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Boron, Molybdenum, and Selenium in Aquatic Food Chains from the Lower San Joaquin River and Its Tributaries, California

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Abstract. Boron (B), molybdenum (Mo), and selenium (Se) were measured in water, sediment, particulate organic detritus, and in various biota—filamentous algae, net plankton, macroinvertebrates, and fishes—to determine if concentrations were elevated from exposure to agricultural subsurface (tile) drainage during the spring and fall 1987, in the San Joaquin River, California. Concentrations of B and Se, but not Mo, were higher in most samples from reaches receiving tile drainage than in samples from reaches receiving no tile drainage. Maximum concentrations of Se in water (0.025 μg/mL), sediment (3.0 μg/g), invertebrates (14 μg/g), and fishes (17 μg/g) measured during this study exceeded concentrations that are detrimental to sensitive warmwater fishes. Toxic threshold concentrations of B and Mo in fishes and their foods have not been identified. Boron and Mo were not biomagnified in the aquatic food chain, because concentrations of these two elements were usually higher in filamentous algae and detritus than in invertebrates and fishes. Concentrations of Se were lower in filamentous algae than in invertebrates and fishes; however, concentrations of Se in or on detritus were similar to or higher than in invertebrates and fishes. These observations suggest that high concentrations of Se accumulated in invertebrates and fishes through food-chain transfer from Se-enriched detritus rather than from filamentous algae.

For several decades, agricultural drainwater—a combination of surface return flows (tailwater) and subsurface (tile) drainage—from about 31,000 ha of irrigated croplands north of Mendota in the San Joaquin Valley, California, was commingled with irrigation water. The commingled water was then transported to the Grassland Water District (Grasslands) for flooding marsh ponds on federal and state wildlife refuges and privately owned duck clubs (Jones and Stokes Associates 1985). This drainwater contains elevated concentrations of many dissolved inorganic constituents, including boron (B), molybdenum (Mo), and selenium (Se) (Deverel *et al.* 1984; Presser and Barnes 1984, 1985). In February 1985, many waterfowl managers ceased using agricultural drainwater after learning that Se in tile drainage was responsible for mortalities and deformities in aquatic birds at the nearby Kesterson Reservoir (Ohlendorf *et al.* 1986).

The State Water Resources Control Board (SWRCB 1987) reported that biological and physicochemical processes in wetlands in the Grasslands had previously removed large quantities of Se and possibly B and Mo from agricultural drainwater. After waterfowl managers discontinued using drainwater on these wetlands, Se conveyed to the San Joaquin River by sloughs flowing through the Grasslands increased approximately two-fold (SWRCB 1987). In 1985, these sloughs supplied 12% of the total flow in the San Joaquin River between Lander Avenue and its confluence with the Merced River, but contributed about 46% of the dissolved salts, 69% of the B, 44% of the Mo, and 81% of the Se (SWRCB 1987).

Resource managers are concerned that food chains in the San Joaquin River have been accumulating toxic concentrations of trace elements. In canals and sloughs within the Grasslands, fishes contain as much as 23 μg Se/g (whole-body dry weight; Saiki 1986), which is nearly twice the concentration (12 μg/g) believed to elicit reproductive failure in sensitive warmwater fishes (Lemly and Smith 1987). Although fishes in the San Joaquin River downstream from the Grasslands contain elevated concentrations of Se, the concentrations are lower than those in fishes from the Grasslands (Saiki 1989; Saiki and Palawski 1990; Saiki *et al.* 1991). Elevated concentrations of B, but not Mo, have also been reported in fishes from some reaches of the San Joaquin River (Saiki and May 1988; Saiki and Palawski 1990).

The primary objective of this study was to determine if food chains of fishes from the San Joaquin River contained elevated concentrations of B, Mo, and Se. A secondary objective was to determine if elevated concentrations of elements in the food chains were associated with exposure to agricultural drainwater.

Study Area and Methods

Seven sampling sites were established on the San Joaquin Valley floor in San Joaquin, Stanislaus, and Merced counties (Fig-

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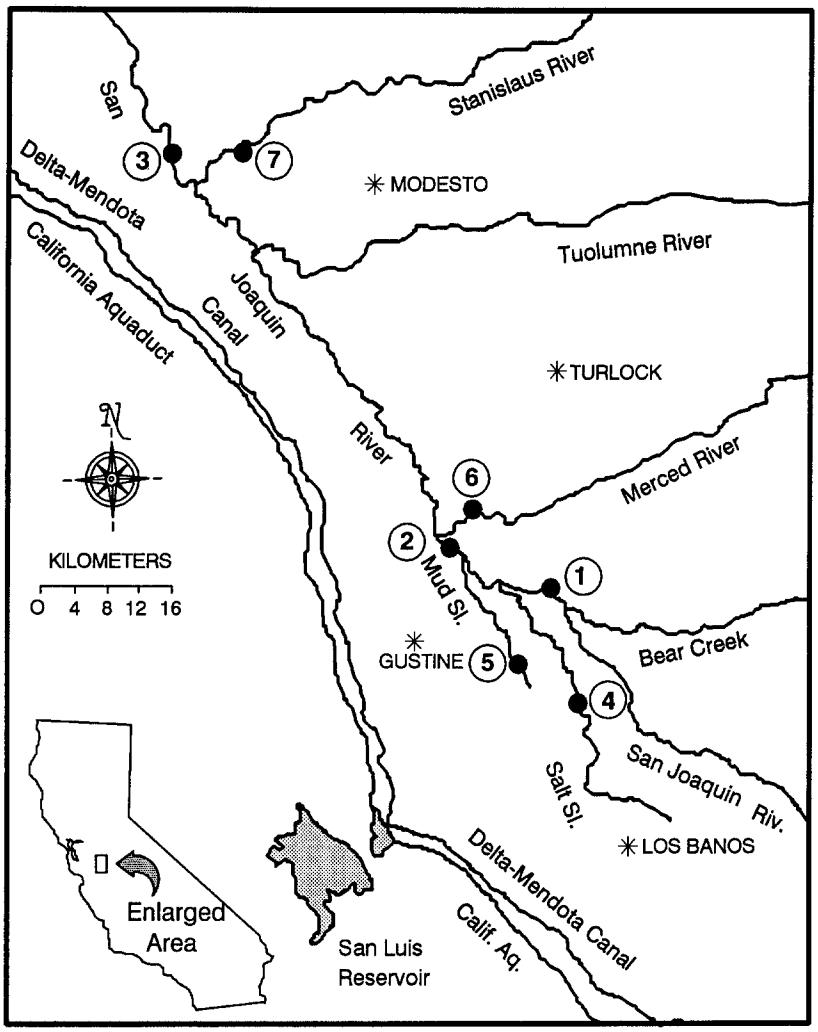

Fig. 1. Locations of sampling sites. Site names and abbreviations are as follows: (1) SJR1, San Joaquin River at Highway 165 (Lander Avenue); (2) SJR2, San Joaquin River above Hills Ferry Road (J-18); (3) SJR3, San Joaquin River at Durham Ferry State Recreation Area; (4) GT4, Salt Slough at the San Luis National Wildlife Refuge; (5) GT5, Mud Slough at Gun Club Road; (6) ET6, Merced River at George J. Hatfield State Recreation Area; and (7) ET7, Stanislaus River at Caswell Memorial State Park

ure 1). Two sites were located on east-side tributaries of the San Joaquin River (the Merced and Stanislaus rivers) whose flows consisted mostly of rainfall and snowmelt from the Sierra Nevada and some tailwater but no tile drainage, two were on west-side tributaries of the lower San Joaquin River (Salt and Mud sloughs) whose flows were derived almost entirely from tailwater and tile drainage, and three were on the San Joaquin River. Sites on the San Joaquin River were as follows: the first (SJR1) was located upstream from the west-side tributaries (during our study, flows consisted mostly of discharge from Bear Creek and groundwater seepage); the second (SJR2) was located immediately downstream from the west-side tributaries, but upstream from the east-side tributaries; and the third (SJR3) was located downstream from the east-side tributaries.

