EVALUATION OF FLUSHING OF A BACKWATER CHANNEL: CONCENTRATIONS OF SELENIUM AND OTHER INORGANIC ELEMENTS IN WATER, SEDIMENT, INVERTEBRATES, FORAGE FISH, AND COLORADO PIKEMINNOW

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EXECUTIVE SUMMARY

Selenium contamination of the upper and lower Colorado River basin has been documented in water, sediment, and biota in studies by U.S. Department of the Interior agencies, and academia. Concern has been raised that this selenium contamination may be adversely affecting endangered fish in the upper Colorado River basin. The objective of the current study (conducted in 1995-1998) was to determine if operation of a water control structure that allowed Colorado River flow through a channel area at Walter Walker State Wildlife Area (WWSWA) would reduce selenium concentrations in aquatic ecosystem components.

The channel area at WWSWA was marked with seven collection stations. Water quality measurements were collected on-site weekly. Samples collected at monthly intervals (sometimes at 60-day or other intervals) included water samples for water quality and analysis of selenium and other inorganic elements, sediment for analysis of selenium and composition, and aquatic invertebrates and forage fish for analysis of selenium and other inorganic elements. Colorado pikeminnow were collected and muscle plug samples taken for selenium analysis. The water control structure was opened on December 5, 1996.

Combining all stations, except the station on the Colorado River and the station at the marsh outflow, selenium concentrations in filtered water were 21.0 µg/L (microgram per liter) in 1995 (range <1-126 µg/L), 23.5 µg/L in 1996 (range <1-135 µg/L), 2.1 µg/L in 1997 (range <1-6 µg/L), and 2.1 µg/L in 1998 (range <1-6.3 µg/L). The major source of selenium to the channel area seemed to be the marsh located east and adjacent to North Pond. Elements in water at the marsh that were elevated during the period when selenium was elevated included boron, chromium, iron, magnesium, manganese, molybdenum, strontium, and vanadium.

Combining all selenium concentrations from mixed samples or the upper most portion of sediment cores and sediment traps from all stations, selenium concentrations were 8.5 µg/g in 1995 (2.4-20.8), 8.2 µg/g in 1996 (0.4-19.6), 4.8 µg/g in 1997 (3.4-5.9), and 1.1 µg/g in 1998 (0.4-1.9). Selenium concentrations in sediment cores collected before operation of the control structure were elevated in the surficial sediment, whereas after structure operation, upper most sections of cores had reduced selenium concentrations and lower sections had elevated concentrations.

Combining all stations, 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 aquatic invertebrates were significantly correlated with selenium in filtered water ($r = 0.83$), unfiltered water ($r = 0.77$), and sediments ($r = 0.81$). No other inorganic elements seemed elevated to concentrations of concern.

Combining all forage fish and stations, selenium concentrations were 27.2 µg/g in 1996, 20.2 µg/g in 1997, and 8.6 µg/g in 1998. Selenium concentrations in forage fish were significantly correlated with filtered water ($r = 0.58$), sediment ($r = 0.75$), and aquatic invertebrates ($r = 0.46$). Between 1996 and 1998, concentrations of inorganic elements in forage fish changed as follows: aluminum 5.8 times lower, selenium 4 times lower, iron 3.7 times lower, manganese 2.0 times lower, vanadium 2.3 times lower, lead 2 times higher, and no change (<two fold) for arsenic, barium, beryllium, boron, cadmium, chromium, copper, magnesium, molybdenum, nickel, strontium, and zinc.

In general from a spatial standpoint, water flow through the water control structure had the greatest effect (i.e., greatest reduction in selenium concentration) on water, sediment, and biota in the upper channel near the location of the control structure. The least change in

selenium concentrations occurred in the lower portion of the channel near its natural connection with the Colorado River.

Combining all selenium concentrations in muscle plugs of Colorado pikeminnow collected from WWSWA, selenium concentrations were 9.8 µg/g in 1995 (n=49), 9.5 µg/g in 1996 (n=40), 9.0 µg/g in 1997 (n=54), and 10.3 µg/g in 1998 (n=3). 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, although a larger sample size of Colorado pikeminnow in 1998 might have revealed a change in selenium concentrations. Selenium concentrations in muscle plugs decreased with increasing fish total length and weight. Selenium concentrations in Colorado pikeminnow repeatedly sampled in the same year or captured in subsequent years did not reveal any significant changes in concentrations. Muscle plug selenium concentrations seemed to be most closely associated with the mean monthly river flow for the March-July period ($r= -0.85$, $P=0.07$).

The objective of the study was met in that selenium concentrations were measured in water, surficial sediments, aquatic invertebrates, and forage fish to determine if concentrations changed after operation of the water control structure. Remediation seemed to be achieved because the process of flushing the backwater channel remedied the presence of high selenium concentrations in water, sediment, aquatic invertebrates, and forage fish, which occurred prior to flushing. Within the context of this study, flushing is defined as the washing out or cleansing of selenium-laden water, sediment, and plankton using water with lower selenium concentration, and remediation is defined as the act of reducing the concentration and bioavailability of selenium at a given locale.

INTRODUCTION

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 has been undertaken in 1987 by the Upper Colorado River Endangered Fish Recovery Program (USFWS 1987). The goal of the 15-year program is 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 to restore floodplain habitats for use by larvae and adults of endangered fish. 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, which after restoration would not pose contaminant problems to the fish, especially from selenium.

Adult Colorado pikeminnow are typically found in deep, fast-flowing waters of the Colorado River and in large pools of tributaries, are slow growing, and are piscivorous (Moyle 1976). Young Colorado pikeminnow <50 mm total length frequent 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 were extirpated from the Colorado River below Glen Canyon Dam (Moyle 1976). The status and trends of the Colorado pikeminnow has been reviewed by Osmundson and Burnham (1998). They estimated numbers of Colorado pikeminnow in the upper Colorado River at 598: 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 suggested in historical accounts. The current population was thought to have a constant adult survival rate, but recruitment was highly variable and may 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 numbers of non-native fish in backwater nursery areas (Osmundson and Burnham 1998).

The life history and status of the razorback sucker has been reviewed by Bestgen (1990). Briefly, the razorback sucker was considered common in the upper and lower Colorado River basins in historical times, but since the 1940s has become rare except for populations in the Green River and lakes Mead and Mohave. Razorback suckers are generally thought to inhabit moderate to large streams and rivers and use a variety of habitats including low-velocity areas (backwaters, sloughs, oxbow lakes), near-shore runs, and shallow channels adjacent to, or over, mid-stream sandbars. The diet of razorback sucker varies depending on life stage, habitat, and food availability, and the diet of adults in rivers may be different than adults in reservoirs. Springtime congregations of razorback sucker have been found in off-channel impoundments and tributaries. Spawning behavior of razorback sucker is apparently influenced by water temperature and flow (Tyus and Karp 1990), but Modde and Wick (1997) suggest that increases in discharge probably have a greater influence on initiating fish movement to spawning sites in late spring such as Razorback Bar in the Green River. The remaining population of razorback

sucker in the middle Green River basin in Utah has been estimated, using similar datasets, at about 1,000 individuals in 1988 (Lanigan and Tyus 1989) and at 300 to 600 in 1992 (Modde et al. 1996). Razorback sucker are rare in the upper Colorado River, where only 10 wild fish were found in the river between 1989 and 1996 (C. McAda, USFWS, personal communication).

Selenium contamination of the upper and lower Colorado River basins has been documented in water, sediment, and biota, in studies by the U.S. Department of the Interior agencies and academia (reviewed in Hamilton 1998). Historic selenium contamination of the upper and lower Colorado River basins prior to the construction of main stem dams has been hypothesized to contribute to the decline of native fish that are currently federally listed as endangered (Hamilton 1999). Other 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 current study was undertaken to determine if flushing a backwater channel contaminated with elevated selenium in water, sediments, invertebrates, and fish would remove selenium from the channel area. The present study was conducted to derive the necessary toxicological information for assessing the suitability of flushing for improving selected flooded bottomlands as habitat for endangered fish. The study was conducted in the backwater channel at Walter Walker State Wildlife Area (WWSWA) near Grand Junction, CO, which is highly contaminated with selenium (Hamilton et al. 2001a, 2001b, Butler and Osmundson 2000). 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 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, i.e., the gravel pit at what is now Walter Walker State Wildlife Area (McAda 1977, Kidd 1977, Valdez et al. 1982, Osmundson and Kaeding 1989).

Objective

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 contamination of biotic and abiotic ecosystem components. The objective of the study was met in that selenium concentrations were measured in water, surficial sediments, aquatic invertebrates, and forage fish to determine if concentrations changed after operation of the water control structure. Remediation seemed to be achieved because the process of flushing the backwater channel remedied the presence of high selenium concentrations in water, sediment, aquatic invertebrates, and forage fish, which occurred prior to flushing. Within the context of this study, flushing is defined as the washing out or cleansing of selenium-laden water, sediment, and plankton using water with lower selenium concentration, and remediation is defined as the act of reducing the concentration and bioavailability of selenium at a given locale.

METHODS

The study was conducted between May 1995 and September 1998 at WWSWA (Figure

1). The site was located about a half km to the southwest of the Grand Junction city limits.

Site description

The sampling stations at WWSWA were designated WW1 through WW10 (Figure 1). The backwater channel is located 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 as shown in Figure 1. During spring runoff, the river backs into the channel area at station WW9 and creates a backwater pool that in some years extends 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 to dilute selenium concentrations in water, sediment, and biota. The water control structure was opened on December 5, 1996. The backwater channel receives inflow of ground water from the underlying cobble aquifer (Phillips 1986). Elevated selenium concentrations in ground water and surface seeps entering the channel area have been documented by Butler and Osmundson (2000).

North Pond is located at WWSWA and is an isolated pond about 1 ha (2.5 acre) in size with a maximum depth of 1.5 m located on a terrace about 2 m above the backwater channel. Water in North Pond was supplied primarily by ground water discharge, which was believed to contain 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 confine fish. A reproduction study with adult razorback sucker was conducted at North Pond in 1995-1996 (Hamilton et al. 2001a), and 1996-1997 (Hamilton et al. 2001b).

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 when water from Independent Ranchman's Ditch was used to maintain water levels for a reproduction study with adult razorback sucker between 1995 and 1997. The sampling station at the outfall of the marsh was designated WW4 (Figure 1) prior to construction and operation of the water control structure was designated WW4a after installation and opening of the water control structure on December 5, 1996, and was at the mixing zone of the water control structure and the marsh outfall (Figure 2). A new station WW4b was established away from the mixing zone and nearer the marsh. Sampling station WW8 (Figure 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 (Figure 2). A staff gage was installed at WW9 to monitor water elevation. Gage heights were recorded daily at WW9 from June 17 to August 3, 1996, and from November 26, 1996, to June 16, 1997. Following operation of the water control structure, it became readily apparent that the water flow through the channel area was creating a relatively uniform mixing of water at sampling stations. Consequently, the sampling of water quality characteristics was discontinued at WW5, WW7, and WW9 in 1997 and 1998.

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, CO. Details of fish collection and the resulting data were given in Mourning (1995), Lloyd (1996), and Scheer (1997, 1998). Briefly, fish were collected by fyke net, trammel net, seining, minnow traps, electrofishing or a combination of two

Figure 1. Map of sampling stations during 1995-1996 at Walter Walker State Wildlife Area near Grand Junction, Colorado.

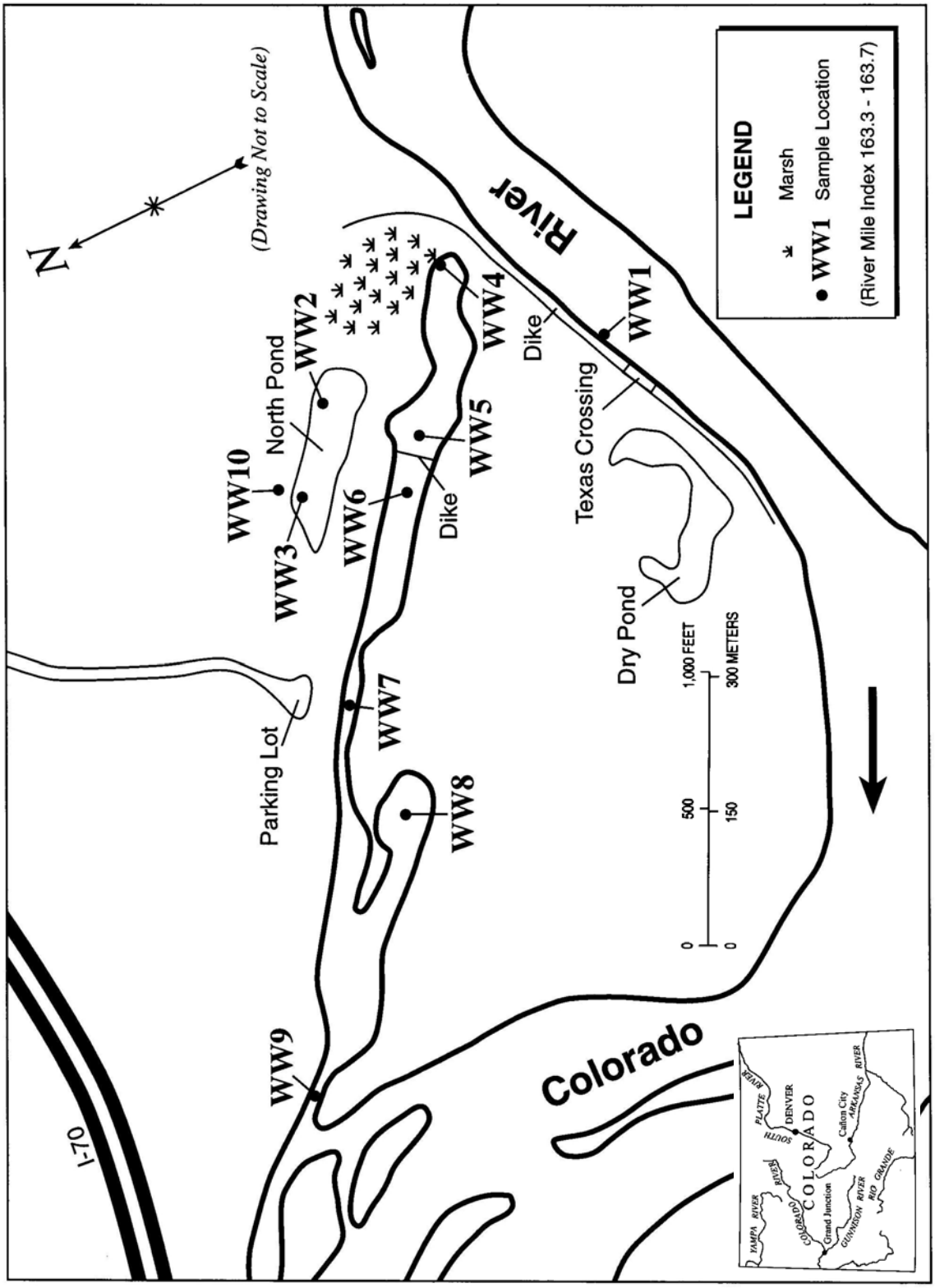
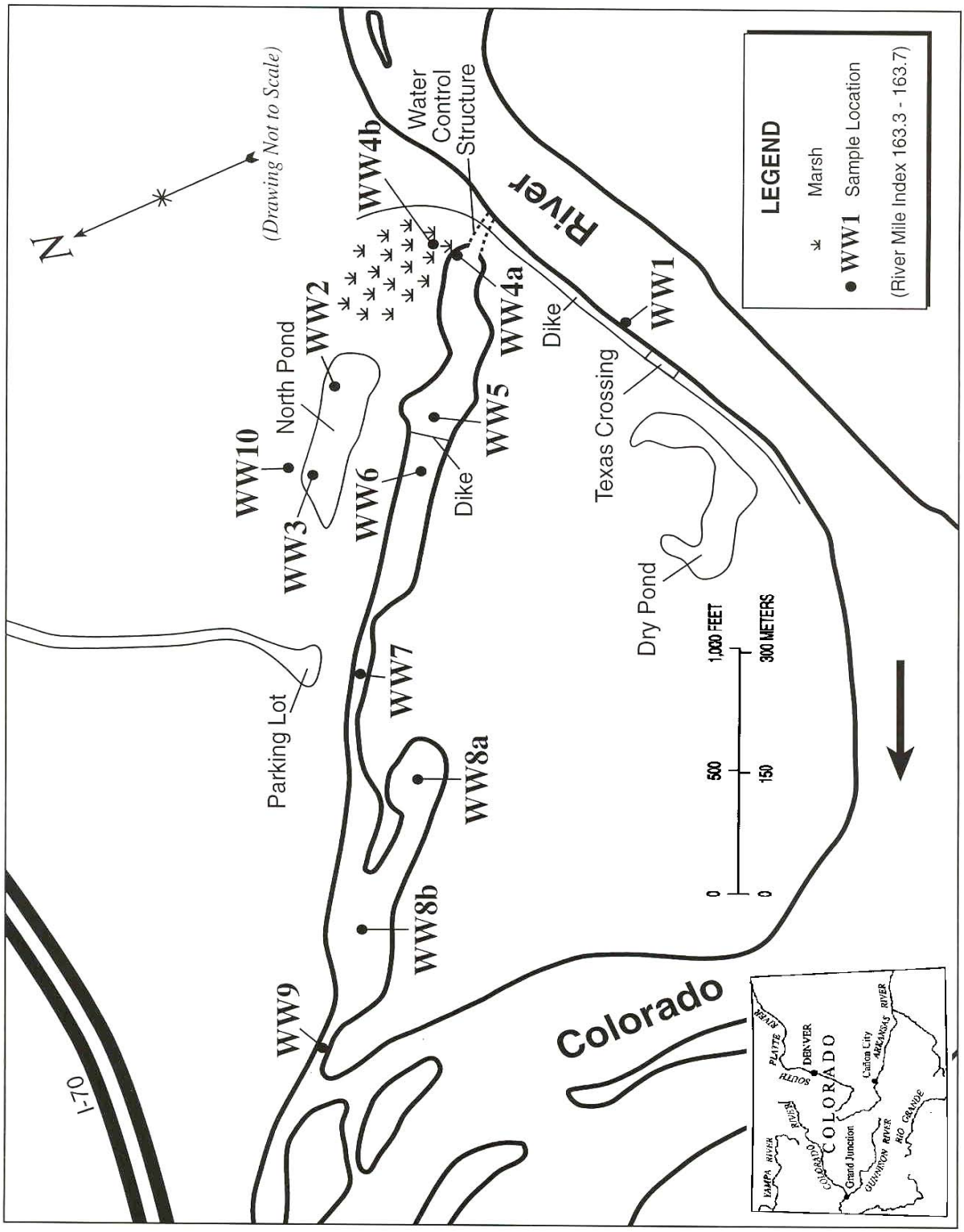


