



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



**CONTAMINANTS AS A LIMITING FACTOR OF  
FISH AND WILDLIFE POPULATIONS IN THE  
SANTA CRUZ RIVER, ARIZONA**

by

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## ABSTRACT

Declining populations of the endangered Gila topminnow in the Santa Cruz River prompted a 1997 study to assess contaminant levels in water, sediment, invertebrates, fish, and birds. Samples were collected from two sites upstream from the Nogales International Wastewater Treatment Plant (NIWWTP) and from five sites downstream from the plant. Water pH ranged from 7.4 to 7.9 and was normal for the area. Un-ionized ammonia concentrations, up to 0.49 mg/L (this study) and 24 mg/L (related studies) were within the range known to be toxic to invertebrates and fish. Independent laboratory toxicity tests run concurrently with our study demonstrated that plant discharges were highly toxic. In 96-hour exposure tests using effluent collected monthly, 100% effluent caused 100% mortality of adult fathead minnows during seven of 12 months. Un-ionized ammonia was identified as the toxicant responsible for fish mortality. We also documented a high proportion of longfin dace, up to 9.1%, with skin and skeletal anomalies at sites downstream from the NIWWTP. Toxicants in NIWWTP effluent appear to have nearly extirpated populations of invertebrates, amphibians, semi-aquatic reptiles, and fish, including the endangered Gila topminnow, at sites closest to the treatment plant outfall.

The entire aquatic ecosystem also was contaminated with chromium; concentrations were highest in sediment from Nogales Wash, 149  $\mu\text{g/g}$  dry weight, a level considerably higher than the 110  $\mu\text{g/g}$  toxic threshold for aquatic invertebrates. Almost one-half (6/13) of all invertebrate samples contained chromium at concentrations that could be toxic to upper trophic-level species. All samples of desert suckers contained elevated concentrations of chromium. The maximum chromium concentration in suckers (13.6  $\mu\text{g/g}$  wet weight) was more than 11-times higher than the 1.2  $\mu\text{g/g}$  toxic concern level. Concentrations of chromium in suckers increased with increasing distance downstream from the NIWWTP indicating that the plant was not a source of chromium contamination. There may be a point-source of chromium contamination between the two most downstream sites of Tubac and Chavez Siding. While sediment, invertebrates, and fish were contaminated with chromium, it did not biomagnify to toxic levels in birds.

Nickel was recovered at relatively low levels in desert suckers from all sites except one. All suckers from Chavez Siding contained higher than background levels of nickel. There may be a source of nickel contamination between Tubac and Chavez Siding. Copper exceeded the National Contaminant Biomonitoring Program 85<sup>th</sup> percentile in 50% of the dace samples and in 95% of the desert sucker samples. Because of its occurrence at relatively high levels at some sites and its propensity to interact with other compounds and elements, copper remains a contaminant of concern in the lower Santa Cruz River.

Current organochlorine compound levels in fish should not present a threat to survival and reproduction nor should current residues present a bioconcentration hazard to upper trophic level species that feed on fish. DDT, DDD, and DDE were not detected in fish from locations upstream from the NIWWTP. Since highest residues of DDT occurred at the site farthest downstream from the NIWWTP, it appears that the source of DDT may be runoff/drainage from contaminated soils downstream of the wastewater treatment plant.

Four of eight killdeer carcasses contained  $>3.4$   $\mu\text{g/g}$  wet weight DDE, a level associated with impaired reproduction and a level that represents a hazard to predatory birds that feed

on killdeer. Concentrations of all metals in killdeer livers were within the normal or background range.

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The Santa Cruz River, located in south-central Arizona, sustains one of the most ecologically diverse riparian areas in the southwest. This riparian zone contains several

endangered species including the Gila topminnow (*Poeciliopsis occidentalis*), cactus ferruginous pygmy-owl (*Glaucidium brasilianum cactorum*), Sonora tiger salamander (*Ambystoma tigrinum stebbinsi*), Huachuca water umbel (*Lilaeopsis schaffneriana* spp. *recurva*), and the Canelo Hills ladies'-tresses (*Spiranthes delitescens*).

A 1994 investigation of fish populations of the Santa Cruz River revealed that more than 50% of the individuals collected immediately downstream from the Nogales International Wastewater Treatment Plant (NIWWTP) had anomalies such as lesions or skeletal deformities associated with poor water quality (Lawson 1995). Fish diversity, density, and age structure varied considerably among sampling sites with a general improvement at sites furthest downstream from the NIWWTP. Density and diversity of aquatic macroinvertebrate populations also varied among sites with a general improvement in taxa richness and individual abundance with increasing distance from the plant (Lawson 1995).

Bioaccumulation of metals and organochlorine compounds at the site has been recently documented. Elevated concentrations of chromium, lead, mercury, and zinc were reported in fish collected from one to three locations on the river (Rector 1997). Avian tissues collected from three locations also contained elevated levels of DDE. Un-ionized ammonia concentrations in effluent water at sites closest to the treatment plant were high enough to be toxic to aquatic life (Lawson 1995). The objectives of our study were: 1) to determine levels of contaminants in sediment, invertebrates, fish, and birds of the Santa Cruz River above and below the NIWWTP; 2) to document bioindicators of fish contamination such as lesions, tumors, and skeletal anomalies; and 3) to assess the potential and actual effects of current contaminant levels on macroinvertebrate, fish, and wildlife populations.

## STUDY AREA

The Santa Cruz River originates in the San Rafael Valley in extreme south-central Arizona. The river flows southward for approximately 10 km before entering Sonora, Mexico. In Sonora, the watercourse continues to flow south then westward around the foothills of the Sierra San Antonio Mountains before looping back to the north to reenter Arizona east of Nogales. The watercourse becomes intermittent close to the U.S./Mexico border at Nogales. Perennial flow begins again where effluent from the NIWWTP reaches the riverbed just north of the City of Nogales (Figure 1). Water from the plant is supplemented by minor flows from Nogales Wash. Our study area encompassed a 46.2 km (28.7 mi) stretch of river from the U.S./Mexico International Boundary northward to Chavez Siding Road (Figure 1). Seven collection sites were selected within the study area; two upstream from the NIWWTP and five downstream from the plant (Table 1, Figure 1). The most upstream site (Border) was located in an intermittent 3 km stretch of river immediately north of the international boundary. A second site was selected in Nogales

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Wash at the Ruby Road crossing, about 3.4 km (2.1 mi) upstream from the confluence of Nogales Wash and the usually dry Santa Cruz River bed. A third site, was established approximately 2.7 km (1.7 mi) downstream from the discharge point of the NIWWTP at Rio Rico Bridge. Four additional sites were located at approximately equidistant intervals downstream from site 3 (Table 1, Figure 1).

## METHODS

Sample collections: Water, sediment, aquatic macroinvertebrate, fish, and bird samples were collected from March to July 1997. Two one-liter containers of water were taken at each location for pH determinations and un-ionized ammonia and residual chlorine analyses. Sulphuric acid was added to the containers of water to maintain a pH of <2 for un-ionized ammonia analyses. Water samples were placed on wet ice in a cooler and delivered to Bolin Laboratories Inc., Phoenix, Arizona on the day of collection and analyzed within 24 hours.

Three to five sediment subsamples were taken at each site using a stainless steel spoon and pan. Approximately the top 5 cm of sediment was collected with each subsample. The subsamples were blended, using spoon and pan, into a single homogenous mixture. Our invertebrate sampling focused on collecting larger macroinvertebrates to provide sufficient biomass for chemical analysis. Invertebrates, including dragonfly larvae (Aeshnidae) and giant water bugs (*Belostoma sp.*), were collected using dip nets. Aquatic snails (*Physa virgata*) were collected by hand. Study sites were visited from one to six times until sufficient mass was obtained. No attempt was made to quantify invertebrate collecting effort during the study. Sediment and invertebrate samples were placed in plastic whirl-packs for storage. Fish, including longfin dace (*Agosia chrysogaster*) and desert sucker (*Pantosteus clarki*), were collected using a backpack electrofisher and dip nets. Longfin dace were counted, weighed, and visually examined for physical anomalies before being combined into a single sample by site. Longfin dace were stored frozen in glass jars until analysis. Desert suckers were weighed and measured and also examined for anomalies. Sucker samples were individually wrapped in aluminum foil and frozen. Killdeer (*Charadrius vociferus*) were collected at selected locations using shotguns and steel shot. Whole bodies were weighed then plucked; and bill, feet, wingtips, and gastrointestinal tract removed and discarded. Bird livers were pooled into a single sample per site and analyzed for metals. Carcasses also were analyzed for metals and for organochlorine compounds. All samples were stored on wet ice in the field until they were transferred to a commercial freezer at the end of the day. Sediment, invertebrates, fish, and bird livers were analyzed for metals. A subsample of fish and all bird carcasses were analyzed for organochlorine compounds.

Chemical analyses: The organochlorine scan included o,p'- and p,p'-DDE, o,p'- and p,p'-

DDD, o,p'- and p,p'-DDT, dieldrin, heptachlor epoxide, hexachlorobenzene (HCB), alpha, beta, delta, and gamma BHC, alpha and gamma chlordane, oxychlordane, *trans*-nonachlor, *cis*-nonachlor, endrin, toxaphene, mirex, and total polychlorinated biphenyls (PCB). Samples were analyzed at Mississippi State Chemical Laboratory, Mississippi State, Mississippi. For each analysis, the sample was homogenized and mixed with anhydrous sodium sulfate and soxhlet extracted with hexane for seven hours. The extract was then concentrated by rotary evaporation to dryness for lipid determination. The weighed lipid sample was dissolved in petroleum ether and extracted four times with acetonitrile saturated with petroleum ether. Lipids were removed by Florisil column chromatography (Cromartie et al. 1975). The column was then eluted with diethyl ether/petroleum ether and separated into two fractions. One fraction was concentrated to appropriate volume for quantification of residues by packed or capillary column electron capture gas chromatography. The other fraction was concentrated and transferred to a SilicAR acid chromatographic column for additional cleanup required for separation of PCBs from other organochlorines for quantification of residues by packed or megabore column, electron capture gas chromatography. The lower limit of quantification was 0.01 µg/g (parts per million) for most organochlorine pesticides and 0.05 µg/g for toxaphene and PCBs. Organochlorine compounds are expressed in µg/g wet weight unless otherwise specified. Organochlorine compounds are primarily stored in body lipids; therefore, lipid levels are presented for each sample.

Sediment, invertebrates, fish, and bird livers were analyzed for aluminum, arsenic, beryllium, boron, cadmium, chromium, copper, iron, lead, mercury, molybdenum, nickel, selenium, strontium, vanadium, and zinc at Research Triangle Institute, Raleigh, North Carolina. Arsenic and selenium concentrations were determined by graphite furnace atomic absorption spectrophotometry (USEPA 1984). Mercury was quantified by cold vapor atomic absorption (USEPA 1984). All other elements were analyzed by inductively coupled plasma atomic emission spectroscopy (Dahlquist and Knoll 1978, USEPA 1987). Blanks, duplicates, and spiked samples were used to maintain laboratory quality assurance and quality control (QA/QC). QA/QC was monitored by Patuxent Analytical Control Facility (PACF). Analytical methodology and reports met or exceeded PACF QA/QC standards. The lower limits of analytical quantification varied by element and by sample and are listed in the appropriate tables. Percent moisture is presented to permit wet weight to dry weight conversions. Wet weight values can be converted to dry weight equivalents by dividing the wet weight values by one minus percent moisture as illustrated in the following equation:

$$\text{Dry weight} = \frac{\text{wet weight}}{1 - \text{percent moisture}}$$

Our 1997 fish data were compared with Schmitt and Brumbaugh's (1990) National Contaminant Biomonitoring Program (NCBP) findings to determine how trace element concentrations in fish from the lower Santa Cruz River compare to national levels.

Concentrations of an element were considered elevated when they exceeded the NCBP 85<sup>th</sup> percentile of the nationwide geometric mean. The 85<sup>th</sup> percentile was not based on toxicity hazard to fish but provides a frame of reference to identify metals of potential concern.

While the NCBP 85<sup>th</sup> percentile was calculated for several elements (Schmitt and Brumbaugh 1990), it was not determined for organochlorine compounds (Schmitt et al. 1990). To facilitate comparison of our organochlorine data in fish with national levels, we calculated the 85<sup>th</sup> percentile for several compounds using raw data reported by Schmitt et al. (1990). We first ordered the data, then multiplied the total number of data points by 0.85. The corresponding residue was considered the 85<sup>th</sup> percentile level.

We also compared our data with those of the USEPA National Study of Chemical Residues in Fish which sampled fish from 314 "targeted" sites with known contaminant problems and from 74 relatively unpolluted (background) sites (USEPA 1992). While NCBP data covered years 1976 to 1984, the USEPA data were collected from 1986-1989. Organochlorine and/or metal concentrations in sediment, invertebrates, fish, and bird samples also were compared with levels detected in comparable samples taken from other Arizona locations.

We recognize that not all the elements listed in this report are "heavy metals" or even true metals. But for the sake of convenience, and to avoid often ambiguous terms such as "trace elements, metalloids, and heavy metals," we refer to all elements simply as metals.

