# CONTAMINANTS IN WATER, SEDIMENT AND, BIOTA

# FROM THE

# BILL WILLIAMS RIVER NATIONAL WILDLIFE REFUGE, ARIZONA

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The University of Arizona, 1994

Director: Dr. O. Eugene Maughan

One hundred sixty two composite samples were analyzed for organochlorine compound residues and 19 trace elements and heavy metals. There was no evidence that flushing of washes in times of flood increased contaminant levels in the Bill Williams River, or that historical mining operations currently contributed to the element load.

There was evidence that Colorado River water increased selenium levels in biota in the delta; one hundred percent of fish collected from the confluence of the Bill Williams River and the Colorado River contained elevated selenium concentrations (geometric mean = 9.98, range 2.80-17.56 æg/g dry weight) . These levels exceed standards set for the protection of predatory species of fish and wildlife.

CONTAMINANTS IN WATER, SEDIMENT, AND BIOTA

FROM THE

BILL WILLIAMS RIVER NATIONAL WILDLIFE REFUGE, ARIZONA

by

Leslie Diane Ruiz

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ABSTRACT

One hundred sixty two composite samples were analyzed for organochlorine compound residues and 19 trace elements and heavy metals. There was no evidence that flushing of washes in times of flood increased contaminant levels in the Pill Williams River, or that historical mining operations currently contributed to the element load.
There was evidence that Colorado River water increased selenium levels in biota in the delta; one hundred percent of fish collected from the confluence of the Bill Williams River and the Colorado River contained elevated selenium concentrations (geometric mean = , range 2.80-17.56 æg/g dry weight). These levels exceed standards set for for the protection of predatory species of fish and wildlife.



INTRODUCTION

Selenium contamination on Kesterson National Wildlife Refuge in California and the dramatic effects of this contamination on resident fish and wildlife (i.e., impaired reproduction and embryonic deformities in birds) led to concern about contaminant levels on other arid refuges (Saiki 1987, Saiki and Lowe 1987). Preliminary surveys on arid refuges along the lower Colorado River have shown elevated selenium levels in water, sediments and biota (Radtke 1988, Rusk 1991, Lusk 1993, Welsh and Maughan 1993, and Martinez 1994). The Bill Williams River National Wildlife Refuge (BWRNWR) is in a desert region, has high natural soil alkalinity, and receives water from irrigation return flows.

Elevated selenium levels along the Colorado River were first verified in 1985 when the Department of the Interior (DOI) investigated contaminant levels in 19 irrigation districts in the western United States. Selenium was the only element that exceeded standards set for the protection of fish and wildlife along the lower Colorado River (Radtke et al. 1988).

Subsequently, the U.S. Fish and Wildlife Service (USFWS), through the Arizona Cooperative Fish and Wildlife Research Unit, conducted a series of contaminant investigations on the refuges along the lower Colorado



River. Fish from waters near Cibola National Wildlife Refuge (NWR) were near the chronic threshold for selenium toxicosis and edible portions exceeded federal and state health advisories (Welsh 1992). The selenium tissue levels in 94% of fishes from Imperial NWR exceeded 3 æg/g dry weight, a standard set to protect aquatic birds from chronic selenium toxicosis (Lemly 1993 and Lusk 1993). Rusk (1991) determined that aquatic birds along the lower Colorado River were at risk of embryonic deformities because of elevated selenium levels in fish and invertebrates. Lusk (1993) and Martinez (1994) found this risk was greater in backwater lakes connected to the river than in seep lakes that do not receive direct inflow from the river.

Radtke et al. (1988) postulated that selenium in the Lower Colorado River Valley originated in the upper basin and not from irrigation return flows. Welsh and Maughan (1994) confirmed that irrigation return flows were not the source of selenium in water, sediment and biota on Cibola NWR. If elevated selenium levels in the Colorado River ecosystem originate from upstream sources, there should not be elevated selenium levels in the Bill Williams River NWR:

the Bill Williams River originates in a different watershed than the Colorado River.

There is potential for heavy metal contamination in the Bill Williams River NWR associated with historic mining



operations in the watershed. The potential for such contamination on the refuge is emphasized by the elevated levels of copper, mercury and zinc in Alamo Lake, 56 km upstream from the Bill Williams River NWR (King et al. 1991). These levels were above the 85th percentile set by the National Contaminant Biomonitoring Program (NCBP) (Lowe et al. 1885, Schmitt and Brumbaugh 1990). In addition, historic mining sites are located in several of the washes that are tributaries to the Bill Williams River. Tailings from these mining areas may contribute heavy metals to the system with runoff.

I began sampling on Bill Williams River NWR in summer 1992 and completed sampling in summer 1993. In December 1992 and January 1993, the area received record amounts of precipitation that resulted in flood flows of over 7000 cubic feet per second (cfs) (ca 2300 cubic meters per second) (Nancy Gilbertson, BWRNWR Manager, personal communication) . These extreme flows caused the river to overflow its banks and rechannelize its course. Comparisons of contaminant levels from before and after this flood event should allow evaluation of the input of contaminants from the mining areas to the river.

The objectives of my study were to:

1. determine baseline contaminant concentrations in sediment, water and biota from aquatic habitats



on the Bill Williams River NWR,

2 determine whether washes that drain into the Bill Williams River during rainfall contribute to the contaminant load within the river system,

3. and determine if the flood in 1993 altered the contaminant levels within sediment, water and biota of the Bill Williams River.

## STUDY AREA

The Bill Williams River NWR is one of four National Wildlife Refuges located on the lower Colorado River below Davis Dam (Figure 1). The Refuge was established concurrently with Havasu NWR by Executive Order 8647, but was not established as an autonomous refuge until 1992. Additions to the Bill Williams River NWR were acquired from The Nature Conservancy (TNC) in 1977. The Refuge is a "..... refuge and breeding ground for migratory birds and other wildlife.. "(Executive Order 8647) and is suitable . . . "for incidental fish and wildlife oriented recreational developments, the protection of natural resources, and conservation of endangered or threatened species" [Refuge Recreation Act, as amended, (Public Law 87-7140)] (Baca 1992).

The Bill Williams River NWR lies in one of the hottest and driest regions of the United States. Annual precipitation averages ca 12 cm (4.63 in) . Temperatures have ranged from -12 to 51 C (9 to 124 F) (Rivers West 1990). Because of these extremes, the sparse upland vegetation contrasts dramatically with the riparian and delta vegetation.

The Bill Williams River NWR is located 4 km east of Parker Dam on the Colorado River at the confluence of the Bill Williams River and Lake Havasu (Figure 1). The Refuge



See Table/Figure

Figure 1. Location of the lower Colorado River Valley and the Bill Williams River NWR.



consists of three principal management units: the Delta Management Unit, which includes a portion of Lake Havasu and associated marsh; the Bill Williams River Management Unit, which includes the Bill Williams River and its floodplain;

and the Desert Uplands Management Unit. I focused on the Delta and Bill Williams River units.

The Bill Williams River basin is recognized statewide in Arizona for its diversity of wildlife: 250 bird, 48 mammal, and 34 reptile and amphibian species have been documented in the basin (Baca 1992). The Bill Williams River NWR is habitat for several federally listed endangered species: Southern bald eagle (Haliaeetus leucocephalus), Yuma clapper rail (Rallus yumanensis), Peregrine falcon (Falco peregrinus), razorback sucker (Xyrauchen texanus) Colorado squawfish (Ptychocheilus lucias), bonytail chub (Gila elegans), and humpback chub (Gila cypha) (Baca 1992). The Yellow-billed cuckoo (Coccyzus americanus), (listed by the State of California as endangered) also occurs on the Refuge.

The refuge (2,475 ha) includes ca 2 km of Lake Havasu and associated marsh and extends upstream along the Bill Williams River for ca 17 kilometers. A 210 ha portion of Lake Havasu is associated with the Delta Management Unit. This area supports a variety of submergent aquatic vegetation, fish, and freshwater clams. The shoreline is

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rocky and the dominant vegetation is salt cedar (Tamarisk spp.) . This area is open to the public and is designated as a "no-wake" zone. The lower end of the refuge consists of open lake and cattail-dominated marsh at the confluence of the river and Lake Havasu. This marsh contains ca 135 ha (Vegetation Map 1989) The dominant vegetation is cattails (Typha spp.); the marsh is bordered by steep rock banks and there is little other shoreline vegetation. The delta supports many species of fish and wildlife, including the endangered Yuma clapper rail, and wintering Canada geese and ducks (USFWS 1989a) . The delta area has expanded over time as sediments are deposited from upstream during high flow events of the Bill Williams River (Rivers West 1990).

Upstream from the delta in the Bill Williams River Management Unit, the riparian vegetation is composed of dense stands (ca 600 ha) of cottonwood (, willow, and salt cedar (USFWS 1989b) . The cottonwood/willow gallery forest provides habitat for the federally endangered Southern bald eagle and Peregrine falcon and state listed species including the Yellow-billed cuckoo and Willow flycatcher. The Refuge also supports many neotropical "song birds"; the Bill Williams River is one of the last vestiges of riparian forest along the lower Colorado River system.

The Bill Williams River originates at Alamo Dam at the



confluence of the Big Sandy Wash and the Santa Maria River. It flows west 56 km from the dam before entering the Colorado River. At the eastern boundary of the Refuge lies Planet Ranch. It is owned by the City of Scottsdale, Arizona and is used to grow alfalfa. Upstream from Planet Ranch, surface flow in the river is dependent on releases from Alamo Dam; generally there is little surface flow. Downstream from the ranch, flows are dependent on the amount of ground water pumped for irrigation at Planet Ranch. In summer of 1992, the river originated on the Refuge ca 50 meters inside the Refuge boundary with Planet Ranch. This area was dominated by cattails and other emergent aquatic vegetation as well as a dense canopy of cottonwood and willow.

Throughout its length, the Bill Williams River was historically perennial, but presently the river is characterized by interrupted stretches where there is no surface flow. The river flows at ca 10 cfs in the summer months (USGS 1979-93). During this time much of the river has only subsurface flow.

The Bill Williams River dissects three mining districts along its reach. The Planet mining district lies within/adjacent to the Refuge boundary. The Planet mineral district contains two of the largest known copper deposits in the southwestern United States (Lehman 1989). The larger



deposit is at Mineral Hill Mine, located ca 0.2 km south of the Bill Williams River along Mineral Wash; the smaller mine, Planet Mine is located southeast of the refuge. Mineral deposits at both mines are typically characterized by massive hematite, $Fe_2O_3$, with fracture filling chrysocolla, a hydrous copper silicate, $CuSiO_3 2H_2O$. High grade copper mineralization was discovered in the Planet Mine in the 1850's. Production from this and other mines in the Planet mineral district mainly occurred between 1923 and 1972. From 1964 to 1970, there were open-pit operations at the Mineral Hill Mine. More than 11-million kg of copper, 11,200 g of gold and 28,000 g of silver were recovered. The total district production was slightly more than 101,600-million kg of ore (Lehman 1989). Mining was discontinued at the Mineral Hill Mine in 1970. However, large tailings piles are exposed in the area of the mine and along the floor of Mineral Wash. These washes all drain into the Bill Williams River.



# METHODS

## Sample Locations

Abiotic and biotic samples were collected at six locations in the Bill Williams River on the refuge and one site 1 km below Alamo Dam at the U.S. Geological Survey (USGS) monitoring station. Collection sites (Table 1) were located upstream and downstream of the confluence of the major washes (Yucca, Mohave, Mineral, and Cave Washes) and the Bill Williams River (Figure 2).

Collection sites were restricted to the areas with surface flow in 1992. The same areas were sampled in 1993 even though the river flowed through its entire length (ca 360 cfs) . Site 2 is located at the eastern boundary of the Refuge. Sites 2 and 3 bracket Yucca Wash from the north. Sites 3 and 4 bracket Mohave Wash which also flows from the north. Sites 4 and 5 bracket Mineral Wash, the site of the inactive copper mine, which flows from the south. Sites 5 and 6 bracket Cave Wash from the north. Site 7 is at the confluence of the Bill Williams River and the Colorado River. Data were collected at all sites in 1992 and at sites 2, 4, 6, and 7 in 1993; other sites were inaccessible because of flood damage to the access road.



See Table/Figure

Figure 2. Location of study sites within Bill Williams River National Wildlife Refuge.

Table 1. Longitude and latitude of collection locations on the Bill Williams River NWR.

| Location | Longitude and Latitude |
|---|---|
| Site 1 | 113ø 36' 29" W<br>34ø 13' 51" N |
| Site 2 | 113ø 57' 23" W<br>34ø 15' 23" N |
| Site 3 | 113ø 58' 23" W<br>34ø 15' 18" N |
| Site 4 | 113ø 59' 23" W<br>34ø 15' 17" N |
| Site 5 | 114ø 0' 45" W<br>34ø 15' 34" N |
| Site 6 | 114ø 1' 33" W<br>34ø 15' 48" N |
| Site 7 | 114ø 4' 45" W<br>34ø 17' 33" N |



Of all mediums sampled, only sediment, algae, mosquitofish, odonates, and snails were collected in both years (Table 2)

Sample Collection and Preparation

Samples were collected in July and August, 1992, and May 1993. They were analyzed for 19 metals (aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, selenium, strontium, vanadium, and zinc) and organochlorine compounds.

Samples were collected from several trophic levels. Species selection was based on availability and abundance in the study area. Samples collected were; sediment, algae, comprised mostly of waternet (Hydrodyctyon sp.) and Cladophora sp., odonate naiads from the families Libellulidae and Gomphidae, snails (Physa sp.), crayfish (Procambarus clarkii), mosquitofish (Gambusia affinis), red shiner (Cyprinella lutrensis), carp (Cyprinus carpio), largemouth bass (Micropteris salmoloides), and bluegill (Lepomis macrochirus) . Samples collected for metal analysis were placed in Whirl-Pak or Zip-Lock bags, stored temporarily on ice and later frozen. Samples collected for organochlorine analysis were placed in aluminum foil and frozen.

