STATUS AND TRENDS OF PERSISTENT ORGANIC POLLUTANTS IN EGGS OF APLOMADO FALCONS FROM SOUTH TEXAS

A Thesis

by

CHELSEA MICHELE HIDALGO

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Chair of Committee,	Miguel A. Mora
Committee Members,	Jose L. Sericano
	Jacquelyn K. Grace
Head of Department,	David Caldwell

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ABSTRACT

Addled Eggs from the endangered Northern Aplomado falcon (*Falco femoralis septentrionalis)* were collected annually during 2004-2017, from Laguna Atascosa National Wildlife Refuge and Matagorda Island in south Texas. Eggs were analyzed for persistent organic pollutants, including PCBs, PBDEs, and organochlorine pesticides. Eggshells were measured to determine thickness and to correlate with p,p'-DDE concentrations. My hypothesis is that environmental contaminants in Aplomado falcon eggs have decreased significantly over time and that eggshell thickness values are near pre-DDT measurements. Sixty egg homogenates were extracted, cleaned- up, and analyzed by gas chromatography-mass spectrometry. Eggshell thickness of 156 shells was measured three times around the equator with a Starrett micrometer. Eggshell thickness ranged from 0.206 mm to a maximum of 0.320 mm. Decreasing eggshell thickness is correlated with increasing p,p'-DDE concentrations. The last reported contaminant concentrations in eggs of Aplomado falcons from south Texas were from 1999 to 2003, with a mean of 821 ng/g ww for p,p'-DDE and 1228 ng/g ww for total PCBs. Current contaminant values for this study show an average of 380 ng/g ww for p,p'- DDE, 368 ng/g ww for PCBs and 13 ng/g ww for PBDEs. This study provides information needed in support of the recovery of the Aplomado falcon in south Texas; populations had been steady at over 30 breeding pairs since 2011, however pairs dropped to 26 in 2018 following Hurricane Harvey. Overall, it appears that contaminant concentrations are low, at levels not likely to impact the recovery of the species.

DEDICATION

To my mom and dad, there aren't words sufficient enough to describe how thankful I am for you two. You have always told me to do whatever I want to in life, and then you helped me get there. Dad, you dropped me off and picked me up every day of school from my first day of kindergarten to my first day of college. Even when I am tired of working I choose to keep going because I want to make you as proud of me as I am of you. Mom, you have shown me what it means to work hard, to sacrifice, and to be kind. My accomplishments are not mine alone, because I would never be here if it wasn't for your encouragement and advice. I love you both, and I'm so glad you have always been on my team.

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All other work conducted for the dissertation was completed by the student independently.

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INTRODUCTION

The Northern Aplomado falcon (*Falco femoralis septentrionalis*) was once an iconic species of the American southwest, but suffered great population losses in the early 1900s due to habitat loss and pesticide contamination (Keddy-Hector et al. 2017). The Northern subspecies had a historical range from southern New Mexico and Arizona and along the southern border of Texas, but now established populations in the U.S. are the result of the recovery program led by the Peregrine Fund. Other subspecies extend to the southernmost tip of Argentina. Aplomado falcon territories within the U.S. are located in Laguna Atascosa National Wildlife Refuge (LANWR) and Matagorda Island (MIWMA) (Figure 1) in south Texas, with some effort to reestablish populations in Big Bend National Park and New Mexico (The Peregrine Fund, unpublished data, Keddy-Hector et al. 2017). Surveys of populations outside the U.S. have been inadequate. For example, population declines have not been documented in Mexico (Keddy-Hector et al. 2017).

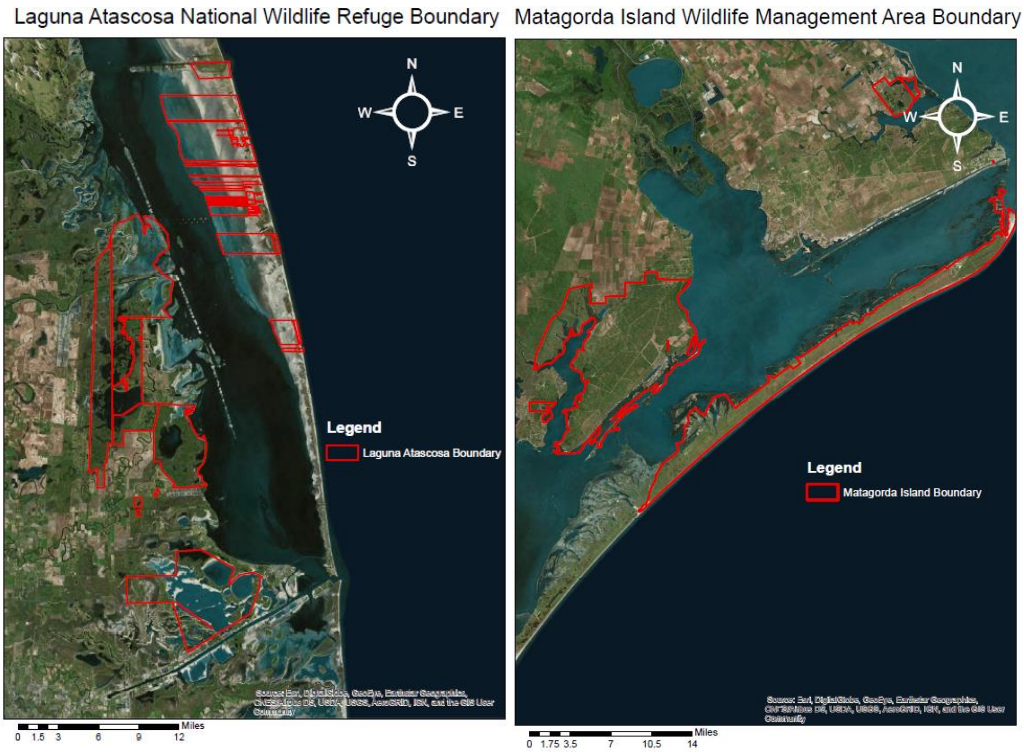

Figure 1. Boundary outlines for two established population areas, Laguna Atascosa and Matagorda Island.

The Aplomado falcon inhabits coastal grasslands, desert grasslands, marshlands and savannahs, much of which has been lost or degraded. This loss and degradation of habitat near the U.S. Mexico border is largely attributed to industrial and agricultural development (USFWS, 1986). Industry presence may also contribute to contamination levels, particularly of polychlorinated biphenyls (PCBs) or polybrominated diphenyl ethers (PBDEs) (Figure 2). The diet of Aplomado falcons consists of medium sized birds, insects, small mammals and reptiles (Keddy-Hector et al. 2017). Specific concerns include contaminants in their habitat that are long-lasting in the environment and have the ability to bioaccumulate. Their position at the top of the food chain makes them vulnerable to persistent organic pollutant (POP) exposure.

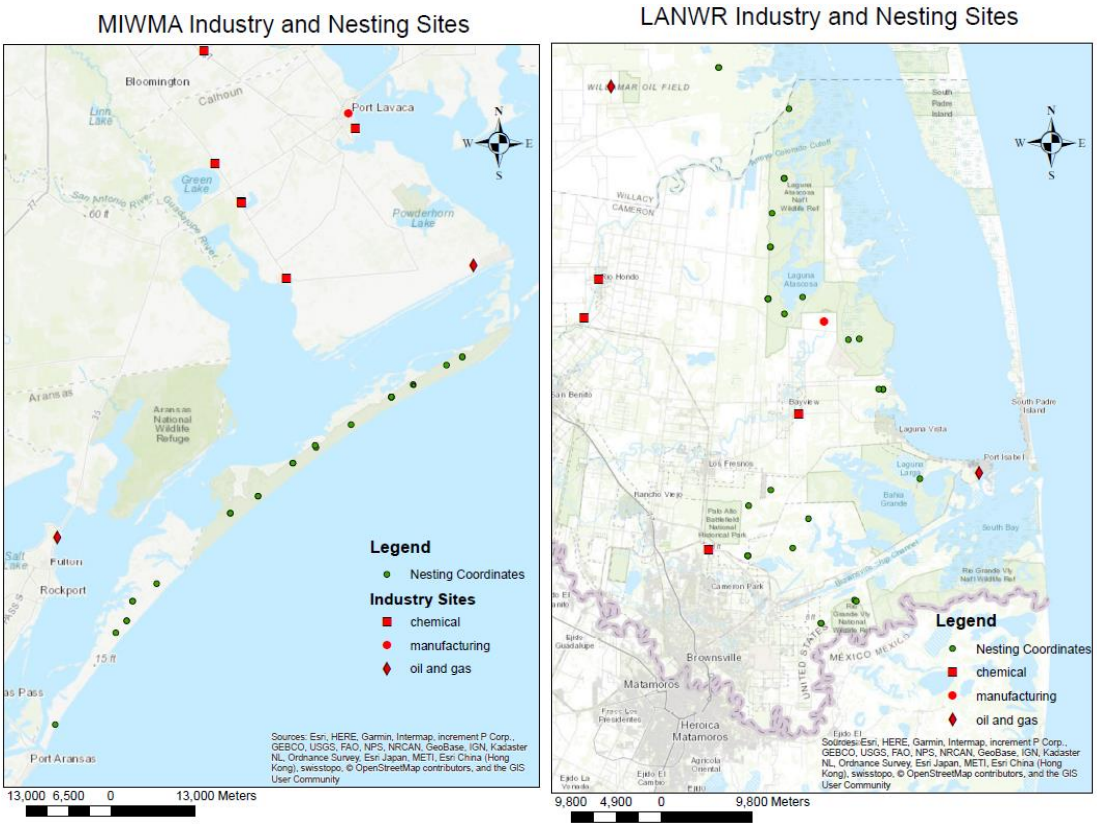

Figure 2. Industrial plants located near nesting sites within Laguna Atascosa and Matagorda Island territories.