Earlier surveys of water quality in the San Joaquin River revealed longitudinal (upstream–downstream) patterns for several physicochemical variables that suggested progressively increasing environmental degradation from inflows of agriculture drainwater (Saiki 1984; Saiki and Palawski 1990). During the spring and fall of 1987, high concentrations of total alkalinity, total hardness, total dissolved solids, and conductivity—which characterize tile drainage (San Joaquin valley Drainage Program 1990)—occurred in Salt and Mud sloughs and the San Joaquin River at SJR2 (Table 1).

Water, Sediment, and Food-Chain Organisms

Samples of water, sediment, particulate organic detritus (detritus; composed mostly of decaying plant material), filamentous algae, net plankton, aquatic macroinvertebrates (chironomids, *Chironomus* spp.; amphipods, *Hyalella azteca, Gammarus fasciatus,* and *Corophium* spp.; and crayfish, *Procambarus clarki*), and fishes (mosquitofish, *Gambusia affinis*; bluegill, *Lepomis macrochirus*; and largemouth bass, *Micropterus salmoides*) were collected during spring (February–May) and fall (September–November) 1987 for chemical determinations of B, Mo, and Se. Spring collections were made during the beginning of the irrigation season when flows of agricultural drainwater into the San Joaquin River were high, whereas fall collections were made after most irrigation had ended and flows of drainwater into the river were somewhat lower.

Sample Collection and Storage

Water samples were collected weekly from each site. Each sample was collected within 15 cm of the surface as a composite of three grab samples (one each from the left and right banks, and in mid-channel), then about 500 mL was filtered

Table 1. Selected physicochemical variables in the San Joaquin River and its tributaries, Spring and Fall 1987. Values are geometric means

	Physical										Chemical									
	Conductivity (μmhos/cm @ 25°C)		Current velocity (m/sec)		Depth (m)		Temperature (°C)		Turbidity (NTUs)		Dissolved oxygen (μg/mL)		pH		Total alkalinity (μg/mL)		Total dissolved solids (μg/mL)		Total hardness (μg/mL)	
Site[a]	Spring	Fall	Spring	Fall	Spring	Fall	Spring	Fall	Spring	Fall	Spring	Fall	Spring	Fall	Spring	Fall	Spring	Fall	Spring	Fall
SJR1	695	199	0.010	0.055	1.98	2.90	11.8	21.1	5.8	9.9	10.40	8.25	7.79	7.36	152	64	296	163	159	55
SJR2	3600	1520	0.430	0.320	0.73	0.61	12.8	17.1	77.0	37.3	10.45	8.91	7.90	7.68	207	173	2050	1090	653	333
SJR3	1050	864	0.160	0.290	1.47	1.50	12.2	13.5	36.5	4.8	9.05	8.70	7.35	7.11	101	115	520	550	199	191
GT4	3610	1710	0.320	0.360	0.62	0.58	10.4	21.6	86.5	13.9	9.40	6.92	7.56	7.49	194	153	2080	1220	689	379
GT5	3830	1200	0.556	0.300	0.27	0.13	14.8	20.2	10.1	9.3	6.35	7.12	7.71	8.96	347	177	2320	845	559	253
ET6	92	111	0.735	0.490	1.10	0.63	12.8	13.3	6.3	1.1	9.65	9.43	6.84	7.06	38	50	56	120	40	52
ET7	2050	189	0.320	0.105	0.52	0.48	13.2	18.2	3.8	1.0	9.80	8.47	6.89	7.10	57	58	94	103	61	59

* See Figure 1 for names and locations of sampling sites

under pressure through a 0.40-μm polycarbonate membrane. About 500 mL of unfiltered water was also collected from each site. All samples were placed in acid-rinsed polyethylene bottles, then acidified with ultrapure nitric acid to pH <2.0 and chilled on ice for transport to the laboratory.

We attempted to collect triplicate samples of the remaining matrices from each site. Sediment samples were collected with a stainless steel Peterson dredge and passed through a 2.0-mm (pore size) polyethylene sieve, then placed in acid-rinsed polyethylene bottles and chilled on ice for transport to the laboratory. Detrital samples were collected by straining sediments through a 3.2-mm mesh dip net, then hand-sorting the remaining materials. Filamentous algae were collected by hand or with dip nets. Net plankton was collected with a 153-μm mesh student plankton net. Aquatic macroinvertebrates were collected with 3.2-mm mesh dip nets, 3.0-m × 1.8-m (2.0-mm square mesh) common sense seines, and baited Gee® minnow traps (crayfish only). Fishes are collected with 3.2-mm mesh dip nets, 5.5-m × 1.8-m (6.4-mm square mesh) bag seines, 30.5-m × 1.8-m (12.7-mm square mesh) beach seines, and backpack fish electroshockers. All biota were sorted from debris and rinsed in site water immediately after collection, then wrapped and double-bagged in polyethylene and chilled on ice for transport to the laboratory. Except for sediment, crayfish, and fishes, we collected composite samples weighing as much as 40 g. For sediment, we collected about 200 mL of sample. For crayfish and fishes, we collected composite samples of 3–5 individuals that collectively weighed at least 40 g and were similar in size or age.

In the laboratory, all samples were stored frozen at −10°C. Within 3 months of collection, biological samples were partially thawed, weighed, measured for carapace length (crayfish only) or total length (bluegill and largemouth bass only), rewrapped, and re-frozen until they were prepared for chemical analyses.

Elemental Determinations

A total of 605 composite samples were analyzed for B, Mo, and Se by the National Fisheries Contaminant Research Center in Columbia, Missouri. Except for water, all samples were lyophilized to facilitate digestion and to determine moisture content. For large (≥150 g wet tissue) organisms such as fishes, frozen samples were cut into cubes with a Hobart® Food-Service band saw and ground with a meat grinder. The ground material was thoroughly mixed by making three passes of the entire sample through the meat grinder, then a portion of the homogenized tissue was lyophilized. Some fish samples were too small for frozen homogenization; these samples were cut open with bone shears and lyophilized directly.

After lyophilization, detritus, filamentous algae, crayfish, and large (>50 g) fishes were dry-blended with an Osterizer® blender. Other matrices—sediment, net plankton, amphipods, and chironomids—did not need additional homogenization. All lyophilized samples were transferred into acid-cleaned glass vials and stored in a desiccator prior to aliquanting for digestion and analysis.

Samples were digested in one of three ways, depending on matrix (water, sediment, or tissue) and element to be determined. For analysis of B, water samples were placed in Teflon® PFA vessels, then digested with nitric acid and microwave heating. Other matrices were digested with a similar procedure, except that hydrogen peroxide was also added to the sample. For analysis of Mo, the various matrices were digested with procedures used to determine B. After digestion was completed, however, an aliquot of digestate was preconcentrated by coprecipitation with an Indium carrier (adapted from Thompson *et al.* 1981). Molybdenum concentrations in detritus were so high that preconcentration of the digestate was not necessary. Both B and Mo were determined from the digestates by inductively coupled plasma emission spectroscopy.

For analysis of Se, water samples were digested by oxidation with persulfate and reduction with hydrochloric acid (Presser and Barnes 1984). The remaining matrices were digested by ashing with nitric acid and magnesium nitrate, and dissolving with hydrochloric acid (Brumbaugh and Walther 1989). Selenium was determined by hydride-generation atomic absorption spectrophotometry.

