Biomonitoring of Legacy and Emerging Toxicants in North Pacific Waters

By

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DISSERTATION

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ABSTRACT

Monitoring physical and biological conditions in the open ocean is an inherently difficult task, particularly when monitoring toxic and harmful compounds. Efforts to use biomonitor species to measure and assess ocean and organismal health require considerable information on habitat use and other life history characteristics to contextualize and interpret contaminant data. A large proportion of biomonitoring research focuses on a single species, a single site, and/or a small range (i.e. 1-3) of contaminant classes. While informative, the scope of such studies can limit their applicability, which is concerning as data suggests the abundance of organic and heavy metal contaminants in the ocean is increasing. Contaminants can have sub-lethal effects that affect population viability, and new, unknown contaminants enter the environment with little knowledge of their possible effects and limited ability to monitor these emerging contaminants.

Seabirds serve as effective biomonitors for contaminants for multiple reasons. First, seabirds feed at high trophic levels, where toxicants are biomagnified. Because most seabird species are long-lived, birds may bioaccumulate toxicant types into tissues (e.g., fat) over a lifetime, much like humans. Contaminants also accumulate in seabird tissues that can be sampled non-lethally and at low cost, including blood, feathers, and non-viable eggs. Thus, it is also easy to assess the sub-lethal effects of low, but chronic levels of contaminants on a variety of ecological parameters, especially when paired with long-term datasets. Additionally, many seabird tissues have enough volume with which to test for multiple contaminant classes in a single sample. Lastly, seabirds

exhibit high breeding site fidelity, so individuals can be sampled and re-sampled with regularity.

My research explores how seabirds may be used as biomonitors for a rapidly-changing ocean environment. In Chapter 1, I show that seabird tissues can be used to indicate the magnitude and extent of a wide range of contaminants at the regional scale in the Southern California Bight. In contrast to single species, single site monitoring, regional assessments maximize the ability to use biomonitoring efforts to meet mandated monitoring objectives, prioritize site remediation, and trace the dispersal and uptake of toxicants in marine food webs. The results suggest at least one species, the California least tern (*Sterna antillarum browni*), may be a robust indicator of contaminant patterns in this region. Chapter 2 investigates blood mercury concentrations as a function of foraging distribution in western gulls (*Larus occidentalis*) nesting at three colonies off the California and Oregon coast. We found that ocean-foraging gulls had elevated mercury concentrations and also lower fidelity to geographic foraging areas, confirming work that suggests aquatic foragers have greater exposure to methylmercury. As mercury exposure and likely exposure to other contaminants differs across the land-sea gradient, species that forage in marine and terrestrial environments may be used to better understand the ecological consequences of contaminant-associated diet. Chapter 3 uses an established nontargeted approach to examine the presence and patterns of legacy and frequently unmonitored halogenated organic compounds in three albatross species that range the North Pacific. The majority of contaminants we found are currently unmonitored, which demonstrates the extent of

chemical contamination beyond urbanized coastal areas to remote coastal regions. We also found support for previous research that suggests differences in broad-scale foraging areas impact contaminant abundance among these three species.

CHAPTER 1

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Seabirds as regional biomonitors of legacy toxicants on an urbanized coastline

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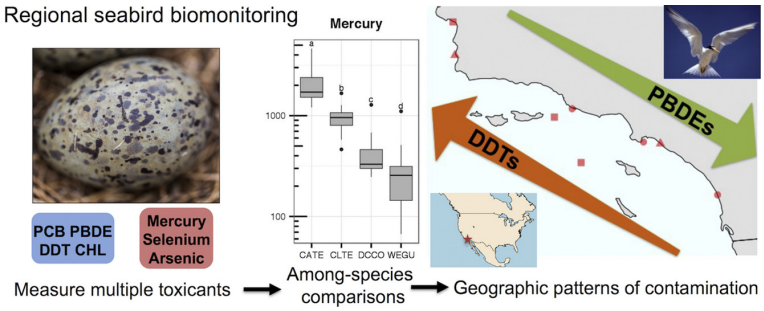
HIGHLIGHTS

- Coastal species are susceptible to mixtures of chemical pollution.
- We compared contaminant concentrations in seabird eggs across a regional water body.
- Legacy contaminants remain dispersed and persistent in seabirds in the SCB.
- Concentrations of contaminant classes and congeners displayed geographic patterns.
- Seabird contaminant monitoring informs remediation & management of coastal regions.