Figure 2. Map of sampling stations during 1996-1998 at Walter Walker State Wildlife Area near Grand Junction, Colorado.



or more methods. Sampling was accomplished from April to late summer when water levels dropped enough to cut off the backwater channel. Fish were identified to species and age class, counted, and measured for total length and weight. 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 was collected in 1995 and did not have a passive integrated transponder (PIT), and was moved to the CRFP's facility at Horsethief Canyon State Wildlife Area. For Colorado pikeminnow collected, the fish's PIT tag was determined, total length and weight recorded, and a muscle plug sample taken from the dorsal area adjacent to the dorsal fin for selenium analysis. If no PIT was found in the fish, a new PIT tag 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.

Sediment 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 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 4, 1995, to September 14, 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 measured *in situ* at each station included pH, conductivity, salinity, air temperature, water temperature, and dissolved oxygen. Water quality measurements 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 <2 with concentrated sulfuric acid. The other sample was used for nitrate, nitrite, sulfate, total suspended solids, volatile solids, and fixed solids 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 Field Research Station (FRS), SD, 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 and following the procedures for low concentration measurements of the electrode manufacturer (Orion 1990, 1991; ATI Orion 1994). Chloride was measured by the mercuric nitrate titration method (Hach Company 1992, 1997).

Subsamples of water collected for water quality analyses from sample stations were taken for selenium analysis and inductively-coupled plasma spectroscopy (ICP) analysis of inorganic elements. Filtered and unfiltered water was collected for selenium analysis. Water was filtered through a 0.4 µm polycarbonate filter using a Geotech Filtration unit and 200 ml of filtered water samples was acidified with 2 ml of ultrapure HCl and stored frozen until analysis of dissolved selenium concentrations. Two hundred ml of unfiltered water samples was acidified with 2 ml of ultrapure HCl and stored frozen until analysis of total selenium concentrations. Samples for ICP analysis were filtered as described above and acidified with 2 ml of ultrapure HNO_3 and stored frozen.

Samples of bottom sediment (hereafter referred to as sediment) were collected between May 4, 1995, and September 9, 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, thoroughly mixed, and large pieces of debris removed (plants, twigs, rocks, etc.). Three subsamples of the homogenized sediment were collected in polyethylene bottles, and stored in a freezer until analysis. One sample was analyzed for total selenium concentrations, and a second sample was analyzed for inorganic element concentrations. A second portion of each of the samples collected in October 1995 and April 1996 was analyzed for total and inorganic carbon, 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. 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, MO, for analysis of total and inorganic carbon; organic carbon was determined by subtraction. Carbon analyses were accomplished with a Coulometrics Carbon model 5020 analyzer.

Total, volatile, and fixed solids 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 determined by drying the sediment overnight in a Fisher Isotemp oven at 105°C. Constant weights were determined by loss of less than 4% or 50 mg, whichever was less. Fixed and volatile solids were determined by ignition at 550°C for 60 minutes in a Thermolyne model FA1730 muffle furnace and then allowed to cool overnight in the furnace before weighing.

Particle size determination of sediments 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 >2.0 mm. Dried sediments were weighed, and stored at 4°C until analysis. Each sample was analyzed in duplicate. Hydrometer analyses were conducted in 1-L sedimentation cylinders or graduated cylinders using ASTM model 152H hydrometers following standard methods (ASTM 1990). Briefly, sediment subsamples were dispersed overnight in 40 g/L sodium hexametaphosphate solution. A Hamilton Beach Scovill mechanical stirrer 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 classification scheme, which is based on the Wentworth grade scale: clay <0.004 mm, silt 0.004 - 0.062 mm, and sand 0.063 mm - 2.0 mm (Guy 1969).

Between late 1996 through 1998, sediment sampling was by coring and traps. Sediment core samples were collected by pushing a 30-cm long, 7.6-cm diameter PVC (polyvinyl chloride plastic) pipe (previously cut in half lengthwise) into the sediment using an apparatus that kept the sides for splitting open as the pipe was forced into the sediments. 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 overlaying water escaped from the pipe as it was inserted in to 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 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 pipe that was capped at one end. The capped end was pushed into the sediments and left to passively collect sediment over a period of time. Sediment traps were capped prior to removal from the sediments, placed in an upright position in a cooler for transport, and stored and shipped frozen. Any frozen overlaying 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, SD, using a Perkin-Elmer model 3300 atomic absorption spectrophotometer equipped with a model MHS-10 hydride generator (AA-HG). 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 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, MO. Similar equipment and procedures were used at ETSL in analyses, except that analysis of selenium concentrations was based on U.S. Environmental Protection Agency (USEPA) method 7000 (USEPA 1983). Quality assurance/quality control measures included determination of limit of detection, 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 at the AA-HG.

For water, the mean limit of detection (LOD) was 1.0 µg/L at both analysis labs (standard error [SE] 0.1, number [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.

Recoveries of selenium from NIST reference material 1643c water, NIST reference material 1643d, and Environmental Resources Associates 9969TM reference water were within CERC recommended ranges, which indicated the digestion and analysis procedure accurately measured selenium concentrations. The mean percent recoveries of digested-spiked sample solutions was 99% (SE 1, n=37), which indicated the digestion procedure did not alter the amount of spiked selenium in the sample, i.e., suggested no loss of selenium in water samples during digestion procedure. Mean selenium recoveries 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. 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 water analyses, and the results are summarized in Table 1.

Analyses of inorganic elements in water, aquatic invertebrates, and forage fish samples were performed by ICP at the Environmental Trace Substances Research Center (University of Missouri), Rolla, MO. The list of elements and LOD are given in Table 2. For water, the procedure 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, MO. All sample preparation prior to neutron activation analyses and the neutron activation method were described in Waddell and May (1995). Samples were transported to MURR for determination of the 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

Table 1. 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 (0.04) [10]	0.16 (0.05) [8]	0.4 (0.7) [45]
% RSD[1]	9.0 (3.5) [10]	3.4 (1.3) [8]	7.6 (1.2) [4]
Reference material	0.41[2] (0.01) [8]	1.30[3] (0.03) [7]	1.20[3] (0) [2]
	1.04[4] (0.16) [2]	5.20[5] (0.06) [4]	5.20[5] (0.06) [4]
Digested spikes[6]	102 (2) [18]	98 (3) [13]	84 (2) [4]
Analysis spikes[7]	102 (3) [8]	108 (2) [5]	-

[1]RSD: Percent relative standard deviation for duplicate or triplicate preparation and analysis.
[2]National Research Council of Canada (NRCC) reference material BCSS-1 (marine sediment; 0.43 ± 0.06 [standard deviation: SD] μg/g).
[3]NRCC reference material DORM-2 (dogfish muscle tissue; 1.40 ± 0.09 [SD] μg/g).
[4]National Bureau of Standards reference material Buffalo River sediment (no certified concentration).
[5]NRCC reference material DOLT-1 (dogfish liver; 6.06 ± 0.49 [SD]μg/g).
[6]% recovery of selenium from samples spiked with selenium at the beginning of preparation for sample analysis.
[7]% recovery of selenium from digested samples spiked with selenium after sample preparation but before instrument analysis.

Table 2. 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

MURR as quality control checks on accuracy and precision. The recovery of selenium was within the NIST recommended range, and the percent relative standard deviation of multiple analyses during one analysis (n=11) was 4.2% and during another analysis (n=5) was 6.5%. Selenium values in µg 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 using computer programs from Statistical Analysis System Institute, Inc (SAS 1990). Analysis of variance testing was used for comparisons of residues in water, sediment, aquatic invertebrates, and forage fish (logarithmically transformed values) among sites. When significant differences ($P \leq 0.05$) were observed, means were compared by the Bonferroni (Dunn) multiple mean comparison test (Snedecor and Cochran 1967). In cases where 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 relations 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 between selenium concentration in sediments (assuming a non-normal distribution of selenium in sediments; Peltz and Waddell 1991, Stephens 1996, Zhang and Moore 1997) and 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, personal communication).

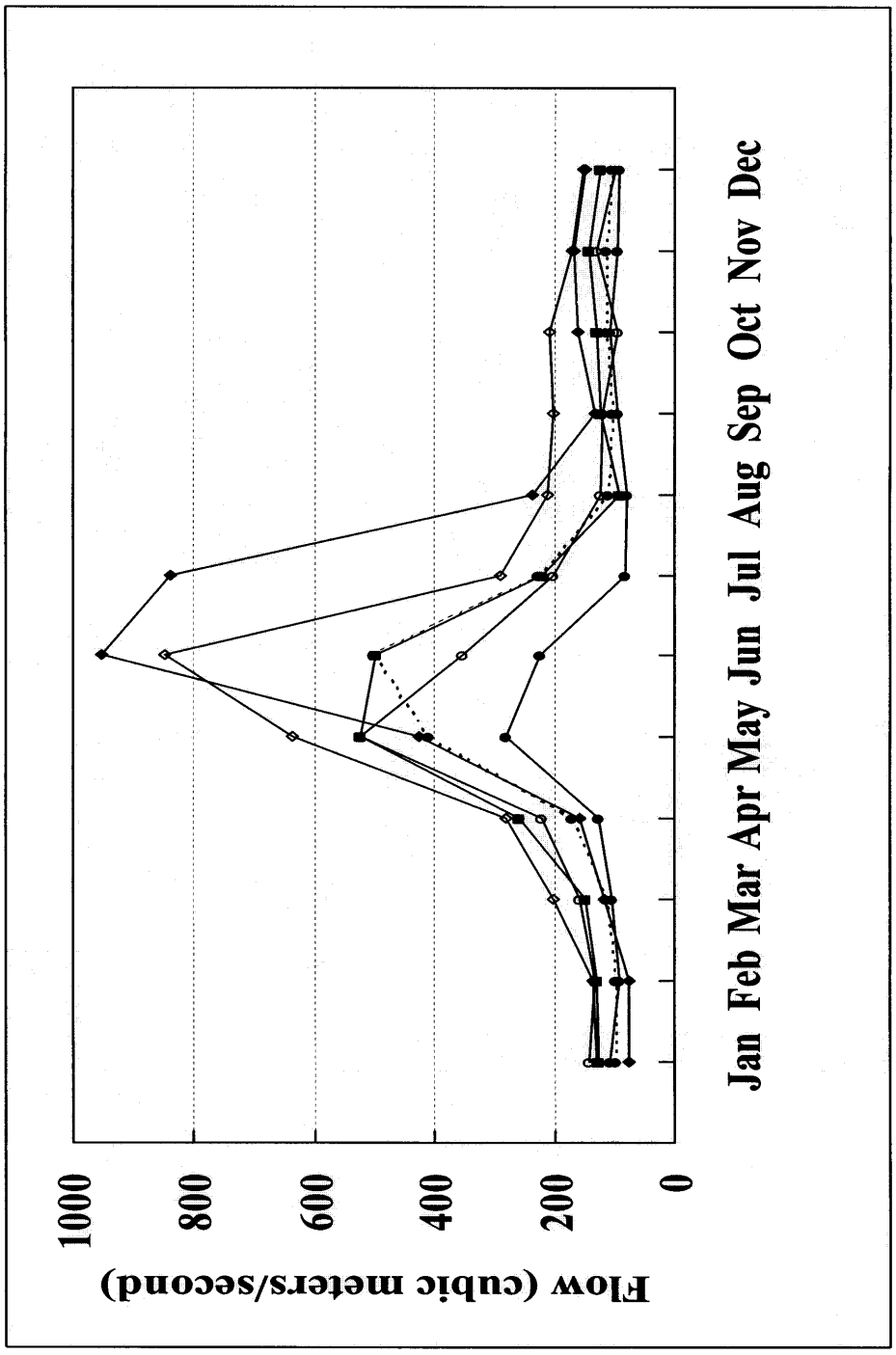
Multiple regression analyses were used to test for relations among sediment characteristics and selenium concentrations in sediment, and among selenium concentrations in water, aquatic invertebrates, and forage fish. A Wilcoxon signed-rank test was used to determine if there were significant differences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

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

RESULTS

Snowmelt runoff in the upper Colorado River basin began approximately on May 1, 1995, and peaked on June 18, 1995 (Appendix A). River runoff peaked on June 18, 1995, and on June 23, 1996. Snowmelt runoff in the Colorado River began in mid-March, 1997, increased in mid-April and increased again on May 7. Staff gage height at WW9 increased from a low of 0.21 m prior to August 3, 1996, to 2.31 m on June 3, 1997. Staff gage height reached a low of 0.37 on July 28 and August 29, 1997. In 1998 snowmelt runoff elevated the river briefly in late March and in earnest in late April and May. High flow years seemed to occur in 1995 and 1997, whereas 1996 and 1998 were average flow years (Figure 3).