Quality Control

During field collections of food-chain organisms for determination of elemental concentrations, we preserved mosquitofish, bluegill, and largemouth bass in 10% formalin for evaluation of stomach contents with methods described by Windell and Bowen (1978). As judged by gravimetric (biomass) measurements, mosquitofish consumed mostly mollusks, adult dipterans, and adult hymenopterans, which collectively accounted

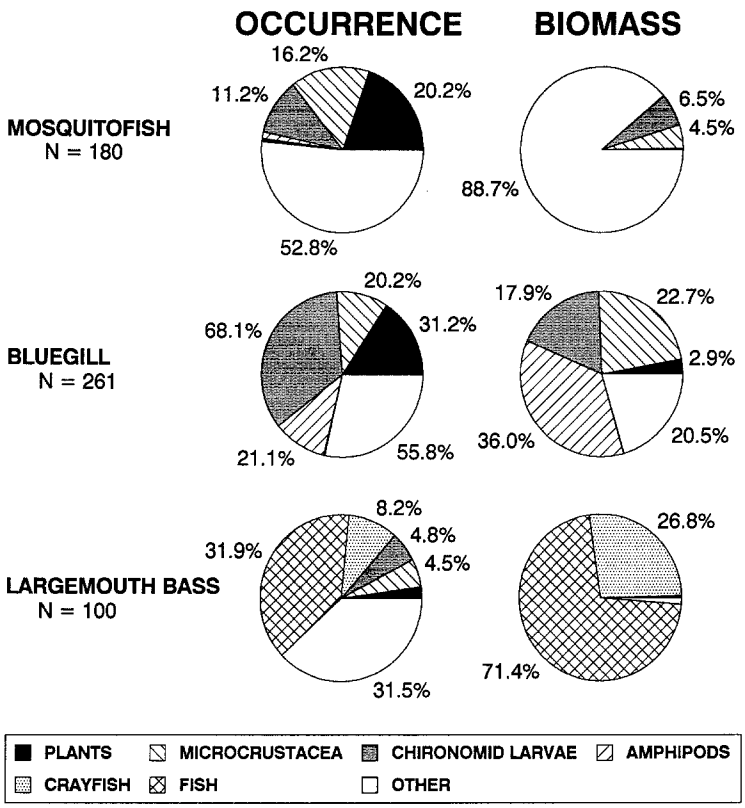

Fig. 2. Frequency of occurrence and biomass of food items in stomachs of mosquitofish, bluegill, and largemouth bass from the San Joaquin River system

for nearly 100% of the Other category (Figure 2). Although relatively unimportant in terms of biomass, mosquitofish also ate plants (primarily diatoms), microcrustacea (cladocerans, copepods, and ostracods), and chironomid larvae. Bluegill ingested mostly amphipods, microcrustacea, and chironomid larvae (Figure 2). The primary foods of largemouth bass were fish (mostly unidentified fish remains) and crayfish (Figure 2). These results demonstrated that the food-chain matrices (*i.e.*, taxa of organisms) selected for chemical determinations during our study were important components of food chains in the San Joaquin River and compared well with previously published information (Moyle 1976; Saiki and Schmitt 1985).

Quality control for the chemical determinations consisted of processing 63 groups of samples, each with their own procedural blanks, calibration solutions, predigestion spikes, analysis spikes, replicate sample preparation and analysis, and appropriate water, tissue, or other certified reference materials. For B and Se, there were no unusual problems associated with the chemical determinations. However, several samples of sediment, detritus, and net plankton were not successfully coprecipitated and analyzed for Mo as revealed by quality control failures. Abnormal color and consistency of the sample mixtures were obtained upon coprecipitation of some of these digestates, possibly from interferences due to high iron or silica content. We therefore do not report Mo for some matrices.

Spectrometers were calibrated with U.S. National Bureau of Standards (NBS) #3107, #3134, and #3149 spectroscopic solutions. U.S. Environmental Protection Agency #1 water and NBS #1643B were used to check the recovery of elements from digested waters. Our measurements of reference solutions were generally within the certified ranges. All procedural blanks for each element were at or less than the limits of detection for the method (Schmitt and Brumbaugh 1990).

Recoveries of B in reference samples (based on Eastman-Kodak® gelatin, the only material certified for this element) were somewhat variable, extending from 20% below to 6% above the certified range. Data for Mo from reference samples indicated that quantitative recovery was not achieved, with most measurements being 10–25% below the certified values. The recoveries of Se from control materials (N = 74) were generally within the recommended or certified ranges; for recoveries exceeding the certified ranges, only one result was not within 19% of the certified range.

Analytical precision, as measured by relative standard deviation (RSD), were as follows (element, sample size, mean, range): B, 17, 5.92%, 0.8–15.5%; Mo, 6, 16.65%, 10.1–24.6%; and Se, 26, 6.43%, 0.7–37.6%. Samples exhibiting RSDs of 20–25% contained concentrations of elements between the limit of detection and the limit of quantification, a region where one expects relatively poor precision. Except for two measurements that were low (B, 54.4%; Mo, 67.0%) and two that were unusually high (B, 232%; Se, 146%), predigestion spike recoveries were as follows (element, sample size, mean, range): B, 90, 102.3%, 77.8–117%; Mo, 90, 95.2%, 74.5–113%; and Se, 161, 94.9%, 77.1–112%. Thus, even though reference samples had somewhat low recoveries for Mo, spikes added prior to digestion of most sample matrices gave good recoveries. Analysis spikes, which checked for matrix enhancement or suppression effects, were as follows (element, sample size, mean, range): B, 49, 104.6%, 92.4–122%; Mo, 25, 97.5%, 89.2–106%; and Se, 40, 96.7%, 82.4–107%. The method limits of detection (μg/mL) for elements in water samples ranged as follows: B, 0.09–0.26; Mo, 0.006–0.020; and Se, 0.0003–0.0010. For other matrices, limits of detection (μg/g dry weight) ranged as follows: B, 0.88–11.8; Mo, 0.20–0.89; and Se, 0.01–0.08.

Table 2. Moisture content in various food-chain matrices from the San Joaquin River and its tributaries, spring and fall 1987. N, sample size; X, mean; Min–Max, minimum–maximum

		Moisture (%)	
Matrix	N	X	Min–Max
Sediment	42	30.5	18–76
Detritus	42	82.1	70–89
Filamentous algae	42	86.3	72–95
Net plankton	36	85.7	76–93
Chironomid larvae	42	83.9	68–89
Amphipods	42	80.9	77–85
Crayfish	40	75.2	67–82
Mosquitofish	42	76.2	73–80
Bluegill	46	73.2	71–75
Largemouth bass	44	74.6	72–78

Statistical Comparisons

Nonparametric tests (*e.g.*, Mann-Whitney-Wilcoxon rank sum [two-sample] test, Kruskal-Wallis test; Spearman rank correlation) were used for all statistical comparisons. The multiple means comparison test described by Conover (1980) was used only if significant ($P \leq 0.05$) chi-square (X^2) values were computed by the Kruskal-Wallis test. If trace element concentrations were below the detection limit, a value of half the detection limit was used to facilitate statistical comparisons and estimation of geometric means (Schmitt and Brumbaugh 1990).

Results

Average moisture content ranged from just under 31% in sediments to more than 86% in filamentous algae (Table 2). Median values for moisture differed significantly ($P \leq 0.05$, based on either Mann-Whitney-Wilcoxon rank sum tests or Kruskal-Wallis tests) among food-chain matrices (14 of 14 comparisons) and collection sites (14 of 20 comparisons), and between seasons (31 of 70 comparisons). To standardize the moisture content of samples, all concentrations of elements are hereinafter reported on a dry weight basis, unless indicated otherwise.

Median concentrations of B, Mo, and Se did not differ significantly ($P > 0.05$, Mann-Whitney-Wilcoxon rank sum tests) between filtered and unfiltered water samples within season and site. Consequently, all references to water will refer to filtered samples.

Boron, Mo, and Se were detected in one or more samples of each matrix during this study (Figures 3–8). Although seasonal patterns were not consistent, the median concentrations of elements from spring and fall collections differed significantly ($P \leq 0.05$, Mann-Whitney-Wilcoxon rank sum tests) in 31 of 80 comparisons for B, 7 of 62 comparisons for Mo, and 40 of 84 comparisons for Se. Therefore, further comparisons of elemental concentrations among matrices and collection sites were made within seasons.