GRAPHICAL ABSTRACT



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ABSTRACT

Seabirds are often cited as sentinels of the marine environment, but are rarely used in traditional ocean and coastal contaminant monitoring. Four classes of persistent organic pollutants (POPs, n = 68) and three trace elements (mercury, selenium, and arsenic) were measured in the eggs of California least terns (*Sterna antillarum browni*), caspian terns (*Hydroprogne caspia*), double-crested cormorants (*Phalacrocorax auritus*), and western gulls (*Larus occidentalis*) that nest in the Southern California Bight. Building on a periodic five year regional monitoring program, we measured contaminant exposure and assessed the utility of seabirds as regional contaminant biomonitors. We found that the eggs of larger, more piscivorous species generally had the highest concentrations of POPs and trace elements while California least terns had the lowest concentrations, except for mercury which was higher in least terns. As expected, DDT concentrations were elevated near the Palos Verdes Superfund site. However, we also detected a previously unknown latitudinal pattern in PBDE concentrations in least terns. POP congener profiles also confirmed differences in contamination in urban least tern colonies closest to urban centers. Though toxicants were at detectable levels across species and sites, concentrations were below those known to cause adverse effects in avian taxa and are steady or declining compared to previous studies in this region. Our results suggest that regional seabird monitoring can inform site-specific remediation and support management and protection of regionally-threatened wildlife and coastal systems. Integration of seabird contaminant data with traditional sediment, water, bivalve and fish monitoring is needed to further our understanding of exposure pathways and food web contaminant transfer.

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Abbreviations

Birds

CATE	Caspian tern
CLTE	California least tern
DCCO	Double-crested cormorant
WEGU	Western gull

Toxicants

POPs	persistent organic pollutants
CHLs	chlordanes
DDTs	dichlorodiphenyltrychloroethanes
PBDEs	polybrominated diphenyl ethers
PCBs	polychlorinated biphenyls
SCB	Southern California Bight

1. Introduction

Human population density continues to increase in coastal areas worldwide, including coastal California (Crossett et al., 2004). Point source pollution, runoff, and atmospheric deposition associated with urban, suburban, agricultural, and industrial development has led to spikes in persistent organic pollutants (POPs) and trace elements in coastal environments (Elliott and Elliott, 2013; Schiff et al., 2001). While production of some toxicants is banned or closely regulated, persistent toxicants remain in coastal waters and sediments for decades and cycle through aquatic food webs. This is especially problematic for long-lived, top predators like seabirds, as many POPs and some trace elements are subject to bioaccumulation and biomagnification (Elliott, 2005; Rowe, 2008). At high concentrations, toxicants can reduce individual survival and reproduction, resulting in population decline (Bustnes et al., 2003; Hellou et al., 2013). Even at sub-lethal levels, these toxicants can impair physiological, immune, and reproductive function (Finkelstein et al., 2007; Tartu et al., 2013; Goutte et al., 2015) and in some species, combinations of toxicants even below effects thresholds have been linked to endocrine disruption (Silva et al., 2002; Bryan et al., 2005). Though effects vary by species, contaminant type, and concentration, the impacts have been observed in multiple taxa and are severe enough to warrant regular screening.

Despite their widespread distribution and ecological effects, multiple contaminant classes are rarely quantified among species or sites for regional analysis (but see Braune et al., 2002, Mallory and Braune, 2012). While single-site, single -species studies can provide data on species' vulnerability in one location, these analyses can overlook regional patterns of contaminant exposure, distant points of contamination, or fail to account for the mobility of marine taxa (Jarvis et al., 2007; Parnell et al., 2008). Given our nascent understanding of the synergistic or additive effects of multiple contaminant types (Finkelstein et al., 2007; Rowe, 2008; Goutte et al., 2015; Noyes and Lema, 2015), a multi-site and species approach can enhance our baseline knowledge of mixtures of toxicants present in impacted ecosystems. This information is particularly relevant along urbanized coastlines, where wildlife have higher exposure to a wide range of anthropogenic toxicants (Phillips et al., 1997; Schiff and Allen, 2000; Jarvis et al., 2007; Millow et al., 2015).

The Southern California Bight (SCB), which extends from Point Conception, CA to Cabo Colnett, Baja California, Mexico, is a seabird biodiversity hotspot that is home to many species of conservation concern, including the California least tern (*Sterna antillarum browni*; Gray, 1997). As high trophic level consumers, seabirds in the SCB are exposed to high concentrations of toxicants and declines in seabird populations in the SCB have been linked to exposure to several compounds, including DDT (dichlorodiphenyltrichloroethane) dispersal from the Palos Verdes Superfund site (Risebrough et al., 1967; Ohlendorf et al., 1985; Fry, 1994). Numerous other toxicants, including mercury (Hotham and Powell, 2000; Komoroske et al., 2012), selenium (Ohlendorf et al., 1985; Hotham and Powell, 2000), arsenic (Komoroske et al., 2011), PCBs (polychlorinated biphenyls, e.g. industrial and electrical byproducts, Fry, 1995, Schiff and Allen, 2000, Brown et al., 2006, Jarvis et al., 2007), PBDEs (polybrominated diphenyl ethers, e.g., flame retardants, Brown et al., 2006) and CHLs (chlordanes, Ohlendorf et al., 1985, Schiff and Allen, 2000), have also been detected in wildlife, sediments, and waters (Zeng et al., 2005; Dodder et al., 2012) in the SCB.