Statistical analysis: Only a single sample of sediment, invertebrates, longfin dace and bird livers was collected per site which precluded statistical analysis. Contaminant concentrations in desert suckers (n = 5 per area) were compared among areas, using 1-way ANOVA. Residue data were normalized by log-transformation before mean comparisons. Geometric means (gmean) were calculated and contaminant concentrations assessed when more than one-half of the individuals from a site contained detectable residues. For those samples in which no residues were detected, a value of one-half the limit of detection was substituted for the "not detected" value to facilitate statistical comparisons.

Because no organochlorine compound or metal differences were detected between normal vs. abnormal longfin dace, we combined the data and compared residues with those in desert suckers to determine possible residue differences between species. Suckers were collected from four areas: Nogales Wash, Santa Gertrudis, Tubac and Chavez Siding (Figure 1). For those compounds and elements for which no differences were detected among areas, the samples were combined and compared to longfin dace. If contaminants in suckers from one area were significantly different from the other three, that area was deleted from the analysis.

Eighteen longfin dace were collected from Tubac and two longfin dace and two mosquitofish were collected at Rio Rico North for histological examination. Fish were examined for the presence of parasites and bacteria to determine any relationship between these pathogens to deformities seen in fish.



## RESULTS

### *WATER*

From March through mid-May 1997, surface water was present at all designated sampling sites. However, by May 28<sup>th</sup>, there was no surface water at sites 1 (Border) and 7 (Chavez Siding). Most biota samples had been collected by this date, but we were unable to collect water samples at these two sites. Chlorine (as total chlorine residuals) was not detected in water samples. Ammonia was not recovered in samples collected upstream from the NIWWTP, but ammonia was present at the first three sites downstream from the NIWWTP and concentrations (0.03 - 0.49 mg/L) were inversely correlated to distance from the treatment plant (Table 2).

### *SEDIMENT*

Sediment samples were collected at each site; however, the sample from Rio Rico North was judged too granular for chemical analysis and was not submitted. Concentrations of 9 potentially toxic elements recovered in sediment are presented in Table 3. A listing of all trace elements and heavy metals recovered in sediment samples is listed in Appendix 1.

### *INVERTEBRATES*

Few aquatic macroinvertebrate species were observed in the Santa Cruz River study area. The three most common invertebrates included dragonfly larvae (Aeshnidae), giant water bugs (*Belostoma* sp.) and snails (*Physa* sp.). At three study sites (Nogales Wash, Rio Rico Bridge, and Rio Rico North), we were able to collect only one species in sufficient numbers to obtain enough material for a sample. Concentrations of nine potentially hazardous metals in invertebrates are presented in Table 4.

We noted significant differences in concentrations of most metals among the various invertebrate species. Snails bioconcentrated arsenic (gmean 7.25  $\mu\text{g/g}$  dry weight) to levels that were more than 5-times higher ( $P = 0.0039$ ) than those in giant water bugs, 1.42  $\mu\text{g/g}$ . Although arsenic concentrations in snails were almost 3-times higher than in dragonfly larvae (2.48  $\mu\text{g/g}$ ), the differences were not statistically significant. Geometric mean chromium concentrations in dragonfly larvae (24.37  $\mu\text{g/g}$  dry weight) were significantly ( $P=0.0355$ ) higher than levels in snails (5.02  $\mu\text{g/g}$ ), but similar to concentrations in giant water bugs (10.77  $\mu\text{g/g}$ ). Average copper concentrations were more than 4-times higher ( $P < 0.0001$ ) in snails (gmean = 106.1  $\mu\text{g/g}$  dry weight) than in dragonfly larvae (22.97  $\mu\text{g/g}$ ) or giant water bugs (23.63  $\mu\text{g/g}$  dry weight). Snails bioconcentrated lead to a geometric mean of 7.11  $\mu\text{g/g}$  dry weight, almost 5-times ( $P = 0.0094$ ) the gmean in giant water bugs (1.46  $\mu\text{g/g}$ ), and 3-times higher than the concentration in dragonfly larvae (2.38  $\mu\text{g/g}$ ). Giant water bugs (gmean = 202  $\mu\text{g/g}$  dry weight) accumulated significantly ( $P < 0.0001$ ) higher levels of zinc than dragonfly larvae (82  $\mu\text{g/g}$ ) and snails (46  $\mu\text{g/g}$ ). Similarly, zinc

concentrations in dragonfly larvae were significantly higher than those in snails. Geometric mean cadmium, mercury, nickel, and selenium concentrations were similar ( $P > 0.05$ ) among invertebrate species.

### *FISH*

Five species of fish were observed including longfin dace, desert sucker, Sonora sucker (*Catostomus insignis*), Gila topminnow, and mosquitofish (*Gambusia affinis*) (Table 5). The relative abundance of each species was standardized by comparing the number of individuals collected per unit-time. Relatively high numbers of longfin dace were present at all but two sampling stations; the two exceptions were the two stations immediately downstream from the NIWWTP. Desert sucker, the second most numerous species, was observed at four of seven sampling sites. Sonora sucker and mosquitofish were present in low numbers at two sites and three sites, respectively. Gila topminnows were recorded at three locations, and breeding males were observed at Tubac and Chavez Siding.

Longfin dace were most abundant at the Border site, upstream from the NIWWTP, and least abundant at the two sites immediately below the treatment plant (Rio Rico Bridge and Rio Rico North, Table 6). Overall abundance of longfin dace ranged from 0.42 to 214 individuals captured per minute of electrofishing time.

During the course of the study, we noticed an usually high proportion of fish, particularly longfin dace, with skin and skeletal anomalies (Table 7). We attempted to quantify these anomalies through close visual examination of all specimens collected. No anomalies were observed in fish from the Border or from Nogales Wash, the two sites upstream from the NIWWTP. The incidence of anomalies could not be assessed at the two sites immediately downstream from the NIWWTP because of the paucity of fish at these locations. At the two sites farthest downstream from the NIWWTP, the proportion of abnormal longfin dace observed was 5.4 and 5.9% (Table 7). Anomalies consisted primarily of reddish lesions on the ventral surface and often on and around the pectoral, anal, and caudal fins, and less frequently around the lips. Few individuals (<1%) had skeletal anomalies such as misshapen heads and spinal curvatures.

Twenty-eight fish, including longfin dace (n=21), desert sucker (n=2), Gila topminnow (n=3), and mosquitofish (n=2) were collected for histopathological investigations by Service fish pathologists from the Pinetop Fish Health Center, Pinetop, Arizona. The only fish parasite consistently found was the white grub (*Posthodiplostomum minimum minimum*) which was present in more than 80% of longfin dace mesenteries. This parasite is common in waters where intermediate snail hosts *Physella* are present, and the final host, herons, egrets, or other waterbirds also are found. Kidneys of three of eight normal appearing fish examined for bacterial infections were positive. Two were carrying motile *Aeromonas* and one had *Staphylococcus*. Only one abnormal fish (longfin dace) was collected for histological studies and no bacterial growth was found in tissue from the lesion.

### *Organochlorines in fish*

Organochlorine compounds are stored primarily in body lipids; therefore, we quantified lipid concentrations in both dace and suckers. Percent lipid in dace samples varied from 2.79 to 12.2 (Table 8). Since only one composite longfin dace sample was collected at each site, we were unable to statistically compare lipid concentrations among areas. Lipid levels in desert suckers ranged from 1.73 to 9.42 percent, and gmean levels were significantly ( $P < 0.0001$ ) lower in suckers from Nogales Wash (2.18%) than in suckers from Santa Gertrudis (6.98%), Tubac (5.48%), and Chavez Siding (6.58%) (Table 9). When the Nogales Wash samples were deleted from the data set, and lipid levels in suckers from Santa Gertrudis, Tubac, and Chavez Siding were compared with those of longfin dace from the same areas, gmean lipid levels were significantly higher in dace (10.0%) than in suckers (6.3%).

Residues of six organochlorine compounds were detected in longfin dace samples (Table 8). Of those, only DDE, DDD, and chlordane were present in more than one-half the samples. The frequency of occurrence of most organochlorine compounds in normal vs. abnormal longfin dace was similar, except that BHC was detected in more than one-half (2 of 3) of the abnormal samples, but was present in only two of six normal samples. There were no statistical differences ( $P \geq 0.19$ ) in DDE, DDD, and chlordane residues in normal vs. abnormal dace (Table 9). Residues of all organochlorine compounds were below the NCBP 85<sup>th</sup> percentile.

Desert sucker samples contained residues of six organochlorine compounds (Table 10). As with longfin dace, only DDE, DDD, and chlordane were detected in more than one-half of the samples. DDE and chlordane were present in all suckers, whereas DDD, while not detected any of the Nogales Wash samples, was present in all suckers from Santa Gertrudis, Tubac, and Chavez Siding. DDT, the parent compound, was detected most frequently in samples from Chavez Siding. Residues of DDE, DDT, chlordane, and PCB were below the NCBP 85<sup>th</sup> percentile. Gmean DDE and chlordane residues were significantly ( $P = 0.001$ ) lower in sucker samples from Nogales Wash than in suckers from Santa Gertrudis, Tubac, and Chavez Siding (Table 11).

### *Metals in fish*

Concentrations of nine potentially harmful metals detected in composite samples of longfin dace and in desert suckers are presented in Tables 12-14. One composite sample of normal-appearing longfin dace was collected at each site except at Rio Rico Bridge, where only nine individuals were captured during three collecting efforts. We also collected and analyzed samples of abnormal-appearing dace from three sites. No significant differences were detected when comparing metals in normal vs. abnormal dace.

Longfin dace contained detectable concentrations of eight of nine potentially harmful metals (Table 12). Arsenic was not recovered in longfin dace samples. Three of six normal dace samples and two of three abnormal samples contained copper at concentrations higher than the NCBP 85<sup>th</sup> percentile (Table 12). Mercury in all but two samples approached or exceeded the NCBP threshold. Lead was detected in only four samples, but the lower limit of detection, 0.26 µg/g wet weight, was greater than the NCBP 85<sup>th</sup> percentile of 0.22 µg/g wet weight. Selenium concentrations were below the NCBP 85<sup>th</sup> percentile in all normal dace samples, but selenium in two of three abnormal samples exceeded the threshold. Zinc was detected in all but one longfin dace sample at concentrations that exceeded the NCBP benchmark.

Desert suckers had sufficient body mass to permit individual whole body chemical analysis. Desert suckers were captured at four sampling stations (Table 5), as opposed to limited numbers of Sonora suckers found at only two sites (n = 4 individuals each). Abnormal appearing desert suckers were infrequently encountered, and we did not quantify the frequency of occurrence of anomalies in suckers and we did not save any abnormal suckers for residue analysis.

In desert sucker, arsenic was detected in fewer than one-half of the samples from each location (Table 13). With one exception, arsenic concentrations in suckers were lower than the NCBP 85<sup>th</sup> percentile of 0.27 µg/g wet weight; one individual collected at Chavez Siding contained 0.29 µg/g arsenic. Chromium was found in all sucker samples and concentrations ranged from 1.45 to 13.6 µg/g. There are no NCBP data for comparisons with current chromium concentrations. Copper concentrations approached or exceeded the NCBP 85<sup>th</sup> percentile threshold in all sucker samples. Mercury and selenium concentrations in sucker samples were all below the NCBP benchmark. Lead was detected in two of five suckers from Nogales Wash, Santa Gertrudis, and Chavez Siding, and lead was present in three of five samples from Tubac. However, the lower limit of detection for lead was 0.25 µg/g wet weight and the NCBP 85<sup>th</sup> percentile is 0.22 µg/g wet weight. Zinc in two of five suckers from Nogales Wash exceeded the NCBP threshold; whereas, zinc concentrations in suckers from the remaining collection locations were relatively low. Geometric mean concentrations of cadmium, copper, and selenium were similar among sites (Table 14). Chromium and nickel concentrations were significantly (P<0.05) higher in suckers from Chevez Siding than in suckers from all other sites. Mercury concentrations were lower (P = 0.001) in desert suckers from Nogales Wash than in suckers from other areas (Table 14). This suggests that Nogales Wash was not a source of mercury contamination for the Santa Cruz River. Zinc was highest (P<0.05) in suckers collected from the Border compared to those from downstream locations.

## BIRDS

Eight adult killdeer were collected from two locations; three individuals were collected from the Border and five individuals from Rio Rico North. To obtain sufficient tissue material for chemical analysis, livers were composited by area. The limited number of samples precluded statistical analysis. Concentrations of only six potentially harmful

metals were detected in killdeer livers (Table 15). Metals recovered in carcass tissues are listed in Appendix 4.

Residues of seven organochlorine compounds were recovered in killdeer carcasses (Table 16). DDE was recovered in more than one-half of the samples from both sites and residues ranged from 0.02 to 28 µg/g wet weight. PCB was not detected in carcasses collected from the Border but was present in four of five samples from Rio Rico North. PCB ranged from not detected (<0.05) to 0.18 µg/g wet weight.

## DISCUSSION

### *WATER*

The Santa Cruz River study area has historically contained stretches with perennial (continuous) and intermittent surface flow (Miller 1961, Bodenchuk 1992). Since the mid-1970s, treated effluent has been the base flow for the perennial river segment downstream from the NIWWTP. Under normal conditions, surface flow also occurs on the Santa Cruz River east of Nogales from the international boundary for about two miles northward. However, groundwater pumping for municipal supplies on both sides of the border frequently depletes this flow (Condes de la Torre 1970, Bodenchuk 1992). The Potrero Creek/Nogales Wash tributary to the Santa Cruz River is perennial and originates from springs near its headwaters (Potrero Creek) and from increasing amounts of grey water and sewage as the watercourse passes through Nogales, Sonora (Bodenchuk 1992).

