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Abstract

Mercury (Hg) and selenium (Se) biomagnify in aquatic food webs and are toxic to fish and wildlife. The authors measured Hg and Se in organic matter, invertebrates, and fishes in the Colorado River food web at sites spanning 387 river km downstream of Glen Canyon Dam (AZ, USA). Concentrations were relatively high among sites compared with other large rivers (mean wet wt for 6 fishes was 0.17–1.59 $\mu g g^{-1}$ Hg and 1.35–2.65 $\mu g g^{-1}$ Se), but consistent longitudinal patterns in Hg or Se concentrations relative to the dam were lacking. Mercury increased (slope = 0.147) with $\delta^{15}N$, a metric of trophic position, indicating biomagnification similar to that observed in other freshwater systems. Organisms regularly exceeded exposure risk thresholds for wildlife and humans (6–100% and 56–100% of samples for Hg and Se, respectfully, among risk thresholds). In the Colorado River, Grand Canyon, Hg and Se concentrations pose exposure risks for fish, wildlife, and humans, and the findings of the present study add to a growing body of evidence showing that remote ecosystems are vulnerable to long-range transport and subsequent bioaccumulation of contaminants. Management of exposure risks in Grand Canyon will remain a challenge, as sources and transport mechanisms of Hg and Se extend far beyond park boundaries.

Introduction

Mercury (Hg) and selenium (Se) contamination of lotic eco-systems pose widespread and persistent exposure risks to aquatic organisms and the terrestrial animals that feed on them [1]. In the United States, for example, Hg concentrations in stream fish exceed wildlife risk thresholds for belted kingfisher (Megaceryle alcyon), a piscivorous bird, in 35% to 75% of stream and river reaches [2,3]. In addition, 1 840 000 km of streams and rivers are under human fish consumption advisories for Hg contamination [4]. Mercury is commonly introduced to lotic ecosystems by atmospheric deposition and watershed runoff [5,6], and Se may be introduced from point sources such as coal ash [7,8] or from irrigation returns in landscapes with seleniferous soils [9].

We investigated Se and Hg exposure in the Colorado River food web in Grand Canyon, Arizona, USA. Mercury and Se concentrations exceed dietary fish and wildlife toxicity thresh-olds throughout the Colorado River Basin, and Se concen-trations are particularly high [10,11]. Data on contaminant exposure are generally lacking from the Grand Canyon segment, owing to the difficulty of collecting samples from such a remote and inaccessible area. Atmospheric deposition is a common vehicle for Hg introduction to aquatic ecosystems in remote areas of the world including western US national parks [12,13]. Potential sources of atmospheric Hg deposition to the Grand Canyon ecosystem include a large regional atmospheric pool, and nearby point sources such as a coal burning power plant located near Page, Arizona, northeast of Grand Canyon [14]. Reactive forms of inorganic Hg in aquatic systems can be converted to methylmercury (MeHg) via microbial processes in sediment, algal mats, or periphyton biofilms [15,16], and MeHg efficiently biomagnifies through aquatic food webs [17]. The primary source of Se to the Grand Canyon segment is runoff associated with irrigation of seleniferous soils in the upriver watershed [9], with Se loads entering Lake Powell, the reservoir upstream of Grand Canyon, approaching 30 MT y^{-1} [18].

We measured Hg and Se concentrations in basal resources and consumers at 6 sites spanning 387 river km downstream of Glen Canyon Dam, which forms Lake Powell on the Colorado River. Our objectives were to describe the magnitude and spatial extent of Hg and Se accumulation in the Colorado River food web, to quantify biomagnification of Hg and Se in the food web, and to compare Hg and Se concentrations in the food web with established risk thresholds for dietary exposure. Glen Canyon Dam operations strongly influence food web structure and ecosystem processes of the Colorado River [19–21], but the degree to which exposure varies downstream of the dam is unknown. Primary productivity and the degree of lentic influence are high near the dam and decline with downstream distance [19,20], and these could affect patterns of Hg and Se exposure in lotic food webs. For example, Hg accumulation in food webs is thought to decline with primary productivity in streams [22]. Concentrations could be higher at the dam because lentic habitats such as Lake Powell are conducive to Hg and Se biotransformation and remobilization, and their bioavailable forms (e.g., MeHg, selenite, and selenoamino forms) are exported to downstream ecosystems [23,24], although that may not always be the case for Hg [25]. This is particularly true for MeHg; stratification and wetting and drying cycles can increase MeHg production and subsequent release to downstream food

webs [26]. Alternatively, higher productivity near the Glen Canyon Dam could lead to either bloom dilution (i.e., whereby algal cell division distributes a fixed amount of contaminant among an increased number [and mass] of cells, resulting in lower contaminant concentration) [27], somatic growth dilution, or a combination of the 2, so concentrations in consumers could be lower in this more productive reach. Lower accumulation with higher productivity has been demonstrated for Hg in lotic systems [22,28], but less is known about how primary productivity affects Se bioaccumulation.

MATERIALS AND METHODS

Study area

Detailed descriptions of the study reach and sample sites (Figure 1) are provided in Cross et al. [19]. Briefly, average thalweg depth and width of the river are 6 m and 89 m, respectively, at a discharge of 225 $m^3 s^{-1}$. River kilometer 0 (RKM0) is located in the clear, tailwater section of the river downstream of Glen Canyon Dam [20]. River kilometer 48 (RKM48) is in Marble Canyon and is downstream of the Paria River, the first perennial tributary entering the Colorado River below the dam. The Paria River contributes suspended sediments and organic matter to the river, and invertebrates and fishes living downstream of this confluence consume less algae and more detrital material compared with those at RKM0 [19,21]. River kilometer 100 (RKM100) is downstream of the confluence of the Little Colorado River, the largest tributary in the Grand Canyon segment, with a drainage area of almost 70 000 km^2. River kilometer 204 (RKM204) is downstream of several additional tributaries and is located within the Middle Granite Gorge section of the river. River kilometer 264 (RKM264) is located downstream of 3 large tributaries, and river kilometer 362 (RKM362) is located in the last accessible reach whose stage is not influenced by Lake Mead, the next reservoir on the Colorado River.