Although seabirds have been recognized as sentinels of marine systems (e.g., Burger and Gochfeld, 2002; Elliott and Elliott, 2013), most contaminant monitoring efforts have yet to include seabirds as part of the typically studied samples, a list that often includes water, sediment, bivalves, and fish (e.g., Zeng et al., 2005; Parnell et al., 2008; Dodder et al., 2012). Here, we assess the loads of the four classes of POPs and three trace elements in four seabird species nesting in the SCB to compare differences in toxicant concentrations within and among species, look for spatial trends in exposure levels within species, and consider the link between contaminant exposure and biological responses. Our research highlights the utility of seabird tissues and ecology in examining spatial, temporal, and biologically-relevant trends in regional contaminant biomonitoring.

2. Methods

2.1. Study species

Salvaged seabird eggs, i.e. eggs left at the end of a breeding season, have been demonstrated to serve as a robust tissue type for toxicant analyses (Hickey and Anderson, 1968; Braune et al., 2002; Burger, 2002; Mallory and Braune, 2012; Millow et al., 2015). Using salvaged eggs, we analyzed the egg contents of four seabird species: California least tern (*Sterna antillarum browni*), Caspian tern (*Hydroprogne caspia*), double-crested cormorant (*Phalacrocorax auritus*), and western gull (*Larus occidentalis*). The selected species differ in foraging strategies and ranges, which are known to influence toxicant load (Mallory and Braune, 2012; Lavoie et al., 2015). For instance, California least terns and Caspian terns are both plunge diving, piscivorous birds, but may consume different prey species (Ohlendorf et al., 1985; Lewison and Deutschman, 2014). Double-crested cormorants are also piscivorous and forage by diving at depth. Western gulls are generalists that forage on the ocean surface as well as on marine, coastal, and terrestrial subsidies. These differences in foraging strategies and prey items may result in varying contamination levels in the eggs of each species.

2.2. Egg collection, processing, and chemical analysis

Salvaged eggs were collected from the nests of the study species from 16 sites in the Southern California Bight (Fig. 1, Table A.1) during spring and summer 2013. Egg collection was executed by permitted individuals at each site in accordance with State, Federal and IACUC guidelines. All collected eggs were determined to be fail-to-hatch eggs due to nest abandonment or were taken as part of a depredation effort. Eggs were placed in cardboard cartons and transported to the US Fish and Wildlife Office in Carlsbad, CA for subsequent morphometric analysis, and other laboratories as described in the Supporting Information for chemical analysis. Eggs were processed using standard protocols for avian egg harvest for chemical analysis, embryo examination, and shell thickness determination. Because a single least tern egg does not contain enough material for all chemical analyses, we combined the contents of multiple least tern eggs into composite samples until sufficient matrix was present for subsequent analyses. Least tern composite samples comprised the egg contents of 2–4 eggs collected from the

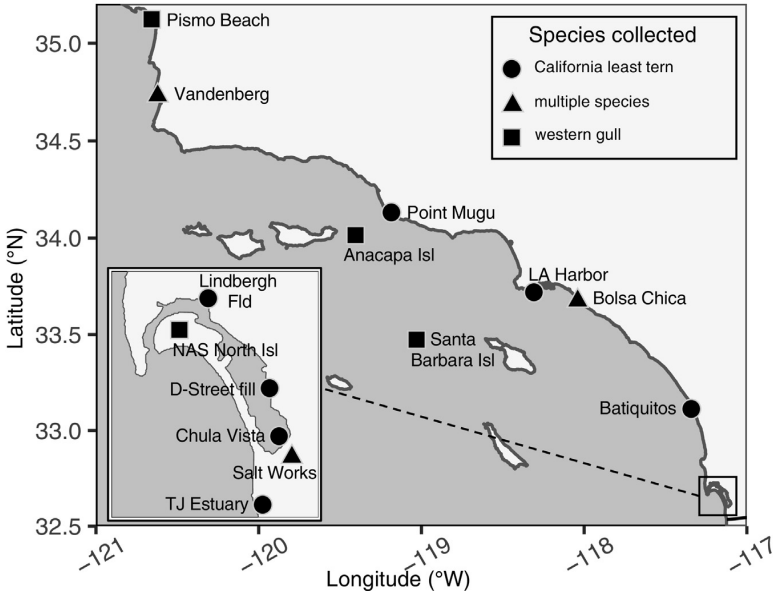

Fig. 1. Egg collection locations in the Southern California Bight.

