al. (1997) and the high hazard of Lemly (1995). After the control structure operation, selenium concentrations in the sediment were substantially reduced at all stations and were near or below the national background level. Selenium concentrations in suspended sediment passing through the water control structure between December 1996 and June 1997 ranged from 0.9 to 1.8 μg/g (geometric mean 1.2 μg/g, Butler and Osmundson, 2000). Thus, relatively low selenium sediment was delivered to the channel from the river. Only in August 1997 was the sediment selenium concentration a concern, when it was 3.8 μg/g, which coincided with elevated selenium in water at 8 μg/L (Butler and Osmundson, 2000). In backwater areas and channels such as at WWSWA, water flow, sediment movement, and delivery of low-selenium sediment would be essential to prevent selenium accumulation in the upper portion of the sediment.

Selenium and Other Elements in Aquatic Invertebrates

Operation of the water control structure facilitated a substantial decrease in selenium concentrations in aquatic invertebrates, which paralleled similar decreases in water and sediment selenium concentrations. The concomitant decrease in selenium concentrations in these three aquatic ecosystem components was reflected in the significant correlations between selenium concentrations in aquatic invertebrates and water and sediment. Two previous studies in the Grand Junction area also reported high correlations between selenium concentrations in aquatic invertebrates, water, and sediments (Hamilton et al., 2001a, 2001b), suggesting a high degree of interconnectedness in the cycling of selenium.

Station WW7 was the only station where selenium concentrations in aquatic invertebrates did not decrease during operation of the water control structure, which was speculated to be because of groundwater seepage of high-selenium water contributing selenium to the food web. Butler and Osmundson (2000) reported that groundwater from a well near our station WW6 was low, whereas selenium in groundwater near our station WW7 was high. Thus, it is likely that this localized elevated selenium in the water near WW7 contributed to the elevated selenium concentrations in the chironomids we sampled.

The likely sources of selenium residues in aquatic invertebrates in the channel area were water, aquatic plants such as algae, bacteria, and particulate matter. Selenium in water is rapidly taken up by algae (Sandholm et al., 1973; Nassos et al., 1980; Foe and Knight, 1986; Riedel et al., 1991; Besser et al., 1993), aquatic plants (Allen, 1991; Ornes et al., 1991), and bacteria (Bender et al., 1991). Typically, algae had taken up maximal selenium concentration within 3–24 h, whereas floating plants took about 1 week to accumulate maximal concentrations. Some of the selenium taken up by aquatic invertebrates was probably waterborne organoselenium compounds released from living algae or by the necrosis of dead cells (Cutter, 1991, 1992; Besser et al., 1994). Zooplankton can rapidly take up selenium from water and accumulate it with no or little adverse effects (Halter et al., 1980; Nassos et al., 1980; Reading and Buikema, 1983; Salki et al., 1985; Foe and Knight, 1986; Boyum and Brooks, 1988; Ingersoll et al., 1990; Dobbs et al., 1996).

Selenium concentrations in aquatic invertebrates collected in 1996 from the WWSWA channel before the control structure was in operation (11.2–52.8 μg/g) were substantially above the proposed dietary toxic threshold concentration of 3 μg/g (Lemly, 1993a, 1996; Maier and Knight, 1994; Hamilton et al., 2000). After the control structure operation, selenium concentrations in channel water (1.6–3.0 μg/L) were found to be below the current USEPA toxic threshold criterion of 5 μg/L; however, selenium concentrations in food organisms during the latter part of this period (mean 4.9 μg/g in 1998) exceeded the proposed dietary toxic threshold. The mean selenium concentration in aquatic invertebrates in 1998 was similar to the selenium concentration in zooplankton (4.6 μg/g), a concentration linked to substantial mortality of larval razorback sucker according to the results of two 30-day toxicity tests using natural food organisms (Hamilton et al., 2001a, 2001b).

Other than selenium, none of the inorganic elements measured in aquatic invertebrates collected from the channel stations were elevated to concentrations of concern. Only barium and zinc in aquatic invertebrates showed significant correlations with selenium concentrations in aquatic invertebrates. However, both these elements were present at relatively low concentrations.

Selenium in Forage Fish

The 68% reduction in selenium concentrations in whole-body forage fish samples (27.2 μg/g in 1996 and 8.6 μg/g in 1998) demonstrated that flushing of the WWSWA channel with river water through the water control structure reduced selenium residues in forage fish. The decrease in selenium concentrations in forage fish probably was a result of the reduction of selenium concentrations in water, sediment, aquatic invertebrates, and forage fish consumed by piscivores.