POPs are those chemical compounds that are resistant to biodegradation and therefore pose risks to wildlife and the environment. POPs were widely used during the economic upturn after World War II, which increased commercial activity (EPA, 2009). POPs such as 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) and metabolites, chlordane, and heptachlor, were widely used as pesticides for their ability to control vectors of typhus and malaria, as well as control of pests on commercial crops and in household settings (Dikshith and Diwan, 2003). In industrial settings, POPs such as PCBs and PBDEs were used in electrical transformers and capacitors, as plasticizers, and as flame retardants (Dikshith and Diwan, 2003). Today, most of

these POPs are not used in the U.S., but remain problematic due to their resistance to degradation and ability to bioaccumulate. POPs often travel long distances from their source by weather and environmental media and by wildlife itself. POPs can be carried when they evaporate from water or land surfaces, and return to the earth via rain (EPA, 2009; Scheringer, 2009). POPs may also be transported from their source by migratory wildlife that accumulate contaminants in one area, then add to the contaminants in another area by becoming prey or dying and releasing the contaminants back to the environment (EPA, 2009). Studies of POP exposures were linked to declines or abnormalities in many wildlife species, including fish, mammals and birds. Exposed fish exhibited mortality, thyroid defects, reproductive disruption, and developmental abnormalities in response to DDT applications (Adams et al. 1949), PCB exposure (Stalling and Mayer 1972), and PBDEs (Usenko et al. 2011). Mammals exhibited reproductive defects in response to DDT exposure (Tiemann, 2008), liver degeneration after PCB exposure (Vos 1972), and immunotoxic effects from PBDEs (de Wit, 2002). Avian species experienced reproductive impacts in response to DDT (Peakall, 1970, Peakall and Kiff, 1988), liver toxicity from PCBs (Vos 1972) and endocrine disruption from PBDE exposure (Fernie et al. 2005). This study addresses the accumulation and potential effects of organochlorine pesticides (OCs), PCBs, and PBDEs in eggs of Aplomado falcons in south Texas.

Organochlorines were most commonly used as commercial pesticides and in industrial settings. Organochlorine pesticides that elicited negative effects on avian reproduction include chemicals such as DDT and its metabolite 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (DDE), dieldrin, aldrin, toxaphene, chlordane, and heptachlor, among others (Fry, 1995). The toxicity mechanism of organochlorine pesticides is mainly by stimulation of the central nervous system. Many of these chemicals attach at specific sites, blocking entry of calcium or magnesium and

thereby disrupting normal nervous system function (Coats, 1990). DDT has been documented to cause effects on embryos including mortality or reduced hatchability, failure of chicks to survive, and physical abnormalities (Fry, 1995). Adult birds exposed to DDT suffered acute mortality, reduced fertility, suppression of egg formation, and eggshell thinning (Fry, 1995). Eggshell thinning was found to be caused by DDE's inhibition of calcium ATPase in the eggshell glands, thereby reducing the amount of calcium allowed to form the egg (Bitman et al, 1970; Lundholm, 1997). This thinning caused the eggs to be weak and frequently crushed, leading to population declines across numerous bird species (Anderson, 1978, Blus et al. 1972, Henny and Nelson, 1981, Henny, 1972).

PCBs were produced commercially primarily for industrial uses for electrical equipment, thermal insulation, paints, plastics, floor finish, and motor oils. Similar to other organochlorines, these chemicals are bio-accumulative and resistant to biodegradation. Dioxin-like PCB congeners such as PCB 77, 126, and 169, act via the Aryl hydrocarbon receptor (AhR). AhR plays a role in mediating the cell cycle, including proliferation and apoptosis (Neal, 1985; Safe et al.1985; Sleight, 1985). Additionally, AhR interacts with other signaling pathways that control hormone receptors and immunosuppression (Safe et al. 1985). In laboratory studies with PCBs on birds, effects included liver failures, edema in chicks, and lymphoid system distresses (Vos, 1972). Studies with wild birds in the U.K. suggested that PCBs accumulated in the kidney and brain, and had visible effects on motor controls (Prestt, et al. 1970). Current PCB levels are likely to be below those which cause toxicity to liver, immunosuppression, or reduction in productivity (Vos, 1972; Elliot and Henny, 2007).

The toxicity and persistence of PBDEs have been of concern as an emerging contaminant due to their bio-accumulative and degradation resistant properties (Hooper and McDonald, 2000,

Chapman, 2006). PBDEs were widely used as flame retardants in many products such as electronics, furnishings, automobiles, plastics and textiles. Some PBDEs do not chemically bond to the materials they are applied to, making dispersal of the compound widespread (Rahman et al. 2001). Others are covalently bonded to the polymer, but still have the ability to leach from the material and absorb to sediments, particulate matter, or fatty tissues (Rahman et al. 2001). The mechanisms of toxicity are not well understood for PBDEs, but they are known to act as endocrine disruptors and neurotoxins, leading to neurodevelopmental delays, thyroid dysfunction and some evidence of carcinogenicity (Costa and Giordano, 2011). One suggested mechanism is that PBDEs interfere with hormone transportation (Costa et al. 2014). Lab studies demonstrated that thyroxin-binding globulin and transthyretin are proteins that transport thyroxine (T4), and may be interacting with PBDE. PBDEs interaction with these proteins likely displaces the binding of T4, disrupting regulation systems of thyroid hormone production (Costa et al. 2014). Additional mechanistic studies have found PBDEs to induce oxidative stress, cause DNA damage and interfere with calcium signaling (Costa et al. 2010, Madia et al. 2004, Smolnikar et al., 2001). Interruption of these systems can have effects on homeostasis, behavior and growth (Guigueno and Fernie, 2017). The negative impacts seen in wildlife are likely due to similar mechanisms, but mechanistic studies in birds are uncommon and known effects are diverse due to species specific differences. Some studies on American kestrels (*Falco sparverius)* showed a correlation between PBDE levels and T4 and triidothyronine (T3) levels (Fernie et al. 2005, Fernie et al. 2015, Fernie and Marteinson, 2016, Marteinson et al. 2011) while a similar study in peregrine falcons *(Falco peregrinus)* showed little or no effect (Smits and Fernie, 2013). Overall, PBDEs have the potential to elicit negative impacts in avian species, but it is currently unknown if contaminant loads in Aplomado falcon eggs are at levels known to cause adverse effects.

The U.S. Fish and Wildlife Service creates recovery plans for listed species as required under the Endangered Species Act Section 4 (ESA, 1972). The recovery plan for the Aplomado falcon is delegated through FWS lead office 2, Texas Coastal Ecological Services Field Office in cooperation with The Peregrine Fund. The Peregrine Fund has worked continuously with the Service to aide in recovery efforts through reintroduction and monitoring plans. Current monitoring efforts are focused in southern Texas (Keddy-Hector et al. 2017). Data is collected annually on population counts and nesting locations, and blood samples are collected for genetic analysis (The Peregrine Fund, unpublished data). Collecting eggs in order to monitor contaminant levels is also an active objective of the FWS recovery plan (USFWS, 1990). In Texas, the first nesting success was recorded in 1995 from a captive reared and released bird (Hunt et al. 2013). The Peregrine Fund began releasing captive bred Aplomado falcons in 1986 to south Texas, west Texas, and New Mexico, and has since successfully released over 1500 captive bred falcons, and banded greater than 400 young. The captive-release program ceased in Texas in 2011 when the population reached 30 breeding pairs along the Texas gulf coast. Releases are ongoing in New Mexico where there is currently one breeding pair (The Peregrine Fund, unpublished data). Sixty sustainable breeding pairs in the U.S. are required to update the endangered status of this bird; currently, there are approximately 26 breeding pairs in MIWMA and LANWR (The Peregrine Fund, unpublished data). Breeding pairs dropped from 39 pairs in 2017 following Hurricane Harvey (The Peregrine Fund, unpublished data.) The Peregrine Fund hopes to complete the Aplomado falcon recovery plan by 2021 by continuing efforts to determine the self-sustainability of the current population, document nest productivity, measure contaminant levels, and maintain quality habitat (The Peregrine Fund, unpublished data).

This study aimed to analyze collected egg samples for OCs, PCBs, and PBDEs, to gain insight into the current contaminant exposure of the Aplomado falcons in Texas. The objectives of this study were to: 1) Analyze egg contents of Aplomado falcons for persistent organic pollutants, including organochlorine pesticides, PCBs and PBDEs, 2) Analyze changes in eggshell thickness by comparing values in eggshells collected before the use of DDT, during the period of DDT use, and during the recovery phase, 3) Compare concentrations of contaminants in eggs across years and locations. This data provides insight into contaminant load differences at the two collection sights, Matagorda Island and Laguna Atascosa Wildlife Refuge.

Monitoring contaminant levels and recording eggshell thickness trends in Aplomado falcons from south Texas aids in prioritizing the objectives of future recovery plans. This data has allowed for comparisons of egg contents and eggshell thickness from pre-DDT exposure to now, almost 50 years since the outlawing of DDT, and has determined the changes to be statistically significant.

METHODS

Field Collection

Egg collections were conducted at Matagorda Island Wildlife Management Area and Laguna Atascosa National Wildlife Refuge by authorized personnel from The Peregrine Fund. Due to the endangered status of the Aplomado falcon, only addled eggs or egg shell fragments were collected for analysis. Eggs were collected during the breeding season, after other eggs have hatched and chicks fledged in order to only collect eggs that did not successfully hatch. Location coordinates of nest sites were recorded. Collected eggs were rinsed with water, placed in chemically cleaned jars and stored at -20º C. The area and territory location GPS coordinates, (MIWMA or LANWR), type of sample (egg or eggshell), date, and name of the collector were all recorded and given a unique sample ID. 99 eggs and 96 eggshells were collected between 2001-2018 (2001, 2004-2010, 2012-2018). 39 eggs were from MIWMA, 58 from LANWR, and 2 from west Texas. Both the individual eggshells (96) and the shells from eggs that were analyzed (60) were measured, totaling 156 shells. 67 eggshells were from MIWMA, 87 from LANWR, one from W. Texas and one from Luna county New Mexico. Eggs were dissected with an acetone rinsed scalpel along the equator when possible. Egg contents were stored in chemically cleaned and labeled jars and shells were placed in correspondingly labeled beakers. Shells were soaked in water for >3 hours to remove debris, then removed from water and rinsed with acetone to remove remaining lipids or proteins. Eggshells were laid on paper towels to dry for >24 hours and stored in labeled egg cartons. Eggshells were measured using a Starrett No.1010M handheld micrometer marketed by L.S. Starrett Company, Athol, MA. Each eggshell was measured at a random location near the equator of the shell three times and recorded in a lab notebook. An average of the three measurements was taken.

