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An evaluation of selenium concentrations in water, sediment, invertebrates, and fish from the Solomon River Basin

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Abstract The Solomon River Basin is located in north-central Kansas in an area underlain by marine geologic shales. Selenium is an indigenous constituent of these shales and is readily leached into the surrounding groundwater. Portions of the Basin are irrigated primarily through the pumping of selenium-contaminated groundwater from wells onto fields in agricultural production. Water, sediment, macroinvertebrates, and fish were collected from various sites in the Basin in 1998 and analyzed for selenium. Selenium concentrations were analyzed spatially and temporally and compared to reported selenium toxic effect thresholds for specific ecosystem components: water, sediments, food-chain organisms, and whole-body fish. A selenium aquatic hazard assessment for the Basin was determined based on protocol established by Lemly. Throughout the Basin, water, macroinvertebrate, and whole fish samples exceeded levels suspected of causing reproductive impairment in fish. Population structures of several fish species implied that successful reproduction was occurring; however, the influence of immigration of fish from low-selenium habitats could not be discounted. Site-specific fish reproduction studies are needed to determine the true impact of selenium on fishery resources in the Basin.

Keywords Bioaccumulation · Fish · Invertebrates · Irrigation · Sediment · Selenium · Solomon River · Toxic effects threshold · Water

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Introduction

Selenium mobilization, bioaccumulation, and effects

Over the past two decades, selenium has been identified as a major contaminant of concern in aquatic ecosystems. Primary anthropogenic sources of selenium resulting in mobilization of the element and contamination of aquatic ecosystems include (1) coal mining and combustion, (2) gold, silver, nickel, and phosphate mining, (3) metal smelting, (4) municipal landfills, (5)

oil transport, refining, and utilization, (6) agricultural irrigation, (7) constructed wetlands, (8) and feedlot wastes (Lemly 1999, 2002). Extensive studies of selenium mobilization and cycling in aquatic ecosystems have indicated that the element is strongly bioaccumulated in food-chain organisms. In several cases of severe contamination, (e.g., Belews Lake, NC; Lemly 1985a; Kesterson National Wildlife Refuge, CA; Saiki 1986a,b) fish reproductive failures and teratogenicity in birds have been documented.

Widespread concern about the ecological effects of selenium in aquatic ecosystems has resulted in numerous published toxic effect thresholds (TETs), which are derived from results of previous toxic effects studies and therefore serve as guidelines for assessing the degree of contamination and relative toxic threat to aquatic life. Published TETs (Table 1) include those by Peterson and Nebeker (1992), Skorupa et al. (1996), Van Derveer and Canton (1997), DeForest et al. (1999), Lemly (1993a, 2002), and U.S. Environmental Protection Agency (2004, 2005). A selenium TET consists of a selenium concentration in a specific environmental component (i.e., water, sediment, food-chain organisms, fish tissues or eggs, aquatic bird liver or eggs) at which toxic effects (i.e., reproductive failure), have been observed to occur in sensitive species of fish and aquatic birds. The selenium TETs reported by different sources for the same ecosystem component vary considerably, and there is current controversy and debate regarding which are the more reliable and thus applicable. For example, Lemly's and Skorupa's TETs on the wholebody fish component have classically been viewed as the more conservative, those by DeForest et al. are considered liberal, and EPA's guidelines are considered as intermediate. The classification system of Lemly (2002) is most robust due to his establishment of TETs for more ecosystem components (e.g., water, sediment, fish diet, fish eggs, bird eggs), the development of hazard profiles for each component, and the development of a protocol for using these profiles in the computation of a selenium aquatic hazard assessment for a study area (Lemly 1993a, 2002). For these reasons, the Solomon River data presented in this study will be primarily evaluated in light of TETs and the hazard profile assessment developed by Lemly. However, due to the uncertainty and debate surrounding the TET issue, the ecosystem components will also be discussed in light of TETs for these matrices established by others as described in Table 1.

Food chain bioaccumulation of selenium in lotic aquatic ecosystems exceeding reported TETs has been found to occur particularly in river basins which are irrigated due to intensive agricultural production and where the underlying and surface outcroppings of geological substrata consist of selenium-containing marine shales. Under alkaline and oxidizing conditions, these shales, especially the Niobrara and Ogallala formations (Fig. 1), lead to the production of primarily selenate (SeO_4^{-2}), which is then easily leached into the surrounding groundwater, or in the case of surface outcroppings of these shales, into the surrounding surface water. Irrigation practices which utilize the resulting selenium-contaminated groundwater and/or surface water serve to disperse

Table 1 Reported toxic effect thresholds for selenium

Matrix	Lemly (2002)	Peterson and Nebeker (1992)	U.S. Environmental Protection Agency 2004, 2005	Van Derveer and Canton (1997)	DeForest (1999)	Skorupa et al. (1996)
Water	2 (inorganic) 1 (organic)	>2	5	–	–	–
Sediment	2	–	–	>4	–	–
Fish Diet (Invertebrates)	3	–	–	–	11 (coldwater anadramous) 10 (warmwater)	3–8
Wholebody Fish	4	–	7.91	–	6 (coldwater anadramous) 9 (warmwater)	4–6
Fish Ovaries	10	–	–	–	17	7–13

the contaminant in the aquatic environment. Numerous irrigation districts in this region are operated and managed by the U.S. Bureau of Reclamation (BOR), which is periodically required to renew district long-term water supply contracts, and as part of this renewal process, to investigate water and soil characteristics which may result in hazardous irrigation project return flows. A recent investigation of the Republican River Basin of Nebraska, Colorado and Kansas (May et al. 2001) illustrated the insidious nature of selenium mobilization and bioaccumulation in an aquatic ecosystem subjected to agricultural irrigation and drainage. That Basin is underlain with shales of marine origin, under intensive agricultural production, and heavily irrigated. Preliminary investigative surveys (1994–1996) and a later extensive investigation (1997–1999) revealed widespread selenium contamination and food-chain bioaccumulation in the Republican River Basin, originating and sustained principally from the pumping of selenium-contaminated groundwater onto fields in agricultural production (May et al. 2001). The confirmation of bioaccumulation of selenium in invertebrates and fish from the Republican River system was based on selenium concentrations in the majority of the samples (≥75%) exceeding published TETs for selenium in biota-3 μg/g dry weight for invertebrates and 4 μg/g dry weight for wholebody fish (Lemly 1993a, 2002). Exceedance of these reported TETs for selenium suggested a high potential for toxicity and reproductive effects in fish and aquatic waterfowl from the Republican River Basin.

In 1998, the BOR began planning for irrigation contract renewal issues in the Solomon River Basin, which is just south of the Republican River in north-central Kansas. Because of the similarities of the Solomon and Republican River Basins regarding selenium-containing geological substrata, lotic habitats; intensive agricultural production; significant irrigated acreage, it was reasonable to anticipate at least the presence of selenium and the potential for food-chain bioaccumulation of selenium to also be occurring in this Basin (Fig. 1). Thus, the BOR, which manages three Irrigation Districts on the Solomon River (Kirwin Unit on the North Fork; Webster Unit on the South Fork; Glen Elder No. 8 on the main stem Solomon River), began a resource management assessment of the Basin to provide environmental data for the

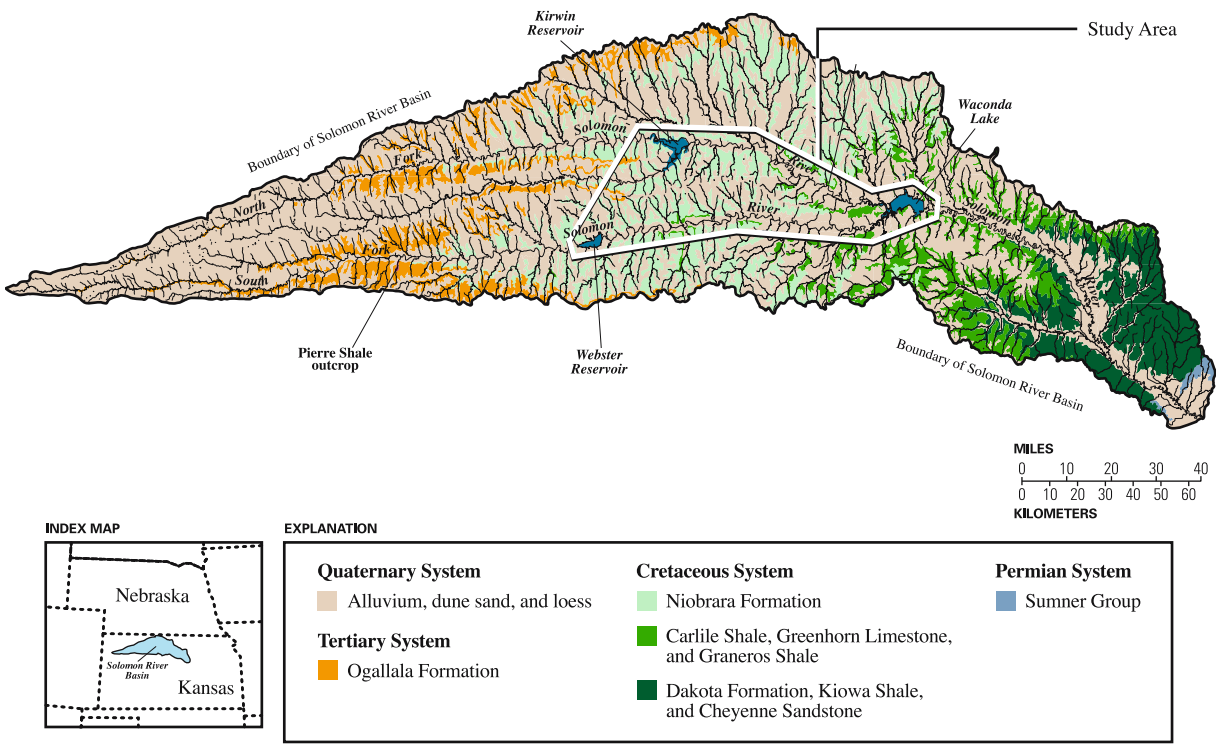

Fig. 1 Location and near-surface geology of the Solomon River Basin, north-central Kansas

National Environmental Policy Act; compliance is required before renewal of long-term water service contracts with these irrigation districts can occur. This study had three objectives: (1) determine and statistically evaluate selenium concentrations in water, sediment, invertebrates, and fish collected from the Solomon River Basin in 1998; (2) evaluate these concentrations in terms of reported TETs for selenium hazards; and (3) perform an aquatic hazard assessment on the Solomon River Basin using protocol developed by Lemly (1993a, 1995, 2002).