Water quality parameters were measured at each sample



Table 2. Numbers of composite samples by medium collected at each site. See text for scientific names. (NC = none collected.)

| | | Location | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Medium | Year | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 6 | Site 7 |
| SEDIMENT | 1992 | NC | 2 | 2 | 2 | 2 | 2 | 2 |
| | 1993 | NC | 3 | NC | 3 | NC | 3 | NC |
| ALGAE | 1992 | 2 | 2 | 2 | 2 | 2 | 2 | NC |
| | 1993 | NC | 3 | NC | 3 | NC | 3 | NC |
| ODONATA | 1992 | NC | NC | 2 | 2 | 1 | 2 | NC |
| | 1993 | NC | 3 | NC | NC | NC | 3 | NC |
| SNAIL | 1992 | 2 | 2 | 2 | 2 | 2 | 2 | NC |
| | 1993 | NC | 3 | NC | 3 | NC | 3 | NC |
| CRAYFISH | 1992 | NC | NC | 3 | 2 | 2 | 1 | 3 |
| REDSHINER | 1992 | NC | 2 | 3 | 3 | 3 | 3 | NC |
| MOSQUITOFISH | 1992 | 1 | 2 | 2 | 3 | 3 | 3 | 3 |
| | 1993 | NC | 3 | NC | 3 | NC | 3 | NC |
| BASS | 1992 | 2 | NC | NC | NC | NC | 2 | 2 |
| BLUEGILL | 1992 | NC | NC | NC | 2 | NC | 1 | 2 |
| CARP | 1992 | NC | NC | 2 | 2 | NC | 2 | NC |
| | 1993 | NC | NC | NC | NC | NC | NC | 2 |
| TADPOLE | 1993 | NC | 3 | NC | 3 | NC | 3 | NC |



site for 1992 and 1993. Temperature, pH, re-dox potential, and specific conductance were measured with a Hach One Combination pH electrode (Hach Company Model 43300). Conductivity was measured with the Hach Model 44600 Conductivity meter.

Alkalinity, total hardness, ammonia, phosphorus, and sulfates were tested with a Hach DREL-1 portable colorimeter kit. Water collected at each site was placed in a 1 L, cleaned (with Alconox), polyethylene jar. The jar was rinsed three times prior to sample collection with the water to be sampled. The sample was collected at ca 0.25 m below the water surface. The jar was sealed tightly and put on ice. Analysis occurred within 24 hours.

Sediment: Sediment was collected at every site except Site 1, below Alamo Dam. Sediment samples were collected in two ways. At riverine sites, sediment was collected from the interface of the river and the bank with a stainless steel spoon. In the confluence area, a brass Eckman dredge was used to collect bottom sediment. Samples from both lentic and lotic sites were picked free of debris and rocks and hand strained through a brass sediment sieve. Sediment samples (collected from a minimum of three areas within each sample site) were thoroughly mixed then divided into 2 or 3 separate subsamples (2 in 1992, 3 in 1993). These composite samples were placed in sterilized Whirl-Pak bags, placed on



ice and subsequently frozen.

Algae: Algae were collected by hand, picked free of debris and aquatic organisms and thoroughly mixed in a large Zip-Loc bag. Two composite algae samples were collected from each site (no algae were present at the confluence) , placed in Whirl-Pak bags, placed on ice and subsequently frozen.

Invertebrates: The number of samples and the location of sites was based on the availability of organisms Each sample was composed of a composite of three subsamples from within each sample site. Odonates (found only in areas with rocky substrate) were collected by hand and with nets. Snails occurred in all wet locations except the confluence area. They were found in algae, on rocky substrate and in small isolated pools. Snails were collected by hand and with nets. Composite samples were placed in Whirl-Pak bags, placed on ice and subsequently frozen.

Crayfish were collected in modified (openings were widened) minnow traps baited with moist cat food

(Lusk 1993). Traps were placed in vegetation along the shoreline in the confluence area and in fallen and submerged brush along the steep banks of the river bed. Traps were checked every 24 hours and crayfish were collected and placed on ice. Crayfish were individually weighed, measured, and uniform sized individuals were used to form composite samples. Crayfish for composite samples were



placed in Whirl-Pak bags and frozen. Pennak (1953) and Merrit and Cummins (1984) were used as the basis for the identification of all invertebrate taxa.

Fish: Mosquitofish, red shiner, largemouth bass, bluegill, and carp were collected. Seines and dip nets were used to collect mosquitofish and red shiners. Bass, bluegill, and carp were collected by gillnetting and electroshocking. A backpack electroshocker was used to collect fish in the river; gill nets and an electroshocking boat were used in marsh and open lake areas. Composite whole body fish samples were composed of either 3 or 5 individuals of the same species of uniform size. All fish collected (except mosquitofish and red shiners) were weighed and measured individually. Mosquitofish were collected at all sites. Red shiners were not collected at Sites 2 and 7 and bass, bluegill, and carp occurred intermittently throughout the study area.

Moisture, Total Organic Carbon, and Metal Analysis

Total organic carbon (TOC) was determined for sediment samples and percent moisture was determined for all mediums. All samples were analyzed for TOC, moisture and metal content by Hazelton Laboratories America. Inc., Madison, Wisconsin. Results of these analyses are reported in Appendix A. Samples from each year were shipped as one unit and analyzed within the same time frame to reduce the "batch



effect": variation due to differences in analyses time and personnel. All sediment and biota samples were analyzed for 19 trace elements (Table 3) and selected samples were analyzed for organochlorine pesticide residues (Appendix A)

Percent moisture was determined by placing the prepared sample in a tared aluminum dish and drying to constant weight (ca 12-18 hr) in an oven. This method is capable of detecting changes of 0.1% moisture.

TOC of sediment was determIned by acidifying an aliquot, drying it in a forced-air oven, and comparing differential weights before and after combustion of organic carbon in an oven. Mercury concentration was determined by cold vapor atomic absorption. The sample was digested with a mixture of sulfuric and nitric acids. Mercury was reduced with sodium borohydride for determination. The amount of mercury was determined at a wavelength of 253.7 nm by comparing the signal of the unknown sample, measured by the atomic absorption spectrophotometer with the MHS-20 hydride generation unit, with the signal of the standard solutions. The lowest detection limit of this assay was 0.025 æg/g for a 2.0 g sample.

Arsenic and selenium were determined by graphite furnace atomic absorption spectrophotometry (HAAS) method. The tissue sample was digested with nitric acid in a microwave digester. Sediment was digested with nitric acid

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Table 3. Detection limits (æg/g dry weight) for trace elements analyzed in sediment and biotic samples collected at Bill Williams River NWR, 1992-93.

| | Detection Limits (æg/g dry weight) | |
|---|---|---|
| Element | Tissue | Soil |
| Aluminum (Al) | 10.00 | 20.00 |
| Arsenic (As) | 0.50 | 0.80 |
| Barium (Ba) | 0.50 | 0.80 |
| Beryllium (Be) | 0.05 | 0.20 |
| Boron (B) | 0.05 | 0.80 |
| Cadmium (Cd) | 0.40 | 0.80 |
| Chromium (Cr) | 0.30 | 2.00 |
| Copper (Cu) | 1.00 | 2.00 |
| Iron (Fe) | 0.20 | 0.40 |
| Lead (Pb) | 0.40 | 0.80 |
| Magnesium (Mg) | 0.50 | 0.80 |
| Manganese (Mn) | 0.10 | 0.20 |
| Mercury (Hg) | 0.17 | 0.20 |
| Molybdenum (Mo) | 0.30 | 0.80 |

| | | |
|---|---|---|
| Nickel (Ni) | 0.30 | 0.80 |
| Selenium (Se) | 0.60 | 1.00 |
| Strontium (Sr) | 0.50 | 0.80 |
| Vanadium (V) | 0.30 | 0.60 |
| Zinc (Zn) | 0.50 | 0.80 |

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and 30% hydrogen peroxide using covered glass beakers on hot plates. Concentrations were determined at a wavelength of 193.7 nm for arsenic and 196.0 nm for selenium by comparing the signal of the unknown sample, measured by graphite furnace atomic absorption spectrophotometer, with the signal of the standard solutions. The lowest detection limit of this assay was 0.1 æg/g for both elements in a 1.00 g sample.

Levels of all other elements were analyzed by inductively coupled plasma spectrophotometry. Plant and animal tissue was digested with nitric acid, diluted with 0.005% Triton X-100 solution and filtered. Sediment samples were digested with nitric acid in covered Teflon beakers on a hot plate. Thirty percent hydrogen peroxide was added until effervescence no longer occurred. Hydrochloric acid was then added, the sample heated, diluted with distilled water and filtered. Concentration for each element in the sample solution was determined by comparing its emission intensity with the emission intensities of a known series of elemental standards. Limits of detection varied for each element.

Analytical Quality Control

Quality control analyses were supplied as a written report by the U.S. Fish and Wildlife Service Patuxent Analytical Control Facility (PACF). Quality assurance

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included the evaluation of analytical precision (as measured by duplicate sample analysis) and accuracy (as measured by spike recovery and standard reference material analysis) The standard reference materials used were NIST 1577B (Bovine liver) for plant and animal tissue and ERA CRM 213 and 215 for sediment analyzed in 1992 and 1993, respectively. Relative percent differences (RPD) were not calculated when concentrations were below detection limits (Table 4). Precision and accuracy were considered acceptable by PACF.



Table 4. Results of duplicate analyses, analyses of spiked samples, and analyses of standard referenCe materials for quality assuranCe/quality control from Hazelton Environmental Laboratories (N = 5).

| | DUPLICATES | SPIKES | REFERENCE MATERIALS |
|---|---|---|---|
| METHOD/ELEMENT | RPD¦ | %RECOVERY | %RECOVERY |
| HAAS[sup]b | | | |
| Arsenic | 0.0-2.46 | ND[sup]d-108.33 | 91.09-108.91 |
| Mercury | ND-7.41 | ND-112.00 | 90.35-134.08 |
| Selenium | ND-33.6 | 82.32-119.10 | 83.24-145.76 |
| ICP[sup]c | | | |
| Aluminum | ND-l.2 | ND-92.86 | ND-142.6 |
| Barium | 0.0-1.7 | ND-96.69 | ND-102.58 |
| Beryllium | ND | 78.47-99.08 | ND-98.45 |
| Boron | ND-3.9 | 83.15-97.29 | ND |
| Cadmium | ND | 76.40-96.69 | 72.00-102.60 |
| Chromium | 0.0-6.20 | ND-93.25 | ND-112.58 |
| Copper | 0.0-2.50 | ND-98.62 | 101.23-107.50 |
| Iron | 0.0-5.90 | ND-95.88 | 98.37-120.78 |
| Lead | ND-5.40 | 78.78-100.20 | ND-102.70 |
| Magnesium | 0.0-1.60 | ND | 83.96-105.91 |
| Manganese | 0.0-2.70 | ND-78.78 | 87.24-97.16 |
| Molybdenum | ND | 80.10-100.00 | 91.71-111.43 |
| Nickel | ND-7.40 | ND-83.47 | ND-102.41 |
| Strontium | 0.0-8.60 | ND | ND |
| Vanadium | ND-6.10 | ND-90.00 | ND-124.68 |
| Zinc | 0.80-4.50 | ND-91.84 | 75.75-110.19 |

¦ RPD = Relative Percent Difference
[sup]b Hydride-generation atomic absorption spectrophotometry
[sup]c Inductively coupled plasma emission spectrometry
[sup]d ND = Not Detected

Analytical Methods: All analyses were performed on loge transformed data. For elements that were below the limit of detection, a value of 1/2 the limit of detection was assigned to that sample in order to allow an estimate of the level of the element in the sample. Analyses were performed on dry weight values to standardize percent moisture content of the sample. Results are reported in æg/g dry weight (Appendix A) . To facilitate comparison to other studies, levels may also be reported in wet weights. To convert data from wet weight to dry weight the following equations are useful:

X = Wet Weight<br>
1.0 æg/g = Dry Weight<br>
70% = Moisture Content<br>
(1.0) (1-(70%/100)) = 0.30 æg/g Wet Weight

X = Dry Weight<br>
0.30 æg/g = Wet Weight<br>
70% = Moisture Content<br>
X = 0.30 + (1 - (70% ö 100)) = 1.00 Dry Weight

To determine if the transformed data were normally distributed, Lilliefors Test for small sample size was used (Milton 1992). Sample sizes for each collection year were unequal. To correct for unbalanced design, the General Linear Model (GLM) approach was used to assess the effects of element, medium, site and year and site/year interactions



(Cody and Smith 1991). Two-way ANOVA models were fit for sediment, algae, snails, and mosquitofish for 7 elements (arsenic, cadmium, copper, lead, mercury, selenium, zinc) Significant main effects and interactions were further analyzed using Tukey's Studentized Range Test (Honestly Significant Difference) . Numbers of composite samples for each medium by site and year are shown in Table 2. to illustrate the unbalanced design. Not all mediums were available for collection at all sites along the river. Therefore, sediment, algae, snails, and mosquitofish were used for comparative analyses.

Analyses were conducted with the Statistical Packages for the Social Sciences (SPSS) and Statistical Analysis System (SAS) software available on the VAX mainframe computer at the University of Arizona, Tucson, Arizona. Unless stated otherwise, statements of statistical significance refer to a 5% Type I error rate (p ó 0.05).



RESULTS

Analytical Results

Water quality and chemistry parameters were similar at all sites except Site 1 (Table 5). I considered Site 1 to be heavily influenced by condition in Alamo Lake. Temperature, specific conductance, hardness, alkalinity, and sulfate measurements from Site 1 were all ca 1/2 the values of these parameters farther downstream on the refuge. Phosphorous values were higher at Site 1 and pH and ammonia were comparable at all sites sampled. A total of 162 biological samples (representing 14 mediums) were analyzed.

Mean total organic carbon in sediment samples was 2.20 in 1992 and 0.54 in 1993 (Table 6). TOC in sediment samples varied considerably across sites and years (p< 0.01).

Percent moisture ranged from 19.5% in sediment to 95.0% in tadpoles (Table 7). Because of the variability in moisture content, results are reported in æg/g dry weight in order to more accurately reflect concentrations.

