

U.S. Fish and Wildlife Service  
Region 2  
Contaminants Program

ENVIRONMENTAL CONTAMINANT INVESTIGATION OF  
WATER QUALITY, SEDIMENT AND BIOTA OF THE  
UPPER GILA RIVER BASIN, ARIZONA

by

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ABSTRACT-Water, sediment, lizard, and avian samples and fish (whole body and fillet) were collected in 1990 from several locations along the Gila and San Francisco Rivers in Arizona and New Mexico for organochlorine and trace element analysis. Arsenic, cadmium and lead concentrations in water were slightly elevated above the 1992 Arizona domestic water source (DWS) criteria. Cadmium was the only element recovered from waters on the San Carlos Apache Reservation that was slightly elevated above the DWS criteria. Concentrations of organochlorine pesticides and selenium were below concentrations known to affect survival and reproduction of fish. Twenty-nine percent of catfish and carp and 62% of lizard samples had elevated levels of cadmium that approached or exceeded the predator protection limit of 0.1  $\mu\text{g/g}$  wet weight. Mercury levels in 69% of whole body fish and 100% of fillet samples equalled or exceeded the threshold limit (0.1  $\mu\text{g/g}$  wet weight) for fish-eating birds. One fish sample had a selenium concentration that exceeded the 3.0  $\mu\text{g/g}$  dry weight level that may be potentially harmful to fish-eating birds.

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#### INTRODUCTION

The objective of this study was to survey the upper Gila River basin to determine if waters from mining and agriculture drainages have the potential to cause significant harmful effects on fish and wildlife resources. Elevated levels of organic and inorganic contaminants have previously been identified in fish from the project area (Schmitt and Brumbaugh 1990, Schmitt et al. 1990). Our study focused on water quality, contaminant impacts to aquatic, reptilian and avian resources on the Gila River and two of its major tributaries, the San Francisco and San Carlos rivers.

#### STUDY AREA

The Gila River headwaters drain the eastern Mogollon and western Black ranges of southwestern New Mexico, flowing south-southwesterly toward Arizona (Minckley and Sommerfeld 1979). The study area begins in the Duncan-Virden Valley near the Arizona/New Mexico state line, in Hidalgo County, New Mexico (Figure 1). The Gila flows northwesterly to its confluence with the San Francisco River. Approximately 32 kilometers downstream from the confluence of the San Francisco and Gila Rivers, near Solomon, Arizona, the river again turns northwest and flows through the Safford Valley, Graham County (Minckley and Sommerfeld

1979). The river continues this course where it enters the San Carlos Reservoir, which is the western boundary of the study area. The San Carlos River flows southward to the San Carlos Reservoir. The study area is generally considered to be within a broad transition between Chihuahuan Desert to the east and Sonoran Desert to the West (Minckley and Sommerfeld 1979).

The San Francisco River originates in the Mogollon Rim of Arizona and New Mexico and flows southerly (LaBounty and Minckley 1972, Minckley and Sommerfeld 1979). The river then diverts west, converging with the Blue River before flowing southwesterly through Clifton, Arizona, to enter the Gila River (Minckley and Sommerfeld 1979). Terrain of the San Francisco River drainage is generally mountainous, and this river is usually restricted to canyons.

The Gila River Basin, lying mostly below 1,500 meters, is dominated by desertscrub (Minckley and Sommerfeld 1979). Riparian woodlands in steep, narrow, mesic side canyons and gorges of larger perennial rivers are present throughout the study area. At lower elevations, slopes adjacent to the streams support pinon-juniper woodlands. Most streams are directly bordered by cottonwood-sycamore forests. In most areas, where the floodplain is relatively level, lands have been modified for agriculture.

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The Gila River and its tributaries represent major lotic waters and important riparian habitats in southeastern Arizona. The Gila River and adjacent flood plain provides a major recreation outlet for local residents. Fishing for catfish is popular along the river from Guthrie to Geronimo, Arizona. San Carlos Reservoir is considered a quality warm water fishery and is utilized by many people from Tucson and Phoenix. Mourning dove (*Zenaidura macroura*)<sup>1</sup> white-winged dove (*Z. asiatica*), and quail (*Callipepla squamata* and *Lophortyx gambelii*) are abundant and migratory waterfowl are often observed in the valley.

This area is valuable for its nongame resources as well. It is popular among bird watchers and wildlife photographers, particularly for its diverse avifauna. Approximately 184 species of birds have been recorded along the upper Gila River (Benham-Blair and Affiliates 1981)

Species of special importance in the study area include two federally threatened fish: spikedace (*Meda fulgida*) and loach minnow (*Tiaroga cobitis*), one federally endangered fish: Gila topminnow (*Poeciliopsis occidentalis occidentalis*), and two federally endangered bird species: peregrine falcon (*Falco peregrinus*) and bald eagle (*Haliaeetus leucocephalus*). One pair of bald eagles nested in the San Carlos Reservoir area during the study period.

HISTORICAL ACCOUNTS OF ENVIRONMENTAL CONTAMINANT DATA

Whole body fish (predator and bottom feeders) from the Gila River at San Carlos Reservoir have been monitored for contaminant residues under the National Contaminant Biomonitoring Program (NCBP) since 1971. Detections included 15 organochlorine insecticides, three polychlorinated biphenyls (PCBs), and seven trace elements. Since 1970, the national mean concentrations of PCBs, other organochlorines, and arsenic, cadmium, lead, and selenium have declined (Schmitt et al. 1990, Schmitt and Brumbaugh 1990). However, arsenic, cadmium and lead remained elevated above national baseline values in the study area.