Figure 3. Mean flow (cubic meter per second) in the Colorado River at the U.S. Geological Survey gauging station near the Colorado-Utah state line during 1994-1998 (● 1994, ♦ 1995, ■ 1996, ◊ 1997, ○ 1998; ● with dashed line average for 1951-1998). Data from Ugland et al. 1995, Crowfoot et al. 1996, 1997, 1998, 1999.



Water quality

Water quality characteristics varied over the years primarily by season. Station WW1 on the Colorado River tended to have high conductivities at low water flow, i.e., ~1000 µmhos/cm, and low conductivities at high water flow, i.e., ~300 µmhos/cm (Table 3, Appendix B), which is typical for western rivers (written communication, J. Yahnke, U.S. Bureau of Reclamation).

Station WW4 was located on the north side of the levee from WW1 at a site where a marsh was formed from ground water discharge. Conductivity in this area varied seasonally with low conductivities in late May to early July 1995, i.e., ~1000-4000 µmhos/cm) and high conductivities in fall through spring, i.e. ~7,000-12,000 µmhos/cm. After the water control structure was opened on December 5, 1996, conductivities at this station were slightly higher than those of the WW1, except when there was reduced water flow through the structure, which resulted in elevated conductivities in the channel. In contrast, station WW4b (started in December 1996 at the marsh outflow) had very elevated conductivities through most of 1997 similar to those at WW4 prior to the opening of the water control structure. After the control structure was opened, conductivity at the marsh station (WW4 in 1995 and 1996; WW4b in 1997 and 1998) decreased: 6,160 µmhos/cm in 1995, 8,810 µmhos/cm in 1996, 7,600 µmhos/cm in1997, and 2,620 µmhos/cm in 1998 (Figure 4). The change in conductivity was more evident in the maximum conductivities at the marsh station: 11,120 µmhos/cm in 1995, 12,780 µmhos/cm in 1996, 14,120 µmhos/cm in 1997, and 5,800 µmhos/cm in 1998.

Conductivity 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 river, but substantially lower than before the structure opening (Figure 4).

Water quality characteristics in samples measured in the mobile laboratory, such as hardness (Figure 5) and alkalinity, followed changes in conductivity measured on-site, being lowest during runoff and highest during low flow periods (Table 4, Appendix C).

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) (Table 5, Appendix D). At WW1, selenium in filtered water samples was consistently lower than in unfiltered water samples in 1995, 1996, and 1997. At WW4b, selenium in filtered water was lower than in unfiltered water in 1997. The higher selenium in unfiltered water was probably due to selenium associated with particulate matter. At stations WW4, WW5, WW6, WW7, WW8, WW8b, and WW9 there was no difference in selenium concentrations between filtered and unfiltered water samples.

There were significant differences in selenium concentrations between years at WW4, WW6, and WW8 (Table 5). Selenium concentrations in water at WW1 was consistent over the 4-year monitoring period at about 2.4 to 3.3 µg/L in unfiltered water. At WW4, selenium concentrations in water before the water control structure was operated were 48-58 µg/L, whereas after operation of the control structure selenium concentrations were 2.0-4.8 µg/L. Similar responses were observed at WW6 (9.2-15 µg/L before and 1.6-2.3 µg/L after) and WW8 (10-29 µg/L before and 1.7-3.0 µg/L after). During the period when the water control structure was operating, water with elevated selenium concentrations was entering the channel area from

Table 3. Mean (range in parentheses and number of samples in brackets) water quality measures *in-situ* 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[1]	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 (270-1,040) [31]	6,160 (380-11,120) [30]	NS	4,990 (340-11,070) [30]	4,470 (310-10,430) [30]	4,500 (280-10,290) [30]	3,860 (270-7,600) [28]	NS	2,960 (270-7,890) [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 (280-1,110) [41]	4,310 (1,160-11,610) [4]	8,810 (1,190-13,650) [41]	6,770 (820-9,830) [28]	4,950 (830-8,460) [41]	5,190 (340-8,660) [28]	5,670 (1,000-9,040) [32]	4,730 (1,010-7,340) [12]	3,680 (340-9,210) [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]

Table 3. Continued.

Year and measure	Station								
	WW1	WW4	WW4b	WW5	WW6	WW7	WW8	WW8b	WW9
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 (270-1,030) [28]	1,120 (280-2,760) [28]	7,600 (330-14,120) [28]	NS	730 (270-1,080) [28]	NS	880 (350-1,400) [21]	820 (270-1,640) [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]	2,620 (970-5,800) [8]	NS	790 (490-1,020) [8]	NS	960 (560-1,150) [7]	1,030 (500-1,810) [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

[1]NS: not sampled.

Figure 4. Conductivity (µmhos/cm) at various sampling stations at Walter Walker State Wildlife Area (● WW1, ♦ WW4, ■ WW4b, ▲ WW6, ▪ WW8).

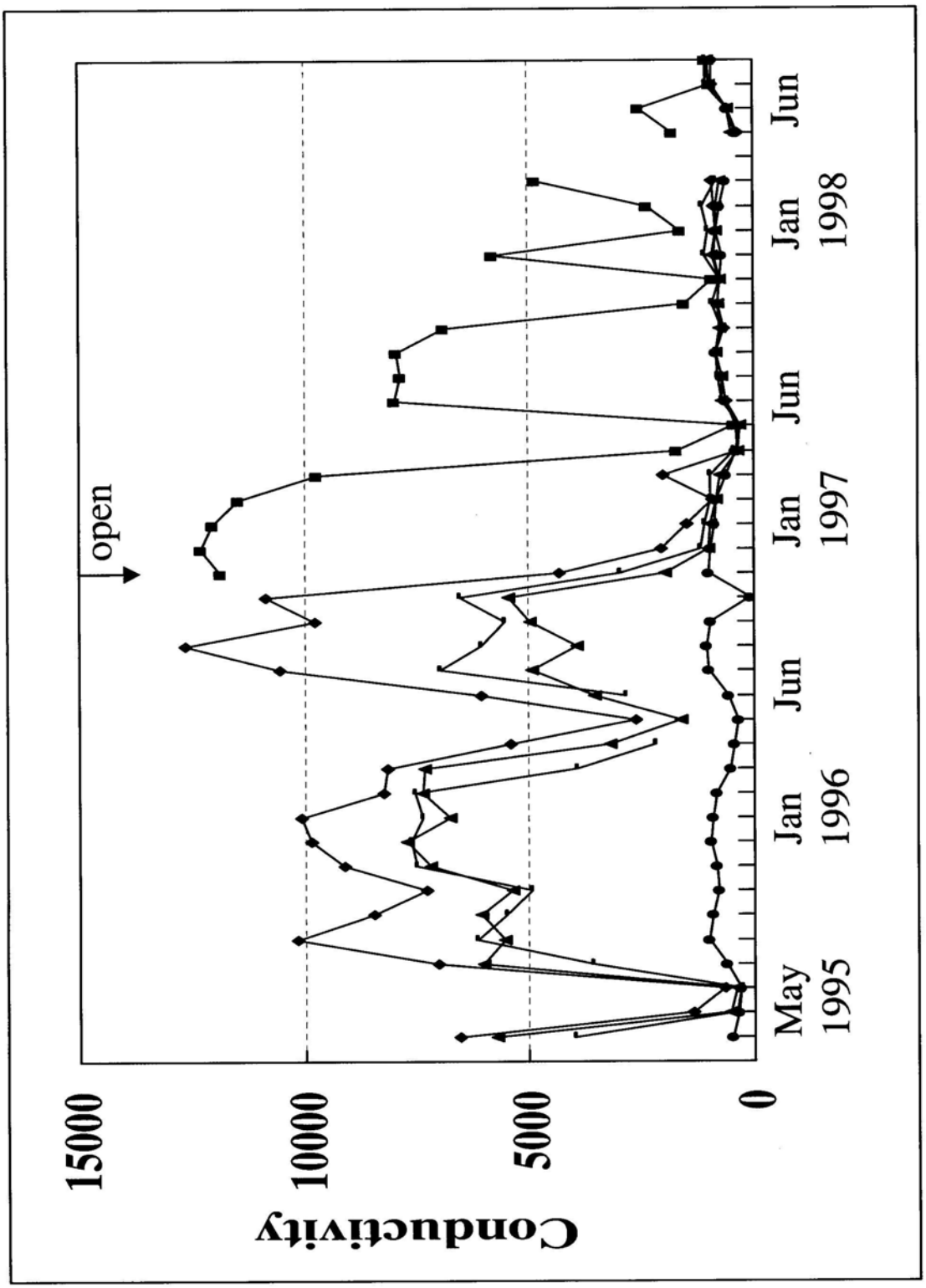


Figure 5. Hardness (mg/L as $CaCO_3$) at various sampling stations at Walter Walker State Wildlife Area (● WW1, ♦ WW4, ■ WW4b, ▲ WW6, ▪ WW8).

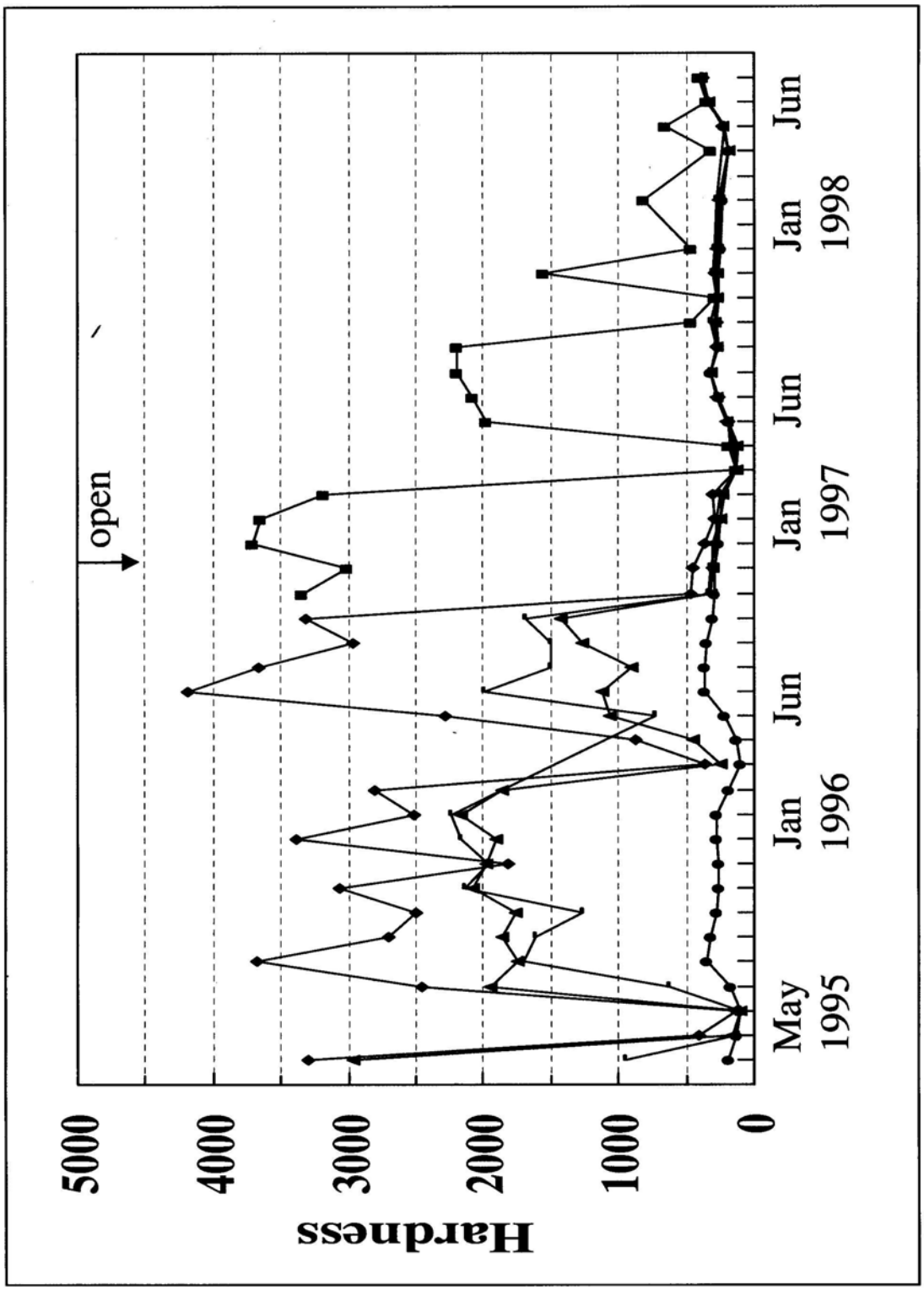


Table 4. Mean (range in parentheses and number of samples in brackets) water quality measured in the laboratory of samples from several stations in the channel at Walter Walker State Wildlife Area. Unionized ammonia was <0.01 µg/L in all samples.

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[1]	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]	7,170 (410-11,120) [8]	NS	6,030 (340-11,070) [8]	5,560 (350-10,430) [8]	5,160 (280-10,290) [8]	3,940 (270-7,570) [8]	NS	2,650 (270-5,710) [8]
Hardness (mg/L as $CaCO_3$)	226 (104-342) [8]	2,280 (130-3,680) [8]	NS	1,680 (124-3,160) [8]	1,580 (109-2,960) [8]	1,420 (106-2,900) [8]	1,060 (104-2,140) [8]	NS	780 (106-1,940) [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 (19-1,150) [8]	NS	583 (18-1,200) [8]	556 (14-1,120) [8]	501 (13-1,140) [8]	354 (13-700) [8]	NS	242 (12-630) [8]
Sulfate (mg/L)	153 (49-264) [8]	3,620 (68-5,900) [8]	NS	2,510 (64-5,880) [8]	2,680 (51-5,280) [8]	2,490 (51-5,240) [8]	1,600 (52-3,700) [8]	NS	1,190 (52-3,450) [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]

Table 4. Continued.