Organochlorine residue analysis was performed on 7 samples; four composite samples sediment (collected from Sites 2, 5, 6, and 7), and three composite fish samples (1 bass sample of five fish from Site 7 and 2 bluegill samples of five fish each, one sample from Site 6 and one from Site 7). Residues for all organochlorine compounds were generally below the limit of detection except for p, p' -DDE



Table 5. Results of water quality tests on water sampled at Bill Williams River NWR, 1992-93. (First value for 1992 and second value fcc 1993 collection periods.)

| | Location | | | | | | |
|---|---|---|---|---|---|---|---|
| Parameter | Site 1 | Site 2 | Site 3 | Site 4 | Site 5 | Site 6 | Site 7 |
| Temp (øC) | 18.8 | 24.3 | 23.4 | 24.7 | 24.9 | 23.6 | 31.6 |
| | | 31.4 | | 31.3 | | 31.5 | |
| pH | 8.52 | 7.75 | 7.54 | 8.84 | 7.71 | 5.24 | 7.53 |
| | | 7.50 | | 5.85 | | 5.95 | |
| Spec. Cond. | 407 | 829 | 897 | 856 | 938 | 952 | 1090 |
| (æS/cm) | | 440 | | 530 | | 594 | |
| Hardness (mg/L | 147 | 248 | 252 | 248 | 240 | 224 | 308 |
| CaCO[sub]3) | | 153 | | 138 | | 231 | |
| Alkalinity | 145 | 313 | 235 | 235 | 246 | 235 | 202 |
| (mg/l CaCo[sub]3) | | 198 | | 233 | | 258 | |
| Ammonia | 0.33 | - | 0.024 | 0.024 | 0.024 | 0.04 | 0.01 |
| (mg/L NH[sub]3) | | 0.009 | | 0.079 | | 0.051 | 6 |
| | | 6 | | 3 | | 2 | |
| Sulfate | 33 | 69 | 108 | 110 | 100 | 106 | 220 |
| (mg/L SO[sub]4ý-) | | 40 | | 52 | | 50 | |
| Phosphorus | 0.425 | 0.15 | 0.15 | 0.16 | 0.11 | 0.11 | 0.12 |
| (Orthophosphate) | | 0.38 | | 0.38 | | 0.46 | 5 |
| (mg/L PO[sub4[sup]3-) | | | | | | | |



Table 6. Total organic carbon levels for sediment samples collected from Bill Williams River NWR, 1992-1993.

| SAMPLE | YEAR | SITE | N | TOC |
|---|---|---|---|---|
| S09 | 1992 | 2 | 5 | 2.13 |
| S10 | 1992 | 2 | 5 | 1.69 |
| S13 | 1993 | 2 | 5 | 0.21 |
| S14 | 1993 | 2 | 5 | 0.23 |
| S15 | 1993 | 2 | 5 | 0.27 |
| S11 | 1992 | 3 | 5 | 1.79 |
| S12 | 1992 | 3 | 5 | 2.05 |
| S07 | 1992 | 4 | 5 | 2.44 |
| S08 | 1992 | 4 | 5 | 1.81 |

| | | | | |
|---|---|---|---|---|
| S16 | 1993 | 4 | 5 | 1.04 |
| S17 | 1993 | 4 | 5 | 1.30 |
| S18 | 1993 | 4 | 5 | 1.34 |
| S05 | 1992 | 5 | 5 | 1.16 |
| S06 | 1992 | 5 | 5 | 1.62 |
| S01 | 1992 | 6 | 6 | 3.91 |
| S02 | 1992 | 6 | 5 | 5.01 |
| S19 | 1993 | 6 | 5 | 0.11 |
| S20 | 1993 | 6 | 5 | 0.13 |
| S21 | 1993 | 6 | 5 | 0.24 |

in fish sampled in 1992 (Table A-b in Appendix A). Levels ranged from 0.04 - 0.11 æg/g dry weight. The limit of detection for p,p'-DDE was 0.039 æg/g dry weight.

With the exception of molybdenum, trace elements were detected in some or all composite samples of sediment and



Table 7. Percent moisture of sediment and biotic samples collected at Bill Williams River NWR, 1992-93. (N = number of composite samples collected, X = arithmetic mean)

| | Percent Moisture | | |
|---|---|---|---|
| Medium | N | X | Minimum-Maximum |
| SEDIMENT | 21 | 36.74 | 19.50-63.20 |
| ALGAE | 23 | 86.31 | 75.30-89.60 |
| NAIAD | 2 | 92.45 | 92.00-92.90 |
| ODONATA | 13 | 84.91 | 80.30-89.20 |
| SNAIL | 21 | 76.10 | 60.50-85.40 |
| CRAYFISH | 11 | 73.35 | 70.80-76.30 |
| RED SHINER | 14 | 76.21 | 72.00-81.50 |
| MOSQUITOFISH | 26 | 81.41 | 73.20-87.60 |
| BASS | 6 | 75.65 | 73.20-77.40 |
| BLUEGILL | 5 | 74.80 | 73.10-78.00 |
| CARP | 9 | 76.20 | 73.40-78.40 |
| TADPOLE | 9 | 78.26 | 54.70-95.00 |
| TURTLE | 2 | 74.45 | 73.60-75.30 |

biota (Table 8). Detectable concentrations (Table 4) of Ba, Cr, copper, Fe, Mg, Mn, Sr, V, and Zn were found in all samples. Limits of detection for elements analyzed are shown in Table 5. Geometric mean, mean, range and standard error for trace element concentrations for all mediums and both years are reported in Appendix B.



Table 8. Trace elements detected in selected samples collected from the Bill Williams River NWR, 1992-1993. (X = element detected at or above the limit of detection in >50% of samples.

| Element | ALGAE | ODO | SNAIL | CRAY | TPOLE | MOSQ | SHINE | BASS | BGILL | CARP | SED |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | x | x | x | x | x | x | x | x | x | x | x |
| As | x | x | x | x | x | x | x | x | x | x | x |
| Ba | x | x | x | x | x | x | x | x | x | x | x |
| Be | | | | | x | | | | | | x |
| B | x | | x | x | x | | | | | | x |
| Cd | | x | x | x | x | | x | | | | x |
| Cr | x | x | x | x | x | x | x | x | x | x | x |
| Co | x | x | x | x | x | x | x | x | x | x | x |
| Fe | x | x | x | x | x | x | x | x | x | x | x |
| Pb | | | | | x | | | | | | x |
| Mg | x | x | x | x | x | x | x | x | x | x | x |
| Mn | x | x | x | x | x | x | x | x | x | x | x |
| Hg | | x | | x | x | x | x | x | x | x | x |
| Mo | | | | | | | | | | | |
| Ni | x | x | x | x | x | | | | | | x |
| Se | | x | | x | | x | x | x | x | x | |
| Sr | x | x | x | x | x | x | x | x | x | x | x |
| V | x | x | x | x | x | x | x | x | x | x | x |
| Zn | x | x | x | x | x | x | x | x | x | x | x |



Statistical Results

Element concentrations showed no consistent differences above and below washes (Figures 3-10) or after the flood (Figures 11-19). However, strong interaction terms between site and year may mask trends. Levels did vary in medium by year, but showed no consistent trends (Tables 9-12).

Site 6 (the location where the river becomes subsurface in dry years) had the highest levels of all sites sampled. Algae collected at Site 2 (the eastern border of the Refuge) had significantly higher mercury concentration than at Site 1 (immediately below Alamo Dam) (p   0.0104). Four of the seven elements-cadmium, copper, lead, and mercury, also differed in snails collected at the two sites. Cadmium was statistically higher in snails at Site 2 ($p < 0.0005$) than at Site 1, but the reverse was true for copper, lead, and mercury ($p < 0.0114$, 0.0312, and 0.0139, respectively) . Cadmium concentrations in algae were higher downstream from Mohave Wash than upstream ($p < 0.0076$).

Concentrations of S of the 7 elements differed in sediment samples collected above and below Mohave Wash. Concentrations of arsenic, copper, lead, selenium, and zinc were significantly lower downstream versus upstream from Mohave Wash ($p < 0.0368$, 0.0161, 0.0036, 0.0417, and 0.0191, respectively)

Mercury was the only element to differ significantly



upstream and downstream from Mineral Wash. The level of mercury in sediment collected upstream from Mineral Wash was significantly ($p < 0.0094$) lower than it was in sediment collected downstream from the wash.

Selenium concentrations were higher in sediment collected downstream versus upstream of Cave Wash ($p < 0.0346$) . Copper concentrations in snails collected upstream from Cave Wash were higher than those in snails collected downstream ($p < 0.0226$). Conversely, zinc concentrations were higher ($p < 0.0057$) in snails downstream versus upstream. Copper and zinc concentrations were higher in mosquitofish collected downstream versus upstream of Cave Wash ($p < 0.0422$ and 0.00.0055, respectively)

Concentration of copper and zinc were higher in sediments from Site 7 ($p < 0.0276$ and 0.0215, respectively) than Site 6. Copper concentration in mosquitofish was also higher at Site 7 than at Site 6 ($p < 0.0164$). Cadmium concentrations were higher in bass at Site 7 than at site 6 (p   0.0338).

Analysis of two-way ANOVA's for arsenic, cadmium, copper, lead, mercury, selenium, and zinc concentrations in sediments, algae, snails, and mosquitofish are shown in Appendix C.

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See Table/Figure

Figure 3. Geometric mean concentration (mg/kg dry weight) of trace elements detected in sediment collected from bill Williams River NWR, 1992. (SE indicated above mean values.)

45

See Table/Figure

Figure 4. Geometric mean concentration (mg/kg dry weight) of heavy metals detected in sediment collected from Bill Williams River NWR, 1992. (SE indicated above mean values.)

46

See Table/Figure

Figure 5. Geometric mean concentration (mg/kg dry weight) of trace elements detected in algae collected from Bill Williams River NWR, 1992. (SE indicated above mean values.)

47

See Table/Figure

Figure 6. Geometric mean concentration (mg/kg dry weight) of heavy metals detected in algae collected from Bill Williams River NWR, 1992. (SE indicated above mean values.)

48

See Table/Figure

Figure 7. Geometric mean concentration (mg/kg dry weight) of trace elements detected in snails collected from Bill Williams River NWR, 1992. (SE indicated above mean values.)

49

See Table/Figure

Figure 8. Geometric mean concentration (mg/kg dry weight) of heavy metals detected in snails collected from Bill Williams River NWR, 1992. (SE indicated above mean values.)

50

See Table/Figure

Figure 9. Geometric mean concentration (mg/kg dry weight) of trace elements detected in mosquitofish collected from Bill Williams River NWR, 1992. (SE indicated above mean values.)

51

See Table/Figure

Figure 10. Geometric mean concentration (mg/kg dry weight) of heavy metals detected in mosquitofish collected from Bill Williams River NWR, 1992. (SE indicated above mean values.)

52

See Table/Figure

Figure 11. Comparison of geometric mean concentration (mg/kg dry weight) of trace elements detected in sediment collected from Bill Williams River NWR, 1992-1993.

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See Table/Figure

Figure 12. Comparison of geometric mean concentration (mg/kg dry weight) of heavy metals detected in sediment collected from Bill Williams River NWR, 1992-1993.

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See Table/Figure

Figure 13. Comparison of geometric mean concentration (mg/kg dry weight) of trace elements detected in algae collected from Bill Williams River NWR, 1992-1993.

55

See Table/Figure

Figure 14. Comparison of geometric mean concentration (mg/kg dry weight) of heavy metals detected in algae collected from Bill Williams River NWR, 1992-1993.

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See Table/Figure

Figure 15. Comparison of geometric mean concentration (mg/kg dry weight) of trace elements detected in snails collected from Bill Williams River NWR, 1992-1993.

57

See Table/Figure

Figure 16. Comparison of geometric mean concentration (mg/kg dry weight) of heavy metals detected in snails collected from Bill Williams River NWR, 1992-1993.

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See Table/Figure

Figure 17. Comparison of geometric mean concentration (mg/kg dry weight) of trace elements detected in mosquitofish collected from Bill Williams River NWR, 1992-1993.

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See Table/Figure

Figure 18. Comparison of geometric mean concentration (mg/kg dry weight) of heavy metals detected in mosquitofish collected from Bill Williams River NWR, 1992-1993.

60

Table 9. Results (p-values, à=0.05) of General Linear Models for sediments collected at Bill Williams River NWR, 1992-93. (Non-significant values are in bold italics.)

| | | SEDIMENT | | |
|---|---|---|---|---|
| ELEMENT | MODEL | SITE | YEAR | SITE*YEAR |
| LOG (As) | 0.0001 | 0.0025 | 0.6675 | 0.0001 |
| LOG (Cd) | 0.0001 | 0.0005 | 0.0001 | 0.0001 |
| LOG (Cu) | 0.0001 | 0.0001 | 0.0078 | 0.0001 |
| LOG (Pb) | 0.0001 | 0.0001 | 0.0001 | 0.0001 |
| LOG (Hg) | 0.0827 | 0.0511 | 0.1185 | 0.4378 |
| LOG (Se) | 0.0001 | 0.0012 | 0.0001 | 0.0001 |
| LOG (Zn) | 0.0001 | 0.0002 | 0.0001 | 0.0001 |

Table 10. Results (p-values, à=0.05) of General Linear Models for algae collected at Bill Williams River NWR, 1992-93. (Non-significant values are in bold italics.)

| | | ALGAE | | |
|---|---|---|---|---|
| ELEMENT | MODEL | SITE | YEAR | SITE*YEAR |

| | | | | |
|---|---|---|---|---|
| LOG (As) | 0.3876 | 0.2876 | 0.1698 | 0.8379 |
| LOG (Cd) | 0.0534 | 0.0376 | 0.2059 | 0.5942 |
| LOG (Cu) | 0.0007 | 0.0049 | 0.0002 | 0.0089 |
| LOG (Pb) | 0.2191 | 0.1858 | 0.3439 | 0.1905 |
| LOG (Hg) | 0.0001 | 0.0001 | 0.0001 | 0.0001 |
| LOG (Se) | 0.0927 | 0.0748 | 0.0178 | 0.7745 |
| LOG (Zn) | 0.0735 | 0.1316 | 0.5140 | 0.0352 |



Table 11. Results (p-values, à=0.05) of General Linear Models for snails collected at Bill Williams River NWR, 1992-93. (Non-significant values are in bold italics.)

| SNAILS | | | | |
|---|---|---|---|---|
| ELEMENT | MODEL | SITE | YEAR | SITE*YEAR |
| LOG (As) | 0.0001 | 0.0466 | 0.0001 | 0.0441 |
| LOG (Cd) | 0.0001 | 0.0001 | 0.0001 | 0.2419 |
| LOG (Cu) | 0.0001 | 0.0011 | 0.0001 | 0.0018 |
| LOG (Pb) | 0.2579 | 0.8202 | 0.3870 | 0.0620 |
| LOG (Hg) | 0.0001 | 0.0097 | 0.0001 | 0.5740 |
| LOG (Se) | 0.0001 | 0.0488 | 0.0001 | 0.0011 |
| LOG (Zn) | 0.0026 | 0.0040 | 0.0024 | 0.0221 |

Table 12. Results (p-values, à=0.05) of General Linear Models for mosquitofish collected at Bill Williams River NWR, 1992-93. (Non-significant values are in bold italics.)

| MOSQUITOFISH | | | | |
|---|---|---|---|---|
| ELEMENT | MODEL | SITE | YEAR | SITE*YEAR |
| LOG (As) | 0.0712 | 0.0906 | 0.0505 | 0.1710 |
| LOG (Cd) | 0.2325 | 0.3779 | 0.4443 | 0.0680 |
| LOG (Cu) | 0.0029 | 0.0643 | 0.0786 | 0.0815 |
| LOG (Pb) | 0.0802 | 0.3020 | 0.7311 | 0.0191 |
| LOG (Hg) | 0.0023 | 0.0608 | 0.0001 | 0.0309 |
| LOG (Se) | 0.0219 | 0.0492 | 0.1400 | 0.0809 |
| LOG (Zn) | 0.0060 | 0.0073 | 0.0017 | 0.1446 |

# DISCUSSION

ORGANOCHLORINES: Organochlorine residues were below the limit of detection in all sediments sampled. There is no evidence of organochlorine contamination in sediments from the Bill Williams River NWR.