Sample collection

Sampling occurred from 12 to 28 June 2008. At each site, we collected representative basal resources (organic matter and primary producers), macroinvertebrates, and fishes. Basal resources included fine benthic organic matter, seston (suspended organic matter), epilithon (benthic biofilm), attached algae (*Cladophora* sp.), and epiphyton (diatoms attached to *Cladophora*). We collected fine benthic organic matter from sandy depositional habitats using a Ponar dredge (0.052 m^2) deployed from a boat. We made a composite of material from 5 dredge samples for a single replicate. We thoroughly mixed sediments, elutriated them several times, and then collected the fine fraction (40–250 μm) using Nitex mesh sieves. We collected seston with a nested Nitex plankton net (243-μm mesh for the inner net; 10-μm mesh for the outer net) deployed

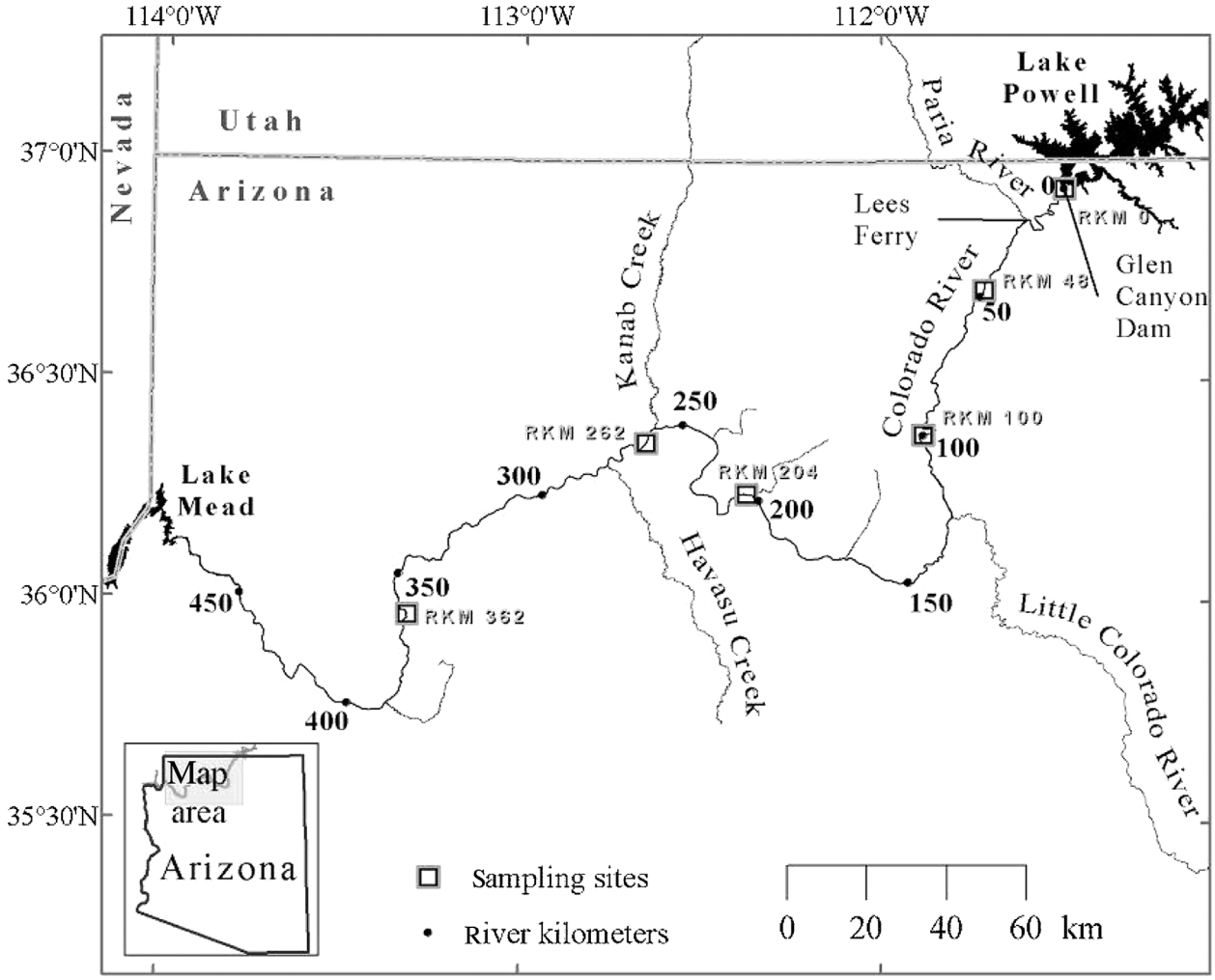

Figure 1. Map of study area showing sample location relative to Glen Canyon Dam on the Colorado River, Grand Canyon (AZ, USA).

in moderate current for up to 10 min. We processed the collected material as described for fine benthic organic matter. We gathered clumps of *Cladophora* by hand and made a composite of them in a plastic bucket with 3 L of river water. We gently squeezed and rinsed *Cladophora* by hand to remove epiphyton, and we removed a subsample for analyses. The material rinsed from *Cladophora* samples was retained and used as the epiphyton sample. The epiphyton sample was visually inspected to remove small macroinvertebrates and *Cladophora* fragments that passed the 250-μm mesh, and the fine fraction (40–250 μm) was retained using Nitex mesh sieves, similar to fine benthic organic matter. For epilithon samples, we collected 5 to 10 river cobbles and gently washed them in river water to remove fine inorganic matter and macroinvertebrates, scrubbed them with a plastic brush into a plastic tub, and processed the resulting slurry as described for fine benthic organic matter.

Macroinvertebrate assemblages near RKM0 are dominated by non-native species and include Lumbricidae, *Gammarus lacustris*, Chironomidae, Simuliidae, and New Zealand mudsnail (*Potamopyrgus antipodarum*) [29]. Soft tissue of New Zealand mudsnails was removed from shells prior to chemical analyses. We collected individuals from these taxa from a variety of river substrates including cobble, wood, and *Cladophora* and made a composite of multiple individuals of each taxon to obtain sufficient biomass for analyses. Macroinvertebrates were sampled using a combination of techniques (fully described in Tsui et al. [16]) including rock and cliff scraping, ponar grab samples, and opportunistic collection of individuals in rocky nearshore habitats.

We collected 6 fish species that are relatively common in Grand Canyon, all of which rely primarily on macroinvertebrates for prey: native bluehead sucker (*Catostomus discobolus*), flannelmouth sucker (*Catostomus latipinnis*), and speckled dace (*Rhinichthys osculus),* and non-native common carp (*Cyprinus carpio*), fathead minnow (*Pimephales promelas*), and rainbow trout (*Oncorhynchus mykiss*). Fishes were collected by boat electrofishing and seining [30], and specimens were identified and measured (total length, mm) in the field. We dissected skinless dorsal muscle tissue for chemical analyses. All fish samples were analyzed as individuals, except for 5 cases (1 rainbow trout, 4 fathead minnow samples), for which we made a composite of material from 2 to 3 individuals to obtain sufficient mass.

