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## East versus West: Organic contaminant differences in brown pelican (*Pelecanus occidentalis*) eggs from South Carolina, USA and the Gulf of California, Mexico

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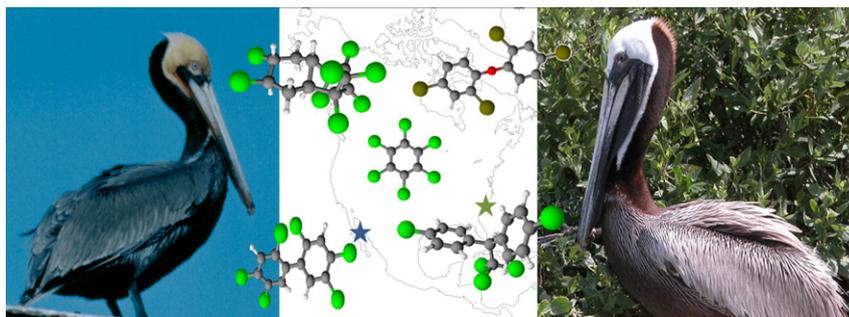
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### HIGHLIGHTS

- ▶ This was the first known analysis of BDEs in the Gulf of California (GofCA).
- ▶ Brown pelicans in southeast U.S. (SC) and GofCA have different population trends.
- ▶ GofCA eggs had higher levels of lower brominated BDEs than SC; patterns also varied.
- ▶ PCBs, chlordanes, dieldrin and mirex were greater in SC eggs; DDTs and HCHs were lower.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Brown pelicans (*Pelecanus occidentalis*) were listed as endangered in the United States in 1970, largely due to reproductive failure and mortality caused by organochlorine contaminants, such as DDT. The southeast population, *P.o. carolinensis*, was delisted in 1985, while the west coast population, *P.o. californicus*, was not delisted until 2009. As fish-eating coastal seabirds, brown pelicans may serve as a biomonitors. Organic contaminants were examined in brown pelican eggs collected from the Gulf of California in 2004 and South Carolina in 2005 using gas chromatography/mass spectrometry (GC/MS). Contaminants were compared using all individual data as well as statistically pooled samples to provide similar sample sizes with little difference in results. Principal components analysis separated the Gulf of California brown pelican eggs from the South Carolina eggs based on contaminant patterns. The South Carolina population had significantly ( $P < 0.05$ ) higher levels of polychlorinated biphenyls (PCBs), chlordanes, dieldrin and mirex, while the Gulf of California eggs had higher levels of dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs). With the exception of dieldrin and brominated diphenyl ether (BDE) 47, this pattern was observed for mussel and oyster tissues from these regions, indicating the need for further study into the differences between east and west coast brown pelican populations and ecosystem contamination patterns.

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### 1. Introduction

In 1970, the brown pelican (*Pelecanus occidentalis*) was listed as endangered in the United States mainly due to reproductive failure and mortality caused by organochlorine pesticides (Gottschalk and Bureau of Sport Fisheries and Wildlife, Fish and Wildlife Service, Department

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of the Interior, 1970; Bureau of Sport Fisheries and Wildlife, Fish and Wildlife Service, Department of the Interior, 1970). Following the banning of many of these contaminants, the southeast population (*P.o. carolinensis*) was delisted in 1985 (Potter and Department of the Interior, Fish and Wildlife Service, 1985), but the remaining brown pelicans, including the west coast population (*P.o. californicus*), were not delisted until 2009 (Eustis and Department of the Interior, Fish and Wildlife Service, 2009). However, since the mid- to late 1980s *P.o. carolinensis* has experienced several important shifts in its population including an expansion in breeding range to the north, establishment of new colonies in Georgia, and a decline in nesting effort in South Carolina (Jodice et al., 2007; Watts and Byrd, 2006). Meanwhile, recent assessment of nesting effort in the Gulf of California population revealed a steady to increasing trend (Anderson et al., 2007). In both populations, it is unclear what mechanism may be underlying these trends, and it is likely that multiple factors are interacting in each population.

