SAN BERNARDINO NATIONAL WILDLIFE REFUGE,

A CASE STUDY OF ACID RAIN IN THE SOUTHWEST.

The San Bernardino National Wildlife Refuge was established in 1982 for the protection and management of endangered desert fishes which are indigenous to the Rio Yaqui drainage. The 2,309-acre refuge is located on the United States-Mexico border 16 miles east of Douglas, Arizona. Collectively, copper smelter emissions in southern Arizona and northern Sonora have a created a regional atmospheric condition where mean annual precipitation pH is 4.7 to 5.0. Background chemistries are largely unavailable and influence of both nonferrous smelter emissions and current agricultural practices and pesticide use remain unexplored. During May and June 1987 water chemistry was determined on-site at each of 13 locations within the refuge (including Leslie Creek) and sediment and selected tissue samples were collected for trace metals and pesticide analysis. Overall, refuge waters were virtually absent of dissolved trace metals and spring chemistries were relatively consistent due to their presumable origin from a common aquifer. Alkalinity exceeded the EPA recommended minimum of 20 mg/1 for freshwater aquatic life by a factor of 10 to 18 and appears to be the mitigating factor which disallows acidic deposition to adversely manifest itself in the aquatic ecosystem. Biota are probably the best integrative indicator of watershed quality, and its ability to neutralize acid. Trace metal residues in tissue matrices were mixed in their occurrence, especially for frogs. However, no evidence of acid-stress in resident organisms on the refuge was observed. Native fish populations exhibited no symptoms of lack of recruitment, incidence of morphological abnormalities, or subnormal growth. Likewise, bullfrogs flourish throughout the refuge and exhibited little in regard to trace metal body burdens. Periodic biological and chemical monitoring is the recommended course of action to evaluate refuge condition and trend relative to environmental quality.

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SAN BERNARDINO NATIONAL WILDLIFE REFUGE

CONTAMINANT STUDY

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Introduction

The San Bernardino National Wiidlife Refuge (Refuge) was established in 1982 for the protection and management of endangered desert fishes which are indigenous to the Rio Yaqui drainage. The 2,309-acre refuge is located on the United States-Mexico border i6 miles east of Douglas. Leslie Canyon (1240 acres) was acquired by the Arizona Chapter of The Nature Conservancy and transferred to the San Bernardino Refuge in May 1988. Leslie Creek is located approximately 17 miles north of Douglas and contains similar Rio Yaqui forms as San Bernardino Refuge (Table 1).

Copper smelter operations in northern Sonora (Cananea and Nacozari) and former operations in southeast Arizona (Douglas) have created acidic atmospheric conditions due to heavy sulfur dioxide (SO_2) emissions (Figure 1). Arizona smelters are currently considered the single largest regional source of SO_2 emissions in the western United States. The San Bernardino Refuge is located within a geographic area where mean annual precipitation pH is 4.7 to 5.0 and is commonly referred to as the “gray triangle” due to the regional haze that occurs there. No studies or routine monitoring to evaluate potential impacts of copper smelter emissions relative to adjacent biotic resources are avaiiable.

Oniy limited water quality information is available and is restricted to a single set of grab samples collected from six springs (Bunting, Cottonwood, Cienega, House, Bathouse, and East Border) on May 9, 1984. Collectively, San Bernardino springs were alkaline (pH 8.01 ± 0.12), clear (less than 1 NTU), moderately hard (92.4 ± 28.5 mg/l as $CaCO_3$), and very low in sulfate (9.1 ± 1.2 mg/l).[1] Alkalinity was considered adequate to maintain pH within tolerabie limits for aquatic life and capable of ameliorating heavy metal toxicity (215.5 ± 11.8 mg/l as $CaCO_3$). No trace metals analyses are available.

Background chemistries are largely unavailable and influence of both nonferrous smelter emissions (Douglas) and current agricultural practices and pesticide use (Mexico) remain unexplored. Reconnaissance monitoring at San Bernardino was identified as a priority need by the Division of Refuge Management in its summary of contaminant issues requiring management attention (U.S. Fish and Wildlife Service 1986). Objectives of the present study were to (1) develop and assess water chemistry information and (2) estabiish baseline organochlorine and metal data for resident biota within the San Bernardino Refuge (including Leslie Canyon).