The NCBP also monitored organochlorine residues in starlings (*Sturnus vulgaris*) collected in the Gila River Valley near Pima, Arizona from 1970 to 1985. Detections have included DDE, dieldrin, and PCBs. DDE residues in starlings collected from this location in 1985 were the eighth highest of 125 sites sampled nationwide.

## METHODS AND MATERIALS

Sampling sites within the Gila River Basin included the San Francisco, Gila (including San Carlos Reservoir) and San Carlos rivers. Water and sediments were sampled at 10 locations from the San Francisco (n=2), Gila (n=7), and San Carlos Rivers (n=1), in New Mexico and Arizona from June to August 1990 (Table 1, Figure 1). Two additional water samples were collected from the Gila River from sites 6 and 8. Fish tissues were sampled from the San Francisco River at site 2, from the Gila River at sites 4, 5, 6, 7, 8, and 9, and from the San Carlos River (Talkalai Lake) at site 10 (Table 1). The Gila River flows through the San Carlos Indian Reservation, and at the request of the San Carlos Apache tribe, We compared water quality with Arizona domestic drinking water standards as well as standard parameters for fish and wildlife health. Whiptail lizards (*Cnemidophorus* spp.) were collected from the San Francisco River St site 2, from the Gila River at sites 3, 4, 5, 6, 7, and 8, and from the San Carlos River (Talkalai Lake) at site 10 (Table 1). Red-winged blackbirds (*Agelaius phoeniceus*) were collected from the Gila River at sites 5, 6, and 7, and from the San Carlos River (Talkalai Lake) at site 10 (Table 1).

Three unfiltered water samples were collected at each location in a one-liter opaque plastic bottle with nitric acid ( $\text{HNO}_3$ ) preservative, a one-liter opaque plastic bottle with no preservative, and a 500-milliliter (ml) opaque plastic bottle with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) preservative. Two additional water samples were collected in 1,000-ml clear glass jars without a preservative and were not filtered. All water samples were kept chilled in the field and later refrigerated in a commercial refrigerator. Water samples collected from all 10 sites in plastic bottles were submitted to Analytical Technologies, Inc., Tempe, Arizona within two days after collection. Water samples containing  $\text{HNO}_3$  preservative were analyzed for arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver; calcium, copper, iron, manganese, magnesium, and zinc. Analytical results for these elements are recorded as total recoverable. Water samples with no preservative were analyzed for fluoride, alkalinity, pH, total dissolved solids, hardness, chloride, and sulfate. Water with  $\text{H}_2\text{SO}_4$  preservative was analyzed for nitrate as nitrogen. Two water samples collected in glass Jars were Submitted to Patuxent Analytical Control Facility (PACF) for organophosphate (OP)/carbamate analyses.

Three sediment samples of similar texture and particle-size were collected and composited into a single sample at each site. Channel catfish (*Ictalurus punctatus*), flathead catfish (*Pilodictis olivaris*), carp (*Cyprinus carpio*), and largemouth bass (*Micropterus salmoides*), were collected by gill net, backpack electric shocker, trot line, and seine and arranged in five-specimen whole body or edible portion (fillet) composites of near equal weight and/or length for each species. Whiptail lizards were collected using a .22 pistol and lead shot shells

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and arranged in five-specimen whole body composites. Red-winged blackbirds were collected using a shotgun and steel shotshells and arranged in five-specimen whole body (without the gastrointestinal tract, feathers, legs, and bill) composites. A 12-gauge shotgun with #4 steel shot was used to collect the blackbirds. All sediment and tissue samples were weighed and measured following collection, kept on ice in the field until frozen in a commercial freezer within the same day.

Sediment and tissue samples were later submitted for chemical analysis through PACF to designated contract laboratories for organochlorine and trace element analyses. Organochlorine analyses were conducted by the Mississippi State Chemical Laboratory, Mississippi State, Mississippi. Trace element analyses were conducted by Hazelton Laboratories America, Inc., Madison, Wisconsin. One fish sample (fillet) was submitted through PACF to Radian Corporation, Austin, Texas

for dioxin/furan analyses. PACF was responsible for assessing quality assurance and control (QA/QC) procedures for all contract labs and QA/QC met PACF standards.

Sediment, fish, lizard, and avian samples were analyzed for organochlorine pesticides, including dicofol and total PCBs (Table 1). Organochlorine pesticides and PCBs were analyzed by electron capture gas chromatography. The lower limit of detection was 0.01  $\mu\text{g/g}$ , wet weight for all organochlorine pesticides and 0.05  $\mu\text{g/g}$ , wet weight for toxaphene and total PCBs. Percent moisture content was determined for all tissue samples. Organochlorine results are reported in  $\mu\text{g/g}$  wet weight for fish, lizard, and avian samples.

Sediment, fish, lizard, and avian samples were also analyzed for trace elements (Table 1). Arsenic and selenium were analyzed by atomic absorption hydride and mercury by cold vapor reduction. All other elements were analyzed by inductively coupled plasma atomic emission spectroscopy. The lower limit of detection for all trace elements varied among samples and is further defined in Tables 5, 6, 7 and 8. Results are reported in  $\mu\text{g/g}$  dry weight for sediment and  $\mu\text{g/g}$  wet weight for fish, lizard, and avian samples.