This paper compares data of organochlorine pesticides, polychlorinated biphenyls (PCBs) and brominated diphenyl ethers (BDEs) from east and west coast pelican eggs. Organochlorine pesticides and PCBs were chosen because each was demonstrated to have negatively affected pelican populations prior to listing as endangered species. BDEs, often used as flame retardants, were chosen because they represent a class of contaminants of emerging concern which the US Environmental Protection Agency (EPA) has begun to regulate due to concerns about the toxicity (US Environmental Protection Agency, 2012). As brown pelicans are mainly fish-eating, long-living, coastal birds (Shields, 2002), these contaminants have the ability to bioaccumulate and biomagnify, which helped lead to the detrimental effects previously observed for the population, but also makes them a good biomonitors, not only for the marine environment, but also for humans that live in similar environments and consume similar food (International Council for the Exploration of the Sea (ICES), 2003). Eggs were collected from two colonies of brown pelicans from South Carolina, USA (one located in a national wildlife refuge, the other in a major industrial port) and from three colonies in the Gulf of California, Mexico. While a comparison of egg morphometrics was previously conducted between these populations (Anderson and Hickey, 1970), no known comparison of organic contaminant differences among these populations has not been conducted. The purpose of this study was to determine if contaminant differences exist between the South Carolina and Gulf of California brown pelican populations which may elucidate a potential mechanism underlying current population trends. Where applicable, literature values and toxicological effects are also included to enhance the breadth of the comparisons.

## 2. Materials and methods

### 2.1. Sample collection and processing

#### 2.1.1. East—South Carolina

Twenty-eight (28) brown pelican (*Pelecanus occidentalis carolinensis*) eggs were collected from newly formed nests in May 2005 from two South Carolina colonies: (1) Crab Bank (n=18) in Charleston Harbor (32° 46' 58.8" N, 79° 53' 20.4" W) and (2) Marsh Island (n=10) in Cape Romain National Wildlife Refuge approximately 35 km northeast of Charleston, SC (32° 59' 24.0" N, 79° 32' 56.4" W; see Table A1, Supplementary data). Only one egg was collected from each nest, and eggs were only collected from clutches with ≥3 eggs. An attempt was made to spread the collection effort over as wide a portion of the colonies as possible to achieve a representative sample of available eggs. The eggs were floated in water to determine freshness. The eggs that sank were suspected to be in a very early stage of development, while those eggs that floated were older and more developed. Only eggs suspected to still be in the early yolk stage were collected. The eggs were stored in a refrigerator (4 °C) until homogenization using a pre-cleaned hand-held blender (Oster, Shelton, CT, USA) following protocols previously

established for the Seabird Tissue Archival and Monitoring Project (STAMP; see Roseneau et al. (2008) and Vander Pol et al. (2009) for further details). Aliquots of the homogenized sample were pipetted with a hexane-rinsed glass pipette into 15 mL Teflon jars and stored at –80 °C until analysis. Aliquots not analyzed were transferred to liquid nitrogen vapor freezers for long-term storage. To test reproducibility, duplicate aliquots from three randomly chosen samples were analyzed.

#### 2.1.2. West—Gulf of California

Fifteen (15) brown pelican (*P.o. californicus*) eggs were collected from active nests in March and April 2004 from three Gulf of California, Mexico colonies: (1) Isla San Luis, Baja California Norte (BCN; 29° 58' 8.4" N, 114° 24' 3.6" W; n=5), (2) Isla Piojo, BCN (29° 1' 1.2" N, 113° 27' 46.8" W; n=5), and (3) Isla San Lorenzo Sur, BCN (28° 40' 1.2" N, 112° 52' 1.2" W; n=5). Colonies ranged from 500 to 15,000 nests in size. To reduce disturbance, sampled sub-colonies were chosen based on the presence of large numbers of eggs in nests (mid- to late-season breeders). Every other nest was sampled with the egg from each nest chosen blindly. Eggs were opened, and contents were homogenized and stored frozen in acetone rinsed glass jars in Ensenada, BCN, Mexico. Based on limited resources at the time of this study and previous studies that have shown limited loss of data for other seabird eggs compared to individual analysis (Sellström et al., 2003; Turle and Collins, 1992), eggs were pooled in sets of three based on number of eggs per clutch, incubation stage, and location (see Table A1, Supplementary data for details). Immediately prior to preparation for analysis at NIST in Charleston, SC, USA three eggs were pooled by using a hexane-rinsed stainless steel spatula to remove approximately 2.4 g of thawed, homogenized sample to a hexane-rinsed glass jar. The pooled sample was stirred with a clean hexane-rinsed stainless steel spatula prior to removing an aliquot for analysis.

While every effort was made to sample eggs that were very early in incubation, the only eggs available for analysis at Isla San Luis in the Gulf of California were incubated to various stages (Table A1, Supplementary data, incubation stage is an approximation factor that should be multiplied by the average incubation of 30 days). For the worst-case (sample CA-3, Table A1, Supplementary data) the calculated expected moisture loss was 5.1% which is within the analytical variation for the environmental contaminants (Table A2, Supplementary data). Due to the large number of variables involved (variable incubation period, imprecision of stage estimates, etc.) the actual field mass versus the calculated fresh mass were used for all analyses.