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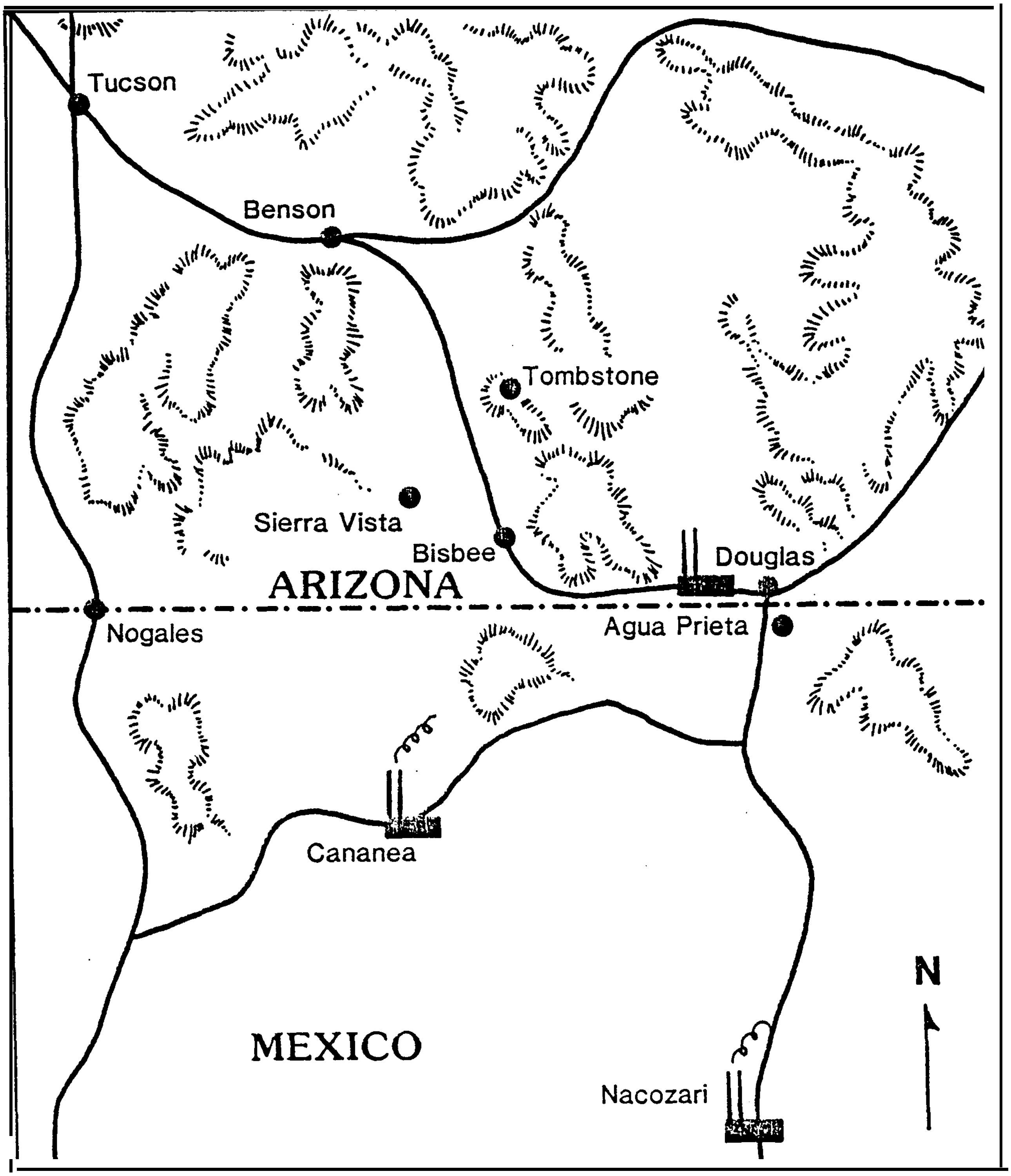
[1] Means foiiowed by ± one standard deviation, as used throughout text and tables.

TABLE 1. Rio Yaqui Fish Distribution, San Bernardino National Wildiife Refuge and Leslie Creek.

Common Name	Scientific Name	Status	Occurrence (X) San Bernardino	Occurrence (X) Leslie Creek
Roundtail chub	Gila robusta robusta		PR	
Yaqui chub	Gila purpurea	FE	X	X
Mexican stoneroller	Campostoma ornatum pricei	c2	X	
Beautiful shiner	Notropis formosus	FT	PR	
Longfin dace	Agosia chrysogaster		X	X
Yaqui catfish	Ictalurus pricei	FT	PR	
Yaqui sucker	Catostomus bernardini	C3(c)	PR	
Yaqui topminnow	Poeciliopsis ocidentalis sonoriensis	FE	X	X

FE Federally Endangered
FT Federally Threatened
C Candidate
PR Proposed for Reintroduction

Figure i. Copper Smelter Locations, Southeast Arizona and Northern Sonora.



Methods and Materials

Water chemistry (temperature, pH, dissoived oxygen, conductivity, orthophosphate, nitrate-nitrogen, total alkalinity, hardness, sulfate, and turbidity) were determined on-site at each of 13 locations (Figure 2) using a Hydrolab Surveyor II and Bausch and Lomb Mini-20 spectrophotometer. Additionally, water samples were fiitered on-site, acid preserved and submitted to the Arizona Game and Fish Department Water Quality Laboratory (Phoenix) for trace metal analysis (cadmium, calcium, copper, iron, lead, magnesium, manganese, mercury, potassium, selenium, silver, sodium, and zinc). Water quality parameters recommended by the U.S. Fish and Wildlife Service Acid Precipitation Mitigation Program were utilized to evaluate surface water impairment relative to their reception of acid deposition (Saunders et al. 1985).

Tissue (Yaqui chub [Gila purpurea], Yaqui topminnow [Poeciliopsis occidentalis sonoriensis] , longfin dace [Agosia chrvsogaster], and bullfrog [Rana catesbeiana]) and sediment samples were collected from House Pond, North Pond, Black Draw, and Lesiie Creek, depending on their availability. All tissue samples were collected as whole body composites of near equai length and weight for each species. Tissue samples were weighed and measured foilowing collection, quick frozen on-site, and later submitted to Mississippi State Chemical Laboratory (Starkville, Mississippi) for organochlorine pesticide analysis and to Environmental Trace Substances Research Center (Columbia, Missouri1 for trace metai analysis. All samples were coilected during May and June i987. Additionaliy, water, sediment, and tissue (Yaqui chub and builfrog) samples were simuitaneously coilected from House Pond for the Environmental Protection Agency (EPA), Region IX, Priority Poliutant Program.

Results

Water Quality

Water quality was, with few exceptions, within levels outlined for state surface water standards for the Whitewater Draw basin, a tributary of the Rio Yaqui (Arizona Administrative Code 1986). Protected uses designated for that watershed generally include aquatic and wildlife, domestic water source, full body contact (aquatic recreation), agricultural irrigation, and agricultural livestock watering. Dissolved oxygen appeared to be the only parameter that was consistently below the 6.0 mg/l state standard for aquatic and wildlife protection (Tabie 2). Dissolved oxygen at spring and pond locations averaged 5.87 ± 1.75 mg/l due to their measurement at the point of surface origin where emanating waters are derived from deoxygenated subterranean sources.

