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SELENIUM IN THE AQUATIC ENVIRONMENT OF QUIVIRA NATIONAL WILDLIFE REFUGE IN 1987

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U.S. Fish and Wildlife Service
Region 6
Contaminants Program



SELENIUM IN THE AQUATIC ENVIRONMENT
OF QUIVIRA NATIONAL WILDLIFE REFUGE
IN 1987

Kansas State Office
Division of Fish and Wildlife Enhancement
315 Houston Street, Suite E
Manhattan, Kansas 66502



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315 Houston Street, Suite A
Manhattan, Kansas 66502

October 1989

ABBREVIATIONS AND CONVERSION FACTORS

Abbreviations

| | |
|---------------------------------|--------|
| parts per million | ppm |
| parts per billion | ppb |
| micrograms per gram | mcg/g |
| micrograms per milliliter | mcg/ml |
| micrograms per liter | mcg/l |
| hectare | ha |

Conversion Factors

| | |
|---------------------------------|-----------|
| micrograms per gram | ppm |
| micrograms per milliliter | ppm |
| micrograms per liter | ppb |
| hectare | 2.5 acres |

SUMMARY

- An investigation by the Kansas Department of Health and Environment (KDHE, 1986) indicated that selenium levels in Rattlesnake Creek below Quivira National Wildlife Refuge in Kansas were elevated. The selenium levels suggested that the refuge might be contaminated or might be a source of selenium contamination in Rattlesnake Creek.
- Twelve water, 12 sediment, 6 filamentous algae, and 12 common carp samples were collected from locations along Rattlesnake Creek in or adjacent to the refuge in July 1987. They were analyzed for percent moisture and dry weight concentration of selenium.
- Selenium concentrations in water (geometric mean=0.69 ppb), sediment (\bar{x} =0.085 ppm dry weight), and filamentous algae (\bar{x} =0.263 ppm dry weight) were low. Half of the sediment samples contained a concentration below the detection limit. Selenium levels in the carp also were low (\bar{x} =1.384 ppm dry weight for whole fish).
- Selenium levels on the refuge were below the levels that are of concern to fish or wildlife resources.
- We believe it unlikely that animals accumulate selenium as a result of their use of the refuge.
- Factors such as rainfall, variations in the flow in Rattlesnake Creek, and water use above the refuge could change the selenium levels found on the refuge and in Rattlesnake Creek below the refuge from those found during this study. However, the source of the selenium measured by KDHE likely is downstream from the refuge.

ACKNOWLEDGMENTS

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INTRODUCTION

Selenium is a widely distributed element generally found at low concentrations in surface waters and soils (Cooper et al. 1974, Kubota 1980, Raptis et al. 1983, Trelease 1945). Selenium has received recent attention from the Department of the Interior and the U.S. Fish and Wildlife Service (Service) because high levels of selenium borne by irrigation return flows have caused serious problems for fish and wildlife (Clark 1987, Hoffman et al. 1988, Lemly 1987, Ohlendorf et al. 1986a,b, 1987, 1988, Saiki and Lowe 1987). Because selenium concentrations can occur in coal deposits, ash from coal-fired powerplants has caused serious selenium contamination problems in several places (Guthrie and Cherry 1979, Lemly 1987, Sorenson et al. 1982).

Selenium occurs at high levels in many Cretaceous sedimentary rocks, such as some limestones, sandstones, phosphate rocks, and shales. It is common in sulfide ores of heavy metals. Across the great plains of the United States there are numerous areas where the soils are high in selenium. In nature, selenium occurs in four important oxidation states: elemental selenium (Se), Se^{-2} , which is often associated with metals, Se^{+4} (selenite), and Se^{+6} (selenate). A variety of natural chemical processes can convert selenium from one inorganic form to another [Callahan et al. 1979, Cutter 1978, 1982, Environmental Protection Agency (EPA) 1987]. The alkaline soils of much of the western United States provide conditions which result in the oxidation of selenium to selenate, which is very soluble and is easily leached from soils. Selenite and selenate are the principal forms of inorganic selenium entering food chains because these forms are taken up by plants [Kansas Department of Health and Environment (KDHE) 1986]. Also, in many cases there are considerable differences in uptake and biological effects of the different forms of selenium (e.g. Butler and Peterson 1967, Kumar and Prakash 1971, Lindstrom 1983). Because selenium is chemically similar to sulfur, selenium taken up by photosynthetic organisms can be converted to an organic form such as selenomethionine, selenocystine, or selenocysteine (e.g. Bottino et al. 1984, Burau 1985, Doran and Alexander 1977, National Research Council 1976, Stadtman 1974, Wrench 1978, 1979). These substituted amino acids are readily incorporated into tissues of consumers, and therefore may be more toxic than the inorganic forms (e.g. Burau 1985, EPA 1987). Selenomethionine is a particularly hazardous organic form (Heinz et al. 1987, Hoffman and Heinz 1988).