Samples collected for metal and metalloid analysis were processed using plastic, Teflon-coated, or rubber gear to minimize metal contamination. When possible, 4 replicate samples of each organic matter type and consumer were collected per site for both metals and stable isotope analyses. We froze metals samples in the field using a portable freezer, placed them on ice until transport to the laboratory, and froze them at –10 °C until analysis. We dried stable isotope samples in the field using a solar oven as a desiccator. Samples of organic matter were placed on filter paper in the laboratory for 1 h to 2 h to drain excess water before obtaining more accurate weight masses prior to Hg and Se analysis.

Sample analyses

Samples were analyzed for total Hg using cold vapor atomic fluorescence (Tekran Model 2600 CVAF spectrometer) following US Environmental Protection Agency method 7474. Quality control was maintained by analysis of method blanks and repeated runs of an internal standard of known concentration (250 $\mu g\ g^{-1}$, continuing calibration verification [CCV]) analyzed after every 10 samples. Matrix spike samples (field samples spiked in the laboratory and analyzed under the same conditions as the field samples) were analyzed on 20% of samples to assess accuracy. Precision was assessed through duplicate analysis of 20% of field samples and measuring the relative percent difference (RPD) of duplicates. All method blanks were less than the reporting limit (0.0001 $\mu g\ g^{-1}$). Measured CCV values averaged 249.3 $\mu g\ g^{-1}$ (± 14.1 standard deviation [SD]), and the percent recovery was 99.7% (± 5.9%). Percent recovery of matrix spikes was 100.2% (± 2.5%), and the RPD of duplicates was 7.8% (± 4.9%). Samples were analyzed for total Se using inductively coupled plasma mass spectrometry (PerkinElmer Elan DRC-e). The instrument was run for 45 min with the plasma on, and then tuned using the Auto Tune function and a 10 $\mu g\ L^{-1}$ tuning solution of Mg, Rh, and Pb in 1% nitric acid to correct for spectral interferences. We followed the same quality control procedures described for Hg analysis, except that the CCV standard was 25 $\mu g\ g^{-1}$. All method blanks were less than the reporting limit (0.0001 $\mu g\ g^{-1}$). Average measured CCV standards were 24.8 $\mu g\ g^{-1}$ (± 1.5), and percent recovery was 99.0% (± 6.1%). Percent recovery was 97.1% (± 12.1%) for matrix spikes, and the RPD of duplicates was 6.0% (± 2.3%). All concentrations (Hg and Se) are reported as $\mu g\ g^{-1}$ wet mass. We freeze-dried, milled, and homogenized samples prior to $\delta^{15}N$ analysis. The resulting homogenates were combusted and reduced to N_2 using a Finnigan Delta Plus XP CHN analyzer online with a Costech EA 1108 Element Analyser isotope ratio mass spectrophotometer. We monitored the reproducibility and accuracy of the $\delta^{15}N$ measurements by analyzing 1 standard (bovine liver, NIST no. 1577b) every 10 samples (precision of 0.04%).

Data analysis

Spatial patterns of Hg and Se accumulation were first assessed qualitatively because of the relatively small sample size ($n = 1$–4) per food web component per site and because not all taxa were present at all sites. We then modeled Hg or Se concentrations in the $\log_{10}$ scale as a linear function of $\delta^{15}N$, including categorical variables for site and a $\delta^{15}N$-by-site interaction term that allows for separate regression relationships among sites with different intercepts and slopes. Fish size can be positively related to Hg concentrations, so we first tested for fish length effects on Hg and Se concentrations using linear regression [31]. We observed no significant relationships between fish length and tissue concentrations, with the exception of a weak negative relationship between Hg and common carp ($r = –0.51$), so fish size was not used as a covariate in spatial models. We parameterized categorical variables for sites so that slope and intercept estimates for sites other than RKM0 were expressed as differences from those for RKM0. Thus, this analysis tests for variation in Hg and Se bioaccumulation among sites and for a given trophic position (using $\delta^{15}N$ as a surrogate) within a food web. This approach explicitly tests for bioaccumulation of Hg and Se bioaccumulation as a function of site or $\delta^{15}N$ against a null model with a common intercept and no slope. We used site means of $\delta^{15}N$, Hg, and Se for each food web component in the analysis. Our iterative modeling approach first compared the separate slopes and intercepts model with a reduced parameter model assuming constant slopes among sites (significant interaction term), and then compared the model with common slopes but different intercepts (significant site effect) with a reduced parameter model that had common slopes and intercepts for $\delta^{15}N$ (no site effect). We evaluated these models using Akaike information criteria (AIC), where a lower AIC indicates the preferred model

[32]. Based on preliminary model results, we further pooled data for δ^{15}N, Se, and Hg across sites to estimate biomagnification of Se and Hg within the Colorado River food web using the equation from Lavoie et al. [17]

$$\log_{10}[\text{Hg or Se}] = \delta^{15}\text{N}\,(b) + a$$

The slope (b) of this model describes the average biomagnification for the entire food web [17,33].

We quantified potential risks of exposure to fish, wildlife, and humans by comparing Hg and Se concentrations in the Colorado River food web with literature-based toxicity thresholds (hereafter termed *risk thresholds*; see Hinck et al. [10]). Again, we pooled data across sites and within food web components for these comparisons because we did not detect consistent patterns among sites. Risk thresholds for Hg (wet wt) are 0.1 $\mu g\,g^{-1}$ for piscivorous mammals, 0.2 $\mu g\,g^{-1}$ for fish (i.e., the concentration in food that could cause harmful exposure to fish), and 0.3 $\mu g\,g^{-1}$ for human consumption. We also included a risk threshold of 0.03 $\mu g\,g^{-1}$ for belted kingfisher [2]. Kingfishers are common in Grand Canyon and serve as a realistic model of avian exposure for consumers of small-bodied fishes. Risk thresholds for Se (wet w) are 0.75 $\mu g\,g^{-1}$ for piscivorous wildlife and 1.0 $\mu g\,g^{-1}$ for larval fish [10]. Larval fish can be exposed via diet or maternal transfer, so this risk threshold can be applied to food items (e.g., macroinvertebrates) or to concentrations in adult, parental fishes.