Figure 2. Water Chemistry Sample Sites, San Bernardino National Wiidlife Refuge, 1987.

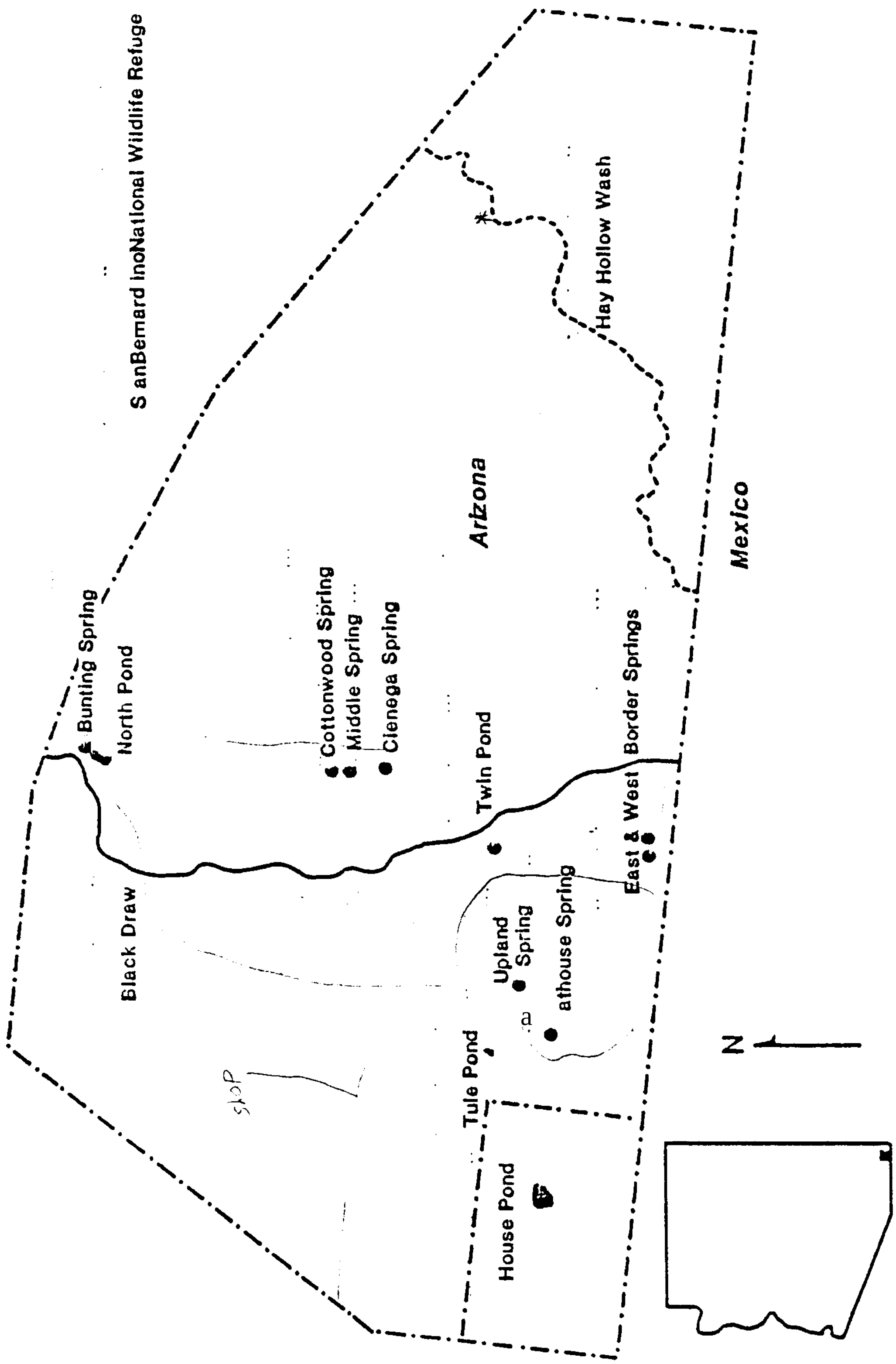


Table 2. Water Quality Data, San Bernardino National Wildlife Refuge, Arizona, June 1987. None detected= -0.99.

								Cations (mg/L)				Trace Metals (µg/L)				Anions (mg/L)			
Station	pH	Conductance (umhos/cm)	DO (mg/L)	AirTemp Celsius	H2OTemp Celsius	Turbidity (NTU)	Hardness (mg/L)	CA	MG	NA	K	FE	HG	PB	ZN	TotalAlk	NitrateN	Sulfate	Orthphos
Cienega	7.43	451	4.28	33.0	27.9	0.3	140	17.3	16.3	54.7	3.2	-0.99	-0.99	100.0	26.0	240	1.4	10	5.3
Middle	7.64	442	5.88	38.0	29.1	0.36	140	17.9	16.1	41.9	2.8	-0.99	1.72	-0.99	-0.99	240	1.4	10	7.0
Cottonwd	7.64	435	5.62	35.0	28.4	0.2	110	14.6	14.2	48.3	2.5	-0.99	-0.99	100.0	26.0	220	1.3	10	5.0
Bunting	7.84	424	3.50	34.0	29.0	0.52	100	12.7	12.5	52.4	2.9	-0.99	-0.99	-0.99	-0.99	200	1.5	10	4.67
NorthPond	8.57	424	5.65	32.0	28.3	0.7	100	11.9	12.6	61.1	2.5	-0.99	1.26	-0.99	-0.99	220	1.1	12	3.25
BlackDraw	7.05	799	1.79	26.0	21.6	0.3	320	34.2	47.4	61.7	10.1	-0.99	-0.99	-0.99	30.0	360	0.6	70	4.0
LeslieCrk	6.75	610	4.32	30.0	17.3	0.9	320	104.0	9.4	17.3	1.8	-0.99	-0.99	100.0	26.0	280	4.6	48	1.97
WstBorder	7.43	431	5.51	32.0	30.5	0.6	100	14.6	10.7	66.4	3.5	-0.99	-0.99	-0.99	-0.99	240	1.0	10	4.83
TwinPond	7.59	451	4.62	36.5	30.5	0.4	80	11.0	9.7	78.0	3.7	-0.99	-0.99	-0.99	26.0	240	1.2	15	7.17
Upland	8.09	513	4.47	35.0	32.3	0.5	40	4.6	3.1	105.0	3.6	-0.99	-0.99	-0.99	26.0	280	1.4	11	5.83
TulePond	7.14	476	8.14	37.0	24.2	2.4	200	18.7	33.1	16.6	9.6	60.0	-0.99	-0.99	26.0	260	0.45	12	5.33
Bathouse	8.36	441	8.14	36.0	32.8	0.2	60	6.9	6.1	87.3	3.7	-0.99	1.17	100.0	-0.99	240	2.2	10	5.0
HousePond	9.63	403	8.79	25.5	24.2	1.4	160	9.8	16.5	43.7	4.3	-0.99	1.43	-0.99	-0.99	220	0.30	14	0.67