Apparently, there is little information about selenium concentrations in Kansas soils. However, in much of the state Cretaceous rocks or soils derived from Cretaceous rocks are at

or near the surface. Water percolating through those rocks or soils can carry selenium to groundwaters (KDHE 1986).

Selenium is an essential trace nutrient for terrestrial and freshwater organisms. However, proper selenium levels in animals fall within narrow ranges, and the acute and chronic effects of organic and inorganic forms of selenium differ on aquatic and terrestrial plants and animals (EPA 1987). Selenium deficiency can produce a variety of symptoms, as can selenium toxicosis. Many of the symptoms are the same (Marier and Jaworski 1983). Numerous cases of selenium poisoning of fish, mammals, and birds have been documented (e.g. Clark 1987, Cumbie and Van Horn 1978, EPA 1987, Hoffman et al. 1988, Lemly 1987, Ohlendorf et al. 1986a,b, 1988, Saiki and Lowe 1987). In contrast, selenium can reduce the toxic effects of arsenic, mercury, and some other environmental contaminants (EPA 1987).

Selenium bioaccumulation¹ occurs in some settings (Cherry and Guthrie 1977, DuBow 1989, Lemly 1985, 1987, Lemly and Smith 1987, Saiki 1986), and concentrations in plants and animals may be progressively greater in organisms higher in the food chain. However, Adams and Johnson (1977) and Kay (1984) suggested that selenium biomagnification does not occur. Whether it does or not, monitoring selenium levels in habitats important to fish or wildlife and in the animals themselves is necessary to determine if selenium concentrations are detrimental to fish or wildlife.

The most recent EPA water quality criteria to protect aquatic life are 5 mcg/l maximum for a 4 day average and 20 mcg/l for a 1 hour average (EPA 1987). Neither value is to be exceeded more than once every three years on the average.

A draft report of the KDHE (1986) indicated that between 1978 and 1985, a site on Rattlesnake Creek near Raymond had a mean selenium concentration of 18.7 mcg/l. The selenium concentration was of concern to the Service because Quivira National Wildlife Refuge is a few miles upstream from the sampling site. Water samples from the Creek above the refuge did not have elevated selenium levels. Therefore, sampling was conducted on the refuge in 1987 to determine if a source of selenium contamination was located on the refuge or if selenium levels on the refuge were hazardous to fish or wildlife.

¹ Bioconcentration is the accumulation of an element or compound by an aquatic organism directly from the water. Bioaccumulation is accumulation from water and from food. Biomagnification refers to increases in body burden of an element or compound in successively higher trophic levels (Biddinger and Gloss 1984, Hall and Burton 1982, Hacek et al. 1979, Rand and Petrocelli 1985).

STUDY AREA AND METHODS

Quivira National Wildlife Refuge is located in northeastern Stafford, southwestern Rice, and northwestern Reno counties in Kansas. Mean annual precipitation in the refuge area is about 61 cm. The approximately 8,600 ha encompassed by the refuge are generally flat, although the terrain is broken by stabilized sand dunes. Rattlesnake Creek flows into the refuge from the southwest, flows north for approximately 14 km, and exits the northeast corner of the refuge (Figure 1). Water diverted from the creek flows through canals with water control structures and into approximately 1800 ha of wetlands in 32 impoundments. Two large saline basins are notable features of the refuge, although their salinity has decreased in recent years due to flushing action of Rattlesnake Creek.

Cooperative farming is practiced on about 500 ha of the refuge. The remaining 6,300 ha of rangeland include native prairie grasses, tree thickets and groves, and scattered shelterbelts.

Quivira supports a variety of nesting, migrating, and wintering bird species. The refuge is a major stopover point for migratory birds in the Central Flyway. Diurnal raptors, sandhill cranes (Grus canadensis), galliformes, mammals, and some reptile species are common on the refuge.

To assess selenium levels on the refuge, six locations believed to be representative of Rattlesnake Creek and its drainage were selected for sampling (Figure 1). We collected water, sediment, filamentous algae, and fish samples in 1987.