Chemical Analyses

60 whole eggs were selected for chemical analysis. Eggs were chosen to create an even sampling across the two main collection areas, with 31 eggs from LANWR and 28 from MIWMA. Additionally, 1 egg from west Texas was included in the study. Samples were chosen to provide a representation across years, with at least one sample from each year that yielded a collection (2004-2008, 2010, 2012-2017), and multiple samples from the same year when possible. In many cases, multiple eggs from the same clutch were collected in the field. Samples that were analyzed were chosen by only selecting one egg from the same clutch.

All chemical analyses and preparation of samples were performed at the Geochemical and Environmental Research Group, Texas A&M University. Whole egg contents were extracted, purified by silica-alumina columns, and run through high performance liquid chromatography, followed by gas chromatography-electron capture detection (GC-ECD) and gas chromatography/mass spectrometry (GC/MS), as described below. Lipid weights, dry weights, and percent moisture were calculated for each sample. All samples were analyzed for OCs, PCBs and PBDEs.

Sample Extraction

Samples were first homogenized with a PRO0250 model tissumizer (Pro Scientific Inc, Oxford, CT). Any embryos were cut into smaller pieces, while frozen, with clean scissors and tweezers and subsequently macerated for 3 min. A 0.5 gram aliquot of homogenized tissue sample was taken and placed into a labeled 200 mL centrifuge bottle. Samples were run in batches of 20, with each batch including a method blank, duplicate, matrix spike, blank spike and Aromatic Pesticide Analytical Control (APAC) as quality control measures. Method blank and blank spike contained no sample, but had all other procedures performed on it. APAC receives

all surrogates, spikes, and internal standards to be used as a control during instrumental analysis but was not carried through other analytical procedures. 100 µL OC spike and PCB spike were added to the matrix spike, blank spike and APAC. 2,2′,4,5′,6-pentachlorobiphenyl (PCB 103), 4,4′-dibromooctafluorobiphenyl (DBOFB), and 2,2′,3,3′,4,5,5′,6-octachlorobiphenyl (PCB 198) were used as surrogate standards. 100 µL of surrogate standard mixture were added to all samples and APAC. 100 mL methylene chloride were added to each bottle. 40-50 grams of combusted, room temperature anhydrous sodium sulfate was added to each sample immediately before extraction. The methylene chloride extracts were decanted into a large funnel filled with room temperature sodium sulfate and collected in a 500 mL flat bottom flask. Another 100 mL methylene chloride was added to the centrifuge bottle and the maceration and decanting step was repeated two more times (a total of three methylene chloride extractions). Entire extract and macerated sample are decanted into funnel after the third extraction.

Extracts were concentrated on a water bath to about 2 mL, changing the solvent from methylene chloride to hexane.

Purification of Sample Extracts

Alumina was deactivated by adding 1% purified water to total weight. Deactivated silica received 5% purified water to total weight. Both chemicals were mixed on rolling table for one hour. Copper was activated by soaking in hydrochloric acid (12 N) for 5 minutes, followed by rinses in purified water, methanol, methylene chloride. Copper was rinsed with each solvent 3 times, and was stored in hexane until ready to use. Sample extracts were added to columns containing deactivated alumina, deactivated silica, dessicated sodium sulfate, and activated copper in pentane. A 200 mL of 50/50 pentane/ methylene chloride solution were run through the columns at a rate of 2 mL/ min. After the column was finished dripping, 2-3 boiling chips were

added to the 250 mL flask, topped with a 3 ball Snyder column, and were boiled down to 15 mL. The concentrate was transferred to a K-D tube and concentrated down on a water bath to exactly 1 mL, and transferred to teardrop vials. The samples were further purified on HPLC and concentrated to 100 µL in hexane. The internal standard tetrachloro-meta-xylene was added to each sample and to APAC before gas chromatographic analysis.

Determination of Percent Dry Weight

Dry weight was determined by placing a 1g sample of homogenized egg contents into a 10 mL beaker. Beakers were placed in a cardboard box, loosely covered with aluminum foil, and placed in a convection oven for 24 hours at 63ºC-65ºC, until constant weight was achieved. Dry weight percent was calculated by the difference of the dry sample weight over wet sample weight.

Determination of Percent Lipid

20 mL of each extract was saved following the extraction process and allowed to evaporate to dryness. 1.0 mL of methylene chloride was added to the dry sample and reconstituted. An aluminum boat was placed on an electro balance and the weight was tared. 100 µL of the sample was transferred into the aluminum boat and placed on a hotplate until constant weight was attained. The aluminum boat plus lipid sample was weighed on the tared electro balance to determine lipid weight.

Instrumental Analysis

Determination of OC, PCB, and PBDE concentrations was conducted with a system that included a temperature programmable gas chromatograph (Hewlett-Packard 5890A). For pesticides and PCBs, analysis was performed by GC-ECD. The injection port was designed for analyses to be conducted in splitless mode. A 30-m long x 0.25 mm I.D. fused silica capillary

column with 0.25 µm DB-5 bonded phase (J&W Scientific) was used. A mass spectrometer operating at 70 eV (nominal) in the electron impact ionization made and tuned to the mass range 10-700 amu was used for PBDE analysis.

PCB 103 was added before extraction as surrogate and 2,4,5,6-Tetrachloro-meta- xylene was added before analysis as internal standard. For OC analysis, aliquots were injected into the capillary column from an initial temp of 100 ºC to 140 ºC at a rate of 5 ºC min^{-1}. A second ramp rate was programmed for 140 ºC to 250 ºC at a rate of 1.5 ºC min^{-1}. Final temperature was brought to 300 ºC at a ramp rate of 10 ºC min^{-1} for a hold time of 10 min. Injector temperature was held at 275 ºC and the detector temperature at 325 ºC. For determination of PCB concentrations, 2 µL aliquots were injected into the capillary column of the gas chromatograph using an initial oven temp of 75 ºC with a ramp rate of 15 ºC min^{-1} to a temperature of 150 ºC. A second ramp rate of 2 ºC min^{-1} was initiated to 260 ºC, and a final ramp rate of 20 ºC min^{-1} up to 300 ºC for a 1 min hold. Injector temperature was held at 270 ºC. For PBDEs, oven temperature was programmed from 130 ºC and raised to 154 ºC at a ramp rate of 12 ºC/min, then ramped at 2 ºC/ min to a temperature of 210 ºC, and a final ramp up to 300 ºC at a rate of 3 ºC/min and held for 5 minutes.

Productivity

Productivity data was gathered from The Peregrine Fund monitoring projects. Biologists collected yearly nesting information including eggs laid, young hatched, fledged, and banded, as well as UTM coordinates for each nest. Coordinates were used to match each analyzed egg to the productivity data from the nest the egg came from in order to compare contaminant concentrations and productivity.

Statistical Analyses

Chemical concentration data for OCs, PCBs and PBDEs were compared among years and locations. Data that met assumptions of normality and homogeneity of variance were analyzed using analysis of variance (ANOVA) to determine differences in concentrations among years within each site. Data that were not normally distributed (Shapiro-Wilk test, $p > 0.05$) were log transformed to meet assumptions of normality and homogeneity of variance. Simple linear regression was used to examine relationships between OC concentrations and eggshell thickness values. Statistical significance was set at $p \leq 0.05$. Statistical analyses were performed in JMP Pro (Version 13.0.0. SAS Institute Inc 2016).

RESULTS

Eggshell thickness values ranged from 0.206 mm to 0.320 mm, with an average of 0.269 ± 0.026 (SD) mm. Average eggshell thickness for MIWMA across all years was 0.266 mm, and for LANWR was 0.272mm. Eggshell thickness for the Luna County, NM sample was 0.260 mm, and the sample from west Texas measured at 0.240 mm. When the 15 years of data were separated into early years (2001, 2004-2009) and later years (2010, 2012-2018), average eggshell values were 0.267 mm and 0.272 mm respectively. When the data were examined for early years vs late years by location, values for LANWR early years averaged 0.269 mm and for late years at 0.268 mm. MIWMA early and late year averages were 0.253 mm and 0.264 mm respectively. There was no significant difference in thickness values between early years and late years. Mean eggshell thickness values from this study (0.269 mm) were significantly below the mean thickness of 0.279 mm reported for pre-DDT (1887-1926) eggshells (t_{155}=-4.86, $p < 0.0001$) (Kiff and Peakall, 1980). By location, both MIWMA eggshells (t_{66}=-4.21, $p <0.0001$) and LANWR eggshells (t_{86}=-2.61, p= 0.0106) were significantly thinner than pre-DDT thickness value.

p,p'- DDE and oxychlordane were present in l00% of the egg samples. Hexachlorobenzene (HCB), heptachlor epoxide, trans-nonachlor, dieldrin and mirex were present in > 50% of samples, although at low levels (Table 1). p,p'- DDE concentrations were significantly different between locations, with LANWR concentrations higher than those of MIWMA (F_1=9.13, p=0.0038) (Figure 3). LANWR and MIWMA concentration values are similar for all other OCs.

Location	n	% Lipid	% Moisture	Thickness (mm)	HCB	HCE	OCD	tNon	Dieldrin	Mirex	p,p'- DDE
LANWR	31	19	79	0.272	3 (0.73-19)	3 (0.70-10)	9 (3-26)	5 (0.61-37)	3 (0.94-11)	11 (2-56)	505 (113-3190)
MIWMA	28	17	80	0.266	3 (0.45-9)	4 (1-14)	10 (2-38)	2 (0.49-4)	3 (0.54-15)	10(2-71)	256 (50-961)

HCB= Hexachlorobenzene. **tNon** = trans-Nonachlor **HCE**= Heptachlor Epoxide **OCD=** oxychlordane

Table 1. Lipid and moisture percent, eggshell thickness, and average concentrations and ranges (ng/g ww) of pesticides found in >50% of samples separated by location.

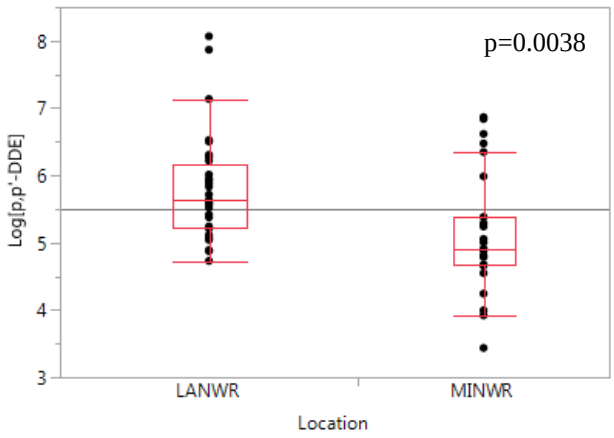

Figure 3. p,p'- DDE concentrations in eggs of Aplomado falcons from two locations in south Texas (LANWR: Laguna Atascosa National Wildlife Refuge; MIWMA: Matagorda Island Wildlife Management Area) Red boxes indicate 25th percentile, median, and 75th percentile. Whiskers indicate interquartile range (IQR).