Standard limnology was comparable to the previous results of 1984. In general, artesian springs were extremely simiiar in chemistry due to their presumabie origin from the same aquifer. Spring chemistries differed from those measured for the surface tributaries, i.e. Black Draw and Leslie Creek. Surface drainages had greater dissolved solute constituents and were, therefore, more highly conductive and harder waters than their spring counterparts (Table 2). For example, waters at Black Draw and Lesiie Creek were very hard (>300 mg/l as $CaCO_3$) compared to moderately hard waters of the eleven springs which measured 112 ± 46 mg/l as $CaCO_3$. Hardness in Leslie Creek was attributed to the prevalence of calcium cations in that system, whereas sodium was the dominant cation at all spring locations and Black Draw. Magnesium, calcium, and potassium contributed to the total hardness of San Bernardino waters, however, they were of lesser influence than sodium at these locations.

Spring water temperatures were consistently thermal (28.8 ± 2.8°C) at their origin and constantly clear (<1 NTU). Specific conductance varied little (403 to 513 µmho/cm) and averaged 445 ± 29 µmho/cm. Spring pH was consistently alkaline (range 7.14 - 9.63). High pH in House Pond is attributed to photosynthetic activity of pond autotrophs which are capable of reducing calcium by precipitation of carbonate and raising pH by removai of carbon dioxide, or in some cases, by production of hydroxyi ions. Low pH at Lesiie Creek presumabiy reflects the location of its measurement at its subsurface origin beiow the stone dam.

Total alkalinity was consistent for all spring sources tested and averaged 236 ± 22 mg/l as $CaCO_3$. All sample locations exhibited excellent buffering capacity relative to their ability to resist changes in pH and all alkalinity concentrations exceeded the recommended minimum standard of 20 mg/l as $CaCO_3$ (EPA 1986). Suifate concentrations were extremely low, i.e. 11 ± 2 mg/l, for desert aquatic systems. Sulfate occurs naturally in water, particularly in the American Southwest, as the result of weathering of calcium suifate deposits or metal suifides, e.g. pyrite. Sulfate is the most oxidized form of sulfur and generally is second to carbonate as a principle anion in freshwater and soil.

Typically, spring sources exhibit high (>16) nitrogen to phosphorus ratios, especially those associated with the Rio Yaqui basin (Grimm and Fisher 1986). Overall, nitrate-N averaged 1.2 ± 0.6 mg/l and ranged from 0 to 4.6 mg/l, however, vaiues varied much less for the San Bernadino artesian springs due to their common connection to a singie aquifer. Leslie Creek exhibited the highest nitrate-N concentration of all sites tested as it aiso did when 157 screams were examined statewide in 1979-81 (Ibid). Orthophosphate concentrations varied little for spring sources versus those measured at ponds and creeks. Overall, orthophosphate averaged 4.9 ± 1.8 mg/l and ranged from 0.57 to 7.17 mg/l. Collectively, phosphorus and nitrogen did not appear to be limiting nutrients for the Rio Yaqui basin. The lowest nitrate-N and orthophosphate values were measured at House Pond, 0.67 and 0 mg/l, respectively. Their concentrations at House Pond are presumably biologically attenuated by autotrophic assimilation.

Dissolved metals were almost completely absent in refuge waters tested. Iron, mercury, zinc, and iead were the only trace metals present within detection limits and cadmium, copper, manganese, selenium, and silver were not detected at any site (Table 2).

Iron was only detected at Tule Pond and mercury at Middle and Bathouse springs and North and House ponds. No state standards exist for iron and those established for mercury are in total versus dissolved forms. Zinc was detected at seven locations and ranged from none detected to 30 µg/l. Zinc concentrations varied little for the sites at which it was detected, i.e. 26.6 ± 1.5 µg/l. All zinc detections were within the 500 µg/l state surface water quality standard for which an aquatic and wildlife protected use is designated. Lead was the only trace substance to exceed a maximum allowable limit for the aquatic and wildlife protected use category. Lead was detected at 4 of 13 locations tested. It was present at the current analytical minimum level of detection, i.e. 100 µg/l, which exceeds the 50 µg/l state standard by two fold.

Organochlorine Pesticides (Tissue and Sediment)

Four of 23 organochlorines tested were detected in tissue samples from San Bernardino Refuge (Table 3). Most vaiues were near the lower level of detection, i.e. 0.01 µg/g wet-weight (Table 4). With the single exception of DDE detected in one longfin dace composite sample from Leslie Creek, all pesticide detections were restricted to tissue samples derived from House Pond. House Pond is the largest surface water on San Bernardino Refuge and located nearest to the International Border. No organochlorines were present in tissue and sediment samples collected from North Pond, the only other lentic water sampled.