The NIWWTP was originally designed to treat 12 million gallons per day (MGD). In the early 1990s, the plant was expanded to accommodate up to 17.2 MGD (Bodenchuk 1992). The plant receives sewage from Nogales, Sonora (67%) and Nogales, Arizona (33%). During our study period, effluent was discharged at an average daily rate of about 12 MGD. Discharge occurs 365 days per year, but rates vary depending on the time of year and local weather conditions.

Un-ionized ammonia (ammonia) is highly toxic in the aquatic environment (USEPA 1998).

It is a common byproduct of decomposition of plant and animal products and is often found at high levels in wastewater treatment facility effluents. Average monthly ammonia concentrations in 1997-98 were the highest recorded since 1993, when monitoring was first initiated (Turner 1997, FO SCR 1999).

Ammonia was not detected at the two collection sites located upstream from the NIWWTP, nor was it recovered in water samples collected from the two sites farthest downstream. Concentrations were highest at the study site immediately below the treatment plant (0.49 mg/L), and ammonia decreased with increasing distance from the plant. Ammonia concentrations found in our study were near the low end of those (<0.5 to 12 mg/L) reported by Lawson (1995) for samples collected from the same general area in 1992-93

and within the 0.03 to 24 mg/L range for samples collected in 1996 (Turner 1997). Our ammonia reading at Rio Rico Bridge (0.49 mg/L) also fell within the range of readings recorded by Boyle (1998) for the same Santa Cruz River site. All four investigators, Lawson (1995), Turner (1997), Boyle (1998), and FO SCR (1999), reported decreasing ammonia levels with increasing distance from the NIWWTP.

Ammonia levels were within the range known to be toxic to a number of species of fish and aquatic invertebrates (USEPA 1985, 1998). Laboratory tests performed on fathead minnows (*Pimephales promelas*) and channel catfish (*Ictalurus punctatus*), species found in both warm and cold waters of Arizona, demonstrated the toxic nature of un-ionized ammonia at concentrations found in our study. Un-ionized ammonia concentrations ranging from 0.7 to 3.4 mg/L were acutely toxic to fathead minnows when pH was above 7; chronic toxicity concentrations ranged from 0.13 to 0.22 mg/L (USEPA 1985). Chronic values for channel catfish ranged from 0.10 to 0.28 mg/L. The un-ionized ammonia concentration at Rio Rico Bridge (0.49 mg/L) was well above the chronic toxicity range for fathead minnows and channel catfish. While our one-point-in-time sampling effort was barely adequate to address ammonia toxicity, our data support those of four other studies (Lawson 1995, Turner 1997, Boyle 1998, FO SCR 1999) that documented potentially toxic ammonia concentrations below the NIWWTP.

Monthly toxicity tests using NIWWTP effluent demonstrated that plant discharges were highly toxic to fathead minnows (Aquatic Consulting and Testing, Inc. 1997-1999). To conduct Whole Effluent Toxicity Tests, effluent was collected over a seven-day period each month. Individual effluent samples were combined into a single composite and used to test acute and chronic toxicity under laboratory conditions. Larval stage fathead minnows were placed in aquaria using various concentrations of effluent at controlled temperatures (averaging about 25°C) and pH (averaging about 7.8). In chronic 96-hour tests conducted monthly from January 1997 through July 1999, 100% effluent caused 22.5 - 100% mortality (Table 17). Toxicity of the effluent was highly variable among monthly testing periods. In May 1997, a mixture of 50% effluent and 50% clean water resulted in 100% mortality. In May 1998, 100% effluent resulted in only 22.5 % mortality.

Effluents discharged in 1997 generally were more toxic than those discharged in 1998 and 1999. One hundred percent mortality was recorded during seven months in 1997; whereas, in 1998, 100% mortality was reported for only two months. Data for 1999 are incomplete, but show a continuing trend towards a lower mortality rate.

Further laboratory testing identified un-ionized ammonia as the toxicant of concern. Toxicity Identification Evaluation (TIE) tests conducted in compliance with the treatment plant's National Pollutant Discharge Elimination System (NPDES) permit concluded, "It is our opinion that the major contributor to chronic toxicity in the effluent sample was un-ionized ammonia." (Aquatic Consulting and Testing, Inc. 1998).

NIWWTP effluents also may be adversely affecting amphibian and reptile populations. In a 1997-98 investigation, Drost (1998) reported that the river and associated riparian habitat

supported at least five species of amphibians and three species of semi-aquatic reptiles. Amphibian diversity and numbers were highest in the flood plain upstream from the NIWWTP and at sites farthest downstream from the plant. The report concluded, "Toxic levels of ammonia are released by the NIWWTP, and no amphibians are found along the river from the waste water outfall downstream for several km."

Ambient pH and temperature can affect the relative toxicity of many metals and compounds in water. The pH values recorded in this study (7.4 - 7.9) fell within the 6.5 - 8.5 range considered optimal for most aquatic organisms (Mitchell and Strapp 1994). Our pH values were similar to those (7.5 - 8.4) reported by Lawson (1995) who documented water quality parameters in the Santa Cruz River in 1992-93 and also similar to the 7.2 - 8.2 range reported by Boyle (1998) for pH values obtained in 1997-98. Arizona water quality standards for waterbodies classified as "Aquatic and Wildlife Warm water" (A&Ww), and "Aquatic and Wildlife Effluent Dependent Waters" (A&Wedw) including the Santa Cruz River, is 6.5 to 9.0. The pH conditions at all sampling sites were within the acceptable range for aquatic organisms expected to be found in southeastern Arizona. Based on our limited sampling, excessive pH apparently was not a factor limiting aquatic organisms in the Santa Cruz River study area.

Chlorine in water also is highly toxic to biological organisms. While chlorine was not detected in any water samples, the lower limit of detection (0.05 mg/L) was not low enough to assess potential adverse impacts to most invertebrates and fish. The 96-hr LC<sub>50</sub> for most invertebrates is 0.01 mg chlorine/L (range = 0.005-0.26) (Wang and Hanson 1985). The 96-hr LC<sub>50</sub> for most fish was <0.20 mg/L (range = 0.07-0.29 mg/L) (Wang and Hanson 1985). Therefore, our analytical methodology for chlorine was not sufficiently sensitive to assess a biological hazard to aquatic invertebrates and was marginal for assessing toxicity to fish.

Low levels of dissolved oxygen in river water, especially at sites nearest the treatment plant outfall, also could have an adverse impact on fish and invertebrate abundance. We did not assess dissolved oxygen levels in our samples. However, results of two previous studies concur that, although lowest dissolved oxygen levels were measured in water collected closest to the NIWWTP outfall (4 mg/L), dissolved oxygen concentrations were well above anoxic conditions and did not appear to be a factor limiting fish populations (Lawson 1995, Boyle 1998).

### *SEDIMENT*

Concentrations of potentially toxic metals in sediment were mostly within the range of background concentrations for Arizona soils as reported by Earth Technology Corp. (1993). One possible exception was a particularly high level of chromium, 149 µg/g dry weight, detected in the sediment sample from Nogales Wash. The mean chromium concentration in Arizona soils is 61.3 µg/g. However, the maximum background concentration recorded in Arizona soils is 300 µg/g. Chromium in the Nogales Wash sediment sample was more than twice as high as the state mean but less than the state maximum.

We assessed relative toxicity of metals in sediment to benthic invertebrates by comparing levels found in our study with toxic thresholds reported in the literature. Under laboratory conditions, Persaud et al. (1993), tested the toxicity of selected metals on more than 100 benthic invertebrates. They separated results into three effect-level categories, 1) the no effect level, 2) the lowest effect level, and 3) the severe effect level. Persaud et al. (1993) defined the lowest effect level as, the level of contamination which has no effect on the majority of the sediment-dwelling organisms; the sediment is clean to marginally polluted. At the severe effect level, the sediment is considered heavily polluted and likely to affect the health of sediment-dwelling organisms. None of the metals in samples collected from the Border equaled or exceeded the lowest effect level established by Persaud et al. (1993). At Nogales Wash, arsenic concentrations slightly exceeded the lowest effect level, and the 149  $\mu\text{g/g}$  chromium concentration was considerably higher than the 110  $\mu\text{g/g}$  severe toxicity threshold. At Rio Rico Bridge, the first site below the NIWWTP, copper concentrations equaled the lowest toxicity threshold of 16  $\mu\text{g/g}$ . At the Santa Gertrudis and Tubac sites, arsenic, cadmium, copper, and lead exceeded the lowest toxicity thresholds of 6, 0.6, 16, and 31  $\mu\text{g/g}$ , respectively. In addition, sediment from Santa Gertrudis, Tubac, and Chavez Siding also contained chromium in excess of the lowest toxicity threshold (26.0  $\mu\text{g/g}$ ). Therefore, with the exception of high levels of chromium detected Nogales Wash sediment, none of the element concentrations approached the severe toxicity threshold.

### *INVERTEBRATES*

We did not quantify the relative abundance of invertebrates at each collection location. However, as the field season progressed, it became apparent that there was an obvious disparity in invertebrate density and diversity among collection sites. For example, only one trip to the Border was needed to collect a minimum 10 gram sample each of dragonfly larvae, giant water bugs, and snails. In contrast, we made four collecting efforts at Rio Rico Bridge and Rio Rico North and were able to secure only one sample of giant water bugs at each site. Invertebrate populations also were relatively low at Nogales Wash. These qualitative observations reflected those of other authors (Lawson 1995, Boyle 1998) who also reported low taxa richness at sites closest to the treatment plant and increasing richness with distance downstream from the NIWWTP. Ephemeroptera are considered pollution sensitive taxa (Merritt and Cummins 1996) and Ephemeroptera populations were severely reduced or non-existent at sites nearer the NIWWTP (Boyle 1998).

Significant differences in accumulation were detected among species for five metals (arsenic, chromium, copper, lead, and zinc). In general, snails bioaccumulated most metals to higher levels than giant water bugs and dragonfly larvae. Snails accumulated higher levels of arsenic, copper, and lead than did giant water bugs or dragonfly larvae. Giant water bugs accumulated only chromium and zinc to higher levels than snails. Dragonfly larvae appeared to be the least efficient bioaccumulators of metals.

We quantified contaminant concentrations in invertebrates, not to assess hazards to the invertebrates themselves, but as a measure of overall ecosystem health. Invertebrates are



prey for many fish and wildlife species; therefore, by quantifying contaminant concentrations in invertebrates, we can estimate the potential hazard to mid- and top-level predators. Fish bioaccumulate contaminants from the surrounding medium via transfer across the gill surface and through the food chain. Because there are two important pathways of exposure, it is difficult to establish safe dietary thresholds for fish under natural conditions. Much of the following discussion focuses on safe, as well as potentially hazardous, dietary thresholds for birds because meaningful dietary thresholds for most contaminants in fish have not been established.

**Arsenic:** Background arsenic concentrations are usually less than 1.0 µg/g wet weight (about 3.3 µg/g dry weight) in freshwater biota (Eisler 1988a). Five of 13 invertebrate samples contained higher than background levels of arsenic. The dietary effect level for arsenic in fish is between 10 µg/g dry weight (no effect) and 30 µg/g (reduced weight gain, SJVDP 1990). The lowest dietary threshold for adverse effects of arsenic on birds (one-day old mallard ducklings (*Anas platyrhynchos*) was between 25 µg/g dry weight (no effect, Stanley et al. 1994) and 30 µg/g (reduced growth rate) (Camardese et al. 1990). Arsenic at levels detected in Santa Cruz River invertebrates should not affect most fish and bird species that consume a large proportion of aquatic invertebrates in their diet.

**Cadmium:** Estimates of the dietary threshold at which cadmium is hazardous to upper trophic level species vary widely. No data are available on toxic thresholds in the diet of fish. Mean cadmium concentrations in two brands of commercial hatchery feed were 0.09 and 0.19 µg/g wet weight (range = <0.06 - 0.20 µg/g wet weight) (Simpson et al. 1998). Birds apparently are relatively resistant to the biocidal properties of cadmium. Beyer and Stafford (1993) reported that 100 µg/g cadmium dry weight in earthworms should be considered hazardous to sensitive species that eat earthworms. Feeding studies with mallards indicated that diets containing 200 µg/g cadmium produced no obvious adverse effects although kidney concentrations approached critical threshold (Eisler 1985). The maximum cadmium concentration in invertebrates collected from the Santa Cruz River was 1.32 µg/g dry weight, well below levels considered potentially hazardous. Cadmium concentrations in invertebrates collected from the Santa Cruz River are relatively low and do not pose a threat to local fish and wildlife species that consume invertebrates in their diet.

**Chromium:** Under laboratory conditions, chromium is mutagenic, carcinogenic, and teratogenic to a wide variety of organisms (Eisler 1986). Pollution of the aquatic environment with chromium results from refining of chromite ore, the use of chromium in electroplating, pigment production, textile manufacturing, tanning, corrosion inhibition in cooling towers, and chromium in urban and residential runoff (Towill et al. 1978). Chromium toxicity to aquatic biota is influenced by abiotic variables such as water hardness, temperature, pH, and salinity. Waterfowl often consume large quantities of aquatic invertebrates and therefore are candidates for bioconcentrating chromium through the aquatic food chain. The maximum chromium concentration recorded in invertebrates collected from the Santa Cruz River was 66.4 µg/g dry weight (14.7 µg/g wet weight) which was well within the dietary range known to adversely affect fish and wildlife.

