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Organochlorine Pesticides and Polychlorinated Biphenyls in American Oystercatchers Nesting Along the Texas Gulf Coast

Miguel A. Mora[1,*], Susan A. Heath[2], Meredith Bohannon[3] and William W. Bowerman[3]

[1]Department of Ecology and Conservation Biology, Texas A&M University, College Station, Texas, 77843, USA

[2]Gulf Coast Bird Observatory, Lake Jackson, Texas, 77566, USA

[3]Department of Environmental Science and Technology, University of Maryland, College Park, Maryland, 20742, USA

[*]Corresponding author; E-mail: mmora@tamu.edu

Abstract.—The American Oystercatcher (*Haematopus palliatus palliatus)* is an important breeding species along the Texas Gulf Coast, particularly between Galveston Bay and Corpus Christi, Texas, USA. American Oystercatchers are considered a species of greatest conservation need and are on the priority list for conservation by the National Fish and Wildlife Foundation. American Oystercatchers feed mainly on oysters (Ostreidae) and other bivalves, which are known to accumulate significant amounts of pollutants. We determined accumulation and potential effects of environmental contaminants, particularly organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs) in blood of American Oystercatchers nesting along the Texas Gulf Coast, USA during 2012 and 2013. Plasma concentrations of OCs and PCBs were low. The most commonly detected OC pesticides were HCB, HCH, α chlordane, endosulfan, methoxychlor, p,p'-DDD, and p,p'-DDE. Total p,p'-DDE concentrations ranged from 2-10 ng/mL ww and total PCB concentrations ranged from 2-54 ng/mL ww. Mean p,p'-DDE concentrations were similar among regions; however, total PCBs were significantly greater ($P = 0.0056$) in blood from adult birds from West Galveston Bay, Texas, USA in 2013 than in blood from young collected in 2012, mostly also from West Galveston Bay. Overall, concentrations of OC pesticides in plasma were low; however, some PCB concentrations were above the NOAEC levels that have been associated with normal reproduction in other bird species. *Received 27 November 2019, accepted 21 May 2020.*

Key words.— American Oystercatcher, organochlorines, PCBs, shorebirds, Texas Gulf Coast.

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Environmental pollution is a continuous concern in the Gulf of Mexico because of increased human activity along the coast including oil exploration, vessel traffic, and various other industrial activities. A variety of environmental pollutants have been reported along the Gulf Coast, Texas, USA, including organochlorine pesticides (OC), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins, furans, and perfluoroctane sulfonates (PFOs) (King and Krynitsky 1986; King *et al.* 1987; Frank *et al.* 2001; Santschi *et al.* 2001; Kannan *et al.* 2002). Other important contaminants include those derived from oil extraction activities, such as, polycyclic aromatic hydrocarbons (PAHs), and metals and metalloids, particularly arsenic, cadmium, selenium, mercury, nickel, and vanadium (Jackson *et al.* 1994; Gohlke *et al.* 2011; Allan *et al.* 2012). Some PAHs are known carcinogens and are highly toxic to birds, marine organisms, and humans. In addition to the direct toxic effects of these substances, the sublethal effects on organisms include disruption of the endocrine system, decreased fertility, embryonic malformations, and decreased productivity in birds and other wildlife (Hoffman *et al.* 1996).

Most environmental contaminant studies on the Texas Gulf Coast have focused primarily on seafood and fish monitoring (Sericano *et al.* 1995; Gohlke *et al.* 2011). To our knowledge, currently there are very few recent studies that provide information on the accumulation and effects of contaminants on upper level organisms such as marine mammals and birds in the Galveston Bay region (Frank *et al.* 2001; Balmer *et al.* 2015; Balmer *et al.* 2018). During 1990, the EPA issued seafood consumption advisories for the upper Galveston Bay and Houston Ship Channel because of elevated concentrations of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-p-furans (PCDFs) in some organisms (Crocker and Young 1990). More recently in 2013, the Texas Department of State Health Services

issued a warning to limit or avoid the consumption of all species of fish and blue crab from the Houston Ship Channel and San Jacinto River because of elevated concentrations of dioxins, pesticides, and PCBs (Texas Department of State Health Services 2013).