Whole-body samples are typically analyzed for Hg, but this was not possible in the present study because of limited space for freezing samples during the boat-based sampling trips required for the present study. The Hg concentration in the muscle tissue we collected are typically higher than whole-body samples [31]. To normalize measured fish concentrations to established risk thresholds and to other data sets, we converted muscle tissue concentration to whole-body concentrations using the equation from Peterson et al. [31]

$$\log\,[\text{filet biopsy Hg}] = 0.2545 + 1.0623\log\,[\text{whole-fish Hg}]$$

where the intercept differing from 0 determines the need for a correction factor. Following this approach, we calculated tissue-corrected risk thresholds for various consumers of fish. These were 0.04 $\mu g\,g^{-1}$ for belted kingfisher, 0.16 $\mu g\,g^{-1}$ for piscivorous mammals, and 0.32 $\mu g\,g^{-1}$ for piscivorous fish. There are no published filet to whole-body Se regressions available, so we analyzed data for 20 bluegill sunfish (*Lepomis macrochirus*) samples published by the North American Metals Council [34] and determined that Se whole-body and muscle tissue concentrations were approximately 1:1 (log[whole body Se] = –0.0282 + 1.057 log [filet biopsy Se]; $r^2 = 0.96$). Thus, we treated muscle and whole-body Se concentrations as equivalent for risk threshold analysis.

RESULTS

Patterns in Hg and Se accumulation

We detected measurable concentrations of Hg and Se throughout the Grand Canyon segment of the Colorado River, and these contaminants were present in all compartments of the food web. Generally, we did not find consistent longitudinal patterns in Hg and Se concentrations in food webs (Figures 2 and 3). The Hg concentrations tended to be either uniform across sites within organic matter types or taxa, or varied across space but without consistent downstream trends. In contrast, Hg

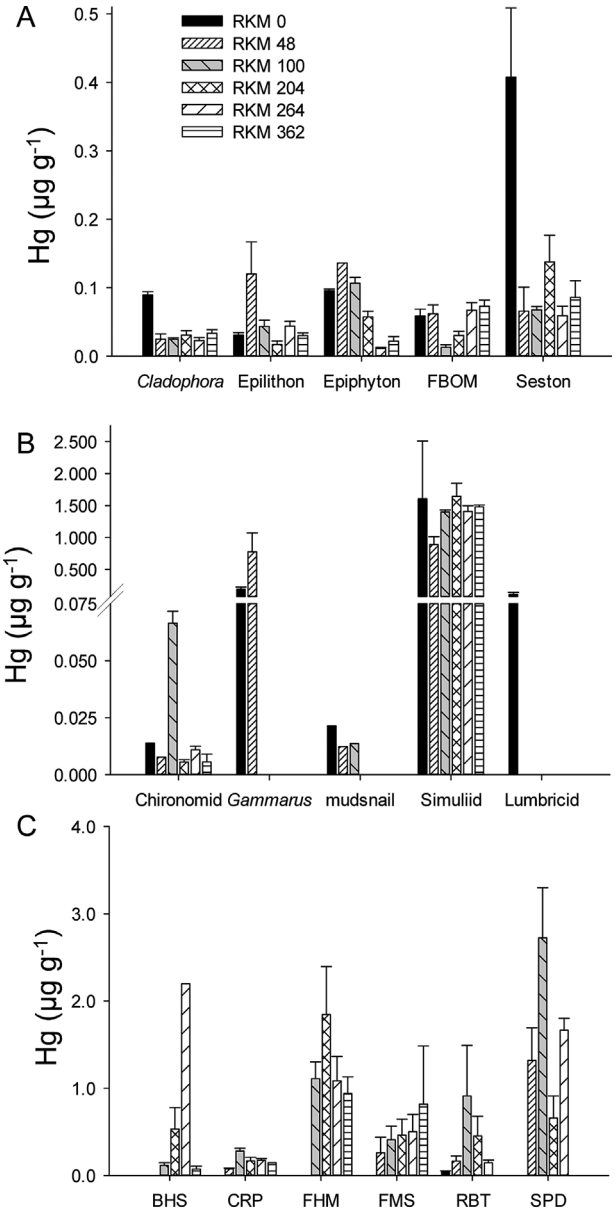

Figure 2. Mercury concentration ($\mu g\,g^{-1}$ wet wt) in (**A**) basal organic matter resources, (**B**) invertebrates, and (**C**) fishes for 6 sites in the Colorado River in Grand Canyon (AZ, USA). Bars show standard error ($n = 3$–4 samples per site). Rainbow trout was the only species collected at RKM0. Missing bars indicate that no samples of that type were collected at a particular site. RKM = river kilometer; BHS = bluehead sucker; CRP = common carp; FHM = fathead minnow; FMS = flannelmouth sucker; RBT = rainbow trout; SPD = speckled dace.

concentrations in seston ($0.41 \pm 0.18\,\mu g\,g^{-1}$) and *Cladophora* ($0.9 \pm 0.009\,\mu g\,g^{-1}$) were considerably higher at RKM0 than at other sites (Figure 2). In addition, Hg concentrations in native flannelmouth sucker showed a consistent, albeit minor, downstream increase. The Se concentrations in seston and fine benthic organic matter were also highest at RKM0 and declined sharply at RKM48 (Figure 3). Similar patterns were apparent for *Gammarus* and simuliids, except that neither showed a peak at RKM0. There were no apparent spatial patterns in the Se concentrations in fish tissues.

We found no effect of site for either Hg or Se concentrations in the multivariate δ^{15}N-site models. For Hg, the slopes for δ^{15}N versus Hg were similar among sites (nonsignificant interaction term), and site was unrelated to Hg concentration (common

intercept). The AIC supported the $\delta^{15}N$ versus Hg concentration model with common slopes and intercepts among sites (AIC = 135.1, with a difference in AIC of 5.8 compared with next best model), and this model showed a positive relationship between $\delta^{15}N$ and Hg ($F_{1,64} = 16.22$, $p = 0.0002$). The model including $\delta^{15}N$ (common slopes and intercepts) indicates bioaccumulation of Hg with trophic position and is superior to the null model (common intercept, no slope) of no bioaccumulation with increasing trophic position. None of the models were significant for Se, but the AIC gave strongest support to the $\delta^{15}N$ versus Se model with common slopes and intercepts among sites (AIC = 144.7, with a difference in AIC of 7.5 compared with next best model), even though the slope did not differ from zero ($F_{1,64} = 1.44$, $p = 0.23$).