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RESULTS AND DISCUSSION

Organophosphates and Carbamates - Water samples collected from sites 6 and 8 did not have detectible levels of organophosphate and carbamate compounds.

Dioxins and Furans - No dioxins and furans were detected in the channel catfish fillets collected from site 7.

Domestic Water Source Standards - General chemistry and trace element concentration results and comparative Domestic Water Source (DWS) standards from the 1992 Arizona Water Quality Standards are presented in Table 2. Waters in the Gila River and its tributaries, San Francisco and San Carlos rivers, are classified as hard water as determined by the total alkalinity as  $\text{CaCO}_3$  (calcium carbonate) results. Total alkalinity results ranged from 151 to 257.

The Arizona Water Quality Standards include DWS criteria for arsenic, barium, cadmium chromium copper, lead and zinc (Table 2). The DWS criteria are written as total recoverable (CT) or dissolved fraction (D). Arsenic concentrations from sites 1 and 3 (0.06T and 0.071T  $\text{mg/l}$ , respectively) exceeded the state DWS criteria for arsenic (0.05T  $\text{mg/l}$ ). Barium concentrations in surface waters ranging from 0.04T to 0.5T  $\text{mg/l}$  were below the DWS criteria of 1.0p  $\text{mg/l}$ . Cadmium was recovered at levels ranging from none detected to 0.009T  $\text{mg/l}$ , however, levels at sites 1, 4, 5 and 10 exceeded the state DWS criteria of 0.005T  $\text{mg/l}$ . Chromium was recovered (none detected to 0.08T  $\text{mg/l}$ ) at levels below the state DWS criteria of 0.1T  $\text{mg/l}$ . The state DWS criteria for copper is 1.0D  $\text{mg/l}$  and values of none detected to 0.21T  $\text{mg/l}$  were below the criteria. Lead recovered from one site (0.078T  $\text{mg/l}$ ) exceeded the DWS criteria of 0.05T  $\text{mg/l}$ . Zinc concentrations ranging from none detected to 0.31T  $\text{mg/l}$  were well below the state DWS standard of 5.0T  $\text{mg/l}$ .

Organochlorines

Sediment - DDE, the only organochlorine compound detected in sediment, was recovered (0.02  $\mu\text{g/g}$ ) in only one sample at site 6.

Fish - Four of 23 organochlorine compounds were detected in whole body fish tissue (Table 3). Heptachlor (as heptachlor epoxide) was present in 55 percent (6/11) of whole body fish samples, primarily channel catfish ( $\bullet$  0.03 $\mu\text{g/g}$ ). The highest heptachlor concentration, 0.03  $\mu\text{g/g}$  in largemouth bass from San Carlos Reservoir (site 9), equaled the estimated NCBP 90th percentile of 0.03  $\mu\text{g/g}$

based on data in Schmitt et al. (1990). Total chlordane was recovered in 55 percent (6/11) of fish samples. However, the maximum chlordane level (0.04  $\mu\text{g/g}$ ) did not exceed the estimated NCBP 90th percentile of 0.24  $\mu\text{g/g}$ . The

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NCBP 90th percentile is a subjective figure considered as a level significantly higher than background concentrations.

DDE was recovered in all whole body and edible fish samples (Table 3). Levels of DDE in whole body fish ranged from 0.01 to 0.25  $\mu\text{g/g}$  from sites 2 and 91 respectively in channel catfish. Concentrations of DDE were below the NCBP 90th percentile of 0.4  $\mu\text{g/g}$  and below the National Academy of Sciences and National Academy of Engineering (1973) DDT and metabolites criterion of 1.0  $\mu\text{g/g}$ , established for the protection of wildlife. Levels of DDE in edible fish tissues ranged from 0.01  $\mu\text{g/g}$  in largemouth bass at site 9 to 0.12  $\mu\text{g/g}$  in flathead catfish from site 7.

Twenty-seven percent (3/11) of whole body fish samples contained DDD (Table 3). Concentrations of DDD did not exceed the NCBP 90th percentile of 0.25  $\mu\text{g/g}$  or the DDT and metabolites criteria (1.0  $\mu\text{g/g}$ ) established for protection of wildlife (National Academy of Sciences and National Academy of Engineering 1973). The fillet samples did not contain detectable levels of DDD.

Lizard - The only organochlorine recovered in whole body western whiptail lizards was DDE (Table 4). Sixty-two percent (5/8) of the samples contained DDE and concentrations ranged from 0.01  $\mu\text{g/g}$  at site 10 to 0.04  $\mu\text{g/g}$  at site 6. Concentrations were below the National Academy of Sciences and National Academy of Engineering (1973) DDT and metabolites criterion of 1.0  $\mu\text{g/g}$ , established for protection of wildlife.

Avian - The only organochlorine detected in whole body red-winged blackbirds was DDE (Table 4). Levels of DDE ranged from 0.11 to 0.33  $\mu\text{g/g}$  at respective sites 10 and 6. Concentrations did not exceed the DDT and metabolites criterion (1.0  $\mu\text{g/g}$ ) for the protection of wildlife (National Academy of Sciences and National Academy of Engineering 1973).

## Inorganic Elements

Sediment - Eighteen of the 23 inorganic elements were detected in sediment samples for nearly all sites (Table 5). Arsenic concentrations ranged from 1.9  $\mu\text{g/g}$  at site 4 to 14.6  $\mu\text{g/g}$  at site 10. All levels exceed the International Joint Commission (IJC) (1988) background level of 1.1  $\mu\text{g/g}$ , dry weight for sediment. However, concentrations of arsenic did not exceed the 95 percent baseline for western soils of 22  $\mu\text{g/g}$  (Shacklette and Boerngen 1984).