### 2.2. Sample preparation and analysis

Approximately 3 g of material from each of the samples were analyzed using methods previously described by Vander Pol et al. (2009). Briefly, the aliquots were extracted by pressurized fluid extraction (PFE), cleaned up using size-exclusion chromatography (SEC), and analyzed by gas chromatography/mass spectrometry (GC/MS) in two injections. The electron impact (EI) GC/MS injection used a 30 m×0.18 mm×0.18 μm i.d. DB-5MS column (J&W Scientific, Folsom, CA, USA) with a 5 m×0.25 mm retention gap added to the beginning of the column and the oven ramp described by Vander Pol et al. (2011). All other GC/MS conditions were as described by Vander Pol et al. (2009). The negative chemical ion (NCI) mode injection used a 30 m×0.18 mm×0.18 μm i.d. DB-XLB column (Agilent, Palo Alto, CA, USA) using the 16 min method described by Vander Pol et al. (2010). Murre Egg Control Material (Vander Pol et al., 2007), procedural blanks, and six calibration solutions were prepared and analyzed along with the egg samples for quality assurance and control.

### 2.3. Statistics

Limits of detection (LODs) were calculated as the maximum of either (1) the lowest observable calibration solution divided by the

sample mass or (2) the mean blank value plus 3 times the standard deviation and then divided by the sample mass. The maximum LODs are given in Table A2, Supplementary data.

To determine if the colonies were statistically different, Multivariate Analysis of Variance (MANOVA) was conducted on the log-transformed wet mass values (to meet normality assumptions) to control for Type 1 error that may occur if multiple individual ANOVAs were conducted. Due to limited degrees of freedom, groups were summed (BDEs, PCBs, dichlorodiphenyltrichloroethanes [DDTs], hexachlorocyclohexanes [HCHs], and chlordanes); hexachlorobenzene [HCB], dieldrin and mirex were individually added. If statistically different ( $P < 0.05$ ), individual ANOVAs and Tukey–Kramer post-hoc tests were used to determine which locations were statistically different. Due to the differences in the sample sizes (5 for the Gulf of California, 18 for Crab Bank, SC and 10 for Marsh Island, SC) that may have affected the first MANOVA, the tests were repeated using the means of 3 egg “virtual pools” for the South Carolina samples. These pools were created by grouping by colony and clutch size and then random assignment to create 6 samples for Crab Bank and 3 for Marsh Island (see Table A1, Supplementary data for sample groupings). The MANOVA and post-hoc tests were repeated as for the individual samples. Principal components analysis was conducted on the percentage of total of all the individual compounds (see Table A2, Supplementary data for list) to help visualize any pattern of the contaminant differences. The individual BDE congeners and PCB homologue groups were also examined using ANOVAs and Tukey–Kramer post-hoc tests on both a mass fraction and percent of the total basis. ANOVAs and Tukey–Kramer post-hoc tests were also used to test the morphological differences of the eggs. For these comparisons, size index was calculated as length  $\times$  breadth to approximate volume as used by Anderson and Hickey (1970) and thickness index was calculated as eggshell mass  $\times 10 / (\text{length} \times \text{breadth})$  as used by Ratcliffe (1967). Statistical tests were conducted using commercially available software (SAS Institute, JMP 7.0.2, Cary, NC, USA).

### 3. Results and discussion

#### 3.1. Contaminant results

The murre egg control material values were within previously reported ranges indicating that the analyses were in control. The three duplicate samples had percent differences that were generally  $< 10\%$  indicating that the processing resulted in homogeneous samples and that analyses were reproducible (Table A2, Supplementary data). Hence, the mean of the replicates is reported hereafter.

The brown pelican eggs had mass fractions ranging from below detection limit to  $1180 \text{ ng g}^{-1}$  wet mass for 4,4'-DDE in sample CA-1 (Table 1 and Tables A3–A5, Supplementary data). There was considerable variation within colonies (overall relative standard deviation [RSD] had a mean  $\pm$  SD of  $74.8\% \pm 29.8\%$  with a range of 14% to 260% with Gulf of California, Crab Bank, SC and Marsh Island, SC colony RSDs shown in Tables A3–A5, Supplementary data, respectively).

