Selenium Contamination

in *Corbicula* Transplanted into Agricultural Drains

in the Imperial Valley, California

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Abstract

Studies of environmental contaminants in the Imperial Valley and Salton Sea area began in 1986 (Setmire et al. 1990), and selenium was identified as the major element of concern. Later studies (Setmire et al. 1993) focused on the potential for impacts from agricultural drainage on migratory and resident birds and their habitats. Studies recently completed (Bennett 1996) focused on black-necked stilts (*Himantopus mexicanus*), colonial waterbirds and desert pupfish (*Cyprinodon macularius*). All of these groups were found to be at risk of reproductive problems as a result of selenium contamination. The study discussed here was designed to examine selenium on the scale of individual drains as opposed to on an ecosystem basis. This study used the Asiatic river clam (*Corbicula* sp.) to evaluate selenium bioaccumulation in several irrigation drains in the Imperial Valley. The clams were obtained from Cibola National Wildlife Refuge on the lower Colorado River.

The lowest concentration of selenium in clams placed in a drain was 6.0 parts per million (ppm), and the highest concentration measured was 15.8 ppm. Reference sample concentrations ranged from 8.5 ppm to 15.5 ppm, and clams collected from the Colorado River as controls ranged from 8.1 ppm to 11.9 ppm. Because the concentrations of selenium in clams from the Colorado River were higher than expected, it is not possible to clearly identify the source of selenium measured in the clams which were placed in the drains. Other studies (Rusk 1991 and Lusk 1993) have found similar selenium concentrations in clams from the lower Colorado River. While this study may not have met the objective of providing drain specific selenium bioavailability information, remediation of specific drains is still a valid approach and should be pursued. Of particular concern are those drains with high habitat value for fish and wildlife resources.

Introduction

Irrigation began in the Imperial Valley in 1901, before the present Salton Sea was formed by an accidental diversion of the Colorado River in 1905. The underground tile system was first installed in 1929 to alleviate salt accumulation in the soils. In the current system water is delivered to 160-acre field plots by 1,675 miles of canals throughout Imperial Valley. The total acreage being irrigated in the Imperial Valley is more than 500,000 acres (Setmire et al., 1990). Alfalfa and Sudan grass make up a large proportion of this total. Other crops being grown in the Imperial Valley include: cotton, sugar beets, wheat, barley, vegetables and melons.

As a result of developmental abnormalities and reproductive failures seen at Kesterson National Wildlife Refuge in 1983 where irrigation drainage was impounded in Kesterson Reservoir, concerns were raised regarding the potential for impacts to wildlife from irrigation drainwater. Several studies followed that identified the effects of high concentrations of selenium in the water or diet to wildlife, particularly birds. Ohlendorf et al. (1986) found high rates of embryo death and external abnormalities of chicks among birds nesting at the Kesterson National Wildlife Refuge. Selenium concentrations in prey items ranged up to 175 parts per million (ppm,

dry weight) at this site. Elevated levels were found in fish at this site (Saiki and Lowe 1987), but the implications of these concentrations to the fish could not be determined. A toxicity threshold of 1 g/L waterborne selenium was found by Peterson and Nebeker (1992) for birds and mammals with food habits that are likely to lead to high exposure. In 1985 the Department of the Interior (DOI) began the National Irrigation Water Quality Program (NIWQP) to study irrigation-induced water quality problems in the western states.

Water quality studies began in the Salton Sea area in 1986 (Setmire et al. 1990), and selenium was identified as the major element of concern in terms of hazards to fish and birds. Tile drain effluent was identified as the source of the elevated selenium concentrations. Later studies (Setmire et al. 1993) focused on the potential for impacts from agricultural drainage on migratory and resident birds and their habitats, and they indicated that selenium concentrations were at levels that could affect reproduction in the endangered Yuma clapper rail, piscivorous birds and shorebirds. Studies recently completed (Bennett 1996) focused on black-necked stilts (*Himantopus mexicanus*), colonial waterbirds and desert pupfish (*Cyprinodon macularius*), and determined the three groups were at risk of reproductive problems as a result of selenium contamination. The colonial waterbirds were also found to be at risk of reduced reproduction from DDE-induced eggshell thinning.