The decrease in selenium in forage fish from 1996 to 1998 that was found in the present study was not consistent with selenium concentrations reported by Butler and Osmundson (2000), who reported selenium concentrations of 7.7–15.0 μg/g (geometric mean 14.2 μg/g, $n = 8$) in forage fish collected in August 1995 from the lower WWSWA channel area. The relatively low selenium concentrations in 1995 may have been partly a result of the small number of fish samples but was more likely to have occurred because of the high river flow in 1995 (Fig. 3).

The initially high selenium residues in forage fish may have decreased because of depuration while living in an environment with lower selenium concentrations, especially in food organisms. An example of selenium depuration was given by Birkner (1978), who conducted a 90-day study with juvenile fathead minnow that initially had a whole-body selenium concentration of 13.9 μg/g. After 90 days of exposure, fish fed zooplankton with selenium concentrations of 1.2 μg/g had whole-body residues of 5.0–5.7 μg/g, those fed zooplankton with 5.7 μg/g had whole-body residues of 5.2–7.0 μg/g, and those fed zooplankton with 11.8 μg/g had whole-body residues of 10.3–11.0 μg/g. Thus, fish depurated selenium from their initial elevated whole-body residue level down to a concentration close to the concentration in their food.

The time after operation of the water control structure allowed selenium concentrations in water, sediment, inver-

tebrates, and forage fish to decrease and may be thought of as a depurating environment during 1997–1998. Loss of selenium from fish tissue during depuration has been reported to be independent of waterborne exposure concentration (Gissel Nielsen and Gissel-Nielsen, 1978; Sato et al., 1980) but to increase with dietary exposure to low concentrations (Hilton and Hodson, 1983). Loss of selenium also was found to be faster in smaller, younger fish (Bennett et al., 1986) than in larger, older fish (Bertram and Brooks, 1986). Depuration of selenium from tissue depends on several factors, including cleanliness of the food and water in the depurating environment, age, size, metabolic activity, season for poikilotherms, initial selenium load of various tissues, and other factors. The half-life of selenium in various species of young fish was reported to be in the range of 19–30 days (Gissel Nielsen and Gissel-Nielsen, 1978; Sato et al., 1980; Hilton et al., 1982; Lemly, 1982; Bennett et al., 1986; Kleinow and Brooks, 1986; Besser et al., 1993). Others have reported longer half-lives, including 49 days for adult fathead minnows exposed to selenium in the diet (Bertram and Brooks, 1986), 63 days in the whole body of adult fathead minnows and the muscle of rainbow trout (*Oncorhynchus mykiss*; Adams, 1976), and greater than 60 days in adult bluegill (*Lepomis macrochirus*; Bryson et al., 1984). In two studies with adult razorback sucker, the half-life of selenium in muscle plugs was found to be greater than 100 days (Hamilton et al., 2001a, 2001b).

The concept of depuration may be misleading in the natural environment because many of those measurements were on fish physically placed in a clean environment for the sole purpose of determining how fast their tissue could remove a contaminant. In the natural environment fish may not be able to move to a clean environment. Sorensen (1988) reported that selenium tissue residues in fish from Martin Lake, in Texas, were only 25% lower after a 5-year period (1981–1986) following the drastic reduction of selenium inputs into the lake in 1978. Likewise, Lemly (1997) assessed selenium concentrations in five ecosystem components of Belews Lake, in North Carolina, 10 years after selenium inputs to that lake were stopped and found elevated selenium concentrations in sediment, benthic invertebrates, and fish, which suggested that a moderate hazard still existed. He also reported teratogenic deformities first observed in 1992 (Lemly, 1993c) were still present at elevated levels in 1996.

Although the selenium concentrations in forage fish investigated in the current study had decreased substantially by 1998, after 2 years of control structure operation, the remaining selenium residues in fish were above the toxic whole-body threshold values of >4 μg/g, proposed by Stephens et al. (1997), and 4 μg/g, proposed by Lemly (1996). Thus, the mean selenium concentration in forage fish of 8.6 μg/g in 1998 should be considered a level of concern for consumption by piscivorous Colorado pikeminnow. Continued operation of the control structure probably would have continued to reduce selenium concentrations in various ecosystem components including forage fish.