A water sample was collected on 23 or 24 July at each of the sampling locations. Each sample was collected in a clean, hand-held plastic cup submerged to a depth of approximately 0.3 m. A battery-operated vacuum pump was used to force the sample through a 0.5 micron filter. Filtrate from each sample was collected in an acid-cleaned 250 ml plastic bottle and fixed with 2 ml of 70% nitric acid. The bottle mouth was covered with cellophane before the top was screwed on. Another water sample was collected at each sampling point on 12 August.

Two sediment samples were collected at each sampling location on 23 or 24 July 1987. A clean steel spade was used to collect sediment from several places along the streambed or lake bed. Approximately 0.5 kg of sediment was collected for each sample and double bagged in plastic bags.

There was no rooted aquatic vegetation at any of the 6 sampling points. However, at locations 2, 3, and 5, for each

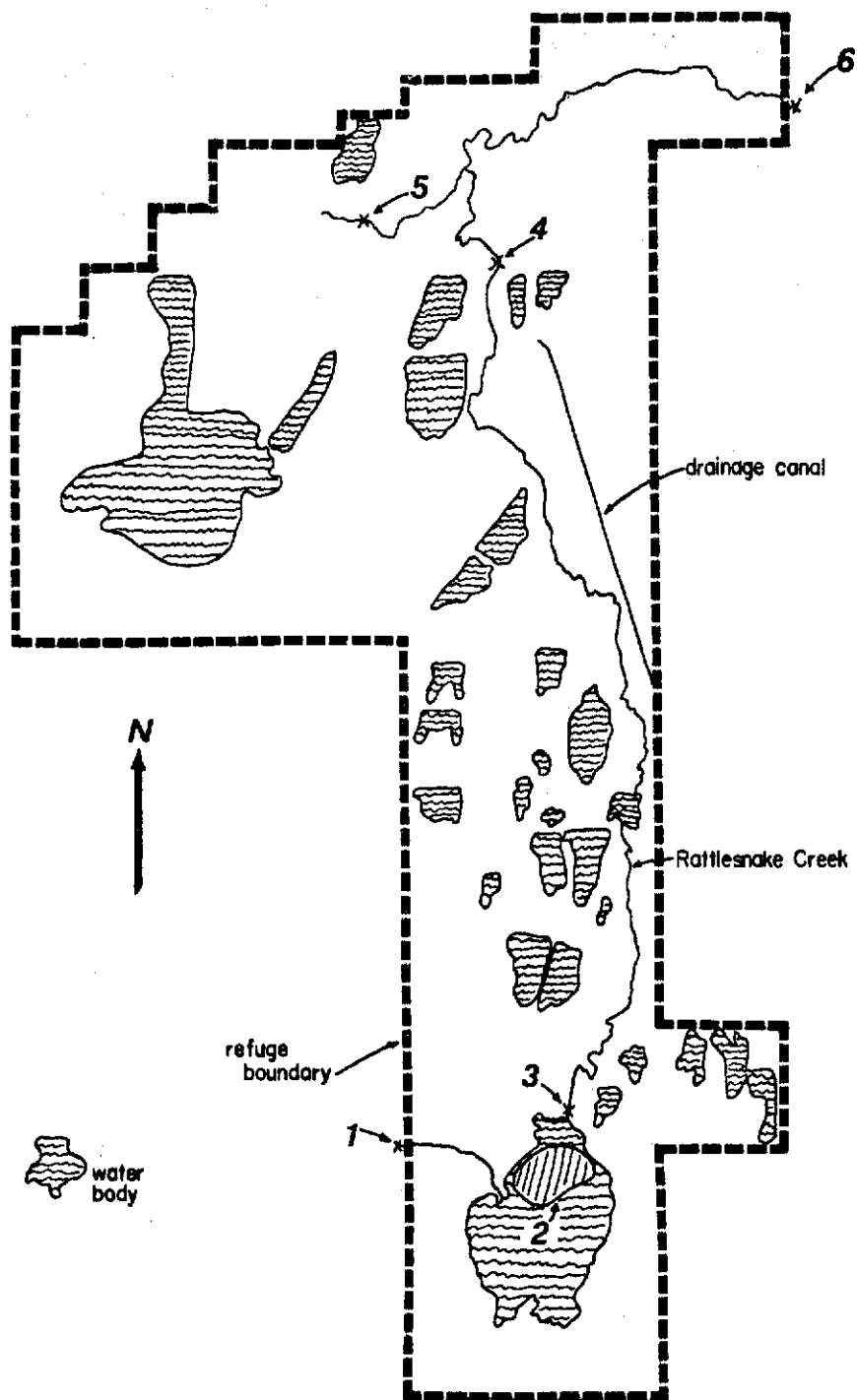


Figure 1. Sampling locations (1-6) at Quivira National Wildlife Refuge, summer 1987.

of 2 samples at each location, approximately 0.25 kg of filamentous algae was collected and double bagged in plastic bags on 23 or 24 July. The algae species were not identified.