The Solomon River Basin

The Solomon River Basin consists of two major tributaries and three reservoirs, encompasses 17 counties, and drains nearly 7,000 mi^2 of primarily farms and ranches in north-central Kansas. The river's two major tributaries, the North Fork and the South Fork, converge immediately above Waconda Lake Reservoir on the main stem of the Solomon River (Fig. 1). Each of the main tributaries also contains a major reservoir – Kirwin Reservoir on the North Fork and Webster Reservoir on the South Fork. Both Kirwin and Webster are managed by the BOR to provide water for irrigation, municipal, industrial, and domestic use; flood control; recreation; and fish and wildlife resources. While wheat is the dominant crop throughout much of the Basin, smaller acreages are devoted to corn, soybeans, alfalfa, sorghum, and sunflowers. In 1995, 3.4% of the Basin was irrigated, predominantly by groundwater pumped from private wells upstream of Kirwin and Webster reservoirs, and by surface water downstream of these reservoirs. While BOR's irrigation districts supplied no water for irrigation upstream of Kirwin and Webster Reservoirs, they did supply water to 48% of the total irrigated acres downstream of the reservoirs, resulting in the irrigation of 12.1% of the total number of irrigated acres (~149,340) in the Basin (Christensen 1999). Irrigation has the effect of accelerating the natural leaching of minerals and trace elements from the marine shale geologic formations (particularly Niobrara and Pierre shales) that are typical of this area of Kansas (U.S. Bureau of Reclamation 2001).

Fishery habitats in the Solomon River Basin consist of low gradient riffle-run habitats with sand, silt, and gravel substrates and periodic pools created by either beaver dams or the scouring effects of water around debris. Native fish species in the Solomon River Basin include plains killifish (*Fundulus zebrinus*), fathead minnow (*Pimephales promelas*), creek chub (*Semotilus atromaculatus*), black bullhead (*Ameriurus melas*), red shiner (*Cyprinella lutrensis*), and white sucker (*Catostomus commersonii*). Native and non-native sport and forage fishes present in the Kirwin and Webster Reservoirs and Waconda Lake and actively managed by the Kansas Department of Wildlife and Parks (KDWP) include walleye (*Sander vitreus*), hybrid striped bass (*Morone chrysops x Morone saxatilis*), largemouth bass (*Micropterus salmoides*), smallmouth bass (*Micropterus dolomieu*), channel catfish (*Ictalurus punctatus*), black crappie (*Pomoxis nigromaculatus*), and white crappie (*Pomoxis annularis*) (U.S. Bureau of Reclamation 2001). The reservoirs and lake remained relatively full of water from 1993 to 2000 but have since experienced drought conditions (Price S, KDWP, personal communication). Being located within the Central Flyway, the Basin provides important habitat for migratory birds, including waterfowl, shorebirds, wading birds, neotropical birds, and some 25 raptor species. Local nesting species include interior least terns (*Sterna antillarun*); piping plovers (*Charadrius melodus*); and raptores (U.S. Bureau of Reclamation 2001).

Materials and methods

Sample collections

Sampling sites collected for the Solomon River study are indicated in Table 2, with geographical locations of each site depicted in Fig. 2. Water sampling was primarily conducted in May and August of 1998, with the same sites visited on each occasion. Water was sampled at all sites on the North Fork except sites 5, 18, and 20, three irrigation drains which were dry in both May and August. In addition, Upper Joy Creek (site 21) was dry and not collected in the August sampling effort. For the South Fork, four drain sites were dry in the May sampling effort (sites 38, 40, 42, and 43), and nine sites were found dry in the August sampling excursion (sites 27, 29, 37–40, 42, 44, 46). A final sampling effort in September collected water from only five sites on each Fork; sites 1, 2, 6, 8, and 24 on the North Fork, and sites 25, 28, 33, 35, and 45 on the South Fork. Sediments and invertebrates were also sampled only from these five sites on each Fork.

Table 2 Sampling sites for the Solomon River Basin (see Fig. 2 for site geographical locations)

North Fork sites			
Site number	Site ID	Site type[a]	Site description
1	KR	R	Kirwin Reservoir
2	NSK	MS	North Fork below Kerwin Reservoir
3	DCK	T	Deer Creek at Kerwin
4	MCC	T	Medicine Creek 1 mi S of Claudell
5	IDC	D	Irrigation Drain 1 mi SE of Claudell
6	NSCU	MS	North Fork W of Cedar above site KWD
7	KWD	D	Pipe Drain 2.5 mi W of Cedar
8	NSCL	MS	North Fork W of Cedar below site KWD
9	CCU	T	Cedar Creek Upper 1 mi NE of Cedar
10	CCL	T	Cedar Creek Lower 1.5 mi E of Cedar
11	BCU	T	Beaver Creek Upper 2 mi NW of Gaylord
12	BCL	T	Beaver Creek Lower at Gaylord
13	SCU	T	Spring Creek Upper W of Harlan
14	SCL	T	Spring Creek Lower W of Harlan
15	DCU	T	Dry Creek Upper W of Harlan
16	DCL	T	Dry Creek Lower W of Harlan
17	IDN	D	Natural Irrigation Drain 2 mi S of Harlan
18	IDH	D	Irrigation Drain 2.5 mi S of Harlan
19	LCH	T	Lawrence Creek@canal 3 mi W of Portis
20	IDP	D	Irrigation Drain 1.5 mi W of Portis
21	JCU	T	Joy Creek Upper
22	JCL	T	Joy Creek Lower
23	LCP	T	Lindley Creek at Portis
24	NSP	MS	North Fork at Portis
South Fork sites			
25	WR	R	Webster Reservoir
26	SWD	MS	South Fork below Webster Reservoir
27	MCW	T	Medicine Creek 3 mi SW of Woodston
28	SSW	MS	South Fork at gauging station near Woodston
29	UCW	T	Un-named Creek – 1 mi SE of Woodston
30	LCW	T	Lucky Creek – 4 mi east of Woodston
31	CAU	T	Crooked Creek Upper – 1 mi north of Alton
32	CAL	T	Crooked Creek Lower – 1 mi south of Alton
33	SSAU	MS	South Fork Upper – 2 mi east of Alton
34	WB	D	Pipe Drain about 2 mi east of Alton
35	SSAL	MS	South Fork Lower – 2 mi east of Alton
36	IDA	D	Irrigation Drain 3 mi east of Alton
37	MCB	T	Medicine Creek 3 mi west of Bloomington
38	IDB	D	Irrigation Drain 1 mi west of Bloomington
39	KCB	T	Kill Creek south of Bloomington
40	IDO	D	Irrigation Drain 1 mi west of Osborne
41	CCO	T	Covert Creek at Osborne
42	NDO-2	D	Natural Drain 3 mi east of Osborne
43	NDO-1	D	Natural Drain 5 mi east of Osborne
44	ICO	T	Indian Creek 5 mi east of Osborne
45	SSO	MS	South Fork 5 mi east of Osborne
46	TCC	T	Twin Creek at Corinth

