

CONCENTRATION OF CONTAMINANTS IN BREEDING BIRD EGGS FROM THE COLORADO RIVER DELTA, MEXICO

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Abstract—Organic contaminants (organochlorine [OC], organophosphorus [OP] pesticides and polychlorinated biphenyls [PCBs]), and metals (As, Cd, Hg, Pb, and Se) are a concern to avian health in the Colorado River delta, Mexico. We determined concentrations of contaminants in eggs of three breeding species of birds from the delta (mourning doves [*Zenaidura macroura*], burrowing owls [*Athene cunicularia*], and marsh wrens [*Cistothorus palustris*]). We collected 27 eggs of mourning doves, eight eggs of burrowing owls, and 18 eggs of marsh wrens for analyses. Polychlorinated biphenyls, OC, and OP pesticides were analyzed by gas chromatography equipped with an electron capture detector, and metals were analyzed by inductively coupled plasma mass spectrometry. The non-ortho PCB congeners (PCB 77 and 126) were found in mourning dove and burrowing owl eggs at concentrations in which hatchability can be affected. Mean selenium concentration found in marsh wren eggs (5.6 µg/g dry wt) exceeded the level of concern. Arsenic and Cd were found at higher than normal concentrations, Hg concentrations did not exceed the level of concern in any of the species, and Pb concentrations were higher in eggs of species subject to hunting. With the exception of lead, marsh wren eggs contained the highest metal concentrations.

Keywords—Colorado River delta Polychlorinated biphenyls Pesticides Selenium Breeding birds

INTRODUCTION

The delta of the Colorado River has experienced unprecedented human development in the last 100 years, from a few hundred early settlers and native Cucapá to more than two million people today. One of the most important factors for this growth was the agricultural development of the Mexican portion of the Colorado River delta, known as the Mexicali Valley [1]. The use of pesticides in the valley beginning in the 1950s contributed to the growth of this development. Reports of pesticide use in the Mexicali Valley in 1971 indicated that 97% of the applications contained DDT. These pesticides were applied to cotton crops during that year [2]. Today DDT is banned for agricultural purposes and is no longer produced in Mexico. Crops in the Valley have changed to predominantly wheat and alfalfa, and pesticide use has changed from DDT to organophosphorus (OP) and carbamate compounds. However, the intensive past use of DDT has left residues (in the form of dichlorodiphenyldichloroethylene [DDE]) in soils and sediments from the Colorado River delta. In 1987, a study by Mora [3] reported eggshell thinning in cattle egrets (*Bubulcus ibis*) from the Mexicali Valley because of elevated concentrations of DDE. Another contaminant of concern in the Colorado River delta is the semimetal selenium (Se), which is a micronutrient at low concentrations but a teratogen for birds at elevated levels. It originates from cretaceous formations in the upper basin of the Colorado River and is transported in a

dissolved form as selenate, with increasing concentrations being observed in the downstream direction [4,5]. A study in the Colorado River delta reported concentrations of selenium in sediments from 0.6 to 5.0 µg/g (dry wt), with 22% of the samples exceeding the EC10 (threshold where sedimentary selenium can cause adverse biological effects in 10% of exposed fish and birds) [6]. In addition, concentrations in fish and invertebrates ranged from 0.5 to 18.3 µg/g (dry wt), with 23% of the samples exceeding 3 µg/g, a value considered a threshold for reproductive impairment in birds from dietary exposure [6].

Recent (1985–2003) higher than normal flows from the Colorado River that reached the Mexican portion of the delta have restored 3,000 ha of riparian native vegetation, and local agricultural runoff maintains approximately 40,000 ha of brackish wetlands [7]. These relatively new ecosystems are protected by the Upper Gulf of California and Colorado River Delta Biosphere Reserve, Mexico. The delta, an important bird area (IBA) in Mexico, is considered a priority site for conservation by the National Commission on Biodiversity (CONABIO), is a Ramsar site [8], and is part of the Western Hemisphere Shorebird Reserves Network [9]. Censuses of bird species in the delta from 1993 to 2004 have registered 358 bird species [10]. The delta provides habitat for migratory and wintering waterbirds and for neotropical migrant land birds [11,12]. Nearly 200,000 shorebirds and 60,000 ducks and geese use these wetlands as wintering grounds or stopover habitat during migration. At least 110 species of neotropical