Common carp (Cyprinus carpio) were collected by seining or by electroshocking. Each carp was measured, weighed, and wrapped in aluminum foil. Two composites of 4 whole fish of approximately equal sizes were collected from each location on 23 or 24 July and double bagged in heavy plastic.

All samples were kept on wet ice while they were in the field. Thereafter, the water samples were kept refrigerated and the sediment, algae, and fish samples were kept frozen until they were delivered to the Environmental Trace Substances Research Center at the University of Missouri for analysis. The laboratory analyses for total selenium were done using atomic absorption spectroscopy. Each sample collected was large enough for the laboratory to determine the dry weight total selenium concentration at the limit of the analytical equipment. No anomalies were reported in the samples. Percent moisture and dry weight selenium concentration were reported by the lab; wet weight concentrations were calculated by multiplying the dry weight concentration by the quantity $(1 - \% \text{ sample moisture})$. Wet weight detection limits were calculated in the same way.

Laboratory quality control was assured through the Service's Patuxent Analytical Control Facility (PACF). The precision and accuracy of the laboratory analyses for the Service are confirmed with procedural blanks, duplicate analyses, test recoveries of spiked materials, and reference material analyses. Round-robin tests among Service and contract analytical labs also are part of the PACF quality control procedures. All Service contaminants analyses receive a PACF quality assurance review. Duplicate analyses of samples we submitted differed by no more than 0.1 ppm. Spike recoveries were 95% in water and sediment, 94% in vegetation, and 96% in fish. Results from analyses of reference standards differed from the expected values by less than 1 ppm.

Geometric mean and arithmetic mean selenium levels and the standard error for the estimate of the mean for each type of sample were calculated from the analytical results. A value of $\frac{1}{2}$ the detection limit was used for calculations of means and standard errors when a sample concentration was below the detection limit.

RESULTS

Selenium concentrations in the water samples were consistent among the 6 sampling locations and between the two sampling dates (Table 1). The concentrations in sediment samples were low. Six of 12 sediment concentrations were below the detection limit (Table 2). Concentrations in algae and common carp also were low (Tables 3 and 4).

Table 1. Selenium concentrations in water samples collected at Quivira National Wildlife Refuge, July and August 1987.

| Sample Number | Collection Location ^a | Concentration | |
|-----------------|----------------------------------|---------------------|--------------------|
| | | mcg/ml ^b | mcg/l ^c |
| 1A-W | 1 | 0.00075 | 0.75 |
| 1B-W | 1 | 0.0007 | 0.7 |
| 2A-W | 2 | 0.0010 | 1.0 |
| 2B-W | 2 | 0.00095 | 0.95 |
| 3A-W | 3 | 0.0007 | 0.7 |
| 3B-W | 3 | 0.00095 | 0.95 |
| 4A-W | 4 | 0.00085 | 0.85 |
| 4B-W | 4 | 0.0004 | 0.4 |
| 5A-W | 5 | 0.0006 | 0.6 |
| 5B-W | 5 | 0.0004 | 0.4 |
| 6A-W | 6 | 0.0006 | 0.6 |
| 6B-W | 6 | 0.00075 | 0.75 |
| geometric mean | | $\bar{x}=0.000693$ | $\bar{x}=0.69$ |
| arithmetic mean | | $\bar{x}=0.000721$ | $\bar{x}=0.72$ |
| | | se=0.000058 | se=0.06 |

^a Collection locations are shown on the study area map.

^b Reported by the analytical laboratory.

^c Shown for comparison to standards.

Table 2. Selenium concentrations in sediment samples collected at Quivira National Wildlife Refuge, July 1987.

| Sample Number | Collection Location ^a | Percent Moisture | Concentration mcg/g | |
|-----------------|----------------------------------|------------------|------------------------|------------------|
| | | | Wet Weight | Dry Weight |
| 1A-S | 1 | 31.5 | 0.06 | 0.09 |
| 1B-S | 1 | 20.7 | ND ^b | ND |
| 2A-S | 2 | 46.0 | 0.16 | 0.29 |
| 2B-S | 2 | 46.1 | 0.11 | 0.20 |
| 3A-S | 3 | 25.1 | 0.07 | 0.09 |
| 3B-S | 3 | 27.9 | 0.07 | 0.1 ^c |
| 4A-S | 4 | 22.0 | ND | ND |
| 4B-S | 4 | 21.5 | ND | ND |
| 5A-S | 5 | 57.9 | 0.08 | 0.2 |
| 5B-S | 5 | 39.3 | ND | ND |
| 6A-S | 6 | 24.2 | 0.08 | ND |
| 6B-S | 6 | 25.2 | ND | ND |
| geometric mean | | \bar{x} =30.45 | \bar{x} =0.060 | \bar{x} =0.085 |
| arithmetic mean | | \bar{x} =32.28 | \bar{x} =0.068 | \bar{x} =0.106 |
| | | se= 3.51 | se=0.011 | se=0.023 |