Elemental Concentrations in Food-Chain Matrices

Overall, concentrations of B were highest in detritus and filamentous algae, and lower in invertebrates (net plankton, chironomids, amphipods, and crayfish) and fishes (mosquitofish, bluegill, and largemouth bass; Figures 3 and 4). In general, concentrations of B in sediment were similar to those in fishes. Water contained the lowest measurable concentrations of B.

Concentrations of Mo were highest in detritus, with lesser amounts in filamentous algae (Figures 5 and 6). Sediment, invertebrates, and fishes contained uniformly low concentrations of Mo. The lowest measurable concentrations of Mo occurred in water.

Although much variation was present, highest concentrations of Se occurred in detritus, mosquitofish, and chironomid larvae (Figures 7 and 8). Lower concentrations of Se were measured in other invertebrates and fishes. Filamentous algae generally contained the lowest concentrations of Se measured in biota. Compared to biota, water and sediment contained little Se.

Elemental Concentrations Among Collection Sites

In general, concentrations of B were relatively high in samples from the Grasslands (GT4 and GT5), whereas concentrations of this element were lower in samples from the eastern tributaries (ET6 and ET7; Figures 3 and 4). However, filamentous algae from ET6 contained unusually high concentrations of this element during the fall (geometric mean, 200 μg B/g; Figure 4). In the San Joaquin River, B concentrations were usually lowest at SJR1 (upstream from the Grasslands) and highest at SJR2 (immediately downstream from the Grasslands). Compared to SJR2, most samples from SJR3 contained less than half as much B, presumably because of dilution with higher quality water (*i.e.*, low in B) from the eastern tributaries.

Median concentrations of Mo in water (fall only), detritus (fall only), filamentous algae (fall only), chironomids (spring only), and bluegill differed significantly ($P \leq 0.05$, Kruskal-Wallis tests) among sites (Figures 5 and 6). Nevertheless, longitudinal (upstream-downstream) patterns were not observed among sites within the San Joaquin River, or among the river, Grasslands, and eastern tributaries. During fall, highest concentrations of Mo were measured in detritus at the uppermost site on the San Joaquin River (SJR1); however, these concentrations were not significantly different ($P \leq 0.05$, Kruskal-Wallis test) from concentrations measured in detritus at GT5.

On average, highest concentrations of Se were measured in samples from the Grasslands (GT4 and GT5), followed by the San Joaquin River immediately downstream from the Grasslands (SJR2), then by the San Joaquin River downstream from the eastern tributaries (SJR3; Figures 7 and 8). Samples from the San Joaquin River upstream from the Grasslands (SJR1) and from the eastern tributaries (ET6 and ET7) contained relatively low concentrations of Se.

Correlations with Physicochemical Variables

Concentrations of B and Se, but not Mo, were frequently correlated ($P \leq 0.05$) with conductivity (B, 6 of 11 comparisons; Se, 10 of 11 comparisons), turbidity (B, 4 of 11 comparisons; Se, 9 of 11 comparisons), pH (B, 8 of 11 comparisons; Se, 10 of 11 comparisons), total alkalinity (B, 9 of 11 comparisons; Se, 11 of 11 comparisons), total dissolved solids (B, 9 of 11 comparisons; Se, 11 of 11 comparisons), and total hardness (B,

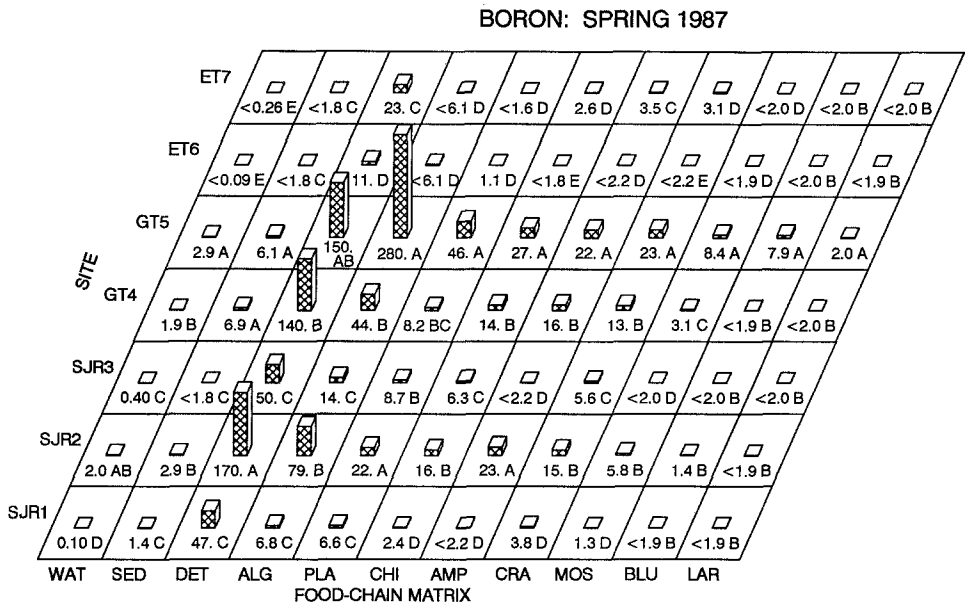

Fig. 3. Concentrations (μg/mL in water, μg/g dry weight in other matrices) of boron in aquatic food chains during spring 1987. Food-chain matrices are as follows: WAT, water; SED, sediment; DET, detritus; ALG, filamentous algae; PLA, net plankton; CHI, chironomid larvae; AMP, amphipods; CRA, crayfish; MOS, mosquitofish; BLU, bluegill; and LAR, largemouth bass. Within each matrix, geometric means followed by the same capital letter are not significantly different ($P > 0.05$)

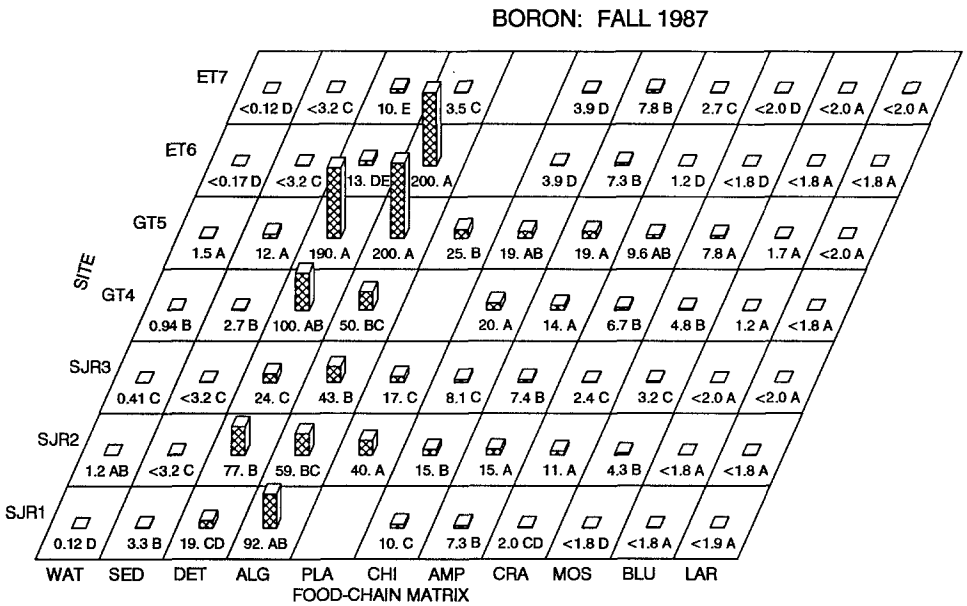

Fig. 4. Concentrations (μg/mL in water, μg/g dry weight in other matrices) of boron in aquatic food chains during fall 1987. Legend is as in Figure 3

8 of 11 comparisons; Se, 10 of 11 comparisons; Tables 3–5). The concentrations of B and Se were either not significantly correlated or rarely correlated with current velocity, depth, temperature, and dissolved oxygen concentrations. In general, concentrations of Mo were not significantly correlated with any physicochemical variables (Table 4).