Another reason that forage fish such as fathead minnow and red shiner had lower selenium concentrations after operation of the water control structure is their high level of reproductivity, enabling them to reproduce two or three times a year. Newly produced fish would start out relatively cleaner than the previous cohort as the channel area was being flushed of selenium in water and sediment. It is also possible that some of the forage fish in the channel came from the river.

Operation of the water control structure seemed to have shifted the proportion of native and nonnative fish in the channel area. Scheer (1997) reported that the percentage of native fish collected by trammel net was 38% in 1995, 28% in 1996, and 64% in 1997. The percentage of native fish collected by trammel nets in the channel area from earlier efforts was 75% in 1992, 53% in 1993, and 58% in 1994 (unpublished data from D. Osmundson, USFWS, given in Lloyd 1996). Scheer (1997) speculated that the reduction in nonnative fish in the channel in 1997 was a result of flow through the channel area and lower water temperatures from input of flowing river water. However, there was a substantial difference in collection efforts, which was most evident in the total number of fish collected—1995, 3294 fish; 1996, 1294 fish; 1997, 1987 fish; 1998, 85 fish—and in the number of hours devoted to the sampling effort, using trammel and trap nets—1995, 163.8 h; 1996, 519.3 h; 1997, 955.7 h; 1998, ~40 h (Mourning, 1995; Lloyd, 1996; Scheer, 1997, 1998). Consequently, the small number of fish collected in 1998 and the reduced sampling effort preclude drawing conclusions about shrifts in species composition after operation of the water control structure.

Selenium in Colorado Pikeminnow

Selenium concentrations in muscle plugs of Colorado pikeminnow did not decrease between 1996 and 1998; however, only three fish were collected in 1998 compared with 40–54 fish collected during the 1995–1997 period. Using data from Osmundson et al. (2000) for 1994, there was a significant decrease in muscle plug selenium between 1994 and the years 1995, 1996, and 1997. Although selenium concentrations in water, sediment, aquatic invertebrates, and forage fish decreased between 1995 and 1998, a similar decrease in selenium concentrations in muscle plugs of Colorado pikeminnow did not occur.

The strongest relation between muscle plug selenium and aquatic ecosystem components seemed to be with river flow for the 1994–1998 period, as shown by the significant correlation with the May stream flow and the similar, but not significant, correlation with the average March–July period stream flow. Osmundson et al. (2000) also thought

high river flow contributed to lower selenium concentrations in muscle plugs of Colorado pikeminnow, but did not give a correlation value. They noted several factors that may have influenced the relation between river flow and selenium in the muscle plugs of Colorado pikeminnow including: (1) selenium concentrations in food items, (2) previous selenium loads in muscle and other tissues, (3) staging and feeding locations of fish prior to capture, (4) feeding rate and weight gain of fish, (5) sex of fish (females can deposit selenium into eggs), and (6) magnitude, duration, and timing of spring runoff and peak flows.

Using the yearly (1995–1998) mean values, muscle plug selenium was not significantly correlated with water, sediment, aquatic invertebrates, or forage fish. Despite these nonsignificant correlations, the selenium residues in Colorado pikeminnow must have come from either water exposure, diet exposure, or combined water and diet exposure. The small number of Colorado pikeminnow collected in 1998 conservatively reduced the overall data set to 4 years (1994–1997). During this period 1994 was a low-flow year, 1995 and 1997 were high-flow years, and 1996 was an average-flow year.

Selenium concentrations in muscle plugs seemed to decrease with increasing fish weight and total length, and the two measures were significantly correlated with selenium in muscle plugs. Larger, presumably older Colorado pikeminnow had relatively low selenium residues, whereas smaller, younger fish had widely varied levels of selenium residue including very elevated concentrations (>12 μg/g). Several questions arise from this pattern of levels of selenium residue: (1) Do young fish with elevated levels of selenium residue fail to live to older ages and larger sizes? (2) Are the few larger, older fish alive because they have a low concentration of selenium residue? (3) Is selenium regulation enhanced with older age? (4) Is the concentration of selenium residues diluted with increased weight? (5) Are the few larger, older fish depurating selenium through egg spawning? (6) Are there diet differences between fish 500–650 mm in length and those whose length is greater than 650 mm?