The study discussed here was designed to examine selenium on the scale of individual drains as opposed to on an ecosystem basis. This study used the Asiatic river clam (*Corbicula* sp.) to evaluate selenium bioaccumulation in several irrigation drains in the Imperial Valley. The technique was similar to work done by Setmire et al. (1993), but the clams were collected at one to four week intervals rather than intervals of up to 11 months as occurred in that study. Clams used by Setmire et al. (1993) were placed in the New River, Alamo River, or the Trifolium drain. The mean concentration for clams removed from the Trifolium drain (6.3 ppm) was slightly elevated over that for clams from the Colorado River (5.3 ppm), whereas the peak concentration (7.5 ppm) was closer to the values seen in this study. The Alamo River clams showed very little change over time in their selenium concentrations.

The objective was to identify drains with high bioavailability of selenium as potential targets for drain-specific selenium remediation. Clams were placed in eighteen drains previously studied by the U.S. Geological Survey (USGS). Clams were placed and were analyzed for selenium concentrations in January and February of 1995 from the same sites where water and sediment samples were collected by USGS in August 1994. Corresponding wildlife surveys were also conducted along some of these same drains from November 1994 to November 1995 (Hurlbert 1996). The majority of the drains were sampled with clams at sites that were at upstream, midstream and downstream locations along the length of the drain in order to evaluate the effects of increasing drainwater inputs on bioaccumulation of selenium in each drain. Because drains vary in terms of the proportions of tile water (water from subsurface drains with the highest selenium load from soil accumulation), tail water (water from the surface of the fields), and canal water (excess irrigation water that never enters the fields); selenium loading was expected to

vary. Identification of drains with high selenium loads would allow for remediation actions to focus on those drains that contribute the most selenium to the system.

Bivalves have been used in other situations to evaluate bioavailability of a variety of contaminants. The California Mussel Watch program uses mussels in coastal marine waters to evaluate contaminant exposure in those areas. A field bioassay using mussels has been proposed to identify contaminant uptake in conjunction with growth measurements (Salazar and Salazar 1993). The Asiatic river clam has been used in field studies by the Santa Ana Regional Water Quality Control Board (Michelle Courtier, pers. comm.). This study required large numbers of clams which limited source options. *Corbicula* sp. is not amenable to laboratory culturing, so a large field source of clams was necessary. For this study, *Corbicula* of approximately 2.5 cm in length or larger were collected from Cibola National Wildlife Refuge, a location on the Colorado River upstream of Imperial Valley irrigation drainage.

Methods and Materials

Clams for use in this study were obtained from the lower Colorado River at Cibola National Wildlife Refuge on January 5-6, 1995. January was chosen because on average the lowest flows in the drains occur at that time. Follow-up sampling was to occur during the highest flows in April, but could not be conducted because high river flows made the clams inaccessible. Clams were obtained from exposed sandbars along the river s edge in the main channel. The most efficient means of finding clams was to dig by hand along the interface between the sand and the riprap which borders the river in this area. Clams were removed from the sand and placed in buckets of river water until they could be transferred to large coolers also containing Colorado River water. Approximately 2,800 clams were collected for use in Imperial Valley drains. These clams were held in coolers with aeration provided by aquarium pumps from Friday evening (January 6) until Monday morning (January 9) when the coolers were loaded into the vehicles for transport to the deployment sites.

The clams were transported as near to the sites of water and sediment collection as possible for deployment. The clams were placed in plastic minnow traps and then mounted vertically on a length of PVC pipe in water over approximately 0.4 m deep or tied to the pipe and placed on the surface of the sediments in a horizontal position in water less than 0.4 m deep. Cable ties were used to prevent clams from exiting the traps via entrance holes in those mounted horizontally. For those traps that were to be sampled on a weekly basis, 50 clams were placed in the traps. A total of four collections were made from these sites. These sites were sampled more intensively because these same drains were used for biological surveys as well. The remainder of the sites were sampled on a biweekly basis, and 25 clams were placed in each cage. Clams were placed in the traps on January 9-11, 1995. At each deployment site dissolved oxygen, pH, temperature and conductivity were measured using hand held instruments.