Growth and survival of second generation black ducks (*A. rubripes*) was reduced when they were fed diets containing 10 and dry weight  $\mu\text{g/g Cr}^{+3}$ , these diets were the same as to those administered to their adult parents (Eisler 1986). Six of 13 invertebrate samples contained 10  $\mu\text{g/g}$  dry weight or more chromium; therefore, chromium concentrations in some Santa Cruz River invertebrates may represent a potential threat to upper trophic level species that consume a large proportion of invertebrates in their diet.

**Copper:** Copper is among the most toxic of the heavy metals in freshwater biota (Eisler 1998a) and often accumulates and causes irreversible harm to some species at concentrations just above levels required for growth and reproduction (Hall et al. 1988). In experimental studies with fish, increased mortality was not observed until dietary concentrations reached 810  $\mu\text{g/g}$  dry weight (Julshamn et al. 1988). Birds and mammals, when compared to lower forms, are relatively resistant to copper. No experimental studies have been conducted on hazardous dietary levels in wild birds, but data are available for domestic fowl and pen-reared waterfowl. NAS (1980) reported that 300  $\mu\text{g/g}$  dry weight copper in the diet is the maximum tolerable level for poultry. The toxic level for ducks was estimated to be  $> 200 \mu\text{g/g}$  (Puls 1988). The maximum safe dietary levels for growing chickens and turkeys is 250 and 500  $\mu\text{g/g}$  (Neathery and Miller 1977). Since the maximum copper concentration recorded in invertebrates in our study was 129  $\mu\text{g/g}$  dry weight, it seems unlikely that copper at levels found in Santa Cruz River invertebrates would have an adverse effect on invertebrate-eating fish and birds.

**Lead:** Although lead is concentrated in biota from water, there is no convincing evidence that lead is transferred through food webs (Eisler 1988b). Lead concentrations tend to decrease with increasing trophic level in both detritus-based and grazing aquatic food chains. Lead was detected in 12 of 13 Santa Cruz River invertebrate samples. Levels of lead below 100  $\mu\text{g/g}$  dry weight in the diet usually cause few significant reproductive effects in birds (Scheuhammer 1987). Starlings nesting near highways exposed to dietary lead levels of about 90  $\mu\text{g/g}$  (dry weight) did not exhibit reproductive impairment (Scheuhammer 1987). Lead in earthworms at 150  $\mu\text{g/g}$  dry weight or more should be considered hazardous to sensitive species that eat earthworms (Beyer and Stafford 1993). Ingestion of food containing biologically incorporated lead, although contributing to the lead burden of carnivorous birds is unlikely in itself to cause clinical lead poisoning. The maximum lead level recorded in invertebrates in our study was 8.99  $\mu\text{g/g}$  dry weight; therefore, lead concentrations are far below acute or chronic levels.

**Mercury:** There is a great deal of conflicting literature regarding the threshold dietary food chain level above which mercury may adversely affect higher predators. Eisler (1987) states, "For the protection of sensitive species of mammals and birds that regularly consume fish and other aquatic organisms, total mercury concentrations in these prey items should probably not exceed 0.1  $\mu\text{g/g}$  fresh weight for birds, and 1.1  $\mu\text{g/g}$  for small mammals." Walsh et al. (1977) suggested, "To protect fish and predatory organisms, total mercury burdens in these organisms should not exceed 0.5  $\mu\text{g/g}$  wet weight." Three  $\mu\text{g/g}$  mercury dry weight ( $\approx 0.9 \mu\text{g/g}$  wet weight) in earthworms should be considered hazardous to sensitive species that eat earthworms (Beyer and Stafford

1993). Mercury in all but one invertebrate sample, giant water bugs from Tubac (0.89  $\mu\text{g/g}$  dry weight, 0.24  $\mu\text{g/g}$  wet weight), was lower than the most conservative threshold, 0.1  $\mu\text{g/g}$ , proposed by Eisler (1987), and none of the samples exceeded food chain toxicity thresholds suggested by Walsh et al. (1977) and Beyer and Stafford (1993).

Nickel: The National Research Council (1980) suggested 100.0  $\mu\text{g/g}$  wet weight (about 333  $\mu\text{g/g}$  dry weight) as the dietary threshold above which toxic effects may be observed in domestic animals. No data are available for background or toxic concentrations of nickel in fish and wildlife. The maximum nickel concentration recorded in our invertebrate samples was 8.73  $\mu\text{g/g}$  dry weight which probably is within the non-toxic range. Nickel concentrations in Santa Cruz River invertebrate samples likely do not pose a significant food chain hazard to higher trophic level species.

Selenium: Based on the known margins of safety between normal and toxic dietary exposure, selenium is potentially more poisonous than either arsenic or mercury (Sorensen 1991). Background concentrations of selenium in aquatic invertebrates range from 0.1 to 4.5  $\mu\text{g/g}$  dry weight (USDI 1998). "Normal" food chain selenium levels in the aquatic environment are  $\leq 2.0$   $\mu\text{g/g}$  dry weight (Ohlendorf et al. 1990). There is an overlap in ambient levels and the toxic biological effects threshold for sensitive species. The estimated biological effects threshold for the health and reproductive success of freshwater and anadromous fish is 3  $\mu\text{g/g}$  dry weight selenium in food chain organisms (Lemly 1993). Organisms containing 3  $\mu\text{g/g}$  dry weight or more also should be viewed as potentially harmful to aquatic birds that consume them (Lemly 1993). The maximum selenium concentration recorded in our invertebrate samples was 2.22  $\mu\text{g/g}$  dry weight; therefore, food chain accumulation of selenium does not appear to be a potential problem in the Santa Cruz River.

Zinc: The toxicity of zinc is difficult to quantify as tissue residues are not always reliable indicators of zinc contamination (Eisler 1993). The optimal amount of zinc in the diet of channel catfish (*Ictalurus punctatus*) and brown trout (*Oncorhynchus mykiss*), raised in aquaculture facilities ranges from 150 - 300  $\mu\text{g/g}$  dry weight (Spry et al. 1988; Gatlin et al. 1989). Rainbow trout (*Oncorhynchus mykiss*) can tolerate relatively high dietary concentrations of zinc (Knox et al. 1982). There was no effect on growth or health of rainbow trout when they were fed a diet containing zinc at a level of 683  $\mu\text{g/g}$  dry weight. Zinc in Santa Cruz River invertebrates ranged from 28.0 to 260  $\mu\text{g/g}$ , well within the non-toxic range for fish. The lowest concentration of zinc in the diet of birds that caused adverse effects is 178  $\mu\text{g/g}$  dry weight (Eisler 1993). When 178  $\mu\text{g/g}$  zinc was fed to domestic breeding hens for 3 weeks, it caused immunosuppression of young progeny. None of the dragonfly larvae or snails contained zinc at levels greater than 178  $\mu\text{g/g}$ , but zinc in 5 of 6 giant water bug samples exceeded this toxic threshold. Therefore, individual birds that prey heavily on giant water bugs could accumulate potentially harmful levels of zinc.

## *FISH*

Fish showed striking differences in distribution and abundance among the sampling sites.

Longfin dace was the most abundant fish species in the Santa Cruz River and were observed at all seven collection sites. Dace were most numerous at the Border (214 individuals captured per minute of electrofishing) and least numerous at Rio Rico North and Rio Rico Bridge (0.42 and 0.52 individuals per minute). There was an overall increase in number of individuals with distance downstream from the NIWWTP; however, density of dace at downstream sites never approached that of upstream locations (Border and Nogales Wash). Desert suckers were recovered in Nogales Wash and the three sites farthest downstream from the NIWWTP. Desert sucker were not observed at the Border possibly because of the intermittent nature of the site. Although not well quantified, the relative abundance of suckers among sites varied from 2.0 - 3.7 individuals per minute of electrofishing. Sonora suckers also were observed in the Santa Cruz River, but their numbers were low relative to populations of desert suckers.

Mosquitofish were the only non-native species observed in the Santa Cruz River and current populations remain relatively low. One individual was observed at Rio Rico Bridge and Rio Rico North and individuals were present but not quantified at Chavez Siding. Mosquitofish populations have declined, at least at one site in the Santa Cruz River, since the early 1990s, as Rector (unpub. data) recorded numerous individuals, including pregnant females, at Rancho Santa Cruz, a site located only 2 km downstream from our Rio Rico North collection site.

Gila topminnow were present at four sites from Rio Rico North downstream to Chavez Siding. Although historic records indicate that Gila topminnow were present in portions of the Santa Cruz River upstream from the current site of the NIWWTP (Chamberlain 1904), we did not observe topminnow at the Border, perhaps because of the intermittent nature of the river at that location. Topminnows also were not observed in Nogales Wash. We have found no historic records indicating that Gila topminnows were ever present in Nogales Wash. The wash is subject to periodic spikes in contamination which may be a limiting factor to some species. A relatively healthy population of topminnow, including breeding males, was observed at Tubac and Chavez Siding.

Gila topminnow populations have declined precipitously within our Santa Cruz River study area since 1993 when the last survey was conducted. In 1993, an abundant population of topminnow, including breeding males, was observed as far upstream as the Rancho Santa Cruz (Rector unpub. data). Despite our intensive electrofishing efforts, we observed only scattered individuals at our collection sites immediately upstream and downstream from Rancho Santa Cruz.

Frequencies of fish with deformities observed during our study were somewhat lower than the 50%+ reported by Lawson (1995) for fish collected in 1994 from the same portions of the Santa Cruz River. Histological investigations of anomalous fish were inconclusive. Lesions and deformities were not related to the presence of the white grub and not enough fish with lesions were collected to assess the role of bacteria as a causative agent.

### *Organochlorines in fish*

Lipid levels in desert suckers ranged from 1.73 to 9.42 percent, and gmean levels were significantly ( $P < 0.0001$ ) lower in suckers from Nogales Wash (2.18%) than in suckers from Santa Gertrudis (6.98%), Tubac (5.48%), and Chavez Siding (6.58%). This suggests that nutrient levels were low in Nogales Wash and may have adversely affected the fish food base. When lipid levels in suckers were compared with those in dace from the same areas, gmean lipid levels were significantly lower in suckers (6.3%) than dace (10.0%).

The use of DDT in Arizona was restricted in 1968 and totally suspended in 1969 (Ware 1974). DDT was not detected in longfin dace but was present in three of five desert suckers from Chavez Siding and in one sucker from Santa Gertrudis. In fish tissue, DDT rapidly metabolizes to DDD and then to DDE; therefore, the occurrence of DDT in fish samples is of concern because it suggests that fish were recently exposed to DDT. None of the fish from collection sites located upstream from the wastewater treatment plant contained DDD, but it was present in all samples collected below the treatment plant. Therefore, DDT and DDD are not entering the system from agricultural use in Mexico via the Santa Cruz River or Nogales Wash. The source of DDT and DDD may be effluent from the NIWWTP, or more likely, runoff/drainage from contaminated soils downstream from the wastewater treatment plant as indicated by increasing concentrations with distance from the plant. DDE was recovered in all fish samples except Border dace, and residues were generally low. Chlordane was the only other organochlorine insecticide present in more than one-half of the samples. PCBs were detected most frequently in fish from Nogales Wash. Residues of all organochlorines were generally low and none of the samples contained concentrations above the NCBP 85<sup>th</sup> percentile. Current organochlorine levels should not present a threat to fish survival and reproduction nor should current residues present a bioconcentration hazard to upper trophic level species that consume a large proportion of fish in their diet.

### *Metals in fish*

**Arsenic:** Arsenic acts as a cumulative poison (Jenkins 1981) and is listed by the USEPA as 1 of 129 priority pollutants (Keith and Telliard 1979). Only one sample exceeded the NCBP 85<sup>th</sup> percentile of 0.27  $\mu\text{g/g}$  (Schmitt and Brumbaugh 1990). Background arsenic concentrations in biota are usually less than 1  $\mu\text{g/g}$  wet weight (Eisler 1988a). Toxic effects of arsenic on aquatic organisms has been reported at concentrations of 1.3 to 5.0  $\mu\text{g/g}$  wet weight. Arsenic was not detected in longfin dace samples and was present in only 25% of the desert suckers at  $\leq 0.29$   $\mu\text{g/g}$  wet weight. Arsenic concentrations in fish were well below the toxic threshold. There appears to be little potential for arsenic related problems in fish at the lower Santa Cruz River sites we sampled.

**Cadmium:** Cadmium was detected in 59% (17/29) of the fish samples; a frequency of occurrence higher than that reported by most other authors for fish collected from

southern Arizona (Radtke et al. 1988, Baker and King 1994, King and Baker 1995, Andrews and King 1997, Andrews et al. 1997, Tadayon et al. 1997). Only one Arizona study documents a higher frequency of occurrence of cadmium in fish than what we encountered during our 1997 Santa Cruz River sampling effort; 77% of the fish samples from three National Wildlife Refuges (NWR) on the Colorado River contained cadmium (King et al. 1993). Cadmium in two of six normal longfin dace samples and in one of 20 desert sucker samples equaled or exceeded the NCBP 85<sup>th</sup> percentile of 0.05 µg/g wet weight. Cadmium concentrations that exceed 2.0 µg/g wet weight in whole fish should be viewed as evidence of probable cadmium contamination (Eisler 1985). Although the frequency of occurrence of cadmium in fish samples was relatively high, overall concentrations were low, and none of the samples exceeded the 2.0 µg/g wet weight threshold of concern.