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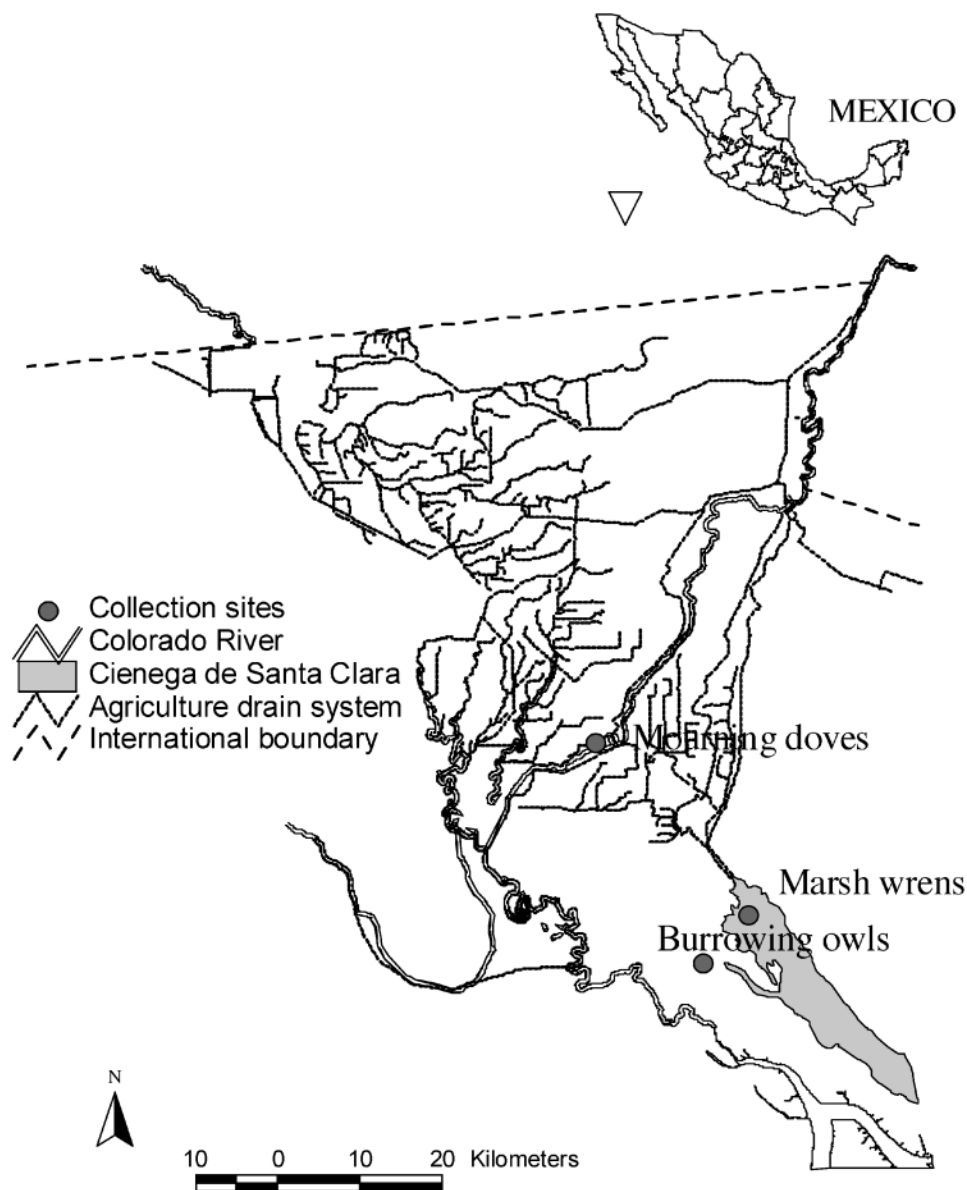


Fig. 1. Study area in the Colorado River delta, Mexico.

migratory land birds visit the area, and 14 species of waterbirds nest in the salt flats, islands, and ponds of the delta [13,14].

One of the major concerns in this ecosystem is the possible detrimental effects of organochlorine (OC) pesticides, selenium, and other contaminants on the reproductive health of its associated species because teratogenesis and decreased hatchability could affect the entire population of a breeding species. Therefore, the objective of this study was to determine concentrations of OC pesticides, polychlorinated biphenyls (PCBs), and heavy metals in the eggs of three breeding species of birds from the Colorado River delta: mourning doves (*Zenaidura macroura*), burrowing owls (*Athene cunicularia*), and marsh wrens (*Cistothorus palustris*).

MATERIALS AND METHODS

We selected for this study bird species that are abundant local breeders and have different food habits. The diet of burrowing owls consists of mammals (70%) and insects (30%) [15]; mourning doves usually feed on grains, seeds, and fruits; and marsh wrens are predominantly insectivorous [16]. The

nests for doves and marsh wrens were accessed from the ground. For burrowing owls, we used 20 artificial burrows, consisting of utility boxes (30 × 30 × 20 cm, length × width × height, available at the local electrical company) and 2-m-long and 15-cm-diameter plastic pipes for tunnels. Each box was buried 0.50 cm to 1 m in an area close to the natural burrows. The pipe was connected to the box, and the entrance was left open at ground level. From April to June 2002, one egg from each nest from the three species was collected for chemical analyses, a total of 27 mourning dove eggs, 18 marsh wren eggs, and eight burrowing owl eggs were collected for analyses. Mourning dove eggs were collected from nests located at the riparian corridor of the Colorado River delta; marsh wrens eggs were collected from the Cienega de Santa Clara, a 4,000-ha cattail wetland on the east side of the delta; and burrowing owl boxes were placed south to the Mexicali Valley, adjacent to an agriculture field (Fig. 1).