WWSWA at river mile 163.3–163.7 had the highest concentrations of selenium residues (9.0–16.1 μg/g) in muscle plugs from Colorado pikeminnow collected from various locations in the upper Colorado River (Fig. 7). In contrast, Colorado pikeminnow collected directly above (river miles 163–168, 8.5 μg/g), farther above (above river mile 168, 4.9–5.4 μg/g), directly below (river miles 158–163, 4.4–6.4 μg/g), and farther below (below river mile 158, 5.3–5.4 μg/g) WWSWA had lower selenium residue levels. A similar pattern of selenium residues in common carp collected in the Green River at Ashley Creek–Stewart Lake area was reported by Stephens and Waddell (1998). They demonstrated that selenium concentrations in whole-body common carp collected immediately downstream (Bonanza and Collier Draw) and immediately upstream (Escalante Bar and Jensen) of Ashley Creek were lower than those in fish from Ashley Creek, and that fish collected farther downstream (Horseshoe–Hammacher and Ouray) and upstream (Echo Park and Browns Park) had still lower selenium concentrations.

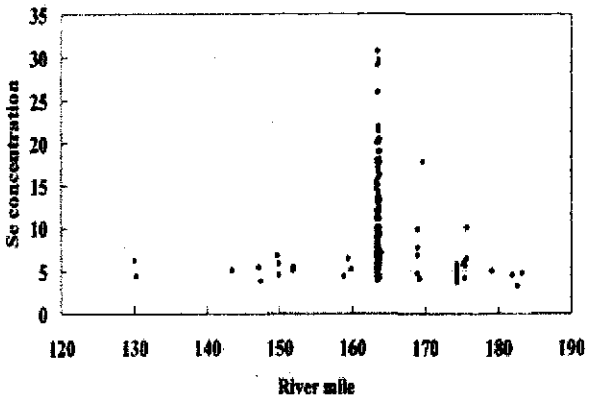

Fig. 7. *Selenium concentrations (μg/g) in muscle plugs from Colorado pikeminnow collected from various locations in the upper Colorado River (n = 211; at Walter Walker State Wildlife Area: river mile 163.3–163.7).*

Selenium residues in muscle plugs of Colorado pikeminnow in the upper Colorado River near WWSWA (4.4–8.5 μg/g) tended to be higher than those in Colorado pikeminnow collected from the lower Gunnison (mean 4.9 μg/g, $n = 7$), Green (3.7 μg/g, $n = 5$), White (3.6 μg/g, $n = 5$), and Yampa (2.3 μg/g, $n = 5$) rivers (Hamilton et al., 2003). Of note is that the Gunnison River, in which Colorado pikeminnow had higher selenium residues than did fish from the other rivers, has been identified as a major source of selenium in the upper Colorado River basin (Butler et al., 1991, 1994, 1996; Engberg, 1999; Butler and Osmundson, 2000).

Depuration does not seem to be occurring in endangered fish in the Colorado River near WWSWA because Colorado pikeminnow recaptured over a period of 2–3 years (1995–1997) seemed to be conserving selenium concentrations in muscle plugs from year to year (this study and Osmundson et al., 2000). This finding seems unusual because selenium concentrations decreased in water, sediment, aquatic invertebrates, and forage fish at WWSWA.

Of 16 fish collected at WWSWA in 1994, all were recaptured in later years (1995–1997). Of 45 fish collected in 1995, 25 were recaptured in other years, but 20 were one-time captures. Of 35 fish collected in 1996, 26 were recaptured in other years, and 9 were one-time captures. Of 54 fish collected in 1997, 21 were recaptured in other years, and 33 were one-time captures. The portion of the Colorado pikeminnow population using WWSWA seems to be dynamic because new fish seemed to be attracted each year, or possibly fish captured one time learned to avoid recapture.

Colorado pikeminnow seem to be highly mobile, and juveniles and subadults in the lower 181 km of the upper Colorado River below Westwater Canyon tend to move to the upper 98 km of the river, mostly in the Grand Junction area, according to Osmundson et al. (1998). They reported that adults in the upper reach of the river tend to be larger and move less than do juveniles and subadults in the lower reach, and they concluded that the relatively small changes in location by larger fish in the upper reach were consistent with the hypothesis that adult Colorado pikeminnow select and maintain fidelity to a home feeding range. This hypothesis seems to supported by the observation in the current study that adults with elevated selenium residues in muscle plugs for 1 year maintained those residues in subsequent years and, conversely, that fish feeding in a low selenium area from year to year had low selenium residues over a multiyear period.

