Bull. Environ. Contam. Toxicol. (1995) 54:198–206

Environmental Contamination and Toxicology

Selenium, Boron, and Heavy Metals in Birds from the Mexicali Valley, Baja California, Mexico

M. A. Mora,* D. W. Anderson

Department of Wildlife and Fisheries Biology, University of California, Davis, California 95616, USA

Received: 10 April 1994/Accepted: 15 July 1994

Trace elements in irrigation drainwater in some areas of the southwestern United States have been detected at concentrations that are associated with reproductive, teratogenic and behavioral anomalies in birds. For example, increased bird mortalities were linked with high concentrations of selenium (Se) at the Kesterson Reservoir in California (Ohlendorf *et al.* 1986a). Agricultural ecosystems in northwestern Mexico resemble closely those of central and southern California because they are also intensively irrigated and there is concern that elevated concentrations of trace elements in these areas could also result in detrimental effects on resident and migratory birds and other wildlife.

The Mexicali Valley is located in northeastern Baja California, south of the Imperial Valley in California. Approximately 70% of the cultivated land in Mexicali (182,000 hectares) is irrigated by gravity flow with water from the Colorado River (Secretaria de Agricultura y Recursos Hidraulicos 1984), and elevated concentrations of trace elements in agricultural drainwaters might be expected. Runoff is discharged directly to canals and to the Hardy River. The Hardy River also receives brine waste with potentially high concentrations of arsenic (As) and boron (B) from a geothermal energy plant located at Cerro Prieto in the middle of the agricultural valley, approximately 30 km south of the city of Mexicali (Comisión Federal de Electricidad 1987).

There are no studies that evaluate the environmental hazards and concentrations of trace elements in wildlife of the Mexicali Valley, except for some data on fish and clams. Concentrations of mercury (Hg) in fish and clams from irrigation canals and drainages of the Mexicali Valley were measured to evaluate the extent of Hg contamination by the Cerro

**Present address:* National Biological Survey, Patuxent Wildlife Research Center, Gulf Coast Research Group, % Department of Wildlife and Fisheries Sciences, Texas A&M University, College Station, Texas 77843, USA
Correspondence to: M. A. Mora

Prieto plant (Gutierrez-Galindo *et al.* 1988), but data on other trace elements were not presented. We undertook this study to evaluate concentrations of trace elements in tissues of aquatic and terrestrial birds of the Mexicali Valley and to determine whether those concentrations are hazardous to birds. We selected five species representing different habitats. Organochlorine pesticides and polychlorinated biphenyls (PCBs) were also analyzed and have been reported elsewhere (Mora and Anderson 1991).

MATERIALS AND METHODS

Double-crested cormorants (Phalacrocorax auritus), cattle egrets (Bubulcus ibis), mourning doves (Zenaida macroura), great-tailed grackles (Quiscalus mexicanus), and red-winged blackbirds (Agelaius phoeniceus) were collected (N=61) during July-August and December 1986 as described previously (Mora and Anderson 1991). We selected species that could be found year-round near agricultural areas and that had diverse food habits. A portion of the liver was taken from the carcasses and was kept frozen until chemical analyses were performed. Fish (Tilapia spp. and Mugil spp.) were also collected during the same period. A portion of fish muscle (midsection) was cut from each fish and frozen until analyzed.

The samples were analyzed at the Agriculture and Natural Resources Diagnostics Laboratory of the University of California at Davis. Zinc (Zn), cadmium (Cd), copper (Cu), chromium (Cr), and B were analyzed by atomic absorption spectrophotometry, according to methods described in Galey *et al.* (1990). Se was analyzed by continuous flow vapor generation with an inductively coupled argon plasma spectrometer as described in Tracy and Moller (1990). Mercury (Hg) was not analyzed at the same time because its analysis required a special technique and the samples were discarded before this analysis could be carried out. The lower limit of detection was 0.2 parts per million (ppm). Recoveries ranged from 90-110%. Residue data are reported on a wet-weight basis (ww).

Concentrations of trace elements were log-transformed for statistical analyses. Seasonal differences in concentrations of trace elements within species were determined by two-sample comparison procedures. Differences in concentrations among species were determined by one-way analysis of variance (ANOVA). Significant differences among means were determined by the Tukey-Kramer method of multiple comparisons (Neter *et al.* 1985).

RESULTS AND DISCUSSION

There were no significant differences in concentrations of trace elements between the summer and winter collection periods for most species, except for mourning doves which had significantly higher concentrations of Cr, Cu, and Zn during the summer than in winter. Thus, summer and winter data for each species were combined for the statistical analysis. Except for Zn, concentrations of trace elements were significantly different ($p<0.05$) among species (Table 1). The pattern of accumulation of each trace element was also different for each species.