The reference site was located along the East Highline canal. This water comes from the Colorado River via the All-American canal and reflects water quality prior to its agricultural use

in the Imperial Valley. Reference clams were collected on a weekly basis. The drain sites were the same as those used by the USGS, but some sites were eliminated as a result of water levels that were too low to support clams. A total of 39 sites were monitored using these clams during January and February representing upstream, midstream and downstream sites. Control clams were collected and held in the same way as reference and drain clams, but were returned to the Carlsbad Field Office and frozen at 0 C following the completion of clam deployment in the drains.

The clams were collected on either a scheduled weekly or biweekly basis. All water quality measurements were repeated at each collection. After removing the clams from the minnow traps, they were placed in plastic bags containing water from the drain and allowed to purge themselves of ingesta for a minimum of 24 hours. After the purging period, the clams were either harvested immediately, or were frozen for 24 hours to facilitate extraction of tissues from the shells. The tissues were placed in chemically clean jars, frozen and shipped on dry ice to the analytical laboratory.

All samples were submitted for selenium analysis and moisture content determinations. A subset of samples was also analyzed using a separate analytical technique for aluminum to determine if adequate purging of ingested sediments had occurred. High aluminum concentrations would indicate that sediments may have been present in the gut and that selenium concentrations may be a combination of sediment selenium and bioaccumulated selenium in the tissues. All analyses were conducted by Hazleton Environmental Services, Inc. of Madison, Wisconsin. The methods are described below, and references are provided in the reference section.

Selenium concentrations were determined by Graphite Furnace Atomic Absorption Spectrophotometer. This method is applicable to animal tissues, plants, sediments, sludges, and soils. For animal tissue 1.00 g is digested with nitric acid in a microwave digester. The amount of selenium is determined at a wavelength of 196.0 nm by comparing the signal of the unknown sample, measured by the graphite furnace atomic absorption spectrophotometer, with the signal of the standard solutions. The method of standard additions is used along with nickel matrix modification in the analysis. Using a 1.00-g sample, the lowest detection limit of this assay is 0.1 ppm.

Moisture determination was performed on all samples. This method is applicable to plant tissue, animal tissue, and soil/sediment. The prepared sample is weighed into a tared aluminum dish and is dried in an oven to constant weight (approximately 12-18 hours) at 100 C. This method is capable of detecting 0.1% moisture.

Aluminum concentrations were determined by Inductively Coupled Plasma Spectroscopy. This method is applicable to plant and animal tissue, soil/sediment, and water. In this study only clam tissue samples were analyzed. Sample preparation began with digestion of 5.00 g of tissue in Teflon vessel with 5 mL nitric acid in a microwave digester. The sample was transferred into a 50 mL volumetric flask and diluted to volume with 0.005% Triton X-100 solution. The final

preparation step was to filter the sample. Aluminum concentration in the sample solution is then determined by comparing its emission intensity with the emission intensities of a known series of aluminum standards. The analytical wavelengths are tabulated with the raw concentration data. Analytical data is corrected for background and interfering element effects by the spectrometer program. The detection limit of each analyte is a function of the instrument detection limit (IDL), the sample mass, and volume to which it is diluted. With each batch of 20 samples of the same matrix type, at least one duplicate, one sample spike, one analytical blank, and one appropriate reference material were assayed.

Results

The selenium concentrations measured in the clams recovered from Imperial Valley drains are presented in Table 1. Geometric means and ranges are provided for each drain and for the sites by the weeks when samples were collected. The lowest concentration of selenium in clams placed in a drain was 6.0 ppm, and the highest concentration measured was 15.8 ppm. Reference sample concentrations ranged from 8.5 ppm to 15.5 ppm, and clams collected from the Colorado River as controls ranged from 8.1 ppm to 11.9 ppm. No pattern emerged regarding upstream sites versus downstream sites or Week 1 or 2 versus Week 3 or 4. No particular area within the Imperial Valley was found to have consistently elevated selenium in the drains of that area. No clear pattern was evident relative to the length of time the clams were in the drains.

At the midstream site on Drain 5, the trap was not relocated until June 27, 1995. The selenium concentration determined for the sample was within the range found at the upstream site on that drain. An additional sample was collected from Drain 16 at the upstream site that was comprised of clams found in the drain sediments. The concentration of selenium was 7.8 ppm which was near the low end of the range measured in clams placed in that drain.