Mean Hg concentration ($\log_{10}$ wet wt) throughout the Colorado River food web was significantly and positively related to $\delta^{15}N$ ($r^2 = 0.32$, $p = 0.02$; Figure 4A), but Se concentration was not ($r^2 = 0.05$, $p = 0.4$; Figure 4B). The relationship with Se was weak because of high variability in Se concentrations among macroinvertebrates. Chironomids and New Zealand mudsnails, in particular, represented large, negative outliers in the regression (studentized residuals > |2.0|). When they were excluded from the analysis, the relationship improved but remained nonsignificant ($r^2 = 0.17$, $p = 0.15$). The slope of this regression was positive, but low ($b = 0.06$), indicating little biomagnification of Se within the food web.

Exposure risks to consumers

Concentrations of Hg in simuliids and *Gammarus* exceeded the risk threshold (0.2 μg g^{-1}) for juvenile and adult fishes (Table 1 and Figure 5A). Mean Hg concentrations for all fish species exceeded the risk threshold for piscivorous mammals (0.16 μg g^{-1}), with individual samples exceeding the threshold in 38% to 100% of cases, depending on the species of fish (Table 1). Mean Hg concentration for all fish species except

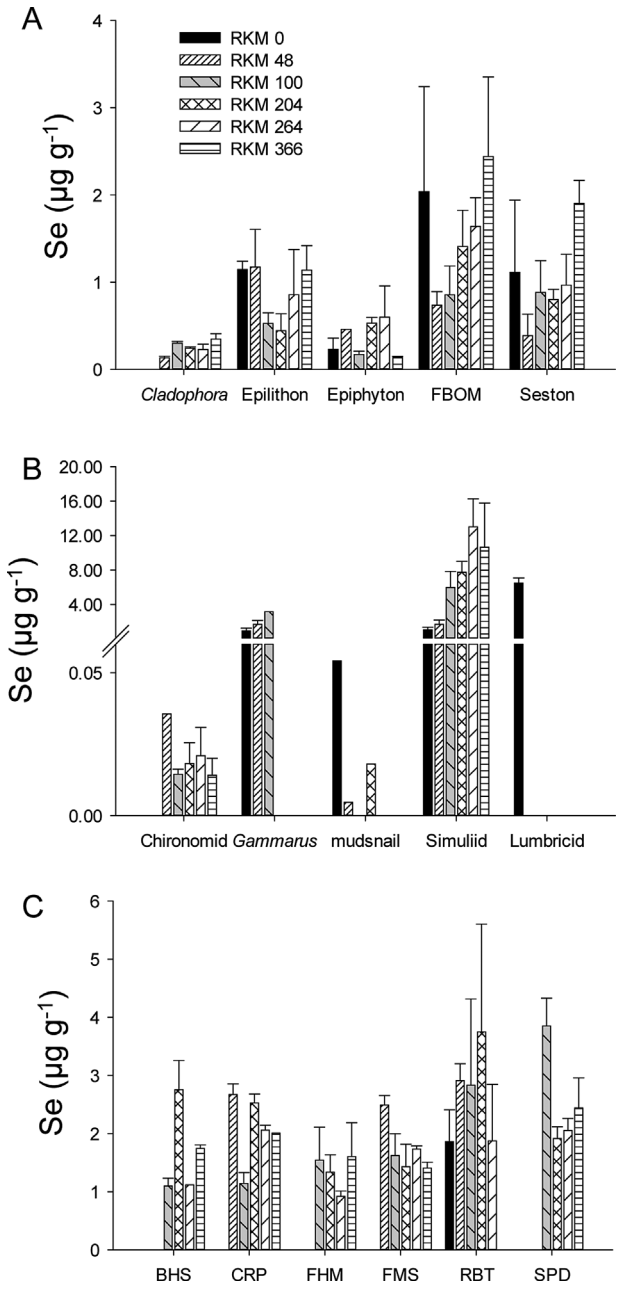

Figure 3. Selenium concentration (μg g^{-1} wet wt) in (**A**) basal organic matter resources, (**B**) invertebrates, and (**C**) fishes for 6 sites in the Colorado River in Grand Canyon (AZ, USA). Bars show standard error ($n = 3$–4 samples per site). Rainbow trout was the only species collected at RKM0. Missing bars indicate that no samples of that type were collected at a particular site. RKM = river kilometer; BHS = bluehead sucker; CRP = common carp; FHM = fathead minnow; FMS = flannelmouth sucker; RBT = rainbow trout; SPD = speckled dace.

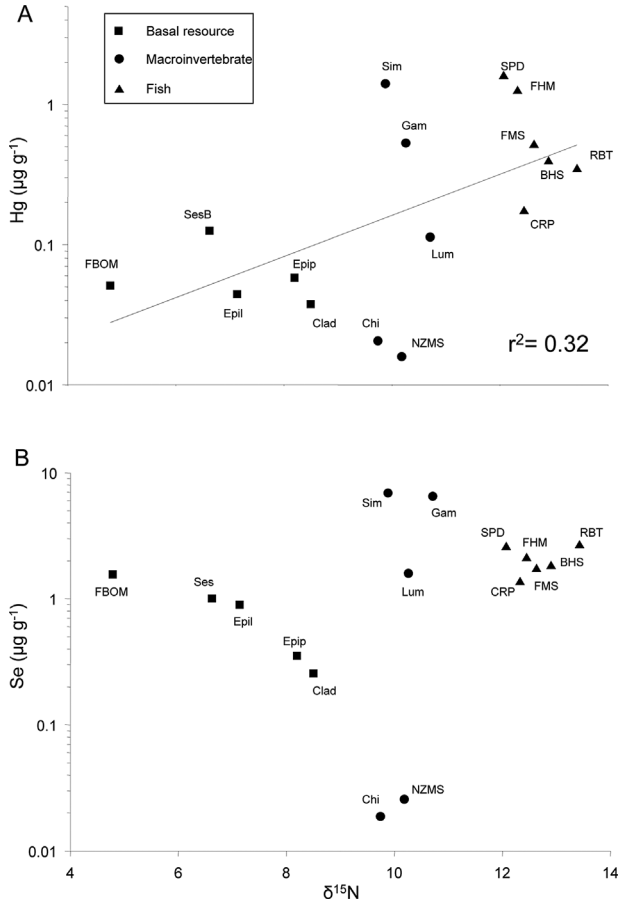

Figure 4. Concentrations (μg g^{-1} wet wt) of Hg (**A**) and Se (**B**) relative to $\delta^{15}N$ for the Colorado River food web in Grand Canyon (AZ, USA). Model regression in (**A**) is: $\log_{10}Hg = 0.147(\delta^{15}N) - 2.259$. BHS = bluehead sucker; Chi = chiromonid; Clad = *Chladophera*; CRP = common carp; Epil = epilithon; Epip = epiphyton; FBOM = fine benthic organic matter; FHM = fathead minnow; FMS = flannelmouth sucker; Gam = *Gammarus;* Se = seston; Lum = lumbricid; NZMS = New Zealand mudsnail; RBT = rainbow trout; Sim = simuliid; SPD = speckled dace.