Year and measure	Station								
	WW1	WW4	WW4b	WW5	WW6	WW7	WW8	WW8b	WW9
1995									
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 (7.8-8.3) [12]	7.7 (7.4-8.1) [12]	7.5 - [1]	7.9 (7.6-8.2) [8]	7.9 (7.7-8.2) [12]	7.8 (7.4-8.2) [8]	8.1 (7.7-8.8) [9]	8.0 (7.8-8.4) [4]	8.0 (7.8-8.3) [8]
Conductivity (µmhos/cm)	800 (280-1,090) [12]	7,930 (1,190-12,780) [12]	11,630 - [1]	6,380 (820-9,450) [8]	4,540 (830-8,460) [12]	4,750 (340-7,390) [8]	5,940 (1,230-8,330) [9]	4,790 (1,060-6,190) [4]	3,330 (340-9,210) [8]
Hardness (mg/L as $CaCO_3$)	259 (98-370) [12]	2,390 (368-4,180) [12]	3,350 - [1]	1,760 (250-2,660) [8]	1,220 (240-2,160) [12]	1,370 (120-2,440) [8]	1,570 (336-2,240) [9]	1,260 (326-1,700) [4]	1,050 (120-2,520) [8]
Calcium (mg/L)	70 (32-101) [12]	295 (72-508) [12]	416 - [1]	222 (54-336) [8]	158 (37-264) [12]	175 (34-312) [8]	189 (84-264) [9]	154 (82-206) [4]	141 (35-276) [8]
Magnesium (mg/L)	20 (4-29) [12]	401 (46-707) [12]	562 - [1]	293 (28-442) [8]	202 (27-377) [12]	227 (9-404) [8]	266 (31-384) [9]	213 (29-288) [4]	169 (8-445) [8]

Table 4. Continued.

Year and measure	Station								
	WW1	WW4	WW4b	WW5	WW6	WW7	WW8	WW8b	WW9
1996									
Alkalinity (mg/L as $CaCO_3$)	129 (81-157) [12]	404 (147-637) [12]	580 - [1]	310 (115-431) [8]	264 (112-372) [12]	286 (84-445) [8]	264 (154-347) [9]	233 (151-296) [4]	189 (84-339) [8]
Chloride (mg/L)	75 (16-106) [12]	792 (91-1,420) [12]	1,020 - [1]	586 (58-850) [8]	417 (54-710) [12]	450 (18-760) [8]	530 (117-720) [9]	451 (115-578) [4]	326 (18-858) [8]
Sulfate (mg/L)	184 (42-294) [12]	3,810 (439-6,890) [12]	5,500 - [1]	2,750 (272-4,000) [8]	1,960 (229-3,570) [12]	2,260 (65-4,080) [8]	2,760 (274-4,120) [9]	2,180 (258-2,840) [4]	1,650 (63-4,430) [8]
Nitrate (mg/L-N)	0.5 (0.2-0.7) [11]	10.9 (0.1-38) [11]	13.9 - [1]	6.1 (<0.1-15) [8]	1.2 (<0.1-4.3) [11]	2.3 (0.1-9.2) [7]	1.8 (0.1-5.9) [9]	0.4 (0.1-0.6) [4]	0.8 (<0.1-2.8) [7]
Nitrite (mg/L-N)	0.01 (<0.01-0.02) [12]	0.15 (0.02-0.38) [12]	0.16 - [1]	0.12 (<0.01-0.25) [8]	0.05 (<0.01-0.16) [12]	0.14 (<0.01-0.46) [8]	0.09 (<0.01-0.20) [9]	0.03 (0.01-0.05) [4]	0.06 (<0.01-0.16) [8]
Total suspended solids (mg/L)	72 (9-283) [11]	26 (12-47) [11]	10 - [1]	71 (33-149) [7]	50 (7-108) [11]	82 (32-144) [7]	42 (8-82) [9]	52 (19-120) [4]	81 (11-162) [7]
Volatile solids (mg/L)	17 (1-129) [11]	6.5 (2.8-13) [11]	1.5 - [1]	14 (5.6-40) [7]	9.5 (0.9-21) [11]	15 (6-31) [7]	10 (1.3-33) [9]	8 (2.0-16) [4]	14 (1.9-33) [7]
Fixed solids (mg/L)	55 (1-256) [11]	20 (9.2-40) [11]	9 - [1]	57 (22-109) [7]	41 (6-96) [11]	67 (17-125) [7]	32 (6.7-64) [9]	44 (17-103) [4]	67 (9.6-129) [7]
1997									
pH	8.2 (7.7-8.5) [12]	8.1 (7.7-8.4) [12]	8.0 (7.6-8.7) [12]	NS	8.1 (7.8-8.4) [12]	NS	8.1 (7.6-8.4) [11]	8.1 (7.8-8.3) [12]	NS

Table 4. Continued.

Year and measure	Station								
	WW1	WW4	WW4b	WW5	WW6	WW7	WW8	WW8b	WW9
1997									
Conductivity (µmhos/cm)	680 (310-920) [12]	920 (300-2,040) [12]	6,460 (390-11,240) [12]	NS	700 (320-930) [12]	NS	780 (350-1,120) [11]	768 (330-1,120) [12]	NS
Hardness (mg/L as $CaCO_3$)	236 (116-322) [12]	278 (130-446) [12]	1,920 (130-3,710) [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 (18-1,120) [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]	3,230 (70-6,450) [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

Table 4. Continued.

Year and measure	Station								
	WW1	WW4	WW4b	WW5	WW6	WW7	WW8	WW8b	WW9
1997									
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]	2,620 (970-5,800) [8]	NS	790 (490-1,020) [8]	NS	960 (560-1,150) [7]	1,030 (500-1,810) [8]	NS
Hardness (mg/L as $CaCO_3$)	266 (192-376) [7]	275 (196-378) [7]	649 (322-1,550) [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

Table 4. Continued.

Year and measure	Station								
	WW1	WW4	WW4b	WW5	WW6	WW7	WW8	WW8b	WW9
1998									
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 (278-2,200) [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

[1]NS: not sampled.

Table 5. 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. Upper case letters within a column indicate significant differences between years ($P \leq 0.05$). Lower case letters within a row indicate significant differences between locations ($P \leq 0.05$).

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

[1]NS: not sampled.

WW4b between December 1996 and September 1998 (84 µg/L in December 1996, 43 µg/L in 1997, and 11 µg/L in 1998).

There were significant differences in selenium concentrations between stations (Table 5). 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 due in part to high selenium concentrations at WW8. However, after the water control structure was operational in 1997 and 1998, selenium concentrations at sampling stations within the channel were not different from each other, except WW4b where elevated selenium concentrations were draining from the marsh area. Overall, selenium concentrations in filtered water decreased in the channel area after the control structure was operational (Figure 6). Combining all stations within the channel, except for WW1 and WW4b, selenium concentrations in filtered water samples were 21.0 µg/L in 1995 (range <1-126 µg/L, n=47), 23.5 µg/L in 1996 (range <1-135 µg/L, n=35), 2.1 µg/L in 1997 (range <1-6 µg/L, n=47), and 2.1 µg/L in 1998 (range <1-6.3 µg/L, n=31).

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

For inorganic elements in water measured by ICP, boron, chromium, iron, magnesium, manganese, molybdenum, strontium, and vanadium were elevated at WW4b during the same periods when selenium concentrations were elevated (Appendix E). Selenium concentrations measured by 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 (r): 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 correlations with other inorganic elements and water quality characteristics suggest that selenium concentrations increased with increasing hardness and conductivity of water associated with irrigation-influenced ground water discharge.

Selenium in sediment

Selenium concentrations in various portions of sediment from the channel area were significantly different from each other (Table 6, Appendix F). Selenium concentrations in sediment cores collected from WW4 on August 23 and November 19, 1996, were elevated in the top (18-19.6 µg/g) and middle (11.3-16.3 µg/g) portions, whereas cores collected on April 6 and September 9, 1998 had 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 selenium was elevated in the top and middle portions of cores at WW8 and WW9 before operation of the water control structure.

Figure 6. Selenium concentrations (µg/L) in filtered water at various sampling stations at Walter Walker State Wildlife Area (● WW1, ♦ WW4, ■ WW4b, ▲ WW6, ▪ WW8).

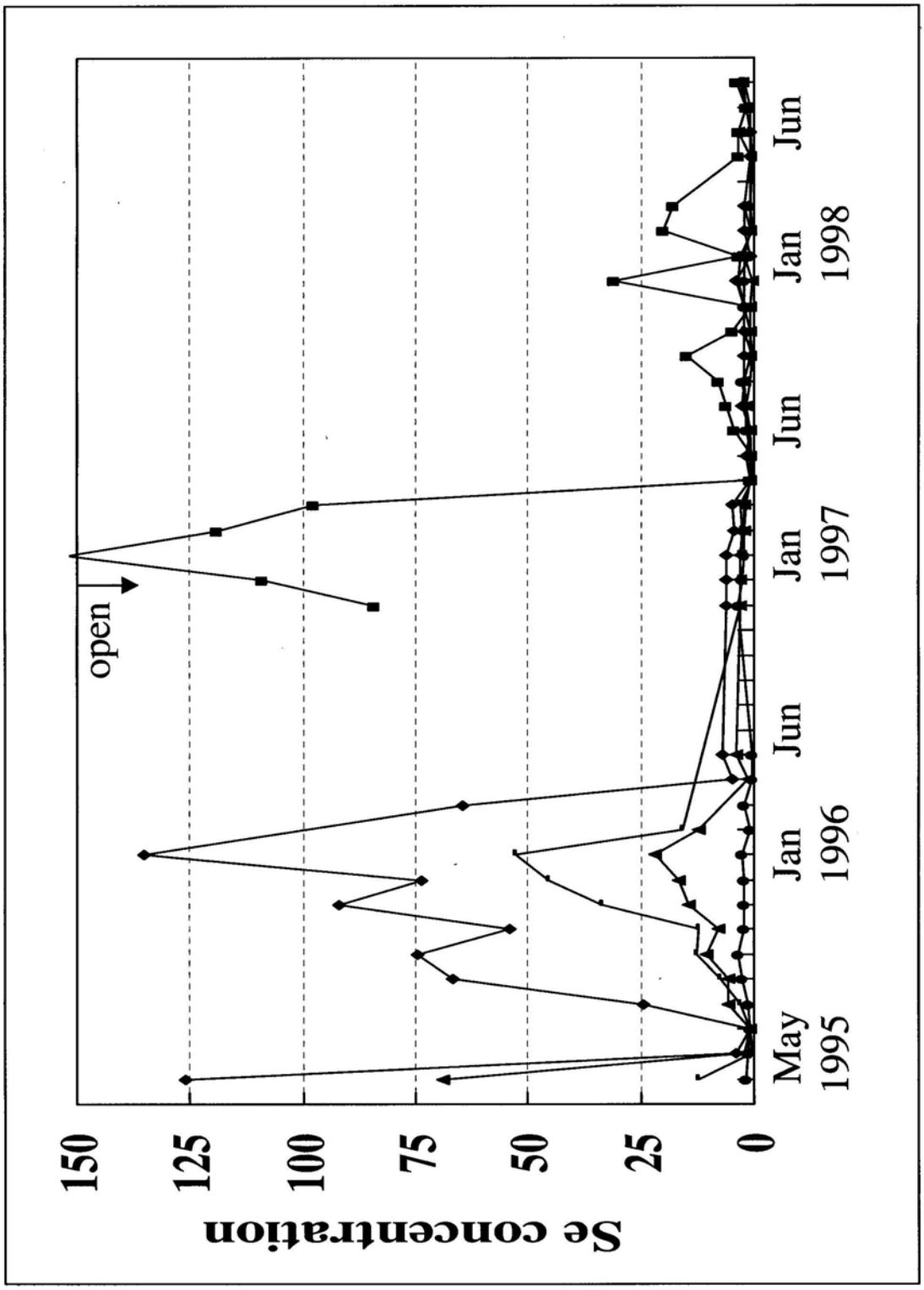


Table 6. Selenium concentrations (µg/g dry weight) in sediment collected from various stations in the channel at Walter Walker State Wildlife Area.

Station	Date	Day of study	Sediment type	Sediment section	Selenium (µg/g)
WW1	04/25/96	358	Mixed[1]		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	560	Trap	Top	3.4
	to	to		Middle	3.8
	03/12/97	679		Bottom	17.2
WW4a	04/06/98	1,062	Core	Top	0.4
				Middle	0.5
				Bottom	0.3
	09/09/98	1,218	Core	Top	0.6
				Middle	0.3
				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	568	Trap	Top	NS[2]
	to	To		Middle	NS
	03/12/97	679		Bottom	4.4
	04/06/98	1,062	Core	Top	1.9
				Middle	3.9
				Bottom	18.0
	09/09/98	1,218	Core	Top	0.5
				Middle	0.6
				Bottom	0.4

Table 6. Continued.

Station	Date	Day of study	Sediment type	Sediment section	Selenium (µg/g)
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
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	559	Trap	Top	5.9
	to	to		Middle	NS
	03/12/97	679		Bottom	5.5
	04/06/98	1,062	Core	Top	1.8
				Middle	0.6
				Bottom	3.4
	09/09/98	1,218	Core	Top	1.1
	09/09/98	1,218	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	559	Trap	Top	5.3
	to	to		Middle	5.8
	03/12/97	679		Bottom	5.8
	04/06/98	1,062	Core	Top	1.4
				Middle	0.5
				Bottom	4.4
	09/09/98	1,218	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

[1]Mixed: The sediment was thoroughly mixed before subsampling for chemical analysis.
[2]NS: Not sampled.

At WW4, a sediment trap deployed between November 13, 1996 and March 12, 1997, had 17.2 µg/g at the bottom (before control structure was opened) and 3.4 µg/g in the top (after the water structure had been opened 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 sediment cores 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 control structure operation (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 sediments after the control structure was operated buried high selenium sediments at WW6, WW8, and WW8b (Table 6). Sediment cores collected at these stations on April 6 and September 9, 1998, generally had low selenium concentrations in the top of the cores and elevated selenium concentrations in the bottom portion.

Most sediment cores tended to have the highest percent volatile solids, total carbon, inorganic carbon, and organic carbon in the upper portion of cores (Appendix F). Selenium concentrations in sediments were positively correlated (r) with volatile solids (0.45, P=0.01, n=31), total carbon (0.61, P=0.0002, n=31), inorganic carbon (0.50, P=0.004, n=31), and organic carbon (0.55, P=0.001, n=31), and negatively correlated with total solids (-0.42, P=0.02, n=31) and fixed solids (-0.45, P=0.01, n=31). There were no significant correlations between selenium concentrations in sediment and sediment particle size. However, selenium concentrations in sediment were correlated with selenium in filtered water samples (r=0.69, P=0.0001, n=29) and unfiltered samples (r=0.68, P=0.004, n=16).

Overall, selenium concentrations in sediments decreased substantially after the water control structure was operated (Figure 7). Combining all sediment selenium concentrations for the upper most portion of the various sediment types (core or trap) and stations within a year, selenium concentrations decreased from 8.5 µg/g (range 2.4-20.8, n=12) in 1995, to 8.2 µg/g (range 0.4-19.6, n=17) in 1996 to 4.8 µg/g (range 3.4-5.9, n=4) in 1997 to 1.1 µg/g (range 0.4-1.9, 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 (ANOVA, F=12.04, P<0.0001).

Selenium and other elements in aquatic invertebrates

Selenium concentrations in aquatic invertebrate samples from channel stations decreased after the water control structure was operated (Table 7, Figure 8, Appendix G). In 1996 before the control structure was operated, 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 7). Although invertebrates were collected at WW8b and WW9 for only 2 years, a decrease in selenium concentrations were also apparent. The only station where selenium concentrations did not decrease was at WW7.