Overall, chlorinated hydrocarbon pesticides were virtually absent in the tissue samples tested. They were completely absent from all sediment samples analyzed. Although DDT degradation products, i.e. DDD and DDE, were detected, collectively their values were 6 to 33 times less than the National Academy of Sciences 1.0 µg/g total DDT criterion established for the protection of aquatic wildlife (National Academy of Sciences 1972). The highest pesticide values detected were for p,p'-DDE in Yaqui chub from House Pond, however, all chub DDE values were less than the 0.2 µg/g national wet-weight average for whole bociy freshwater fish (Schmitt et al. 1985).

Table 3. Organochlorine Analysis, San Bernardino National Wildlife Refuge, Arizona (1987).

*	p,p'-DDE		Dieldrin
*	p,p'-DDD		Dicofol
	p,p'-DDT		Heptachlor epoxide
	o,p'-DDE		Oxychiordane
	o,p'-DDD		aipha-Chlordane
	o,p'-DDT		gamma-Chiordane
	Hexachlorobenzene (HCB)	*	trans-Nonachlor
	Hexachlorocyclohexane (BHC)		cis-Nonachlor
	alpha-BHC	*	Endrin
	beta-BHC		Mirex
	gamma-BHC (Lindane)		Toxaphene
	delta-BHC		PCBs (total)

* Detected

Table 4. Organochlorine Pesticide Analysis, San Bernardino National Wildlife Refuge, Arizona. Data collected May through June, 1987. AI.1 pesticide values=µg/g wet weight. None detected=-0.99; data not available=NA.

Station	ID #[1]	Matrix[2]	N	Mean (g) Weight	Mean (mm) Length	Percent Moisture	Percent Lipid	t-Nonachl.	p,p'DDE	p,p'DDD	Endrin
BlackDraw	SANB11	Sediment	3	56.3	NA	50.6	NA	-0.99	-8.99	-8.99	-8.99
HousePond	PP12	Sediment	3	NA	NA	56.6	NA	-8.99	-8.99	-8.99	-8.99
HousePond	SANB05	sediment	3	51.7	NA	48.6	NA	-8.99	-0.99	-0.99	-8.99
HousePond	SANB06	Sediment	3	44.0	NA	60.0	NA	-0.99	-0.99	-0.99	-0.99
LeslieCrk	SANB18	Sediment	3	51.7	NA	23.8	NA	-0.99	a.99	-8.99	-8.99
NorthPond	SANB15	Sediment	3	45.0	NA	51.3	NA	-0.99	-0.99	-8.99	-8.99
BlackDraw	SANB10	RANCAT	5	289.4	141.8	79.6	O.n	-8.99	-8.99	-8.99	-8.99
HousePond	PP14	RANCAT	5	390.0	162.8	NA	NA	-0.99	0.0056	-8.99	0.004
HousePond	SANB04	RANCAT	5	198.6	130.4	79.2	2.00	-0.99	-8.99	-8.99	-8.99
NorthPond	SANB14	RANCAT	5	343.4	152.0	78.4	1.21	-8.99	-0.99	-8.99	-0.99
BlackDraw	SANB08	POESON	150	1.28	42.85	75.0	6.03	-8.99	-0.99	-8.99	-0.99
HousePond	SANB03	POESON	125	0.86	40.2	79.0	2.54	-8.99	0.02	0.01	-8.99
LeslieCrk	SANB19	POESON	10	1.7	52.2	76.9	5.25	-8.99	-8.99	-8.99	-8.99
NorthPond	SANB13	POESON	160	0.69	36.05	79.0	2.08	-8.99	-8.99	-8.99	-8.99
BlackDraw	SANB07	GILPUR	5	12.0	95.6	70.0	10.0	-8.99	-8.99	-8.99	-8.99
HousePond	PP13	GILPUR	5	34.0	136.8	NA	NA	-8.99	0.152	0.023	-8.99
HousePond	SANB01	GILPUR	5	14.6	99.6	74.2	5.34	0.01	0.09	0.01	-8.99
HousePond	SANB02	GILPUR	5	14.4	101.6	73.2	4.88	0.01	0.06	0.01	-8.99
LeslieCrk	SANB16	GILPUR	5	13.2	96.8	78.0	1.9	-8.99	-8.99	-8.99	-0.99
NorthPond	SANB12	GTLPUR	5	6.06	78.6	79.2	2.66	-8.99	-0.99	-0.99	-0.99
BlackDraw	SANB09	AGOCHR	63	2.9	60.9	70.6	13.1	-0.99	-0.99	-0.99	-8.99
LeslieCrk	SANB17	AGOCHR	69	3.0	-68.1	74.6	7.06	-8.99	0.02	-8.99	-8.99

Pesticide columns: t-Nonachl., p,p'DDE, p,p'DDD, Endrin.

[1] PP12-14 are EPA, Region IX, Priority Pollutant samples.

[2] RANCAT=bullfrog, POESON=Yaqui topminnow, GILPUR=Yaqui chub, and AGOCHR=longfin dace.

Trace Metals (Tissue and Sediment)

Eleven of 21 metals were analyzed for all tissue and sediment matrix types (Table 5). The remaining 10 metals were either analyzed for sediments only (boron, barium, magnesium, molybdenum, siiver, strontium, and vanadium) or restricted to EPA samples (arsenic, mercury, and selenium). Thallium was the only trace metal of the 11 analyzed for all matrix types that was consistently undetected.