WATER: Water quality measurements collected in this study in 1992 and 1993 were comparable to water quality data for 1992 and 1993 reported by the USGS at the water monitoring station located at Mineral Wash (USGS 1993) (Tables 5 and 13).

ARSENIC: Arsenic is widely distributed in the environment in both organic and inorganic compounds in its trivalent or pentavalent form. Arsenic occurs naturally as complex sulfides of iron, nickel, and cobalt. Soil arsenic levels are normally elevated near arseniferous deposits and in mineralized zones containing gold, silver, and sulfides of lead, zinc, and especially pyrite. Arsenic levels may be increased 10-fold in soils derived from pyritic shales (Eisler 1988a) Inorganic arsenic is released into the environment by copper, zinc and lead smelting, and glass and chemical manufacturing (Menzer 1991).

Toxicity of arsenic is a function of the size of fish, chemical form and concentration of the metalloid, temperature, water hardness, pH, and exposure time and level



Table 13. Water quality and Chemistry parameters for Bill Williams River NWR, 1992-93. (As, Cd, Cu, Pb, Hg, Se, and Zn dissolved æg/l).

See Table/Figure



(Sorensen 1991) . Smaller fish are more vulnerable to arsenic poisoning than larger fish of the same species, probably due to increased metabolic rates in smaller fish. Organic forms of arsenic ate considered less toxic than inorganic forms, and the pentavalent more toxic than the trivalent form. Trivalent forms of arsenic react with sulfhydryl protein groups, resulting in enzyme inactivation and structural damage, whereas pentavalent forms may inhibit phosphate insertion into nucleotide chains, resulting in false formation of DNA (Sorensen 1991) . Acute arsenic exposure in fish may result in "coagulation film anoxia": mucus buildup on the gill surface, and suffocation due to inadequate oxygen exchange at the secondary lamellae (Sorensen 1991).

There was little evidence of arsenic contamination in any of the sediment samples collected from the Bill Williams River NWR. Arsenic concentrations in sediment from the Bill Williams River NWR (mean = 4.37 æg/g, geometric mean = 4.25 æg/g, dry weight) were consistently lower than those reported in other studies in the region (Radtke 1988, King et al. 1993), in Arizona (King et al. 1991), and U.S. background levels (Shacklette and Boerngen 1984) (Table 14). Long and Morgan (1990) reported an ER-L (Effects Range-Low) for arsenic in sediments of 33 æg/g dry weight (Table 15). An ER-L is defined as the low end of a range of

Table 14. Comparison of concentrations æg/g dry weight) of selected elements in sediments collected from Bill Williams River
NWR, 1992-93 and other studies in the lower Colorado River Valley.

See Table/Figure



Table 15. Summary of ER-L, ER-M, and overall apparent effects threshold concentrations (æg/g dry weight) for selected element in sediment (Taken from Long and Morgan 1990).

| Element | ER-L¦ | ER-L[sup]b | ER-L:ER-M | Overall Effects (Apparent Threshold) | Degree of Confidence in ER-L/ER-M Values |
|---|---|---|---|---|---|
| As | 33 | 8.5 | 2.6 | 50 | Low/Moderate |
| Cd | 5 | 9 | 1.8 | 5 | High/Moderate |
| Cu | 70 | 390 | 5.6 | 300 | High/Moderate |
| Pb | 35 | 110 | 3.1 | 300 | Moderate/High |
| Hg | 0.15 | 1.3 | 8.7 | 1 | Moderate/High |
| Zn | 120 | 270 | 2.2 | 260 | High/High |

¦ Effects Range-Low
[sup]b Effects Range-Median

concentrations where effects to aquatic organisms occurred.

Based on these data, arsenic concentrations in sediments collected from the Bill Williams River NWR do not appear to be at levels high enough to cause environmental concern.

Certain fish and crustaceans contain very high levels of organic arsenic, often as arsenobetaine (Ishinishi et al. 1986), a water-soluble organoarsenical that poses little risk to the organism or its consumer (Eisler 1988). Arsenic concentrations in invertebrates collected at Bill Williams NWR ranged from 0.22 æg/g in odonate larvae to 2.74 æg/g in snails. Eisler (1988) reported that most living organisms normally contain arsenic concentrations of approximately



Table 16. Comparison of concentrations (æg/g wet weight) of selected elements in fish collected from Bill Williams River NWR.
1992-93 with the National Contaminant Biomonitoring Program and other studies in the lower Colorado River Valley.

| | Trace element concentration, æg/g wet weight | | | | | | |
|---|---|---|---|---|---|---|---|
| Area and Species | As | Cd | Cu | Pb | Hg | Se | Zn |
| NCBP¦ | | | | | | | |
| 85th Percentile | 0.27 | 0.05 | 1.0 | 0.22 | 0.17 | 0.73 | 34.2 |
| Geometric Mean | 0.14 | 0.03 | 0.65 | 0.11 | 0.10 | 0.42 | 21.7 |
| Maximum | 1.5 | 0.22 | 23.1 | 4.88 | 0.37 | 2.30 | 118.4 |
| Predator Protection Limit[sup]b | | | | | | | |
| Bill Williams River National Wildlife Refuge | | | | | | | |
| Bill Williams River NWR[sup]c | | | | | | | |
| Largemouth Bass | 0.258 | 0.0249 | 0.558 | 0.247 | 0.126 | 0.790 | 14.25 |
| Carp | 0.571 | 0.0296 | 1.495 | 0.250 | 0.061 | 1.421 | 73.08 |
| Bill Williams River[sup]d | | | | | | | |
| Carp | 0.115 | 0.05 | 0.79 | 0.15 | 0.077 | 1.167 | 51.67 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| lower Colorado National Wildlife Refuges[sup]e | | | | | | | |
| Martinez Lake | | | | | | | |
| Largemouth Bass | 0.02 | 0.01 | 0.30 | ND | 0.02 | 2.02 | 16.1 |
| Carp | 0.10 | 0.01 | 9.69 (4.75)[sup]f | ND | 0.01 | 2.28 | 72.5 |
| Cibola Lake | | | | | | | |
| Largemouth Bass | 0.12 | 0.02 | 0.30 | 0.68 | 0.01 | 1.53 | 15.5 |
| Carp | 0.10 | 0.02 | 0.70 | 0.84 | 0.02 | 1.17 | 48.8 |
| Topock Marsh | | | | | | | |
| Largemouth Bass | 0.12 | 0.02 | 0.3 | 0.75 | 0.01 | 2.18 | 13.6 |
| Carp | 0.09 | 0.05 | 0.7 | 0.94 | 0.01 | 1.54 | 45.0 |
| Alamo Lake[sup]f | | | | | | | |
| Largemouth Bass | 0.19 | ND | 0.34 | NA | 0.20 | 0.43 | 11.76 |
| Carp | 0.08 | 0.07 | 21.47 (7.46) | NA | 0.175 | 0.475 | 76.15 (73.90) |

¦ National Contaminant Biomonitoring Program 85th percentile (Schmitt and Brumbaugh 1990)
[sup] b Walsh et al. 1977
[sup] c This study
[sup] d Radtke et.al. 1988
[sup] e King et.al. 1993
[sup] f King et.el. 1991
[sup] g Geometric mean used because of extreme difference in values.



Table 17. Baseline concentrations (æg/g wet weight) of trace elements in fish (Schmitt and Brumbaugh 1990).

| Element and collection Period | Geometric Mean | Minimum | 85th Percentile | Maximum |
|---|---|---|---|---|
| Arsenic | | | | |
| 1978-79 | 0.16 | 0.04 | 0.23 | 2.08 |
| 1980-81 | 0.14 | 0.05 | 0.22 | 1.69 |
| 1984-85 | 0.14 | 0.02 | 0.27 | 1.50 |
| cadmium | | | | |
| 1978-79 | 0.04 | 0.01 | 0.09 | 0.41 |
| 1980-81 | 0.03 | 0.01 | 0.06 | 0.35 |
| 1984-85 | 0.03 | 0.01 | 0.05 | 0.22 |

| | | | | |
|---|---|---|---|---|
| copper | | | | |
| 1978-79 | 0.86 | 0.29 | 1.14 | 38.75 |
| 1980-81 | 0.68 | 0.25 | 0.90 | 24.10 |
| 1984-85 | 0.65 | 0.06 | 1.00 | 23.10 |
| Lead | | | | |
| 1978-79 | 0.19 | 0.10 | 0.32 | 6.73 |
| 1980-81 | 0.17 | 0.10 | 0.25 | 1.94 |
| 1984-85 | 0.11 | 0.01 | 0.22 | 4.88 |
| Mercury | | | | |
| 1978-79 | 0.11 | 0.01 | 0.18 | 1.10 |
| 1980-81 | 0.03 | 0.01 | 0.06 | 0.35 |
| 1984-85 | 0.10 | 0.01 | 0.17 | 0.37 |
| Selenium | | | | |
| 1978-79 | 0.46 | 0.09 | 0.70 | 3.65 |
| 1980-81 | 0.47 | 0.09 | 0.71 | 2.47 |
| 1984-85 | 0.42 | 0.08 | 0.73 | 2.30 |
| Zinc | | | | |
| 1978-79 | 25.63 | 7.69 | 46.26 | 168.10 |
| 1980-81 | 23.82 | 8.82 | 40.09 | 109.21 |
| 1984-85 | 21.70 | 9.60 | 34.20 | 118.40 |



1.00 æg/g (wet weight)

Arsenic concentrations in fish collected at Bill Williams River NWR ranged from 0.05 æg/g in red shiners collected at Site 5 in 1992 to 1.08 æg/g in carp collected at Site 3 in 1992 (wet weight). Arsenic levels were generally higher in carp than in other fish species collected. Differences were not site specific. Arsenic levels in fish collected at Bill Williams River NWR were generally higher, especially in carp, than reported in other studies from the region (Radtke et al. 1988, King et al. 1991, 1993) (Table 16).

The NCBP showed that the whole body geometric mean concentration of arsenic in fish was 0.14 æg/g and the 85th percentile was 0.27 æg/g (wet weights) (Schmitt and Brumbaugh 1990) (Table 17). The maximum arsenic concentration reported by the NCBP was 1.50 æg/g and occurred in bloater (Coregonus hoyi) from Lake Michigan.

Walsh et al. (1977) considered whole body arsenic at concentrations >0.50 æg/g arsenic to be potentially harmful to predatory species of fish and wildlife (predator protection limit). Four out of nine carp contained arsenic concentrations higher than 0.50 æg/g (0.58, 0.83, 1.07, and 1.08 æg/g arsenic): other species generally were below the predator protection limit. Although arsenic levels in carp exceeded Walsh's predator protection limit, levels are



within expected levels reported by Eisler (1988a) of 1.00 æg/g in most organisms. My data indicate that levels of arsenic were slightly elevated at a few sites, but even in these areas levels were not high enough to cause environmental concern.

CADMIUM: Cadmium, long recognized as a toxic element, is similar to zinc and occurs with zinc, copper, and lead in sulfide ores (Friberg et al. 1986). It is recovered as a by-product of the smelting process for those metals. Natural soil concentrations are generally <1 æg/g and average about 0.40 æg/g cadmium (Menzer 1991).

Compared to other metals, cadmium is mobile in the aquatic environment and, in natural waters may exist as the hydrated ion; as complexes with carbonate, chloride, or sulfide; and complexes with humic acids (Menzer 1991). Cadmium is widely dispersed in the environment and is bioaccumulated in organisms, especially invertebrates such as mollusks and crustaceans. cadmium concentrations in fresh waters are generally <1 æg/kg (parts per billion) (Fleisher et al. 1974). Higher concentrations of cadmium are usually suggestive of anthropogenic contamination.

There is little evidence of cadmium contamination in sediments collected at the Bill Williams River NWR. cadmium concentrations in sediments from the Bill Williams River have a mean and geometric mean of 0.25 æg/g and 0.30 æg/g,



respectively. Sediments from Martinez Lake in the lower

Colorado River Valley (King et al. 1993) had 0.77 æg/g arsenic concentration. There are no Arizona or U.S. baseline values available, however, Long and Morgan (1990) reported an ER-L (Effects Range-Low) for cadmium at 5.0 æg/g dry weight (Table 15). Cadmium levels in sediments collected from the Bill Williams River NWR do not appear to be at levels high enough to cause environmental concern.

Cadmium concentrations in invertebrates collected at Bill Williams River NWR ranged from 0.05 æg/g in odonates collected at Site 4 in 1992 to below the limit of detection in crayfish collected at Site 7 in 1992 (wet weight). cadmium concentrations in fish collected at Bill Williams River NWR were generally below the limit of detection in mosquitofish, bass, bluegill and carp. Red shiner collected at Sites 4 and 5 contained levels of 0.13 æg/g cadmium (wet weight) . These levels were generally at or below levels found in fish collected in other studies in the region (Table 16). The NCBP found a geometric mean whole-body concentration of 0.03 æg/g (wet weight) of cadmium in fish. The 85th percentile concentration was 0.05 æg/g (wet weight) (Schmitt and Brumbaugh 1990). Walsh et al. (1977) considered whole-body concentrations >0.50 æg/g cadmium (wet weight) in biota to be potentially harmful to predatory species of fish and wildlife. Based on these data, cadmium



concentrations in fish collected from Bill Williams River NWR do not exceed the predator protection limit of 0.50 æg/g cadmium, therefore, cadmium concentrations do not appear to be high enough to cause environmental concern.