The Gulf of Mexico is one of the most important regions in North America for birdwatching and outdoor activities. Bird conservation along the Gulf Coast is of primary importance because it contributes to the conservation of natural resources and provides an economic incentive to the coastal communities by increasing tourism, including bird-watchers and nature lovers, to the region. Therefore, maintaining healthy bird populations along the coast is important from an economic and ecological standpoint. Fish-eating birds are among some of the primary bird groups along the coast, which are also at the top of the food chain and often accumulate more contaminants than other species at lower trophic levels (Borga *et al.* 2004).

The coastal wetland areas, estuaries, and islands in bays along the Texas Gulf Coast represent a primary nesting and feeding ground for many North American birds. The American Oystercatcher (*Haematopus palliatus palliatus)* is an important species that breeds along the Texas Gulf Coast, particularly between Galveston Bay and Corpus Christi Bay, Texas, USA. American Oystercatchers (hereafter oystercatcher) are on the priority list for conservation by the National Fish and Wildlife Foundation and are considered a species of greatest conservation need (Texas Parks and Wildlife Department 2019). American Oystercatchers are restricted to the narrow band of the coastal zone throughout their range where they feed mainly on oysters (Ostreidae) and other bivalves. The threats to their survival are many and include a low overall population size, low reproductive success, delayed breeding (3+ years of age), and environmental pollution. An aerial survey conducted in 2003 estimated that the oystercatcher population in Texas represented approximately 5% of the U.S.A. population (Brown *et al.* 2005). Previous studies reported Galveston Bay as one of the major hotspots for bioaccumulation of chlorinated pesticides and PCBs in oysters in the coastal areas of the Gulf of Mexico (Sericano *et al.* 1990). Schulte *et al.* (2007) indicated that contamination of the primary food source for oystercatchers was among the five major threats to the health of the species. Other major threats involve habitat loss, disturbance from human activities, predation, and rising water levels associated with climate change. The main objectives of this study were: 1) to determine accumulation of environmental contaminants, particularly OC pesticides and PCBs in blood of oystercatcher chicks and adults from colonies along the Texas Gulf Coast; and 2) to evaluate potential sublethal or lethal effects on the species.

METHODS

Study Sites and Blood Sampling

During 2012 and 2013, oystercatchers nesting locations were identified on the Upper Texas Coast in Dickinson Bay, Swan Lake, Galveston Bay, West Galveston Bay, Bastrop Bay, and Drum Bay, and on the Central Texas Coast in East Matagorda Bay. Texas, USA (Fig. 1). Oystercatchers nested on islands in bays in close proximity to the Houston Ship Channel, the Gulf Intra Coastal Waterway, and many major industrial areas. One of the nesting areas in Galveston Bay was adjacent to a superfund site in Texas City, Texas, USA. We collected blood from oystercatcher chicks (n = 9*)* and adults during 2012 (n = 20) from East Matagorda Bay (n = 6), Drum Bay (n = 2), Bastrop Bay (n = 2), West Galveston Bay (n = 14), Jones Bay (n = 2), and Moses Lake (n = 3); and during 2013 (n =11, all adults) from West Galveston Bay (n = 5), Drum Bay (n = 3), Jones Bay (n = 1), Moses Lake (n = 1), and Dickinson Bay (n = 1) (Fig. 1). The samples from chicks collected in 2012 were from Galveston Bay (n = 6), Jones Bay (n = 2), and east Matagorda Bay (n =1). Birds were captured with the use of whoosh nets, noose carpets, and a box trap on the nest (Mills *et al.* 1979; McGowan *et al.* 2005). We took blood from the brachialis vein with a syringe and stored it in heparinized 3 ml vials. Immediately after collection the blood was placed on ice. After transport to a laboratory the blood was placed in a centrifuge and separated into plasma and red blood cells which were stored in separate heparinized vials and then frozen at -20°C. Bird handling and blood collection was accomplished in accordance with training provided by members of the American Oystercatcher Working Group.