Eggshell thickness decreased as p,p'- DDE concentrations increased ($F_{1,55}$=12.4, p=0.0009) with an R^2 of 0.19.(Figure 4).

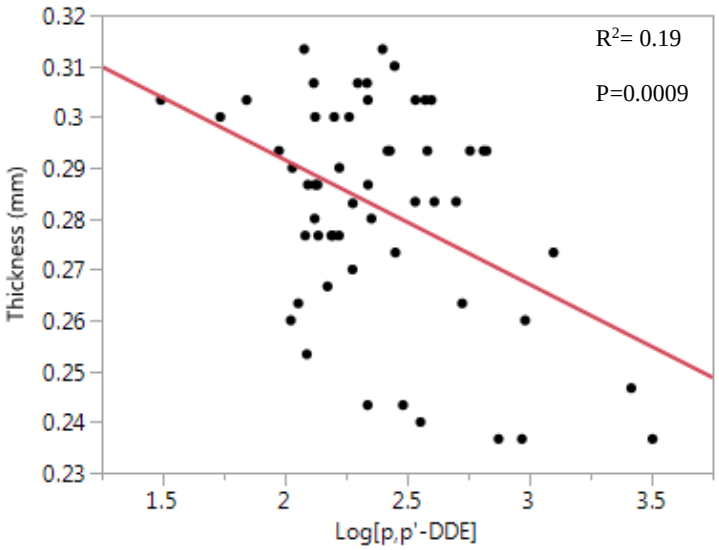

Figure 4. Relationship between eggshell thickness (mm) and p,p'- DDE concentrations (ng/g ww) in eggs of Aplomado falcons from south Texas

Total PCBs in eggs from all locations averaged 368 (range:28-2209) ng/g ww. Mean total PCB concentrations were lower in eggs from MIWMA than in those from LANWR, although not significantly ($F_{1,57}$=1.78, p=0.1873). PCB concentrations in eggs from LANWR averaged 439 ng/g ww and those from MIWMA averaged 297 ng/g ww. PCB Congener 153 was most prevalent in samples, representing about 25% of total PCBs, followed by PCB 180 (14%), PCB 194 (10%) and 138 (8%) (Figure 5). For each location, PCBs 153, 180, 194 and 138 were the most common congeners representing about 57% and 55% of total PCBs for LANWR and MIWMA respectively (Figure 6). Twenty-one PCB congeners were found in > 50% of samples (Table 2). Thirty-three other PCB congeners were detected in < 50% of samples. Hexa- hepta- and octa- chlorinated homologues had the greatest contribution to the total sum of PCBs for both LANWR and MIWMA (Figure 7).

PCB Congener	Average (ng/g ww)
Total PCBs	368 (28-2722)
PCB 99	8 (1-32)
PCB 118	14 (2-91)
PCB 146	8 (1-61)
PCB 153	93(17-666)
PCB 138/160	30 (5-204)
PCB 175	1 (0.7-3)
PCB 187	16 (2-108)
PCB 183	8 (1-67)
PCB 128	4 (0.6-20)
PCB 167	5 (0.8-30)

PCB Congener	Average (ng/g ww)
PCB 171/202	3 (0.5-19)
PCB 156	9 (1-49)
PCB 180	51 (7-422)
PCB 197	6 (1-42)
PCB170/190	22 (5-167)
PCB 199	24 (5-126)
PCB 195/208	12 (1-63)
PCB 207	22 (7-61)
PCB 194	37 (6-228)
PCB 206	10 (1-60)
PCB 209	6 (0.8-34)

Table 2. Total PCB and individual PCB congener concentrations and ranges (ng/g ww) detected in more than 50% of the samples. PCBs grouped together by slashes indicates co-eluting congeners.

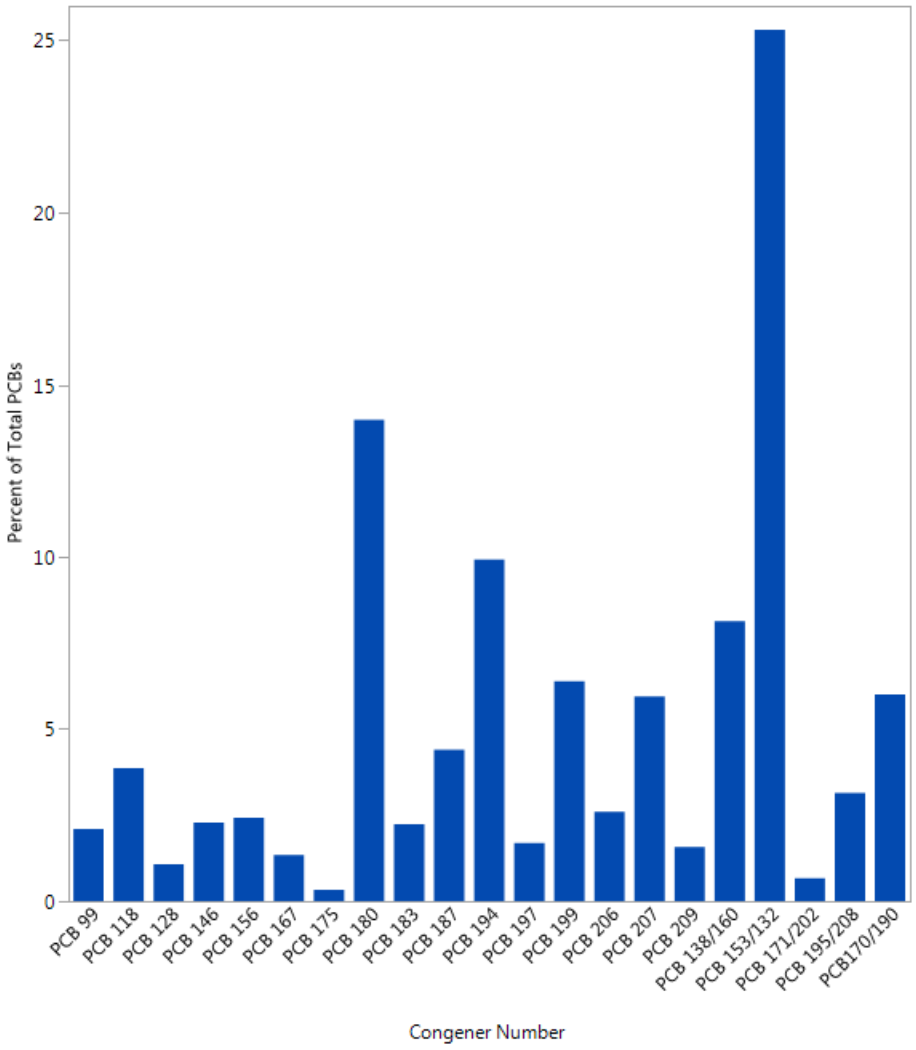

Figure 5. Percent of the total PCB concentration for congeners found in greater than 50% of samples.

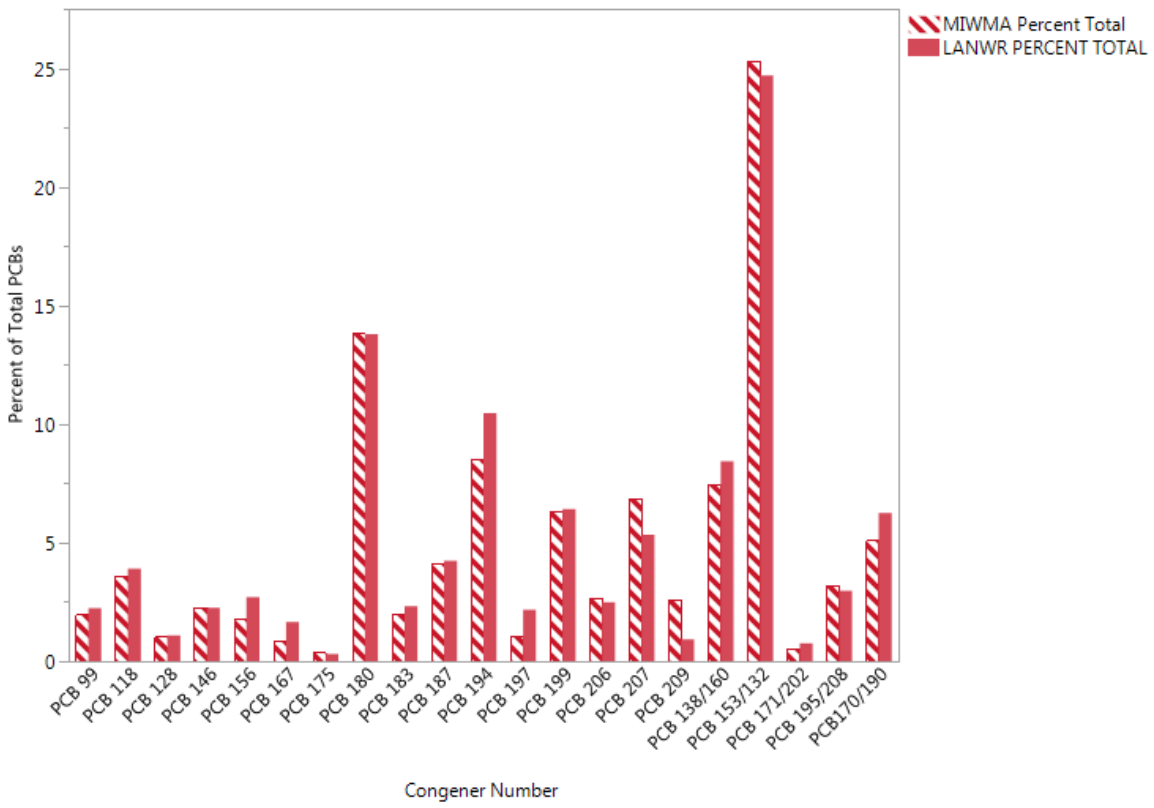

Figure 6. Comparison of percent of the total PCB concentration for PCB congeners found in >50% of samples between LANWR and MIWMA.