^a Collection locations are shown on the study area map.

^b Not detected. Detection limit was 0.1 mcg/g dry weight.

^c Decimal values are shown as reported by the analytical laboratory.

Table 3. Selenium concentrations in filamentous algae samples collected at Quivira National Wildlife Refuge, July 1987.

| Sample Number | Collection Location ^a | Percent Moisture | Concentration mcg/g | |
|-----------------|----------------------------------|------------------|------------------------|------------------|
| | | | Wet Weight | Dry Weight |
| 2A-V | 2 | 85.4 | 0.03 | 0.2 ^b |
| 2B-V | 2 | 78.3 | ND ^c | ND |
| 3A-V | 3 | 89.4 | 0.06 | 0.55 |
| 3B-V | 3 | 94.7 | 0.03 | 0.54 |
| 5A-V | 5 | 91.6 | 0.03 | 0.37 |
| 5B-V | 5 | 93.6 | 0.02 | 0.3 |
| geometric mean | | $\bar{x}=88.65$ | $\bar{x}=0.027$ | $\bar{x}=0.263$ |
| arithmetic mean | | $\bar{x}=88.83$ | $\bar{x}=0.030$ | $\bar{x}=0.335$ |
| | | se= 2.50 | se=0.007 | se=0.080 |

^a Collection locations are shown on the study area map.

^b Decimal values are shown as reported by the analytical laboratory.

^c Not detected. Detection limit was 0.1 mcg/g dry weight.

Table 4. Selenium concentrations in common carp collected at Quivira National Wildlife Refuge, July 1987.

| Sample Number | Collection Location ^a | Percent Moisture | Concentration mcg/g | |
|--------------------|----------------------------------|------------------|------------------------|------------------|
| | | | Wet Weight | Dry Weight |
| 1A-FT ^b | 1 | 75.7 | 0.32 | 1.3 ^c |
| 1B-FT | 1 | 76.0 | 0.50 | 2.1 |
| 2A-FT | 2 | 76.3 | 0.35 | 1.5 |
| 2B-FT | 2 | 72.6 | 0.44 | 1.6 |
| 3A-FT | 3 | 78.9 | 0.29 | 1.4 |
| 3B-FT | 3 | 77.8 | 0.31 | 1.4 |
| 4A-FT | 4 | 76.4 | 0.26 | 1.1 |
| 4B-FT | 4 | 78.8 | 0.32 | 1.5 |
| 5A-FT | 5 | 80.0 | 0.15 | 0.73 |
| 5B-FT | 5 | 80.1 | 0.18 | 0.89 |
| 6A-FT | 6 | 77.6 | 0.45 | 2.0 |
| 6B-FT | 6 | 76.7 | 0.42 | 1.8 |
| geometric mean | | $\bar{x}=77.22$ | $\bar{x}=0.315$ | $\bar{x}=1.384$ |
| arithmetic mean | | $\bar{x}=77.24$ | $\bar{x}=0.333$ | $\bar{x}=1.443$ |
| | | se= 0.61 | se=0.031 | se=0.119 |

^a Collection locations are shown on the study area map.

^b Each fish sample is a composite of 4 fish.

^c Decimal values are shown as reported by the analytical laboratory.

DISCUSSION

Brooks (1984) stated that most fresh waters average about 1 mcg/l selenium, although some waters contain as much as 160 mcg/l. Fishbein (1984) reported that in ground waters and surface waters selenium ranges from 0.01 to 400 mcg/l. Robberecht and Von Grieken (1982) reported selenium concentrations in rivers across the United States ranging from less than 0.01 mcg/l to 30 mcg/l. Lake waters in the United States were reported to contain 0.04 to 1.4 mcg/l (National Academy of Sciences 1976). Concentrations at the uncontaminated Volta Wildlife Area in California were about 0.04 to 0.1 mcg/l (Saiki and Lowe 1987). In North Carolina, two uncontaminated lakes contained 0.32 and 0.67 mcg/l (Lemly 1985). Halter *et al.* (1980) found that Daphnia magna were apparently unaffected by concentrations up to 500 ppb, although Hyallolela azteca were harmed by a concentration of 40 ppb. Dunbar *et al.* (1983) found that selenite concentrations as high as 2000 ppb apparently did not harm Daphnia magna. Concentrations greater than 50 ppb affected the green alga Selenastrum capricornutum (Foe and Knight 1986).