Two South Carolina samples, 21–05 and 15–05, had high levels of most contaminants (Tables A4 and A5, Supplementary data) and data from each were originally listed as outliers for Crab Bank and Marsh Island, respectively. However, even after removal, the colonies were not normally distributed. Therefore, these samples were re-included, the values were log-transformed, and subsequently the colonies were log-normally distributed allowing parametric statistical tests to be performed. Egg 23–05 had very high mass fractions and proportions of the lower chlorinated PCBs. Fortunately this sample was randomly chosen for the duplicate analysis (Table A2, Supplementary data), so the values obtained apparently are correct, even though it appears as an outlier on the principal components analysis (Fig. 1). This egg was found outside a nest (Table A1, Supplementary data), but the other two eggs collected from outside a nest (21–05 and 22–05) did not exhibit a similar pattern (Fig. 1 and Table A4, Supplementary data).

Brown pelican eggs from Marsh Island were at least an order of magnitude lower than those reported for eggs collected from this location in the 1970s for DDTs ( $[38.8\text{--}541] \text{ ng g}^{-1}$  vs.  $[360\text{--}11,190] \text{ ng g}^{-1}$ ), dieldrin ( $[5.43\text{--}39.6] \text{ ng g}^{-1}$  vs.  $[<100\text{--}2890] \text{ ng g}^{-1}$ ), and PCBs ( $[172\text{--}1490] \text{ ng g}^{-1}$  vs.  $[700\text{--}36,500] \text{ ng g}^{-1}$ ; see Table 1) (Blus, 1982). Similarly, DDT in the eggs from the Gulf of California were an order of magnitude lower than those reported previously ( $[2.7\text{--}13.6] \mu\text{g g}^{-1}$  lipid mass vs.  $[96.1\text{--}1204] \mu\text{g g}^{-1}$  lipid mass) (Anderson et al., 1975). Based on the maximum residue reported by Blus (1982) that still resulted in nest success for PCBs (18,600  $\text{ng g}^{-1}$ ), DDTs (4840  $\text{ng g}^{-1}$ ), and dieldrin (940  $\text{ng g}^{-1}$ ), current levels are well below those determined to adversely affect reproduction in brown pelicans.

As a class of emerging concern, the BDE data were further analyzed by comparing percentage of the individual congeners to the total BDEs (Fig. 2). BDE 47 was the major congener (mean  $\pm$  SD:  $65.0\% \pm 2.88\%$ , range: 61.0% to 72.1%), followed by BDE 100 ( $18.0\% \pm 1.78\%$ ; 13.3% to 21.2%). The remaining congeners had mean compositions of less than 5% of the total. This pattern is identical to that recently reported for brown pelican eggs from the Chesapeake Bay region along the mid-Atlantic coast of the USA (Chen et al., 2010). The same study reported nearly identical levels of total BDEs as the South Carolina brown pelican eggs (median  $27.5 \text{ ng g}^{-1}$  wet mass with a range of  $6.8 \text{ ng g}^{-1}$  to  $67.9 \text{ ng g}^{-1}$  wet mass; see Table 2 for comparison). These levels are far below those reported to have toxicological effects (lowest observable effect level [LOEL]  $\geq 1000 \text{ ng g}^{-1}$ ) (Chen and Hale, 2010).

#### 3.2. East versus West comparisons

The eggshell morphometrics between the South Carolina and Gulf of California eggs followed the pattern observed by Anderson and Hickey (1970) with no differences in shell size index, but significantly ( $P < 0.0001$ ) lower eggshell masses and hence thickness indices in eggs from South Carolina (Table 2). While eggshells from both regions were still 1% to 5% thinner and lighter than those collected before the use of DDT in 1943, they were thicker and heavier than those collected in the 1950s and 1960s, the latter being 12% to 29% less than the pre-DDT eggshells (Anderson and Hickey, 1970).

A MANOVA comparing the contaminants in the Gulf of California and South Carolina eggs revealed significant differences (Wilks'  $\lambda = 0.0167$ ,  $F_{16,46} = 19.4$ ,  $P < 0.0001$ ). Brown pelican eggs from the Gulf of California had significantly ( $P < 0.05$ ) lower concentrations of  $\Sigma$ chlordanes,  $\Sigma$ PCBs, dieldrin, and mirex and significantly higher levels of  $\Sigma$ DDTs and  $\Sigma$ HCHs compared to the South Carolina colonies while HCB was not significantly different (Table 1). The MANOVA for the “virtual pools” was still significant (Wilks'  $\lambda = 0.00575$ ,  $F_{16,8} = 6.09$ ,  $P = 0.0071$ ) and only the Tukey–Kramer post-hoc test for  $\Sigma$ PCBs was different; this test no longer separated Gulf of California and South Carolina samples although the ANOVA was still significant ( $P = 0.0467$ ; Table 1). Thus pooling samples did not result in much statistical difference and may be a valid option for large sample sizes where the individual data are not required. Similar lack of statistical difference for individual versus pooled samples have previously been shown for guillemot (*Uria lomvia*) (Sellström et al., 2003) and herring gull (*Larus argentatus*) eggs (Turle and Collins, 1992).