Discussion

The concentrations measured in the *Corbicula* are in the dietary range that has been found to cause reproductive effects in birds. A diet including 10 ppm selenium (as selenomethionine) was found to cause adverse effects when fed to mallards (Lemly and Smith 1987). Skorupa et al. (1996) found in a review of the literature that dietary levels as low as 2.5-8 ppm resulted in reproductive impairment in birds. Impacts may be occurring to birds using the Colorado River and the drains. Lusk (1993) raised particular concern about the Imperial National Wildlife Refuge and recommended captive feeding studies to evaluate the potential risk.

Because the concentrations of selenium in clams from the main channel of the Colorado River were higher than expected, it is not possible to clearly identify the source of selenium measured in the clams which were placed in the drains. The reference clams were placed in the East Highline canal and are believed to have only been exposed to Colorado River water from the All-American canal. When considering the range of values seen in the reference and Colorado River clams, it is possible that the selenium quantified in the clams placed in the drains was already

present at the time of placement because the range of selenium in the clams placed in the drains was very similar to the reference and river clams. Drain mean selenium concentrations ranged from 7.2 ppm to 11.7 ppm. The reference mean selenium concentration was 10.9 ppm, and the Colorado River samples had a mean selenium concentration of 9.8 ppm.

Based on the aluminum concentrations found in the samples for which this was determined, purging of ingesta appears to have been adequate (Roy Schroeder, pers. comm.). The aluminum concentrations ranged from 10.9-130 ppm, with a single sample measuring 1,875 ppm. However, the selenium measured in that sample was very similar to the concentrations found at other sites in the drain where the aluminum measured only 10.9-12.0 ppm. Selenium concentrations are therefore considered to be the concentrations in the tissues.

A clam sample composited from the same collection sites as used in this study was found to have a concentration (9.5 ppm) similar to the reference concentrations determined in this study (Roy Schroeder, pers. comm.). Clams were also deployed at two sites in the New River with similar results (8.6-9.7 ppm selenium). Rusk (1991) found clam tissue residues of 2.94-6.54 ppm selenium in and above the Imperial Reservoir. The two drain sample concentrations in this study were within that range, but that range is below the range found in the reference and river clams. Lusk (1993) found concentrations similar to those found in this study. Clams collected from backwater areas of the lower Colorado River had concentrations of selenium of 5.8-26.5 ppm (geometric mean 11.1). Clams collected from the river itself had concentrations of 7.6-12.7 (geometric mean 9.5). In this study clams placed in the drains had selenium concentrations of 6.0-15.8 ppm (geometric mean 9.6), and reference and river clams ranged 8.1-15.5 ppm (geometric mean 10.4). All clams used in this study were collected from the main river channel.

In comparing the data from the clam tissue samples with the water and sediment results from the same sites (Jim Setmire, pers. comm.), no significant correlations were found. There did not appear to be a relationship between the selenium concentrations found in clam tissues and those measured for the water or sediments of the drains. This may be because the clams started with high tissue concentrations as evidenced by the concentrations found in the river and reference clams. Water and sediment concentrations were collected at a different time from the clam deployment, and the clams may have been exposed to different waterborne selenium concentrations as a result of different irrigation regimes. The suspended sediment loads may also have been different thus affecting what was collected in sediment samples versus what the clams were exposed to in the drains.

In this study the clams collected from the Colorado River did not have sufficiently low body burdens of selenium to permit observation of additional uptake during their relatively short exposures to Imperial Valley drainwater. The technique would have been more useful if a sufficiently large source of uncontaminated clams were available. Additional options for future selenium bioaccumulation studies include collecting species such as sailfin mollies (*Poecilia latipinna*) or juvenile tilapia (*Tilapia zillii* or *Sarotherodon mossambica*) from areas with and without drainwater influences. Efforts could also be made to collect composite invertebrate

samples from the drains. This would encompass the variety of prey items bird species feeding in the drains are likely to consume. Future drain studies should focus on drain areas likely to attract wildlife. Some drains do not provide habitat due to their depth, configuration and/or lack of vegetation. By concentrating research efforts on those areas where receptors are found, research funds can be used most cost effectively.

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