[a] *R* Reservoir, *T* Tributary, *MS* Main stem, *D* Irrigation drain

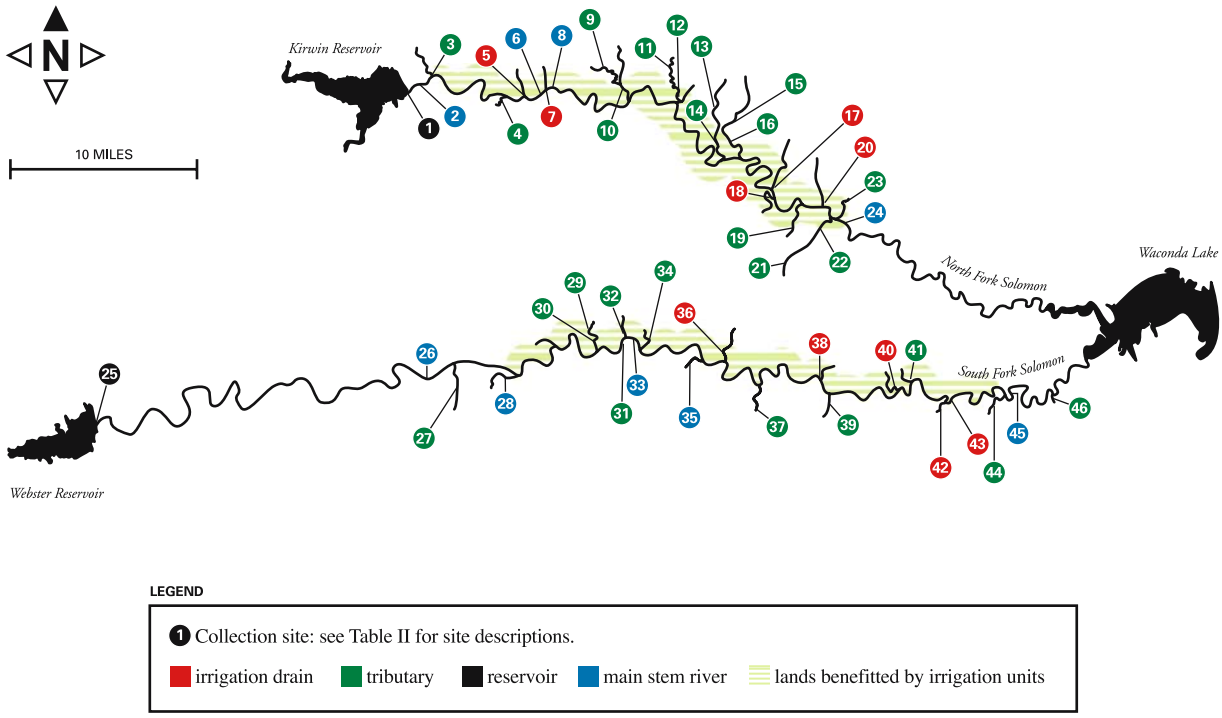

Fig. 2 Sample collection sites for the Solomon River Basin: Summer 1998

Unfiltered water samples at each site were collected in 250 ml high density polyethylene containers (Consolidated Plastics, Twinsburg, OH), preserved with nitric acid to a pH <2, and placed on ice. Quality control (QC) samples introduced during field collection for water included sample splits, duplicates, and deionized water blanks. Sediment samples were collected with a large plastic spoon, with 4–5 scoops being composited into a single sample. Four to five spots were selected at the sample site from a water depth of 2.5–60 cm, and one scoop of sediment was collected from each spot. The tributaries and main forks of the river are characterized as shallow with high flow, resulting in a bottom composed largely of sand, gravel, and solid rock. Thus, an effort was made to select sediment consisting of fine particles with high organic material, which would have the highest potential of selenium accumulation. After compositing the four or five scoops in a 250 ml high density polyethylene pre-cleaned container (Environmental Sampling Supply, Oakland, CA), the sediment was thoroughly mixed and preserved on ice in the field. Following collection, water and sediment samples and associated field QC samples were shipped to the BOR Soil and Water Laboratory in Bismarck, ND, for the determination of selenium.

Benthic invertebrates were collected by sweep-netting of underwater substrates such as submerged vegetation and rocks. In addition, invertebrates were manually removed from submerged structures, such as logs, branches, and large rocks; duplicate samples were collected at each site. Collected specimens were placed in pre-cleaned plastic jars and frozen with dry ice. Fish were collected using either electro-shocking (Smith-Root Inc., Vancouver, WA, Model 12-B battery powered backpack shocker) or seining. Fish samples at each site were sorted by species into individual (n=165) or composite samples (shiners, sunfish, and killifish; n=30) and placed in plastic bags and frozen with dry ice. All biota samples were shipped to the United States Geological Survey's Columbia Environmental Research Center (CERC) in Columbia, MO for the determination of selenium.

Sample preparation and analysis

Water and sediment

Preparation and analysis of all water and sediment samples were conducted by the BOR Soil and Water Laboratory in Bismark, ND. Water samples were

digested using Method 3030E from *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association 1995). Sediment digestions followed Method 3050B from *EPA SW-846 Test Methods for Evaluating Solid Waste* (U.S. Environmental Protection Agency 1996). Water and sediment digestates were analyzed for total recoverable selenium by graphite furnace atomic absorption spectrophotometry following Method 270.2 as described in *Methods for Chemical Analysis of Water and Wastes* (U.S. Environmental Protection Agency 1998).

Biological samples

Preparation and analysis of all biota samples was conducted by CERC. Small fish samples were chopped and minced with a meat cleaver, but larger samples were processed through a Hobart band saw and meat grinder. Invertebrate samples needed no initial homogenization. All samples were lyophilized, and percent moisture was determined in conjunction with the lyophilization procedure. Following lyophilization, invertebrate samples and small samples of fish were placed in a Bamix® mixer/blender and mechanically ground to a coarse powder. For larger fish samples, the dried cake product was hand-kneaded in a plastic bag to a coarse uniform powder. Each ground sample product was stored in a 40 ml glass vial in a dessicator prior to further treatment.

Dried fish or invertebrate samples (~0.5 g each) were subjected to a nitric acid-magnesium nitrate dry ashing procedure (Brumbaugh and Walther 1989). The determination of selenium in fish and invertebrates was accomplished by flow-injection hydride generation atomic absorption spectroscopy. In this procedure, the digestate was mixed with a hydrochloric acid carrier solution and then reduced by sodium tetrahydridoborate which had been stabilized with sodium hydroxide. The resulting volatile hydrogen selenide was transferred with argon carrier gas into a heated quartz cell mounted on an atomic absorption spectrophotometer for decomposition and measurement.

Statistics

Data were analyzed using the SAS/SYSAT (Version 6.0; Carey, NC). Prior to statistical analysis the data were tested for normality and homogeneity of variance using the Shapiro-Wilkes statistic. Water data was not normally distributed and were therefore log-transformed. Invertebrate, sediment, and fish data met the assumptions of the model and were not transformed. Differences among main effects (fork; site; habitat type) were analyzed using analysis of variance (ANOVA) using the General Linear Models procedure. Relationships among matrices (fish, invertebrates, sediment, and water) were analyzed using bivariate correlation. Statistical significance was judged at the $p \leq 0.05$ level.

Quality control

Quality control for water and sediments consisted of sample blanks, spikes, duplicates, and reference solutions. Blank concentrations were all less than the method detection limits (1 μg/L for water; 0.2 μg/g dry wgt for sediments). Spike recoveries of Se averaged 97% for water ($n=24$) and 98% for sediment ($n=11$). Recoveries of Se from reference solutions (Environmental Resource Associates, #ERA433; CPI International, #CPI-01) averaged 100% for water ($n=64$) and 98% for sediment (n=11). Relative percent differences for duplicate sample analyses averaged 12% for water and 10% for sediment.

Quality control for all biota samples included digestion blanks, reference tissues, duplicates, replicates, pre-digestion spikes, and post-digestion spikes. All digestion blanks exhibited selenium concentrations less than the method detection limits. Analysis of four reference tissue materials (CERC Striped Bass, IAEA MA-A-1 Copepod, NIST 1566a Oyster Tissue, and NRCC DORM01) resulted in selenium recoveries ranging from 100 to 107%. Duplicates ranged from 1.2 to 26% relative percent difference (RPD) and averaged 9% RPD. The percent relative standard deviation (%RSD) from the triplicate preparation and analysis of biota samples (replicates), ranged from 0.3 to 5.9% and averaged 2.4%RSD. Recoveries from pre-digestion tissue spikes ranged from 97 to 106% and averaged 100%. Post-digestion (analysis) spikes, used to check for suppression or enhancement of the selenium signal at the instrument, ranged from 92 to 110% recovery and averaged 108%. The biota method detection limit varied with each analytical run and ranged from 0.03 to 0.17 μg/g. All quality control results were within acceptable limits for the types of samples and analyses involved.

Results and discussion

Water

The Solomon River, like the Republican River to the north, is a lotic system characterized as having shallow tributaries and main forks with flowing water and virtually no deep pools, resulting in a bottom composed largely of sand, gravel, and solid rock. The main source of selenium is from cretaceous marine shales which underlie and surface outcrop into the Solomon River Basin. These shales contain selenium mostly as the soluble oxyanion selenate (SeO_4^{-2}), which is highly mobile and easily leached from soils by irrigation return flows (Masscheleyn et al. 1991; Christensen 1999) or through contact of surface water with shale outcroppings. Once in surface water, existence and maintenance of the SeO_4^{-2} form is augmented by the shallow oxygenated nature of the tributary-river system.

Concentrations of selenium in water from each collection site are presented in Table 3. Selenium in water averaged 6.75±5.56 μg/L selenium (n=81) over the entire Solomon River Basin dataset. Over all habitat types and dates, selenium concentrations in North Fork water averaged 9.22±6.17 μg/L selenium (n=45) and were significantly greater (one-way ANOVA; $p \leq 0.001$) than concentrations in the South Fork which averaged 3.34±1.85 μg/L (n=36).