Selenium concentrations in water from our investigation contrast sharply with the 18.7 mcg/l mean value reported by the KDHE from Rattlesnake Creek downstream of the refuge. All values from this study are below the 3.0 mcg/l lowest value reported by the KDHE for the Rattlesnake Creek sampling station.

Our results indicate that the level of selenium in refuge waters is well below the 1987 EPA standard for selenium for protection of aquatic life and also is below the 2 to 5 mcg/l level of concern for fish and wildlife suggested by Lemly and Smith (1987) (Figure 2).

The geometric mean selenium concentration in the sediment samples from this study was below the 0.23 mcg/g dry weight geometric mean for the western United States reported by Shacklette and Boerngen (1984) and below the 0.45 mcg/g mean reported for the northern Great Plains by Severson and Tidball (1979). The mean at Quivira also was well below the means for both pothole (\bar{X} =0.89 mcg/g dry weight, range 0.13 to 2.1) and riverine (\bar{X} =0.52, range 0.03 to 5.1) wetlands in the north-central United States (Martin and Hartman 1984). Most sediment concentrations reported for other water bodies (e.g. Furr *et al.* 1979, Nriagu and Wong 1983, Saiki and Lowe 1987) also were higher than we found at Quivira. Lemly and Smith (1987) recommended a 4 mcg/g dry weight level of concern in sediment for protection of fish and wildlife. Selenium concentrations in sediments of Quivira (Figure 3) were well below that level.

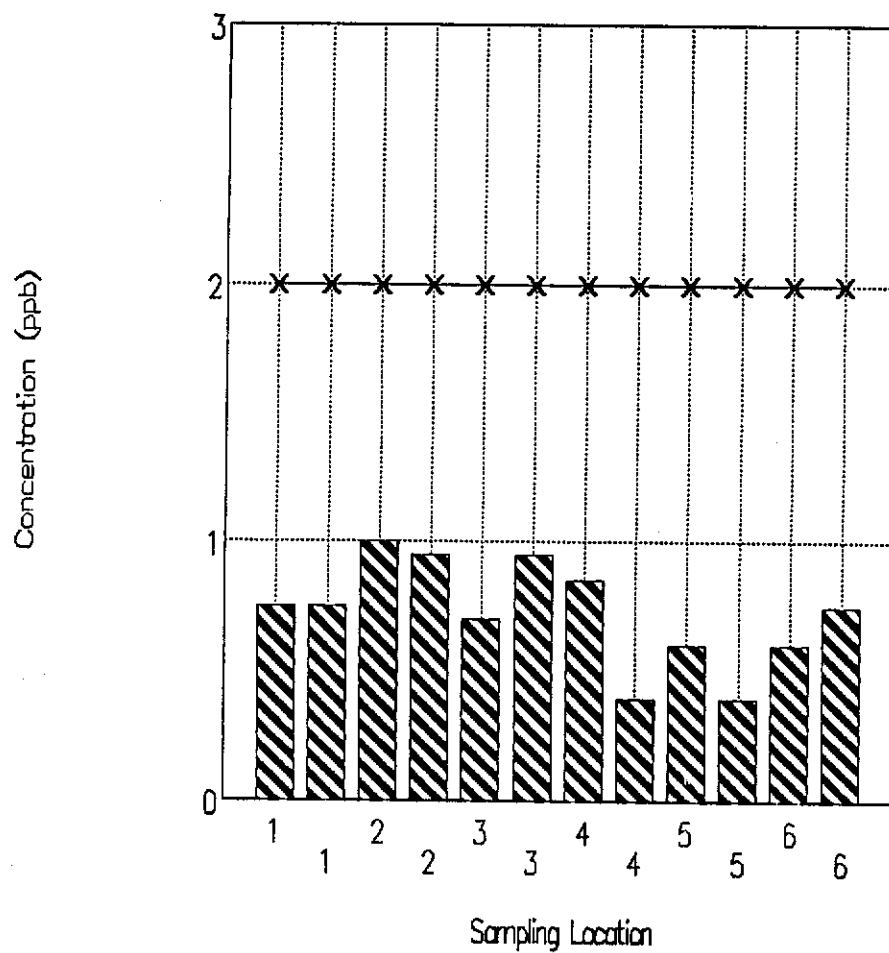


Figure 2. Selenium concentrations in water samples collected at Quivira National Wildlife Refuge, July and August 1987. The line at 2 ppb represents the lowest level of concern in water (Lemly and Smith 1987).