Chemical Analysis

Extraction and cleanup of oystercatcher plasma was performed using the solid-phase micro extraction

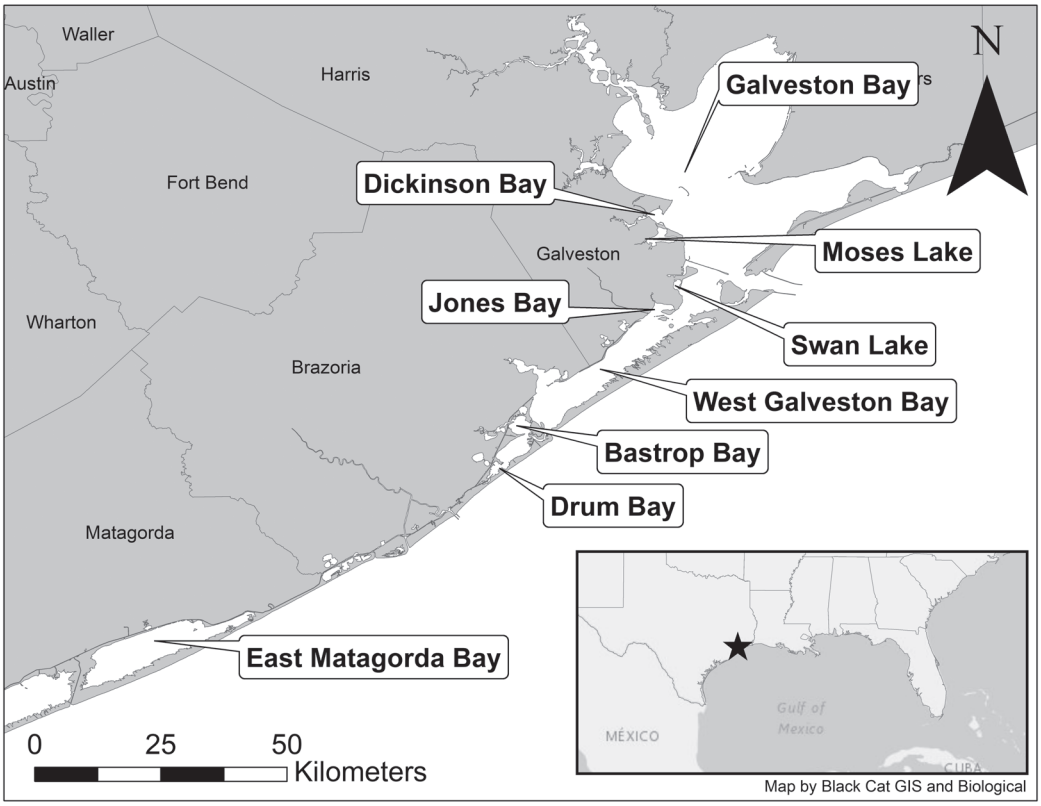

Fig. 1. Map of the Dickinson-Galveston Bay and east Matagorda Bay, Texas areas where the blood samples from American Oystercatcher (*Haematopus palliatus*) chicks and adults were collected, 2012-2013.