Se concentrations were significantly higher ($p<0.05$) in double-crested cormorants and lower in mourning doves than in other species. It is not surprising that cormorants were high because cormorants were the most aquatic species sampled, and Se accumulates primarily in aquatic food chains (Ohlendorf *et al.* 1986a; Saiki *et al.* 1993). Se concentrations were similar among cattle egrets, great-tailed grackles, and red-winged blackbirds. These species are all intermediate in types of habitat used and probably share common food sources. The effects of Se on aquatic birds have been well documented (Ohlendorf *et al.* 1986a, b, 1987; Heinz *et al.* 1987, 1989; Hoffman and Heinz 1988). American coots (Fulica americana) with mean Se concentrations in livers of 24.7 ppm ww (range 5.8-48.5) failed to nest at the Kesterson Reservoir during 1984; black-necked stilts (Himantopus mexicanus) and American avocets (Recurvirostra americana) from the same area also showed reproductive problems and embryotoxic effects at mean Se concentrations in livers of 14 ppm ww and 24 ppm ww, respectively (Ohlendorf et al. 1987). Birds nesting at irrigation drainwater ponds in the San Joaquin Valley California, had mean Se levels of 19 to 130 ppm dry weight in liver (5.7-39 ppm ww) which were associated with missing or abnormal wings, beak, legs, and feet (Ohlendorf *et al.* 1986a). In the laboratory, 100 ppm of Se as sodium selenite in the diet of mallards (Anas platyrhynchos) resulted in high adult mortality, and hatching was reduced when adult hens received 10 ppm of Se as selenomethionine (Heinz *et al.* 1987). Selenomethionine (16 ppm Se) in the diet of mallards also caused malformations in near 70% of unhatched eggs (Heinz *et al.* 1989). Levels of Se in fish from the Mexicali Valley (Table 2) were below the dietary levels that caused mortality and reproductive effects in laboratory birds. The concentrations of Se in double-crested cormorants from the Mexicali Valley were below the threshold at which reproductive effects were apparent in American coots at Kesterson Reservoir (Ohlendorf *et al.* 1987, 1990). Concentrations of Se in cormorants from Mexicali were also lower than those reported in livers of double-crested cormorants from the Salton Sea in 1986 (mean=9.7 ppm ww) (White et al. 1987), and from the Alamo and New rivers in 1986-1987 (mean= approximately 8.1 ppm ww) (Setmire et al. 1990).

Table 1. Trace elements in livers of birds from the Mexicali Valley, Baja California, 1986[1].

Species[2]	Trophic level Habitat	N	Moisture %	Se	Zn	Cd	Cu	Cr	B
Double-crested	F,A	9	69.5	5.1 A	24.7 A	0.7 BC	5.1 A	1.7 B	4.2 BC
Cormorant				(2.9-7.3)	(18-45)	(0.5-1.7)	(1.7-12.2)	(1-3.6)	(2.9-8.2)
Cattle Egret	O,W	15	71.9	1.3 B	23.3 A	0.5 B	3.0 B	2.1 B	5.3 B
				(0.5-2.2)	(9-35)	(0.5-1.2)	(1.2-6.8)	(1-5.1)	(2.6-8.7)
Red-winged	O,W	8	70.8	1.5 B	28.8 A	2.1 A	7.6 A	3.1 A	3.9 BC
Blackbird				(1.1-4.4)	(25-33)	(1.5-3.3)	(5.2-13.5)	(2.4-5.5)	(2.6-7.9)
Great-tailed	O,U	14	69.8	1.6 B	26.1 A	0.9 BC	5.0 A	2.0 B	2.3 C
Grackle				(1-3.2)	(18-36)	(0.5-5.2)	(3.4-7.4)	(1-3.9)	(1.2-7.6)
Mourning Dove	H,U	15	69.5	0.7 C	24.6 A	0.9 C	7.4 A	4.6 A	10.0 A
				(0.2-1.0)	(9-35)	(0.5-2.3)	(3.9-16.9)	(1.9-7.2)	(4.3-28.5)

1 Geometric means, ppm ww, ranges in parentheses. Means not sharing the same letter (among species) are significantly different.

2 Species are ordered according to their estimated trophic positions and general habitat as follows: (F) fish-eating, (O) omnivorous, (H) herbivorous; (A) aquatic, (W) wetland, (U) upland.