Metals were present in tissue samples, virtually absent in water samples, and apparently concentrated in sediment samples, particularly at House Pond. The greatest preponderance of metals in Yaqui topminnow also occurred at House Pond, whereas metals were more prevalent in longfin dace and Yaqui chub samples collected from Leslie Creek. Metals were mixed in their occurrence for the three locations, i.e. House Pond, North Pond and Black Draw, at which bullfrogs were sampled.

Copper, zinc, and lead in San Bernardino fishes appear to be elevated in relation to national-baseline vaiues on a wet-weight basis [wet-weight concentration = (l-percent sample moisture) (dry-weight concentration)].

Copper in Yaqui chub, Yaqui topminnow, and longfin dace exceeded the 0.68 µg/g geometric mean concentration for National Contaminant Biomonitoring Program (NCBP) freshwater fish samples for 1980-81 (Lowe et al. 1985). However, none of the San Bernardino fishes exceeded the maximum 24.10 µg/g value detected within the monitoring network. The lowest copper value detected for fish during the present study was 0.83 µg/g in longfin dace from Black Draw.

Zinc exceeded the 1980-81 geometric mean of 23.82 µg/g for all San Hernardino fish samples except Yaqui topminnow at Black Draw. Values varied between 7.78 and 61.21 µg/g wet-weight and ail were less than the NCBP 109.21 µg/g maximum concentration.

Lead values in fish at San Bernardino varied from none detected to 1.37 µg/g. Although several samples exceeded the 0.17 µg/g national-baseline value, none exceeded the 1.94 µg/g NCBP maximum value.

Cadmium residue values exceeded the NCBP geometric mean of 0.03 µg/g for fish at Black Draw and Leslie Creek. Cadmium in Yaqui chub (0.69 µg/g) and longfin dace (0.48 µg/g) at Leslie Creek were particularly elevated and also exceeded the 1980-81 national-baseline maximum concentration of 0.35 µg/g.

Table 5. Trace Metal Analysis, San Bernardino National Wildlife Refuge, Arizona, May-September 1987. All trace metal values=µg/g dry-weight. None detected=-0.99; data not available=NA.

								Trace Metal							
Station	ID [1] #	Matrix [2]	N	Mean (g) Weight	Mean (mm) Length	Percent Moisture	Percent Lipid	AG	AL	AS	B	BA	BE	CD	CR
BlackDraw	SANB11	Sedimnt	3	56.3	NA	50.6	NA	-0.99	21100.0	NA	-0.99	151.0	1.5	-0.99	31.0
HousePond	PP12	Sediment	3	NA	NA	56.6	NA	-8.99	NA	6.78	NA	NA	-0.93	3.34	81.6
HousePond	SANB05	Sediment	3	51.7	NA	48.6	NA	-0.99	38200.0	NA	-8.99	194.0	1.7	0.5	74.[illegible]
HousePond	SANB06	Sedimnt	3	44.0	NA	60.0	NA	-0.99	45103.0	NA	2.0	198.0	1.7	9.61	79.0
LeslieCrk	SANB18	Sediment	3	51.7	NA	23.8	NA	-0.99	130Q0.0	NA	-8.99	161.0	0.88	0.3	6.1
NorthPond	SANB15	Sediment	3	45.0	NA	51.3	NA	-0.99	12500.0	NA	-0.99	197.3	0.82	5.2	51.0
BlackDraw	SANB10	RANCAT	5	289.4	141.8	79.6	0.77	NA	124.0	NA	NA	NA	-8.99	0.11	-0.93
HousePond	PP14	RANCAT	5	390.0	162.8	NA	NA	-0.99	NA	-8.99	NA	NA	-8.99	-0.99	0.9[illegible]
HousePond	SANB04	RANCAT	5	198.6	130.4	79.2	2.00	NA	43.4	NA	NA	NA	-8.99	0.13	1.2
NorthPond	SANB14	RANCAT	5	343.4	15a.0	78.4	1.21	NA	69.2	NA	NA	NA	0.01	0.08	1.5
BlackDraw	SANB08	POESON	150	1.28	42.85	75.0	6.03	NA	803.0	NA	NA	NA	0.03	0.11	2.3
HousePond	SANB03	POESON	125	0.86	40.2	79.0	2.54	NA	912.0	NA	NA	NA	0.03	C.l	3.6
LeslieCrk	SANB19	POESON	10	1.7	52.2	76.9	5.25	NA	NA	NA	NA	NA	NA	NA	NA
NorthPond	SANB13	POESON	160	0.69	36.05	79.0	2.08	NA	452.0	NA	NA	NA	0.02	0.088	2.3
BlackDraw	SANB07	GILPUR	5	12.0	95.6	70.0	10.0	NA	0.4	NA	NA	NA	-0.99	0.13	4.93
HousePond	PP13	GILPUR	5	34.0	136.8	NA	NA	-0.99	NA	-8.99	NA	NA	-0.99	-0.99	1.10
HousePond	SANB01	GILPUR	5	14.6	99.6	74.2	5.34	NA	25.0	NA	NA	NA	-0.99	0.13	0.2
HousePond	SANB02	GILPUR	5	14.4	101.6	73.2	4.88	NA	10.0	NA	NA	NA	-8.99	0.09	-0.39
LeslieCrk	SANB16	GILPUR	5	13.2	96.8	78.0	1.9	NA	119.0	NA	NA	NA	-8.99	3.14	cl.57
NorthPond	SANB12	GILPUR	5	6.06	78.6	79.2	2.66	NA	53.8	NA	NA	NA	-8.99	0.14	2.4
BlackDraw	SUB09	AGOCHR	63	2.9	60.9	70.6	13.1	NA	56.4	NA	NA	NA	0.01	0.17	0.71
LeslieCrk	SANB17	AGOCHR	69	3.0	68.1	74.6	7.06	NA	212.0	NA	NA	NA	-8.99	1.9	0.2

[1] PP12-14 are EPA, Region IX, Priority Pollutant samples.