After collection, eggs were measured and weighed, and their contents were removed and kept frozen until chemical analyses. Contents were classified as yolk or embryo with

Table 1. Range and mean \pm SD concentrations of selected organochlorine and organophosphorus pesticides in eggs of mourning doves and burrowing owls from the Colorado River delta, Mexico

| Pesticide | Concentration (ng/g wet wt) ^a | |
|---|--|-------------------------------|
| | Mourning dove (<i>n</i> = 27) | Burrowing owl (<i>n</i> = 8) |
| ΣDDE (dichlorodiphenyldichloroethylene) | 4.30–58.60 23.08 \pm 14.8 A | 3.90–40.80 22.33 \pm 12.2 A |
| ΣDDD (dichlorodiphenyldichloroethene) | 0.60–35.00 11.04 \pm 9.2 A | 0.10–27.00 9.25 \pm 9.3 A |
| ΣDDT | 0.20–58.90 26.99 \pm 10.7 A | 0.10–36.20 16.51 \pm 13.5 A |
| Lindane | 13.6–58.00 32.79 \pm 12.8 A | 1.00–25.30 14.16 \pm 8.8 B |
| Heptachlor | 0.10–32.40 2.72 \pm 7.3 A | 0.10–39.60 8.26 \pm 15.2 A |
| Dieldrin | 0.80–18.20 3.70 \pm 4.3 A | 0.10–1.20 0.50 \pm 0.4 B |
| Diazinon | 0.60–28.10 3.93 \pm 6 A | 0.40–19.40 3.37 \pm 6.5 A |
| Dimethoate | 1.00–22.90 7.64 \pm 5 A | 0.10–4.10 2.00 \pm 1.6 B |
| Malathion | 1.70–112.10 26.4 \pm 26 A | 0.20–10.90 3.96 \pm 3.9 B |

^a Each of the organochlorine and organophosphorus pesticides were detected in each of the egg samples. Different uppercase letters mean statistical differences ($p < 0.0001$).

different stages of development. Signs of abnormal development in embryos were recorded (abnormal eyes, beak, feet, or wings). Egg contents were mixed with an Ultra-Turrax® homogenizer (IKA Staufen, Germany) and separated into two parts: one for pesticides and PCB analyses and one for heavy metals. Because marsh wren egg contents were less than 0.5 g, they were used for heavy metals analyses only.

In preparation for OC and OP pesticides and PCB analyses, egg samples were homogenized with activated anhydrous sodium sulfate and extracted with pentane three times. Extracts were separated from samples by vacuum filtration and concentrated to 1 ml by rotary evaporation. Lipid contents were determined for all samples gravimetrically. Lipids were removed with an alumina–silica gel column. Alumina and silica gel were activated, followed by 1 and 5% deactivation, respectively. The microcolumns were prepared in the laboratory with 1 g of deactivated alumina, 2 g of deactivated silica gel, and 1 g of activated anhydrous sodium sulfate. The column was conditioned with dichloromethane, and the concentrated extract was transferred onto the column and eluted with pentane:dichloromethane (50:50, v/v).

Sample extracts were analyzed with a Hewlett-Packard HP-6890 (Avondale, PA, USA) gas chromatograph equipped with an electron capture detector and a DB-5MS fused silica capillary column (60 m \times 0.32 mm \times 0.25 μ m). Preliminary OC results were confirmed with a second polar capillary column (DB-35MS), and OP results were confirmed with a nitrogen phosphorus detector. Analyte recoveries were determined with the use of egg samples spiked with pesticide and PCB standards. The recoveries were 76 to 105%, with relative standard deviations of 8 to 13%. The method detection limit was less than 0.2 ng/g.

For heavy metal analyses, approximately 0.5 g of thawed egg homogenates were digested with 4 ml of HNO₃, 4 ml of H₂O₂, and 2 ml of distilled water in a microwave digestion system (MARS X CEM, Matthews, NC, USA). Digested samples were analyzed with a Perkin Elmer 6100 DRC inductively coupled plasma mass spectrometer (ICP-MS; Perkin Elmer Sciex, Norwalk, CT, USA) for As, Cd, Hg, Pb, and Se. The accuracy of the method was more than 5%, the precision more than 3%, and the method detection limit ranged from 1 to 5 μ g/g. Recoveries for heavy metal analyses ranged from 72 to 129%.

Concentrations of pesticides and PCBs were compared between species by Student's *t* test, and metals were compared by one-way analysis of variance. When differences were

found, the Tukey–Kramer test with $\alpha = 0.05$ was used for all pairwise multiple comparisons. Concentrations were log-transformed to normalize their distribution. Statistical analyses were performed with JMP® software of the SAS Institute (Cary, NC, USA) [17].