Osmundson et al. (1998) also noted that Colorado pikeminnow do not seem to be highly territorial as shown by their concentrating in limited backwater habitats during the spring runoff (April–June), their congregating prior to and during spawning in summer, and individuals occasionally being found beside one another. This finding of nonterritoriality is consistent with the wide range of selenium residues found in adults captured from the WWSWA in the present study.

Osmundson et al. (1997) reported that growth rates of adult Colorado pikeminnow were highest (42.7 mm/year) for fish 400–449 mm in length, declined in fish 500–549 mm in length (19.8 mm/year), and were lowest for fish 550 mm in length and larger (9.5 mm/year). This reduced growth in larger, older fish suggests they were putting less food resources into growth and possibly were consuming less food. Consumption of less food, especially high-selenium food from areas such as WWSWA, would allow depuration of selenium residues over long periods of time, assuming depuration is slow in large-bodied fish. In the present study fish whose total length was about 680 mm and larger had substantially less selenium in muscle plugs than did fish whose length was in the range of 500–630 mm. Consequently, the reduced growth of large, older Colorado pikeminnow may allow depuration of selenium residues to occur. Alternatively, it may be adult Colorado pikeminnow 500–650 mm in length with low selenium residues that live to be older and larger, whereas adults with elevated selenium residues, those greater than 12–15 μg/g, may disappear from the population because of long-term contaminant stress.

The adult annual survival rate of adult Colorado pikeminnow in the upper reach of the upper Colorado River has been estimated to be high (0.86; Osmundson and Burnham, 1998). A similar survival rate (0.85) was estimated by Osmundson et al. (1997) for Colorado pikeminnow greater than 550 mm in length . Adult fish can usually withstand higher levels of stress, including contaminants, than can younger fish, and so this high survival rate seems reasonable despite high selenium residues in some adult Colorado pikeminnow.

Stress during the younger life stages of Colorado pikeminnow in the upper reach seems to have increased since the 1970s. Osmundson and Burnham (1998) noted that in the mid-1970s smaller size classes (250–450 mm) were more prominent (about one-third), whereas fish shorter than 450 mm were rare in the upper reach in the early 1990s. They presented two hypotheses to explain the changes in size class distribution: (1) the nursery habitat in the upper reach was of a higher quality and quantity early than in later years, and so a smaller proportion of larvae drifted to the lower reach; and (2) reproduction or hatching success in the upper reach was formerly much greater than that today, and a substantial number of larvae were retained in the upper reach even though proportions drifting to the lower reach might have been similar to those in recent years. Stress from contaminants such as selenium could be contributing to the lack of smaller size classes of Colorado pikeminnow in the upper Colorado River noted by Osmundson and Burnham (1998). They suggested that changes in runoff patterns in the Colorado River, that is, fewer high spring runoff events, may influence Colorado pikeminnow populations by reducing the creation of fresh cobble bars for spawning and inadequately cleansing fines from existing bars, reducing flushing events to remove contaminants from agricultural (selenium) and urban areas from backwater nursery areas, reducing channel diversity and biological diversity of river bottomlands, and reducing the number of nonnative minnows that now dominate backwater nursery habitats.

Comparison to Selenium in Colorado River

In the present study selenium concentrations in muscle plugs of fish collected at WWSWA (9.0–16.6 μg/g) and outside WWSWA in the upper Colorado River (4.4–8.5 μg/g) exceeded the 85th percentile (arbitrary point distinguishing relatively "high" concentrations) in the National Contaminant Biomonitoring Program (NCBP) for the years 1971–1984 (Walsh et al., 1977; May and McKinney, 1981; Lowe et al., 1985; Schmitt and Brumbaugh, 1990). The NCBP has documented temporal and geographic trends in concentrations of persistent environmental contaminants, including selenium, in whole body of fish that may threaten fish and wildlife. The 85th percentile concentrations of selenium in samples from the NCBP were 2.9 μg/g [reported as wet weight, converted to dry weight assuming 73% moisture ([average of percent moisture in 1978–1981 and 1984 samples)] in 1972–1973, 3.0 μg/g (converted to dry weight assuming 73% moisture) in 1976–1977, 2.5 μg/g (converted to dry weight based on a mean moisture of 72% for 591 samples in the 1978–1981 collection) in 1978–1981, and 2.8 μg/g (converted to dry weight based on a

mean moisture of 74% for 315 samples in the 1984 collection) in 1984, the last year of the program (Walsh et al., 1977; May and McKinney, 1981; Lowe et al., 1985; Schmitt and Brumbaugh, 1990).