[2] RANCAT=bullfrog, POESON=Yaqui topminnow, GILPUR=Yaqui chub, and AGOCHR=longfin dace.

Table 5 (cont.).

Station	ID #[1]	Matrix[2]	Trace Metal												
			cu	FE	HG	MG	MN	MO	NI	PB	SE	SR	TL	V	ZN
BlackDraw	SANB11	Sediment	16.0	22100	NA	8460.0	200.0	-0.99	31.0	10.0	NA	100.0	-0.99	49.3	41.9
HousePond	PP12	Sediment	119.0	NA	-0.99	NA	NA	NA	63.2	32.0	-0.99	NA	-0.99	NA	95.0
HousePond	SANB05	Sediment	89.7	35100.0	NA	14600.0	722.0	-0.99	68.0	31.0	NA	132.0	-0.99	52.8	72.8
HousePond	SANB06	Sediment	91.4	38200.0	NA	15100.0	709.0	-0.99	74.0	32.0	NA	134.0	-0.99	58.8	78.3
LeslieCrk	SANB18	Sediment	29.7	165000.0	MA	4850.0	1450.0	-0.99	6.6	15.0	NA	98.0	-0.99	29.0	39.9
NorthPond	SANB15	Sediment	24.5	15300.0	NA	4360.0	168.0	-0.99	14.0	24.0	NA	136.0	-0.99	54.1	41.5
BlackDraw	SANB10	RANCAT	6.32	225.0	NA	NA	33.3	NA	0.41	0.5	NA	NA	-0.99	NA	91.1
HousePond	PP14	RANCAT	3.63	NA	0.2	NA	NA	NA	-0.99	-0.99	-0.99	NA	-0.99	HA	19.7
HousePond	SANB04	RANCAT	17.9	145.0	NA	NA	10.6	NA	3.6	-0.99	NA	NA	-0.99	NA	84.7
NorthPond	SANB14	RANCAT	1.7	147.0	NA	NA	6.88	NA	0.2	0.7	NA	NA	-0.99	NA	79.7
BlackDraw	SANB08	POESON	10.5	860.0	NA	NA	57.4	NA	1.6	0.6	NA	NA	-0.99	NA	31.1
HousePond	SANB03	POESON	14.4	1030.0	NA	NA	35.2	NA	1.9	1.0	NA	NA	-0.99	NA	205.0
LeslieCrk	SANB19	POESON	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
NorthPond	SANB13	POESON	11.7	482.0	NA	NA	27.5	NA	0.62	1.0	NA	NA	-0.99	NA	246.0
BlackDraw	SANB07	GILPUR	11.1	83.6	NA	NA	6.14	MA	-0.99	-0.99	NA	NA	-0.99	NA	111.0
HousePond	PP13	GILPUR	12.4	NA	0.2	NA	NA	NA	-0.99	-0.99	-0.99	NA	-0.99	NA	49.6
HousePond	SANB01	GILPUR	20.2	134.0	NA	NA	5.51	NA	-0.99	-0.99	NA	NA	-0.99	NA	142.0
HousePond	SANB02	GILPUR	13.1	94.1	NA	NA	5.33	NA	-0.99	5.1	NA	NA	-0.99	NA	114.0
LeslieCrk	SANB16	GILPUR	23.4	265.0	NA	NA	19.0	NA	0.74	2.9	NA	NA	-0.99	NA	224.0
NorthPond	SANB12	GILPUR	6.53	147.0	NA	NA	4.1	NA	0.96	-0.99	NA	NA	-0.99	NA	217.0
BlackDraw	SANB09	AGOCHR	2.82	123.0	NA	MA	10.3	NA	0.42	-0.99	NA	NA	-0.99	NA	155.0
LeslieCrk	SANB17	AGOCHR	5.89	235.0	NA	NA	29.6	NA	0.88	2.0	NA	NA	-0.99	NA	241.0

[1] PP12-14 are EPA, Region IX, Priority Pollutant samples.

[2] RANCAT=bullfrog, POESON=Yaqui topminnow, GILPUR=Yaqui chub, and AGOCHR=longfin dace.

Cadmium in bullfrogs was three times less than the normal range (0.10 - 0.36 µg/g wet-weight) associated with whole body ranid frogs collected from uncontaminated locations (Hail and Mulhern 1984). Bullfrog cadmium concentrations were approximately equal to those found in San Bernardino fishes except for those taken from Leslie Creek where fish exhibited cadmium elevations.

Lead and manganese values in bullfrog varied from none detected to 0.15 µg/g and 1.49 - 6.79 µg/g wet-weight, respectively. Both ranges were less than the normal values (0.88 - 3.2 µg/g as lead and 14 - 42 µg/g as manganese) associated with whole body ranid samples from nonpolluted areas (Ibid).

Levels of copper and zinc were within the normal range of concentrations reported for both elements in adult ranid frogs, i.e. 1.2 - 3.5 µg/g as copper and 6.2 - 31 µg/g as z inc. Copper can reach high concentrations in adult anurans, however, their values are also known for the high variability, even in contaminated areas. In contrast, zinc levels in amphibians exhibit little variation between tadpole and adult forms or between background and metal-contaminated areas (Ibid). Zinc concentrations in adult bullfrogs from San Bernardino Refuge were more than two times less than those of fish collected from the refuge.

Summary and Recommendations

In summary, surface waters located within the San 3ernardino Refuge (including Leslie Creek) are of excellent quality. With little exception, water quality was within state surface water quality standards for protected uses associated with the Rio Yaqui basin. Dissolved oxygen and lead appear to be the oniy two parameters which exceed allowable limits for the aquatic and wildlife protected use. Low dissolved oxygen may be an artifact of its measurement location, i.e. spring sources, whereas, the occurrence of lead may be more associated with its gross ievel of detection (100 µg/l).