Although many factors can influence trace element concentrations in sediments (Martin and Hartman 1984, 1987), selenium concentrations in the sediments from Quivira do not appear to be of concern.

Furr *et al.* (1979) recorded selenium concentrations in algae of 0.6 mcg/g dry weight in an uncontaminated pond and 0.9 mcg/g dry weight in a nearby contaminated pond. Aquatic insects contained 1.5 ppm. At Volta Wildlife Area in California, Saiki and Lowe (1987) collected algae samples with selenium concentrations that ranged from below the detection limit to 1.4 mcg/g dry weight. Lemly (1987) suggested a chronic no-effect level for dietary selenium for warm water fishes of 3 to 6 mcg/g dry weight. Although uptake and toxicity concentrations differ widely among aquatic plants and animals (EPA 1987), the filamentous algae concentrations we report for Quivira imply that aquatic biota in refuge waters contain dry weight selenium concentrations below 3 mcg/g.

The nationwide geometric mean wet weight selenium concentrations in fish were 0.60 mcg/g (range 0.57 to 0.64) in 1971-1973, 0.58 mcg/g (range 0.53 to 0.62) in 1976-1977, 0.46 mcg/g (range 0.09 to 3.65) in 1978-1979, and 0.47 (range 0.09 to 2.47) in 1980-1981 (Lowe *et al.* 1985, May and McKinney 1981, Walsh *et al.* 1977). The mean wet weight concentration in the composites from Quivira were below these nationwide means. Wet weight selenium levels in the carp from Quivira were far below the 2 mcg/g wet weight level of concern suggested by Baumann and May (1984) and well below the 12 mcg/g dry weight whole body value suggested as a level of concern by Lemly and Smith (1987) (Figure 4). The maximum body burden of 2.1 mcg/g dry weight in composite samples indicates that common carp on the refuge are not exposed to high levels of selenium.

There was no apparent trend in the selenium content of any sample medium from the south (upstream) end to the north (downstream) end of the refuge. The uniformity of concentrations suggests that the source of selenium contamination of Rattlesnake Creek is not on Quivira NWR. Therefore, although we did not evaluate selenium concentrations in nesting birds or in other resident animals, we believe it unlikely that they accumulate selenium as a result of their use of the refuge. Additional research would be necessary to evaluate selenium levels in terrestrial plants and animals on the refuge.