Cadmium in sediments ranged from none detected to 9.9  $\mu\text{g/g}$  (Table 5). All concentrations exceeded the IJC sediment background level of 0.6  $\mu\text{g/g}$ . Sediments from site 2 (9.9  $\mu\text{g/g}$ ) were approximately 16.5 times the background level.

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Chromium was recovered from 9 to 41  $\mu\text{g/g}$  in sediments with site 10 having the highest concentration. Lead concentrations ranged from 7 to 22  $\mu\text{g/g}$  with site 8 showing the highest concentration. Both chromium and lead concentrations were below the IJC background level of 37.1 and 27.5  $\mu\text{g/g}$ , respectively.

Sediments from sites 1, 2, and 5-10 contained elevated ( $\neq$  IJC background level) copper residues (Table 5). The highest concentration of copper (521  $\mu\text{g/g}$ , site 2) was nearly 25 times greater than the background level (20.8  $\mu\text{g/g}$ ). Copper in sediments from sites 1, 2, and 9 also exceeded the 95 percent baseline of 90  $\mu\text{g/g}$  for western soils (Shacklette and Boerngen 1984). Sediments from site 2

are located downriver from the active Phelps-Dodge copper mine in Morenci, Arizona therefore, copper exposed from the mine activities may be settling into sediments downstream. Site 1 is located above the Phelps-Dodge copper mine. Soils in this area may be rich in copper thus resulting in high copper levels.

Mercury was recovered in sediments from sites 1, 2, and 9 (Table 5) and exceeded the IJC background level of 0.03  $\mu\text{g/g}$ . The highest concentration from site 2 (0.16 $\mu\text{g/g}$ ) was below the 95 percent baseline for western soils (Shacklette and Boerngen 1984).

The highest concentrations of vanadium (86  $\mu\text{g/g}$ ) and zinc (177  $\mu\text{g/g}$ ) were recovered from site 2 sediments. Sediment at this location exceeded the IJC background level for zinc by 1.5 times. There is no IJC background level for vanadium. Aluminum, beryllium, iron, magnesium, nickel, and strontium were recovered at their highest concentration from site 2 (Table 5). No IJC sediment background levels have been established for these elements.

Barium and thallium in sediments were recovered at the highest concentration from site 10 (Table 5). Manganese (1,072  $\mu\text{g/g}$ ) was recovered at its highest concentration from site 8. Boron was recovered (18.4 $\mu\text{g/g}$ ) at its highest concentration from San Carlos reservoir (site 9). Established IJC sediment background levels have not been determined for barium, boron, manganese and thallium.

Fish - Sixteen of 21 inorganic elements were recovered in fish tissue (Table 6). Twenty-eight individual samples contained trace elements above the NCBP 85th percentile (Schmitt and Brumbaugh 1990). Aluminum was recovered in all whole body and fillet samples. Whole body concentrations ranged from 7 $\mu\text{g/g}$  in largemouth bass to 163 $\mu\text{g/g}$  in carp from San Carlos Reservoir (site 9). Aluminum concentrations were similar among fillet samples. No comparable data are available to assess whether aluminum concentrations reported in this study were elevated or within normal background range.

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Arsenic was detected in all whole body and fillet samples (Table 6). Concentrations in whole body largemouth bass (0.3 $\mu\text{g/g}$ ) from San Carlos Reservoir (site 9) exceeded the NCBP 85th percentile of 0.27 $\mu\text{g/g}$ . Arsenic levels in whole body tissue declined slightly from 1984 to 1990 in carp (1984 = 0.14-0.18 $\mu\text{g/g}$ , 1990 = 0.01  $\mu\text{g/g}$ ) and in largemouth bass (1984 = 0.43, 1990 - 0.3 $\mu\text{g/g}$ ) collected from San Carlos Reservoir (Schmitt and Brumbaugh 1990). The fillet samples contained similar levels of arsenic.

Barium was present in all whole body and fillet samples (Table 6). Concentrations in whole body samples were highest in carp (4.3  $\mu\text{g/g}$ ) from San Carlos Reservoir (site 9) and lowest in flathead catfish (0.5  $\mu\text{g/g}$ ) from sites 5 and 7. Each fillet sample contained 0.5 $\mu\text{g/g}$  of barium. No comparable data are available to assess whether barium concentrations reported in this Study were elevated or within normal background range.

Cadmium was detected in 38 percent (5/13) of the whole body samples (Table 6). The 0.1  $\mu\text{g/g}$  cadmium level in carp collected from San Carlos Reservoir in 1990 was slightly lower than the 0.16 $\mu\text{g/g}$  levels reported in two carp collected from the same area in 1984 (Schmitt and Brumbaugh 1990). Cadmium was not detected in San Carlos Reservoir largemouth bass whole body samples collected in 1990, but 0.01  $\mu\text{g/g}$  cadmium was reported in bass samples collected from the same area in 1984. These data suggest a possible decline in cadmium in fish from San Carlos Reservoir from 1984 to 1990. Cadmium in channel and flathead catfish and carp (0.1  $\mu\text{g/g}$ ) exceeded the NCBP 85th percentile by 2-fold. These five samples contained cadmium at levels (0.1  $\mu\text{g/g}$ , wet weight) considered to pose secondary hazards of cadmium poisoning to avian predators (Eisler 1985). Fillet samples did not contain detectable levels of cadmium.