Table 1. Percentage of collected samples exceeding risk thresholds for mercury and selenium exposure in the Colorado River food web, Grand Canyon

	Mercury[a]			Selenium[b]	
	% > PM	% > fish	% > human	% > PW	% > larval fish
Basal resources					
Cladophora	n.a.	0	n.a.	n.a.	0
Epilithon	n.a.	0	n.a.	n.a.	39
Epiphyton	n.a.	0	n.a.	n.a.	5
FBOM	n.a.	0	n.a.	n.a.	59
Seston	n.a.	17	n.a.	n.a.	43
Macroinvertebrates					
Chironomid	n.a.	0	n.a.	n.a.	0
Gammarus	n.a.	57	n.a.	n.a.	86
Lumbricid	n.a.	0	n.a.	n.a.	100
New Zealand mudsnail	n.a.	0	n.a.	n.a.	0
Simuliid	n.a.	100	n.a.	n.a.	88
Fish[c]					
Bluehead sucker	38	23	23	100	85
Common carp	71	6	6	94	94
Fathead minnow	100	100	100	81	56
Flannelmouth sucker	67	52	52	95	95
Rainbow trout	55	40	20	100	80
Speckled dace	100	94	94	100	100

[a]Mercury risk thresholds: PM (piscivorous mammals) = 0.16 μg g^{-1}; fish = 0.2 μg g^{-1}; human = 0.3 μg g^{-1}.
[b]Selenium risk thresholds: PW (piscivorous wildlife) = 0.75 μg g^{-1}; larval fish = 1.0 μg g^{-1}.
[c]Percentages for fish species under "% > fish" are based on a risk threshold of 0.32 μg g^{-1} Hg to account for differences between fish tissue and whole-body concentrations.
n.a. = not applicable; FBOM = fine benthic organic matter.

common carp exceeded the risk threshold for humans (0.3 μg g^{-1}). Although mean rainbow trout Hg concentrations exceeded the human risk threshold, only 20% of individual trout exceeded the threshold. All these samples came from downstream reaches in Grand Canyon. Concentrations in 100% of speckled dace and fathead minnow greatly exceeded the risk threshold for belted kingfisher (0.04 μg g^{-1}), and average Hg concentrations for these small-bodied fish species were 30- to 40-fold higher than the risk threshold.

Selenium concentrations were 5- to 10-fold higher than Hg concentrations for organic matter resources and macroinvertebrates (Figure 5B), except that Hg and Se concentrations were similar for chironomids (0.02 μg g^{-1} for both Hg and Se) and New Zealand mudsnails (0.02 μg g^{-1} Hg and 0.03 μg g^{-1} Se). Among organic matter types, for example, Se concentration was lowest for *Cladophora* (0.26 ± 0.10 μg g^{-1}) and highest for fine benthic organic matter (1.56 ± 1.37 μg g^{-1}). Selenium concentrations for macroinvertebrates were again highest for simuliids (6.90 ± 6.53 μg g^{-1}), and values for lumbricids were similarly high (6.49 ± 1.0 μg g^{-1}). Concentrations in these taxa were more than 2 orders of magnitude higher than those in New Zealand mudsnails and chironomids and were approximately 2-fold higher than concentrations measured in fishes.

Selenium concentrations were similar among fishes, ranging from 1.35 μg g–1 (± 0.84 μg g^{-1}) in fathead minnow to 2.65 μg g^{-1} (± 2.22 μg g^{-1}) in rainbow trout. Mean Se concentrations of all species were approximately 2- to 4-fold higher than the risk threshold for piscivorous wildlife (0.75 μg g^{-1}), with individual samples exceeding the threshold in 81% to 100% of cases among species (Table 1). The risk value for larval fishes, which can be exposed via maternal transfer of Se to eggs or via diet, is 1.0 μg g^{-1}. Mean concentrations in all fishes (e.g., maternal transfer vector) exceeded this threshold, with individual samples exceeding the threshold in 56% to 100% of cases among species (Figure 5B and Table 1). Likewise, mean concentrations of simuliids, *Gammarus*, and lumbricids (dietary vectors) also exceeded this threshold (e.g., mean concentrations of simuliids were approximately 7-fold higher), with individual samples exceeding the threshold in 86% to 100% of cases among these invertebrate taxa.

DISCUSSION

Mercury and Se are leading causes of impairment of lotic ecosystems [4], and the present study demonstrates that these contaminants are pervasive in food webs of the Colorado River in Grand Canyon. Measurable concentrations of Hg and Se were detected in all food web compartments and across all sites, and concentrations commonly exceeded risk thresholds. Mercury and Se concentrations in some basal resources were greatest just downstream from Lake Powell (RKM0), suggesting that this reservoir is exporting bioavailable forms of these elements to the downstream ecosystem, although other local processes, such as methylation of mercury in *Cladophora* beds, could play a role as well [16]. In either case, this did not translate into elevated concentrations of these elements in invertebrates or fish at this site. Moreover, Hg and Se concentrations in rainbow trout at RKM0, a popular sport fishery, were the lowest for any site, and Hg concentrations were well below risk thresholds for human consumption. Concentrations of Hg and Se in native and non-native fishes present in downstream reaches of Grand Canyon often exceeded risk thresholds for humans and wildlife. A positive relationship between δ^{15}N and Hg concentrations indicates that biomagnification contributes to elevated Hg concentrations observed in fish in Grand Canyon. Collectively, these results demonstrate that aquatic food webs in Grand Canyon have elevated concentrations of Hg and Se, and additional research into pathways of exposure is warranted. These data represent an advance in our understanding of contamination of Hg and Se in food webs of large southwestern rivers and in particular food webs downstream of large dams.