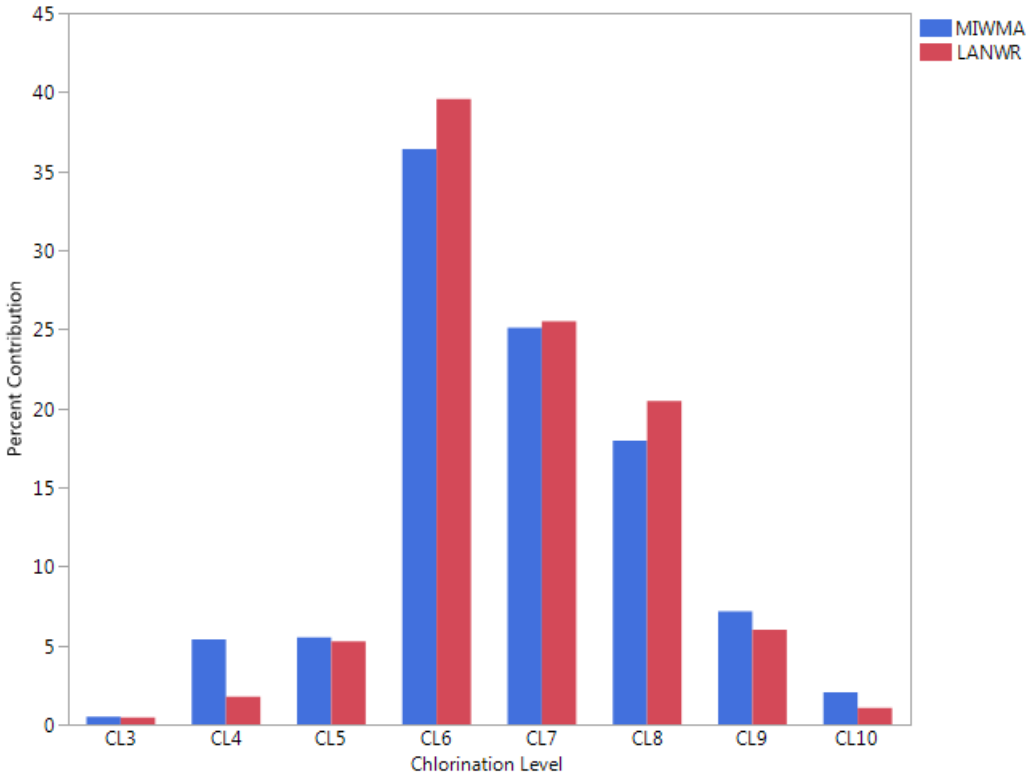

Figure 7. Percent contribution of PCB homologues in both MIWMA and LANWR

Six different PBDE congeners were detected in samples. BDE 47 was detected in all but one sample. BDE 99 and 153 were detected in >85% of samples. BDE 100 was detected in 76% of samples, and BDE 154 was detected in about 50% of samples. BDE 49 was detected in 10% of samples. PBDE totals ranged from 1 to 42 ng/g ww. Total PBDEs for the six congeners present averaged 13 ng/g ww for all south Texas samples. PBDE totals were similar for LANWR (15 ng/g ww) and for MIWMA (10 ng/g ww). PBDE concentrations from early years (2004-2007,2010, 2012) were 2.7 ng/g ww and were significantly different ($F_{1,57}$=5.3, p=0.0250) than later years (2013-2017) at 2.2 ng/g ww.

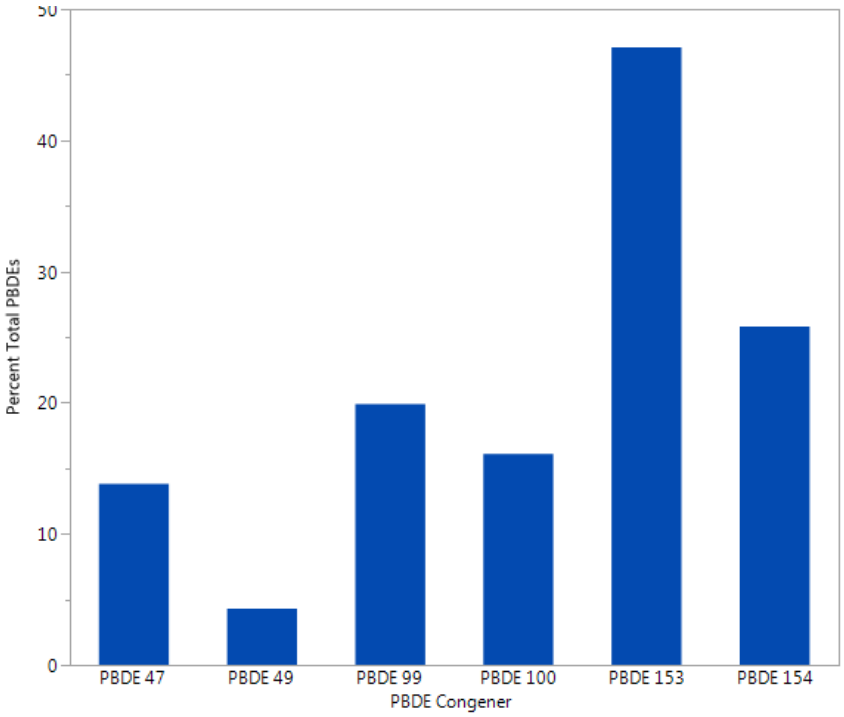

Figure 8. Percentage of the total PBDE concentration for PBDE congeners found in >50% of samples

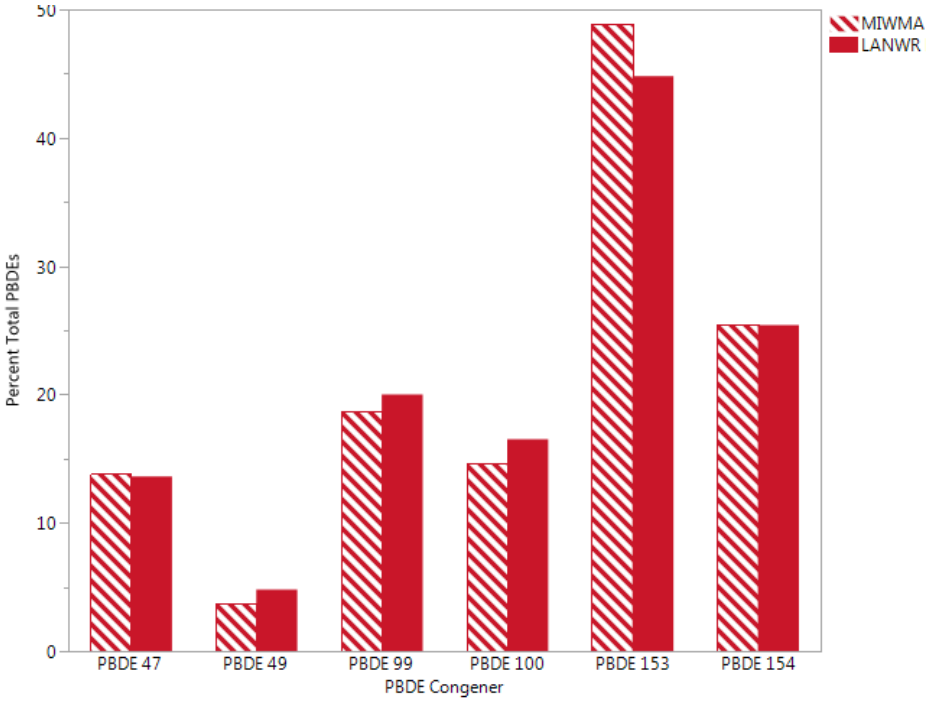

Figure 9. PBDE congener patterns in LANWR and MIWMA

Several nesting sites were used on several occasions by breeding Aplomado falcons, however, we could not determine if it was the same pair returning every year, or if other pairs were using the same nesting site. There were seven nesting locations with repeated nesting activity throughout the collection years in both locations. One egg was collected from each repeated nest site location.

Of the seven nest sites that were reused in LANWR, two nest locations (nest sites 2, 4) showed lower p,p'- DDE concentrations from earlier years to later years, while one other site (nest site 5) had a lower value from 2014 to 2016, while remaining steady for 2017 with no noticeable change (Table 3). Three other sites (sites 1, 3, 7) showed a slightly higher value in p,p'-DDE from early years to later years (Table 3). One nest site (nest site 6) from which an egg was first sampled in 2014 had continuously higher p,p'-DDE in 2015 and 2016, and a lower value in 2017, though the 2017 value did not drop below the value recorded in 2014 (Table 3). Values for other major pesticides followed a similar trend as p,p'- DDE.

NEST SITE	DATE	LOCATION	Hexachloro benzene	Heptachlor Epoxide	Oxychlor dane	Trans-nonachlor	Dieldrin	Mirex	p,p'- DDE
1A	2014	LANWR	2	1	4			4	166
1B	2015	LANWR	3	2	4	37	4	4	358
2A	2016	LANWR	2	2	5	0.47	1	5	281
2B	2017	LANWR	0.89	2	3		1	3	167
3A	2013	LANWR	2.	2	4		1	3	263
3B	2017	LANWR	2	3	7	2	3	6	531
4A	2007	LANWR	2	3	9	1		5	683
4B	2017	LANWR	0.82	1	4	0.68		3	159
5A	2014	LANWR		2	5	1	2	6	183
5B	2016	LANWR	19	1	5			3	131
5C	2017	LANWR	2	2	6	1	1	4	133
6A	2014	LANWR	3	1	5	2		9	189
6B	2015	LANWR	4	2	17	7	2	11	283
6C	2016	LANWR	5		26	0.63	3	21	382
6D	2017	LANWR	2	2	15	4	1	15	219
7A	2014	LANWR	2	3	7	1	1	30	217
7B	2015	LANWR	3	2	9	1		71	251

Table 3. Organochlorine concentrations (ng/g ww) for nest sites at the same location in Laguna Atascosa during different years. Blank spaces are samples with non-detected concentrations.