Overall, combining all invertebrates and all stations the selenium concentrations 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 the

Figure 7. Selenium concentrations (µg/g) in sediment at various sampling stations at Walter Walker State Wildlife Area (● WW1, ♦ WW4, ▲ WW6, ■ WW8).

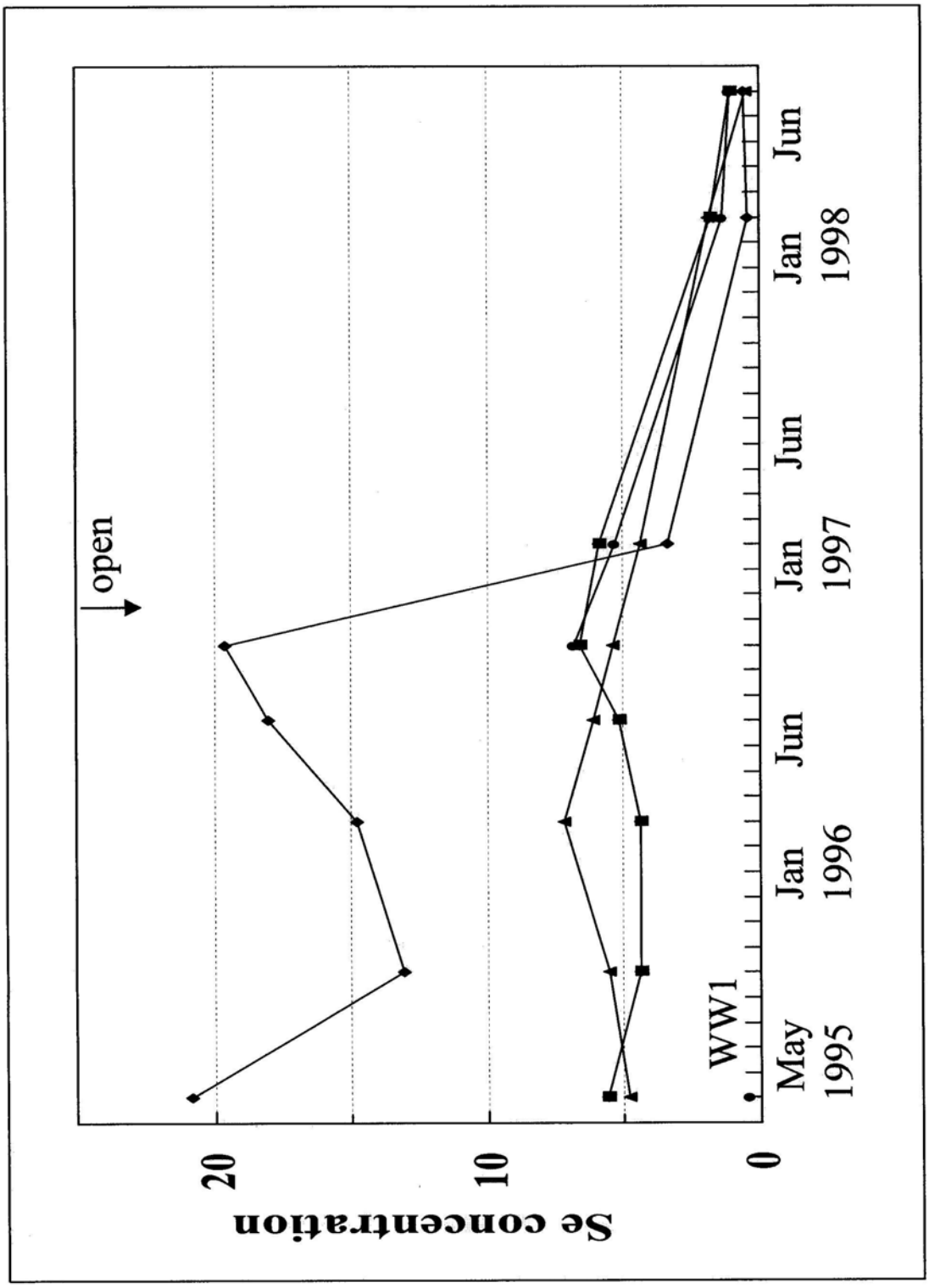
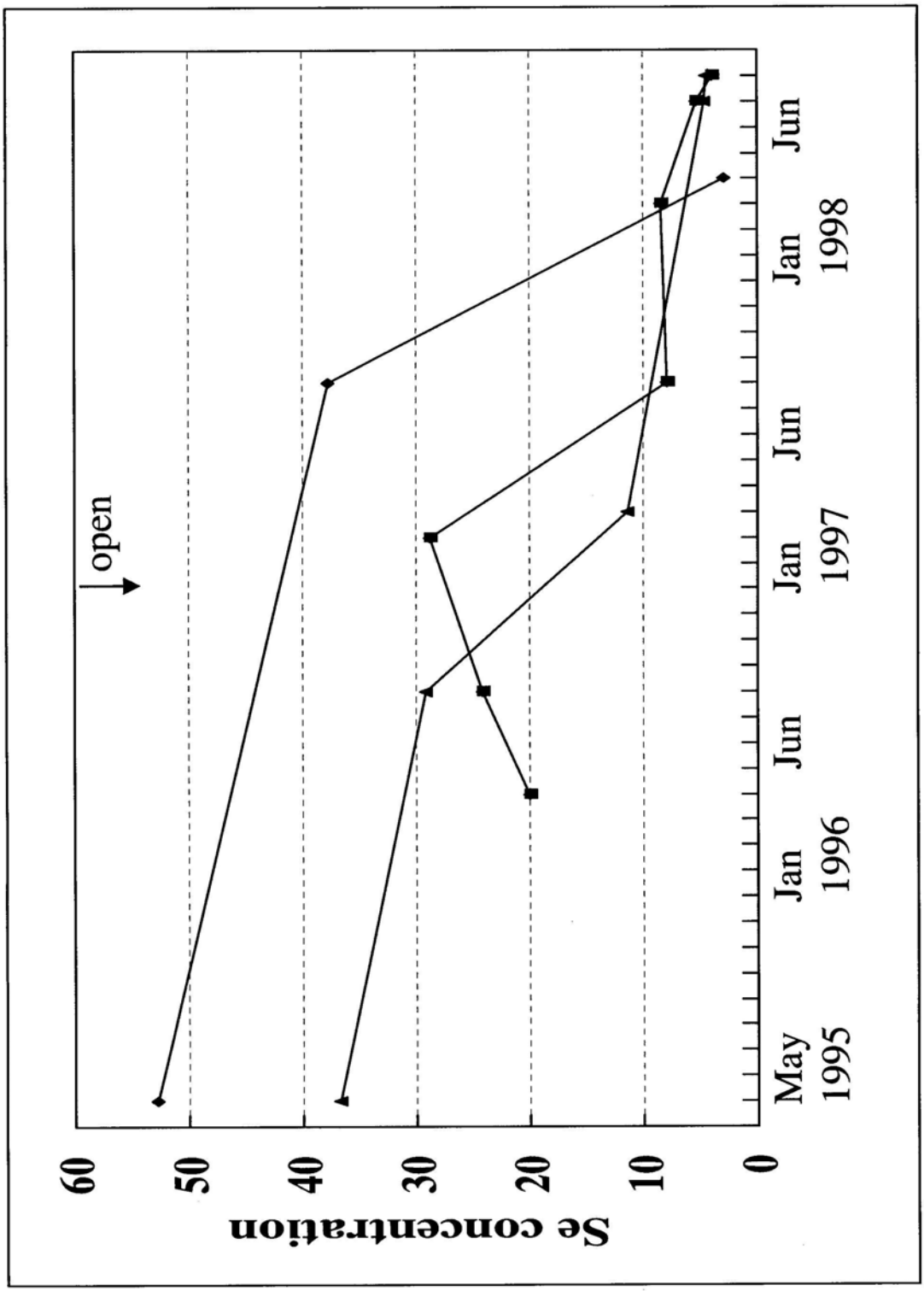


Table 7. Mean (range in parentheses and number of samples in brackets) selenium concentrations (µg/g dry weight) in aquatic invertebrates collected from various stations in the channel at Walker Walter State Wildlife Area.

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

[1]NS: no sample.

Figure 8. Selenium concentrations (µg/g) in aquatic invertebrates at various sampling stations at Walter Walker State Wildlife Area (♦ WW4, ▲ WW6, ■ WW8).



selenium concentrations in 1997 and 1998, but 1997 was not significantly higher than the selenium concentration in 1998.

In contrast to previous studies, chironomids accumulated similar amounts of selenium as zooplankton (Appendix G). The correlation between selenium concentrations in aquatic invertebrates and selenium in filtered water was r=0.83 (P=0.0001, n=18) and for selenium 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).

Inorganic elements in aquatic invertebrates collected after operation of the water control structure seemed consistent among stations (Appendix H). 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 water control structure operation, and decreased after operation (Table 8, Figure 9, Appendix I). 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 mosquitofish (*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.

Interesting occurrences in the forage fish collection included a fathead minnow containing 40 µg/g of selenium that was regurgitated from a Colorado pikeminnow collected at WW8 on May 21, 1996. A composition sample of five male red shiner collected at WW6 on July 30, 1998 contained 8.9 µg/g of selenium, whereas a composition of five gravid females contained 12 µg/g selenium. Thirteen sets of fathead minnows were collected as 2 to 3 individual or composite samples over the 3-year period, and 12 sets of samples had consistent selenium concentrations (coefficient of variation 0-25 in 12 sets and 48 in 13th set), which demonstrated little variability in selenium concentrations (Appendix I).

Selenium concentrations in forage fish were highest in 1996 and 1997 at WW4 where elevated selenium in water entered the channel area from the marsh (Table 8, Figure 9). Selenium in forage fish tended to decrease to the lowest concentrations at WW9, except for one sample collected in the WW6 area in 1996 (Table 8). Within a station, selenium tended to decrease between 1996 and 1998, except for one sample at WW6 in 1996. Overall, combining all forage fish and stations by year, 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 those in 1997, but both were significantly higher than concentration in forage fish in 1998 (ANOVA, F=9.11, P<0.0014).

Selenium concentrations in forage fish were positively correlated with selenium in filtered water samples (r=0.58, P=0.02, n=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 aquatic invertebrates (r=0.46, P=0.10, n=14).

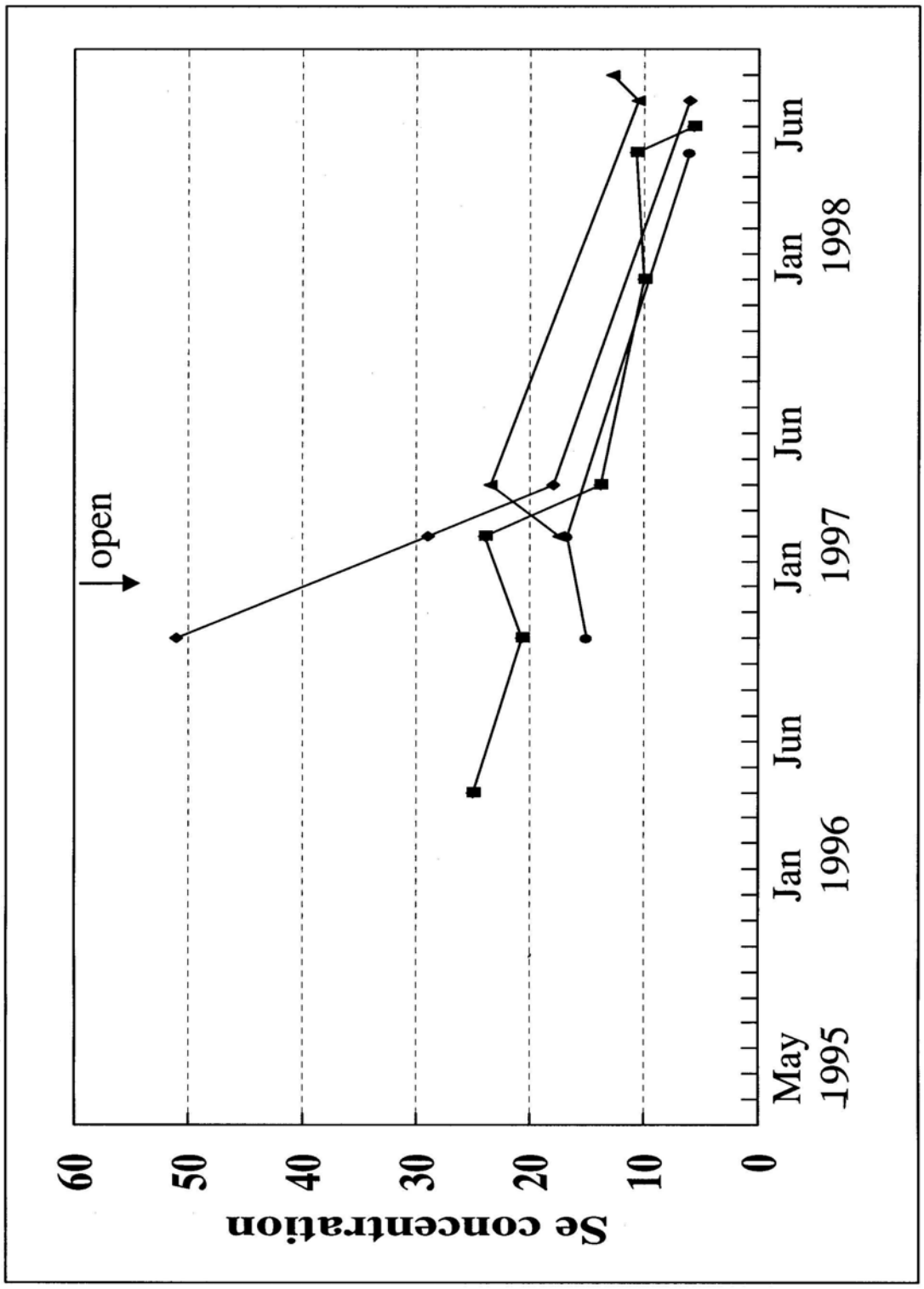
Most inorganic elements in forage fish decreased between 1996 and 1998 (Appendix J). Combining all stations within a year, four elements had greater than two-fold decreases between 1996 and 1998 including aluminum (5.8 times lower), iron (3.7 times lower), manganese (2.0

Table 8. 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 (29-66) [4]	NS[1]	31.5 (30-33) [4]	4.8 - [1]	25.3 (17-32) [3]	22.9 (11-40) [8]	15.0 (13-19) [3]	14.0 - [1]
1997	22.9 (10-35) [7]	NS	NS	21.5 (16-29) [6]	NS	18.1 (5.1-39) [7]	16.7 (10-21) [3]	NS
1998	NS	6.1 - [1]	NS	11.6 (5.6-20) [4]	6.2 (5.9-6.6) [2]	9.8 (5.7-19) [8]	6.1 (5.1-8.0) [3]	6.4 (2.8-13) [3]

[1]NS: no sample.