Damming of river systems has the potential to increase Hg and Se accumulation in stream food webs by linking lotic ecosystems to lentic habitats that often serve as sources of bioavailable forms of these elements [24,35–38]. This is particularly true in the Colorado River Basin, where large reservoirs proliferate [39] and sources of contaminants are abundant (e.g., Se) [18] or proximate to reservoirs (e.g., Hg) [14,40]. In the present study we found no significant differences in Hg and Se accumulation among sites throughout the Grand Canyon. Although this is only 1 study, these findings suggest that there is little evidence for spatial gradients downstream of large impoundments characterized by hypolimnetic releases; however, it is likely that Lake Powell contributes disproportionately to bioavailable Hg entering the food web near the dam (RKM0). Mercury concentration in seston was 4-fold higher at RKM0 than other sites, and primary and secondary production is also high compared with downstream sites [19]. Seston is consumed by aquatic invertebrates in the river [21]. Moreover, diatoms derived from Lake Powell constitute the majority of the seston in this reach (60% by biomass) [21]. Filter-feeding simuliids are an important prey item for fishes throughout the segment we studied (nearly all simuliid production in the river is consumed by fishes) [19], and consumption of simuliids could be an important pathway for Hg into fishes. Mercury

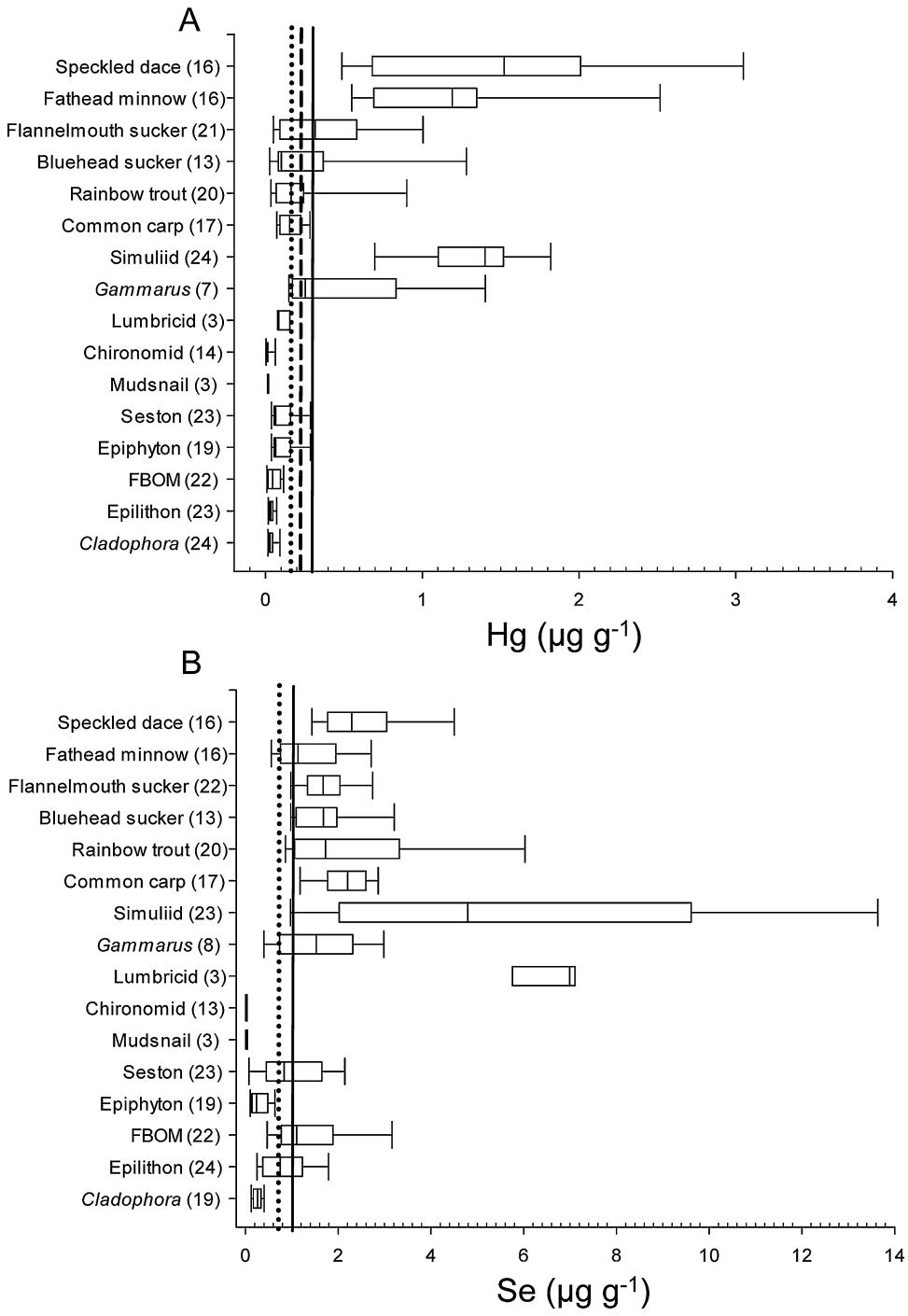

Figure 5. Concentrations (µg g^{-1} wet wt) of Hg (**A**) and Se (**B**) in organic matter and consumers among all sites sampled in the Colorado River, Grand Canyon (AZ, USA). Numbers in parentheses indicate number of replicates analyzed for each component. Lines within the boxes are the median, and horizontal whiskers indicate the 90th and 10th percentiles. Vertical lines in the Hg plot are risk thresholds for piscivorous mammals (0.16 µg g^{-1}; dotted line), fish (0.2 µg g^{-1}; dashed line), and humans (0.3 µg g^{-1}; solid line). The whole-body–corrected risk threshold for kingfisher (0.04 µg g^{-1}) is not included in the figure because all fishes exceeded this threshold. Vertical lines in the Se plot are risk thresholds for piscivorous wildlife (0.75 µg g^{-1}; dotted line) and larval fish (1.0 µg g^{-1}; solid line). FBOM = fine benthic organic matter.

concentrations in fish were generally lower than those in simuliids, possibly because these fishes are relatively omnivorous and consume other resources (e.g., diatoms, *Cladophera*, and fine benthic organic matter) [19] with relatively low Hg concentrations.