MIWMA also had seven nesting locations reused for different years. Of the seven, three nest sites (sites 2,4,7) had lower values in p,p'- DDE and most other OC's from early years to late years (Table 4). Two sites (sites 3, 6) had higher values in all OCs, while one other site (site 1) had a similar value for p,p'- DDE but a lower value in other OC's (Table 4). Another nest site (nest site 5) had a change in p,p'- DDE from 398 ng/g ww in 2013 to a lower value of 132 ng/g ww in 2014, but was higher at 572 ng/g ww in 2015 (Table 4).

NEST SITE	DATE	LOCATION	Hexachlorobenzene	Heptachlor Epoxide	Oxychlordane	Trans-nonachlor	Dieldrin	Mirex	P,P'- DDE
1A	2015	MINWR	7	4	38	3	1	10	120
1B	2017	MINWR	2	2	4	0.49		6	121
2A	2014	MINWR	1	2	5	0.88	0.72	5	107
2B	2014	MINWR	1	2	7	1	0.74	7	133
2C	2016	MINWR	1	2	4		0.85	5	54
2D	2017	MINWR	0.45		2			2	31
3A	2013	MINWR	2	3	2	4		4	50
3B	2016	MINWR	1	3	8	3	1	10	157
4A	2014	MINWR	3	14	25	1	15	7.	748
4B	2015	MINWR	7		13			7	189
5A	2013	MINWR	3	5	7		8	8	398
5B	2014	MINWR	1	3	8	1	0.86	10	132
5C	2015	MINWR	7	6	15	2	6	15	572
6A	2013	MINWR	2	3	7			4	136
6B	2016	MINWR	2	4	11	1	2	8	649
7A	2016	MINWR	1	2	9	1	0.69	7	149
7B	2017	MINWR	1	2	5		0.55	7	137

Table 4. Organochlorine concentrations (ng/g ww) for nest sites at the same location in Matagorda Island during different years. Blank spaces are samples with non-detected concentrations.

Concentrations of OCs were similar in eggs collected from nests located in the same territory from early years to later years.

An analysis of the productivity data showed that nests with 2 or fewer eggs had an average DDE value in the analyzed egg of 445 ng/g ww, while nests with >2 eggs had an average of 283 ng/g ww. DDE values for the analyzed eggs were between 225-485 ng/g ww for nests that had 0, 1, 2, or 3 fledglings (Figure 10). For PCB averages, nests with 2 or fewer eggs had an average of 562 ng/g ww in the analyzed eggs and those with >2 eggs had 366 ng/g ww. PCB values in eggs from this study were 189-573 ng/g ww for nests with 0, 1, 2 or 3 fledglings (Figure 11). An ANOVA of contaminant values as a function of eggs laid and young fledged yielded no significant results for both p,p'-DDE and PCBs.

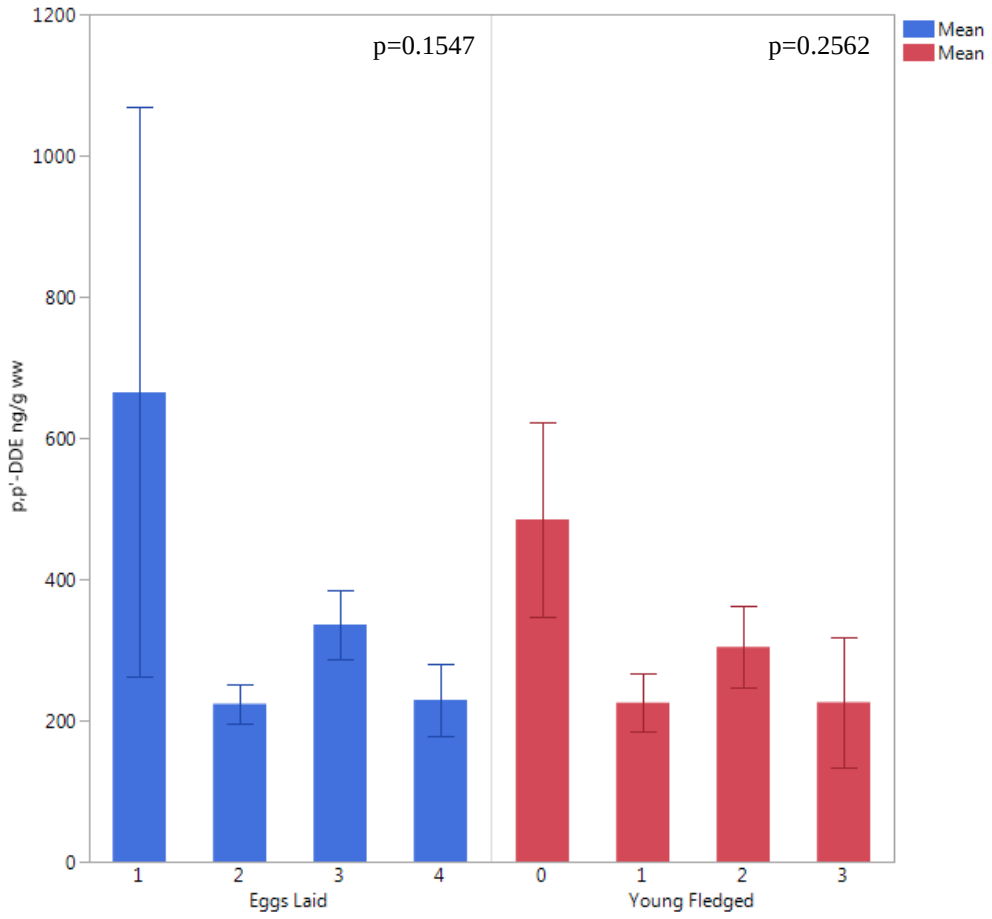

Figure 10. p,p'- DDE averages from eggs analyzed in this study as a function of eggs laid and young fledged. Bars represent standard error.

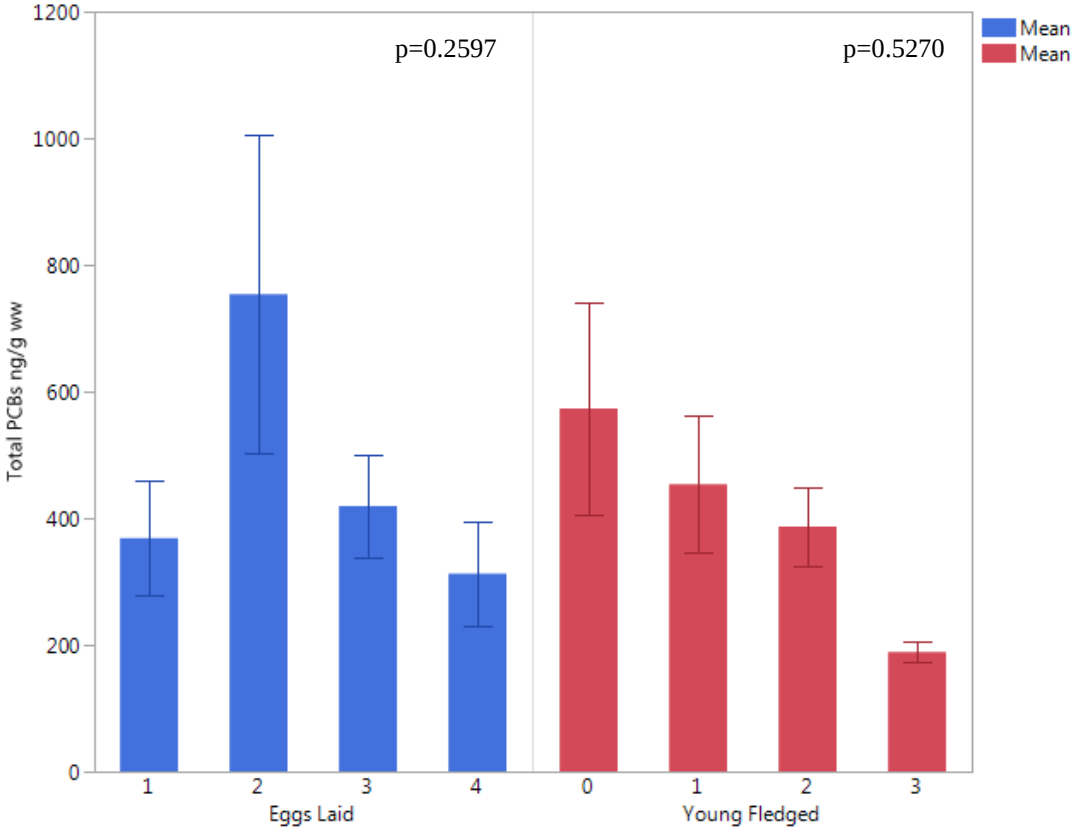

Figure 11. Total PCBs from eggs analyzed in this study as a function of eggs laid and young fledged. Bars represent standard error.

DISCUSSION

The Aplomado falcon used to be a common species in southern Texas but declined during the early 1900s and was considered mostly absent north of Mexico by 1930 (Hector, 1987, Mutch et al. 2001). The reason for the decline of this species is not well known; however, it is suspected the species declined due to habitat loss and degradation, as well as pesticide use. Eggs collected in Mexico from 1957 to 1966 had p,p'-DDE levels as high as 15000 ng/g ww and eggshells averaging 0.223 mm (Kiff and Peakall, 1980). Eggs from south Texas collected in 1995 and 1996 averaged 1410 and 1750 ng/g ww p,p'-DDE, and eggshell thickness 0.295 mm (Mora et al. 1997). Later egg collections (1999-2003) in south Texas and northern Mexico reported eggshell values 0% to 33.7% thinner than pre-DDT eggs, with DDE concentrations in eggs from south Texas ranging 262-6131 ng/g ww (Mora et al. 2008). Concentrations of DDE known to affect eggshell thickness and reproduction in other raptor species is between 200-1200 ng/g ww and 2400-12000 ng/g ww respectively (Fyfe et al. 1976, 1988).

Average eggshell thickness values from this study were 0.269 mm (n=156), however eggshells collected from the same locations in 1995-1996 recorded thickness values of 0.295 mm (n=2). The larger sample size and timespan in this study may have resulted in more accurate thickness values. Samples in this study had a mean DDE concentration of 381 ng/g ww, representing a 92% decrease from the most recent study in 1999-2003 (t_{58}=-9.21, $p < 0.0001$). In this study, LANWR contamination values were higher for nearly every OC when compared to MINWR, though not significantly. In studies from 1999-2003, DDE concentrations were higher in LANWR than MIWMA, but other major OC's (HCB, HCH, Mirex, etc) were higher in MIWMA. The Lower Rio Grande Valley has historically been one of the most intensely farmed areas in south Texas (USFWS, 1986). Lower OC contaminant values from LANWR compared to

MIWMA in 1999-2003 studies could be a reflection of sample size (n=4 MIWMA, n=3 LANWR), as low sample size might not provide a comprehensive view of the territory areas.