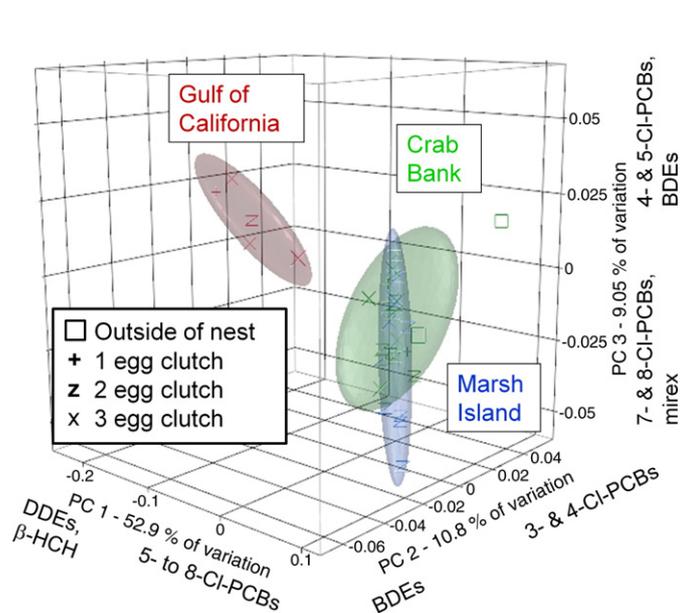
The patterns of contaminants clearly separated the Gulf of California brown pelican eggs from the South Carolina eggs (Fig. 1). The first three principal components accounted for 72.7% of the total variation. Most eggs were well grouped within the respective colonies with the exception of egg 23–05 from Crab Bank, SC. This egg was collected from outside of a nest and had very high proportions of lower chlorinated PCBs ( $\leq 4\text{-Cl-PCBs}$  were 32% of the total PCBs compared to  $< 10\%$  for the other samples). The Gulf of California eggs contained significantly ( $P < 0.05$ ) higher proportions of all DDTs (except 2,4'-DDT/4,4'-DDD was not significantly different), HCHs, HCB, and BDEs 28, 47, 99, and 100 and lower proportions of all PCBs (except 28/31 and 44 which were not significantly different), BDE 155, all chlordanes compounds,

**Table 1**  
Contaminant levels (geometric means in  $\text{ng g}^{-1}$  wet mass with ranges shown in parentheses) in brown pelican (*Pelecanus occidentalis*) eggs. ANOVA F ratios and probabilities are shown following significant MANOVAs (original data: Wilks'  $\lambda = 0.0167$ , approximate  $F_{16,46} = 19.4$ ,  $P < 0.0001$ ; virtual pooled data: Wilks'  $\lambda = 0.00575$ , approximate  $F_{16,8} = 6.10$ ,  $P = 0.0071$ ) and groups with different letters were significantly different based on Tukey–Kramer HSD post-hoc tests. Note: for  $\Sigma$  PCBs, the colonies could not be differentiated by the post-hoc test for the virtual pooled data.