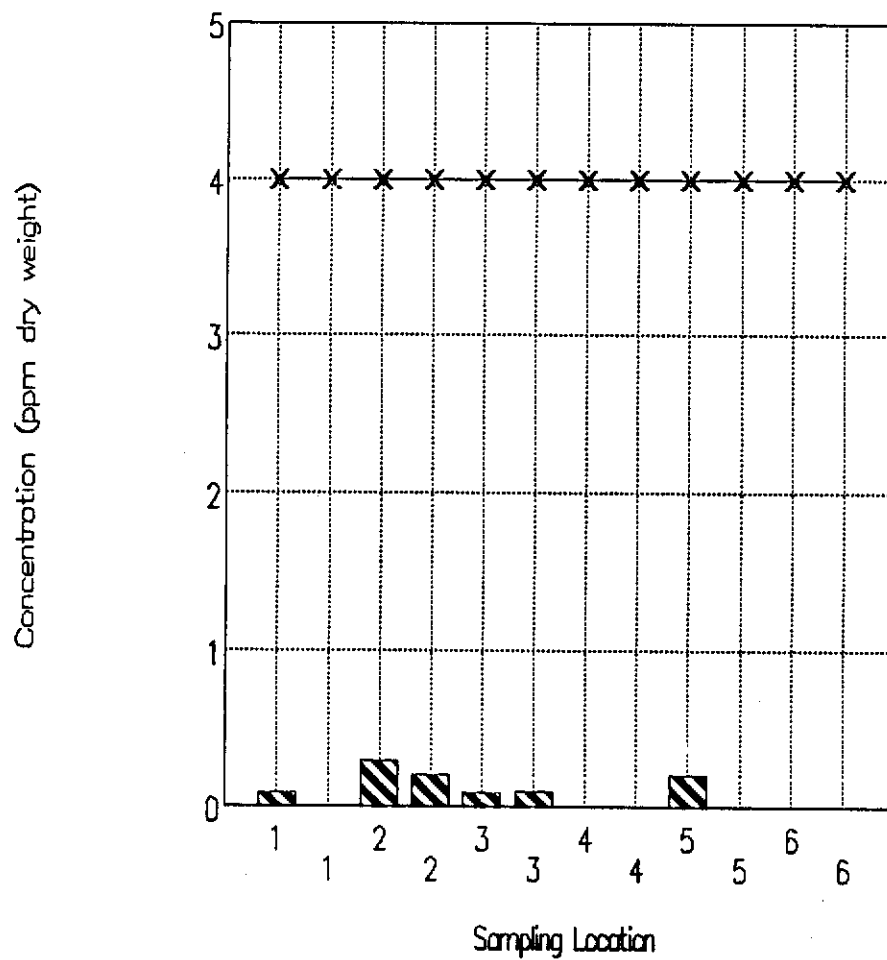


Figure 3. Selenium concentrations in sediment samples collected at Quivira National Wildlife Refuge, July and August 1987. The line at 4 ppm represents the level of concern in sediments (Lemly and Smith 1987).

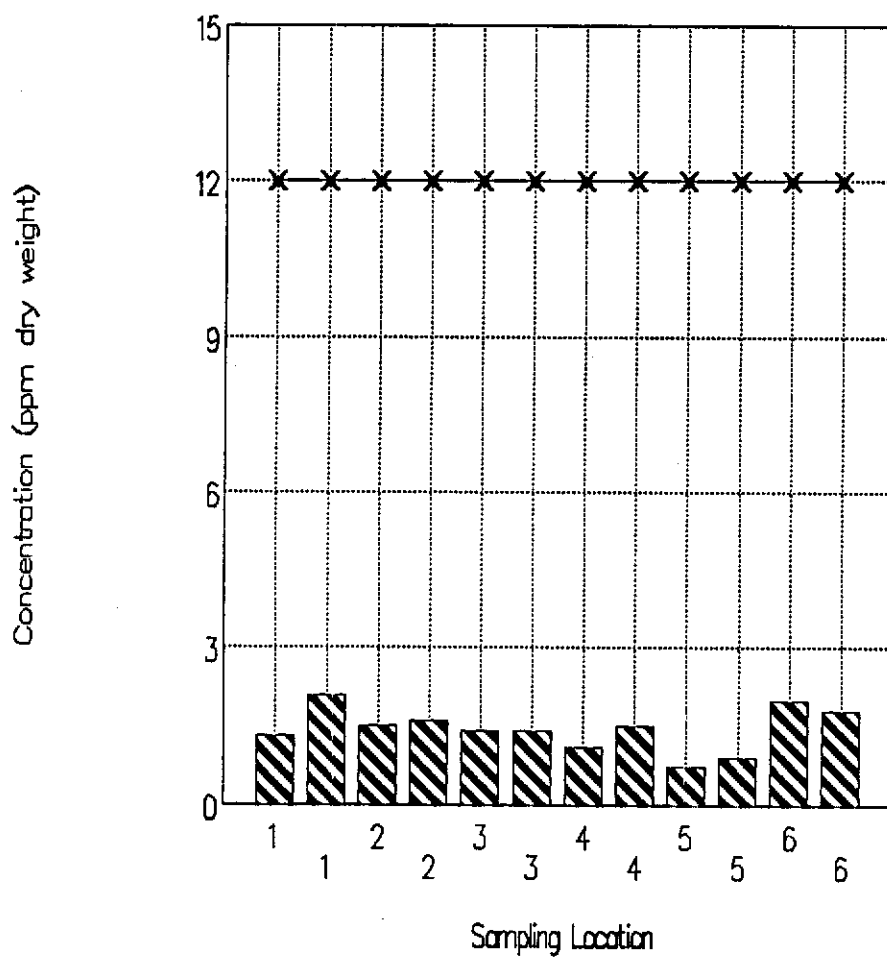


Figure 4. Selenium concentrations in common carp collected at Quivira National Wildlife Refuge, July and August 1987. The line at 12 ppm represents the level of concern in whole fish (Lemly and Smith 1987).

Variations in precipitation, stream flows, and water use could affect the selenium concentrations observed on the refuge and in Rattlesnake Creek. However, the Kansas Department of Health and Environment has suggested that the most likely source of the high selenium concentrations recorded at the monitoring station near Raymond is a "...mineral intrusion immediately downstream of the refuge" (S. Cringan, personal communication). Based on the information available, we concur with that assessment.

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