Selenium water concentrations in the mainstem of the North Fork averaged 9.08±4.69 μg/L (n=12) and were significantly greater than concentrations in the South Fork mainstem (average 3.34±1.33 μg/L; n=12). A two-way analysis of variance of selenium in tributary water revealed a significant effect of fork (p=0.0039) and month (p=0.03111) with highest levels observed in both forks in late summer months. However, there were no significant differences between the mainstem sites (average 9.08±4.69 μg/L; n=12) and tributary sites (average 9.05±6.46 μg/L; n=26) of the North Fork. Similarly, there were no significant differences between mainstem sites (3.34±1.33 μg/L; n=12) and tributary sites (average 3.17±1.47 μg/L; n=14) of the South Fork.

Due to extreme drought conditions only a minimum number of irrigation drain sites (n=5 total) could be sampled for water. Highest observed concentrations occurred at site 7 (KWD) where selenium averaged 20.75±0.07 μg/L across two sampling dates. This concentration was significantly higher ($p \leq 0.001$) than selenium in water at the North Fork site 17 (IDN; mean 3.15±0.22 μg/L). In contrast, overall concentrations of selenium in the South Fork were much lower than in the North Fork and varied significantly by site [site 36 (IDA) averaged 4.30±0.28 μg/L; and site 34 (WB) averaged 3.10±0.42 μg/L]. Only one sample was taken at the South Fork site 43 (NDO-1; 0.10 μg/L selenium) which was the lowest selenium concentration in water observed during the study.

Two reservoirs, Kerwin (North Fork) and Webster (South Fork), were sampled in May, August, and September. Selenium concentrations in reservoirs did not differ significantly and averaged 6.1±1.2 μg/L (n=3) in Kerwin Reservoir and 5.3±4.7 μg/L in Webster Reservoir (n=3).

Samples from 85% of the sites where water was present (n=69) exhibited selenium concentrations that exceeded the water TET of 2 μg/L for one or more collection periods. In addition to the published water TET value, Lemly (1995, 2002) has also reported a hazard profile for selenium accumulation from water into the planktonic food chain, with resultant toxicity to fish and aquatic birds. The profile has five hazard categories: high, >5 μg/L; moderate, 3–5 μg/L; low, 2–3 μg/L; minimal, 1–2 μg/L; none, <1 μg/L. Classifying the selenium water concentrations with these designations (Fig. 3), there were two North Fork sites with a least one water measurement of no hazard (sites 21 and 22); two with minimal hazard (sites 2 and 22); six sites with moderate hazard (sites 1, 4, 10, 15, 16, and 17); and all remaining sites (n=17) had at least one water measurement that was a high hazard. Similarly, for the South Fork, three sites had at least one water measurement of no hazard (sites 26, 29, 43); four with minimal hazard (sites 25, 41, 44, 46); eight with low hazard (sites 26, 28, 30, 31, 33, 34, 35, 45); 12 with moderate hazard (sites 25, 27, 28, 30, 32, 33, 34, 35, 36, 39, 41, 45); and two with high hazard (sites 25, 45). Thus, water samples collected from 20 sites on the Solomon River exceeded the high hazard profile level of 5.0 μg/L on one or more dates (Fig. 3); the average of these concentrations was 11.5 μg/L ± 5.2 (n=34). This is a very similar pattern to that observed for water from the Republican River Basin in 1997–1998, where 26 samples from 16 sites exceeded 5.0 μg/L and averaged 11.8 ± 7.2 (May et al. 2001).

Lemly reported an average lake water concentration of 10 μg/L selenium in a power plant cooling reservoir

Table 3 Concentrations (μg/L) of selenium in water from the Solomon River Basin

Site ID	Site[a] number	Site type[b]	Date collected	Se
North Fork				
NSK	2	MS	May-98	1.1
			Aug-98	<1.0
			Sep-98	14.9[c]
NSCU	6	MS	May-98	5.4[c]
			Aug-98	11.5[c]
			Sep-98	11.8[c]
NSCL	8	MS	May-98	6.5[c]
			Aug-98	11.5[c]
			Sep-98	13.4[c]
NSP	24	MS	May-98	7.7[c]
			Aug-98	11.4[c]
			Sep-98	12.7[c]
CCU	9	T	May-98	–[d]
			Aug-98	13.1[c]
CCL	10	T	May-98	4.8[c]
			Aug-98	11.6[c]
BCU	11	T	May-98	14.5[c]
			Aug-98	25.0[c]
BCL	12	T	May-98	13.8[c]
			Aug-98	22.3[c]
SCU	13	T	May-98	10.1[c]
			Aug-98	18.4[c]
SCL	14	T	May-98	8.1[c]
			Aug-98	15.6[c]
DCU	15	T	May-98	4.9[c]
			Aug-98	8.0[c]
DCL	16	T	May-98	4.0[c]
			Aug-98	6.3[c]
LCH	19	T	May-98	3.3[c]
			Aug-98	9.4[c]
JCL	22	T	May-98	0.6
			Aug-98	1.9
LCP	23	T	May-98	5.3[c]
			Aug-98	7.2[c]
DCK	3	T	May-98	5.8[c]
			Aug-98	13.6[c]
MCC	4	T	May-98	4.1[c]
			Aug-98	2.9[c]
JCU	21	T	May-98	0.7
			Aug-98	–[d]
IDN	17	D	May-98	3.0[c]
			Aug-98	3.3[c]
KWD	7	D	May-98	20.8[c]
			Aug-98	20.7[c]
KR	1	R	May-98	4.7[c]
			Aug-98	6.9[c]
			Sep-98	6.8[c]
South Fork				
SWD	26	MS	May-98	2.8[c]
			Aug-98	<1.0
SSW	28	MS	May-98	3.1[c]
			Aug-98	2.2[c]
			Sep-98	2.5[c]
SSAU	33	MS	May-98	2.7[c]
			Aug-98	3.4[c]
			Sep-98	4.6[c]
SSAL	35	MS	May-98	3.0[c]
			Aug-98	2.8[c]
			Sep-98	4.2[c]
SSO	45	MS	May-98	2.2[c]
			Aug-98	4.0[c]
			Sep-98	6.3[c]
UCW	29	T	May-98	<1.0
			Aug-98	–[d]
LCW	30	T	May-98	2.9[c]
			Aug-98	3.6[c]
CAL	32	T	May-98	4.1[c]
			Aug-98	5.7[c]
CCO	41	T	May-98	1.9
			Aug-98	4.8[c]
MCW	27	T	May-98	3.6[c]
			Aug-98	–[d]
CAU	31	T	May-98	2.1[c]
			Aug-98	2.8[c]
MCB	37	T	May-98	5.0[c]
			Aug-98	–[d]
KCB	39	T	May-98	4.0[c]
			Aug-98	–[d]
ICO	44	T	May-98	1.2
			Aug-98	–[d]
TCC	46	T	May-98	1.7
			Aug-98	–[d]
WB	34	D	May-98	2.8[c]
			Aug-98	3.4[c]
IDA	36	D	May-98	4.5[c]
			Aug-98	4.1[c]
NDO-1	43	D	May-98	–[d]
			Aug-98	<1.0
WR	25	R	May-98	4.3[c]
			Aug-98	1.2
			Sep-98	10.5[c]

[a] Number corresponds to Fig. 2 site number which depicts geographical location; listed sites had water present for at least one collection period

[b] *R* Reservoir; *T* Tributary, *MS* Main stem, *D* Irrigation drain

[c] Exceeding TET of 2 ug/L, where toxic effects, i.e., reproductive failure, begin to occur in sensitive species of fish and aquatic birds (Lemly 2002)