RESULTS AND DISCUSSION

Pesticide concentrations

Residual concentrations of OC and OP pesticides analyzed (DDE, dichlorodiphenyldichloroethene [DDD], DDT, lindane, heptachlor, dieldrin, diazinon, dimethoate, and malathion) were present in each egg sample of the three species (Table 1). Concentrations of lindane, dieldrin, dimethoate, and malathion were greater in mourning dove eggs than in burrowing owl eggs, and no differences were found in DDT, DDE, DDD, heptachlor, and diazinon concentrations (Table 1). During our fieldwork, we observed that at least a portion of the population of burrowing owls migrate to other areas in late summer after they reproduce, whereas mourning doves are present year-round in the delta. These species differences in bird movement could account for the greater concentrations of some pesticides found in mourning dove eggs.

Maximum concentrations of DDE in burrowing owls were well below critical levels associated with eggshell thinning for raptors' eggs (10 μ g/g) [18]. Concentrations in mourning doves were also lower than the no adverse effects level (NOAEL) observed for terrestrial birds (2.2 μ g/g) [19]. Lethal concentrations of DDT in birds vary from 6 to 40 μ g/g in brain tissue, depending on the species [20]. However, none of the samples analyzed exceeded 0.06 μ g/g DDT in egg/embryo concentration. Previous work by Mora [3] in the Mexicali Valley in 1987 [3] showed that concentrations of DDE in cattle egret eggs ranging between 2.3 and 4.5 μ g/g, and concentrations of DDT between 0.024 and 0.045 μ g/g resulted in 9.3% eggshell thinning. The author attributed this high DDE/DDT ratio (97) to elevated DDE concentrations present in soils of the Valley because of intensive DDT use in the past, before its ban from Sonora and Baja California, Mexico, in 1978. Our results show a significant decrease in DDE concentrations in eggs of mourning doves and burrowing owls from the Colorado River delta, resulting in a DDE/DDT ratio of 0.80 for mourning doves and 1.5 for burrowing owls. On the other hand, mean concentrations of DDT in egg samples from our study (0.027 and 0.017 μ g/g) remained similar to the concentrations found in 1987 (0.033 μ g/g) [3], which provides evi-

Table 2. Number of samples detected, range and mean \pm SD concentrations of non- and mono-*ortho* polychlorinated biphenyls (PCBs) in mourning dove and burrowing owl eggs from the Colorado River delta, Mexico^a

| PCB congener | Mourning dove (<i>n</i> = 27) | | | Burrowing owl (<i>n</i> = 8) | | |
|-------------------------------|--------------------------------|-----------------------------|-----------------------------|-------------------------------|---------------------|-----------------------------|
| | No. detected | Range (ng/g wet wt) | Mean \pm SD (ng/g wet wt) | No. detected | Range (ng/g wet wt) | Mean \pm SD (ng/g wet wt) |
| Non-<i>ortho</i> PCBs | | | | | | |
| 37 | 27 | 1.0–14.6 | 3.1 \pm 2.7 A | 8 | 0.3–7.4 | 1.5 \pm 2.4 B |
| 77 | 26 | <Detection limit (DL)–1,157 | 77.1 \pm 217.4 A | 4 | <DL–18.5 | 4.6 \pm 6.5 A |
| 81 | 26 | <DL–358.7 | 23.4 \pm 71.4 A | 6 | <DL–1.8 | 0.7 \pm 0.6 A |
| 126 | 26 | <DL–193.5 | 25.4 \pm 47.5 A | 8 | 0.3–5.0 | 3.3 \pm 1.6 A |
| 169 | 5 | <DL–3.7 | 0.55 \pm 1.2 A | 2 | <DL–1.1 | 0.26 \pm 0.48 A |
| Mono-<i>ortho</i> PCBs | | | | | | |
| 87 | 27 | 2.6–340.9 | 67.4 \pm 71.5 B | 8 | 36.9–1,716 | 651.1 \pm 644.8 A |
| 179 | 27 | 21.9–7,940 | 486.9 \pm 1,497.4 A | 5 | <DL–1,642 | 244.7 \pm 572.2 A |
| 158 | 27 | 7.4–1,138 | 133.2 \pm 261.3 A | 8 | 4.9–59.4 | 19.5–18.6 A |
| 180 | 27 | 1.8–192.4 | 39.4 \pm 45.2 A | 8 | 0.7–65.1 | 16.12 \pm 24.52 B |
| Total PCBs ^b | 27 | 198–11,697 | 968 \pm 2,168.9 A | 8 | 125–2,815 | 967.6 \pm 1,044.2 A |

^a Different uppercase letters mean statistical differences ($p < 0.0001$).

^b Σ_{egg} [PCBs 8, 28, 37, 44, 49, 52, 60, 66, 70, 74, 77, 81, 82, 87, 99, 101, 105, 114, 118, 126, 128, 138, 153, 156, 158, 169, 170, 179, 180, 183, 187, 189].

dence for the persistence of this compound in the ecosystem and through the food chain. Although cattle egret nests could not be found during the period of sampling, they were recently observed nesting in agricultural hedgerows, which is also nesting habitat for mourning doves and burrowing owls in the Mexicali Valley [21]. This common habitat could presumably reflect similarities in pollutant exposure in these different species.