**Chromium:** Chromium was not quantified in the NCBP program (Schmitt and Brumbaugh 1990); therefore, comparisons with national levels are not possible. The organs and tissues of fish and wildlife that contain >4.0 µg/g total chromium dry weight (about 1.2 µg/g wet weight) should be viewed as presumptive evidence of chromium contamination (Eisler 1986). Two normal longfin dace samples contained elevated concentrations of chromium; the composite sample collected at the Border contained 7.99 µg/g and the sample from Rio Rico North had 6.76 µg/g wet weight. All samples of desert sucker contained concentrations of chromium in excess of the 1.2 µg/g wet weight threshold. In suckers, concentrations of chromium increased with increasing distance downstream from the NIWWTP. Mean concentrations in desert suckers from Chavez Siding were significantly higher than levels suckers from Nogales Wash, Santa Gertrudis, and Tubac. The maximum chromium concentration in suckers (13.6 µg/g wet weight at Chavez Siding) was more than 11-times higher than the 1.2 µg/g concern level. These data suggest that the entire lower Santa Cruz river is contaminated with chromium. Also, there may be a source of chromium contamination between the Tubac and Chavez Siding as indicated by the high frequency of occurrence and elevated levels of chromium in suckers from Chavez Siding. Field measurements of temperature and specific conductance within a 1000 meter section of the Santa Cruz River near Tubac indicated a localized area of possible groundwater inflow (Gebler 1998).

**Copper:** Copper is among the most toxic of metals to freshwater biota (Schroeder et al. 1966, Eisler 1998a) and often accumulates and causes irreversible harm to some species at concentrations just above levels required for growth and reproduction (Hall et al. 1988). Specific sources of environmental contamination include mining and smelting, industrial and sewage treatment plant discharges (Eisler 1998a). Copper can combine with other contaminants such as ammonia (common in wastewater effluent), mercury, and zinc to produce additive toxic effects on fish (Skidmore 1964, Hilmy et al. 1987, Eisler 1997). Copper exceeded the NCBP 85<sup>th</sup> percentile (Schmitt and Brumbaugh 1990) in 50% of the normal dace samples and in 95% of the desert sucker samples. Because of its occurrence at relatively high levels at some sites and its propensity to interact with other compounds and elements, copper remains a contaminant of concern in the lower Santa Cruz River.

Lead: Lead has been known for centuries as a cumulative metabolic poison. Acute exposure to environmental lead (as opposed to exposure to lead shot) is seldom a current issue, but continuous exposure to low concentrations is still a major concern (Eisler 1988b). Although lead is concentrated by biota from water, there is no evidence that environmental lead is transferred through the food web (Eisler 1988b). Lead concentrations tend to decrease with increasing trophic level in the aquatic food base. Lead was detected in three of six dace samples (50%) and in 9 of 20 (45%) of the sucker samples. The frequency of occurrence of lead in Santa Cruz River fish (45-50%) was much greater than in fish from other southern Arizona areas including the lower Colorado River, 0, 10 and 36%, (Radtke et al. 1988, King et al. 1993, Tadayon et al. 1997), the lower Gila River, 0% (King et al. 1997), and the middle Gila River, 0% (King and Baker 1995). Only fish collected from Arizona streams associated with mining activities contained a higher proportion of samples with detectable concentrations of lead (Rector 1997). Our analytical methodology was not sufficiently precise to allow a meaningful comparison of lead concentrations in Santa Cruz River fish with the NCBP 85<sup>th</sup> percentile. The lower limit of detection for lead in our study was  $\leq 0.37 \mu\text{g/g}$  wet weight. The NCBP 85<sup>th</sup> percentile was  $0.22 \mu\text{g/g}$ . Although lead was not detected in 16 of 29 samples, these samples may have contained lead in excess of the NCBP 85<sup>th</sup> percentile. Data are not available on body burdens of lead in fish associated with chronic toxicity and reproductive effects (Eisler 1988b). Dietary thresholds for upper trophic level organisms vary greatly;  $50 \mu\text{g/g}$  lead in the diet is the recommended threshold for the protection of avian species (NRC 1980), but concentrations above  $0.3 \mu\text{g/g}$  in fish to be consumed by humans is considered hazardous (Eisler 1988b). Fish from heavily polluted areas can contain from 20 to  $128 \mu\text{g/g}$  dry weight lead (about 6 to  $38 \mu\text{g/g}$  wet weight) (Eisler 1988b). Therefore, while the frequency of occurrence and concentrations of lead in Santa Cruz River fish appear to be elevated, concentrations are far below those in seriously contaminated areas.

Mercury: Mercury concentrations are of special concern because mercury can bioaccumulate in organisms and biomagnify through the aquatic food chain. Mercury has no known biological function, and its presence in cells of living organisms is undesirable and potentially hazardous (Eisler 1987). Mercury in the environment exists in a wide range of inorganic and organic forms with varying degrees of stability and toxicity (Thompson 1996). It is generally accepted that methylmercury is the most stable form and the form most toxic to wildlife. From 95-99% of the mercury in fish is methylmercury (Wiener and Spry 1996). Only one sample of normal longfin dace (Chavez Siding,  $0.50 \mu\text{g/g}$  wet weight) exceeded the NCBP 85<sup>th</sup> percentile of  $0.17 \mu\text{g/g}$  and none of the sucker samples approached the NCBP 85<sup>th</sup> percentile threshold. The highest concentration of mercury detected in lower Santa Cruz River fish,  $0.50 \mu\text{g/g}$  wet weight, was well within the  $\leq 1.0 \mu\text{g/g}$  range generally accepted as the concentration in biota from unpolluted environments (Eisler 1987). There is probably little potential for adverse effects of mercury on adult fish survival or reproduction. Mercury, however, when ingested in combination with other compounds and elements such as parathion, cadmium, and copper can have additive or synergistic toxic effects (Hoffman et al. 1990, Calabrese and Baldwin 1993).

Nickel: Nickel is listed by the USEPA as one of 129 priority pollutants (Keith and Telliard 1979). Freshwater fish from uncontaminated habitats usually contain  $\leq 1.3 \mu\text{g/g}$  wet weight nickel compared to 9.5-31.7  $\mu\text{g/g}$  nickel in tissues of fish collected from a highly polluted site near a nickel smelter in Canada (Eisler 1998b). None of the longfin dace samples exceeded the 1.3  $\mu\text{g/g}$  wet weight threshold. It is interesting to note that nickel in all five desert sucker samples from Chavez Siding exceeded the lower threshold but none of the concentrations (1.55 - 4.98  $\mu\text{g/g}$ ) fell within the range of residues reported in fish from the contaminated Canadian site. Nickel, by itself, is not a potentially threatening contaminant at current levels. Nickel, however, can combine with zinc to have additive toxic effects on fish (Eisler 1998b). Our fish data suggest that there is a source of nickel contamination in the Santa Cruz River between the Tubac and Chavez Siding sites.

Selenium: Selenium is an essential trace element in animal diets, but it is toxic at concentrations only slightly above required dietary levels. None of the normal fish samples exceeded the NCBP 85<sup>th</sup> percentile threshold (Schmitt and Brumbaugh 1990). In a comprehensive summary of selenium threshold effect levels, Lemly and Smith (1987) reported that selenium induced reproductive failure in fish was associated with whole body selenium concentrations of 12  $\mu\text{g/g}$  dry weight (about 3.6  $\mu\text{g/g}$  wet weight). Based on a later review of more than 100 papers, Lemly (1996) suggested a toxic effects threshold of 4  $\mu\text{g/g}$  wet weight in the whole body for the protection of overall health and reproductive vigor of freshwater and anadromous fish. The highest wet weight whole body selenium concentration (in normal fish) recorded in this study was 0.70  $\mu\text{g/g}$ , well below the 4.0  $\mu\text{g/g}$  wet weight threshold recommended by Lemly (1996). There is little potential for selenium toxicity to fish populations in the lower Santa Cruz River at current contaminant levels.

Zinc: Zinc was present in all fish samples. Five of 6 dace and 2 of 20 suckers exceeded the NCBP 85<sup>th</sup> percentile level of 34.2  $\mu\text{g/g}$  wet weight (Schmitt and Brumbaugh 1990). Zinc may interact with other elements and compounds, and the patterns of accumulation, metabolism, and toxicity from zinc interactions greatly differ from those produced by zinc alone. Zinc in combination with other elements can have antagonistic, additive, or synergistic effects as reviewed by Eisler (1993, 1997). Zinc is more toxic to embryos and juveniles of aquatic organisms than to adults, and zinc is more toxic in the presence of nickel, cadmium, chromium, copper, and mercury (Eisler 1997). The toxicity of zinc also is modified by ambient environmental factors. Zinc is more toxic under conditions of comparatively low dissolved oxygen (Spear 1981), a condition that is chronic at sites downstream of the NIWWTP (Lawson 1995, Boyle 1998). Also, zinc is more toxic at elevated temperatures (NAS 1980, Spear 1981, Hilmy et al. 1987), a condition common in the desert southwest. The toxicity of zinc to fish is species dependent (Eisler 1997) and no information has been located on hazard thresholds to longfin dace or desert suckers or closely related species.

## *BIRDS*



Assessing exposure of birds to environmental contaminants is difficult because birds are highly mobile, often migratory, and may accumulate contaminants over broad geographic areas. Killdeer are common throughout the winter months in the Santa Cruz River area (Tucson Audubon Society 1995). All killdeer sampled were adults, but we cannot be certain that their contaminant burdens reflect only local conditions. We could not be certain if we sampled overwintering birds, migrants, or residents.

### *Organochlorines in birds*

Organochlorine residues, particularly DDE, in birds collected from the southwestern United States have historically been higher than those from the rest of the nation (Cain 1981, Fleming et al. 1983, Fleming and Cain 1985, White and Krynitsky 1986, Bunck et al. 1987). European starlings (*Sturna vulgaris*) collected near the lower Gila River during a 1982 nationwide survey of 129 sites contained the highest (8.4 µg/g wet weight) DDE concentrations in the United States (Bunck et al. 1987). DDE in five of eight killdeer carcasses (0.36 - 28 µg/g wet weight) exceeded the upper 95% confidence interval (0.23 µg/g wet weight) of the nationwide average for bird carcasses reported by Bunck et al. (1987).

Four of eight killdeer samples contained >3.4 µg/g DDE wet weight; the level associated with impaired reproductive performance in other species of birds, particularly the American black duck (*A. rubripes*) (Longcore and Stendell 1977). Also, one-half of the killdeer carcasses contained more than 3.0 µg/g DDE, a level that represents a hazard to predatory birds that feed on killdeer (Wiemeyer and Porter 1970, McLane and Hall 1972, Mendenhall et al. 1983). Killdeer have been recorded in the diet of the once endangered peregrine falcon (Anderson et al. 1982, DeWeese et al. 1986) and the Santa Cruz River study area is within the range of the peregrine falcon.

### *Metals in birds*

The elements most likely to be toxic to birds include cadmium, lead, mercury, and selenium (Eisler 1987, 1988b, Scheuhammer 1987, Ohlendorf et al. 1988). The concentration of cadmium in liver tissues of birds considered to represent normal background levels is <3 µg/g dry weight (Ohlendorf 1993). Cadmium was recovered in both killdeer liver samples, but levels were low, 1.43 and 2.33 µg/g dry weight. Cadmium is not considered a contaminant of concern for killdeer nesting and wintering in the lower Santa Cruz River ecosystem.

The normal background level of lead in livers of adult birds living in relatively uncontaminated environments ranges from 0.5 to 5.0 µg/g dry weight (Scheuhammer 1987, Ohlendorf 1993). The liver is the tissue of choice for assessing recent exposure to lead; whereas, bone is preferred for assessing long-term exposure. Lead was detected in six of eight livers and concentrations were ≤ 2.60 µg/g dry weight which is well within the normal background range indicating minimal recent exposure. There is little

evidence to indicate that lead is a contaminant of concern for birds on the Santa Cruz River.

Background concentrations of mercury in bird livers ranges from <1 - 10 µg/g dry weight, but concentrations greater than 6 µg/g dry weight may be toxic to sensitive species (Ohlendorf 1993). Reproductive effects usually occur at lower doses than those that produce pathological effects (Scheuhammer 1987). Liver concentrations of about 2 µg/g dry weight mercury were associated with decreased hatchability due to early embryonic mortality and an increased number of unfertilized eggs. Mortality was associated with 30 to 130 µg/g mercury in the liver (Scheuhammer 1987). The maximum concentration of mercury in killdeer livers was 0.48 µg/g, well within the nontoxic range. Mercury does not present a threat to the health and reproductive success of killdeer nesting along the Santa Cruz River.

Selenium usually averages 3 - 10 µg/g dry weight in livers of birds from selenium normal environments (Skorupa et al. 1990, Ohlendorf 1993). Concentrations above 3 µg/g wet weight (approximately 10 µg/g dry weight) in the livers of laying females has been associated with reproductive impairment (Heinz 1996). Concentrations of selenium greater than 10 µg/g wet weight (approximately 33 µg/g dry weight) in the liver can be considered harmful to the health of young and adult birds. Selenium in livers of killdeer (8.66 - 9.46 µg/g dry weight) were within the normal or background range and selenium should not pose a problem for aquatic birds nesting on the Santa Cruz.