[d] Site found dry

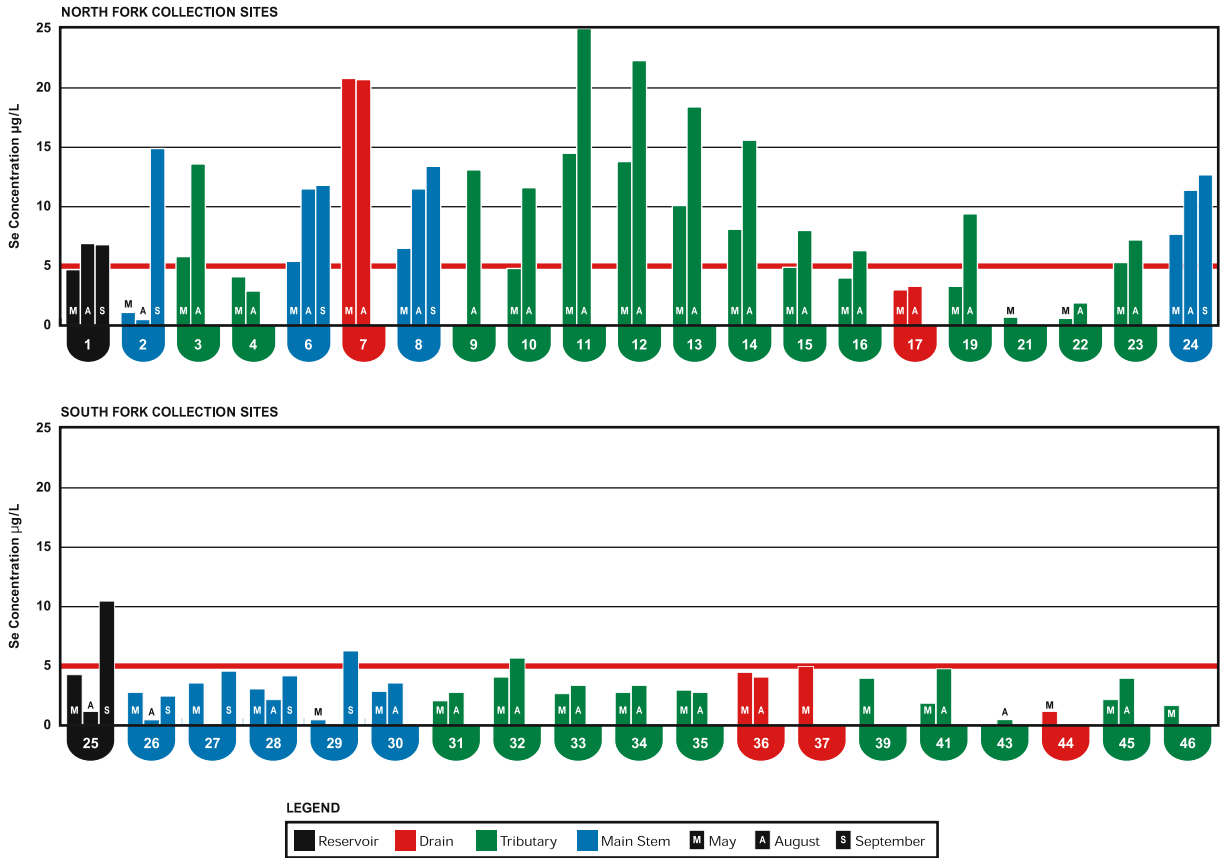

Fig. 3 Concentrations of selenium in water from the Solomon River Basin relative to the >5 µg/L high hazard

in North Carolina which exhibited marked bioaccumulation of the element in fishes, insects, benthic invertebrates, periphyton, and plankton (Lemly 1985b). In contrast, Hoffman et al. (1990) reported significant selenium bioaccumulation in sediments, insects, and birds in the Stillwater National Wildlife Refuge, even though selenium in filtered surface and ground water was below the analytical reporting limit (1 µg/L). Bioaccumulation of selenium can occur from water containing very low dissolved selenium concentrations, as Besser et al. (1993) reported that disproportionately high selenium concentrations accumulated in algae, daphnids, and bluegills (*Lepomis macrochirus*) during aqueous exposures based on 1 µg/L dissolved organoselenium (selenomethionine). Water from the Solomon river contained >2 µg/L selenium in 85% of samples and an average of ~12 µg/L in 42% of samples (or those >5 µg/L), suggesting the potential for bioaccumulation of selenium from water through the planktonic food chain in this river system. For example, Bennett et al. (1986) demonstrated in laboratory testing the rapid and effective transfer of waterborne sodium selenate from algae, to rotifers, to fathead minnow larvae, with rotifers reaching 91 µg/g Se and fathead minnow larvae 61 µg/g Se. Based on Lemly's selenium hazard profile (Lemly 1995, 2002), water from the Solomon River Basin receives a high hazard rating, or a numerical score of 5.

Sediment

Selenium in sediments (Table 4) averaged less than 1 µg/g: 0.90±0.63 µg/g (n=5) in the North Fork and 0.93±0.34 µg/g (n=6) in the South Fork; there was no statistical difference among the two forks. Sediment selenium concentrations from all sites were less than the 2 µg/g TET reported by Lemly (2002).

The incorporation of waterborne selenium into the sediment is highly dependent on sediment redox conditions. Masscheleyn et al. (1991) incubated selenium-contaminated sediments from Hyco Reservoir under controlled redox and pH conditions.

Table 4 Concentrations (μg/g dry weight) of selenium in sediment collected from the Solomon River

	Collection site	Site number	Site type[a]	Se
North Fork	KR	1	R	1.2
	NSK	2	MS	<0.2
	NSCU	6	MS	0.3
	NSCL	8	MS	1.7
	NSP	24	MS	1.1
South Fork	WR	25	R	1.3
	SWD	26	MS	0.4
	SSW	28	MS	1.0
	SSAU	33	MS	1.4
	SSAL	35	MS	0.9
	SSO	45	MS	0.6

[a] *R* reservoir, *MS* main stem of river

Selenium solubility as Se^{+6} reached a maximum under highly oxidized conditions, but under strongly reduced conditions the insoluble elemental selenium and/or metal selenides predominated. More alkaline conditions resulted in greater selenium concentrations in solution. Low redox environments (reducing conditions) are prevalent in lentic systems, such as sediments of ponds, wetlands, and reservoirs, where reduction into the sediment is often a major pathway for removal of soluble selenium oxyanions from the water column into sediments where microbial methylation of selenium to organoselenium is enhanced. In contrast, the Solomon River and its tributaries constitute a shallow, flowing system virtually devoid of any deep pool areas. In such a system, selenium would be expected to remain in the water column as predominately selenate (Masscheleyn et al. 1991), with reduction and selenium accumulation in sediments expected to occur in any downstream reservoirs, such as Waconda Lake. However, Christensen (1999) reported that although mean concentrations of selenium in sediment cores from Kirwin Reservoir, Webster Reservoir, and Waconda Lake showed an increase from 1964 to 1998 due to major irrigation development in the Solomon River Basin, recent mean concentrations were below the 2 μg/g sediment TET suggested by Lemly (2002). Similarly, Juracek and Ziegler (1998) showed a trend of increasing selenium in the sediment cores from three reservoirs in the neighboring Republican River Basin to the north. Recent mean selenium concentrations were 1.0 μg/g in Swanson Lake, 1.8 μg/g in Harlan County Lake, and 1.0 μg/g in Milford Lake, all less than the 2 μg/g TET. Out of 53 sediment samples collected by the BOR from the Republican River Basin in 1997–1998, all but four exhibited selenium concentrations less than the TET of 2 μg/g (May et al. 2001). Following a similar pattern, selenium concentrations in Solomon River sediment did not exceed 1.7 μg/g in this collection effort. There may well be different sediment-biota selenium relationships in these two river systems, as opposed to lentic systems, due to the presence of little detrital material (Canton and Van Derveer 1997; Van Derveer and Canton 1997). This would further emphasize the importance of waterborne selenium in planktonic food web residue dynamics over a sediment-detrital pathway in both the Republican and Solomon river basins.

Whereas selenium concentrations in sediment greater than or equal to the 2 μg/g TET (dry wgt basis) are reported to present a hazard for selenium accumulation from sediments into the benthic food chain, the more definitive hazard profile for the sediment matrix has the following five hazard categories: high, >4 μg/g; moderate, 3–4 μg/g; low, 2–3 μg/g; minimal, 1–2 μg/g; no hazard, <1 μg/g (Lemly 1995). Applying Lemly's protocol for selenium hazard profile assessment (Lemly 1995, 2002), sediment from the Solomon River Basin receives a minimal hazard rating, or a numerical score of 2, and shows little evidence for bioaccumulation of the element from this matrix into the benthic food chain.

Benthic invertebrates

Selenium concentrations in benthic invertebrates collected from the Solomon River are presented in Table 5. Mean Selenium concentrations are presented

Table 5 Concentrations of selenium (μg/g dry weight) in invertebrates collected from the Solomon River

a. Invertebrates by site

Collection site	Site number	Site type[a]	Fork	Mean Se Conc	Conc SD
KR	1	R	North	17.2[b]	1.5
NSK	2	MS	North	8.81[b]	3.4
NSC-U	6	MS	North	10.5[b]	1.2
NSC-L	8	MS	North	10.7[b]	0.8
NSP	24	MS	North	16.0[b]	1.1
WR	25	R	South	10.3[b]	0.2
SSW	28	MS	South	7.60[b]	4.2
SSA-U	33	MS	South	8.35[b]	1.1
SSA-L	35	MS	South	11.5[b]	0.7
SSO	45	MS	South	10.0[b]	2.8

[a] *R* reservoir, *MS* main stem of river

[b] Site mean (n=2) exceeds TET of 3 μg/g for food chain organisms in fish, and 7 μg/g for birds, levels at which toxic effects, i.e., reproductive failure, begin to occur in sensitive species of fish and aquatic birds (Lemly 2002).

in a longitudinal (i.e., upstream to downstream) basis. Selenium in invertebrates averaged 11.1±3.4 μg/g selenium (n=20) over the entire data set. Selenium concentrations in invertebrates differed significantly by fork (one-way ANOVA; p=0.0412), averaging 12.7±3.7 μg/g in North Fork invertebrates and 9.55± 2.3 μg/g (n=10) in South Fork invertebrates.

Concentrations of selenium in invertebrates collected from the Solomon River Basin clearly exceed the 3 μg/g published TET for dietary selenium transferred to fish and the 7 μg/g TET for dietary selenium transferred to aquatic birds through aquatic food chains (Lemly 1993a, 2002). Benthic invertebrates serve as a primary food source for a variety of fishes and aquatic wildlife, and numerous studies have indicated that the majority of selenium residues in fish tissue originates from selenium in the diet (Besser et al. 1993; Coyle et al. 1993; Hamilton et al. 1986, 1990; Lemly 1982). Benthic invertebrates can harbor substantial levels of selenium without apparent toxic or population effects and in doing so provide a major dietary source of selenium to fish and wildlife species that consume them. For example, aquatic insects collected from the Kesterson Reservoir and San Luis Drain contained selenium exceeding 300 μg/g dry weight (Saiki 1986a,b; Saiki and Lowe 1987). Benthic invertebrates (damselfly nymphs (*Zygoptera*), dragonfly nymphs (*Anisoptera*) and diptera fly larvae) from Kesterson Reservoir exhibited selenium concentrations ranging from 48 to 180 μg/g dry weight (Schuler 1989; Schuler et al. 1990). Macroinvertebrates from the Solomon River exhibited selenium concentrations less than these examples, e.g., <20 μg/g. However, these selenium levels were quite similar to those found in the Republican River Basin to the north, where invertebrate selenium concentrations ranged from 1.53 to 18.0 μg/g and averaged 7.57 μg/g; 95% of that sample set collected in 1997–1998 exceeded the 3 μg/g TET (May et al. 2001).