N Compound	Crab Bank, South Carolina		Marsh Island, South Carolina		Gulf of California	F ratio probability	
	18	6 virtual pools of 3	10	3 virtual pools of 3	5 pools of 3	33	14
						Original data	Virtual pooled
$\Sigma$ Chlordanes	43.2 <sup>A</sup> (22.8–148)	48.7 <sup>A</sup> (31.8–70.7)	35.8 <sup>A</sup> (11.0–118)	44.6 <sup>A</sup> (30.2–66.5)	13.6 <sup>B</sup> (6.20–25.1)	7.70 0.0020*	10.4 0.0029*
$\Sigma$ DDTs	132 <sup>B</sup> (53.8–466)	150 <sup>B</sup> (96.6–215)	119 <sup>B</sup> (38.8–541)	158 <sup>B</sup> (104–266)	489 <sup>A</sup> (223–1210)	9.93 0.0005*	9.26 0.0044*
$\Sigma$ HCHs	1.05 <sup>B</sup> (0.542–3.42)	1.15 <sup>B</sup> (0.812–2.20)	0.830 <sup>B</sup> (0.486–1.30)	0.914 <sup>B</sup> (0.725–1.05)	13.6 <sup>A</sup> (6.46–36.7)	61.3 <0.0001*	43.0 <0.0001*
$\Sigma$ PBDEs	25.8 (10.6–66.6)	29.1 (15.6–48.8)	25.3 (10.2–69.8)	30.0 (22.3–44.4)	61.5 (11.7–262)	2.96 0.0669	1.15 0.351
$\Sigma$ PCBs	565 <sup>A</sup> (262–1800)	620 <sup>A</sup> (444–940)	512 <sup>A</sup> (162–1490)	628 <sup>A</sup> (491–941)	135 <sup>B(A)</sup> (28.6–945)	7.60 0.0021*	4.10 0.0467*
Dieldrin	16.7 <sup>A</sup> (9.26–56.8)	18.2 <sup>A</sup> (13.3–27.2)	15.0 <sup>AB</sup> (5.43–39.6)	17.8 <sup>AB</sup> (13.8–24.9)	5.42 <sup>B</sup> (3.15–9.96)	3.92 0.0306*	6.27 0.0152*
HCB	1.54 (0.819–3.66)	1.68 (1.42–2.29)	1.45 (0.563–3.60)	1.76 (1.29–2.44)	2.73 (1.06–5.16)	2.93 0.0687	2.10 0.1694
Mirex	5.53 <sup>A</sup> (2.56–14.2)	6.21 <sup>A</sup> (4.14–8.73)	4.80 <sup>A</sup> (1.92–18.6)	6.08 <sup>A</sup> (4.02–10.6)	0.287 <sup>B</sup> (0.146–0.629)	59.2 <0.0001*	65.1 <0.0001*

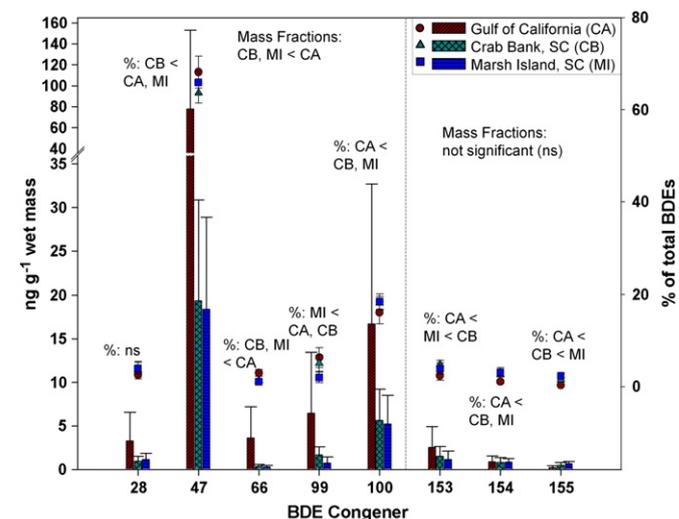
dieldrin, and mirex than the South Carolina eggs. The only significant differences between the South Carolina colonies were higher proportions of BDE 155, and PCBs 154, 178, and 187 at Marsh Island than at Crab Bank.

The Gulf of California brown pelican eggs had significantly ( $P < 0.05$ ) higher mass fractions of the lower brominated BDE congeners (28, 47, 66, 99, and 100) compared to the South Carolina eggs while BDE congeners 153, 154, and 155 were not statistically different (Fig. 2). The proportions of these congeners to the total also followed a similar pattern with the exception of BDE 28 not being significantly different and BDE 100 had higher proportions in the South Carolina eggs. This is believed to be the first study of flame retardants in the Gulf of California, so it is uncertain if this pattern is indicative of the local ecosystem. However, based on the California state government requirements that furniture and bedding sold in the state be flame-retardant (State of California, 2011), it is not surprising that this increased consumer use of BDEs has affected the wildlife in the region.



**Fig. 1.** Principal components analysis of brown pelican (*Pelecanus occidentalis*) eggs from Gulf of California, Mexico and South Carolina, USA. Compounds contributing to the loadings are shown along the axes.