Chromium was present in all whole body samples and ranged from 0.1 pg/g in channel catfish from the San Francisco River (site 2), to 1.0 µg/g in carp from San Carlos Reservoir (Table B). The only fillet sample with chromium (0.2 µg/g) was flathead catfish from site 7. Cadmium in fish tissue from this Study did not exceed the 4.0 µg/g dry weight (approx 0.8 µg/g wet weight) level considered as evidence of chromium contamination (Eisler 1986).

Copper was equal to or exceeded the NCBP 85th percentile (1.0 µg/g) in 62 percent (8/13) of the whole body samples (Table 6). The highest concentration in carp (2.1 µg/g) from site 6 exceeded the 85th percentile by 2-fold. Carp collected from San Carlos Reservoir in 1990 contained 1.6 µg/g copper. Two carp samples collected from the same area in 1984 contained 0.92 and 1.15 µg/g copper. While copper levels in San Carlos Reservoir carp increased from 1984 to 1990, copper in largemouth bass declined slightly from 0.88 to 0.6 µg/g during the same time period (Schmitt and Brumbaugh 1990). Copper was detected at 0.03 µg/g in all fillet samples.

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Iron, magnesium, and manganese were present in all whole body samples and concentrations varied from 19-226, 305-562, and 2-8.3 µg/g, respectively (Table 6). Iron and magnesium varied from 4-16 and 231-315 µg/g, respectively, for all fillet samples. Molybdenum concentrations in whole body fish ranged from none detected to 1.0 µg/g and molybdenum was not detected in fillet samples. Manganese and molybdenum were not detected in fillet samples. Background levels for these trace elements in fish and their tendency to bioaccumulate through the aquatic food chain to predators are not well known.

Lead ranged from 0.02 to 0.27 pg/g in two carp and one largemouth bass collected from San Carlos Reservoir in 1984 (Schmitt and Brumbaugh 1990). In

contrast, lead was not detected in any fish collected from the Gila River basin including San Carlos Reservoir in 1990. These data suggest a decrease of lead in fish from San Carlos Reservoir from 1984 to 1990.

Mercury concentrations in whole body fish samples were similar to or exceeded the NCBP 85th percentile of 0.11 µg/g in 54% (7/13) of the samples (Table 6). Mercury levels in carp collected from San Carlos Reservoir in 1990, 0.08 µg/g, were similar to carp collected from the same area in 1984, 0.08-0.1 µg/g. In addition, mercury in largemouth bass from the San Carlos Reservoir collected in 1990, contained similar mercury levels (0.17 µg/g) to bass (0.18 µg/g) from the same area in 1984 (Schmitt and Brumbaugh 1990) therefore, concentrations of mercury appear to be stable. All fillet samples contained 0.3 µg/g mercury (Table 6). Schmitt and Finger (1987) stated that mercury is one of the few heavy metals that tends to concentrate in the axial muscles of fish. The levels of mercury present in fish from the Gila River basin (0.1-0.3 µg/g) are equal to or exceed the 0.1 µg/g concentration that may cause adverse effects on fish-eating birds (Eisler 1987). Therefore, bald eagles, ospreys, and other fish-eating birds foraging in the upper Gila River Basin may be ingesting potentially harmful levels of mercury.

Selenium was detected in all fish samples and concentrations ranged from 0.14 to 0.77 µg/g in whole body fish (Table 6). A channel catfish sample from site 4 (0.77 µg/g) was elevated above the NCBP 85th percentile of 0.73 µg/g (Schmitt and Brumbaugh 1990). Selenium in carp from site 6 (0.68 µg/g) had a dry weight value of 3.4 µg/g. This concentration exceeds the 3.0 µg/g, dry weight value considered potentially lethal to fish-eating birds (Lemly 1993). Selenium levels in carp from San Carlos Reservoir increased slightly from 1984 (0.37-0.38 µg/g) to 1990 (0.51 µg/g) but selenium in bass however, declined slightly during the same time period from 0.52 to 0.45 µg/g (Schmitt and Brumbaugh 1990). Selenium concentrations in fillets ranged from none detected in flathead catfish to 0.51 µg/g in largemouth bass from San Carlos Reservoir (site 9). Selenium

concentrations detected in fish wholebody and fillet samples were below the toxic effect threshold of 4  $\mu\text{g/g}$ , dry weight (whole body) and 8  $\mu\text{g/g}$ , dry weight (fillet) for health and reproduction of freshwater fish (Lemly 1993).

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Strontium was present in all whole body and fillet fish tissues and concentrations varied from 14-55 and 0.3-1.0  $\mu\text{g/g}$ , respectively. Tin was recovered in whole body and fillet samples at levels from none detected to 3.9 and 3.0  $\mu\text{g/g}$ , respectively. Vanadium was present in whole body samples but not in fillets (Table 6). No comparable data are available to assess whether strontium, tin, and vanadium concentrations reported in this study were elevated or within the normal background range.

Zinc concentrations in all whole body carp (41.1-59.5 $\mu\text{g/g}$ ) from sites 6-10 exceeded the NCBP 85th percentile of 34.2 $\mu\text{g/g}$  (Schmitt and Brumbaugh 1990). Zinc concentrations in carp collected from San Carlos Reservoir increased slightly from 1984 (46.23 and 50.34  $\mu\text{g/g}$ ) to 1990 (54.3  $\mu\text{g/g}$ ). Zinc in San Carlos Reservoir largemouth bass also increased slightly during the same time period from 13.38 to 14.8  $\mu\text{g/g}$  (Schmitt and Brumbaugh 1990).