COPPER: Copper is widely distributed in nature and is an essential element and part of about 30 enzymes and glycoproteins (e.g., amine oxidases, cytochrome oxidase, feroxidases, and superoxide dismutase (Aaseth and Norseth 1986, Sorensen 1991). Copper is required in oxidative enzymes for hydrogen peroxide/organic substance destruction and energy production. The daily requirement of copper has been estimated to be about 2 mg for adult humans (Aaseth and Norseth 1986).

copper contamination of aquatic environments is usually associated with mining, urban runoff, industrial discharges, landfills, and wastewater treatment plants. The most toxic species of copper is the cupric form, Cu+ý. Hardness, alkalinity, pH, and the amount of clay or organic material regulate the toxicity of copper in aquatic organisms (Sorensen 1991). Copper complexes with carbonates, hydroxides and humic materials. complexation of copper with inorganic carbon increases with alkalinity and pH, therefore, at high alkalinity and a pH of 8 or more, (conditions at Bill Williams River NWR) , most copper is probably complexed, leaving small amounts of Cu+ý present



(Sorensen 1991). Fish and other aquatic organisms accumulate copper from ingesting contaminated food and sediment-bound or suspended copper (Irwin 1988).

Copper concentrations in the sediments of the Bill Williams River NWR were elevated compared to those for Arizona (King et al. 1991, 1993) and the U.S. (Shacklette and Boerngen 1984) (Table 14). copper concentrations at Bill Williams River NWR have a mean and geometric mean of 47.1 æg/g and 54.9 æg/g (dry weight). These values exceed concentrations found in sediments at other locations in the lower Colorado River Valley. However, they are within baseline concentrations of 4.9-90.0 æg/g (dry weight) reported by Shacklette and Boerngen (1984). Sediments with copper concentrations greater than 60 æg/g are considered elevated. Long and Morgan (1990) (Table 25) reported an ER-L for copper at 70 æg/g (dry weight). Based these data, copper concentrations in sediment from Bill Williams River NWR are not high enough to cause environmental concern.

Copper concentrations in invertebrates collected at Bill Williams River NWR ranged from 2.92 æg/g in snails at Site 6 to 42.30 æg/g in crayfish at Site 3 (wet weight). However, copper levels in whole body fish samples do not reveal any biomagnification of copper. Copper concentrations in fish ranged from 0.35 æg/g in bass collected at Site 6 in 1992 to 3.19 æg/g in carp from Site 6



in 1992 (wet weight). The NCBP found a whole-body geometric mean concentration of 0.65 æg/g wet weight and the 85th percentile of 1.00 æg/g (wet weights) in fish (Schmitt and Brumbaugh 1990). The maximum copper concentration reported by the NCBP was 23.1 æg/g in tilapia (Tilapia mossambica) from Hawaii. Although copper levels in carp from this study exceed the NCBP 85th percentile, they are well below the maximum levels reported. There is no predator protection limit for copper.

The toxicity of copper to aquatic organisms is inversely correlated to the ionic concentration of the water. The lowest hardness recorded was 74 mg/L CaCO[sub]3 (during flooding), the median hardness value was 160 mg/L CaCO[sub]3 and normal (not flood conditions) hardness values for the Bill Williams River were ÷ 260 mg/L CaCO[sub]3 (Table 13) Under normal hardness, it would not become toxic until it reached concentrations at or above 26.75 æg/L (Table 18). Copper concentration in water never exceeded 5 æg/L in the Bill Williams River in pre- or post-flood conditions.

LEAD: Lead is present in practically all phases of the environment, and in all biological systems (Goyer 1991). Lead was detected in all sediment samples collected. Lead concentrations in the sediments of the Bill Williams River NWR were generally at or above concentrations found for



Table 18. Water quality Criteria for the designated uses of the Bill Williams River, Arizona, based on Numeric Water Quality Criteria For Arizona, 1991-1993. (FC = Fish consumption, human; FBC = Full body Contact, i.e. swimming; A&W = Aquatic and wildlife uses.)

See Table/Figure



Arizona (King et al. 1991, 1993) and the U.S. (Shacklette and Boerngen 1984) (Table 14). Lead concentrations at Bill Williams River NWR have a mean and geometric mean of 21.2 æg/g and 16.5 æg/g (dry weight). However, they are within baseline concentrations of 5.2-55.0 æg/g (dry weight) reported by Shacklette and Boerngen (1984). Long and Morgan (1990) (Table 15) reported an ER-L for lead at 35 æg/g (dry weight). Lead concentrations in sediments collected from Bill Williams River NWR were roughly half this amount (mean 16.5 æg/g, geometric mean 21.2 æg/g, dry weight). Based on these data, lead concentrations in sediment from Bill Williams River NWR are not high enough to cause environmental concern

Lead concentrations in invertebrates collected at Bill

Williams River NWR generally were below the limit of detection in all mediums sampled. Lead concentrations in fish ranged from ca 0.24-0.25 æg/g in all fish collected at Bill Williams River NWR. The NCBP found a whole-body geometric mean concentration of 0.11 æg/g (wet weight) of lead in fish and the 85th percentile was 0.73 æg/g (wet weights) (Schmitt and Brumbaugh 1990). The maximum lead concentration reported by the NCBP was 4.88 æg/g wet weight. Lead concentrations in fish from Bill Williams River NWR are generally below levels reported in fish from other studies in the region (Table 16). A predator protection limit of



0.30 æg/g (wet weight) has been defined by Eisler (1988). Lead concentrations in fish collected from Bill Williams River NWR do not exceed NCBP values or the predator protection limit, therefore, lead levels do not appear to merit environmental concern.

MERCURY: Mercury occurs as elemental mercury, and as inorganic and organic compounds, all having different toxicological properties. Mercury is circulated naturally in the biosphere, with 30,00-150,00 tons being released into the atmosphere by degassing from the earth's crust and the oceans (Berlin 1986).

In nature, methylmercury is produced from inorganic mercury as a consequence of microbial activity (Berlin 1986). In fish, the major amount of mercury is methylmercury. Factors determining the methylmercury concentration in fish are mercury content of the water and bottom sediment; pH and redox potential of water; species, age and size of fish.

There was little evidence of mercury contamination in any of the sediment samples collected from the Bill Williams River NWR. Mercury concentrations in sediment from the Bill Williams River NWR (mean = 0.05 æg/g, geometric mean = 0.04 æg/g, dry weight) were generally equivalent to concentrations in sediments from other studies in the region (Radtke 1988, King et al. 1993), in Arizona (King et al.



1991), and U.S. background levels (Shacklette and Boerngen

1984) (Table 14). Long and Morgan (1990) reported an ER-L (Effects Range-Low) for mercury in sediments of 0.15 æg/g dry weight (Table 15). Based on these data, mercury concentrations in sediments collected from the Bill Williams River NWR do not appear to be at levels high enough to cause environmental concern.

Mercury concentrations in invertebrates collected at Bill Williams River NWR were 0.01 æg/g in crayfish collected at Site 3 in 1992 to 0.22 æg/g in odonates collected at Site 6 in 1993 (wet weight) . Mercury concentrations in fish collected at Bill Williams River NWR ranged from 0.0099 æg/g in mosquitofish collected at Site 2 in 1992 to 0.238 æg/g red shiners collected at Site 1 in 1992 (wet weight)

Mercury levels in fish collected at Bill Williams River NWR generally were higher than those reported in other studies from the region (Radtke et al. 1988, King et al. 1991, 1993), with the exception of carp collected at Alamo Lake (Table 16).

The NCBP showed that the whole body geometric mean concentration of mercury in fish was 0.10 æg/g and the 85th percentile was 0.17 æg/g (wet weights) (Schmitt and Brumbaugh 1990) (Table 16). The maximum mercury concentration reported by the NCBP was 0.37 æg/g. The predator protection limit for mercury is 0.10 æg/g (wet



weight) (Eisler 1987) . Generally, all fish collected on the refuge contained mercury levels <0.1 æg/g. Red shiners with elevated mercury levels collected at Site 1 are probably reflective of conditions in Alamo Lake, which has elevated levels of mercury (King et al. 1991). The data indicate that levels of mercury were slightly elevated at a few sites, but even in these areas levels were probably not high enough to cause environmental concern.

SELENIUM: Selenium is chemically very similar to sulphur and many of its compounds are analogous to organic and inorganic sulphur compounds (Goyer 1991). Selenium is an essential trace element, and has been shown to be a natural component in the enzyme glutathione peroxidase (GSH-px) and other proteins (Hogberg and Alexander 1986).

Exposure concentrations and duration determine if selenium is toxic or essential for good health (Goyer 1991).

Sorensen (1991) reported that dietary levels of 0.07 æg/g and/or aqueous levels of 0.004 æg/g selenium are essential for rainbow trout (Oncorhynchus mykiss) . The nutritive role of selenium is linked to the presence of four gram atoms of selenium per mole of GSH-px. Trace levels of selenium protects lipids and nucleic acids from peroxidation and hepatocellular lysis. Selenium is thought to act as an intercellular antioxidant to prevent free radical damage to cell membranes (Sorensen 1991). It is also thought that

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selenium protects against the toxicity of heavy metals such as arsenic, cadmium, mercury, platinum, and silver (Hogberg and Alexander 1986, Menzer 1991).

Selenium deficiencies in fish include increased mortality, reduced growth, hepatic injury, muscle lesions, and depressed GSH-px activity. Conversely, excess levels of selenium are more toxic than arsenic or mercury. Toxic levels of selenium are ca 43 times the essential dietary level or 1000 times the aqueous level (Sorensen 1991). For a review of selenium toxicosis to fish and wildlife see Lemly and Smith (1987).

Selenium concentrations in natural water depend largely on the occurrence of seleniferous soils (Radtke (1988, Menzer 1991). Menzer reports average concentrations of selenium in natural waters are generally less than 1.00 æg/L. Selenium occurs naturally in the environment at trace amounts rarely exceeding 2 æg/kg in soils (Eisler 1985b) however, soils originating from seleniferous shales are generally higher.

There was no evidence of selenium contamination in sediments collected at Bill Williams River NWR. Selenium levels in all sediment samples (N = 21) were below the limit of detection, less than 0.20 æg/g selenium, and generally lower than other studies in the region (Radtke 1986, King et al. 1993), in Arizona (King et al. 1991), and U.S.

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background levels (Shacklette and Boerngen 1984) (Table 14).

Selenium concentrations in invertebrates collected at

Bill Williams River NWR ranged from below the detection limit to 0.79 æg/g in crayfish collected at Site 7 in 1992 (wet weight). The NCBP showed that the whole-body geometric mean concentration of selenium in fish was 0.42 æg/g and the 85th percentile concentration was 0.73 æg/g (wet weights) (Schmitt and Brumbaugh 1990). The maximum selenium concentration found by the NCBP was 2.30 æg/g in carp collected from Martinez Lake, Arizona.

Fish collected from the area of the confluence of the Bill Williams River with the Colorado River contained elevated levels of selenium. With the exception of red shiners, fish from upstream areas of the Bill Williams River did not. These data confirm that elevated selenium levels in biota originate from contact with water from the Colorado River and not from that from the Bill Williams River. of the fish sampled in the confluence, carp, bass, and bluegill had elevated selenium levels. Two carp samples collected in 1993 from the delta contained 3.62 and 4.67 æg/g (wet weight) selenium, respectively.

Selenium levels in red shiners were consistently elevated (<3.00 æg/g wet weight) throughout the study area. Red shiners were the only species to consistently contain selenium levels higher than 3.00 æg/g (dry weight) across

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all sites. Ninety-three percent (13/14 samples) of red shiner samples collected exceeded 3.00 æg/g and 71% (10/14 samples) exceeded 4.00 æg/g, a threshold level set by Lemly (1994) to protect fish from chronic selenium toxicosis.

Selenium levels in carp and bass were generally at or below levels found in fish collected in other studies in the region (Table 16).

Lemly (1993) set a predator protection limit of 3.0 æg/g (dry weight) in samples of food items of aquatic birds and fish and found selenium concentration greater than 4.00 æg/g (dry weight) whole body concentration as the biological effects threshold for the health and reproductive success of fish. Therefore, selenium concentrations in fish collected from the confluence of the Bill Williams River and the Colorado River and red shiners throughout the Bill Williams River suggest health risks to the organisms and predators that may feed upon them.

ZINC: Zinc is an essential metal, necessary for the function of various enzymes (carbonic anhydrase, superoxide dismutase, phosphatase and glutamate dehydrogenase) (Goyer 1991, Sorensen 1991). Zinc is found in large quantities in the vertebrate body, second only to iron. arsenic a component of carbonic anhydrase, zinc plays a role in binding carbon dioxide in teleost cells, combining it with water to form carbonic acid, and releasing carbon dioxide

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from the gills (Sorensen 1991).

Zinc is associated with mining, urban runoff, sewage sludge, industrial discharges, soil erosion, and leachates from municipal landfills (Menzer 1991). The toxicity of zinc is affected by chemical factors such as pH and hardness. In natural waters zinc is less toxic as hardness increases.

Zinc concentrations in the sediments of the Bill Williams River NWR were elevated compared to those for Arizona (King et al. 1991, 1993) and the U.S. (Shacklette and Boerngen 1984) (Table 14). Zinc concentrations at Bill Williams River NWR have a mean and geometric mean of 79.9 æg/g and 74.5 æg/g (dry weight). These values exceed zinc concentrations found in sediments at other locations in the lower Colorado River Valley. However, they are within baseline concentrations of 17-180 æg/g (dry weight) reported by Shacklette and Boerngen (1984). Long and Morgan (1990) (Table 15) reported an ER-L for zinc at 120 æg/g (dry weight). Based these data, zinc concentrations in sediment from Bill Williams River NWR do not appear high enough to cause environmental concern.

Zinc concentrations in invertebrates collected at Bill Williams River NWR ranged from 4.53 æg/g in snails collected at Site 6 in 1992 to 28.30 æg/g in crayfish at Site 7 in 1992 (wet weight). Zinc concentrations in fish ranged from

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13.8 æg/g in bass collected from Site 1 in 1992 to 298 æg/g in carp collected from Site 7 in 1992. The NCBP found a whole-body geometric mean concentration of 21.7 æg/g of zinc and an 85th percentile concentration if 34.2 æg/g (wet weights) in fish (Schmitt and Brumbaugh 1990). Zinc levels in carp and bass were generally higher than reported in other studies done in this region (Table 26). However, carp collected at Alamo Lake contained concentrations similar to those collected from Bill Williams River NWR. Levels of zinc in all carp collected in this study (whole body samples) exceeded the 85th percentile in fish, levels in carp generally exceed this level in carp (Schmitt and Brumbaugh 1990). The maximum zinc concentration reported by the NCBP was 118.4 æg/g wet weight in carp from Minnesota. The NCBP also reported that zinc levels were generally higher in carp compared to other species. Although zinc levels in carp exceed the NCBP values, there is no predator protection limit for zinc.