Polychlorinated biphenyl homologue groups were also investigated further for differences among the colonies. This time the lower chlorinated groups showed no statistical differences in either the mass fractions or proportions to the total PCBs (Fig. 3). The hexa-PCBs comprised a greater proportion of total PCBs in the Gulf of California brown pelican eggs compared to the South Carolina eggs, while the latter had higher proportions of the hepta- and octa-PCBs. The Marsh Island, South Carolina eggs also had significantly greater mass fractions of the octa-PCBs than the Gulf of California eggs. While studies on PCBs in loggerhead turtles (*Caretta caretta*) have occurred both in the Gulf of California and Cape Romain NWR South Carolina, the tissues examined differed with liver in the former and eggs and chorioallantoic membranes (CAM) in the latter and a decade elapsed between studies (Cobb and Wood, 1997; Richardson et al., 2010). However, as no other studies were as similar for the regions, the proportions of the PCBs to the total contribution were compared based on the means reported. The Gulf of California turtles had



**Fig. 2.** Mean  $\pm 1$  standard deviation of mass fractions ( $\text{ng g}^{-1}$  wet mass) and percentage of total brominated diphenyl ether (BDE) congeners in brown pelican (*Pelecanus occidentalis*) eggs. All the percentages, except BDE 28, had significant ANOVAs ( $P < 0.05$ ). Tukey–Kramer HSD post-hoc test results are shown for colony differences. Mass fractions of BDE congeners 153, 154, and 155 were not significant; the rest had significantly higher values in the Gulf of California eggs. See Table A1 Supplementary data for sample information.

**Table 2**

Brown pelican (*Pelecanus occidentalis*) morphological summary information with ANOVA F ratios and probabilities. Colonies with different letters were significantly ( $P < 0.05$ ) different based on Tukey–Kramer post-hoc tests.

	Crab Bank, South Carolina	Marsh Island, South Carolina	Gulf of California	F ratio probability
N	18	10	15	43
Measurement				
Whole egg (g)	99.3 (88.2–117.5)	97.5 (82.8–115.2)	97.3 (75.5–111.5)	0.225 0.7994
Eggshell (g)	9.2 <sup>B</sup> (7.2–11.4)	8.5 <sup>B</sup> (7.0–9.2)	10.3 <sup>A</sup> (8.9–11.8)	11.9 <0.0001*
Length (cm)	7.68 (6.98–8.24)	7.42 (6.96–7.77)	7.63 (6.95–8.58)	2.00 0.1489
Breadth (cm)	4.92 (4.71–5.29)	4.96 (4.77–5.25)	5.00 (4.76–5.18)	1.60 0.2138
Size index (cm <sup>2</sup> )	37.8 (34.2–41.8)	36.8 (34.1–40.8)	38.1 (33.1–42.8)	1.19 0.3153
Thickness index	2.44 <sup>B</sup> (2.07–2.86)	2.32 <sup>B</sup> (1.92–2.62)	2.71 <sup>A</sup> (2.28–2.97)	12.1 <0.0001*

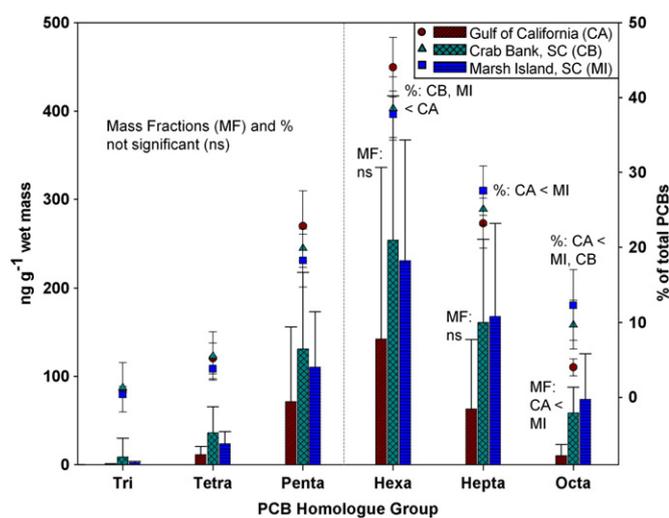
slightly higher proportion of hexa-PCBs (41.4% vs. 27.2% in the eggs and 35.4% in the CAM), similar to the brown pelican eggs. However the opposite trend was observed for penta-PCBs with lower proportions in the Gulf of California turtles (23.0% vs. 30.1% in the eggs and 37.0% in the CAM) and higher proportions of the octa-PCBs (3.6% vs. 2.0% in the eggs and 3.6% in the CAM). Aside from the confounding factors of different tissues and the temporal differences, the PCB congeners used in these studies may also have differed affecting the ability to truly make accurate comparisons, again indicating that more work is needed in determining contaminant levels in both of these regions. There is a superfund site south of the South Carolina colonies in Brunswick, GA that used Aroclor 1268, which is uniquely comprised of higher chlorinated PCBs, and surrounding wildlife has been found to reflect this unique PCB pattern (Kannan et al., 1998), which may help explain the higher proportion of these compounds in the South Carolina eggs compared to the Gulf of California eggs (Fig. 3), although this was not reflected as strongly in the turtle eggs and CAM collected from the same region in 1993.