Discussion

Routine disposal of agricultural drainwater into west-side tributaries of the San Joaquin River has raised concerns that aquatic food chains are accumulating toxic concentrations of B, Mo, and Se. Although aquatic plants can concentrate chemicals directly from water and sediment, animals also accumulate chemicals from food (Baudo 1983, 1985). Fish are known to accumulate elevated concentrations of Se by consuming contaminated food (Lemly 1985; Lemly and Smith 1987).

Comparisons with Other Studies

Boron: The average or background concentration of B in surface freshwaters of the U.S. has been reported as either 0.01 μg/mL (Wetzel 1975; Forstner and Wittmann 1979) or 0.1 μg/mL (Sprague 1972; U.S. Environmental Protection Agency 1986). According to Sprague (1972), the concentration of B in most soils is 10–30 μg/g, but marine shales may contain as much as 300 μg/g. Yamamoto *et al.* (1973) reported that phytoplankton averaged 467 μg B/g and zooplankton averaged 6 μg B/g in a freshwater lake in Japan. In the San Joaquin Valley, filamentous algae accumulated 390–787 μg B/g when exposed

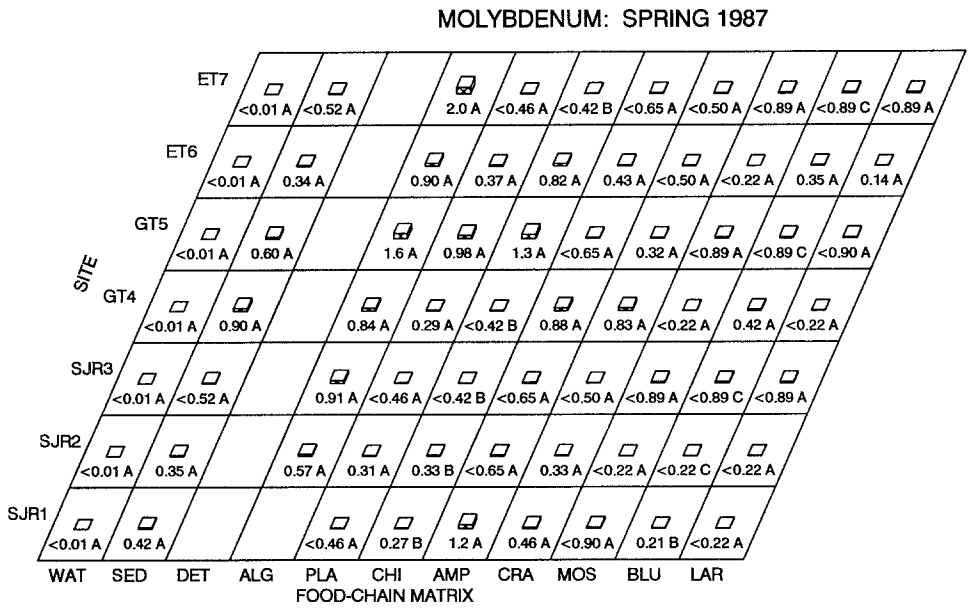

Fig. 5. Concentrations (μg/mL in water, μg/g dry weight in other matrices) of molybdenum in aquatic food chains during spring 1987. Legend is as in Figure 3

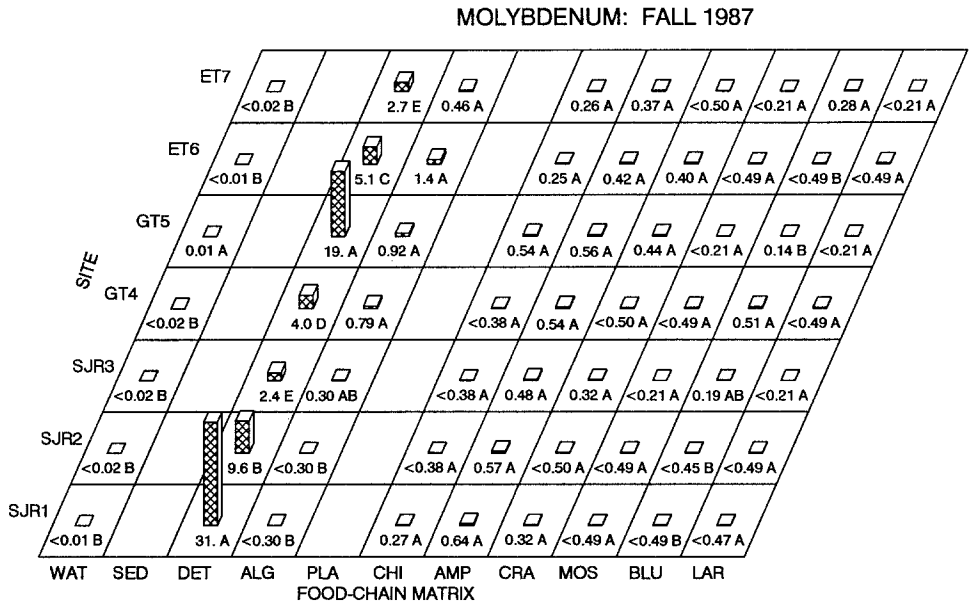

Fig. 6. Concentrations (μg/mL in water, μg/g dry weight in other matrices) of molybdenum in aquatic food chains during fall 1987. Legend is as in Figure 3

to brackish tile drainage containing 12–41 μg B/mL, whereas this taxon accumulated 64–140 μg B/g when exposed to fresher water containing 1.4–2.2 μg B/mL (Schuler 1987). Aquatic insects living in tile drainage contained 22–340 μg B/g but those living in freshwater untainted by tile drainage contained 6–47 μg B/g (Ohlendorf et al. 1986; Schuler 1987; Hothem and Ohlendorf 1989). Jenkins (1980) reported that a freshwater crayfish (*Potamobius fluviatilis*) contained 31.3 μg B/g, and muscle tissue from lake trout (*Salvelinus namaycush*) contained 0.25–0.63 μg B/g wet weight (about 1.0–2.5 μg/g dry weight, assuming 75% moisture). Based on a limited number of field surveys in the San Joaquin Valley and elsewhere, Saiki and May (1988) concluded that whole-body samples of freshwater fishes usually contain <4 μg B/g. As judged by these comparisons, concentrations of B in several matrices that we sampled (water, filamentous algae, net plankton, mosquitofish, and bluegill) at SJR2, SJR3, GT4, and GT5 were slightly elevated.

Concentrations of B in water exceeding 1.0 μg/mL, the limit recommended by Eisler (1990) to protect sensitive species of aquatic life, were measured at SJR2, GT4, and GT5 (Figures 3 and 4). To our knowledge, no one has proposed similar limits for B in sediment or in fishes and their foods. According to Thompson *et al.* (1976), coho salmon (*Oncorhynchus kisutch*) alevins succumbing during a 283-h exposure to 328–656 μg B/mL (from sodium metaborate) accumulated whole-body concentrations of 900–1,560 μg/g (assumes 75% moisture). Chinook salmon (*Oncorhynchus tshawytscha*) and striped bass (*Morone saxatilis*) fingerlings experienced poor growth and survival after accumulating as much as 200 μg B/g during 28 days of exposure to tile drainage from the San Joaquin Valley but other variables in the tile drainage (*e.g.*, unusual ratios of major ions) could not be excluded as potential contributors to toxicity (Saiki *et al.* 1992).