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# CONCLUSIONS

## Subsurface Effects

In years of average precipitation, the Bill Williams River has only subsurface flow for most of the distance between Alamo Dam and Site 2 (45 km); there is generally surface flow at Site 2. Higher elemental concentrations at Site 2 than at Site 1 may be related to interactions that take place in the subsurface water column.

## Runoff Effects

Few data supported the hypothesis that flows from the washes increased element levels. Even in Mineral Wash (Sites 4 and 5), the site of an inactive copper mine and exposed mine tailings, copper levels were not significantly higher downstream than upstream. In fact, the converse was true for copper levels in sediment, algae, snails and mosquitofish and mercury levels in sediment. Only algae showed differences between upstream and downstream sites near Yucca Wash. There were differences in sediment concentrations of arsenic, copper, lead, selenium, and zinc upstream and downstream of Mohave wash, but most concentrations decreased.

Elemental concentrations consistently increased from upstream to downstream of Cave Wash. The downstream site where the Bill Williams River sank into the sand in 1992 had the characteristics of an evaporation pond; fish and other



organisms were seen stranded and dying as the water receded.

Flood flows did not result in consistent changes in element levels in the Bill Williams River. In December 1992 and January 1993, above average precipitation resulted in the Bill Williams River reaching the 100-year flood crest (well over 4000 cfs or ca 1300 cms) (Dean Radtke, pers. comm. Figure 19). The river over flowed its banks and formed a new channel in two areas on the Refuge. During all of 1993 the Bill Williams River flowed above ground throughout its entire length to the confluence of the Colorado River.

My data showed no consistent differences in contaminant levels before or after the flood, however samples were collected 3 months after the peak flows. Conditions at the time of collection were probably not reflective of the actual flood. There were complex interactions between site and year which may have masked changes. There was a general decrease in arsenic, cadmium, selenium, and zinc concentrations after the flood. Such decreases would seem to be consistent with flushing associated with high flows. In contrast, levels of copper and mercury generally increased. Such increases would seem to be consistent with increased deposition of materials eroded from the watershed.

Selenium was the only element that reached levels of concern in the Bill Williams River and then only at sites 6



See Table/Figure

Figure 19. Mean annual discharge (cubic feet per second) values for releases from Alamo Dam into the Bill Williams River for years 1982-93. (Data taken from U.S. Geological Survey Water Resources Data for Arizona, 1981-1993.)

and 7. At Site 6, the Bill Williams River went underground in 1992 (the river flowed its entire length in 1993), and Site 7 is the delta where the Bill Williams River joins the Colorado River. One might expect elevated selenium levels at site 7 given other data that show elevated selenium levels throughout the lower Colorado River. However, selenium concentrations (geometric means, dry weight) were 5.05 æg/g and 7.59 æg/g for mosquitofish at Sites 6 and 7, respectively and 3.43 æg/g and 3.82 æg/g for bass at Sites 6 and 7, respectively. Differences were not significant (p > 0.07 for mosquitofish and p > 0.09 for bass) . Elevated selenium levels at Site 6 may result from concentration via evaporation or be an artifact resulting from movement of biota out of the Colorado River into the lower portion of the Bill Williams River during periods of surface flow.

The fact that selenium levels were low in all biota except at Sites 6 and 7 indicates that there is little cause for concern over potential contaminant levels on the Bill Williams River NWR. However, most waterbirds nest and feed in the delta rather than on the Bill Williams River and would be exposed to elevated selenium levels. There is also potential concern over selenium levels in neotropical migrants. Martinez (1994) has hypothesized that elevated selenium levels in two nighthawk eggs collected on Imperial NWR are the result of adult birds feeding on the aerial



phase of aquatic insects in the riparian corridor. Such a pattern could also occur if neotropical migrants feed on insects emerging from the delta of the Bill Williams River.



## APPENDIX A



Appendix A-1. Analytical results (ug/g, dry-weight) of elements in samples of vegetation from Bill Williams River NWR, 1992-93. [N = number per composite; SITE = reference number for site location; YEAR = year of sample collection; %MSTR = percent moisture; TOC = total organic carbon; Length = mean length for sample; WEIGHT = total weight (in grams) of sample.]

See Table/Figure



Appendix A-1.  Continued.

See Table/Figure

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Appendix A-1.  Continued.



See Table/Figure



Appendix A-2.  Analytical results (ug/g, dry-weight) of elements in samples of odonate larvae from Bill Williams River NWR, 1992-93.  [CODE # = sample identification; N = number per composite; SITE = reference number for site location; YEAR = year of sample collection; WEIGHT = total weight (in grams) of sample; %MSTR = percent moisture.]

See Table/Figure



Appendix A-2.  Continued.

See Table/Figure



Appendix A-2.  Continued.

See Table/Figure

Appendix A-2. Continued.

See Table/Figure



Appendix A-3. Analytical results (ug/g, dry-weight) of elements in samples of snails from Bill Williams River NWR, 1992-93. [N = number per composite; SITE reference number for site location; YEAR = year of sample collection; %MSTR = percent moisture; TOC = total organic carbon; Length = mean length for sample; WEIGHT = total weight (in grams) of sample.)

See Table/Figure



Appendix A-3. Continued.

See Table/Figure



Appendix A-3. Continued.

See Table/Figure



Appendix A-3. Continued.

See Table/Figure



Appendix A-4. Analytical results (ug/g, dry-weight) of elements in samples of crayfish from Bill Williams River NWR, 1992-93. [N = number per composite; SITE reference number for site location; YEAR = year of sample collection; %MSTR percent moisture; TOC = total organic carbon; Length = mean length for sample; WEIGHT = total weight (in grams) of sample.]

See Table/Figure

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Appendix A-4. Continued.

See Table/Figure

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Appendix A-4. Continued.

See Table/Figure

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Appendix A-4. Continued.

See Table/Figure

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Appendix A-5. Analytical results (ug/g, dry-weight) of elements in samples of tadpoles from Bill Williams River NWR, 1992-93. [N = number per composite; SITE reference number for site location; YEAR = year of sample collection; %MSTR = percent moisture; TOC = total organic carbon; Length = mean length for sample; WEIGHT = total weight (in grams) of sample.]

See Table/Figure

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Appendix A-5. Continued.

See Table/Figure

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Appendix A-6. Analytical results (ug/g, dry-weight) of elements in samples of mosquitofish from Bill Williams River NWR, 1992-93. [N = number per composite; SITE = reference number for site location; YEAR = year of sample collection; %MSTR = percent moisture; TOC = total organic carbon; Length = mean length for sample; WEIGHT = total weight (in grams) of sample.]

See Table/Figure



Appendix A-6. Continued.

See Table/Figure



Appendix A-6. Continued.

See Table/Figure



Appendix A-6. Continued.

See Table/Figure



Appendix A-7. Analytical results (ug/g, dry-weight) of elements in samples of red shiners from Bill Williams River NWR, 1992-93. [N = number per composite; SITE = reference number for site location; YEAR = year of sample collection; %MSTR = percent moisture; TOC = total organic carbon; Length = mean length for sample; WEIGHT = total weight (in grams) of sample.]

See Table/Figure

Appendix A-7. Continued.

See Table/Figure

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Appendix A-7. Continued.

See Table/Figure

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Appendix A-7. Continued.

See Table/Figure

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Appendix A-8. Analytical results (ug/g, dry-weight) of elements in samples of bass, bluegill, and carp from Bill Williams River NWR, 1992-93. [N = number per composite; SITE = reference number for site location; YEAR = year of sample collection; %MSTR = percent moisture; TOC = total organic carbon; Length = mean length for sample; WEIGHT = total weight (in grams) of sample.]

See Table/Figure

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Appendix A-8. Analytical results (ug/g, dry-weight) of elements in samples of bass, bluegill, and carp from Bill Williams River NWR, 1992-93. [N = number per composite; SITE = reference number for site location; YEAR = year of sample collection; %MSTR = percent moisture; TOC = total organic carbon; Length = mean length for sample; WEIGHT = total weight (in grams) of sample.]

See Table/Figure

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Appendix A-8.  Continued.

See Table/Figure



Appendix A-8.  Continued.

See Table/Figure



Appendix A-9.  Analytical results (ug/g, dry-weight) of elements in samples of sediment from Bill Williams River NWR, 1992-93.   [N = number per composite; SITE = reference number for site location; YEAR = year of sample collection; %MSTR   percent moisture; TOC = total organic carbon; Length = mean length for sample; WEIGHT = total weight (in grams) of sample.]

See Table/Figure



Appendix A-9.  Continued.

See Table/Figure



Appendix A-9.  Continued.

See Table/Figure



Appendix A-9.  Continued.

See Table/Figure

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Appendix A-10. Analytical results (ug/g, dry-weight) of elements in samples of Clark's grebe and turtle embryos from Bill Williams River NWR, 1992-93. [N = number per composite; SITE = reference number for site location; YEAR = year of sample collection; %MSTR = percent moisture; TOC = total organic carbon; Length = mean length for sample; WEIGHT = total weight (in grams) of sample.]

See Table/Figure

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Appendix A-10. Continued.

See Table/Figure

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Appendix A-11. Analytical results (ug/g, dry-weight) of organochlorine residues in selected samples collected at Bill Williams River NWR, 1992-93. [CODE = code number for sample; Medium = type of sample; YEAR = year of sample collection; WEIGHT = total weight (in grams) of sample; %MSTR = percent moisture.]

See Table/Figure

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Appendix A-11. Continued.

See Table/Figure

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APPENDIX B

Appendix B-1. Aluminum concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 19659 | 20982 | 9560-37759 | 1617 |
| ALGAE | 23 | 1090 | 1628 | 331.8-6207 | 361.6 |
| SPINY NAIAD | 2 | 1097 | 1101 | 1008-1194 | 92.65 |
| ODONATA | 13 | 406.67 | 637.9 | 106.9-1950 | 174.7 |
| SNAIL | 21 | 881.83 | 1112 | 151.9-2313 | 146.3 |
| CRAYFISH | 11 | 265.07 | 309.6 | 114.1-675.1 | 58.17 |
| MOSQUITOFISH | 26 | 97.13 | 161.3 | 14.86-579.4 | 34.75 |
| CARP | 9 | 21.09 | 34.03 | 6.39-155.3 | 15.51 |
| BASS | 6 | 13.68 | 20.68 | 1.87-44.77 | 6.58 |
| BLUEGILL | S | 36.97 | 45.67 | 11.59-90.45 | 13.53 |
| RED SHINER | 14 | 75.34 | 84.69 | 34.81-154.10 | 10.65 |
| TADPOLE | 9 | 8062.67 | 9064 | 2699-17403 | 1424 |
| TURTLE | 2 | 5.81 | 9.87 | 1.89-17.84 | 7.96 |



Appendix B-2. Arsenic concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 4.25 | 4.367 | 2.96-6.41 | 0.221 |
| ALGAE | 23 | 8.93 | 10.42 | 4.81-48.76 | 1.836 |
| SPINY NAIAD | 2 | 1.79 | 1.80 | 1.62-1.97 | 0.175 |
| ODONATA | 13 | 3.49 | 3.81 | 1.48-5.93 | 0.396 |
| SNAIL | 21 | 7.31 | 8.37 | 3.19-16.85 | 0.90 |
| CRAYFISH | 11 | 2.89 | 3.14 | 1.50-5.38 | 0.40 |
| MOSQUITOFISH | 26 | 1.83 | 2.05 | 0.67-4.89 | 0.20 |
| CARP | 9 | 1.97 | 2.46 | 0.49-4.95 | 0.54 |
| BASS | 6 | 1.06 | 1.06 | 0.89-1.19 | 0.04 |
| BLUEGILL | 5 | 1.08 | 1.09 | 0.83-1.23 | 0.07 |
| RED SHINER | 14 | 0.75 | 0.95 | 0.095-1.65 | 0.13 |
| TADPOLE | 9 | 11.70 | 13.72 | 5.16-29.31 | 2.78 |
| TURTLE | 2 | 0.51 | 0.51 | 0.45-0.57 | 0.06 |

Appendix B-3. Barium concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 214.65 | 217.9 | 145-296.7 | 8.314 |
| ALGAE | 23 | 100.89 | 172.3 | 18.86-747.80 | 29.76 |
| SPINY NAIAD | 2 | 126.73 | 126.8 | 123.30-130.30 | 1.50 |
| ODONATA | 13 | 26.10 | 31.21 | 8.36-56.60 | 4.68 |
| SNAIL | 21 | 95.01 | 98.64 | 60.22-219.40 | 7.02 |
| CRAYFISH | 11 | 213.79 | 233.00 | 132.10-411.60 | 32.34 |
| MOSQUITOFISH | 26 | 17.03 | 18.33 | 9.72-35.97 | 1.50 |
| CARP | 9 | 10.92 | 11.89 | 4.07-18.96 | 1.53 |
| BASS | 6 | 5.41 | 5.98 | 2.42-8.97 | 1.09 |
| BLUEGILL | 5 | 10.76 | 10.80 | 9.43-12.01 | 0.48 |
| RED SHINER | 14 | 9.09 | 9.14 | 7.20-11.14 | 0.28 |
| TADPOLE | 9 | 228.38 | 247.90 | 95-436.40 | 33.33 |
| TURTLE | 2 | 20.09 | 20.11 | 19.23-21 | 0.80 |



Appendix B-4. Beryllium concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 0.736 | 0.873 | 0.48-1.47 | 0.059 |
| ALGAE | 23 | 0.092 | 0.107 | 0.04-0.30 | 0.0153 |
| SPINY NAIAD | 2 | 0.132 | 0.133 | 0.125-0.14 | 0.003 |
| ODONATA | 13 | 0.074 | 0.075 | 0.05-0.10 | 0.005 |
| SNAIL | 21 | 0.078 | 0.043 | 0.035-0.055 | 0.002 |
| CRAYFISH | 11 | 0.034 | 0.038 | 0.035-0.04 | 0.0007 |
| MOSQUITOFISH | 26 | 0.055 | 0.056 | 0.035-0.09 | 0.0023 |
| CARP | 9 | 0.043 | 0.043 | 0.04-0.045 | 0.0009 |
| BASS | 6 | 0.041 | 0.041 | 0.035-0.045 | 0.00.15 |
| BLUEGILL | 5 | 0.039 | 0.040 | 0.035- | 0.0016 |

| | | | | | |
|---|---|---|---|---|---|
| | | | | 0.045 | |
| RED SHINER | 14 | 0.042 | 0.043 | 0.035- | 0.0015 |
| | | | | 0.055 | |
| TADPOLE | 9 | 0.580 | 0.663 | 0.22-1.32 | 0.112 |
| TURTLE | 2 | 0.037 | 0.038 | 0.035-0.04 | 0.0025 |