Concentrations of OP pesticides (diazinon, dimethoate, and malathion) were detected in egg samples at low concentrations ($<1 \mu\text{g/g}$). Mourning doves exhibited higher concentrations of malathion and dimethoate than burrowing owls ($p < 0.001$; Table 1). The most widely used pesticide on wheat crops in the Mexicali Valley in the 2003 to 2004 season was methamidophos, which accounted for 90% of the total pesticide applied. Dimethoate accounted for 2% of the pesticide used in wheat, and malathion was used in the summer cotton crops in limited amounts (M. Vega-Cázares, MS thesis, Centro de Investigación en Alimentación y Desarrollo, Mazatlán, Sinaloa, Mexico, unpublished data). Despite the low amounts of these two compounds used in the Valley and their low persistence in the environment, trace concentrations were still detected in egg samples, which might reflect continuous usage of these pesticides throughout the year. For future studies, we recommend the analysis of methamidophos in egg samples because it is the most widely used pesticide in the Mexicali Valley. We also recommend examination of cholinesterase inhibition in birds as an endpoint of avian exposure and response to OP pesticides.

PCB concentrations

Concentrations of non- and mono-*ortho* polychlorinated biphenyls in egg samples from the Colorado River delta are shown in Table 2. Non-*ortho* PCB 37 and mono-*ortho* PCB 180 were higher in mourning dove than in burrowing owl eggs, and the mono-*ortho* PCB 87 was higher in burrowing owl eggs ($p < 0.001$; Table 2). Polychlorinated biphenyl 77 and 126 are two of the most toxic congeners, with similarities in structure to dioxins. These compounds are persistent in the food chain, resisting bacterial and chemical breakdown, and are readily absorbed into fats of organisms [22]. In mourning

doves, the most frequently detected non-*ortho* PCB congener was PCB 77, whereas in burrowing owls, it was PCB 126 (Fig. 2). Differences in diet (granivorous vs carnivorous–insectivorous) or the migratory nature of the burrowing owl population could explain differences in the amount of PCBs accumulated and in the type of congeners present in egg tissues.

Diets of 20 $\mu\text{g/g}$ of Aroclor 1242 to white leghorn hens resulted in whole-egg concentrations of 0.87 $\mu\text{g/g}$ [23]. This concentration did not affect egg production, egg weight, shell thickness, and weight, but hatchability was affected within two weeks [23]. Mean concentrations of PCBs (non- and mono-*ortho* congeners) found in mourning doves and burrowing owls were below a concentration of 1 $\mu\text{g/g}$. However, the sample egg from a single nest of a mourning dove contained the highest PCB 77 (1,157 ng/g), PCB 179 (7,940 ng/g), and PCB 158 (1,138 ng/g) concentrations of all the samples. This nest was the closest to the Colorado River (200 m). Egg samples from three burrowing owl artificial nests (40% of the total eggs sampled) also exceeded 1 $\mu\text{g/g}$ for PCBs 87 (1,716 ng/g) and 179 (1,642 ng/g).

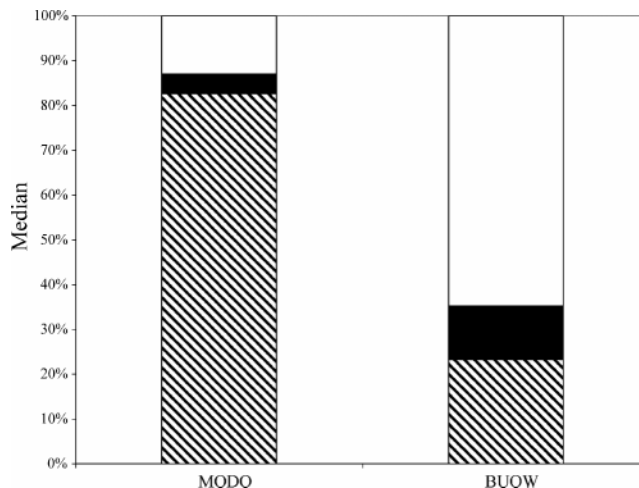


Fig. 2. Median percentage of non-*ortho* polychlorinated biphenyl (PCB) concentrations from mourning dove (MODO) and burrowing owl (BUOW) eggs. (□) PCB 126; (■) PCB 81; (▨) PCB 77.

These results suggest that a portion of the population of breeding birds from the Colorado River delta might be subject to reduced hatchability because of high PCB concentrations in the environment. Possible sources of these compounds are the urban and industrial activities present on the United States/Mexico border. More studies are needed to evaluate the distribution of these compounds in the wetlands and in bird food items.