Chromium is a contaminant of concern in the Santa Cruz River ecosystem, particularly in fish, but chromium did not bioaccumulate in killdeer liver tissues. Chromium, if present in killdeer liver samples, was below the detection limit of 0.05 µg/g dry weight.

## SUMMARY

- ! Effluent from the NIWWTP has an overall positive effect on the Santa Cruz River riparian habitat and fish and wildlife values. Effluent provides perennial surface flow for about a 16 mile stretch of river that would otherwise be a dry river bed.
- ! Concentrations of arsenic, cadmium, lead, mercury, and selenium were present at relatively low concentrations in sediment, invertebrates, fish, and birds. Current levels of these elements do not pose a significant hazard to the health of fish and wildlife.
- ! Effluent from the NIWWTP does not appear to be a source of metal contamination in the Santa Cruz River ecosystem.
- ! The pH values recorded in this study (7.4 - 7.9) fell within the 6.5 - 8.5 range considered optimal for most aquatic organisms
- ! Dissolved oxygen concentrations were well above anoxic conditions and did not appear to be a factor limiting fish populations.
- ! TIE tests conducted by an independent laboratory identified un-ionized ammonia as the primary toxicant responsible for fish mortality.
- ! Toxicity tests using NIWWTP effluent demonstrated that plant discharges were highly toxic to fish. Monthly testing from January 1997 - July 1999 indicated that 100% effluent caused 22.5 - 100% mortality of adult fathead minnows after 96 hours of exposure.
- ! NIWWTP effluent appears to have limited populations of invertebrates, amphibians, semi-aquatic reptiles, and fish, especially at sites closest to the treatment plant outfall. Populations of the endangered Gila topminnow have declined precipitously since 1993 when the last survey was conducted. Associated with this decline was an increase in un-ionized ammonia concentrations in river water.
- ! Fish showed striking differences in distribution and abundance among sampling sites. Dace were most numerous at the Border and least numerous at the two collection sites immediately downstream from the NIWWTP. There was an overall increase in number of individuals with distance downstream from the treatment plant; however, density of dace at downstream sites never approached that of upstream locations.
- ! A high proportion of fish with skin and skeletal anomalies was documented at sites downstream from the NIWWTP. Anomalous fish were not observed at sites upstream from the treatment plant. Histological investigations to assess the cause of the anomalies were inconclusive.
- ! The entire lower Santa Cruz River aquatic ecosystem was contaminated with chromium. Chromium concentrations were highest in sediment from Nogales

- Wash, but chromium bioaccumulated in invertebrates and fish to higher than background levels at almost all collection sites. Almost one-half of all invertebrate samples contained chromium at concentrations that could be harmful to upper trophic level species.
- ! Two of five longfin dace samples and all desert sucker samples were contaminated with higher than background levels of chromium. Concentrations increased with increasing distance from the NIWWTP.
  - ! There may be a source of chromium and nickel contamination between the Tubac and Chavez Siding collection sites as indicated by significantly higher concentrations of those metals in desert suckers from Chavez Siding, the most downstream site.
  - ! Chromium did not accumulate in killdeer liver samples.
  - ! Nickel was recovered in all desert suckers from Chavez Siding at higher than background concentrations, but below toxic levels.
  - ! Copper exceeded the NCBP 85<sup>th</sup> percentile in 50% of the dace samples and in 95% of the desert sucker samples. Because of its occurrence at relatively high levels at some sites, and its propensity to interact with other compounds and elements, copper remains a contaminant of concern.
  - ! Current levels of organochlorine compounds do not present a threat to fish survival and reproduction nor should current residues present a bioconcentration hazard to upper trophic level species that consume a large proportion of fish in their diet. DDT family compounds were not detected in fish from upstream locations. A possible source of DDT may be effluent from the NIWWTP; but more likely, the source is related to runoff/drainage from contaminated soils downstream from the plant as indicated by increasing DDT/DDE concentrations with increasing distance from the plant.
  - ! Four of eight killdeer carcasses contained DDE at levels associated with impaired reproduction. Current residues represent a hazard to predatory birds that feed on killdeer.
  - ! Concentrations of all metals in killdeer livers were within the normal or background range. Metals do not appear to pose a hazard to killdeer survival or reproduction.

## RECOMMENDATIONS

The NIWWTP should be upgraded to reduce ammonia concentrations to levels that are nontoxic to invertebrates and fish. An upgrade is scheduled for completion by March 31, 2002. We recommend and encourage USIBWC to move forward as soon as possible and upgrade the treatment plant to lower the concentrations of ammonia and improve overall water quality in the Santa Cruz River.

We also recommend initiation of a follow-up Fish and Wildlife Service investigation within one year following completion of treatment plant facility improvements. In addition to organochlorine and metal determinations, the new study should be expanded to include assessments of petroleum hydrocarbons, dioxins, PAHs, and other potentially harmful compounds.

NIWWTP is operating in compliance with its NPDES permit regarding acute and chronic tests. It is clear that current permit provisions are not protective of the environment as evidenced by several km of river almost devoid of fish and invertebrates below the treatment plant outfall. Laboratory tests confirmed that treatment plant effluent is chronically toxic to fish. The current "toxicity trigger" is based on acute toxicity; we recommend that chronic toxicity be given equal consideration in future permit provisions.

Field measurements of temperature and specific conductance within a 1000 meter section of the Santa Cruz River near Tubac indicated a localized area of possible groundwater inflow (Gebler 1998). Chromium, nickel, and DDT/DDE were highest in fish collected downstream from the Tubac site. Additional research is needed in this area to identify potential point- source(s) of elevated chromium, nickel, and DDT/DDE contamination.

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Table 1. Sample collection sites, Santa Cruz River, 1997

Site name	Latitude	Longitude	Approx. distance from NIWWTP <sup>1</sup>		Location description
			Km	Miles	
Border	N 31°20'39"	W 110°51'05"	23.7	14.7	0.8 km (½ mile) stretch of river north of international boundary
Nogales Wash	N 31°25'47"	W 110°57'38"	3.4	2.1	Nogales Wash south of Ruby Road
NIWWTP <sup>2</sup>	N 31°26'10"	W 110°56'30"	0.0	0.0	Nogales International Wastewater Treatment Plant
Rio Rico Bridge	N 31°28'10"	W 110°59'33"	2.7	1.7	Santa Cruz River downstream from Rio Rico Bridge
Rio Rico North	N 31°32'11"	W 111°01'19"	7.7	4.8	Appx. 1 km (¾ mile) downstream from Peck's Canyon
Santa Gertrudis	N 31°34'35"	W 111°02'48"	14.6	9.1	About 0.8 km (½ mile) upstream from Carmen
Tubac	N 31°36'33"	W 111°02'20"	18.2	11.3	Appx 0.4 km (¼ mile) upstream from Tubac Bridge
Chavez Siding	N 31°38'30"	W 111°02'33"	22.5	14.0	Santa Cruz River downstream of Chavez Siding Road

<sup>1</sup>Distance from Nogales International Wastewater Treatment Plant was estimated from a map and represents straight-line mileage, not river miles.

<sup>2</sup>The Nogales International Wastewater Treatment Plant was not a collection site. It is included in this table to provide a frame of reference to the other collection sites.

Table 2. Santa Cruz River water quality parameters, May 30, 1997

Site No.	Site Name	Un-ionized Ammonia (mg/L)	Std. Unit pH	Residual Chlorine (mg/L)	Water Temp. (°C)
1	Border	NA <sup>1</sup>	NA	NA	NA
2	Nogales Wash	<0.01	7.9	<0.05	20.5
----	NIWWTP <sup>2</sup>	----	----	----	----
3	Rio Rico Bridge	0.49	7.8	<0.05	23.3
4	Rio Rico North	0.23	7.5	<0.05	23.8
5	Santa Gertrudis	0.03	7.6	<0.05	23.8
6	Tubac	<0.01	7.4	<0.05	23.8
7	Chavez Siding	NA	NA	NA	NA

<sup>1</sup>NA = Data not available. This segment of the Santa Cruz River was dry during the collection period.

<sup>2</sup>NIWWTP = Nogales International Wastewater Treatment Plant. This site was not a sampling location. It is included in the table to provide a frame of reference to other collection sites.



Table 3. Metals in sediment collected from the Santa Cruz River, Arizona, 1997

Site	Contaminant concentration $\mu\text{g/g}$ dry weight <sup>1</sup>						
	As	Cd	Cr	Cu	Ni	Pb	Zn
lowest/highest toxic threshold <sup>2</sup>	6/ 33	0.6/ 10	26/ 110	16/ 110	16/ 75	31/ 250	120/ 820
Border	1.68	0.23	3.04	7.88	3.87	5.81	25.4
Nogales Wash	6.12	0.13	149.00	6.42	11.30	7.63	19.5
Rio Rico Bridge	3.20	0.39	61.20	16.00	8.38	11.20	40.3
Santa Gertrudis	13.10	1.18	16.70	48.80	14.20	35.30	115.0
Tubac	12.10	1.06	38.60	45.40	12.40	32.40	98.1
Chavez Siding	3.40	0.20	37.60	9.39	8.16	9.99	23.8

<sup>1</sup>A suitable sediment sample could not be obtained from the Rio Rico North site. Only the sample from Santa Gertrudis contained mercury (0.11  $\mu\text{g/g}$ ). Selenium was not detected in any samples at a lower limit of detection of 0.51  $\mu\text{g/g}$ .

<sup>2</sup>Data based on Persaud et al. 1993.

Table 4. Metals in invertebrates collected from the Santa Cruz River, Arizona, 1997

Sample and area collected	Contaminant concentration $\mu\text{g/g}$ dry weight									Prcent moist
	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn	
<i>Dragonfly larvae</i>										
Border	3.33	0.42	35.40	22.50	0.14	8.73	1.90	1.35	73.3	74.0
Santa Gertrudis	2.49	0.34	26.80	22.00	0.14	6.81	2.96	2.07	92.1	75.2
Tubac	2.65	0.19	66.40	22.30	0.11	8.66	4.49	1.24	83.2	77.8
Chavez Siding	1.73	0.28	5.60	25.20	0.18	3.07	1.26	1.87	81.5	77.3
<i>Giant water bug</i>										
Border	1.63	0.47	12.70	29.80	0.32	4.36	<1.00	0.88	225.0	77.4
Nogales Wash	2.39	0.64	15.30	22.40	0.29	5.89	1.56	1.35	180.0	74.6
Rio Rico Bridge	0.81	0.31	8.66	15.40	0.25	6.01	2.86	1.47	174.0	79.6
Rio Rico North	1.21	0.19	7.97	15.60	0.24	3.84	1.08	2.22	197.0	73.8
Santa Gertrudis	0.60	0.80	6.91	42.00	0.16	2.69	1.54	0.96	191.0	78.5
Tubac	3.62	0.28	16.80	25.80	0.89	5.90	2.65	1.60	260.0	72.6
<i>Snail</i>										
Border	9.63	0.54	3.36	103.00	<0.10	3.19	8.99	1.31	28.0	70.2
Santa Gertrudis	5.68	1.32	4.10	129.00	<0.10	3.14	4.60	1.20	48.3	69.0
Chavez Siding	6.96	0.53	9.20	89.90	0.15	6.90	8.69	1.14	73.9	75.5

Table 5. Comparison of fish species abundance at selected sampling sites, Santa Cruz River, Arizona, 1997

Site name	Approx. distance from NIWWTP <sup>1</sup>		No. sample efforts	Total shock time (sec)	Longfin dace	Desert sucker	Sonora sucker	Gila top-minnow	Mosquito-fish
	km	mi							
Border	<del>23.7</del>	<del>14.7</del>	1	65	232	-0-	-0-	-0-	-0-
Nogales Wash	3.4	2.1	3	517	473	17	-0-	-0-	-0-
NIWWTP <sup>1</sup>	NA	NA	NA	NA	NA	NA	NA	NA	NA
Rio Rico Bridge	2.7	1.7	3	1,030	9	-0-	-0-	-0-	1
Rio Rico North	7.7	4.8	4	2,012	14	-0-	-0-	17	1
Santa Gertrudis	14.6	9.1	3	1,378	318	86	4	P <sup>2</sup>	-0-
Tubac	18.2	11.3	4	2,317	322	22+	-0-	166+	-0-
Chavez Siding	22.5	14.0	3	1,081	547	47	4	30+	P

<sup>1</sup>The river at the NIWWTP was not sampled for fish. This location is included to provide a frame of reference for other sites.

<sup>2</sup>P = Present. Individuals were present but numbers were not quantified.

Table 6. Relative abundance of longfin dace at selected sampling sites, Santa Cruz River, Arizona, 1997

Site name	Approx. distance from NIWWTP <sup>1</sup>		No. of sample efforts	Total shock time (sec)	Total indiv.	Individuals per minute
	km	mi				
Border	23.7	14.7	1	65	232	214.2
Nogales Wash	3.4	2.1	3	517	473	54.9
NIWWTP <sup>2</sup>	NA	NA	NA	NA	NA	NA
Rio Rico Bridge	2.7	1.7	3	1,030	9	0.52
Rio Rico North	7.7	4.8	5	2,012	14	0.42
Santa Gertrudis	14.6	9.1	3	1,378	318	13.8
Tubac	18.2	11.3	4	2,317	322	8.3
Chavez Siding	22.5	14.0	3	1,081	547	30.4

<sup>1</sup>NIWWTP = Nogales International Wastewater Treatment Plant.