The hazard profile for dietary toxicity and reproductive failure from ingestion of selenium-contaminated macroinvertebrates considers >5 μg/g a high hazard; 4–5 μg/g moderate; 3–4 μg/g low; 2–3 μg/g minimal; and <2 μg/g no hazard. This places one sample in the moderate category (SSW, South Fork, 4.64 μg/g), and all other samples in the high hazard category. Overall, according to the reported TET and selenium hazard profile for macroinvertebrates (Lemly 1995, 2002), selenium concentrations in benthic invertebrates from the Solomon River Basin receives a high hazard rating, or a numerical score of 5, indicating strong evidence of food chain bioaccumulation of the element that could cause adverse effects on fish and bird populations.

Fish

Concentrations of selenium in wholebody fish collected from the Solomon River Basin are presented in Table 6a (by fish species) and b (by site). Out of 195 samples collected, selenium concentrations ranged from 2.68 to 16.4 μg/g and averaged 9.5 μg/g.

Table 6 Concentrations of selenium (μg/g dry weight) in fish collected from the Solomon River in 1998: Categorization by fish species (a) and by site (b)

a. Fish by species

Species	Number collected	Number sites	Percent of total	Se Conc range	Mean Se Conc	SD	Mean Se Conc fish egg basis[b]
Orangespotted Sunfish	12	3	6.2	11.0–15.4	12.9[a]	1.3	42.6
Green Sunfish	16	3	8.2	6.0–16.1	12.3[a]	2.3	40.6
White Bass	1	1	0.5	12.2	12.2[a]	–	40.3
Freshwater Drum	6	4	3.1	10.5–13.2	12.1[a]	1.1	39.9
Creek Chub	8	2	4.1	10.4–13.1	11.7[a]	0.9	38.6
Bluegill	12	2	6.2	7.9–14.3	11.4[a]	1.9	37.6
Plains Killfish	1	1	0.5	10.0	10.0[a]	–	33.0
Common Carp	33	10	16.9	5.8–13.3	9.70[a]	1.5	32.0
Black Crappie	3	1	1.5	6.6–11.8	9.50[a]	2.6	31.4
Black Bullhead	7	2	3.6	5.5–11.1	9.07[a]	1.8	29.9
Fathead Minnow	8	8	4.1	6.2–10.6	8.79[a]	1.5	29.0
Flathead Catfish	5	3	2.5	6.5–10.8	8.68[a]	1.8	28.6
Sand Shiner	5	5	2.5	7.1–10.3	8.60[a]	1.3	28.4
River Carpsucker	11	6	5.6	4.9–11.1	8.31[a]	2.0	27.4
Red Shiner	31	10	15.9	5.6–3.2	8.27[a]	1.9	27.3
White Crappie	2	2	1.0	7.0, 8.1	7.52[a]	0.8	24.8
Central Stoneroller	4	1	2.0	5.5–12.4	7.45[a]	3.3	24.6
Channel Catfish	27	8	13.8	2.8–16.4	7.42[a]	3.3	24.5
Gizzard Shad	1	1	0.5	6.81	6.81[a]	–	22.5
Longnose Gar	2	2	1.0	2.7–3.6	3.12	0.6	10.3

b. Fish by site

Collection site	Site number	Site type	Fork	Number of fish species	Se Conc range	Mean Se Conc	Conc SD
KR	1	R	North	8	5.50–13.8	9.14[c]	2.6
NSK	2	MS	North	6	4.87–9.91	6.79[c]	1.9
NSC-U	6	MS	North	7	2.68–11.5	8.13[c]	2.1
NSC-L	8	MS	North	5	4.24–12.7	8.34[c]	3.1
NSP	24	MS	North	6	3.57–11.0	8.34[c]	2.5
WR	25	R	South	11	3.14–16.1	9.69[c]	2.7
SSW	28	MS	South	12	2.76–15.4	10.7[c]	2.7
SSA-U	33	MS	South	4	7.59–12.6	9.15[c]	1.9
SSA-L	35	MS	South	7	6.45–16.4	10.5[c]	2.4
SSO	45	MS	South	9	3.97–13.1	8.61[c]	2.6

[a] Species mean exceeding TET of 4 μg/g for wholebody fish, where toxic effects, i.e., mortality of juveniles and reproductive failure, begin to occur in sensitive species of fish (Lemly 2002).

[b] fish mean Se egg concentration = fish wholebody mean Se concentration × 3.3 (Lemly and Smith 1987; Skorupa et al. 1996).

[c] Site mean exceeding TET of 4 μg/g for wholebody fish, where toxic effects, i.e., mortality of juveniles and reproductive failure, begin to occur in sensitive species of fish (Lemly 2002).

Examining fish species and frequency of capture (Table 6a), the most common species collected were common carp (*Cyprinus carpio*), red shiners, and channel catfish, which together represented 47% of the sample set, followed by green sunfish (*Lepomis cyanellus*), orangespotted sunfish (*Lepomis humilis*), bluegill, and river carpsucker (*Carpiodes carpio*) (together an additional 26% of the sample set). The two most abundant species in the Solomon River Basin were common carp and red shiner, based on

Table 7 Selenium concentrations in Carp and Red Shiners categorized by fork and site

Species	Fork	Site	Site number	Site type[a]	Mean Se Conc	SD
Common Carp	North	KR	1	R	7.78	2.3
	North	NSK	2	MS	9.33	0.8
	North	NSCU	6	MS	10.6	0.8
	North	NSCL	8	MS	10.8	1.8
	North	NSP	24	MS	10.3	0.7
	South	SSW	28	MS	10.4	1.8
	South	SSAU	33	MS	7.59	–
	South	SSAL	35	MS	10.5	0.8
	South	SSO	45	MS	8.48	0.5
Red Shiner	North	KR	1	R	7.03	1.6
	North	NSK	2	MS	5.81	–
	North	NSCU	6	MS	7.24	1.1
	North	NSCL	8	MS	7.36	–
	North	NSP	24	MS	8.62	–
	South	SSW	28	MS	10.0	2.4
	South	SSAU	33	MS	11.2	1.9
	South	SSAL	35	MS	9.00	2.6
	South	SSO	45	MS	7.16	–

[a] *R* reservoir, *MS* main stem of river

number of sites collected in main-stem habitats (Table 7). Since these two species constituted the most statistically robust dataset, we conducted a 2-way ANOVA with fork and species as main effects. Selenium concentrations did not differ by fork (p=0.4270) but did differ by species (p=0.0452) and fork x species interaction (p=0.0344). Overall, selenium concentrations averaged 9.75±1.17 μg/g (n=8 sites) in carp and 8.30±1.75 μg/g (n=8 sites) in red shiner. Selenium concentrations in the North Fork were significantly higher in carp (9.76± 1.24 μg/g; n=5) than in red shiner (7.21±1.00 μg/g; n=5). Selenium concentrations in the South Fork were similar between carp (9.24±1.44 μg/g; n=4) and red shiner (9.34±1.71 μg/g; n=4). There were no significant longitudinal relationships in selenium concentrations in main-stem habitats. Carp and red shiners were only sampled in one of the two reservoirs in the Solomon Basin (Kerwin, North Fork) and averaged 7.78 μg/g in carp and 7.03 μg/g in red shiner. Collectively, the data indicated that selenium concentrations in carp and red shiner were lower in the reservoir compared to main-stem habitats.

Correlation analysis indicated that there were no significant relationships between fish, invertebrates, sediments, or water when all main-stem habitats were combined. However, when analyzed by fork there was a significant, positive correlation between carp and sediment in the South Fork r=0.997; p=0.043, n=3); no other significant correlations were found. The lack of significant relationships among sample compartments is due to two factors: (1) drought conditions, which limited the overall number of sites where insectivorous fishes were collected (Table 6a), and (2) the lack of variation in selenium concentrations among habitats within each fork.

Overall, 97% of the fish sample set, or 189 samples, exhibited selenium concentrations exceeding the 4 μg/g TET for the health and reproductive success of freshwater fish. Fish collected at all sites exhibited mean selenium concentrations exceeding the 4 μg/g dry weight TET for the health and reproductive success of freshwater fish (Table 6b). On a species mean basis (Table 6a), the concentrations of selenium in all fish species except longnose gar (*Lepisosteus osseus*) collected from the Solomon River ranged from 6.81 to 12.9 μg/g, thus exhibiting selenium concentrations exceeding the 4 μg/g TET. Based on the TET of 4 μg/g for the health and reproductive success of freshwater fish (Lemly 1993a, 2002), selenium concentrations in fish collections indicated strong evidence of food chain bioaccumulation with potential dietary toxicity and/or reproductive effects on fish populations.