procedure for organochlorine compounds as described in Sundberg *et al.* (2006). Briefly, 100 µL of plasma samples were fortified with the surrogate compounds 2,4,5,6-tetrachloro-m-xylene (TCMX), 4,4'-dibromooctafluorobiphenyl (DBOFB), and 2,2',4,5',6-pentachlorobiphenyl (PCB 103) at a final concentration of 20 ppb for each compound, to assess consistency in the extraction and cleanup process. Two 100-µL volumes of sterile chicken (*Gallus gallus*) plasma were treated in the same way for use as control samples in every batch (n = 20) of oystercatcher samples. Additionally, two 100-µL volumes of chicken plasma were fortified with surrogate compounds as well as known amounts of all analytes of interest at a final concentration of 20 ppb, to assess analyte recovery from the extraction and cleanup process for quality assurance purposes. 400 mL of an 8M urea solution was then added to the sample and the sample was further diluted with 900 mL Nanopure water and mixed on a stir plate for 25 minutes for protein denaturation. Each sample was passed through a 30 mg Oasis HLB solid-phase micro-extraction cartridge and both sample vials and cartridges were rinsed with Nanopure water to ensure full application of analytes to the cartridge. Analytes were eluted from the cartridges using 2 ml of dichloromethane (DCM). The sample elutions were concentrated under a gentle stream of nitrogen gas until dry. Finally, an internal standard compound composed of 1-bromo-2-nitrobenzene (BrNB) and 2,2',4,4',5,5'-hexabromobiphenyl (HBB) was added to monitor Gas Chromatograph (GC) performance, for a final concentration of 40 ppb. The sample was further dried under nitrogen, and the sample composed of the surrogate compounds, analytes of interest, and the internal standard compounds was reconstituted to a final volume of 100 µL with hexane.

Sample extracts were analyzed for OCs and PCBs using an Agilent 7890 GC (Agilent Technologies, Santa Clara, California) with an Electron Capture Detector (ECD). The GC settings were consistent with the quantification methods described in EPA method 8081 and 8082. The GC was configured with a split injection, dual columns, and dual ECD detectors to confirm the detection of each analyte. Individual analyte calibration curves were used for individual analyte quantification. One blank solution composed solely of hexane as well as calibration solution composed of the surrogate, spike, and internal standard solutions in their final sample concentrations in hexane were also analyzed with every set of extracted samples to monitor for calibration performance and possible GC contamination. Method detection limits (MDL) were calculated for each analyte, however the quantification limit (QL) for

the Agilent GC is 2 ppb, which is higher than all the MDLs, therefore if a sample is detected by the GC below 2 ppb, then it was given a value of 1, which is half the MDL. Quality assurance protocols required that the blank and spike sample recoveries are between 70 and 130% of the initial concentration added, as well as the calibration solution recoveries. If any of the surrogate, spike, or internal standard compounds did not meet these criteria within a batch, a new aliquot of each of the samples went through the extraction and cleanup method again.

Statistical Analysis

The data were combined for several locations close in latitude because of small sample sizes to facilitate statistical comparisons. For the year 2012, the samples from hatch year individuals ($n = 9$, mostly from Galveston Bay) were separated from adults, and the adults were separated in three regions: East Matagorda Bay ($n = 5$), Drum Bay ($n = 4$, including Bastrop Bay), and West Galveston Bay ($n = 11$, including Galveston Bay and Moses Lake). In 2013 the data were separated in two regions: Drum Bay and West Galveston Bay (including three samples from Jones Bay, Moses Lake, and Dickinson Bay). Concentrations of PCBs were compared between years, age class, and among regions or locations by one-way analysis of variance of normal data with JMP Pro 15 (SAS Institute Inc, Cary, North Carolina). Significant differences among means were determined by the Tukey-Kramer HSD procedure in JMP. Other OCs concentrations could not be compared statistically since they were detected in less than 50% of the samples.

RESULTS

Concentrations of organochlorine pesticides and PCBs in oystercatcher plasma were low. The most commonly detected OC pesticides were hexachlorobenzene (HCB, $n = 9$ of 40), hexachlorcyclohexane (HCH, $n = 11$), alpha chlordane ($n = 4$), endosulfan ($n = 3$), methoxychlor ($n = 4$), p,p'-DDD ($n = 5$), and p,p'-DDE ($n = 20$). Concentrations of these OC pesticides, except for p,p'-DDE, ranged from 2-5 ng/mL and percent detection ranged from 1 to 50%. p,p'-DDE (range 2-10 ng/mL) was the most commonly detected and at greater concentrations than the rest of the OC pesticides. PCBs were detected in 95% ($n = 38$) of the samples and total concentrations ranged from 2-54 ng/mL. Mean p,p'-DDE concentrations were similar between years and among regions in 2012 and 2013 (Fig. 2); however, only two of the 9 blood samples from chicks (mostly from west Galveston Bay) had detectable levels of p,p'-DDE (mean = 3.1 ng/mL, Fig. 3). For PCBs, the lowest mean concentrations were observed in birds from Jones Bay in 2012 and the highest concentrations in Dickinson Bay in 2013 (Fig. 2). However, when blood from young was considered separately from adults, total PCB concentrations were significantly greater in blood from adults from West Galveston Bay in 2013 than in blood from young collected in 2012 ($P = 0.0056$,