DDE concentrations decreased over time at each location, but concentrations from other pesticides did not show any particular trend. In Laguna Atascosa, HCB averaged 2 ng/g ww in previous studies (Mora et al. 2008), and the average for this study was 3±0.37 (SE) ng/g ww. Heptachlor epoxide averages increased in LANWR from 2 ng/g ww (Mora et al. 2008) to 3±0.34 ng/g ww. Oxychlordane increased in LANWR from 8 ng/g ww (Mora et al. 2008) to 9±0.93 ng/g ww. All MIWMA OC values were lower in this study than in previous studies (Mora et al. 2008). Additionally, eggs collected from 1997-2003 detected HCH in 100% of samples, while this study found HCH in less than <50% of samples. Thus, pesticides loads other than p,p'- DDE have appeared to drop in MIWMA, while remaining steady in LANWR.

While the pesticides in this study are no longer in use, perturbation of soil surfaces has the potential to bring buried contaminated soil to the surface, allowing for redistribution of the contaminant. This process may occur through the disturbance of the soil during agricultural practices. MIWMA had a 3 fold increase in agriculture from 2002 to 2017, and the LANWR area had over a 5 fold increase in agricultural production (USDA, 2002; USDA 2018). This could account for some of the differences in OC contaminant values between LANWR and MINWR over time. Generally higher values in LANWR likely reflect differences in agricultural practices in these surrounding areas. For 2017, Calhoun County (Matagorda Island) recorded 107,784 tons of agricultural yields (corn, sorghum, cotton). For the same year, Cameron County (Laguna Atascosa) recorded 508,304 tons (cotton, sugarcane) (USDA, 2018). Cattle production in 2018 in the two counties was approximately the same at 16,500 and 16,200 respectively (USDA, 2018). Soil contaminant monitoring studies are scarce, but 1996 soil samples from Cameron County

averaged 2720 ng/g dw for all OCs including DDT, dieldrin, endrin, chlordane, mirex, and toxaphene (Garcia et al. 2001). We were not able to obtain similar data for Calhoun County. Additionally, the Arroyo Colorado (AC) watershed extends through the northern half of Cameron County leading to the Laguna Madre. The AC has been listed on Texas' list of impaired water bodies since the early 1970s (Enciso et al. 2014). In the late 1970s, fish collected in the AC watershed had 7000 ng/g ww of DDE in fillet tissue samples (White et al., 1983a). Laughing gull *(Leucophaeus atricilla)* carcasses from the same location had DDE concentrations as high as 81000 ng/g ww, whereas Franklin's gull (*Leucophaeus pipixcan*) carcasses had up to 37000 ng/g ww (White et al., 1983a). Long-billed dowitcher *(Limnodromus scolopaceus)* carcasses collected near agricultural drainages in the Laguna Madre near the AC had elevated DDE concentrations of 68000 ng/g ww (White et al. 1983b).

PCB concentrations in eggs that are known to cause significant reduction in productivity range from 20000 ng/g ww to 40000 ng/g ww in other raptor species (Elliott and Henny, 2007). Concentration levels that cause significant effects vary widely among species, and linking PCB concentrations to adverse effects proves difficult due to strong correlations with other contaminants as well as outside environmental factors. The most predominant PCBs in this study were congeners 153, 180, 194, and 138. This is consistent with previous studies that reported similar predominance of congeners (Mora et al. 1997, 2008). Total PCB concentrations in this study (mean 368 ng/g ww), were lower than previously reported at 1003 ng/g ww in 1995-1996 and 1049 ng/g ww in 1999-2003 (Mora et al. 1997, 2008). PCB values reported in this study have declined significantly (t_{58}=-12.66, $p<0.0001$) from collections in 1999-2003.

Eggs collected in this study had higher PCB values in LANWR, but eggs collected in 1999-2003 had higher PCBs in MINWR. Other studies from the early 2000s showed similar

results to this study. White wing doves *(Zenaida asiatica)* collected in Cameron County (MIWMA) in 2003 contained no traceable PCB concentrations (Fredricks et al. 2009). Total PCBs in swallow *(Petrochelidon pyrrhonota)* carcasses collected during 1999 and 2000 from the Brownsville, TX (near LANWR) area averaged 245 ng/g ww (Mora et al. 2006). Doves and swallows represent at least one trophic level lower than that of Aplomado falcons, which could help explain the lower PCB loads. The lower PCB values in Cameron County than in Brownsville supports the trend seen in this study, but not the trend reported for the same time frame from for the 1999-2003 study.

Lower PCB concentration values in MIWMA seen in this study could be explained by greater average distance from nesting sites to industry sites. A review of industry in the area (chemical plants, oil/gas, and manufacturing) (Figure 2) showed that nests were on average 14 miles away from any industry in MIWMA, and LANWR sites to be an average of 6 miles away. This could possibly account for PCB concentration data, but agricultural sources impacting pesticide loads are unclear. Overall, however, a simple linear regression showed there was no correlation between distance to industry and PCB concentration level.

For both DDE and PCB concentrations, there were no significant results indicating that contaminant levels had any impact on productivity. Falcon nests that had at least one addled egg were observed to have between 1-4 eggs total, with 3 being the most common. Assuming that eggs from the same clutch would receive similar environmental conditions, they would likely have similar contaminant loads, although clutch order may produce slight differences in deposition of contaminants (Bryan et al. 2003, Van den Steen et al., 2006). Nests in early years (2004-2007, 2010, 2012) averaged 2 eggs laid and later years (2013-2017) averaged 3 eggs laid. Although one-third of the nests from which addled eggs were collected resulted in 0 fledglings,

productivity data for nests with at least one addled egg showed that the number of young fledged averaged 2 for both early and later years (The Peregrine Fund, unpublished data).

Concentrations of PBDEs in Aplomado falcon eggs from south Texas (13 ng/g ww) were very low and most likely not considered hazardous. PBDE levels of Aplomado falcon eggs in Mexico measured at 101-430 ng/g ww and were likewise not of concern to falcons there (Mora et al. 2011). Osprey (*Pandion haliaetus*) carcasses found dead in Sweden had total PBDE loads of 2,100 ng/g lw (Jansson et al. 1993). Cormorant (*Phalacrocorax auritus*) eggs from northern California contained PBDE concentrations from 3,425 to 5,550 ng/g lw (Klosterhaus et al. 2012). In lab studies, PBDE dosages of 10000-20000 ng/g in eggs of American kestrels seemed to decrease pipping and hatching success, as well as elicited edema and deformities in chicks that failed to hatch (McKernan et al. 2009).

To my knowledge PBDEs have not been reported previously in Aplomado falcon eggs from south Texas, but in this study the concentrations were low. PBDEs in Aplomado falcon eggs collected during 2004-2007 in Northern Veracruz, Mexico averaged 304 ng/g lw, while those in Chihuahua Mexico measured 116 ng/g lw (Mora et al. 2011). PBDEs for this current study averaged 13 ng/g ww, much lower than the Mexican averages. PBDE concentrations in swallow carcasses collected in 2003 from Laredo, Texas averaged 4.4 ng/g ww (Mora et al. 2012). Resident song bird carcasses in Brazos, Burleson, and Brazoria counties of Texas collected in 2011-2013 averaged 34.9 ng/g dw for total PBDEs (Maldonado et al. 2017). Peregrine falcon eggs collected near the Chesapeake Bay averaged much higher PBDE concentrations (182 ng/g ww) than falcon eggs in this study, (12 ng/g ww)(Chen et al. 2010). Osprey eggs collected in Oregon and Washington states in the early 2000s had PBDE totals ranging from 97.7 to 897 ng/g ww (Henny et al. 2009). Compared to these values, my results

show that PBDE levels are very low in eggs of Aplomado falcons in south Texas and not a current concern.

POPs are still prevalent in raptors worldwide; Cooper's hawks *(Accipiter cooperii)* and peregrine falcon carcasses collected in British Columbia from 1999-2010 had DDE values of 47200 ng/g lw and 65900 ng/g lw respectively (Elliot et al. 2015) From the same study, PCBs measured around 16000 ng/g lw for both birds and PBDEs measured 19000 ng/g lw (Cooper's hawk) and 9000 ng/g lw (peregrine falcon). Burrowing owl *(Athene cunicularia)* eggs from Idaho in 2007 and 2008 had DDE concentrations up to 3500 ng/g ww (Stuber et al. 2018). Eurasian sparrowhawk *(Accipiter nisus)* liver tissue collected in Spain in 2009-2012 had 1955.8 ng/g ww DDE and PCBs of 35.6 ng/g ww (Luzardo et al. 2014). Peregrine falcons, eagle owls *(Bubo bubo),* and osprey eggs from Germany in 2014 had total PBDEs of 480 ng/g lw, 289 ng/g lw, and 18 ng/g lw respectively (Vetter et al. 2017).

Aplomado falcon populations have steadily been increasing in the two decades since recovery efforts began. Since 2000, the population has been stable with over 28 pairs, up to a high of 44 in 2005. There are currently 8 pairs in MIWMA, and 18 pairs in LANWR. (The Peregrine Fund, unpublished data). The Peregrine Fund will continue in recovery efforts including habitat management, genetic analyses, and population modelling to continue towards the goal of 60 sustainable breeding pairs outlined in the species recovery plan (The Peregrine Fund, unpublished data).

Mixture toxicity and additive effects of contaminants is complex, and most risk assessment is primarily based on hazards of individual chemicals (Feron and Groten, 2002). Chemical mixtures have been described to act independently or by additive mechanisms, resulting in multiple responses. Many studies that have attempted to address mixture toxicity

focus on human health, often using lab mice or rats as study subjects, therefore mixture toxicity specific to avian species is lacking (Carpenter et al. 1998, Cedergreen, 2014, Hallgren and Darnerud, 2002, Hernandez et al. 2013). Mixture toxicity assessments of multiple organochlorines have not supported concerns of risk presented by mixtures well below their observed affect levels (Carpy et al. 2000). Additionally, reviews of organochlorine pesticide mixtures appeared to overestimate toxicity and risk (Carpy et al. 2000). PCB and PBDEs both have the potential to act as thyroid disrupting agents, but whether their combination has additive, antagonistic or synergistic effects is not well studied. Miller et al. (2012) found that mixtures of PCBs and PBDEs did have additive effects on endocrine systems in rodent model systems at doses at or above observed effect levels; however, exposure in this study was below levels known to affect other raptors.