Heavy metal concentrations

Concentrations of As, Cd, Hg, Pb, and Se were detected in each of the egg samples of the three species analyzed (Table 3). Only one sample of marsh wren egg had a concentration of arsenic (2.2 µg/g) within the range considered to be the level of concern (1.3–2.8 µg/g) in bird eggs [24]. The rest of the samples of the three species did not exceed the 1.3 µg/g NOAEL [24]. High arsenic concentrations are rarely found in eggs, even in those collected close to contaminated agricultural drain water evaporation ponds [25]. However, studies indicate that arsenic is extremely toxic to avian eggs when injected [26]. Although levels of arsenic found in bird eggs were low, it is important to continue monitoring arsenic concentrations in water, sediment, and bird food items from the Colorado River delta.

Cadmium concentrations in birds are generally highest in the kidneys, where chronic toxicity occurs, and lowest in eggs [27,28]. Therefore, apparently birds do not transfer cadmium into eggs [27]. Cadmium concentrations in eggs from different reservoirs in the Lower Colorado River were all below detection limits [29]. However, in this study, samples from mourning doves, burrowing owls, and marsh wren eggs from the Colorado River delta exhibited concentrations that ranged from 0.3 to 4.6 µg/g dry weight, with no significant differences between the three species (Table 3), although mean concentrations were higher in marsh wren eggs (0.8 µg/g dry wt) than in mourning dove (0.6 µg/g dry wt) and burrowing owl (0.5 µg/g dry wt) eggs. It is possible that cadmium enters the delta wetlands through raw sewage discharge of cities and communities along the river and agricultural drains. Although transfer of this metal from the parent to the embryo is apparently limited [27], eggs from aquatic species could be exposed to cadmium through direct immersion of the egg to surface water, parent breast feathers, feet, or nesting materials [30]. Marsh wren nests from this study were all above water level (between 0.5 and 1.6 m); however, the contact of the parents and nesting materials could have increased the concentrations of cadmium in embryos compared with eggs from the other two species. In a study, mallard eggs immersed in water with 5 µg/L of cadmium resulted in a 27% increase in embryonic death, and eggs injected with 0.5 ng of Cd had an increase in embryonic death of 40% [30]. Therefore, even relatively low environmental concentrations of Cd in eggs are of concern for embryonic survival. Because a highly significant positive correlation exists between renal cadmium and metallothionein in birds [27], our recommendation is to estimate metallothionein concentrations as an assay of the toxic potential of cadmium in different species of birds from the delta.

Concentrations of mercury in bird eggs from the Colorado River delta did not exceed the valid lowest observed adverse effect level for mercury in bird eggs (0.5 µg/g wet wt) [31]. Reports have indicated that in 1973, the maximum mercury losses from the Cerro Prieto geothermal plant were 47 kg/year, most of which is lost to the atmosphere and the remainder to

Table 3. Range and mean \pm standard deviation concentrations of trace metals in mourning dove, burrowing owl, and marsh wren egg samples from the Colorado River delta, Mexico

| Element | Concentration (µg/g) ^a | | | | | | | | | | | |
|---------|-----------------------------------|---------------------|--------------------------|------------------|------------------------|---------------------|-----------|-----------------|------------|-------------------|-----------|-----------------|
| | Mourning dove (n = 27) | | Burrowing owl (n = 8) | | Marsh wren (n = 18) | | | | | | | |
| | Wet wt | Dry wt ^b | Wet wt | Dry wt | Wet wt | Dry wt | | | | | | |
| As | 0.02–0.19 | 0.04 \pm 0.03 C | 0.09–0.99 | 0.21 \pm 0.16 | 0.006–0.02 | 0.015 \pm 0.004 B | 0.03–0.10 | 0.07 \pm 0.02 | 0.06–0.44 | 0.11 \pm 0.08 A | 0.29–2.2 | 0.57 \pm 0.42 |
| Cd | 0.05–0.58 | 0.12 \pm 0.08 A | 0.28–2.92 | 0.61 \pm 0.44 | 0.05–0.14 | 0.11 \pm 0.02 A | 0.28–0.74 | 0.56 \pm 0.13 | 0.05–0.92 | 0.15 \pm 0.15 A | 0.26–4.6 | 0.77 \pm 0.78 |
| Hg | 0.003–0.06 | 0.013 \pm 0.015 B | 0.015–0.285 | 0.061 \pm 0.07 | 0.003–0.11 | 0.02 \pm 0.04 AB | 0.01–0.6 | 0.12 \pm 0.18 | 0.01–0.30 | 0.03 \pm 0.06 A | 0.05–1.5 | 0.18 \pm 0.33 |
| Pb | 0.01–0.17 | 0.05 \pm 0.04 A | 0.06–0.855 | 0.23 \pm 0.2 | 0.008–0.04 | 0.02 \pm 0.01 AB | 0.04–0.22 | 0.12 \pm 0.06 | 0.006–0.07 | 0.01 \pm 0.01 B | 0.03–0.36 | 0.09 \pm 0.07 |
| Se | 0.18–0.77 | 0.33 \pm 0.11 B | 0.93–3.85 | 1.66 \pm 0.56 | 0.19–0.39 | 0.33 \pm 0.07 B | 0.96–1.96 | 1.65 \pm 0.34 | 0.67–2.1 | 1.1 \pm 0.37 A | 3.3–10.5 | 5.6 \pm 1.8 |

^a Each of the metals was detected in each of the egg samples. Different capital letters mean statistical differences ($p < 0.0001$).