Overall, there are clearly differences in contaminants between the east and the west populations of brown pelicans. While contaminant levels should be below those causing an effect on the population levels, the different trajectories of the population sizes was a driver in

undertaking this study (Anderson et al., 2007; Jodice et al., 2007; Watts and Byrd, 2006), so the observed differences between the populations is still intriguing and worthy of further study. Explanations for these differences cannot be readily obtained, but one may suspect that proximity to industrial sources or areas of use would be the main reason. Unfortunately, very little data is available to compare and contrast either the sources of contamination or other studies that have data for similar species and similar times. One other source of data that is available for both the Gulf of California region and the South Carolina region is the Mussel Watch Program which conducted a special international assessment that included mussels from San Felipe, Mexico in 1992 (International Mussel Watch Committee, 1995). These data were compared to data for oysters from Charleston, South Carolina also collected in 1992 (Center for Coastal Monitoring and Assessment, 2011). While Σchlordanes, ΣPCBs, dieldrin, and mirex were significantly higher in brown pelicans from South Carolina (Table 1), the Mussel Watch data had similar levels for these compounds at both locations, with the exception of dieldrin where the South Carolina oysters had [3.76 and 4.24] ng g<sup>-1</sup> dry mass while the Gulf of California mussels were below the detection limit of 0.25 ng g<sup>-1</sup> dry mass. The east coast oysters also had higher levels of DDTs ([24.9 and 29.4] ng g<sup>-1</sup> dry mass), and γ-HCH ([1.93 and 1.98] ng g<sup>-1</sup> dry mass) compared to the Gulf of California mussels ([9.18 and <0.25] ng g<sup>-1</sup> dry mass, respectively), opposite of the trend for the brown pelicans (Table 1). Unfortunately many of the compounds studied in the Mussel Watch were below detection limits or at trace levels so more thorough comparisons were not possible for the PCB homologue group patterns or even major compounds to the sum of the classes (brown pelican egg data are shown in Figs. 3 and A1, Supplementary data, respectively). BDEs were also not measured in the special international collection, but in 2004, BDE 47 was measured in southern California mussel tissue and ranged from [6.8 to 777] ng g<sup>-1</sup> dry mass while South Carolina oyster tissue in 2004 ranged from [0.7 to 4.9] ng g<sup>-1</sup> dry mass which did follow the pattern observed for the brown pelicans (Fig. 2) (Center for Coastal Monitoring and Assessment, 2011).

#### 4. Conclusions

This is the first known study to directly examine contamination differences between the southeast United States and the Gulf of California, as well as the first known one to examine BDEs in the latter ecosystem. Brown pelicans in these regions have very different population trends and may be useful biomonitors in these ecosystems. While eggs from the Gulf of California had higher levels of lower brominated BDEs, DDTs, and HCHs, South Carolina eggs had higher levels of PCBs, chlordanes, dieldrin and mirex. The patterns of the contaminants also varied between the regions. More research is needed to clearly understand the differences in the east and west coast populations and ecosystem



**Fig. 3.** Mean  $\pm 1$  standard deviation of mass fractions (ng g<sup>-1</sup> wet mass) and percentage of total polychlorinated biphenyl (PCB) homologue groups in brown pelican (*Pelecanus occidentalis*) eggs. Only the higher chlorinated PCB homologue groups had significant ANOVAs ( $P < 0.05$ ) for the percentage of total PCBs. Tukey–Kramer HSD post-hoc test results are shown for colony differences. Mass fractions were significantly different for only the octa-PCBs with Gulf of California eggs having lower values than Marsh Island, South Carolina eggs. See Table A1, Supplementary data for sample information.

contamination patterns. Future research is needed in both of these ecosystems to examine these contaminants in the prey fish and other top predators. Examination of current use of pesticides and other contaminants of emerging concern, such as perfluorinated chemicals or other flame retardants, and stable isotopes or fatty acid analyses may also help elucidate the differences in the brown pelican population status between the Gulf of California and the southeast United States.

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## Disclaimer

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.scitotenv.2012.08.055>. These data include Google maps of the most important areas described in this article.

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