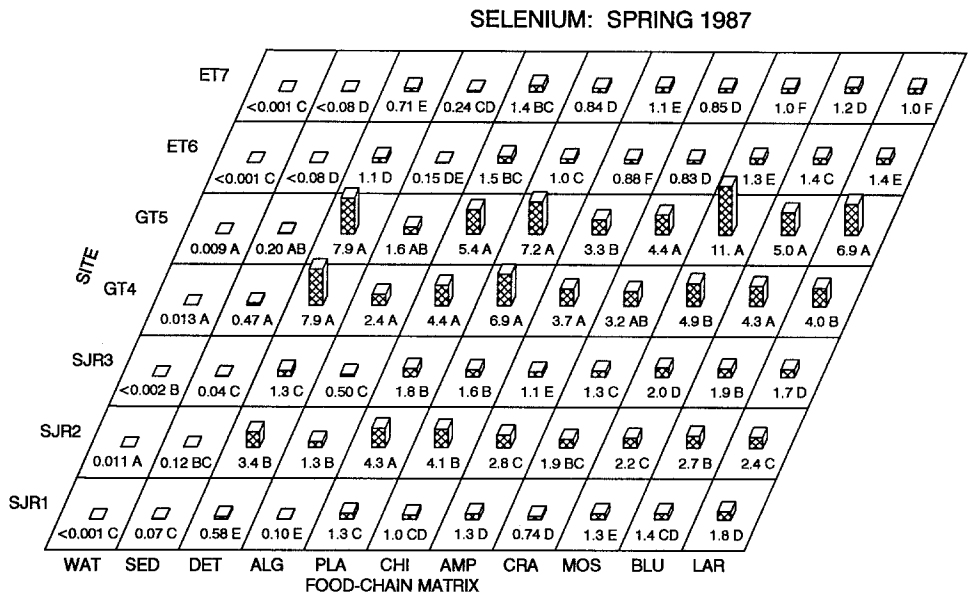

Fig. 7. Concentrations (μg/mL in water, μg/g dry weight in other matrices) of selenium in aquatic food chains during spring 1987. Legend is as in Figure 3

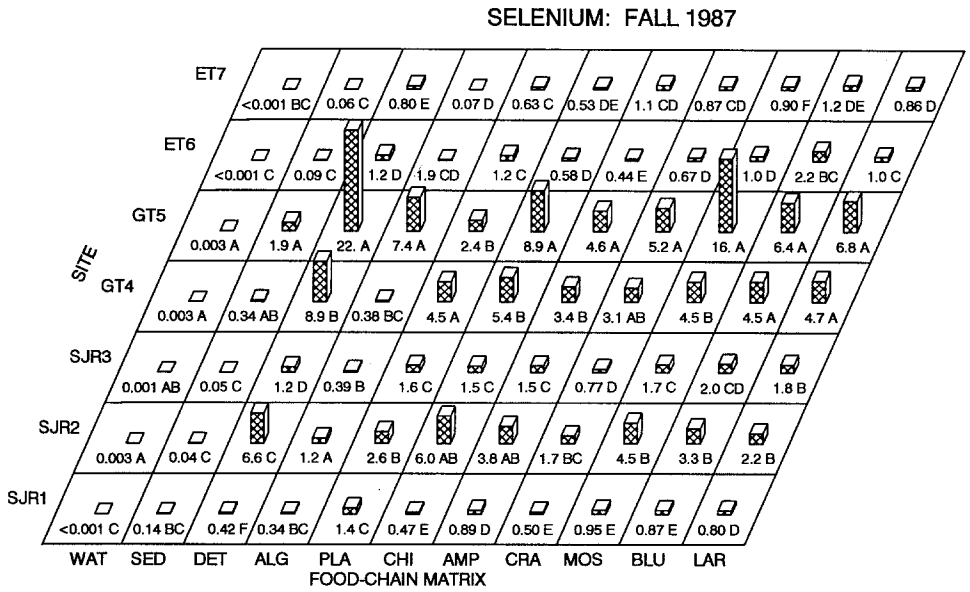

Fig. 8. Concentrations (μg/mL in water, μg/g dry weight in other matrices) of selenium in aquatic food chains during fall 1987. Legend is as in Figure 3

In terrestrial food chains, B accumulates in plants but not in animals (Underwood 1977). Our results indicate a similar pattern in aquatic food chains (Figures 3 and 4). Schuler (1987) also mentioned that concentrations of B were higher in aquatic plants than in most aquatic insects. Collectively, these findings suggest that B does not biomagnify in aquatic food chains.

High concentrations of B in filamentous algae and detritus (which consisted mostly of decaying vegetation) may be associated with its importance in plant nutrition. Boron is an essential micronutrient for higher plants and some algae, fungi, and bacteria (Boyd and Walley 1972). Although the function of B in plants is uncertain, this element is important in organs where growth occurs (*i.e.*, at the meristem; Sprague 1972). According to Rajaratnam *et al.* (1971), B is required for synthesis of flavonoid compounds, which are unique to plants. Boron deficiency has been reported for several mammals, including man, where it appears to affect membrane function and calcium and magnesium metabolism (National Research Council 1989). The importance of B to other vertebrates, including fishes, is not known.

Molybdenum: According to Forstner and Wittmann (1979) and Wetzel (1975), the background concentration of Mo in freshwater is about 0.001 μg/mL. Chappell (1975), however, reported the background concentration of dissolved Mo in water as <0.010–0.020 μg/mL, whereas Eisler (1989) stated that natural Mo concentrations in surface waters rarely exceeded 0.020 μg/mL. In the U.S., soils average 1.2 μg Mo/g, but concentrations can range as high as 40 μg/g (Eisler 1989). Webb et al. (1968) proposed a background concentration of <2 μg Mo/g in stream sediment. In the San Joaquin Valley, where dissolved concentrations of Mo averaged 0.017 μg/mL, filamentous algae contained as much as 5.7 μg Mo/g and aquatic insects as much as 1.6 μg Mo/g (Schuler 1987). In Colorado streams containing <0.001 μg Mo/mL, aquatic insects accumulated as much as 1.65 μg Mo/g (Colborn 1982). Lynch *et al.* (1988) reported that benthic insects downstream from spills of

Table 3. Spearman rank correlation coefficients (r_s) that describe the relations between concentrations of boron in 11 sample matrices and 10 physicochemical variables[a]

	Physical					Chemical				
Sample matrix	Conductivity	Current velocity	Depth	Temperature	Turbidity	Dissolved oxygen	pH	Total alkalinity	Total dissolved solids	Total hardness
Water	0.68**	0.30	−0.26	0.02	0.78**	−0.32	0.72**	0.89**	0.90**	0.85**
Sediment	0.46	0.05	−0.35	0.38	0.41	−0.53	0.61*	0.71**	0.70**	0.57*
Detritus	0.67**	0.14	−0.31	>0.01	0.75**	−0.26	0.87**	0.91**	0.85**	0.85**
Filamentous algae	0.35	−0.16	−0.44	0.58*	0.28	−0.69**	0.61*	0.64*	0.57*	0.46
Net plankton	0.52	−0.01	−0.48	0.65*	0.42	−0.65*	0.62	0.75*	0.78**	0.66*
Chironomid larvae	0.60*	0.26	−0.38	0.46	0.64*	−0.63*	0.63*	0.80**	0.86**	0.74**
Amphipods	0.56*	0.43	−0.48	0.25	0.49	−0.32	0.57*	0.77**	0.78**	0.70**
Crayfish	0.66*	0.37	−0.26	−0.16	0.80**	−0.13	0.73**	0.86**	0.87**	0.83**
Mosquitofish	0.62*	0.39	−0.39	0.12	0.48	−0.28	0.71**	0.83**	0.82**	0.75**
Bluegill	0.36	0.57*	−0.34	0.08	0.11	−0.21	0.28	0.40	0.43	0.36
Largemouth bass	0.04	0.35	−0.05	−0.27	−0.12	−0.07	−0.02	0.09	0.13	0.00

[a]Codes: $*P \leq 0.05$; $**P \leq 0.01$

Table 4. Spearman rank correlation coefficients (r_s) that describe the relations between concentrations of molybdenum in 11 sample matrices and 10 physicochemical variables[a]