Cadmium, mercury and selenium concentrations in fish were detected at levels that may pose a threat to fish-eating birds in the Gila River basin. Cadmium may pose a threat to fish-eating birds, however, cadmium levels have decreased slightly in fish tissue. Data suggest that aluminum, arsenic, chromium, iron, magnesium, molybdenum strontium, tin and vanadium concentrations in the Gila River basin are highest at the San Carlos Reservoir. These data suggest a possible decreasing trend in arsenic, a possible increasing trend in zinc and relatively stable levels of copper, mercury and selenium in fish from an Carlos Reservoir. However, additional samples are needed to determine if these trends are real or simply short-term fluctuations.

Lizards - Nineteen of 22 inorganic elements were detected in whole body western whiptail lizard tissues (Table 7). Aluminum concentrations ranged from 134 at site 10 to 225  $\mu\text{g/g}$  at site 4. No comparable data are available to assess whether aluminum concentrations reported in this study were elevated or within normal background range.

Antimony (31  $\mu\text{g/g}$ ), arsenic (5 $\mu\text{g/g}$ ), barium (3.7 $\mu\text{g/g}$ ), cadmium (0.3 $\mu\text{g/g}$ ) and chromium (1.9  $\mu\text{g/g}$ ) concentrations were highest at site 3 (Table 7). No comparable data on antimony, arsenic and barium are available to assess whether concentrations of these elements reported in this study were elevated or within normal background range. Concentrations of cadmium equal to or greater than 0.1  $\mu\text{g/g}$  were detected in 62 percent (5/8) of the samples and may pose as a secondary hazard of cadmium poisoning to avian predators in the Gila River Basin (Eisler 1985).

Copper and thallium concentrations were highest in lizards from site 2. Copper ranged from 1.8-5.3  $\mu\text{g/g}$ . Site 2 is located downstream from the Phelps-Dodge copper mine on the San Francisco River. Concentrations of iron, magnesium,

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and manganese ranged from 154-278, 486-581, and 3.7-6.1  $\mu\text{g/g}$ , respectively. Mercury levels in all lizard samples ranged from 0.03 to 0.07  $\mu\text{g/g}$  and were below the maximum concentration (0.1  $\mu\text{g/g}$ ) for protection of avian predators (Eisler 1987).

Molybdenum and strontium were detected in most lizard samples (Table 7) and varied from none detected-3.1 and 8-23 $\mu\text{g/g}$ , respectively. Background levels for these trace elements in animals and their tendency to bioaccumulate through the food chain to predators are not well known.

Selenium was detected in all samples with the highest concentration of 1.1  $\mu\text{g/g}$  at site 10 (Table 7). The dry weight equivalents of these values were below the 5  $\mu\text{g/g}$  (dry weight) dietary level considered to be toxic to predatory animals (Ohlendorf et al. 1988).

Nickel was recovered in one-half the lizard samples (Table 7). Concentrations ranged from none detected to 2.5  $\mu\text{g/g}$ . Vanadium and zinc were present in nearly all lizard samples (Table 7). Concentrations varied from none detected to 40-53  $\mu\text{g/g}$ , respectively. Background levels for these trace elements in animals and their tendency to bioaccumulate through the food chain to predators are not well known.

Avian - Fifteen of 22 inorganic elements were detected in whole body red-winged blackbird samples (Table 8). Highest concentrations of barium, chromium, magnesium, molybdenum, strontium, and vanadium were present in red-winged blackbirds from site 6. However, blackbirds from site 7 had the highest concentrations of aluminum, cadmium, copper, iron, manganese, and selenium. Arsenic was recovered at 0.2  $\mu\text{g/g}$  from all four sites and was within the reported range (<0.05-1.4  $\mu\text{g/g}$  wet weight) for 1973 National Pesticide Monitoring Program (NPMP) sampling of starlings (White et al. 1977). All arsenic concentrations exceeded levels reported for starlings (0.05  $\mu\text{g/g}$  wet weight) collected in Phoenix, Arizona (White et al. 1977).

Cadmium in red-winged blackbirds was within the reported range (<0.05-0.2  $\mu\text{g/g}$  wet weight) for 1973 NPMP sampling of starlings (White et al. 1977). However, cadmium concentrations from sites 6 and 7 exceeded levels reported for starlings (0.05  $\mu\text{g/g}$  wet weight) collected in Phoenix, Arizona (White et al. 1977). Cadmium levels were below the dietary protection limit (0.1  $\mu\text{g/g}$ ) for predators (Eisler 1985).

One-half of the red-winged bird samples had mercury concentrations (Table 8) greater than the reported range (<0.01-0.2  $\mu\text{g/g}$  wet weight) for 1973 NPMP sampling of starlings (White et al. 1977). All levels in this study exceeded those

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reported for starlings (<0.01  $\mu\text{g/g}$  wet weight) collected in Phoenix, Arizona (White et al. 1977).

Selenium concentrations ranged from 0.3 to 1.0  $\mu\text{g/g}$  and were within the reported range (0.1-1.1  $\mu\text{g/g}$  wet weight) for 1973 NPMP sampling of starlings (White et al. 1977). Selenium in starlings from site 7 exceeded the reported concentration by 2-fold for starlings collected in Phoenix, Arizona (White et al. 1977).