Selenium concentrations in muscle plugs measured in the present study probably underestimate the concentrations in whole-body fish. One report stated that fillets (i.e., muscle) had more selenium than did whole-body bluegill and largemouth bass (*Micropterus salmoides*) collected at a variety of sites in central California associated with irrigation drainage (Saiki et al., 1991), which was the opposite of what the majority of articles in the literature reported. In general, muscle tissue contains less selenium than does the whole body because of the relatively high amounts of selenium found in the spleen, liver, kidney, heart, and other tissues, especially mature ovaries (Adams, 1976; Sato et al., 1980; Lemly, 1982; Hilton et al., 1982; Hilton and Hodson, 1983; Kleinow and Brooks, 1986; Lemly and Smith, 1987; Hermanutz et al., 1992). Consequently, the estimated whole-body selenium concentrations in Colorado pikeminnow in the present study would be about 15.0–27.7 μg/g for fish collected in WWSWA and 7.3–14.2 μg/g for fish collected outside WWSWA (based on a conversion factor of 1.667 × muscle concentration = whole body concentration; Lemly and Smith 1987). Other conversion factors are 2.355 for rainbow rout, based on data from Adams (1976), and 1.745 for bluegill and largemouth bass, from Lemly (1982). Both of factors would have increased the estimated whole-body selenium concentrations in Colorado pikeminnow. Thus, using a conservative conversion factor, the Colorado pikeminnow in the present study would have had selenium residues over 5–9 times higher than the NCBP 85th percentile for fish collected in WWSWA and 2–5 times higher for fish collected outside WWSWA.

Selenium concentrations in whole-body fish in the Colorado River basin, measured as part of the NCBP, have been among the highest in the nation (Walsh et al., 1977; Lowe et al., 1985; Schmitt and Brumbaugh, 1990). They exceeded the 85th percentile in whole-body fish collected in 1972–1973 at 5 of 6 Colorado River basin stations [the Green River at Vernal, UT (only upper basin station), and the Colorado River at Imperial Reservoir, Lake Havasu, Lake Mead, and Lake Powell, all in Arizona]. Selenium concentrations in whole-body fish also exceeded the 85th percentile in 1978–1981 and in 1984 at six of seven stations (same five as above plus the Colorado River at Yuma, AZ).

The fish investigated in the present study may have reached an equilibrium between selenium concentrations in muscle tissue and those in food chain organisms because the concentrations of selenium in the fish, based on using selenium concentrations in muscle to calculate whole-body concentrations, were found to be close to those in food organisms. The results of most laboratory studies of dietary exposure to selenium have shown that selenium accumulates to concentrations in whole-body fish similar to those in the diet (Bennett et al., 1986; Hamilton et al., 1990; Crane et al., 1992; Lemly, 1993b). In field studies where fish have had time to equilibrate with the environmental conditions, they often accumulate selenium concentrations from 1.4 to 2.6 times greater than the selenium concentrations in their food (Barnhart, 1957; Birkner, 1978; Woock, 1984; Saiki, 1986). It is possible that if the selenium concentrations in water, sediment, aquatic invertebrates, and forage fish had remained low, as occurred in 1998, that selenium concentrations in Colorado pikeminnow using WWSWA would decrease.

Although it was found that flushing the WWSWA channel lowered selenium concentrations in several aquatic ecosystem components, others have reported that flushing of channels and backwaters has not had similar effects. Villegas (1997) reported that the flushing of the 243-ha Cibola Lake, on Cibola National Wildlife Refuge, in California and Arizona, with Colorado River water did not consistently reduce selenium concentrations in sediment and fish during three intermittent flushings. He also reported that continuous flushing of Mittry Lake, in Arizona, with Colorado River water held selenium concentrations in sediment and fish at the lower end of the range of concentrations observed at Cibola Lake. NIWQP (2002) reported that remediation efforts such as draining, drying, flushing, tilling, or adding lime did not measurably reduce selenium concentrations in sediments at selenium-contaminated Stewart Lake, on the Green River in Utah. In fact, selenium in the sediment rapidly accumulated in phytoplankton and zooplankton, which resulted in a 10-fold increase in selenium concentrations in 300-g razorback sucker after 30 days of exposure (from 0.9 μg/g prerelease to 9.0 μg/g). In the present study the decreased selenium concentrations in water, sediment, and biota at WWSWA were probably a result of the efficient, continuous flushing of the long narrow channel.

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