Zn levels were not different among birds from the Mexicali Valley, which may indicate that Zn is uniformly distributed in that ecosystem or well regulated metabolically. Zn concentrations in livers of birds from Mexicali were lower than Zn concentrations in livers of common eiders (Somateria mollissima), approximately 62 and 111 ppm ww, from a heavy metal contaminated site in Norway (Lande 1977). Common eiders did not show any biological effects at those Zn concentrations.

Cd was significantly greater ($p<0.05$) in red-winged blackbirds than in other species (Table 1). Red-winged blackbirds feed primarily on seeds and insects near agricultural fields and marshes; thus, both seeds and insects may have represented the main source of Cd for red-winged blackbirds. Cd concentrations were also significantly different between mourning doves and cattle egrets ($p<0.05$) with cattle egrets having the lowest concentrations among all species. The Cd threshold concentrations for effects in wildlife are relatively high. Adult female mallards fed 200 ppm Cd for 13 weeks accumulated up to 110 ppm ww of Cd in their livers and stopped egg laying, but no other effects were observed (White and Finley 1978). Mallard ducklings fed 20 ppm for 12 weeks accumulated approximately 42 ppm ww in the liver and had mild to severe kidney lesions (Cain *et al.* 1983). The Cd levels observed in birds from Mexicali were probably not of concern.

Cu levels were lower ($p<0.05$) in cattle egrets than in the other four species, which had similar concentrations (Table 1). The significance of these Cu levels in livers of birds has not been established.

Cr was significantly higher in mourning doves and red-winged blackbirds ($p<0.05$) than in cormorants, egrets, and grackles, which had similar concentrations. Mourning doves are primarily seed-eaters, whereas red-winged blackbirds feed on seeds and insects (Martin *et al.* 1951); thus, the similarities in Cr content of their livers might be explained by their similar preferences for seeds at Mexicali. We did not, however, study the food habits of any species. Cr in the environment results primarily from industries, coal combustion, municipal incinerators, and cooling towers (Eisler 1986). Growth patterns and survival of young black ducks (Anas rubripes) were altered when they were fed diets containing 10 or 50 ppm Cr^{+3}; these diets were similar to those administered to their adult parents, which seemed to have normal survival and reproduction (Haseltine *et al.* unpubl., Eisler 1986). Similarly, up to 200 ppm Cr^{+3} in diets did not significantly affect the avoidance behavior of young black ducks (Heinz and Haseltine 1981). However, we did not find any data that correlate concentrations of Cr in bird livers with biological effects; hence, the significance of levels of Cr in livers cannot be established.

Boron was significantly greater in mourning doves ($p<0.05$) than in any other species (Table 1). Because mourning doves are primarily seed-eaters, it is likely that the main source of B resulted from high concentrations in agricultural seed crops. At Kesterson Reservoir, California, B accumulated in plants more than in fish or invertebrates (Hothem and Ohlendorf 1989), thus, herbivores such as mourning doves probably have greater exposure to B than other birds. B concentrations were also significantly different ($p<0.05$) between cattle egrets and great-tailed grackles, which had the lowest concentrations of all species. In some areas of California and the southwestern United States, agricultural drainwaters are considered major sources of B and Se (Eisler 1990, Saiki *et al.* 1993); that also may be true for the Mexicali Valley. Adult mallards fed B in the diet at 30 ppm dw had less than 5 ppm dw (similar to controls) in liver (Smith and Anders 1989). However, at a diet of 300 ppm dw mean residues in liver were 17 ppm dw (5.1 ppm ww). B levels of 30 and 300 ppm dw in the diet of mallards did not affect reproduction, but levels above 1000 ppm dw significantly impaired reproduction (Smith and Anders 1989). Based on our results and on the experiments described above, mourning doves at the Mexicali Valley were probably ingesting significant amounts of B, although analytical differences also may be a factor. Differences in metabolism and sensitivity to trace elements may occur among species; thus, the possible effects of the concentrations of B observed in mourning doves need further study, including sampling in other areas for comparison.