Appendix B-5. Boron concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 10.99 | 12.19 | 3.87-23.44 | 1.123 |
| ALGAE | 23 | 114.66 | 125.7 | 19.01- | 9.55 |
| | | | | 219.3 | |
| SPINY NAIAD | 2 | 24.41 | 24.5 | 22.38- | 2.12 |
| | | | | | 26.62 |
| ODONATA | 13 | 2.10 | 2.453 | 1.12-4.69 | 0.41 |
| SNAIL | 21 | 2.61 | 2.941 | 0.995-6.25 | 0.32 |
| CRAYFISH | 11 | 4.65 | 4.743 | 3.34-6.61 | 0.29 |
| MOSQUITOFISH | 26 | 1.99 | 1.109 | 0.745- | 0.04 |
| | | | | | 0.224 |
| CARP | 9 | 0.462 | 0.843 | 0.75-0.925 | 0.02 |
| BASS | 6 | 0.813 | 0.814 | 0.745- | 0.02 |
| | | | | 0.875 | |
| BLUEGILL | 5 | 0.904 | 0.948 | 0.730-1.59 | 0.16 |
| RED SHINER | 14 | 0.834 | 0.840 | 0.710- | 0.03 |
| | | | | | 1.075 |
| TADPOLE | 9 | 7.434 | 8.124 | 3.15-15.19 | 1.18 |
| TURTLE | 2 | 0.735 | 0.735 | 0.72-0.755 | 0.02 |



Appendix B-6. Cadmium concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 0.246 | 0.296 | 0.09-0.58 | 0.0342 |
| ALGAE | 23 | 0.281 | 0.311 | 0.16-0.87 | 0.034 |
| SPINY NAIAD | 2 | 0.332 | 0.333 | 0.315-0.35 | 0.018 |
| ODONATA | 13 | 0.685 | 0.712 | 0.34-1.03 | 0.053 |
| SNAIL | 21 | 0.331 | 0.382 | 0.12-0.76 | 0.045 |
| CRAYFISH | 11 | 0.371 | 0.479 | 0.105-0.92 | 0.087 |

| | | | | | |
|---|---|---|---|---|---|
| MOSQUITOFISH | 26 | 0.148 | 0.162 | 0.095-0.67 | 0.021 |
| CARP | 9 | 0.124 | 0.125 | 0.095-0.14 | 0.004 |
| BASS | 6 | 0.102 | 0.103 | 0.095-0.16 | 0.003 |
| BLUEGILL | 5 | 0.099 | 0.100 | 0.095-0.16 | 0.004 |
| RED SHINER | 14 | 0.335 | 0.371 | 0.11-0.57 | 0.039 |
| TADPOLE | 9 | 0.347 | 0.380 | 0.11-0.60 | 0.048 |
| TURTLE | 2 | 0.113 | 0.113 | 0.11-0.115 | 0.003 |

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Appendix B-7. Chromium concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 29.77 | 30.32 | 17.81-42.46 | 1.282 |
| ALGAE | 23 | 3.281 | 4.477 | 1.31-17.22 | 0.91 |
| SPINY NAIAD | 2 | 2.387 | 1.66 | 1.09-2.93 | 0.090 |
| ODONATA | 13 | 1.476 | 1.748 | 0.63-3.69 | 0.29 |
| SNAIL | 21 | 2.054 | 2.122 | 1.32-3.08 | .012 |
| CRAYFISH | 11 | 1.122 | 1.132 | 0.89-1.44 | 0.048 |
| MOSQUITOFISH | 26 | 1.610 | 1.66 | 1.09-2.93 | 0.09 |
| CARP | 9 | 1.374 | 1.39 | 1.02-1.85 | 0.087 |
| BASS | 6 | 1.406 | 1.42 | 1.16-1.76 | 0.09 |
| BLUEGILL | 5 | 1.609 | 1.612 | 1.45-1.71 | 0.05 |
| RED SHINER | 14 | 1.259 | 1.261 | 1.14-1.39 | 0.21 |
| TADPOLE | 9 | 12.025 | 13.35 | 4.14-25.06 | 2.001 |
| TURTLE | 2 | 0.789 | 0.79 | 0.79-0.79 | 0 |

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Appendix B-8. Copper concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 47.09 | 54.93 | 18.97-131.2 | 7.157 |
| ALGAE | 23 | 9.53 | 13.73 | 3.07-40.08 | 2.61 |
| SPINY NAIAD | 2 | 6.67 | 6.67 | 6.60-6.73 | 0.065 |
| ODONATA | 13 | 30.72 | 31.62 | 22.66-45.09 | 2.26 |
| SNAIL | 21 | 60.95 | 68.63 | 20-139.20 | 6.89 |
| CRAYFISH | 11 | 105.32 | 109.30 | 62.45-151 | 9.14 |

| | | | | | |
|---|---|---|---|---|---|
| MOSQUITOFISH | 26 | 7.34 | 7.43 | 5.75-10.73 | 0.25 |
| CARP | 9 | 5.76 | 6.23 | 3.78-13.07 | 0.98 |
| BASS | 6 | 2.17 | 2.39 | 1.29-3.49 | 0.38 |
| BLUEGILL | 5 | 2.44 | 2.46 | 2.12-3.20 | 0.19 |
| RED SHINER | 14 | 4.54 | 4.59 | 3.32-5.78 | 0.18 |
| TADPOLE | 9 | 33.15 | 35.72 | 13.37-57.27 | 4.35 |
| TURTLE | 2 | 4.93 | 4.97 | 4.37-5.57 | 0.60 |



Appendix B-9. Iron concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 24221 | 24705 | 15274-36904 | 1109 |
| ALGAE | 23 | 1548 | 2245 | 528-9924 | 436.8 |
| SPINY NAIAD | 2 | 1728 | 1734 | 1606-1863 | 128.4 |
| ODONATA | 13 | 716 | 1039 | 198-3031 | 264.6 |
| SNAIL | 21 | 1213 | 1426 | 236-3307 | 167.7 |
| CRAYFISH | 11 | 276 | 347.4 | 112-885 | 80.35 |
| MOSQUITOFISH | 26 | 167 | 237.9 | 56-839 | 46.68 |
| CARP | 9 | 110 | 128.7 | 61-381 | 32.28 |
| BASS | 6 | 55 | 59.71 | 30-102 | 10.53 |
| BLUEGILL | 5 | 89 | 98.29 | 55-188 | 23.36 |
| RED SHINER | 14 | 133 | 141.2 | 75-222 | 12.73 |
| TADPOLE | 9 | 11510 | 12509 | 47-22078 | 1723 |
| TURTLE | 2 | 107 | 107.3 | 103-112 | 4.455 |



Appendix B-10. Lead concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 16.50 | 21.15 | 9.20-48.99 | 2.509 |
| ALGAE | 23 | 2.07 | 2.26 | 1.01-6.22 | 0.26 |
| SPINY NAIAD | 2 | 3.27 | 2.27 | 3.07-3.48 | 0.21 |
| ODONATA | 13 | 1.85 | 1.89 | 1.29-2.54 | 0.12 |
| SNAIL | 21 | 1.41 | 1.48 | 0.80-2.35 | 0.10 |
| CRAYFISH | 11 | 0.93 | 0.93 | 0.85-1.03 | 0.21 |
| MOSQUITOFISH | 26 | 1.36 | 1.39 | 0.94-2.17 | 0.05 |

| | | | | | |
|---|---|---|---|---|---|
| CARP | 9 | 1.05 | 1.05 | 0.94-1.16 | 0.02 |
| BASS | 6 | 1.02 | 1.02 | 0.94-1.09 | 0.03 |
| BLUEGILL | 5 | 0.98 | 0.99 | 0.92-1.13 | 0.04 |
| RED SHINER | 14 | 1.04 | 1.05 | 0.89-1.35 | 0.03 |
| TADPOLE | 9 | 11.11 | 12.54 | 3.48-23.12 | 1.92 |
| TURTLE | 2 | 2.72 | 4.58 | 0.89-8.26 | 3.68 |

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Appendix B-11. Magnesium concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 8825 | 90966 | 5138-12969 | 469.3 |
| ALGAE | 23 | 2827 | 3127 | 1325-5946 | 303 |
| SPINY NAIAD | 2 | 3656 | 3657 | 3577-3737 | 80.02 |
| ODONATA | 13 | 1210 | 1280 | 710.7-2258 | 129.7 |
| SNAIL | 21 | 1666 | 1702 | 1046-2394 | 78.72 |
| CRAYFISH | 11 | 2267 | 2321 | 1826-3298 | 165.6 |
| MOSQUITOFISH | 26 | 1548 | 1570 | 1161-2221 | 54.62 |
| CARP | 9 | 1295 | 1302 | 1053-1566 | 50.12 |
| BASS | 6 | 1284 | 1309 | 953.4-1615 | 110.6 |
| BLUEGILL | 5 | 1318 | 1328 | 1041-1459 | 77.09 |
| RED SHINER | 14 | 1347 | 1349 | 1217-1475 | 21.22 |
| TADPOLE | 9 | 6393 | 7038 | 2288-13507 | 1035 |
| TURTLE | 2 | 791 | 791.7 | 757.6-825.9 | 34.16 |

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Appendix B-12. Manganese concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 491.08 | 525.30 | 252.5-959.2 | 42.53 |
| ALGAE | 23 | 1059 | 3122 | 162.9-16903 | 1017 |
| SPINY NAIAD | 2 | 367 | 367.1 | 359.2-375 | 7.93 |
| ODONATA | 13 | 421 | 580 | 113-1616 | 133.5 |
| SNAIL | 21 | 502 | 749.7 | 111.3-3397 | 165.7 |
| CRAYFISH | 11 | 417 | 455.4 | 266-992.8 | 67.40 |
| MOSQUITOFISH | 26 | 75 | 308.2 | 26.56-6306 | 240.00 |

| | | | | | |
|---|---|---|---|---|---|
| CARP | 9 | 9.76 | 17.60 | 4.52-27.19 | 2.26 |
| BASS | 6 | 34.23 | 92.63 | 8.21-268.7 | 50.57 |
| BLUEGILL | 5 | 55.65 | 61.70 | 28.75-100 | 13.38 |
| RED SHINER | 14 | 42.73 | 45.10 | 21.89-73.73 | 4.06 |
| TADPOLE | 9 | 1066.35 | 1188 | 524.6-1725 | 171.7 |
| TURTLE | 2 | 3.38 | 3.38 | 3.32-3.44 | 0.06 |

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Appendix B-13. Mercury concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 0.040 | 0.0468 | 0.0135-0.10 | 0.005 |
| ALGAE | 23 | 0.069 | 0.097 | 0.02-0.025 | 0.016 |
| SPINY NAIAD | 2 | 0.066 | 0.067 | 0.063-0.071 | 0.004 |
| ODONATA | 13 | 0.197 | 0.46 | 0.035-1.38 | 0.148 |
| SNAIL | 21 | 0.052 | 0.063 | 0.018-0.13 | 0.009 |
| CRAYFISH | 11 | 0.096 | 0.101 | 0.05-0.15 | 0.01 |
| MOSQUITOFISH | 26 | 0.237 | 0.286 | 0.05-0.50 | 0.0352 |
| CARP | 9 | 0.234 | 0.259 | 0.13-0.51 | 0.044 |
| BASS | 6 | 0.477 | 0.51 | 0.26-0.74 | 0.079 |
| BLUEGILL | 5 | 0.196 | 0.214 | 0.12-0.37 | 0.047 |
| RED SHINER | 14 | 0.196 | 0.262 | 0.07-0.85 | 0.068 |
| TADPOLE | 9 | 0.360 | 0.486 | 0.17-1.46 | 0.150 |
| TURTLE | 2 | 0.055 | 0.055 | 0.05-0.06 | 0.005 |

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Appendix B-14. Molybdenum concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 0.859 | 0.963 | 0.61-2.25 | 0.0998 |
| ALGAE | 23 | 1.533 | 1.585 | 0.81-3.04 | 0.0~1 |
| SPINY NAIAD | 2 | 2.609 | 2.615 | 2.45-2.78 | 0.165 |
| ODONATA | 13 | 1.462 | 1.496 | 1.04-2.03 | 0.091 |
| SNAIL | 21 | 0.919 | 0.989 | 0.50-2.37 | 0.091 |
| CRAYFISH | 11 | 0.742 | 0.744 | 0.675-0.820 | 0.017 |

| | | | | | |
|---|---|---|---|---|---|
| MOSQUITOFISH | 26 | 1.089 | 1.109 | 0.75-1.74 | 0.044 |
| CARP | 9 | 0.998 | 1.179 | 0.75-3.85 | 0.334 |
| BASS | 6 | 0.813 | 0.814 | 0.745-<br>0.875 | 0.021 |
| BLUEGILL | 5 | 0.787 | 0.789 | 0.730-<br>0.905 | 0.03l |
| RED SHINER | 14 | 0.834 | 0.839 | 0.710-<br>1.075 | 0.026 |
| TADPOLE | 9 | 1.275 | 1.700 | 0.425-4.95 | 0.488 |
| TURTLE | 2 | 0.735 | 0.735 | 0.715- | 0.02<br>0.755 |



Appendix B-15. Nickel concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 22.56 | 23.05 | 14.79-<br>34.65 | 1.079 |
| ALGAE | 23 | 3.03 | 3.46 | 1.24-9.31 | 0.426 |
| SPINY NAIAD | 2 | 4.76 | 4.93 | 3.68-6.17 | 1.245 |
| ODONATA | 13 | 2.09 | 2.58 | 0.85-5.80 | 0.487 |
| SNAIL | 21 | 3.52 | 3.811 | 1.62-6.18 | 0.318 |
| CRAYFISH | 11 | 1.64 | 1.77 | 1.00-3.11 | 0.228 |
| MOSQUITOFISH | 26 | 0.480 | 0.635 | 0.26-3.54 | 0.134 |
| CARP | 9 | 0.502 | 0.856 | 0.23-3.33 | 0.351 |
| BASS | 6 | 0.245 | 0.245 | 0.225-<br>0.265 | 0.006 |
| BLUEGILL | 5 | 0.464 | 0.536 | 0.24-1.02 | 0.142 |
| RED SHINER | 14 | 0.283 | 0.307 | 0.22-0.69 | 0.042 |
| TADPOLE | 9 | 18.81 | 20.84 | 6.93-39.87 | 3.169 |
| TURTLE | 2 | 0.223 | 0.23 | 0.22-0.26 | 0.015 |