Numerous studies have shown that levels of selenium in fish exceeding the 4 μg/g wholebody TET can result in growth inhibition, tissue damage in major organs, reproductive impairment, or mortality. For example, Hamilton et al. (1990) observed mortality in chinook salmon (*Oncorhynchus tshawytscha*) having wholebody selenium residues exceeding 10 μg/g dry weight; growth was impaired at 2–3 μg/g. Fathead minnows showed inhibited growth at wholebody selenium concentrations of 6–8 μg/g (Ogle and Knight 1989), and reproductive failure at 16 μg/g (embryos) and 24 μg/g (ovaries) (Schultz and Hermanutz 1990). Striped bass (*M. saxatilis*) fed red shiners from selenium affected areas of Belews Lake NC accumulated wholebody residues of 15 μg/g, resulting in mortality within 78 days (Coughlan and Velte 1989). Lemly (1985b, 2002) reported 10-fold higher incidence (compared to fish from reference lakes) of teratogenic defects in centrarchids having wholebody selenium residues of 15 μg/g (12–16 μg/g selenium in skeletal muscle) and the eventual elimination of all nine species of centrarchids from Belews Lake NC. Coyle et al. (1993) reported severely reduced survival in bluegill fry from female adults that had accumulated 16–18 μg/g selenium.

In addition to the growth inhibition, tissue and organ damage, and mortality due to elevated selenium in fish, there is the additional injury and mortality from the combination of elevated selenium levels in conjunction with low water temperature, the so-called "Winter Stress Syndrome." Lemly (1993b) reported that in juvenile bluegill, elevated selenium in combination with low water temperature (4°C) substantially reduced activity and feeding during cold weather, caused depletion of 50–80% body lipid, and significant mortality occurred within 60 days. Whereas concentrations of 10–16 μg/g dry wgt dietary selenium and 5–10 μg/L waterborne selenium will likely cause reproductive failure of bluegill under temperate water conditions, only about half these amounts can be lethal to young-of-year and juvenile bluegills exposed to falling water temperatures. Wholebody selenium concentrations associated with mortality ranged from 5.9 μg/g in summer to 7.9 μg/g in winter, which served as the basis for the EPA fish tissue-based criterion. The Solomon River Basin, given its geographical position in north-central Kansas, is subjected to winter temperatures that are frequently below freezing, which would increase the importance of Winter Stress Syndrome as a significant mortality factor among numerous fish species. Thus, elevated selenium in both temperate and especially periodic cold environments can result in repeated loss of year classes which can ultimately deplete fish populations.

Besides the harmful effects of elevated selenium and elevated selenium + cold water on juvenile and adult fishes, there are the additional deleterious effects of the element specifically directed at fish reproduction. In waters of a power plant cooling reservoir contaminated with 9–12 μg/L selenium, female bluegills preferentially concentrated selenium in ovary tissues (40–48 μg/g dry wgt) compared to remaining carcass samples (24–28 μg/g). Similarly, selenium concentrations in carcasses of female largemouth bass averaged 16 μg/g, whereas ovaries contained 30 μg/g. Selenium concentrations were always higher in the ovaries than in the carcasses and showed no relative decline as carcass levels increased (Baumann and Gillespie 1986). In selenium water dosing experiments with fathead minnows, Schultz and Hermanutz (1990) reported that embryos from fish reared in dosed streams (10 μg/L Na_2SeO_3) contained selenium levels 13X higher than embryos from fish reared in control streams (1.24 vs 15.6 μg/g dry wgt). There was a similarity in residues of selenium between embryos and ovaries within the same treatment, and control embryos did not significantly accumulate selenium when exposed to the 10 μg/L dosing water. The transfer of selenium from fathead minnow ovaries to embryos resulted in increased incidence of edema and lordosis, conditions leading to mortality of larvae in natural systems. When adult bluegills were exposed to 33.3 μg/g selenomethionine through the diet and 10 ug/L waterborne selenium (Coyle et al. 1993), fry from such adults exhibited a mean survival of only 7%. As with the previous study, selenium was preferentially accumulated in reproductive organs (30–40 μg/g dry wgt) over other body tissues. The dietary organoselenium was transferred to the eggs in the ovary, and the selenium was incorporated into the stored eggs at the time of deposition and fertilization, resulting in reproductive impairment due to substantial fry mortality from failure to survive past swim-up stage at 5–7 days post-hatch. Lemly (2002) has concluded that fish ovarian or egg selenium levels greater than 10 μg/g may result in reproductive impairment.

For the Solomon River Basin, 97% of the fish collected exceeded the 4 μg/g wholebody TET. In Lemly's

"Protocol for Aquatic Hazard Assessment" (Lemly 2002), there is no selenium hazard profile for whole-body fish because the hazard profile for reproductive impairment is based instead on fish eggs. However, no fish eggs were collected from the Solomon River Basin. In absence of selenium residues from actual fish eggs, and recognizing the difficulty in obtaining gravid fish ovaries, the protocol allows for the conversion of wholebody fish selenium residues to approximate egg concentrations using the formula: fish egg selenium = fish wholebody selenium × 3.3 (Lemly and Smith 1987; Skorupa et al. 1996). Thus, Solomon River wholebody fish selenium concentrations (mean basis) converted to approximate fish egg concentrations (mean basis, dry wgt) are presented in Table 6a and range from 10.3 to 42.6 μg/g selenium. The hazard profile for selenium-induced reproductive impairment in fish, based on fish egg concentrations (μg/g dry wgt), is as follows (Lemly 1995, 2002): >20 μg/g, high; 10–20 μg/g, moderate; <5–10 μg/g, low; 3–5 μg/g, minimal; and <3 μg/g, none. Since 19 out of 20 fish species collected from the Solomon River exhibited computed mean selenium concentrations in fish eggs >20 μg/g, the fish egg component receives a high hazard rating, or a score of 5.

Aquatic hazard assessment for the solomon river basin: Lemly method

The Solomon River Basin has been the subject of a selenium concentration monitoring survey. This study has reported the collection and evaluation of that monitoring data based on published TETs and selenium hazard profiles developed by Lemly (1995, 2002). The numerical ranking for each ecosystem component from the hazard profiles was conducted with results as follows: water, 5; sediment, 2; macroinvertebrates, 5; fish eggs, 5. The aquatic hazard assessment for the entire Basin was then determined by adding up the numerical ranking of each ecosystem component from the profiles, the sum of which was 17. This sum was then compared to the aquatic hazard assessment ranking scale: 15–20=high hazard – sufficient to cause reproductive failure in sensitive species of fish and birds; 11–14=moderate hazard – sufficient to impair but not eliminate reproductive success; 8–10=low hazard – some sensitive species could have reproductive success marginally affected, but most species unaffected; 5–7=minimal hazard – concentrations of selenium may be marginally elevated in one or more ecosystem components but no imminent toxic threat; 4 =no hazard – selenium concentrations are not elevated in any ecosystem component, thus no toxic threat identified. The sum of 17 obtained from adding up the four ecosystem component numerical rankings for water, sediment, macroinvertebrates, and fish eggs determined from the individual component selenium hazard profiles falls within the 15–20 high hazard ranking, classifying the Solomon River Basin as a "high hazard" for selenium.

Assessment of data with other toxic effect thresholds

In addition to the work of Lemly, TETs have been reported by others (Table 1), and these include TETs for water (Peterson and Nebeker 1992; U.S. Environmental Protection Agency 2005), sediment (Van Derveer and Canton 1997), and fish diet, wholebody fish, and fish ovaries (DeForest et al. 1999; Skorupa et al. 1996). Whereas the TET for water has been determined at 2 μg/L by Lemly (2002) and Peterson and Nebeker (1992), the U.S. Environmental Protection Agency (2005) has established a criteria continuous concentration (CCC) of 5 μg/L for total recoverable selenium in water. For the North Fork, 31 out of 45 collected water samples (69%) exhibited selenium concentrations exceeding 5 μg/L. In contrast, in the South Fork, only three samples out of 36 (8%) exceeded 5 μg/L. While selenium concentrations in sediment were <Lemly's 2 μg/g TET, they were also well under the >4 μg/g TET proposed by Van Derveer and Canton (1997). For fish diet (invertebrates), mean selenium concentrations from all sites well exceeded Lemly's 3 μg/g TET (Table 5). While one site was within Skorupa's 3–8 μg/g TET (7.60 μg/g ± 4.2), mean selenium concentrations from all other sites exceeded the upper TET limit of 8 μg/g. Invertebrate selenium means from seven out of the 10 sites equalled or exceeded the 10 μg/g TET proposed by DeForest et al. (1999) for warmwater fishes. On a site mean basis (Table 6b), all selenium concentrations in fish exceeded both Lemly's and Skorupa's TETs of 4 μg/g and 4–6 μg/g, all but one site exceeded the EPA chronic criterion value of 7.91 μg/g, and five sites exceeded the 9 μg/g warmwater fish TET proposed by DeForest et al. On a species mean basis (Table 6a), selenium concentrations in all but one species (long-nose gar, *L. osseus*) exceeded the 4 μg/g and 4–6 μg/g TETs, 75% of the species exceeded the 7.91 μg/g EPA

chronic criterion, and 50% exceeded the 9 μg/g TET for warmwater fishes. On a fish egg mean basis, all species exceeded Lemly's 10 μg/g TET for fish ovaries, and all but one species exceeded the 17 μg/g TET for this matrix proposed by DeForest et al. Thus, even when using less conservative TETs proposed by others, the Solomon River Basin ranks as a watershed highly contaminated with selenium.