Overall, refuge waters were virtually absent of dissoived trace metais and consistently alkaline (pH 7.78 ± 0.75). Spring chemistries were relatively consistent due to their presumable origin from a common aquifer. Springs differed chemically from surface drainages which have watersheds under greater hydrological influence than underground aquifers.

Sodium was the dominant cation at all spring locations and Black Draw, whereas calcium was prevalent in Leslie Creek. Coiiectively, phosphorus and nitrogen did not appear to be iimiting nutrients to primary production. The highest nitrate-N was detected at Leslie Creek and the lowest at House Pond. Suifate was relatively absent within refuge waters, particularly at spring sources. Alkalinity exceeded the EPA recommended minimum of 20 mg/l for freshwater aquatic life by a factor of 10 to 18. it.5 presence at these concentrations buffers San Bernardino waters against acidic atmospheric conditions and complexes dissoived heavy metals into insolubie nontoxic forms.

Trace metal residues in tissue matrices were mixed in their occurrence, especially for frogs. Trace metais were more prevaient in topminnow and sediment samples at Rouse Pond and greatest in dace and chub samples from Leslie Creek. Copper, zinc, and lead in fish samples were consistently elevated reiative to NCBP nationai-baseiine values for freshwater fish. Cadmium was only elevated in fish collected from surface drainages, i.e. Black Draw and Lesiie Creek. Cadmium in chub from Leslie Creek was almost two times greater than the 1980-81 national-baseline maximum concentration (Lowe et al. 1985).

Trace metais in bullfrogs were less than or equai to those detected in fish. All metal residues were within the normal range for ranid frogs associated with uncontaminated areas (Hall and Mulhern 1984).

Four of 23 organochlorine pesticides were detected in tissue samples from San Bernardino Refuge; none were detected in sediment samples. All but one of the detections occurred in samples collected from House Pond. The highest pesticide values detected were for p,p'-DDE in chub, however, all DDE residues were iess than the 0.2 µg/g nationai wet-weight average for freshwater fish (Schmitt et al. 1985). All values were aiso iess than the National Academy of Sciences total DDT criterion for aquatic wildlife protection.

Aithough iong term records of precipitation pH for Arizona are largely unavailable, recent data developed via the National Acid Deposition Program (NADP) have deiineated an area of precipitation acidity (pH range 4.7 to 5.0) in southeast Arizona (Roth et al. 1985). High suifate deposition and acidity at the Tombstone, Arizona NADP site are among the highest within the western portion of the network. Sulfate emissions result almost entireiy from non-ferrous metals smelting in Arizona, where over half the western copper smeiters are located.

Admittedly, Arizona smelters are currently the single iargest regionai sulfate emission source in the western United States. However, surface water alkalinity appears to be the mitigating factor which disaiiows acidic deposition to adverseiy manifest itseif in the aquatic ecosystem. Sulfate ranged from 10 to 70 mg/l within the refuge and averaged 11 ± 2 mg/l at spring sources. Ninety-five percent of the waters of the United States that support excellent fisheries contain less than 90 mg/l sulfate (Hart et al. 1945). Trace metals were virtually absent and pH was near neutrai or above. Surface water alkalinity exceeded the 10 mg/l criterion which separates aquatic ecosystems into sensitive and non-sensitive categories (Hendrey et al. 1980). San Bernardino Refuge waters were consistently above this acidification sensitivity level by a factor of 20 to 36. Roth et al. (1985) also found that alkalinity was the best indicator of sensitive surface waters in their review of acid precipitation in the American West. Collectively, they found southeast Arizona waters were not sensitive to chronic acidification due to a variety of factors, i.e. soil characteristics, climate, geologic contact, terrain, and surface water alkalinity.

Lastly, biota are probably the best integrative indicator of watershed quality, and in this instance, its ability to neutralize acid. Some researchers have attributed the decline of native ranids in southern Arizona and northern Mexico to copper smelter emissions (Hale and May 1983), however, we found no evidence of acid-stress in resident organisms on the refuge. Native fish populations exhibited no symptoms of lack of recruitment, incidence of morphological abnormalities, or subnormal growth. Likewise bullfrogs, albeit non-native, flourish throughout the refuge and exhibited little in regard to trace metal body burdens. All metal residues were less than or equal to normal ranges associated with similar ranid frogs from uncontaminated areas.

Despite the fact that refuge waters are of superior quality and that its resident biota exhibit no symptoms of acid-stress or pesticide and trace metal toxicity, clear evidence currently exists relative to localized acidic atmospheric conditions. Although damage to the aquatic portions of the refuge is not apparent, the terrestriai counterpart remains unstudied. Perhaps further study of terrestrial systems is warranted, however, our single recommendation is to monitor the aquatic ecosystem. Conceivably, this would include the foliowing:

1. Xater Quaiity

   Standard limnology (including pH, total alkalinity, and sulfate) and trace metals, especially lead, mercury (total recoverable), and zinc should be determined for each spring, pond, and surface tributary within the refuge (including Leslie Creek) every three years.

2. Sediment and Tissue Residue Chemistry

   Trace metals should be determined for sediment, fish, and bullfrogs at selected locations, e.g. House Pond, Black Draw, and Leslie Creek every five years.

3. Population Censusing

   Fish and frog popuiation estimates shouid be determined annually at selected sites within the refuge. Long-term datasets for biotic populations are largely unavailable, particularly for sites under imminent or potential influence of environmental contaminants. Population monitoring, especialiy for federally listed and candidate species, will match biological information to water and residue chemistries and will ailow for more complete evaluation of refuge conditions and trends relative to environmental quaiity.

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