Figure 9. Selenium concentrations (µg/g) in forage fish at various sampling stations at Walter Walker State Wildlife Area (♦ WW4, ▲ WW6, ■ WW8, ● WW8b).



times lower), and vanadium (2.3 times lower), whereas little change (less than two-fold differences) was noted for arsenic, barium, beryllium, boron, cadmium, chromium, copper, magnesium, molybdenum, nickel, strontium, and zinc. Lead was the only inorganic element that had a 2-fold increase between 1996 and 1998 in forage fish. In contrast, selenium measured by AA-HG in forage fish had a four-fold reduction between 1996 and 1998.

Combining all stations within a year, zinc, but not any of the other 16 elements, was significantly and negatively correlated with selenium concentrations in forage fish (r= -0.41, *P*=0.04, n=26). The low correlation value was due in part to the small, less than two-fold, 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=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 9, Appendix K). There were no significant differences in selenium concentrations in muscle plugs collected between 1995 and 1998. However, selenium concentrations in muscle plugs collected in 1995, 1996, and 1997, but not 1998, were significantly less than those in muscle plugs of Colorado pikeminnow collected from WWSWA in 1994 prior to the current study, which contained 16.1 µg/g (n=17, Osmundson et al. 2000).

Several Colorado pikeminnow were captured repeatedly during the 1994-1998 period (Table 10). Selenium in muscle plugs of fish captured in 1994 were significantly different than those in 1995, 1996, and 1997, but the later 3 years were not different from each other. As with other measures above, 1994 seemed to be an unusual year with low flows in the river and elevated selenium residues in muscle plugs of Colorado pikeminnow.

Selenium concentrations in muscle plug 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) using the yearly mean values for the period 1995-1998.

Selenium concentrations in muscle plugs of Colorado pikeminnow for the 1994-1998 period 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). Correlations between muscle plug selenium and the average river flow during the May-July period were r= -0.74 (*P*=0.16), the April-July period were r= -0.79 (*P*=0.11), and the March-July period were r= -0.85 (*P*=0.07).

Selenium concentrations in muscle plugs seemed to decrease with increasing fish weight (Figure 10) and fish total length (Figure 11). Combining data for 1994-1998, 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 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, as characterized by conductivity, in the

Table 9. 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 of the upper Colorado River near Grand Junction, CO.

	Year				
Segment	1994[1]	1995[1]	1996[1]	1997	1998
RM <158	5.3 (4.4-6.2) [2]	NS[2]	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

[1]Data from Osmundson et al. (2000).
[2]NS: no sample.

Table 10. 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[1]	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[2]	6/14	980	17.8	7/10	1150	15.0	5/13	1225	17.2	5/7	1200	18.0			
1F4041312F[3]	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			

Table 10. Continued.

PIT tag number	1994			1995			1996			1997			1998		
	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)
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

[1]Fish captured at rm 130.1 in 1994.
[2]Fish captured at rm 169.5 in 1994.
[3]Fish captured at rm 163.9 in 1994.

Figure 10. 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).

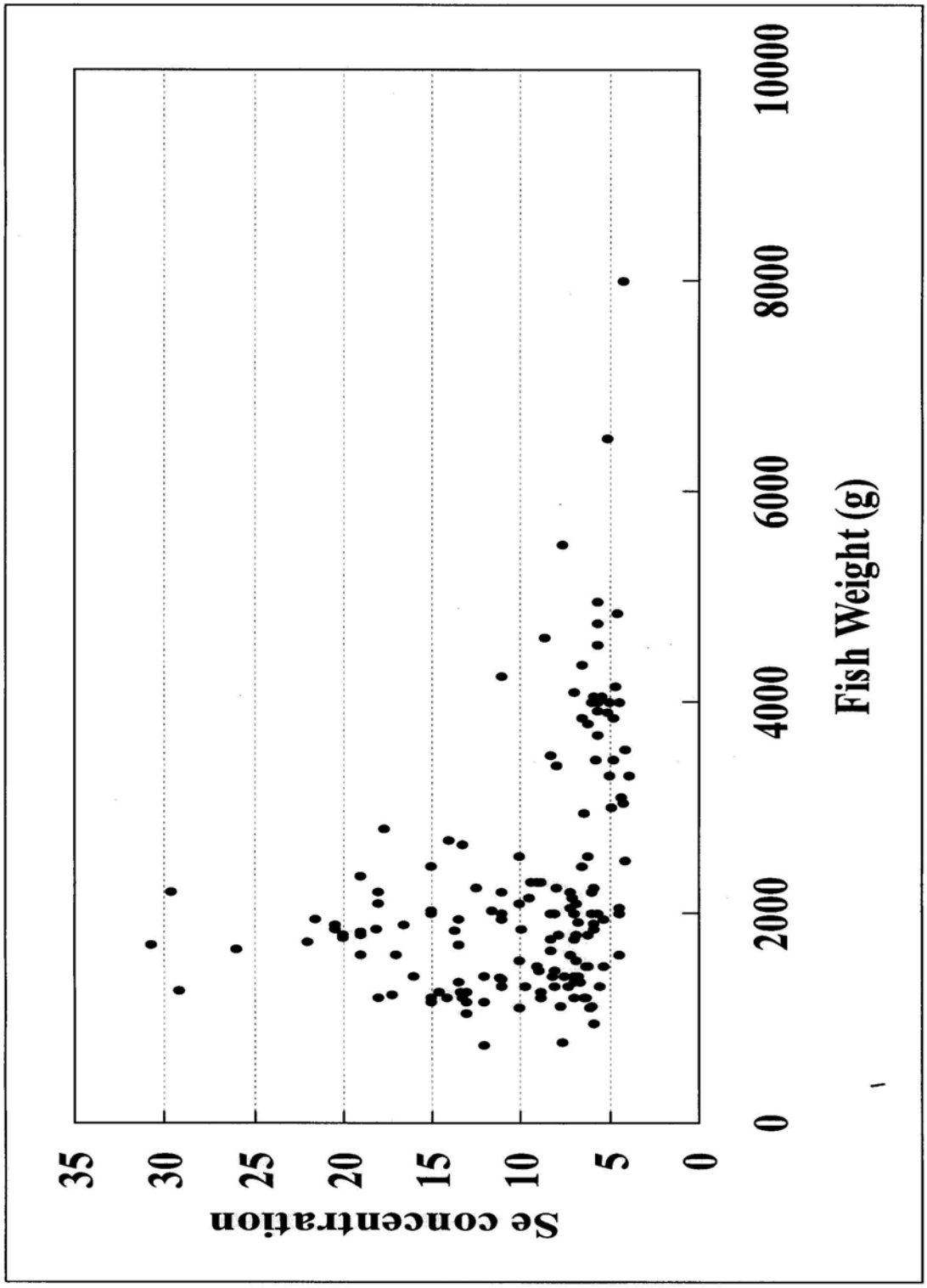
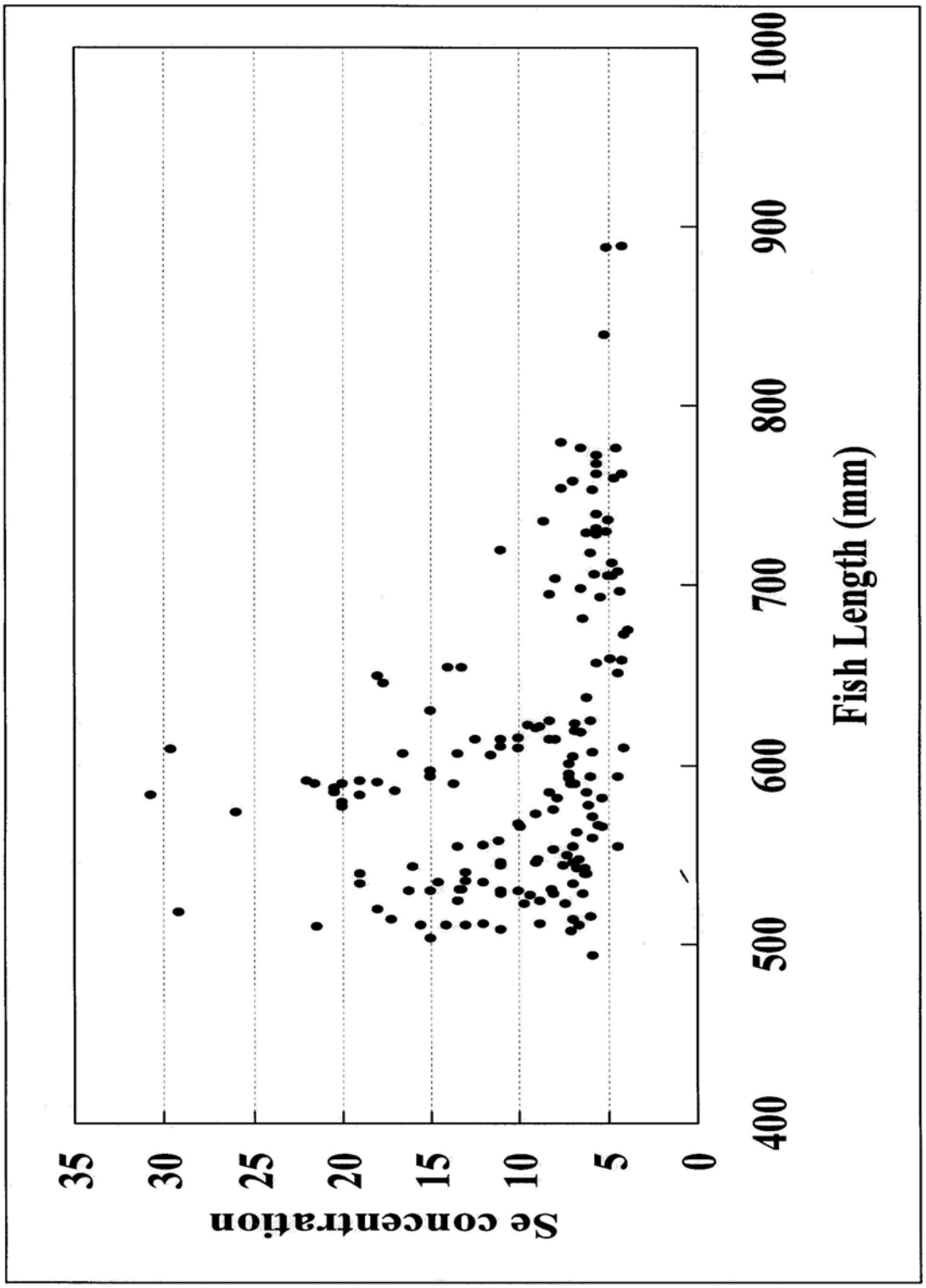


Figure 11. Selenium concentrations (µg/g) in muscle plugs versus fish total length (mm) of Colorado pikeminnow collected during 1994-1998 at Walter Walker State Wildlife Area (n=163).



channel area were dominated by ground water 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 due to inflow of ground water from the underlying cobble aquifer (Phillips 1986). Water in the cobble aquifer sampled as part of the NIWQP in 1992 at a location about 5.5 km north of WWSWA had conductivities of 4,370 to 5,720 µmhos/cm, as well as elevated alkalinity (430-490 mg/L as $CaCO_3$), calcium (480-540 mg/L), sulfate (2,500-3,400 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 ground water influence (e.g., reduced conductivity) between January 1997 and June 1998 due to river influences from the operation of the water control structure, water quality characteristics were still elevated in ground water 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, alkalinity (380-1,090 mg/L as $CaCO_3$), calcium (370-540 mg/L), sulfate (5,000-7,600 mg/L), and chloride (900-3,300 mg/L) (Butler and Osmundson 2000).

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 a discharge area for high selenium ground water (Butler and Osmundson 2000). Water quality characteristics were elevated in the marsh area, i.e., conductivity 3,590-3,930 µmhos/cm, sulfate 1,600 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 demonstrate that the channel area was receiving ground water with elevated cation and anions probably derived from up-gradient irrigated areas.

Based on the above discussion, if ground water were to become the dominant water recharge mechanism of the WWSWA backwater, the water quality characteristics along with 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) and with investigations of flowing water systems at Kesterson Reservoir, CA (Fujii 1988, Moore et al. 1990). Saiki et al. (1993) also reported no difference in selenium concentrations between filtered and unfiltered water samples collected from seven riverine sites associated with irrigation drainage in the San Joaquin Valley, CA.

The difference in selenium concentrations between filtered and unfiltered water samples at WW1 in 1995-1997 and WW4a in 1997 was probably due to selenium 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, compared to dissolved selenium, to the sorption of selenium onto suspended solids and selenium contained in plankton.

The selenium concentrations in water in the channel area were reduced substantially by

operation of the water control structure. For example, selenium in water at WW6 declined from 15 µg/L in 1995 to 9.8 µg/L in 1996 to 1.6-1.8 µg/L in 1997-1998. River water passing through the control structure generally had low selenium concentrations, which ranged from <1 to 3 µg/L between December 11, 1996 and April 2, 1998 (Butler and Osmundson 2000). Only two samples had elevated selenium concentrations: 8 µg/L on August 6, 1997 and 5 µg/L on September 17, 1997 (Butler and Osmundson 2000).

Elevated selenium in water was entering the channel area at WW4 before and at WW4b after operation of the control structure: 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). Ground water in one well up-gradient of the marsh contained 120-200 µg/L selenium in 1997-1998, whereas a second, close well contained 4-7 µg/L, which illustrated the variability of ground water sources in the cobble aquifer.

Elevated selenium in water from stations WW7, WW8, and WW8b compared to upstream station WW6 was observed in the present study, which suggested ground water input of selenium downstream of WW6. Butler and Osmundson (2000) demonstrated this ground water input in sampling conducted in 1997-1998: selenium in ground water from a well near our station WW6 was <1-4 µg/L, whereas selenium in ground water 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 influenced by irrigation activities. Selenium concentrations were 4-7 µg/L (median 5 µg/L, n=11) in the Colorado River at the CO-UT 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).

Some people have suggested that native fish in the Colorado River basin may have evolved in a selenium-rich aquatic environment because of the presence of high selenium soils derived from Mancos Shale (e.g., A. Archuleta, USFWS, written communication). The issue of background waterborne selenium concentrations in streams and water bodies in Mancos Shale areas in the Grand and Uncompahgre valleys with no irrigation activity has been investigated. David Butler of the U.S. Geological Survey searched the area extensively and located seven areas for sampling (Butler and Osmundson 2000). At Wells Gulch adjacent to Fools Hill at Highway 50 west of Delta in the Gunnison River basin in an area with some grazing activity, selenium concentrations in water were <1 µg/L [additional sampling at Wells Gulch found median selenium concentrations of 2.6 µg/L, range <1-10 µg/L, n=8 (Butler and Leib 2002)]. At Cheney Reservoir in the Uncompahgre River basin in an area with no grazing or irrigation, selenium concentrations were <1-1 µg/L in water, 2-2.4 µg/g in sediments composed almost exclusively from Mancos Shale, and 4.2 µg/g in aquatic invertebrates. At Little Salt Wash above Government Highline Canal in the Grand Valley in an area with no irrigation and minimal grazing activity, selenium concentrations in water during runoff events on February 20, 1996,

(1.5 cfs) were 3 µg/L and on March 24, 1997, (0.99 cfs) were 1 µg/L. At Big Salt Wash above Government Highline Canal in the Grand Valley in an area with no irrigation activity, four selenium measurements in water ranged from 2 to 3 µg/L, but perennial flows were low, ranging from 0.08 to 0.14 cfs. At East Salt Creek downstream from Camp Gulch in the Grand Valley in an area with little irrigation activity, selenium concentrations in water were <1 µg/L during runoff events on December 4, 1995 (2.2 cfs) and February 16, 1996 (5.4 cfs). At West Salt Creek downstream below Prairie Canyon in the Grand Valley in an area with no irrigation and some grazing, selenium concentrations in water were <1 µg/L during runoff events on December 4, 1995 (0.99 cfs) and March 13, 1997 (5.3 cfs). In only one area with low flows (0.16-0.24 cfs) at West Salt Creek near S Road in the Grand Valley, selenium concentrations in water were elevated (9-10 µg/L) due to the presence of salt crusts. Because selenium concentrations in water draining high selenium soils were relatively low, i.e., ~1 µg/L, the hypothesis of aquatic environments with naturally elevated selenium, i.e., selenium enriched, enhancing the possibility of selenium adaptation by native fish seems unlikely. These waterborne selenium concentrations were lower than those in streams and rivers below areas influenced by irrigation activities and close to the national background concentrations of 1 µg/L.