<sup>2</sup>The NIWWTP was not a collection site. It is included in this table to provide a frame of reference for the other collection sites.

Table 7. Proportion of longfin dace with anomalies at selected sampling sites Santa Cruz River, Arizona, 1997

Site name	Approx. distance from NIWWTP <sup>1</sup>		Total number of individuals examined <sup>2</sup>	Abnormal	
	km	mi		No.	Percent
Border	23.7	17.7	232	-0-	-0-
Nogales Wash	3.4	2.1	221	-0-	-0-
NIWWTP <sup>3</sup>	NA	NA	NA	NA	NA
Rio Rico Bridge	2.7	1.7	9	-0-	-0-
Rio Rico North	7.7	4.8	11	1	9.1
Santa Gertrudis	14.6	9.1	200	5	2.5
Tubac	18.2	11.3	185	10	5.4
Chavez Siding	22.5	14.0	547	32	5.9

<sup>1</sup>NIWWTP = Nogales International Wastewater Treatment Plant.

<sup>2</sup>The total number of individuals examined differs from the total captured (Table 6) because anomalies were not quantified on the first collecting trip of the season.

<sup>3</sup>The Nogales International Wastewater Treatment Plant was not a collection site. It is included in this table to provide a frame of reference for the other collection sites.

Table 8. Organochlorine compounds in normal and abnormal longfin dace collected from the Santa Cruz River, Arizona, 1997

Sample and area	N <sup>2</sup>	Concentration (µg/g wet weight <sup>1</sup> )						
		p,p' - DDE	p,p' - DDD	Total chlor	BHC	Total PCB	Moist (%)	Lipid (%)
NCBP 85th <sup>3</sup>	NA <sup>4</sup>	0.33	NC <sup>5</sup>	0.17	NC	0.80	NA	NA
<u>Normal</u>								
Border	10	ND <sup>6</sup>	ND	ND	ND	ND	77.5	3.21
Nogales Wash	10	0.04	ND	0.02	ND	0.01	77.5	2.84
Rio Rico	5	0.05	0.03	0.01	ND	ND	76.5	2.79
Santa	10	0.12	0.12	0.12	0.01	ND	69.5	12.20
Tubac	10	0.11	0.11	0.10	0.02	ND	70.5	11.30
Chavez Siding	10	0.10	0.09	0.08	ND	0.08	73.0	7.36
<u>Abnormal</u>								
Santa	5	0.12	0.11	0.09	ND	ND	68.5	9.89
Tubac	5	0.11	0.11	0.12	0.01	ND	64.0	11.90
Chavez Siding	12	0.12	0.10	0.09	0.01	0.08	69.5	7.59

<sup>1</sup>One normal and one abnormal dace from Chavez Siding contained 0.01 µg/g dieldrin.

<sup>2</sup>N = number of individuals per composite sample.

<sup>3</sup>NCBP = National Contaminant Biomonitoring Program 85<sup>th</sup> percentile as calculated using data from Schmitt et al. 1990.

<sup>4</sup>NA =Data not available.

<sup>5</sup>NC = Not calculated.

<sup>6</sup>ND = Not detected. Lower limit of detection was 0.01 µg/g for insecticides and 0.05 for PCBs.

Table 9. Mean concentration of organochlorine compounds in normal and abnormal longfin dace collected from the Santa Cruz River, Arizona, 1997

Sample	N <sup>2</sup>	Concentration (µg/g wet weight) (n) <sup>1</sup>				
		p,p'-DDE	p,p'-DDD	Total chlordane	BHC	Total PCB
<u>Normal</u>						
Mean	6	0.05 (6)	0.03 (4)	0.03 (5)	--- (2)	--- (2)
Range		0.04-0.12	ND-0.12	0.01-0.10	ND-0.02	ND-0.10
<u>Abnormal</u>						
Mean	3	0.12 (3)	0.11 (3)	0.10 (3)	--- (2)	--- (1)
Range		0.11-0.12	0.10-0.11	0.09-0.12	ND-0.01	ND-0.08

<sup>1</sup>Geometric mean. n = number of samples with detectible residues.

<sup>2</sup>N = number of fish per sample.

Table 10. Organochlorine compounds in individual whole body desert suckers collected from the Santa Cruz River, Arizona, 1997

Site and sample No. <sup>1</sup>	Organochlorine concentration, µg/g wet weight						Prcent moist	Prcent lipid
	p,p'-DDE	p,p'-DDD	p,p'-DDT	Chlor-dane	Gamma BHC	Total PCB		
NCBP 85th <sup>2</sup> <u>Nogales W.</u>	0.33	NC <sup>3</sup>	0.03	0.17	NC	0.80	NA <sup>4</sup>	NA
DS1	0.03	<0.01	<0.10	0.04	<0.10	0.12	77.0	1.73
DS2	0.03	<0.01	<0.10	0.02	<0.01	0.10	77.0	1.81
DS3	0.01	<0.01	<0.10	0.02	<0.01	0.07	75.5	2.76
DS4	0.02	<0.01	<0.10	0.02	<0.01	0.08	75.0	2.13
DS5	0.03	<0.01	<0.10	0.03	<0.01	0.11	77.5	2.69
<u>Santa G.</u>								
DS1	0.07	0.06	<0.01	0.12	<0.01	<0.05	71.0	7.04
DS2	0.07	0.07	<0.01	0.10	0.01	<0.05	73.0	7.83
DS3	0.09	0.07	0.01	0.14	0.04	<0.05	71.5	6.66
DS4	0.06	0.07	<0.01	0.09	0.04	<0.05	70.5	8.84
DS5	0.10	0.09	<0.01	0.12	<0.01	<0.05	73.5	5.10
<u>Tubac</u>								
DS1	0.06	0.03	<0.01	0.04	<0.01	<0.05	74.5	3.67
DS2	0.08	0.07	<0.01	0.10	<0.01	<0.05	74.5	5.24
DS3	0.11	0.06	<0.01	0.10	<0.01	<0.05	73.5	5.95
DS4	0.06	0.06	<0.01	0.10	<0.01	<0.05	72.5	5.92
DS5	0.07	0.10	<0.01	0.10	0.01	<0.05	71.0	7.32
<u>Chavez S.</u>								
DS1	0.06	0.07	<0.01	0.09	0.01	<0.05	70.5	9.42
DS2	0.05	0.06	0.02	0.06	<0.01	<0.05	70.5	5.67
DS3	0.06	0.06	0.02	0.06	<0.01	<0.05	71.5	6.89
DS4	0.04	0.05	0.01	0.09	<0.01	<0.05	70.5	7.10
DS5	0.07	0.09	<0.01	0.14	<0.01	0.07	75.0	4.71

<sup>1</sup>DS = Desert sucker.

<sup>2</sup>Calculated 85<sup>th</sup> percentile based on data in Schmitt et al. 1990.

<sup>3</sup>NC = Not calculated.

<sup>4</sup>NA = Data not available.



Table 11. Statistical comparison of organochlorine residues in individual whole body desert suckers collected from the Santa Cruz River, Arizona, 1997

Area	N <sup>2</sup>	Gmean concentration, µg/g dry weight (n) / range <sup>1</sup>			Percent lipid
		DDE	DDD	Chlordane	
Nogales Wash	5	0.02 (5) A <sup>3</sup> 0.01 - 0.03	---- (0) ND	0.02 (5) A 0.02 - 0.04	2.2 (5) A 1.73 - 2.76
Santa Gertrudis	5	0.08 (5) B 0.06 - 0.10	0.07 (5) A 0.06 - 0.09	0.11 (5) B 0.09 - 0.12	7.1 (5) B 5.10 - 8.84
Tubac	5	0.07 (5) B 0.06 - 0.11	0.06 (5) A 0.03 - 0.10	0.08 (5) B 0.04 - 0.10	5.6 (5) B 3.67 - 7.32
Chavez Siding	5	0.06 (5) B 0.04 - 0.07	0.06 (5) A 0.05 - 0.09	0.08 (5) B 0.06 - 0.14	6.8 (5) B 4.71 - 9.42

<sup>1</sup>Geometric mean concentration, (n) = number of samples with detectable residues, range = low and high concentrations.

<sup>2</sup>N= number of individuals analyzed from each site.

<sup>3</sup>Means sharing the same letter are not significantly different from one another (P> 0.05).

Table 12. Metals in composite whole body samples of longfin dace collected from the Santa Cruz River, Arizona, 1997

Sample and area	N	Concentration (µg/g wet weight) <sup>1</sup>								Prent moist
		Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn	
NCBP 85th <sup>2</sup>	NA	0.05	NA	1.0	0.17	NA	0.22	0.73	34.2	NA
<i>Normal</i>										
Border	10	0.06	7.99	1.12	0.05	0.76	<0.26	0.70	36.1	74.7
Nogales Wash	10	0.05	0.58	1.04	0.05	0.16	0.27	0.51	43.1	77.0
Rio Rico N.	7	0.04	6.76	1.02	0.13	0.53	0.26	0.51	53.6	76.0
Santa Gertrudis	10	0.04	1.06	0.82	0.16	<0.16	<0.32	0.67	42.4	68.1
Tubac	10	<0.03	0.28	0.89	0.16	<0.16	<0.37	0.63	36.7	68.6
Chavez Siding	10	0.04	0.57	0.95	0.50	0.16	0.50	0.55	32.6	73.6
<i>Abnormal</i>										
Santa Gertrudis	5	0.04	0.20	0.89	0.17	<0.15	0.52	.074	41.6	70.2
Tubac	6	0.04	0.29	1.11	0.19	<0.19	<0.37	0.80	51.5	62.6
Chavez Siding	12	<0.03	5.54	1.06	0.14	0.53	<0.30	0.54	43.2	68.4

<sup>1</sup>Arsenic was not detected in any samples at a lower limit of detection (LLOD) of 0.51µg/g.

<sup>2</sup>NCBP 85<sup>th</sup> = National Contaminant Biomonitoring Program 85<sup>th</sup> percentile (Schmitt and Brumbaugh 1990)

Table 13. Metals in desert suckers collected from the Santa Cruz River, Arizona, 1997

Site and sample <sup>1</sup>	Concentration $\mu\text{g/g}$ wet weight									Prct moist
	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn	
NCBP 85th <sup>2</sup>	0.27	0.05	NA	1.0	0.17	NA	0.22	0.73	34.2	NA
<i>Nogales W.</i>										
DS1	<0.12	0.03	3.72	1.05	0.05	0.68	0.38	0.20	32.0	76.3
DS2	<0.12	<0.12	1.29	1.10	0.04	0.51	0.26	0.27	25.1	76.5
DS3	<0.13	0.06	2.65	1.36	0.04	0.94	<0.25	0.28	41.4	74.8
DS4	<0.13	0.04	2.93	1.24	0.04	0.85	<0.26	0.19	23.3	74.4
DS5	<0.13	0.03	1.53	1.10	0.03	0.43	<0.26	0.24	46.1	74.8
<i>Santa G.</i>										
DS1	0.14	0.03	1.45	1.43	0.06	0.43	<0.28	0.24	23.9	72.5
DS2	<0.16	<0.03	2.78	1.00	0.10	0.37	<0.32	0.41	27.1	68.2
DS3	<0.14	0.04	2.76	1.22	0.09	0.50	<0.28	0.28	21.5	72.0
DS4	<0.14	<0.03	6.29	1.20	0.13	0.72	0.30	0.30	27.1	73.2
DS5	0.18	0.04	2.37	1.11	0.07	0.44	0.36	0.29	23.3	71.2
<i>Tubac</i>										
DS1	<0.14	0.03	5.60	1.06	0.10	0.47	0.33	0.38	27.6	71.2
DS2	<0.14	<0.03	4.24	1.40	0.07	0.46	0.48	0.31	25.2	72.0
DS3	0.15	0.04	2.94	1.45	0.13	0.58	0.36	0.32	24.1	72.4
DS4	<0.15	<0.03	4.10	1.15	0.09	0.39	<0.30	0.28	26.7	70.2
DS5	<0.15	<0.03	4.17	1.03	0.10	0.76	<0.30	0.22	22.9	70.2
<i>Chavez S.</i>										
DS1	<0.16	<0.03	8.83	0.99	0.08	2.26	<0.32	0.21	22.2	67.3
DS2	<0.13	<0.03	7.66	1.02	0.08	1.55	0.49	<0.13	26.7	74.0
DS3	0.17	0.04	11.70	1.13	0.09	3.14	<0.28	0.22	25.2	71.7
DS4	<0.14	<0.03	11.80	1.13	0.12	2.51	0.29	0.29	20.2	72.2
DS5	0.29	<0.03	13.60	1.24	0.06	4.98	<0.32	0.29	20.5	68.2

<sup>1</sup>DS = Desert sucker.