	Physical					Chemical				
Sample matrix	Conductivity	Current velocity	Depth	Temperature	Turbidity	Dissolved oxygen	pH	Total alkalinity	Total dissolved solids	Total hardness
Water	0.20	0.09	−0.30	0.48	−0.09	−0.43	0.17	0.24	0.31	0.17
Sediment	0.72	−0.16	−0.41	−0.21	0.36	−0.11	0.58	0.76*	0.74	0.70
Detritus	0.14	−0.46	−0.14	0.57	0.39	−0.39	0.57	0.36	0.07	0.04
Filamentous algae	0.02	0.32	−0.49	−0.21	−0.21	−0.08	−0.06	−0.06	−0.15	−0.06
Net plankton	0.82*	0.41	−0.93**	0.69	0.00	−0.15	0.22	0.56	0.52	0.33
Chironomid larvae	0.25	0.11	−0.30	−0.01	−0.18	0.06	0.27	0.16	−0.02	−0.02
Amphipods	0.03	−0.59*	0.16	0.11	0.08	−0.08	0.33	0.17	0.11	0.10
Crayfish	0.19	−0.40	−0.04	−0.21	0.08	0.02	0.57*	0.50	0.34	0.36
Mosquitofish	−0.09	−0.13	0.23	−0.19	0.15	>0.01	0.09	−0.02	−0.07	−0.08
Bluegill	0.08	0.40	−0.14	−0.03	0.11	−0.26	−0.43	−0.22	−0.04	−0.04
Largemouth bass	0.07	0.19	−0.12	0.10	0.21	−0.26	−0.10	−0.04	−0.02	−0.01

[a]Codes: $*P \leq 0.05$; $**P \leq 0.01$

Mo mill tailings in the Red River, New Mexico, averaged as much as 29 μg Mo/g. In a laboratory study, rainbow trout (*Oncorhynchus mykiss*) held in 0.006 μg Mo/mL accumulated about 0.56 μg Mo/g (assumes 75% moisture) in their tissues (Ward 1973). In general, concentrations of Mo in whole freshwater fishes average <0.6 μg/g (Saiki and May 1988). According to Eisler (1989), adverse effects from waterborne exposure usually occur in aquatic organisms at concentrations exceeding 50 μg Mo/mL. However, newly fertilized eggs of rainbow trout, which may be extremely sensitive to Mo, suffer from reduced survival at concentrations as low as 0.79 μg/mL (Birge *et al.* 1980, cited by Eisler 1989). By comparison, concentrations of Mo in water from our study sites never exceeded 0.01 μg/mL. To our knowledge, the toxic threshold concentrations for Mo in sediment or in fishes and their foods have not been determined. The concentrations of Mo that we measured in water, sediment, and biota were well within background or nontoxic concentrations, indicating that fishes were not exposed to harmful concentrations of this element.

As shown by our results, concentrations of Mo were higher in plants than in animals (Figures 5 and 6). Schuler (1987) also reported that higher concentrations of Mo occurred in filamentous algae than in aquatic insects. These limited observations suggest that Mo does not biomagnify in aquatic food chains.

Plants (including algae) and animals require Mo for proper nutrition (Phillips and Russo 1978; Gough *et al.* 1979; National Research Council 1989). The role of Mo in plants is apparently to stimulate nitrogen fixation and nitrate reduction (Chappell 1975). Moreover, at least seven enzymes found in plants—nitrogenase, nitrate reductase, xanthine oxidase, aldehyde oxidase, NADH-dehydrogenase, xanthine dehydrogenase, and sulfite oxidase—require Mo as a cofactor (Chappell 1975). The biological role of Mo in animals is less understood. Animals efficiently regulate Mo over a wide range of environmental concentrations, with excessive amounts occurring in their tissues only after toxic or lethal doses are administered (Gough *et al.* 1979). Goettl and Davies (1977, cited by Phillips and Russo 1978) exposed rainbow trout to various Mo concentrations in water for as long as 492 days and measured Mo accumulations in liver; trout exposed to the highest concentration (18.7 μg Mo/mL) accumulated significantly more Mo than controls, but lower exposures resulted in insignificant Mo uptake. Studies with mammals (cattle, sheep, rats) indicate that high concentrations of dietary sulfate can reduce uptake and increase excretion

Table 5. Spearman rank correlation coefficients (r_s) that describe the relations between concentrations of selenium in 11 sample matrices and 10 physicochemical variables[a]

	Physical					Chemical				
Sample matrix	Conductivity	Current velocity	Depth	Temperature	Turbidity	Dissolved oxygen	pH	Total alkalinity	Total dissolved solids	Total hardness
Water	0.69**	0.28	−0.33	−0.10	0.72**	−0.21	0.67**	0.88**	0.93**	0.90**
Sediment	0.39	0.00	−0.38	0.37	0.29	−0.50	0.59*	0.63*	0.60*	0.51
Detritus	0.70**	0.26	−0.66*	0.21	0.55*	−0.46	0.53*	0.73**	0.77**	0.82**
Filamentous algae	0.66**	0.13	−0.34	0.06	0.74**	−0.38	0.67**	0.81**	0.79**	0.79**
Net plankton	0.86**	0.38	−0.38	0.07	0.78**	−0.35	0.58*	0.82**	0.87**	0.89**
Chironomid larvae	0.79**	0.24	−0.56*	0.02	0.63*	−0.33	0.69**	0.83**	0.81**	0.86**
Amphipods	0.55*	0.21	−0.30	0.07	0.65*	−0.27	0.71**	0.78**	0.78**	0.75**
Crayfish	0.67**	0.53	−0.59*	0.01	0.60*	−0.27	0.53	0.70**	0.74**	0.75**
Mosquitofish	0.77**	0.16	−0.49	0.03	0.66**	−0.35	0.75**	0.87**	0.83**	0.87**
Bluegill	0.71**	0.19	−0.72**	0.25	0.46	−0.50	0.64*	0.80**	0.77**	0.82**
Largemouth bass	0.78**	0.25	−0.49	0.03	0.57*	−0.31	0.77**	0.88**	0.85**	0.86**

[a]Codes: $*P \leq 0.05$; $**P \leq 0.01$

rate of Mo, resulting in lower body burdens of this element (Underwood 1977). Although the mechanism is unknown, sulfate interferes with or prevents the transport of Mo across cell membranes (Underwood 1977). Excess Mo in diets of ruminants and humans also causes symptoms of copper (Cu) deficiency (Underwood 1977; National Research Council 1989). Little is known about the toxic effects of high concentrations of Mo in fish (Eisler 1989).

Selenium: Selenium concentrations in most freshwaters range from 0.0001 to 0.160 μg/mL and average about 0.001 μg/mL (Brooks 1984). Swaine (1955, cited by the National Research Council 1983) reported that soils usually contain 0.1–2 μg Se/g. Background concentrations of Se in filamentous algae and aquatic invertebrates have not been established; however, concentrations reported in these matrices from non-seleniferous habitats usually averaged <5 μg Se/g (Lemly 1985; Saiki and Lowe 1987; Schuler 1987; Hothem and Ohlendorf 1989; Schuler *et al.* 1990). Selenium concentrations in whole freshwater fish from throughout the U.S. average 0.70–0.82 μg/g wet weight (about 2.8–3.3 μg/g dry weight, assuming 75% moisture; Schmitt and Brumbaugh 1990). Lemly and Smith (1987) reported that Se concentrations >0.002–0.005 μg/mL in water, ≥4 μg/g in sediment, ≥5 μg/g in food, and ≥12 μg/g in whole fish can cause reproductive failure and other toxic problems among sensitive fishes such as centrarchids. However, adverse effects on survival and growth of juvenile chinook salmon can occur at threshold whole-body concentrations as low as 3–8 μg Se/g (Hamilton and Wiedmeyer 1990). As judged by these comparisons, elevated and potentially toxic concentrations of Se occurred at SJR2, GT4, and GT5 during our study (Figures 7 and 8). Selenium concentrations were especially high in detritus (maximum, 23 μg/g) and mosquitofish (maximum, 17 μg/g) from GT5.