The accumulation levels for OCs, PCBs, and PBDEs in this study are well below observed effect levels, and mixture toxicity from the particular POPs measured are likely not of concern. However, this study does not address other potential contaminants that Aplomado falcons may be exposed to in south Texas, including heavy metals and current-use pesticides such as neonicotinoids, and therefore the mixture toxicity effects of all potential chemical exposure is unknown. Further studies on a wide variety of mixtures, particularly in avian species, would be helpful in identifying and modeling risks posed to exposed wildlife.

These results indicate that OC pesticides, PCBs, and PBDEs are likely not a threat to Aplomado falcon reproduction in south Texas. The mean contaminant levels in eggs from this study are below levels known to affect other raptor species. Future studies would be improved by reporting on levels of heavy metals and neonicotinoid insecticides in prey of the Aplomado falcon and in addled eggs. Overall, this study provides an assessment of the potential impacts of

environmental contaminants, particularly OC pesticides, PCBS, and PBDEs on Aplomado falcon populations in south Texas. This information should be useful in future revisions and updates to the Aplomado falcon recovery plans.

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APPENDIX A

ID	Year	Percent Moisture	Percent Lipids	Location	Eggshell Thickness (mm)	HCB	HCE	OCD	tNon	Dieldrin	Mirex	p,p'-DDE	Total PCBs	Total PBDEs
1	2004	78.07	22.81	LANWR	0.28	1.75	1.81	4.78			2.20	408.53	233.31	14.80
2	2004	81.83	13.13	MINWR	0.26	1.35	2.93	6.81	0.95		5.21	105.62	228.99	11.26
3	2005	78.69	18.34	LANWR	0.27	3.70	5.75	20.06	4.37	10.71	56.00	1255.35	2722.15	32.77
4	2005	67.92	17.17	LANWR	0.25	2.96	9.53	21.13	4.42	7.57	4.82	2611.38	294.03	23.14
5	2005	78.46	23.30	LANWR	0.32	2.24	6.84	25.62	16.20	2.74	5.38	548.86	298.25	30.51
6	2006	79.17	22.61	MINWR	0.26	1.94	5.35	12.71	1.30	1.81	13.11	960.72	509.09	23.07
7	2006	78.86	17.59	MINWR	0.31	2.50	3.17	9.77	1.24		5.14	198.42	243.89	17.74
8	2006	80.24	15.96	LANWR	0.28	2.00	2.17	5.40	1.12		5.42	341.07	212.93	10.73
9	2006	81.06	17.81	LANWR	0.30	1.18	2.10	5.14	0.61	2.20	2.94	374.51	107.56	1.66
10	2007	82.59	12.65	LANWR	0.31	1.82	2.69	8.51	1.26		4.52	683.11	178.23	11.68
11	2010	73.83	18.61	LANWR	0.24	3.23	2.66	8.43		1.21	25.18	667.01	742.46	28.13
12	2012	71.18	17.54	MINWR	0.29	9.34	11.04	20.41	4.44	2.71	25.09	932.06	1112.44	24.88
13	2012	78.12	20.50	LANWR	0.24	1.12	1.70	6.36			3.23	341.79	168.00	5.05
14	2013	79.19	16.55	LANWR	0.30	2.04	1.49	3.60		1.35	2.57	262.73	95.22	5.42
15	2013	77.07	12.54	MINWR	0.29	2.01	2.89	7.22			4.41	135.80	252.64	12.50
16	2013	80.00	20.67	MINWR	0.29	2.75	4.58	7.09		8.24	7.56	397.57	421.86	19.91
17	2014	81.17	16.08	LANWR	0.30	2.84	1.27	5.03	2.18		8.46	189.35	345.93	13.69
18	2014	78.95	20.81	LANWR	0.28	1.95	1.37	3.64			3.55	166.26	168.68	7.70
19	2014	79.37	16.24	LANWR	0.28	1.75	2.99	7.40	1.26	1.35	29.95	216.51	1061.10	21.95
20	2014	80.00	21.11	MINWR	0.31	1.88	2.30	6.65			5.17	124.01	270.65	10.65
21	2014	80.54	19.58	LANWR	0.29		1.95	4.94	1.04	1.97	5.75	182.98	329.37	8.76
22	2014	80.15	23.55	MINWR	0.30	3.13	13.73	25.43	1.32	14.79	7.22	747.97	475.13	7.61
23	2015	78.88	21.70	LANWR	0.24	3.74	2.07	17.37	7.42	1.91	10.48	282.86	510.61	17.47
24	2015	80.63	18.32	MINWR	0.27	6.68	6.11	15.03	2.01	5.90	15.45	571.57	772.76	15.28
25	2015	69.60	11.97	MINWR	0.29	7.39		12.69			7.02	188.85	402.27	12.54
26	2015	82.16	14.76	MINWR	0.27	6.63	4.30	38.29	2.50	1.11	9.41	119.77	469.64	10.67
27	2015	76.21	23.14	LANWR	0.31	6.78	3.93	10.25		1.95	35.02	303.99	1577.68	26.26
28	2015	77.14	25.69	MINWR	0.24	2.71	2.11	8.96	1.30		70.51	250.79	2443.55	41.87
29	2016	78.97	22.65	LANWR	0.31	4.59		25.55	0.63	3.11	20.97	382.33	714.11	25.77
30	2016	85.46	12.57	LANWR	0.29	18.87	1.20	4.49			3.16	131.08	154.93	6.10
31	2016	81.92	17.52	MINWR	0.31	1.45	1.65	3.65		0.85	4.94	54.34	184.01	6.80
32	2016	82.02	16.75	MINWR	0.30	2.14	3.88	11.06	0.98	1.55	7.51	649.16	301.65	9.39
33	2016	75.85	28.81	LANWR	0.29	1.85	2.42	4.85	0.47	1.01	5.13	280.65	209.28	9.13
34	2017	82.67	12.60	LANWR	0.31	2.10	1.77	15.23	4.13	0.94	14.49	218.54	600.34	21.68

ID	Year	Percent Moisture	Percent Lipids	Location	Eggshell Thickness (mm)	HCB	HCE	OCD	tNon	Dieldrin	Mirex	p,p'-DDE	Total PCBs	Total PBDEs
35	2017	83.77	13.02	MINWR	0.29	0.45		1.51			1.99	31.06	135.98	7.63
36	2017	82.26	20.43	MINWR	0.30	1.52	1.48	4.28	0.49		5.71	121.01	295.29	8.91
37	2017	78.92	18.89	LANWR	0.28	0.90	1.64	2.88		1.00	3.31	166.81	142.01	8.40
38	2017	78.92	15.06	LANWR	0.29	0.82	0.98	3.52	0.68		3.24	159.01	129.75	6.38
39	2017	82.68	23.13	LANWR	0.30	1.49	1.66	5.69	0.89	0.97	3.64	132.93	155.87	11.21
40	2005	80.60	18.21	LANWR	0.30	1.88	4.66	15.92	5.52	5.29	7.43	501.49	486.62	16.85
41	2005	77.73	19.62	LANWR	0.28	0.89	8.68	12.89	4.20	10.70	11.30	3190.44	369.40	14.60
42	2013	81.45	7.09	MINWR	0.24	1.47	2.54	2.42	3.56		4.26	50.46	214.18	8.68
43	2014	79.14	24.56	LANWR	0.25			4.00		1.75	5.26	268.77	191.50	14.11
44	2014	78.80	21.27	MINWR	0.29	1.38	1.97	4.38	0.85		6.47	217.80	262.36	5.05
45	2014	79.46	22.10	MINWR	0.24	1.21	2.80	8.32	1.40	0.86	9.96	132.24	437.97	6.48
46	2014	79.17	15.57	MINWR	0.28	1.08	2.07	5.09	0.88	0.72	4.65	107.19	228.51	1.65
47	2014	79.90	18.89	MINWR	0.29	1.01	2.39	6.55	1.01	0.74	6.60	132.87	307.89	6.66
48	2015	82.95	10.95	MINWR	0.29	2.36	3.50	7.58	1.76	2.07	7.05	122.81	368.07	13.14
49	2015	79.01	23.89	LANWR	0.25	3.05	1.53	3.51	37.41	4.01	3.74	358.44	161.78	11.67
50	2015	81.44	19.01	LANWR	0.24	1.87	0.70	4.40		1.19	14.96	225.65	608.45	11.05
51	2015	83.55	12.40	MINWR	0.28	1.10	3.78	6.52		0.70	5.07	94.45	254.93	5.39
52	2016	79.88	17.35	MINWR	0.29	1.40	3.18	7.95	2.88	1.20	10.16	156.94	544.46	5.29
53	2016	82.05	14.36	MINWR	0.28	1.17	2.16	8.69	1.21	0.69	6.85	149.22	227.75	5.23
54	2016	80.45	15.62	LANWR	0.27	0.73	1.56	2.96	0.76	2.38		113.28	135.27	0.94
55	2016	78.92	20.74	MINWR	0.26	2.33	3.38	7.78	0.66	1.48		218.25	239.92	2.79
56	2017	77.63	18.24	LANWR	0.30	2.03	2.82	7.03	1.99	2.61	6.26	531.00	295.68	13.45
57	2017	78.64	21.74	MINWR	0.26	1.21	1.95	3.71		0.57	4.56	69.64	191.57	4.01
58	2017	79.38	15.03	MINWR	0.30	1.12	1.78	4.76		0.54	7.29	136.77	270.00	3.32
59	2017	78.54	21.77	LANWR	0.28	1.02	2.89	13.62	1.93	0.84	23.22	154.85	905.57	11.40
60	2008	80.45	13.34	W TX	0.28			9.84	6.96	7.98		**	27.65	1.53

**Concentration could not be confirmed

HCB= Hexachlorobenzene. **tNon** = trans-Nonachlor **HCE**= Heptachlor Epoxide **OCD=** oxychlordane