<sup>2</sup>NCBP 85<sup>th</sup> = National Contaminant Biomonitoring Program 85<sup>th</sup> percentile (Schmitt and Brumbaugh 1990)

Table 14. Geometric mean concentration of metals in whole body desert suckers collected from the Santa Cruz River, Arizona, 1997

Area <sup>1</sup>	N <sup>2</sup>	Geometric mean concentration, µg/g dry weight (n) / range <sup>1</sup>								
		Al	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn
Nogales Wash	5	294. (5) A <sup>3</sup> 188-618	0.08 (4) A ND-0.22	9.12 (5) A 5.50-15.70	4.70 (5) A 4.36-5.43	0.16 (5) A 0.11-0.20	2.65 (5) A 1.68-3.72	---- (2) ND-1.62	0.95 (5) A 0.86-1.17	131. (5) A 91.2 - 183
Santa Gertrudis	5	190. (5) A 42-326	0.13 (3) A ND-0.14	9.75 (5) A 5.28-23.50	4.14 (5) A 3.14-5.19	0.31 (5) B 0.24-0.50	1.68 (5) A 1.16-2.68	---- (2) ND-1.24	1.05 (5) A 0.89-1.30	86. (5) B 76.7-101.
Tubac	5	275. (5) A 193-468	---- (2) ND-0.13	14.29 (5) A 10.60-19.4	4.19 (5) A 3.43-5.26	0.33 (5) B 0.24-0.46	1.79 (5) A 1.30-2.52	1.36 (3) ND-1.71	1.02 (5) A 0.72-1.33	88. (5) B 76.4-95.7
Chavez Siding	5	265. (5) A 168-399	---- (2) ND-0.15	35.92 (5) B 27.0-42.9	3.77 (5) A 3.03-4.08	0.28 (5) B 0.20-0.38	9.16 (5) B 5.94-11.1	---- (2) ND-1.88	0.82 (4) A ND-1.03	83. (5) B 67.3-74.0

<sup>1</sup>Geometric mean concentration, (n) = number of samples with detectable residues, range = low and high concentrations. Arsenic was detected in fewer than one-half of the samples at each location.

<sup>2</sup>N= number of individual fish analyzed at each site.

<sup>3</sup>Means sharing the same letter are not significantly different from one another (P > 0.05).

Table 15. Metals in composite samples of killdeer liver tissues, Santa Cruz River, Arizona, 1997

Area	N <sup>2</sup>	Concentration, µg/g dry weight <sup>1</sup>					
		Al	Cd	Cu	Hg	Se	Zn
Border	3	7.94	1.43	15.8	0.48	9.46	71.1
Rio Rico North	5	22.90	2.33	22.3	0.47	8.66	85.5

<sup>1</sup>Arsenic, boron, beryllium, chromium, nickel, lead, and vanadium were not detected.

<sup>2</sup>N = Number of individual livers in each composite sample.

Table 16. Organochlorine compounds in killdeer carcasses collected from selected sites from the Santa Cruz River, Arizona, 1997

Area and sample	Organochlorine compound, $\mu\text{g/g}$ wet weight						
	p,p'-DDE	p,p'-DDD	p,p'-DDT	Total Chlor	Diel-drin	Hept epox.	Total PCB
<u>Border</u>							
Sample 1	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.05
Sample 2	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.05
Sample 3	0.36	<0.01	<0.01	0.01	<0.01	<0.01	<0.05
<u>Rio Rico N.</u>							
Sample 1	8.5	0.02	<0.01	0.04	0.01	<0.01	0.09
Sample 2	18.0	0.01	0.12	0.07	0.03	<0.12	0.10
Sample 3	28.0	<0.01	0.21	0.13	<0.06	<0.21	0.17
Sample 4	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.05
Sample 5	4.7	<0.01	<0.01	0.07	0.01	<0.01	0.18

Table 17. Effects of Nogales International Wastewater Treatment Plant effluent on fathead minnows

Percent mortality after 96-hours exposure to 100% effluent <sup>1</sup>			
Month	1997	1998	1999
January	100	97.5	NA <sup>2</sup>
February	85	57.5	NA
March	100	85	55
April	100	100	45
May	82	22.5	45
June	80	22.5	62.5
July	100	100	40
August	100	67.5	NA
September	100	65	NA
October	67.5	40	NA
November	100	38.5	NA
December	75	80	NA

<sup>1</sup>Data from Aquatic Consulting and Testing, Inc. Temperature averaged about 25 °C and pH averaged 7.8.

<sup>2</sup>NA = Data not available.

Appendix 1. A complete listing of trace elements and heavy metals in sediment collected from the Santa Cruz River, Arizona, 1997

Site <sup>2</sup>	Contaminant concentration, $\mu\text{g}$ dry weight <sup>1</sup>																
	Al	As	B	Ba	Be	Cd	Cl	Cu	Fe	Mg	Mn	Mo	Ni	Pb	Si	V	Zn
Border	4,728	1.68	3.19	77.3	0.24	0.23	3.04	7.88	3,539	1,376	174	<0.50	3.87	5.81	34.5	9.05	25.4
Nogales Wash	2,402	6.12	5.22	61.9	0.25	0.13	149.	6.42	4,502	722	374	0.59	11.30	7.63	18.6	7.39	19.5
Rio Rico Bridge	3,417	3.20	3.64	52.4	0.29	0.39	61.2	16.0	5,393	1,576	193	<0.50	8.38	11.2	22.3	9.95	40.3
Santa Gertrudis	13,940	13.10	10.5	210.	1.29	1.18	16.7	48.8	18,460	3,939	944	0.77	14.20	35.3	96.6	18.6	115.
Tubac	9,874	12.10	8.51	138.	0.97	1.06	38.6	45.4	15,690	3,237	531	0.87	12.40	32.4	61.0	19.2	98.1
Chaves Siding	3,359	3.40	4.40	80.3	0.25	0.20	37.6	9.39	4,745	1,384	363	<0.51	8.16	9.99	32.6	9.58	23.8

<sup>1</sup>Only the sample (Santa Gertrudis) contained mercury (0.11  $\mu\text{g}/\text{g}$ ). Selenium was not detected in any samples at a lower limit of detection of 0.51  $\mu\text{g}/\text{g}$ .

<sup>2</sup>A suitable sediment sample was not obtained from the Rio Rico North site.



Appendix 2. Trace elements and heavy metals in composite whole body samples of longfin dace collected from the Santa Cruz River, Arizona, 1997

Sample and area	Concentration, µg/g wet weight <sup>1</sup>																
	N	Al	Ba	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Ni	Pb	Se	Sr	V	Zn	
NCBP 85 <sup>th</sup>	NA	NA	NA	NA	NA	NA	1.0	NA	0.17	NA	NA	NA	0.22	0.73	NA	NA	34.2
<u>Normal</u>																	
Border	10	42.9	2.13	0.06	7.99	1.12	109	0.05	365	25.00	0.76	<0.26	0.70	8.37	0.22	36.1	
Noglaes Wash	10	19.5	2.67	0.05	0.58	1.04	39.5	0.05	357	13.70	0.16	0.27	0.51	8.70	<0.12	43.1	
Rio Rico N.	7	14.5	2.43	0.04	6.76	1.02	81.5	0.13	415	13.60	0.53	0.26	0.51	11.9	<0.12	53.6	
Santa Gertrudis	10	11.1	1.22	0.04	1.06	0.82	39.8	0.16	288	4.71	<0.16	<0.32	0.67	8.45	<0.16	42.4	
Tubac	10	25.5	1.43	<0.03	0.28	0.89	46.6	0.16	314	4.82	<0.16	<0.37	0.63	8.52	<0.16	36.7	
Chavez Siding	10	27.2	1.44	0.04	0.57	0.95	50.5	0.50	299	4.82	0.16	0.50	0.55	8.19	<0.13	32.6	
<u>Abnormal</u>																	
Santa Gertrudis	5	15.4	1.34	0.04	0.20	0.89	39.3	0.17	302	4.25	<0.15	0.52	0.74	8.90	<0.15	41.6	
Tubac	6	14.7	1.67	0.04	0.29	1.11	39.9	0.19	387	6.61	<0.19	<0.37	0.80	9.85	<0.19	51.5	
Chavez Siding	12	37.7	4.46	<0.03	5.54	1.06	101	0.14	391	8.07	0.53	<0.30	0.54	17.8	0.18	43.2	

<sup>1</sup>Arsenic, beryllium, boron, and molybdenum were not detected in any samples. The lower limit of detection (LLOD) was 0.51 for arsenic, 0.03, for beryllium, 0.75 for boron, and 0.19 for molybdenum.

Appendix 3. Trace elements and heavy metals in desert suckers collected from the Santa Cruz River, Arizona, 1997

Site and sample <sup>1</sup>	Concentration, µg/g wet weight															
	Al	As	Ba	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Ni	Pb	Se	Sr	V	Zn
<u>Nogales W.</u>																
DS1	54.0	<0.12	6.09	0.03	3.72	1.05	88.1	0.05	470.	92.9	0.68	0.38	0.20	23.5	0.25	32.0
DS2	79.4	<0.12	5.44	<0.02	1.29	1.10	104.	0.04	388.	35.6	0.51	0.26	0.27	15.1	0.25	25.1
DS3	155.	<0.13	9.08	0.06	2.65	1.36	176.	0.04	526.	74.0	0.94	<0.25	0.28	23.3	0.42	41.4
DS4	63.8	<0.13	6.29	0.04	2.93	1.24	98.3	0.04	421.	50.0	0.85	<0.26	0.19	18.7	0.25	23.3
DS5	47.5	<0.13	9.34	0.03	1.53	1.10	61.5	0.03	394.	31.9	0.43	<0.26	0.24	19.0	0.17	46.1
<u>Santa G.</u>																
DS1	89.6	0.14	2.63	0.03	1.45	1.43	137.	0.06	355.	17.6	0.43	<0.28	0.24	11.7	0.81	23.9
DS2	13.3	<0.16	1.98	<0.03	2.78	1.00	42.2	0.10	334.	9.6	0.37	<0.32	0.41	17.4	<0.16	27.1
DS3	67.8	<0.14	2.96	0.04	2.76	1.22	109.	0.09	355.	12.2	0.50	<0.28	0.28	18.7	0.21	21.5
DS4	79.6	<0.14	2.69	<0.03	6.29	1.20	155.	0.13	389.	11.8	0.72	0.30	0.30	17.6	0.31	27.1
DS5	71.6	0.18	3.00	0.04	2.37	1.11	118.	0.07	355.	14.7	0.44	.036	0.29	19.0	0.24	23.3
<u>Tubac</u>																
DS1	60.2	<0.14	2.96	0.03	5.60	1.06	111.	0.10	417.	27.5	0.47	0.33	0.38	22.8	0.22	27.6
DS2	92.9	<0.14	3.56	<0.03	4.24	1.40	152.	0.07	355.	27.5	0.46	0.48	0.31	19.3	0.26	25.2
DS3	130.	0.15	2.93	0.04	2.94	1.45	197.	0.13	450.	23.8	0.58	0.36	0.32	18.1	0.36	24.1
DS4	75.4	<0.15	3.02	<0.03	4.10	1.15	125.	0.09	365.	19.1	0.39	<0.30	0.28	18.1	0.21	26.7
DS5	57.8	<0.15	2.94	<0.03	4.17	1.03	108.	0.10	366.	16.6	0.76	<0.30	0.22	19.1	0.19	22.9
<u>Chavez S.</u>																
DS1	55.1	<0.16	2.57	<0.03	8.83	0.99	140.	0.08	310.	15.2	2.26	<0.32	0.21	17.3	0.23	22.2
DS2	56.5	<0.13	2.85	<0.03	7.66	1.02	118.	0.08	399.	14.6	1.55	0.49	<0.13	23.7	0.23	26.7
DS3	113.	0.17	4.66	0.04	11.70	1.13	218.	0.09	337.	15.2	3.14	<0.28	0.22	19.0	0.41	25.2
DS4	63.3	<0.14	2.01	<0.03	11.80	1.13	167.	0.12	300.	11.0	2.51	0.29	0.29	13.1	0.23	20.2
DS5	126.	0.29	3.22	<0.03	13.60	1.24	238.	0.06	273.	19.1	4.98	<0.32	0.29	21.2	0.41	20.5

<sup>1</sup>DS = Desert sucker.

Appendix 4. Trace elements and heavy metals in killdeer carcass tissues, Santa Cruz River, Arizona, 1997<sup>1</sup>

Concentration in µg/g dry weight <sup>2</sup>															
Area	Al	Ba	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Mo	Ni	Pb	Se	Sr	Zn
Border															
1	32.8	5.95	0.25	88.4	5.37	909.	0.12	720.	15.1	0.91	5.06	2.60	2.73	22.0	63.1
2	32.8	2.11	<0.10	168.	6.99	1494.	0.20	761.	22.9	1.93	15.7	1.39	1.13	14.0	75.6
3	42.1	4.89	0.11	77.2	6.74	864	0.19	739.	13.3	0.88	5.55	<1.03	2.50	16.1	73.8
RRN															
1	129.	5.48	0.30	5.48	8.47	342	0.22	1080.	5.78	0.57	1.38	1.16	2.60	30.6	90.9
2	55.2	3.96	0.30	9.51	7.26	267	0.20	899.	3.86	<0.50	0.84	<1.00	1.83	23.2	69.9
3	40.7	4.13	<0.10	27.0	6.44	394	0.15	922.	5.42	<0.51	0.81	1.30	1.68	26.6	71.8
4	70.9	4.10	0.26	12.7	5.37	264	<0.10	728.	4.76	<0.51	0.61	1.11	2.41	15.2	43.4
5	111.	3.36	<0.10	62.9	6.76	818	0.14	873.	17.9	0.96	1.40	1.10	1.48	16.8	72.1

<sup>1</sup>Plucked carcass with bill, wingtips, feet, gastrointestinal tract and liver removed.

<sup>2</sup>Elements not detected in any samples: arsenic (LLOD = 0.51) and boron (LLOD = 2.05). Vanadium was detected in Border sample 2 at 0.92 µg/g, LLOD = 0.5.

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