Appendix B-16. Selenium concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 0.146 | 0.166 | 0.125-0.27 | 0.0087 |
| ALGAE | 23 | 0.610 | 0.783 | 1.10-2.04 | 0.109 |
| SPINY NAIAD | 2 | 1.091 | 1.18 | 0.730-1.63 | 0.45 |

| | | | | | |
|---|---|---|---|---|---|
| ODONATA | 13 | 2.672 | 3.305 | 0.80-5.49 | 0.526 |
| SNAIL | 21 | 0.886 | 1.38 | 0.26-3.55 | 0.26 |
| CRAYFISH | 11 | 1.618 | 1.77 | 1.00-3.11 | 0.228 |
| MOSQUITOFISH | 26 | 3.511 | 3.96 | 1.92-13.04 | 0.473 |
| CARP | 9 | 4.023 | 5.75 | 2.04-17.56 | 2.003 |
| BASS | 6 | 3.168 | 3.24 | 2.06-3.93 | 0.28 |
| BLUEGILL | 5 | 0.847 | 2.41 | 0.20-7.14 | 1.406 |
| RED SHINER | 14 | 4.993 | 5.25 | 2.20-7.44 | 0.415 |
| TADPOLE | 9 | 0.886 | 1.60 | 0.22-5.80 | 1.896 |
| TURTLE | 2 | 5.286 | 5.295 | 5.02-5.57 | 0.275 |

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Appendix B-17. Strontium concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 126.23 | 135.0 | 59.30-315.20 | 11.60 |
| ALGAE | 23 | 178.40 | 291.9 | 51-984 | 61.99 |
| SPINY NAIAD | 2 | 188.11 | 188.3 | 180-196 | 7.99 |
| ODONATA | 13 | 23.83 | 26.29 | 10-48 | 11.70 |
| SNAIL | 21 | 509.79 | 525.2 | 277-849 | 28.93 |
| CRAYFISH | 11 | 838.82 | 858.5 | 664-1227 | 61.00 |
| MOSQUITOFISH | 26 | 123.10 | 128.1 | 79-218 | 7.56 |
| CARP | 9 | 166.33 | 176.3 | 89-262 | 19.50 |
| BASS | 6 | 127.87 | 136.1 | 79-213 | 20.81 |
| BLUEGILL | 5 | 168.17 | 172.9 | 116-238 | 20.14 |
| RED SHINER | 14 | 124.46 | 124.9 | 107-146 | 3.043 |
| TADPOLE | 9 | 122.98 | 132.3 | 54-236 | 17.21 |
| TURTLE | 2 | 61.50 | 61.54 | 59-65 | 2.830 |

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Appendix B-18. Vanadium concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 67.66 | 69.38 | 46.35-100.70 | 3.452 |
| AL~AE | 23 | 7.~32 | 11.17 | 2.40-38.67 | 2.125 |
| SPINY NAIAD | 2 | 5.130 | 5.15 | 4.77-5.52 | 0.375 |
| ODONATA | 13 | 2.540 | 3.16 | 1.06-7.23 | 0.571 |

| | | | | | |
|---|---|---|---|---|---|
| SNAIL | 21 | 5.601 | 5.86 | 3.12-9.21 | 0.387 |
| CRAYFISH | 11 | 1.471 | 1.51 | 1.04-2.12 | 0~100 |
| MOSQUITOFISH | 26 | 0.643 | 0.84 | 0.22-2.74 | 0.142 |
| CARP | 9 | 0.365 | 0.42 | 0.11-0.93 | 0.078 |
| BASS | 6 | 0.139 | 0.15 | 0.10-0.31 | 0.035 |
| BLUEGILL | 5 | 0.695 | 0.77 | 0.38-1.15 | 0.157 |
| RED SHINER | 14 | 0.557 | 0.57 | 0.36-0.82 | 0.036 |
| TADPOLE | 9 | 27.41 | 30.13 | 11.10-59.22 | 4.64 |
| TURTLE | 2 | 0.138 | 1.05 | 0.10-0.20 | 0.053 |

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Appendix B-19. Zinc concentrations (æg/g dry weight) in selected samples from Bill Williams River NWR, 1992-93.

| Medium | N | GMEAN | MEAN | RANGE | SE |
|---|---|---|---|---|---|
| SEDIMENT | 21 | 74.54 | 79.92 | 37.06-129.90 | 6.398 |
| ALGAE | 23 | 14.66 | 16.62 | 5.26-37.55 | 1.86 |
| SPINY NAIAD | 2 | 22.35 | 22.45 | 21-24.51 | 2.06 |
| ODONATA | 13 | 76.71 | 77.28 | 63-89.08 | 2.64 |
| SNAIL | 21 | 26.39 | 27.08 | 18-52.21 | 1.54 |
| CRAYFISH | 11 | 73.26 | 74.23 | 60-102 | 3.97 |
| MOSQUITOFISH | 26 | 121.88 | 123.30 | 95-169 | 3.86 |
| CARP | 9 | 229.75 | 298.40 | 118-1146 | 106.80 |
| BASS | 6 | 58.62 | 58.75 | 52-64 | 1.80 |
| BLUEGILL | 5 | 81.94 | 82.74 | 67-102 | 5.72 |
| RED SHINER | 14 | 159.02 | 159.50 | 14-179 | 3.35 |
| TADPOLE | 9 | 80.48 | 87.55 | 33-165 | 12.46 |
| TURTLE | 2 | 79.28 | 79.28 | 79-80 | 0.49 |

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# APPENDIX C

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Appendix C-1. Statistical results from General Linear Model for all trace elements analyzed in sediment collected at the Bill Williams River NWR, 1992-1993. Insignificant values are in italics (à = 0.05).

| Element | Model | Year | Site | Site*Year | Normality |
|---|---|---|---|---|---|
| Aluminum | 0.0001 | 0.0051 | 0.0001 | 0.0016 | >0.2000 |
| Arsenic | 0.0001 | 0.6775 | 0.0025 | 0.0001 | >0.2000 |
| Barium | 0.0076 | 0.0391 | 0.0350 | 0.0509 | 0.1712 |
| Beryllium | 0.0001 | 0.6696 | 0.0003 | 0.0017 | >0.2000 |
| Boron | 0.0001 | 0.0001 | 0.0033 | 0.0001 | >0.2000 |
| cadmium | 0.0001 | 0.0001 | 0.0005 | 0.0001 | 0.0393 |
| chromium | 0.0054 | 0.6826 | 0.0049 | 0.0144 | >0.2000 |
| copper | 0.0001 | 0.0078 | 0.0001 | 0.0001 | >0.2000 |
| Iron | 0.0006 | 0.1791 | 0.0009 | 0.0014 | >0.2000 |
| Lead | 0.0001 | 0.0001 | 0.0001 | 0.0001 | >0.2000 |
| Magnesium | 0.0002 | 0.3405 | 0.0005 | 0.0059 | 0.0045 |
| Manganese | 0.0002 | 0.0001 | 0.0008 | 0.0001 | >0.2000 |
| Mercury | 0.0827 | 0.1185 | 0.0511 | 0.4378 | >0.2000 |
| Molybdenum | 0.0016 | 0.0003 | 0.0566 | 0.0009 | 0.0033 |
| Nickel | 0.0013 | 0.0282 | 0.0005 | 0.2518 | 0.0111 |
| Selenium | 0.0001 | 0.0001 | 0.0012 | 0.0001 | >0.2000 |
| Strontium | 0.0001 | 0.0001 | 0.0805 | 0.0001 | >0.2000 |
| Vanadium | 0.0011 | 0.0006 | 0.0106 | 0.0109 | >0.2000 |
| Zinc | 0.0001 | 0.0001 | 0.0002 | 0.0001 | >0.2000 |

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Appendix C-2. Statistical results from General Linear Model for all trace elements analyzed in algae collected at the Bill Williams River NWR, 1992-1993. Insignificant values are in italics (à = 0.05)

| Element | Model | Year | Site | Site*Year | Normality |
|---|---|---|---|---|---|
| Aluminum | 0.2209 | 0.3453 | 0.0967 | 0.8150 | >0.2000 |
| Arsenic | 0.3876 | 0.1698 | 0.2876 | 0.8379 | 0.1173 |
| Barium | 0.0001 | 0.0001 | 0.0499 | 0.4703 | >0.2000 |
| Beryllium | 0.0044 | 0.1202 | 0.0017 | 0.1317 | 0.0001 |
| Boron | 0.0634 | 0.0413 | 0.1022 | 0.0336 | >0.2000 |
| cadmium | 0.0534 | 0.2059 | 0.0376 | 0.5942 | 0.0952 |
| Chromium | 0.0028 | 0.2246 | 0.0011 | 0.1485 | 0.0344 |
| Copper | 0.0007 | 0.0002 | 0.0049 | 0.0089 | 0.0976 |
| Iron | 0.1524 | 0.2822 | 0.0738 | 0.4783 | >0.2000 |
| Lead | 0.2191 | 0.3439 | 0.1858 | 0.1905 | 0.0001 |
| Magnesium | 0.0063 | 0.0002 | 0.0401 | 0.6050 | >0.2000 |
| Manganese | 0.0001 | 0.0001 | 0.0014 | 0.3343 | 0.0873 |
| Mercury | 0.0001 | 0.0001 | 0.0001 | 0.0001 | >0.2000 |
| Molybdenum | 0.0081 | 0.0024 | 0.0535 | 0.0062 | 0.1480 |
| Nickel | 0.4853 | 0.6667 | 0.3329 | 0.5413 | 0.0001 |
| Selenium | 0.0927 | 0.0178 | 0.0748 | 0.7745 | 0.2000 |
| Strontium | 0.0001 | 0.0001 | 0.0001 | 0.1127 | 0.0397 |

| | | | | | |
|---|---|---|---|---|---|
| Vanadium | 0.0101 | 0.0196 | 0.0698 | 0.3334 | >0.2000 |
| Zinc | 0.0735 | 0.5140 | 0.1316 | 0.0352 | >0.2000 |

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Appendix C-3. Statistical results from General Linear Model for all trace elements analyzed in snails collected at the Bill Williams River NWR, 1992-1993. Insignificant values are in italics (à = 0.05)

| Element | Model | Year | Site | Site*Year | Normality |
|---|---|---|---|---|---|
| Aluminum | 0.0972 | 0.0867 | 0.1266 | 0.9975 | >0.2000 |
| Arsenic | 0.0001 | 0.0001 | 0.0466 | 0.0441 | >0.2000 |
| Barium | 0.0242 | 0.7389 | 0.0629 | 0.0069 | 0.0352 |
| Beryllium | 0.0001 | 0.0001 | 0.6423 | 0.2820 | 0.0975 |
| Boron | 0.0080 | 0.0059 | 0.0452 | 0.0975 | >0.2000 |
| Cadmium | 0.0001 | 0.0001 | 0.0001 | 0.2419 | >0.2000 |
| Chromium | 0.0044 | 0.0004 | 0.0350 | 0.6817 | >0.2000 |
| Copper | 0.0001 | 0.0001 | 0.0011 | 0.0018 | >0.2000 |
| Iron | 0.3025 | 0.0716 | 0.8760 | 0.2233 | >0.2000 |
| Lead | 0.2579 | 0.3870 | 0.8202 | 0.0620 | >0.2000 |
| Magnesium | 0.0001 | 0.0002 | 0.0016 | 0.0043 | >0.2000 |
| Manganese | 0.0001 | 0.0017 | 0.0001 | 0.0124 | >0.2000 |
| Mercury | 0.0001 | 0.0001 | 0.0097 | 0.5740 | >0.2000 |
| Molybdenum | 0.0030 | 0.0002 | 0.1153 | 0.0363 | >0.2000 |
| Nickel | 0.0001 | 0.0001 | 0.0009 | 0.0002 | 0.0832 |
| Selenium | 0.0001 | 0.0001 | 0.0488 | 0.0011 | 0.0071 |
| Strontium | 0.1241 | 0.0283 | 0.4529 | 0.4381 | >0.1910 |
| Vanadium | 0.0001 | 0.0002 | 0.0004 | 0.0001 | >0.2000 |
| Zinc | 0.0026 | 0.0024 | 0.0040 | 0.0221 | >0.2000 |

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Appendix C-4. Statistical results from General Linear Model for all trace elements analyzed in mosquitofish collected at the Bill Williams River NWR, 1992-1993. Insignificant values are in italics (à = 0.05).

| Element | Model | Year | Site | Site*Year | Normality |
|---|---|---|---|---|---|
| Aluminum | 0.0001 | 0.8283 | 0.0001 | 0.4956 | >0.2000 |
| Arsenic | 0.0712 | 0.0505 | 0.0906 | 0.1710 | >0.2000 |
| Barium | 0.0001 | 3.6443 | 0.0001 | 0.0043 | 0.0539 |
| Beryllium | 0.0301 | 0.5583 | 0.1359 | 0.0096 | >0.2000 |
| Boron | 0.0813 | 0.7248 | 0.3086 | 0.0189 | 0.1382 |
| cadmium | 0.2325 | 3.4443 | 0.3779 | 0.0680 | 0.0008 |

| | | | | | |
|---|---|---|---|---|---|
| chromium | 0.0001 | 0.0396 | 0.0001 | 0.0290 | 0.0651 |
| Copper | 0.0029 | 0.0786 | 0.0643 | 0.0185 | 0.0799 |
| Iron | 0.0001 | 0.2332 | 0.0001 | 0.1465 | 0.0001 |
| Lead | 0.0802 | 0.7311 | 0.3020 | 0.0191 | 0.1391 |
| Magnesium | 0.0015 | 0.5593 | 0.0010 | 0.0352 | >0.2000 |
| Manganese | 0.1593 | 0.8362 | 0.1240 | 0.2408 | 0.0001 |
| Mercury | 0.0023 | 0.0001 | 0.0608 | 0.0309 | >0.2000 |
| Molybdenum | 0.0813 | 0.7248 | 0.3086 | 0.0189 | 0.1882 |
| Nickel | 0.0001 | 0.0311 | 0.0001 | 0.2933 | 0.0001 |
| Selenium | 0.0219 | 0.1400 | 0.0482 | 0.0809 | 0.1116 |
| Strontium | 0.0001 | 0.2201 | 0.0001 | 0.0461 | 0.1038 |
| Vanadium | 0.0001 | 0.0010 | 0.0001 | 0.6676 | 0.0240 |
| Zinc | 0.0060 | 0.0017 | 0.0073 | 0.1446 | >0.2000 |



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