Population impacts

Generally, fish produce excess numbers of young to sustain the population, but most of the offspring undergo rapid mortality from predation, starvation, and environmental fluctuations so that only a few individuals survive until recruitment into the reproductive cohort. Thus, eventual reproductive success is dependent upon demographic factors such as fecundity, survival, reproductive life-span and immigration/emigration rates (Berryman 1981). The addition of a contaminant can result in localized mortality or possibly total absence of a fish year class, but populations usually persist due to immigration or alternating years of strong year classes. However, if the contaminant is selenium, the effect can be repeated loss of year classes and depletion of the fish population. In these cases the resulting population undergoes an alteration in normal structure to one either dominated by mature adults (Gillespie and Baumann 1986) or a complete eradication of the fish population (Lemly 1985b, 2002). The sampling of fish populations and comparing population structures from high and low selenium areas enables an analysis of population-level effects and a determination of whether population impacts are occurring.

Population profiles from four of the most prevalent collected species from the Solomon River Basin are presented in Fig. 4. These plots of selenium

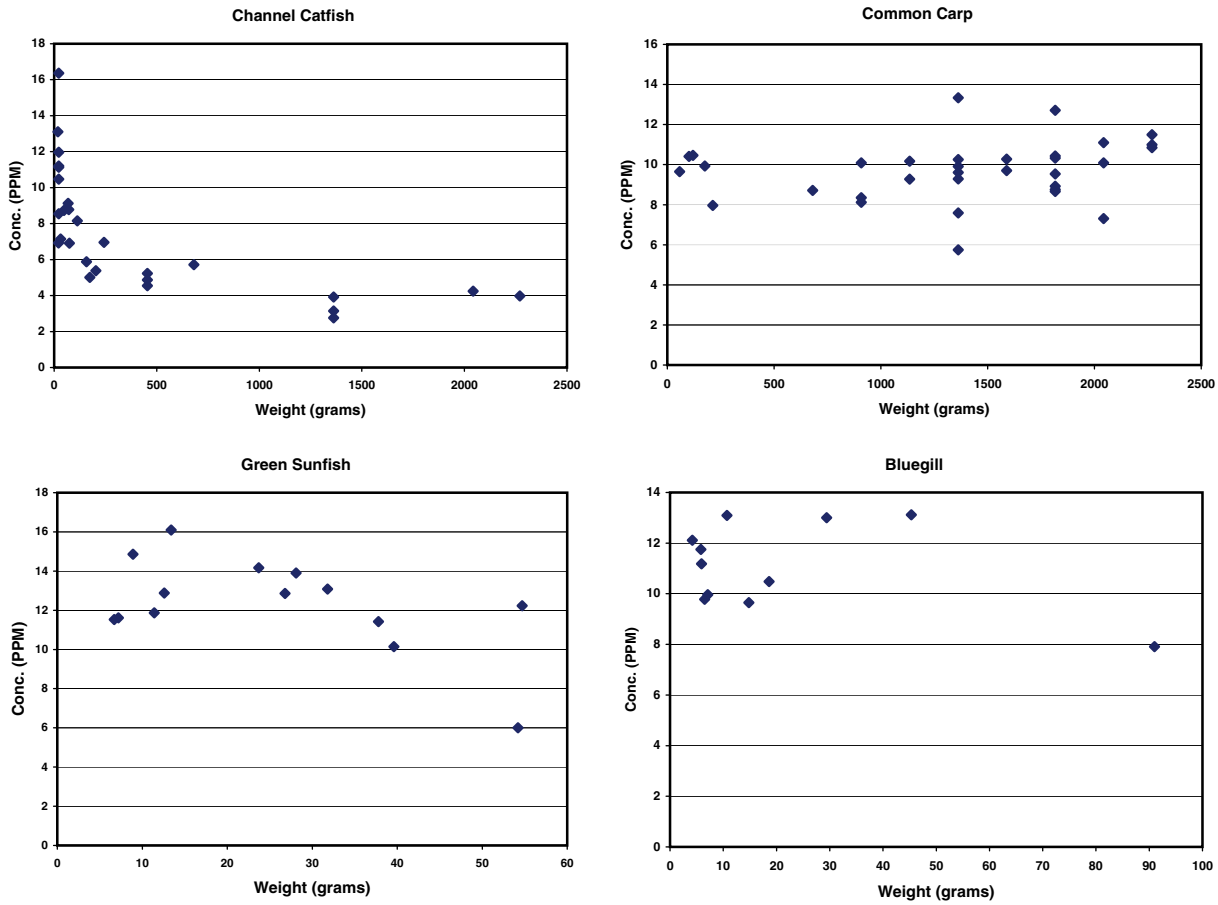

Fig. 4 Selenium concentrations vs weight for four species of individual fish collected from the Solomon River Basin, 1998

concentration vs individual fish weight show the presence of apparently very young fish, some in significant numbers, containing concentrations of selenium that clearly exceed the TET of 4 μg/g. For most species, selenium concentrations did not vary with size of fish; one exception, however, is channel catfish where selenium concentrations begin to decrease at the size of approximately 100 g. This supports ecological observations that channel catfish switch from feeding on invertebrates at early life stages (e.g.<100 g) but eventually switch to omnivory at adulthood (Bailey and Harrison 1948). Our observation that selenium concentrations decrease at larger sizes in channel catfish further confirms the existing literature indicating that selenium concentrations are higher in species that feed on aquatic insects or forage fishes.

Similar patterns were seen in the Republican River Basin (May et al. 2001) and indicates the need in both river Basins for further research to actually access reproductive impairment. The observation of very young fish with high levels of selenium might suggest some successful recruitment, in spite of wholebody selenium levels exceeding TETs. However, no fish studies have been initiated in the Solomon River Basin to determine if reproductive impairment or other population impacts have actually occurred. Hamilton and Lemly (1999) have indicated that faunal surveys, by themselves, are insufficient to detect the presence or lack of contaminant impacts in an open river system due to the possibility of immigration of individuals from the population in nonaffected river reaches or tributary streams. Skorupa (1998) also has reported that instream studies commonly report the "counterintuitive combination" of high selenium fish levels associated with a normal and diverse fish fauna. Furthermore, monitoring of fish populations in rivers is "an insensitive measure of contaminant effects unless substantial effort is made to assess the health of the fish community" (Hamilton and Lemly 1999). Thus, there is a growing need for the results of monitoring surveys on open river systems, as reported here for the Solomon River and elsewhere for the Republican River (May et al. 2001), to be augmented by detailed biological studies which will define and confirm the presence and degree of reproductive impairment among indigenous fish species. The results from such research will provide resource managers with scientifically-derived information necessary for the continued evaluation and growth of fishery and aquatic waterfowl resources in the region as well as directions for adaptive management of irrigation systems.

Conclusions

Water collected from 85% of the sites in the Solomon River Basin had selenium concentrations exceeding the 2 μg/L TET for one or more collection periods. The North Fork exhibited many more sites (42%) than the South Fork where selenium concentrations exceeded 5 μg/L. Values >5 μg/L on the selenium hazard profile ranked water in the Basin as a high hazard for accumulation of selenium in the planktonic food chain with resultant dietary toxicity to fish and aquatic birds. All sediment samples from either fork of the river were less than the 2 μg/g TET, presumably due to the shallow, flowing oxygenated character of this lotic system. Based on the sediment hazard profile, sediment in the Basin was ranked to be a minimal hazard for accumulation of selenium in benthic food-chain and dietary toxicity to fish and aquatic birds. Thus, in the Solomon River Basin, a planktonic food chain dynamic takes precedence over a sediment-detrital food chain dynamic. All invertebrate samples had selenium concentrations exceeding the 3 μg/g TET, and all except one sample exceeded 5 μg/g. According to the invertebrate hazard profile, any invertebrate selenium concentration in excess of 5 μg/g ranks this matrix as a high hazard of selenium from dietary toxicity and reproductive impairment in fish and aquatic birds. Virtually the entire fish sample set (97%) exhibited selenium concentrations exceeding the 4 μg/g TET for health and reproductive success of freshwater fish. To utilize the fish egg hazard profile for selenium, fish egg concentrations were computed from wholebody fish concentrations. On a species mean basis, all fish egg selenium concentrations, except for longnose gar, exceeded 20 μg/g. The hazard profile states that any fish egg concentration exceeding 20 μg/g ranks this ecosystem component as a high hazard for selenium-induced reproductive impairment in freshwater fish. Given the high hazard ranking for the water, macroinvertebrate, and fish egg ecosystem components, the Solomon River Basin ranked as a high hazard for selenium being a toxic threat sufficient to cause reproductive failure in sensitive species of fish and aquatic birds. An examination of population structures for several

fish species revealed the presence of very young fish with high levels of selenium. This may indicate that proposed thresholds for protection of fish are conservative; alternatively, this may imply that fish have emigrated from low exposure environments into high exposure environments where they were caught. These same patterns, both in ecosystem component selenium levels and in fish population structures, were evident also for the Republican River Basin just to the north (May et al. 2001). To date, detailed biological studies have not been conducted on either Basin. Such studies are needed to determine the true impact of selenium on fish and wildlife resources.

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