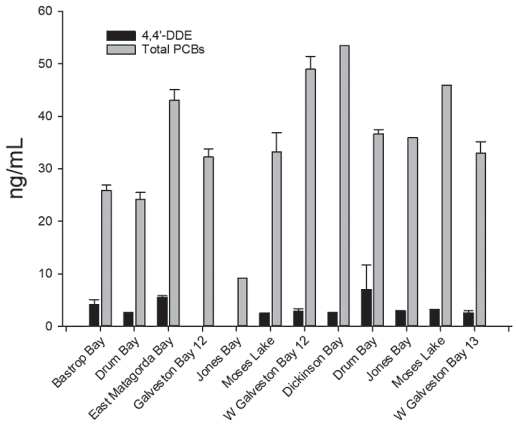

Fig. 2. Mean (arithmetic) p,p'-DDE and total PCB concentrations (ng/mL) ± SD in blood of American Oystercatchers (*Haematopus palliatus*) collected in 2012 and 2013 in various regions in Matagorda and Galveston Bay, TX. Bars with no SD represent individual values.

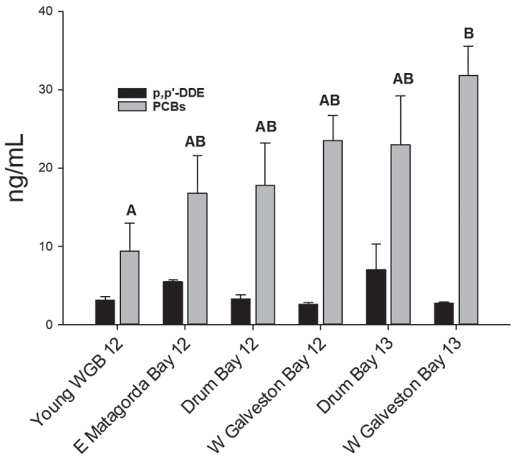

Fig. 3. Mean (arithmetic) p,p'-DDE and total PCB concentrations (ng/mL) ± SE in blood of American Oystercatcher (*Haematopus palliatus*) chicks and adults collected from various colonies in Matagorda and Galveston Bay, TX in 2012-2013. For total PCBs, means not sharing the same letter are significantly different.

Fig. 3). Six of the 9 blood samples collected from chicks were from Galveston Bay; two from Jones Bay and East Matagorda Bay had no detectable levels of PCBs. Mean total PCB concentrations were not significantly different in blood from adults collected during both years and among all regions (Fig. 3). Of 22 PCB congeners analyzed, the following were detected in plasma samples: 8, 18, 28, 52, 44, 66, 101, 153, 105, 126, 187, 156, 180, 195, 206, 118, and 138; and the most common PCB congeners were 18, 28, 52, 44, 66, 153, and 118 (Fig. 4).