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 measured by AA-HG were significantly correlated with 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 relation ($r^2 = 0.80$) between 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, i.e., elevated elements in soil will generally leach out in proportion to their concentration in soil depending on adsorption coefficients. Reviews of the relation between geologic sources of selenium and their movement and potential consequences have been described in 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 in the present study (alkalinity, calcium, chloride, conductivity, hardness, magnesium, nitrate, nitrite, and sulfate; range r=0.57-0.90, all *P*=0.0001) were similar to those in 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 between 1995 to early 1996 and mid 1996 to 1998 is an important consideration in the interpretation of selenium concentrations in

sediments. 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 portion of cored samples are readily available to biota such as benthic invertebrates and bottom dwelling fish, and thus are more easily incorporated in the food web than is selenium disposed in deeper sediments.

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 sediments were buried by deposition of low-selenium sediments carried or moved by river flows through the control structure. Maintenance of low-selenium sediments probably would depend on continued low selenium sediment deposit because ground water recharge by high selenium water could cause re-elevation of selenium concentrations in sediments. For example, selenium concentrations in sediment 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 concentrations in sediment can be variable (Peltz and Waddell 1991, Stephens 1996, Zhang and Moore 1997), the decrease observed in October 1995 was thought due to 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. A similar 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 U.S. 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 sediments. 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 sediments 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 sediments 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 initial selenium concentrations of 40 mg/L were undetectable in water after 27 days of microbial activity.

The mechanism of selenium incorporation into the organic component of sediments is by microbial activity. Microbes have been shown to be able to synthesize organic selenium compounds, i.e., selenomethionine, from inorganic selenium, which are incorporated into amino acids and proteins (Foda et al. 1983). Next, the amino acid ratio for methionine, and presumably selenomethionine, has been shown to increase as much as 69% in fully developed plant detritus relative to live plant material (de la Cruz and Poe 1975). Finally, the protein content of marsh grass enriched from 6% in dead leaves to about 24% in detritus due to the presumed buildup of microbial populations (Odum and de la Cruz 1967). The incorporation of selenium into the organic component of sediments and the positive relation between sediment selenium and organic carbon content of sediment has been reported by Besser et al. (1989), Stephens et al. (1992), Zhang and Moore (1996, 1997), Hamilton et al. (2001a), and similarly, for selenium and carbon on suspended particulate matter (Zawislanski et al. 2001), which becomes part of the sediment after settling. Selenium accumulated in the top layer of sediments can contribute to selenium uptake in the aquatic food web (Peters et al. 1999) beginning with bacterivorous and algivorous predators (protozoa) (Sanders and Gilmour 1994).

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 control structure operation, selenium concentrations in sediment were substantially reduced at all stations and were near or below the national background. Selenium concentrations in suspended sediment passing through the water control structure between December 11, 1996, and June 24, 1997, ranged from 0.9 to 1.8 µg/g (geometric mean 1.2 µg/g, Butler and Osmundson 2000). Thus, relatively low selenium sediments were delivered to the channel from the river. Only in August 6, 1997, were sediment selenium concentrations a concern when they were 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 sediments would be essential to prevent selenium accumulation in the upper portion of sediments.

Selenium and other elements in aquatic invertebrates

Operation of the water control structure facilitated a substantial decrease in selenium concentrations in aquatic invertebrates (27.4 µg/g in 1996 to 15.5 µg/g in 1997 to 4.9 µg/g in 1998), 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 (r=0.77-0.83) and sediment (r=0.81). 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), thus 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 and was speculated to be due to ground water seepage of high selenium water contributing selenium to the food web. Butler and Osmundson (2000) reported selenium concentrations in several wells monitoring ground water and seepage in the WWSWA channel area. They reported ground water from a well near our station WW6 had <1-4 µg/L, whereas selenium in ground water near our station WW7 contained 22-190 µg/L. Thus, it is likely that this localized, elevated selenium in water near WW7

contributed to the absence of decreased selenium concentrations in the chironomids that 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 took up maximal concentrations in 3-24 hours, whereas floating plants took about 1 week to accumulate maximal concentrations. Part of the selenium taken up by aquatic invertebrates was probably waterborne organoselenium compounds released from living algae or necrosis of dead cells (Cutter 1986, 1989, 1991, 1992, Besser et al. 1994). Zooplankton can rapidly take up selenium from the 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 control structure 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 control structure operation, selenium concentrations in water in the channel (1.6-3.0 µg/L) were below the current USEPA 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 (3 µg/g). The mean selenium concentration in aquatic invertebrates in 1998 was similar to the selenium concentration in zooplankton (4.6 µg/g) linked with substantial mortality of larval razorback sucker in two 30-day toxicity tests using natural food organisms (Hamilton et al. 2001a, 2001b).

Selenium concentrations in aquatic invertebrates from the WWSWA channel after operation of the water control structure were similar to aquatic invertebrates in the Uncompahgre River near Delta, CO, which contained selenium concentrations of 4.1 µg/g, and in the Gunnison River at Delta, CO, which contained 5.6-6.8 µg/g (Butler et al. 1991).

Similar to conditions in the WWSWA channel area in 1998 when waterborne selenium was low (i.e., <3 µg/L) but selenium concentrations in aquatic invertebrates were elevated (i.e., 3-5.8 µg/g), Butler et al. (1994) reported two examples of low selenium concentrations in water, yet elevated concentrations in aquatic invertebrates from the Uncompahgre Valley: Horsefly Creek (<1 µg/L, 6.1 µg/g, respectively) and South Fork (<1 µg/L, 4.8 µg/g, respectively). Stephens et al. (1992) reported four examples from the Green River valley: Sheppard Bottom pond 5 (3-4 µg/L, 4.4-8.9 µg/g, respectively), Desilting Basin (3-5 µg/L, 3-9 µg/g, respectively), Big Island Pond (2-5 µg/L, 5-6 µg/g, respectively), and Felters, Shoveler, and Pintail ponds (1-5 µg/L in adjacent waters, 6-11 µg/g, respectively). Birkner (1978) reported two examples from the Grand Valley: Mac Mesa Reservoir (2.2 µg/L, 7.7 µg/g, respectively), and Highline Reservoir (4.2 µg/L, 7.7 µg/g, respectively), as well as four other locations in Colorado and two in Wyoming. Similar examples were reported in Peltz and Waddell (1991) and Hamilton et al. (1996, 2001a, 2001b).

These examples from locations in the Uncompahgre, Grand, and Green River valleys were similar to the selenium loading study of Maier et al. (1998), which revealed that aquatic invertebrates exposed to low waterborne selenium concentrations can accumulate selenium residues that reach or exceed the proposed dietary toxicity threshold of 3 µg/g. Outside of the upper Colorado River basin, other examples of low waterborne selenium concentrations (<5 µg/L) associated with elevated selenium concentrations in food organisms above the proposed

dietary toxic threshold (3 µg/g) have been reported by Holland (1979), Schroeder et al. (1988), Zhang and Moore (1996), and Lemly (1997a).

None of the inorganic elements measured in aquatic invertebrates, other than selenium, collected from the channel stations were elevated to concentrations of concern. Only barium and zinc in aquatic invertebrates had significant correlations with selenium concentrations in aquatic invertebrates. However, both of 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 the selenium residues in forage fish. The decrease in selenium concentrations in forage fish probably was a result of reductions in selenium concentrations in water, sediment, aquatic invertebrates, and other forage fish consumed by piscivores.

The decrease in selenium in forage fish from 1996 (27.2 µg/g, n=24) to 1997 (20.2 µg/g, n=23) to 1998 (8.6 µg/g, n=21) in the present study was not consistent with selenium concentrations reported by Butler and Osmundson (2000). They reported the selenium concentrations of 7.7 to 15.0 µg/g (geometric mean 14.2 µg/g, n=8) in forage fish collected on August 5, 1995, from the lower WWSWA channel area. The relatively low selenium concentrations in 1995 may be due in part to the low sample number, but more likely to the high river flows in 1995 (Figure 3).

The initially high selenium residues in forage fish may have decreased due to depuration of initially high selenium residues in forage fish in 1996 while living in an environment with lower selenium concentrations, especially in food organisms. An interesting example of selenium depuration was given in 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 a whole-body residue of 5.2-7.0 µg/g, and those fed zooplankton with 11.8 µg/g had a whole-body residue of 10.3-11.0 µg/g. Thus, fish depurated selenium from their initial elevated whole-body residue to close to the concentration in their food.

The time period after operation of the water control structure allowed selenium concentrations in water, sediments, invertebrates, 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 increased with dietary exposure to low concentration (Hilton and Hodson 1983). Loss of selenium also was faster in small, younger fish (Bennett et al. 1986) than in larger, older fish (Bertram and Brooks 1986). Depuration of selenium from tissues 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. Half-lives of selenium reported in fish range from 19 to 30 days in various species of young fish (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 whole

body of adult fathead minnows and 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 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 tissues can 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, TX, were only 25% lower after a 5-year period (1981-1986) following the drastic reduction of selenium inputs to the lake in 1978. In 1983, 2 years after selenium inputs to Martin Lake, TX, were stopped, selenium concentrations in ovary of redear sunfish (*Lepomis microlophus*) were 20-24 µg/g (reported as wet weight, converted to dry weight assuming 75% moisture) (Sorensen and Bauer 1984), which are two times higher than the toxicity threshold of 10 µg/g in ovary or eggs. Likewise, Lemly (1997b) assessed selenium concentrations in five ecosystem components of Belews Lake, NC, 10 years after selenium inputs to the lake were stopped and found elevated selenium concentrations in sediment, benthic invertebrates, and fish that suggested a moderate hazard still existed. He also reported teratogenic deformities that were first observed in 1992 (Lemly 1993c) were still present at elevated levels in 1996.

Although the selenium concentrations in forage fish had decreased substantially in 1998 after 2 years of control structure operation, the remaining selenium residues in fish were above the toxic whole-body threshold of >4 µg/g proposed by Stephens et al. (1987) and 4 µg/g proposed by Lemly (1996). Thus, the mean selenium concentration in forage fish of 8.6 µg/g 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 because they are highly reproductive and could reproduce two to 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. Some of the forage fish in the channel could have come from the river also.

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 due to flow through the channel area and the lower water temperatures due to the 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: 3,294 fish; 1996: 1,294 fish; 1997: 1,987 fish; 1998: 85 fish), and the hours of sampling effort with trammel and trap nets (1995: 163.8 hours; 1996: 519.3 hours; 1997: 955.7 hours; 1998: ~40 hours) (Mourning 1995, Lloyd 1996, Scheer 1997, 1998). Consequently, the low numbers 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. Using the Wilcoxon signed-rank test, there was a significant difference in selenium concentrations in muscle plugs collected from the same fish from 1994 compared to 1995, 1996, and 1997, but not among the later three years. 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.

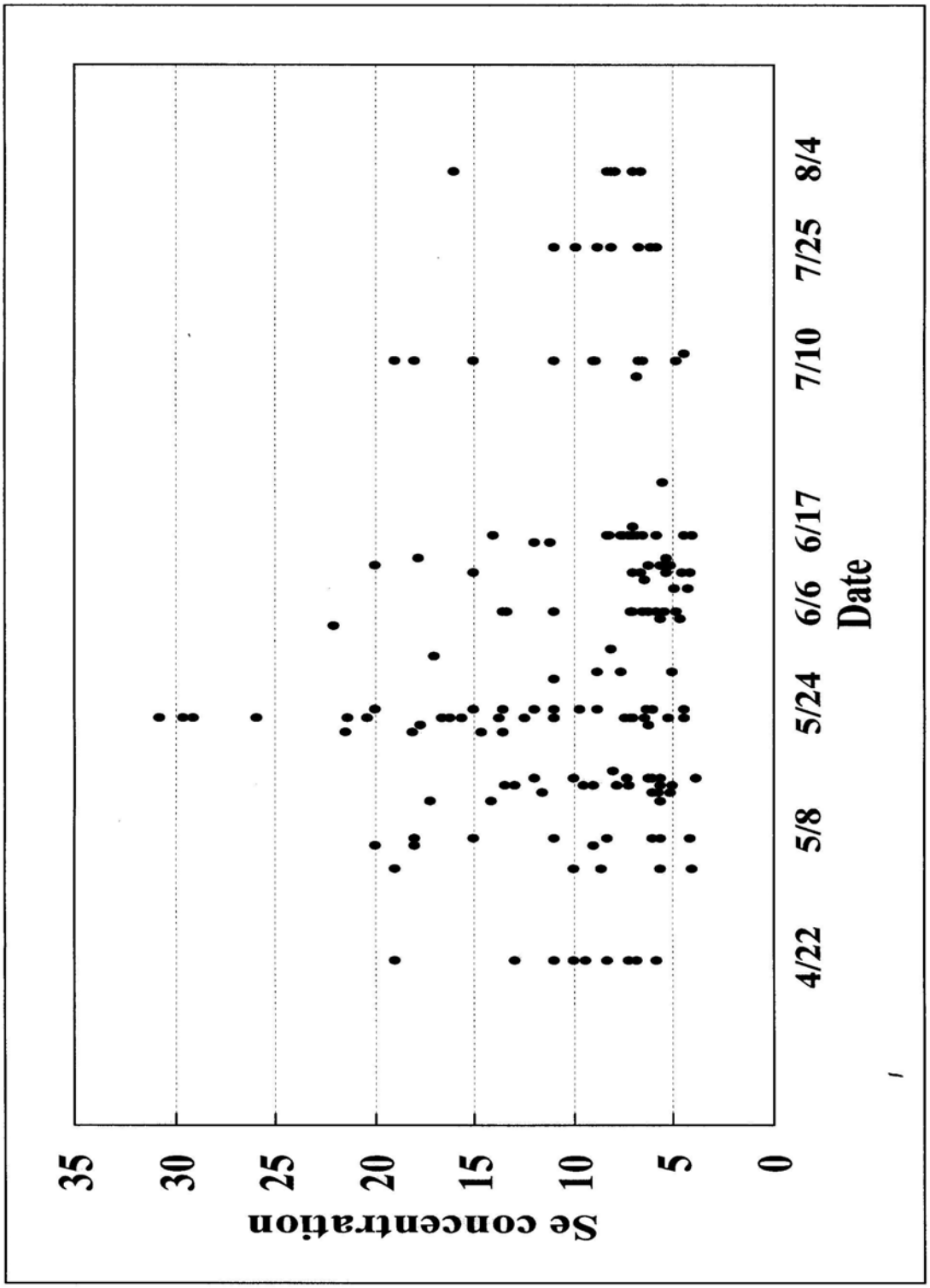
The strongest relation between muscle plug selenium and aquatic ecosystem components seemed to be with river flow for the 1994-1998 period, as evidenced by the significant correlation with the May stream flow (r= -0.87, *P*=0.05) and similar, but not significant, correlation with the average March-July period stream flow (r= -0.85, *P*=0.07). Osmundson et al. (2000) also thought high river flows 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 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 (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). In spite of these non-significant correlations, the selenium residues in Colorado pikeminnow must have come from either water exposure, diet exposure, or combined water and diet exposure. The low number of Colorado pikeminnow collected in 1998 conservatively reduced the overall dataset 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 (Figure 10) and total length (Figure 11) and the two measures were significantly correlated with selenium in muscle plug. Larger, presumably older, Colorado pikeminnow had relatively low selenium residues, whereas smaller, younger fish had a wide variety of selenium residues including very elevated residues (>12 µg/g). Several questions arise from this pattern of selenium residues: (1) do young fish with elevated selenium residues fail to live to older ages and larger sizes; (2) are the few, larger, older fish alive because they have low selenium residues, (3) is selenium regulation enhanced with older age; (4) are selenium residues diluted with increased weight; (5) are the few, larger, older fish depurating selenium through egg spawning; (6) are there diet differences between 500 to 650 mm fish and those >650 mm?