Relatively high concentrations of Se were measured in detritus during our study (Figures 7 and 8). Saiki and Lowe (1987) reported a similar occurrence of high Se concentrations in detritus collected from the San Luis Drain, a canal that previously carried seleniferous tile drainage from irrigated croplands in the San Joaquin Valley to Kesterson Reservoir. Inorganic Se compounds generally do not form complexes with organic matter; however, they may be adsorbed on detrital particles. More probable is that bacteria and other microbial organisms living on detrital particles accumulated high concentrations of Se. Burton *et al.* (1987) reported a high incidence of Se-resistant bacteria in water, sediment, and algal mats from Kesterson Reservoir, and suggested that the bacteria were able to accumulate Se. Baudo (1983) also cautioned that bacterial growth on aquatic plants can account for a significant fraction of elemental concentrations improperly referred to as occurring in plant tissues.

As judged by field evidence, several investigators have stated that Se is biomagnified through aquatic food chains (Elwood *et al.* 1976; Cherry and Guthrie 1977; Lemly 1985; Lemly and Smith 1987). However, Kay (1984) argued that conclusive evidence of biomagnification (specifically defined as an increase in the concentrations of a contaminant from one trophic level to the next higher one) is not yet available. Bertram and Brooks (1986) reported that, after 11 weeks of exposure under laboratory conditions, fathead minnow (*Pimephales promelas*) accumulated only about one-third of the Se present in their food (*Daphnia*). Based on these findings, Bertram and Brooks (1986) concluded that the fathead minnow probably does not accumulate Se to concentrations greater than that in its food. Adams and Johnson (1977) suggested that differences in Se concentrations between two adjacent trophic levels might reflect species-specific accumulation rates. The National Academy of Sciences (1976) also mentioned that there is little evidence of Se biomagnification. We suspect that Se concentrations in higher trophic levels can exceed those in filamentous algae if invertebrates and fishes accumulate this element through a Se-enriched detrital food chain. Although the food habits of chironomid larvae, amphipods, and crayfish were not determined during our study, Pennak (1978) indicated that these omnivorous macroinvertebrates (which are important fish foods; Figure 2) consume large quantities of organic detritus.

Selenium is important to plants and animals (including fishes) for biochemical and physiological functions such as protein synthesis, mitochondrial transport of electrons, facilitating the metabolic union of oxygen and hydrogen, and catalyzing reactions that protect cell membranes from oxidation damage (National Academy of Sciences 1976). This element also protects against toxicity from arsenic, cadmium, Cu, lead, mercury, silver, thallium, zinc, and the herbicide paraquat (Na-

tional Research Council 1983; Eisler 1985). Dietary sulfate may protect against selenate (the predominant form of inorganic Se in tile drainage; Deverel *et al.* 1984; Presser and Barnes 1984) toxicity, but does not influence the toxicity of selenite and organoselenium (National Academy of Sciences 1976). Inorganic Se is transformed into organic forms (*e.g.*, selenocysteine and selenomethionine and, ultimately, into proteins) by aquatic plants. Although the relative toxicity of organic and inorganic Se is poorly defined, bioaccumulation is most pronounced when it is ingested by fish in an organic form (Bennett *et al.* 1986). Moreover, organic forms of Se are retained in the body to a greater degree than inorganic forms (National Academy of Sciences 1976). In fish, sublethal effects from exposure to excessive concentrations of Se include reproductive abnormalities (*e.g.*, congenital malformations, edema, and growth retardation), lesions or other pathological changes in internal organs, and behavioral modifications (Eisler 1985). Disruption or alteration of biochemical and metabolic processes, which result in sublethal effects, are poorly understood (Eisler 1985).

Relation of Elements in Food Chains to Agricultural Drainwater

Spatial (geographic) patterns of B and Se in food-chain matrices (*i.e.*, high concentrations at SJR2, GT4, and GT5; somewhat lower concentrations at SJR3; and lowest concentrations at SJR1, ET6, and ET7) resemble the pattern for agricultural drainwater as it exits the Grasslands and becomes diluted with higher quality water from the San Joaquin River and the eastern tributaries. These observations suggest that agricultural drainwater is a major source of B and Se in food-chain matrices (especially those from SJR2, GT4, and GT5). By comparison, concentrations of Mo in food-chain matrices do not exhibit a recognizable spatial pattern.

Physicochemical variables that are strongly influenced by agricultural drainwater (*e.g.*, conductivity, total alkalinity, total dissolved solids, and total hardness; San Joaquin Valley Drainage Program 1990) were significantly ($P \leq 0.05$) correlated with concentrations of B and Se, but not with Mo, in food-chain matrices (Tables 3–5). These results provide corroborating evidence that high concentrations of B and Se (but not Mo) in aquatic food chains resulted from exposure to agricultural drainwater.

Filamentous algae collected from ET6 contained high concentrations of B in the fall (geometric mean, 200 μg/g; Figure 4) but not in the spring. We are not aware of any local sources of B-enrichment at ET6. Boyd (1967) noted that some algal genera (e.g., *Lyngbya* and *Pithophora*) can contain as much as 65–112 μg B/g even though other algal genera from the same vicinity contain less than 10 μg B/g.

Conclusions

Our study revealed that concentrations of B and Se, but not Mo, were elevated in food-chain organisms from the Grasslands and the San Joaquin River immediately downstream from the Grasslands. We were not able to fully assess the potential toxicity of elevated B concentrations, because toxic threshold concentrations for this element have not been determined. Maximum concentrations of Se in fish (especially mosquitofish) and in two fish-forage invertebrates (chironomid larvae and crayfish) exceeded concentrations that, according to Lemly and Smith (1987), can adversely affect reproduction, growth, and survival of sensitive fish.

With few exceptions, concentrations of B, Mo, and Se did not progressively increase from lower trophic levels (detritus and filamentous algae) to higher trophic levels (invertebrates and fish). Although Se concentrations generally increased from filamentous algae to invertebrates, the concentrations from invertebrates to fish did not usually increase. Baudo (1983) also stated that B, Mo, and Se were among several elements that did not exhibit evidence of biomagnification. For these reasons, we doubt that B, Mo, and Se were biomagnified in food chains from the San Joaquin River system. As judged by our results, the elevated concentrations of Se that we found in fish and some invertebrates may have occurred without magnification through food-chain transfer from Se-enriched detritus.

Highest concentrations of B and Se in food-chain matrices occurred at reaches exposed to inflows of concentrated agricultural drainwater. In addition, concentrations of these two elements were significantly ($P \leq 0.05$) correlated with physicochemical variables that are characteristic of agricultural drainwater (e.g., conductivity, total alkalinity, total dissolved solids, total hardness, and turbidity). These data strongly implicate agricultural drainwater as the source of elevated concentrations of B and Se in aquatic food chains from the San Joaquin River.

In the future, agricultural drainwater entering the San Joaquin River may increase in volume if additional irrigated lands are drained to rejuvenate crop production on waterlogged soils. In 1987, about 342,800 ha on the western side of the San Joaquin Valley floor had groundwater levels within 1.5 m of the land surface, an increase from 217,300 ha only 10 yr earlier (San Joaquin Valley Drainage Program 1989). If current trends continue, water tables will be within 1.5 m of the land surface on about 399,800 ha by the year 2000 (San Joaquin Valley Drainage Program 1989). Recent studies indicate that prolonged (28-day) exposure of juvenile chinook salmon and striped bass to tile drainage from the San Joaquin Valley results in high mortality, poor growth, and increased body burdens of B and Se (Saiki et al. 1992). Therefore, any increase in the volume of tile drainage discharged to the San Joaquin River may further increase elemental concentrations in fish and their foods, and adversely affect their survival.

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