DISCUSSION

The results from our study suggest that concentrations of OC pesticides and PCBs in blood of oystercatcher chicks and adults along the Texas Gulf Coast between Galveston and Corpus Christi Bays were low, but PCB concentrations were close to threshold effects associated with negative reproduction in other species. Mean total PCB values in plasma of oystercatchers from East Matagorda Bay, west Galveston Bay, Dickinson Bay, and Moses Lake were above the no observed adverse effect concentration (NOAEC = 36.4 ng/g ww) in plasma of Bald Eagles (*Haliaeetus leucocephalus*) nestlings at which productivity was considered healthy in Bald Eagles from the Great Lakes and the Pacific coast of Canada (Elliott and Norstrom 1998; Bowerman *et al.* 2003). Interestingly, during our study in 2012, productivity in the oystercatcher colonies was one of the worst along the Texas Gulf coast (S. A. Heath, unpubl. data), and PCB concentrations were higher in adults than in chicks, although they were significantly different only in 2013. Fifty-three pairs were monitored each year during the breeding season; the majority of them were in West Galveston Bay. Productivity, measured as the number of chicks fledged divided by the number of nesting pairs, was higher in the West Galveston Bay area in 2013 (0.5) than in 2012 (0.2) (S. A. Heath, unpubl. report). We are not aware of any studies on PCBs and their effects on oystercatcher productivity; however other studies in Texas have suggested that the main factors affecting oystercatcher reproduction (nest and brood loss) include overwash, depredation, and starvation (Koczur *et al.* 2014).

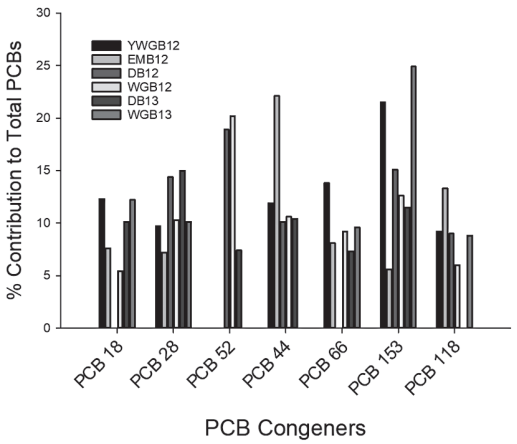

Fig. 4. Percent contribution of the most common PCB congeners to total PCBs detected in blood of American Oystercatchers (*Haematopus palliatus*) collected in 2012 and 2013 from various colonies in Matagorda and Galveston Bay, TX. YWGB (Young West Galveston Bay), EMB (East Matagorda Bay), DB (Drum Bay), WGB (West Galveston Bay).

Very few studies have reported contaminant concentrations and their effects on oystercatchers. The earliest published study provided contaminant data on carcass and follicles of one oystercatcher found dead in South Carolina in 1973; with low levels of p,p'-DDE (0.45 and 0.88 μg/g) observed in carcass and follicles, respectively (Blus *et al.* 1978). OC pesticides and PCBs in blood samples of oystercatchers from Georgia and South Carolina were below detection limits; however, Hg also was measured in blood but at low concentrations (Carlson-Bremmer *et al.* 2010). The contaminant levels detected in oystercatcher blood were consistent with the low levels reported in mussels from the same regions in Georgia and South Carolina (Kimbrough *et al.* 2008). Nonetheless, in a study with oystercatchers in Argentina, elevated concentrations of cadmium (Cd) were observed and were attributed to the diet and to a potential increase of Cd in suspended particular matter over time (Simonetti *et al.* 2015).

Overall, our study shows that persistent organic pollutants, particularly organochlorine pesticides, do not accumulate in oystercatcher chicks and adults on the western Gulf Coast at levels that can affect their growth and survival. However, total PCB concentrations in plasma of adults from four regions were above the NOAEC values at which healthy populations of Bald Eagles are sustained; thus, continued monitoring of oystercatcher colonies in Texas is necessary to determine whether PCBs or other industrial contaminants could be affecting their reproduction.

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All applicable ethical guidelines for the use of birds in research have been followed, including those presented in the "Ornithological Council Guidelines to the Use of Wild Birds in Research" (Fair *et al.* 2010). All birds were handled and captured under approved permits from United States Department of the Interior, Geoloical Survey (banding permit # 23712) and from the Texas Parks and Wildlife Department (SPR-1210-217). We thank Amanda Hackney of Black Cat GIS for help with Fig. 1.

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