The apparent disconnect between high Hg and Se concentrations in basal resources and low concentrations in consumers at RKM0 is likely because of food web structure and the trophic ecology of invertebrates in this segment. Specifically, *Cladophora*, seston, and fine benthic organic matter, the 3 basal resources with elevated Hg or Se at RKM0, do not constitute a substantial portion of invertebrate diets [21], with the exception of seston-feeding simuliid larvae. Concentrations of Hg and Se were high in simuliids across all sites, including RKM0, and we attribute this pattern to their reliance on seston that is partially sourced from Lake Powell. Coupling energy flow food webs [41] with our metal concentration data would be an effective way to test this hypothesis [42]. Alternatively, this pattern could be

related to the form of mercury present in basal resources at RKM0. In the present study we measured total Hg, but the relative contribution of bioavailable MeHg in organic matter and invertebrates can be highly variable among food web compartments and sites. For example, MeHg can account for anywhere from 10% to 70% of total Hg in invertebrates among inland lakes [43]. Thus, a large and variable proportion of Hg can be in the inorganic form, which is minimally accumulated compared with MeHg.

The accumulation of Hg and Se in the Colorado River food web is consistent with prior studies of freshwater ecosystems, including rivers. The slope of the $\log_{10}$Hg/δ^{15}N model was 0.147, in line with global means for other river ecosystems (0.12) and freshwater food webs in general (0.15 [17]). Trophic magnification slopes are steeper (1.5 times higher, on average) and less variable for studies on MeHg than total Hg [17], and this may partially explain the high degree of variability that we observed between δ^{15}N and Hg in the present study. Stewart et al. [44] developed a generalized, nonlinear model of Se accumulation in freshwater food webs that is characterized by a large concentration factor of 10^2 to 10^6 fold between water and primary producers, a 5- to 10-fold increase between primary producers and primary consumers, and little additional trophic accumulation from primary consumers to higher order predators. Our data are consistent with the Stewart model. Average Se concentrations in organic matter and primary producers (0.2–1.8 $\mu g\, g^{-1}$) were approximately 4 orders of magnitude higher than average Se concentration in water below Glen Canyon Dam (2.3 $\mu g\, L^{-1}$). Concentrations in primary consumer macroinvertebrates were approximately 4-fold higher than in organic matter, and remained relatively level across macroinvertebrate and fish consumers. The invasive *P. antipodarum* (New Zealand mudsnail) and chironomids did not follow this trend and had much lower concentrations of Hg and Se than would be expected (i.e., they represented large negative outliers in the Hg and Se food web accumulation models). It is not clear why these taxa had lower Hg and Se concentrations, because δ^{15}N signatures indicate that they are feeding at a similar trophic level as the other invertebrates.

Food webs of the Colorado River in Grand Canyon contain high levels of Hg and Se in comparison with other rivers. For example, Hg concentrations in the Colorado River fishes (mean 0.17–1.59 $\mu g\, g^{-1}$ among species) were consistently higher than in fishes in large rivers around the United States (mean 0.21 $\mu g\, g^{-1}$, whole-body concentrations normalized to muscle tissue) [1] or in the great rivers (Missouri, Mississippi, and Ohio Rivers) of the central United States (mean small fish and large fish 0.06 $\mu g\, g^{-1}$ and 0.11 0.1 $\mu g\, g^{-1}$, respectively) [3], even though these rivers drain much more intensively developed landscapes (e.g., agriculture, urban, and industrial uses). One reason why Hg and Se concentrations in the food web are of concern is because this segment of the Colorado River supports the largest population of endangered humpback chub (*Gila cypha*) anywhere [11]. Mitigating threats to humpback chub population viability is crucial for conserving this species. Although we did not measure concentrations of Hg and Se in humpback chub, aquatic invertebrates are an important component of humpback chub diets [19], and consumption of simuliids, in particular, may pose a risk to this species. Specifically, simuliids exceeded risk thresholds for fish consumption in 100% of samples for Hg and 88% of samples for Se. Although Hg concentrations in organisms often exceeded risk values for wildlife, such as piscivorous mammals and birds, it is possible that any potential adverse effects of Hg on consumers would be mitigated by the correspondingly high Se concentrations found in this system. There is a well-documented antagonistic interaction between Se and Hg, whereby Se protects animals from Hg toxicity [45] when Hg:Se molar ratios are approximately 1 or less. The Hg:Se molar ratios were typically much lower than 1 in the present study (results not shown), ranging from 0.04 (rainbow trout) to 0.38 (fathead minnow) among fish species. Assuming that Se and Hg in prey are equally transferred to consumers, this large excess of Se in this system suggests that the risks of Hg toxicity could be considerably lower than the Hg wildlife risk values alone would indicate. In addition to posing potential exposure risks for aquatic animals, terrestrial consumers of aquatic organisms are also at risk for Hg and Se exposure. In arid ecosystems such as Grand Canyon, rivers are ribbons of productive habitat embedded in relatively unproductive terrestrial environments [46]. Emergent insects and fish are key food resources for terrestrial consumers such as spiders, lizards, bats, and birds [47,48], all of which are common in Grand Canyon [49,50]. Terrestrial consumers in riparian zones tend to rely heavily on these aquatic resources [48], and adult aquatic insects, as well as fish, likely represent an important flux of aquatic Hg and Se to riparian food webs [51]. Aquatic insects are prone to dumping most metals via excretion and other pathways during metamorphosis, but Hg and Se tend to be conserved (i.e., similar concentrations in larval and adult tissues) [52]. Thus species such as simuliids and small fishes that have high concentrations of Hg and Se are likely vectors of contaminant flux to riparian animals.

CONCLUSIONS

The Colorado River in Grand Canyon runs through a remote wilderness, and the area around Grand Canyon itself remains sparsely populated. Our findings demonstrate that Hg and Se occur in Grand Canyon food webs. Moreover, these concentrations are sufficient to pose exposure risks for fish, wildlife, and humans. Our research adds to a growing body of evidence showing that remote ecosystems are vulnerable to long-range transport and subsequent bioaccumulation of contaminants [53,54]. Airborne transport and deposition is most commonly identified as the mechanism for contaminant introduction to remote ecosystems [13], and this is a potential pathway for Hg entering the Grand Canyon food web [14]. In addition, long-range downstream transport from upstream sources can play a significant role in delivering contaminants to lotic ecosystems, particularly in the case of Se transport within the Colorado River Basin [18,55]. Protecting fish and wildlife in Grand Canyon from contaminant exposure driven by processes occurring beyond park and other political boundaries will remain an ongoing challenge.

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Disclaimer—This research was subjected to USGS review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. Handling of animals was in conformance with applicable permits (Arizona Game and Fish Permit SP565911, National Park Service Permit 2006-SCI-0003) with protocols approved by the Idaho State University Animal Care and Use Committee (Project 626R1008). The authors have no conflicts of interest to report.

Data availability—Readers may contact D. Walters (waltersd@usgs.gov) to request further data.

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