High concentrations of B in the Mexicali Valley also may result from brine discharges from the Cerro Prieto geothermal energy plant. During 1986-1987, the Federal Electrical Commission (CFE) of Mexico conducted an evaluation of the environmental impacts of the brine discharged by the geothermal plant in Cerro Prieto (CFE, unpublished report). Concentrations of As and B were monitored for three periods at several sampling stations along the Hardy River. Levels of B and As in Hardy River sediments reached maximum concentrations of 26 and 1.4 ppm ww (averages of three sampling periods from September 1986 through March 1987) at the site closest to the brine discharge of the geothermal plant. Concentrations of B and As diminished with increasing distance from the discharge point, but remained high for most of the river throughout the valley. As concentrations decreased to less than 1 ppm at approximately 40 km downstream from the discharge. B, however, remained above 1 ppm for a longer stretch and did not reach levels below 0.5 ppm until beyond the confluence with the Colorado River (CFE, unpublished report). Unfortunately, we did not analyze As in bird livers. However, three fish (Tilapia spp.) from the Hardy River had mean As levels of 2.42 ppm ww in muscle. It has been suggested that B does not accumulate in terrestrial or aquatic food chains (Saiki *et al.* 1993); thus, the high levels of B detected, particularly in mourning doves, at the Mexicali Valley could probably be explained by high daily B dietary intakes. It is also possible that some bioaccumulation of B occurs in environments where high B concentrations exist. This possibility also requires further study.

The results for pooled fish (Table 2) also suggest increased exposure to Se, B, and Zn. Concentrations of Se in tilapia from Mexicali were similar to those observed in tilapia (whole fish) from the New River, near the Salton Sea, California, during 1986-1987 (1.3-3 ppm ww) (Setmire *et al.* 1990). Concentrations of Se in fish from the Mexicali Valley were above the U.S. national mean of 0.42 ppm ww in whole fish during 1984, and were close to the maximum concentration observed in carp (2.3 ppm ww) from the Colorado River in Arizona (Schmitt and Brumbaugh 1990). Levels of Zn and Cu in muscle of fish from Mexicali during 1986 were somewhat similar to levels in whole fish from the Colorado River, near Yuma, Arizona, in 1986 (Schmitt and Brumbaugh 1990). Cd was somewhat higher at Mexicali. However, differences in concentrations in muscle (this study) and in whole fish (Schmitt and Brumbaugh 1990) may occur.

Table 2. Trace elements (ppm ww) in muscle samples of fish from the Mexicali Valley, Baja California.

Species	N	Se	Zn	Cd	Cu	Cr	B
Tilapia spp.	6	1.7	14.0	0.9	2.2	1.4	2.9
Mugil spp.	4	2.1	7.0	0.9	2.2	1.6	1.9

In conclusion, concentrations of Zn, Cd, Cu, and Cr in livers seem to be well below thresholds for biological effects in birds. Levels of Se were somewhat high in cormorants, but they were below the threshold suggested to cause anomalies and reproductive impairment in birds from the San Joaquin Valley. Levels of B were also high in mourning doves and could be associated with potential biological effects. No data were obtained on reproduction of double-crested cormorants or mourning doves. A recent review suggested that As bioaccumulates only slightly in eggs and that concentrations of B in eggs of birds exposed to high B diets were not high enough to be of concern for embryotoxic effects (Ohlendorf *et al.* 1993). Field studies on reproductive success of aquatic birds and other species at the Mexicali Valley are necessary to determine whether there are effects of Se, B, and As which are present in high concentrations in that ecosystem.

Acknowledgments. This research was supported by a fellowship from CONACYT, Mexico, UCMEXUS (University of California Institute for Mexico and the United States), and Jastro-Shields grants from the

University of California, Davis. This manuscript has been improved by comments from D. Boellstorff, D. Clark, G. Heinz, D. Hoffman, and H. Ohlendorf.

REFERENCES

Cain BW, Sileo L, Franson JC, Moore J (1983) Effects of dietary cadmium on mallard ducklings. Environ Res 32:286-297

Comisión Federal de Electricidad (1987) Informes de los resultados de las campañas de monitoreo intensivo efectuadas durante 1986-1987, para el estudio del impacto ambiental de las descargas de agua geotérmica de desecho en el Río Hardy. Superintendencia General de Estudio, Coordinadora Ejecutiva de Cerro Prieto, Mexicali, Baja California

Eisler R (1986) Chromium hazards to fish, wildlife, and invertebrates: a synoptic review. U S Fish Wildl Serv Biol Rep 85(1.6) 60 pp

Eisler R (1990) Boron hazards to fish, wildlife, and invertebrates: a synoptic review. U S Fish Wildl Serv Biol Rep 85(1.20) 32 pp

Galey FD, Slenning BD, Anderson ML, Breneman PC, Littlefield ES, Melton LA, Tracy ML (1990) Lead concentrations in blood and milk from periparturient dairy heifers seven months after an episode of acute lead toxicosis. J Vet Diagn Invest 2:221-226