^b Dry weight value was estimated from wet weight values considering 80% water content in egg samples.

water effluents [32]. However, concentrations of mercury in sediment, fish, invertebrates [6,32], and bird eggs (Table 3) from the Colorado River delta did not exceed 1.0 $\mu\text{g/g}$ wet weight. Studies have shown that the toxicity of mercury can be alleviated with selenium in different matrices, such as aerobic and anaerobic sediments [33], and in fish [34]. In sediments, small amounts of selenium (Na_2SeO_3) can reduce the methylation rate of mercury, gradually detoxifying an ecosystem [33]. Although in this study, no statistical relationship was found between selenium and mercury concentrations in egg samples of each of the three species, we recommend investigating the Se–Hg relationship in sediment and fish from this ecosystem. Mercury concentrations were higher in marsh wren eggs (0.18 $\mu\text{g/g}$ dry wt) than in mourning dove eggs (0.06 $\mu\text{g/g}$ dry wt; $p < 0.0001$). Burrowing owl egg concentrations (0.12 $\mu\text{g/g}$ dry wt) were no different from either of these two species (Table 3). Contaminated wetlands receive atmospheric Hg derived from regional industrial sources, and this element is transformed in sediments through methylation processes to methylmercury, which is the toxic form of mercury made available for biotic uptake [35]. Marsh wrens were probably exposed to higher concentrations of methylmercury by consuming aquatic insects, compared with mourning doves, which consume grains, seeds, and fruits mainly from the agricultural fields and hedgerows.

Lead concentrations in eggs found in the Lower Colorado River are generally below detection limit [31]. In this study, samples of eggs from the three species of birds analyzed contained Pb concentrations from 0.03 to 0.86 $\mu\text{g/g}$ dry weight. Concentrations were higher in mourning dove eggs (0.23 $\mu\text{g/g}$ dry wt) than in burrowing owls (0.09 $\mu\text{g/g}$ dry wt; $p < 0.0001$); concentrations in marsh wren eggs (0.12 $\mu\text{g/g}$ dry wt) were no different from either of the two species (Table 3). Hunting of mourning and white-winged dove, gambel's quail, and ring-necked pheasant is a high-demand activity in the Mexicali Valley (www.turismobc.gob.mx). The current Mexican Federal Firearms and Explosives law (<http://info4.juridicas.unam.mx>) does not specify the type of shot allowed for hunting. This omission has allowed for the use of lead shot for hunting purposes in the Mexican territory, including the Mexicali Valley, as confirmed by local outfitters. Lead poisoning in birds other than waterfowl can result from direct consumption of spent lead shot and consumption of lead shot embedded in food items [36]. It is possible that higher lead concentrations found in mourning dove eggs compared with the other two species in this study resulted from direct consumption of lead shot by the parent bird. However, this problem could be more serious if predators and scavengers fed on unretrieved dove carcasses or wounded doves. More studies are needed to establish possible lead exposure in these species. Burrowing owls are not targeted for hunting. Their food items are primarily insects and mammals (mice, rats, ground squirrels, gophers, chipmunks, shrews, prairie dogs, cottontails, and even bats), although they occasionally ingest other birds, including doves [15]. Burrowing owl egg samples were collected from a remote area in which hunting is not common; however, burrowing owls from other sites in the Mexicali Valley could contain higher lead concentrations. Hunting of ducks in the Cienega de Santa Clara was an important activity as well; however in 1993, the Biosphere Reserve of the Colorado River delta and upper Gulf of California was created and hunting was banned from the Cienega de Santa Clara. This has probably contributed to the reduced concentrations for lead found

in fish [6] and is probably the reason for low lead concentrations in marsh wren eggs found in this study.

Bird eggs collected from selenium-normal study areas usually average $<3 \mu\text{g/g}$ dry weight [24]. Mourning doves and burrowing owls presented levels considered to be collected from a normal area (Table 3). However, marsh wren eggs had all 18 samples with concentrations above 3 $\mu\text{g/g}$, and 90% of the samples ranged from 3.3 to 8.6 $\mu\text{g/g}$ dry weight and were significantly higher than the concentrations found in mourning dove and burrowing owl eggs ($p < 0.001$; Table 1). Results suggest that the main sources of Se in the delta are via the aquatic ecosystems of the Colorado River and its associated wetlands, rather than the local soils. This observation is supported by other studies in which higher Se concentrations were found in sediments from the Colorado River compared with sediments collected from agricultural drains [4,6].