Larger, older Colorado pikeminnow may feed over a wider area of river, and thus, may not feed on high selenium forage fish, whereas, young adults may concentrate their feeding in areas of abundant small forage fish such as WWSWA. Selenium residues in Colorado pikeminnow seem to vary between 5 and 20 µg/g somewhat uniformly between late April to mid July at WWSWA (Figure 12). This pattern suggests that adults are not accumulating selenium

Figure 12. Selenium concentrations (µg/g) in muscle plugs from Colorado pikeminnow collected on various dates during 1994-1998 at Walter Walker State Wildlife Area (n=164).



residues to higher concentrations over the summer at WWSWA. Similar findings were reported by Osmundson et al. (2000) who found that for six adults sampled two to three times in 1995, only two increased selenium residues in muscle plugs (defined here as an increase of about 2 µg/g) and four did not (Table 11). In 1996 they sampled four fish two to three times, and only one fish had increased selenium residues. Several factors may have influenced the accumulation of selenium in these fish.

WWSWA at river mile 163.3-163.7 had the highest selenium residues (9.0-16.1 µg/g) in muscle plugs from Colorado pikeminnow collected from various locations in the upper Colorado River (Figure 13). In contrast, Colorado pikeminnow collected directly above (river mile 163-168, 8.5 µg/g), farther above (river mile >168, 4.9-5.4 µg/g), directly below (river mile 158-163, 4.4-6.4 µg/g), and farther below (river mile <158, 5.3-5.4 µg/g) WWSWA had lower selenium residues (Table 9). 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 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 in fish from Ashley Creek, and that fish collected further downstream (Horseshoe-Hammacher and Ouray) and upstream (Echo Park and Browns Park) had still lower selenium concentrations.

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 River (mean 4.9 µg/g, n=7), Green River (3.7 µg/g, n=5), White River (3.6 µg/g, n=5), and Yampa River (2.3 µg/g, n=5) (Appendix L, unpublished data from the National Irrigation Water Quality Program). It is interesting to note that Colorado pikeminnow from the Gunnison River had higher selenium residues than fish from the other rivers because the Gunnison River has been identified as 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 2 or 3-year period (1995-1997) seemed to be conserving selenium concentrations in muscle plugs from year to year, i.e., if the selenium concentrations were elevated one year, they were elevated in subsequent years (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. Waddell and May (1995) and Stephens and Waddell (1998) did not collect muscle plugs from any adult razorback sucker in the Green River that were recaptured, thus it is unknown if any changes in selenium concentrations have occurred over time (B. Waddell, USFWS, personal communication).

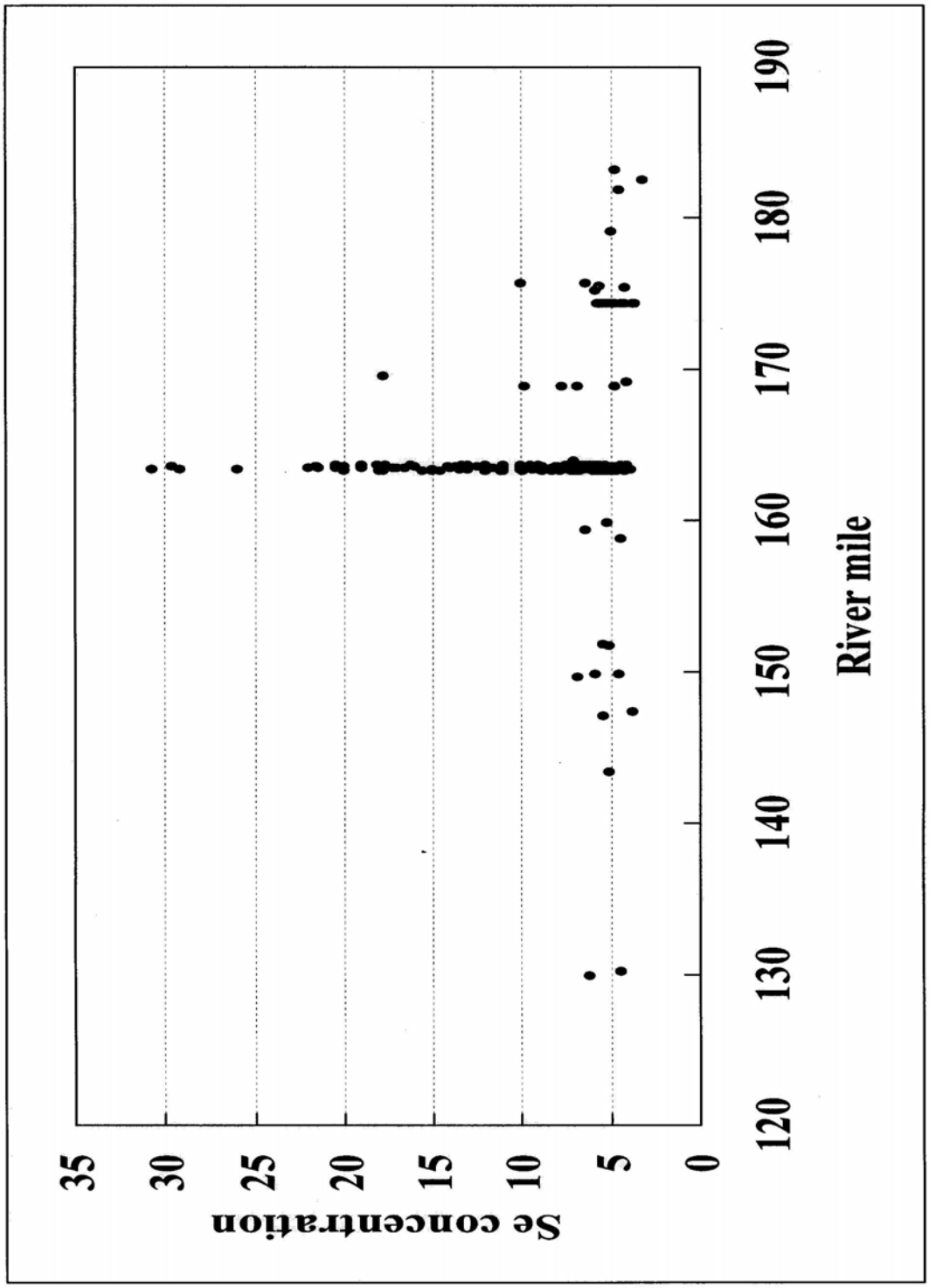
Of 16 fish collected at WWSWA in 1994, all were recaptured in later years (1995-1997). Of 45 fish collected in 1995, 25 were recaptured in other years, but 20 fish were one-time captures. Of 35 fish collected in 1996, 26 were recaptured in other years and 9 were one-time captures. Of 54 fish collected 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 learn 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 river, mostly in the Grand Junction area (Osmundson et al. 1998). They reported that adults in

Table 11. Selenium concentrations (µg/g dry weight) in muscle plugs from Colorado pikeminnow sampled multiple times at Walter Walker State Wildlife Area (data from Osmundson et al. 2000).

1995				1996			
PIT tag no.	Date	Se (µg/g)	Weight (g)	PIT tag no.	Date	Se (µg/g)	Weight (g)
1F407C7530	5/25	6.3	1200	1F46515A70	5/13	5.7	3450
	6/12	6.6	1300		6/6	4.8	3450
	7/10	6.7	1400	1F732C2D15	6/5	4.6	4150
1F412B787D	6/13	7.7	2200		6/6	5.8	4050
	8/4	7.9	2250	1F74342COD	5/14	13.4	1250
7F7D072F30	5/25	12	1150		5/21	14.6	1250
	8/4	16	1400		6/6	13.5	1350
7F7D073E2E	5/25	6.3	1500	7F7D22513D	5/13	11.6	2025
	6/13	6.2	1500		5/24	13.5	1950
7F7D152D61	5/25	20	1775				
	6/13	20	1775				
7F7F362E6D	6/1	17	1600				
	7/10	19	1800				

Figure 13. Selenium concentrations (µg/g) in muscle plugs from Colorado pikeminnow collected from various locations in the upper Colorado River (n=211; Walter Walker State Wildlife Area: river mile 163.3-163.7).



the upper reach of river tend to be larger and move less than juveniles and subadults in the lower reach. Osmundson et al. (1998) concluded the relatively small changes in location by larger fish in the upper reach was consistent with the hypothesis that adult Colorado pikeminnow select and maintain fidelity to a home feeding range. This hypothesis seems to be supportive of the observation in the current study that adults with elevated selenium residues in muscle plugs one year maintained those residues in subsequent years, and conversely, fish feeding in a low selenium area from year to year had low selenium residues over a multi-year period.

Osmundson et al. (1998) also noted that Colorado pikeminnow do not seem to be highly territorial because they concentrate in limited backwater habitats during spring runoff (April-June), they congregate prior to and during spawning in summer, and individuals were occasionally located beside one another. This finding was 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 for fish 400-449 mm (42.7 mm/year), declined in 500-549 mm fish (19.8 mm/year), and were lowest for fish 550 mm and larger (9.5 mm/year). Thus, reduced growth in larger, older fish suggests that they were putting less food resources into growth, and possibly 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 with total length of about 680 mm and larger had substantially less selenium in muscle plugs than fish in the 500 to 630 mm range. Consequently, the reduced growth of large, older Colorado pikeminnow may allow depuration of selenium residues to occur (Figure 11). Alternatively, adult Colorado pikeminnow that are 500-650 mm and have low selenium residues may be the individuals that continue to live to older ages and larger sizes, whereas the adults with elevated selenium residues, i.e., greater than 12-15 µg/g, may disappear from the population due to long-term contaminant stress.

A high estimated adult annual survival rate (0.86) of adult Colorado pikeminnow in the upper reach of the upper Colorado River has been reported (Osmundson and Burnham 1998). A similar survival rate (0.85) for Colorado pikeminnow greater than 550 mm was estimated by Osmundson et al. (1997). Adult animals can usually withstand higher levels of stress, including contaminants, than younger fish, so the high survival rate seems reasonable in spite of high selenium residues in some adult Colorado pikeminnow. However, chronic selenium exposure in animals can lower the immune response to opportunistic infections. For example, Green and Albers (1997) reported extensive histopathologic lesions in lymphoid organs of mallards (*Anas platyrhynchos*) exposed to dietary selenium that they concluded "could cause profound immunologic inhibition or suppression." Fairbrother and Fowles (1990) reported impaired cell-mediated immunity in mallards exposed to selenium via drinking water, and speculated that selenium-induced immunosuppression could be a contributing factor in the continuing epidemics of avian cholera and other diseases affecting free-ranging waterfowl and shorebird populations in the agricultural drain water basins of California. Selenium-induced immunosuppression has also been reported in mice (Schamber et al. 1995) and other birds (Whiteley and Yuill 1991). Exposure to dietary selenium has been reported to reduce a fish's survival due to exaggerated hatchery-type stresses such as extra handling stress, water temperature increases, and bright light (Felton et al. 1989).

Stress on 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) nursery habitat in the upper reach was formerly of higher quality and quantity than in later years and 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 substantial numbers 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, i.e., 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 numbers of nonnative minnows that now dominate backwater nursery habitats.

Comparison to selenium in the 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 to 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 (reported as wet weight, converted to dry weight assuming 73% moisture) in 1976-1977, 2.5 µg/g (reported as wet weight, 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 (reported as wet weight, 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 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 the majority of the literature. In general, muscle tissue contains less selenium than whole-body due to the relatively high amounts of selenium found in 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 to 27.7 for fish collected in WWSWA and 7.3 to 14.2 µg/g fish collected outside of WWSWA (based on a conversion factor of 1.667 × muscle concentration = whole body concentration, Lemly and Smith 1987). Other conversion factors are 2.355 based on data from Adams (1976)

for rainbow trout, and 1.745 from Lemly (1982) for bluegill and largemouth bass. Both of these 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 for fish collected in WWSWA and 2-5 times higher for fish collected outside WWSWA than the NCBP 85th percentile.

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 (Green River at Vernal, UT [only upper basin station], and Colorado River at Imperial Reservoir, Lake Havasu, Lake Mead, Lake Powell, all AZ). Selenium concentrations in whole-body fish also exceeded the 85th percentile in 1978-1981 and 1984 at 6 of 7 stations (same five as above) plus Colorado River at Yuma, AZ.

The fish in the present study may have reached an equilibrium between selenium concentrations in muscle tissue and those in food chain organisms because selenium concentrations in fish, based on conversion of selenium concentrations in muscle to those in whole-body, were close to those in food organisms. In most laboratory studies with dietary exposure to selenium, 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 environmental conditions, fish often accumulate selenium concentrations from 1.4 to 2.6 times selenium concentrations in their food (Barnhart 1957, Birkner 1978, Woock 1984, Saiki 1986). It is possible that if the selenium concentrations in water, sediments, aquatic invertebrates, and forage fish continued to remain low as occurred in 1998, that selenium concentrations in Colorado pikeminnow using WWSWA would decrease.

CONCLUSIONS

1. Selenium concentrations in water, sediments, aquatic invertebrates and forage fish collected from the channel area at WWSWA were substantially reduced after operation of a water control structure was installed and operated to allow Colorado River water to flow through the channel.
2. Selenium concentrations in muscle plugs of adult Colorado pikeminnow did not decrease in spite of the selenium reductions in water, sediments, aquatic invertebrates, and forage fish.
3. Flushing backwaters and channels to reduce selenium concentrations in water, sediments, aquatic invertebrates, and forage fish should be considered a helpful approach to reducing stresses in selenium-sensitive species.

RECOMMENDATIONS

Backwater and channel areas that may pose contaminant problems due to selenium contamination can be remediated by flushing flows as one option. Monitoring should be conducted to determine if reductions in selenium in important components such as invertebrates and forage fish occur after flushing.

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