Residue implications for human health - Arsenic, cadmium and lead recovered from the Gila and San Francisco rivers upstream from Safford, Arizona were slightly elevated above the DWS criteria for AWQS. Cadmium was the only element recovered from waters on the San Carlos Apache Reservation (Talkalai Lake) that was slightly elevated above the DWS criteria. However, based on the sampling techniques used, it is difficult to determine if these levels pose any threat to the drinking water source on the San Carlos Apache Reservation. Mercury concentrated at higher levels in the fillets than in whole body fish samples. The highest mercury concentration detected in fish fillets was 0.32  $\mu\text{g/g}$  wet weight from San Carlos Reservoir. However, these levels were well below the U.S. Food and Drug Administration (FDA) action level of 1.0  $\mu\text{g/g}$  wet weight (FDA 1982).

Concentrations vary from 0.03 to 0.1  $\mu\text{g/g}$  wet weight for the normal dietary intake of total chromium in the human diet (Langar and Norseth 1979). One flathead catfish fillet sample from site 7 exceeded the 0.1  $\mu\text{g/g}$  dietary intake level.

Except for a domestic water source standard of 10  $\mu\text{g/l}$  (USEPA 1986) there is no current FDA action level for selenium if food for human consumption (FDA 1982).

Residue implications for fish - Organochlorine (heptachlor, chlordane, and DDE) concentrations were generally higher in whole body fish from the San Carlos Reservoir (site 9) than in fish from other sites. However, levels of these organochlorine pesticides were below concentrations known to effect survival and reproduction of most fish species (National Academy of Sciences and National Academy of Engineering; 1973).

Selenium concentrations detected in fish whole body and fillets from the Gila River basin were below the respective 4 and 8  $\mu\text{g/g}$  dry weight levels associated with selenium-induced reproductive failure of fish (Lemly 1993).

Residue implications for avian and mammalian predators - The trace elements in diets of birds and mammals that are most likely to cause reproductive and survival problems are arsenic, cadmium, mercury and selenium (Eisler 1985, 1987, 1988; Ohlendorf et al 1986, 1988). While the acute effects of arsenic have

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been investigated, little is known about its sublethal chronic effects except that arsenic is readily accumulated by aquatic organisms. Based on data summarized by Eisler (1988), arsenic at concentrations recovered in upper Gila River fish apparently poses little hazard of secondary poisoning to avian and mammalian predators. Secondary hazards of cadmium poisoning to predators might be expected if dietary levels reach 0.1  $\mu\text{g/g}$  wet weight (Eisler 1985). Twenty-nine percent of the catfish and carp and 62% of the lizard samples from the Gila River basin contained concentrations of cadmium that approached or exceeded this threshold level. The minimum concentration of mercury which may cause effects on predatory fish-eating birds and mammals is 0.1 and 1.1  $\mu\text{g/g}$  wet weight, respectively (Eisler 1987). Mercury levels in 69% of whole body fish (0.1  $\mu\text{g/g}$ ) and 100% of fillet samples (0.3  $\mu\text{g/g}$ ) throughout the Gila River basin equalled or exceeded the threshold limit for fish-eating birds but not mammals. Fish throughout the Gila River basin including San Carlos Reservoir contained levels of mercury considered hazardous to foraging osprey, bald eagle and herons. One fish sample had a selenium concentration exceeding the 3.0  $\mu\text{g/g}$  dry weight level that may be potentially lethal to fish-eating birds (Lemly 1993).

#### RECOMMENDATIONS

Cadmium concentrations detected in fish and reptiles in the study area exceed the dietary level for the protection of predatory wildlife in the Gila River basin. Mercury concentrations observed in fish throughout the study area are within the range that affect survival and reproduction of fish-eating birds, resident or wintering in the area. Based on current high cadmium and mercury concentrations that approach the critical reproductive effect threshold level in more than one-half the samples, regular monitoring of fish on the upper Gila River on a three-year basis is recommended. Selenium concentrations in one fish sample exceeded the dietary level for protection of avian predators. Therefore, monitoring for selenium in fish tissue should be done in conjunction with the cadmium and mercury monitoring.

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[See Table/Figure](#)

Figure 1. Gila River Basin study area and collection sites, Arizona and New Mexico, 1990

(SEE ORIGINAL)

Table 1. Gila River Basin collection locations Arizona and New Mexico, media tested and 1990.

W = water, S = sediment, F = fish tissue, L = lizard tissue and A = avian tissue.

| Site Number | Station Location                  | Water Chemistry | OC & Trace Elements <sup>[sup]1</sup> | PCDD/PCDF <sup>2</sup> | OP/<br>Carbamates <sup>[sup]3</sup> |
|-------------|-----------------------------------|-----------------|---------------------------------------|------------------------|-------------------------------------|
| 1           | San Francisco River above Clifton | W               | S                                     |                        |                                     |
| 2           | San Francisco River below Clifton | W               | S,F,L                                 |                        |                                     |
| 3           | Gila River above Virden           | W               | S,L                                   |                        |                                     |
| 4           | Gila River at Guthrie             | W               | S,F,L                                 |                        |                                     |
| 5           | Gila River at San Jose            | W               | S,F,L,A                               |                        |                                     |
| 6           | Gila River at Pima                | W               | S,F,L,A                               | F                      | W                                   |
| 7           | Gila River at Ft. Thomas          | W               | S,F,L,A                               |                        |                                     |
| 8           | Gila River at Bylas               | W               | S,F,L                                 |                        | w                                   |
| 9           | San Carlos Reservoir              | W               | S,F                                   |                        |                                     |
| 10          | Talkalai Lake at San Carlos River | W               | S,F,L,A                               |                        |                                     |

<sup>[sup]1</sup> bc - Organochlorine pesticide scan (includes 20 pesticides and total PCBs).