Selenium is a common element found in birds from the lower Colorado River. Concentrations ranging from 2.9 to 10.7 $\mu\text{g/g}$ (dry wt) were found in egg samples from american coot (*Fulica americana*), least bittern (*Ixobrychus exilis*), cliff swallow (*Hirundo pyrrhonota*), great blue heron (*Ardea herodias*), and great-tailed grackle (*Quiscalus mexicanus*) from Cibola and Havasu National Wildlife Refuges in 2000 to 2001 [29]. In the Cienega de Santa Clara, Se was reported in water (median 11 $\mu\text{g/L}$, $n = 10$), sediment (median 1.3 mg/kg , $n = 10$), cattail (median 0.10 mg/kg , $n = 7$), tilapia (median 3 $\mu\text{g/g}$, $n = 2$), carp (median 3.3 mg/kg , $n = 3$), and largemouth bass (median 5.1 mg/kg , $n = 3$). Bioaccumulation was evident in this marsh; higher concentrations were found in carnivorous fish compared with herbivorous or detritivorous fish [37]. *Cistothorus palustris* major food items are bees, ants, and wasps (Hymenoptera); beetles (Coleoptera); leafhoppers (Homoptera); flies (Diptera); moths (Lepidoptera); and bugs (Hemiptera) [38]. This is the first record of selenium concentrations in an insectivorous organism from the Cienega de Santa Clara. Results found in marsh wren eggs were similar to concentrations reported by carnivorous fish in the marsh [37]. It is possible that insects bioaccumulate high levels of Se (comparable with small fish) by feeding on algae and detritus from the sediment.

The embryo is the avian life stage most sensitive to Se poisoning because it is the Se in the egg rather than in the parent bird that causes developmental abnormalities and death of avian embryos; therefore, selenium in the egg gives the most sensitive measure for evaluating hazards in birds [39]. Minimum estimates of real-world (in situ) toxic exposures have been documented for natural populations of birds [24]. Hatchability was affected in black-necked stilts (*Himantopus mexicanus*) from Tulare (Lake Basin, CA, USA) with concentrations in eggs as low as 4.2 to 9.7 $\mu\text{g/g}$ dry weight, and in the Salton Sea (which receives Colorado River water), with average concentrations in eggs of 6 $\mu\text{g/g}$ dry weight [24]. Marsh wrens from the Cienega de Santa Clara had a Se average of 5.6 $\mu\text{g/g}$ dry weight with a maximum of 10.5 $\mu\text{g/g}$ dry weight. Therefore, Se could possibly cause some hatchability problems in marsh wrens from the Cienega de Santa Clara. However, true threshold points for Se toxicity are generally higher than real-world toxic exposures. A laboratory study concluded that the highest mean Se concentration in eggs not associated with reproductive impairment was 3.4 $\mu\text{g/g}$ wet weight and the lowest mean toxic concentration was 11 $\mu\text{g/g}$ wet weight [39]. Most of the marsh wren samples in our study (94%) were less than 1.2 $\mu\text{g/g}$ wet weight, the highest having

a concentration of 2.1 $\mu\text{g/g}$ wet weight. Therefore, on the basis of laboratory data, concentrations of Se found in marsh wren eggs from the Ciénega de Santa Clara are not likely to cause reproductive impairment. Nevertheless, laboratory studies are made on different species (i.e., Mallards, *Anas platyrhynchos*), and environmental conditions such as fluctuating water levels and changes in salinity are not accounted for. We recommend monitoring the reproductive success of marsh wrens and other aquatic birds from the Ciénega de Santa Clara to determine selenium toxicity.

It is important to note that embryos (when found in eggs) of the three species of birds monitored did not exhibit any physical abnormalities.

CONCLUSION

Concentrations of OC pesticides in eggs from granivorous (mourning dove) and a carnivorous bird species (burrowing owl) were all below the NOAEL for terrestrial birds. Organophosphorus pesticide residues were found in egg tissues, suggesting intensive use of these pesticides in the area. The highly toxic non-ortho PCB congeners (PCB 77 and 126) were found in eggs of mourning doves and burrowing owls, respectively, and a single mourning dove egg contained a PCB 77 concentration that exceeded the 1 $\mu\text{g/g}$ threshold for potential reduction in hatchability. Of all metals analyzed, only selenium was present at two to three times normal background concentrations in marsh wren eggs. Arsenic was found in one egg sample (marsh wren) within the range considered to be a level of concern. Cadmium was present in all egg samples at low concentrations, although this element is known to cause embryonic mortality at low environmental levels. Mercury did not exceed the valid lowest observed adverse effect level; higher concentrations were found in aquatic birds. Lead concentrations were higher in mourning dove eggs, probably as a result of lead shot usage. With the exception of lead, marsh wren eggs contained the highest concentrations of metals. These results suggest that wetlands within our study area are more susceptible to metal bioaccumulation than terrestrial ecosystems.

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