Gutierrez-Galindo EA, Flores Munoz G, Aguilar Flores A (1988) Mercury in freshwater fish and clams from the Cerro Prieto geothermal field of Baja California, Mexico. Bull Environ Contam Toxicol 41:201-207

Heinz GH, Haseltine SD (1981) Avoidance behaviour of young black ducks treated with chromium. Toxicol Let 8:307-310

Heinz GH, Hoffman DJ, Krynitsky AJ, Weller DMG (1987) Reproduction in mallards fed selenium. Environ Toxicol Chem 6:423-433

Heinz GH, Hoffman DJ, Gold LG (1989) Impaired reproduction of mallards fed an organic form of selenium. J Wildl Manage 53:418-428

Hoffman DJ, Heinz GH (1988) Embryotoxic and teratogenic effects of selenium in the diet of mallards. J Toxicol Environ Health 24:477-490

Hothem RL, Ohlendorf HM (1989) Contaminants in foods of aquatic birds at Kesterson Reservoir, California, 1985. Arch Environ Contam Toxicol 18:773-786

Lande E (1977) Heavy metal pollution in Trond-heimsfjorden, Norway, and the recorded effects of the fauna and flora. Environ Pollut 12:187-198

Martin AZ, Zim HS, Nelson AL (1951) American Wildlife and Plants. Dover Publications Inc., New York

Mora MA, Anderson DW (1991) Seasonal and geographical variation of organochlorine residues in birds from northwest Mexico. Arch Environ Contam Toxicol 21:541-548

Neter JW, Wasserman W, Kutner ME (1985) Applied Linear Statistical Models. Second edition, RD Irwin Inc., Homewood, IL

Ohlendorf HM, Hothem RL, Aldrich TW, Moore JF (1986a) Relationships between selenium concentrations and avian reproduction. Trans North Amer Wildl Nat Res Conf 51:330-342
Ohlendorf HM, Hoffman DJ, Saiki MK, Aldrich, TW (1986b) Embryonic mortality and abnormalities of aquatic birds: apparent impacts of selenium from irrigation drainwater. Sci Total Environ 52:49-63
Ohlendorf HM, Hothem RL, Aldrich TW, Krynitsky AJ (1987) Selenium contamination of the Grasslands, a major California waterfowl area. Sci Total Environ 66:169-183
Ohlendorf HM, Hothem RL, Bunck CM, Marois KC (1990) Bioaccumulation of selenium in birds at Kesterson Reservoir, California. Arch Environ Contam Toxicol 19:495-507
Ohlendorf HM, Skorupa JP, Saiki MK, Barnum DA (1993) Food-chain transfer of trace elements to wildlife. In: Allen RG, Neale CMU (eds) Management of Irrigation and Drainage Systems: Integrated Perspectives, Proc 1993 National Conference on Irrigation and Drainage Engineering, Park City, Utah, American Society of Civil Engineers, New York, p 596-603
Saiki MK, Jennings MR, Brumbaugh WG (1993) Boron, molybdenum, and selenium in aquatic food chains from the lower San Joaquin River and its tributaries, California. Arch Environ Contam Toxicol 24:307-319
Secretaría de Agricultura y Recursos Hidráulicos (1984) Guía para la asistencia técnica agrícola, área de influencia del campo agrícola experimental Valle de Mexicali. Campo Agrícola Experimental Valle de Mexicali, Mexicali, Baja California, Mexico. 154 pp
Setmire JG, Wolfe JC, Stroud RK (1990) Reconnaissance investigation of water quality, bottom sediment, and biota associated with irrigation drainage in the Salton Sea area, California, 1986-1987. U.S. Geological Survey, Sacramento, California, Water-resources Investigations Report 89-4102
Schmitt CJ, Brumbaugh WG (1990) National contaminant biomonitoring program: Concentrations of arsenic, cadmium, copper, lead, mercury, selenium, and zinc in U.S. freshwater fish, 1976-1984. Arch Environ Contam Toxicol 19:731-747
Smith GJ, Anders VP (1989) Toxic effects of boron on mallad reproduction. Environ Toxicol Chem 8:943-950
Tracy ML, Moller G (1990) Continuous flow vapor generation for inductively coupled argon plasma spectrometric analysis. Part I, Selenium. J Assoc Off Anal Chem 73:404-410
White DH, Finley MT (1978) Uptake and retention of dietary cadmium in mallard ducks. Environ Res 17:53-59
White JR, Hofmann PS, Hammond D (1987) Selenium verification study, 1986. A report to the California State Water Resources Control Board. California Department of Fish and Game, Fish and Wildlife Water Pollution Control Laboratory, Rancho Cordova, California