Trace elements - include 14

elements (Al, As, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sc, TI, Zn)

<sup>2</sup>PCD/PCDF - Polydilorinated dibuldodioxin and fliran scan

<sup>[sup]3</sup> OP/Carbamates - Organophosphate pesticide scan (includes 24 compounds),

carbamate pesticide scan (includes  
6 compounds)

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Table 2. General chemistry and trace element concentration water results (mg/l) compared with 1992 Arizona domestic water source criteria (mg/l) from Upper Gila River Basin, Arizona and New Mexico, 1990.

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Table 3. Organochlorine concentrations in fish whole body and edible portion tissue (†g/g wet weight) from the Upper Gila River Basin, Arizona, 1990.

| Site & Species               | Heptachlor | Total chlordane | p,p' DDE | p,p' DDD | Percent Moisture |
|------------------------------|------------|-----------------|----------|----------|------------------|
| NCBP 90 Percent <sup>2</sup> | 0.03       | 0.24            | 0.4      | 0.25     |                  |
| 2                            |            |                 |          |          |                  |
| Channel catfish              | 0.02       | 0.01            | 0.01     | <0.01    | 73.0             |
| Flathead catfish*            | <0.01      | <0.01           | 0.02     | <0.01    | 79.0             |
| 4                            |            |                 |          |          |                  |
| Channel catfish              | 0.02       | 0.02            | 0.03     | <0.91    | 74.0             |
| Flathead catfish             | <0.01      | <0.01           | 0.03     | <0.01    | 79.0             |
| 5                            |            |                 |          |          |                  |
| Channel catfish              | 0.02       | 0.02            | 0.03     | <0.91    | 72.5             |
| Flathead catfish             | <0.01      | <0.01           | 0.02     | <0.91    | 77.0             |
| 6                            |            |                 |          |          |                  |
| Carp                         | <0.01      | <0.01           | 0.15     | <0.91    | 80.5             |
| 7                            |            |                 |          |          |                  |
| Flathead catfish             | <0.01      | 0.01            | 0.12     | 0.91     | 78.0             |
| Carp                         | <0.01      | <0.01           | 0.09     | 0.01     | 75.5             |
| Flathead catfish*            | <0.01      | <0.01           | 0.12     | <0.01    | 80.0             |
| 8                            |            | <0.01           |          |          |                  |
| Carp                         | <0.01      |                 | 0.03     | <0.01    | 76.0             |
| 9                            |            |                 |          |          |                  |
| Channel catfish              | 0.02       | 0.03            | 0.25     | 0.01     | 73.0             |
| Carp                         | <0.01      | <0.01           | 0.12     | <0.01    | 76.0             |
| Largemouth bass              | 0.03       | 0.04            | 0.10     | <0.01    | 71.5             |
| Channel catfish*             | <0.01      | <0.01           | 0.11     | <0.91    | 78.5             |
| Largemouth bass*             | <0.01      | <0.01           | 0.01     | <0.01    | 78.5             |
| 10                           |            |                 |          |          |                  |
| Carp                         | 0.01       | <0.01           | 0.05     | <0.91    | 73.5             |

[sup]1 Hepatachlor as heptachior epoxide

<sup>2</sup>National Contaminant Biomonitoring Program 90th percentile 1984, estimated, †g/g wet weight (Schmitt et al. 1990)

\*Edible portion

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Table 4. Concentrations of p,p' DDE in lizard and avian whole body tissues (†g/g wet weight) from Upper Gila River Basin, Arizona, 1990.

| Site | Western Whiptail Lizard | Percent Moisture | Red-winged Blackbird | Percent Moisture |
|------|-------------------------|------------------|----------------------|------------------|
| 2    | <0.01                   | 71.5             | NA <sup>1</sup>      | NA               |
| 3    | <0.01                   | 72.5             | NA                   | NA               |
| 4    | <0.01                   | 71.0             | NA                   | NA               |
| 5    | 0.02                    | 69.0             | 0.26                 | 69.0             |
| 6    | 0.04                    | 70.0             | 0.33                 | 69.5             |
| 7    | 0.02                    | 72.5             | 0.20                 | 71.7             |
| 8    | 0.02                    | 69.0             | NA                   | NA               |
| 10   | 0.01                    | 71.5             | 0.11                 | 69.0             |

<sup>1</sup> NA - not analyzed

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[See Table/Figure](#)

Table 5. Trace element concentrations in sediment (†g/g dry weight) from the Upper Gila River Basin, Arizona, 1990.

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[See Table/Figure](#)

Table 6. Trace element concentrations in channel catfish (C catfish), flathead catfish (FH catfish), carp and largemouth bass (LM bass) tissue (†g/g wet weight) from Upper Gila River Basin, Arizona, 1990.

(SEE ORIGINAL)

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[See Table/Figure](#)

Table 7. Trace element concentrations in whiptail lizard<sup>1</sup> tissue (†g/g wet weight) from Upper Gila River Basin, Arizona, 1990.

(SEE ORIGINAL)

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[See Table/Figure](#)

Table 8. Trace element concentrations in red-winged blackbird tissue (†g/g wet weight) from Upper Gila River Basin, Arizona, 1990.

(SEE ORIGINAL)