same site. Egg morphometrics of each egg in the composite sample were averaged to obtain mean measurements per composite sample. The majority of samples (92/102) were either not fertilized or in the early stages of development. The analytical methods and quality assurance/quality control (QA/QC) protocols closely followed those of the Southern California Bight Program (Dodder et al., 2016). The analytes included 41 polychlorinated biphenyl (PCB) congeners, 15 polybrominated biphenyl ether (PBDE) congeners, 7 dichlorodiphenyltrichloroethane (DDT) related compounds, 5 chlordanes (CHLs), mercury, selenium, and arsenic. Additional information on egg processing, analysis, and quality assurance is available in Appendix B: Supplementary methods.

2.3. Statistical analysis

All statistical analysis was performed in R (R Core Team, 2015). Results from Physis Environmental Labs were reported on a wet weight basis; the percent lipid was also determined. All concentrations were standardized to unadjusted dry weight, ng/g (ppb), to account for desiccation based on differences in egg collection dates. Summed concentrations by contaminant class were $\log_{10}$-normalized to fit test and model assumptions of normality. For non-detect samples, we set values to zero for statistical analysis and summary statistics (Table A.2). For log-scaled graphing purposes only, we added 1 ng/g dry weight to all CHL values.

Based on results from Wilk-Shapiro and Levene's test which showed that data among species were nonparametric ($p < 0.05$), we used Kruskal-Wallis ANOVAs with post-hoc Dunn's test and Holm's correction to compare differences in toxicant concentrations among species across all sites, among species at a single site, and within a species across multiple sites. We used Welch's *t*-tests to assess differences in contaminant concentrations between two species at a single site.

We conducted spatial analyses for California least terns and western gulls as sample size and egg collection distribution were sufficient to allow for spatial comparison. To assess spatial relationships with toxicant concentrations within species, we used linear mixed models with latitude, distance to urban areas, and the type of collection site (e.g., designated marine protected area) as fixed effects and site as a random effect. We compared models using Akaike's Information Criterion (AIC) and described significant predictors using likelihood ratio tests and the importance function in the R package "AICcmodavg" (Mazerolle, 2016). The ratio test yields the relative importance of the predictor variables in each model set based on the sum of Akaike weights that include the variable of interest ($w+$). We set a $w+$ critical value of 0.75 for high relative importance for each predictor. We performed two additional analyses to further evaluate geographic toxicant patterns: Mantel tests and principal components analysis (PCA). Mantel tests examine the relationship between distances between sites and mean toxicant concentrations by site; only CLTE had sufficient data to perform these tests. PCAs were used to examine loadings of individual POP congeners and the resulting groupings of individual samples based on the similarity in individual congener profiles. For this analysis, congener concentrations were converted to a percent of the summed POP concentration per sample to normalize abundance that would otherwise obscure variation among congener profiles. For CLTE, we performed PCA on samples from urban sites only, as these are the areas of greatest potential for contaminant exposure (Dodder et al., 2012).

2.4. Biological response

To consider potential biological responses to toxicant exposure we compared toxicant concentrations to eggshell thickness measurements and published toxicant concentrations associated with adverse effects in other avifauna. Because both PBDEs and DDTs have been associated with decreased eggshell thickness in avifauna, we ran linear regressions to compare eggshell thickness and Ratcliffe's index to log-normalized PBDE and DDT concentrations (Ratcliffe, 1970; Harris and Elliott, 2011). Because eggshell thickness is species-specific, we did not compare eggshell thicknesses between species. Effect levels can be used to delineate the toxicant concentrations at which adverse effects may occur. To put our results in this context, we compare our detected toxicant levels to previously published contaminant effect levels associated with adverse effects in other avifauna. Although effect levels vary by species and toxicant, and there are limited data available on effect levels for particular species or toxicants, the selected thresholds are ones that have been established by published research on toxicant levels in avian eggs. Two sets of thresholds were used in this analysis: No Observed Adverse Effect Concentration (NOAEC) and Lowest Observed Adverse Effect Concentration (LOAEC). NOAEC indicates a concentration

threshold where there is no concern of adverse effects and LOAEC indicates the lowest level at which adverse effects may occur. Levels between NOAEC and LOAEC suggest the toxicant merits additional consideration. We compared the range and mean for our focal species to estimates from other avian species (Table 1).

3. Results

3.1. POPs: levels detected among species

We detected all targeted toxicants by class in every egg sample except CHLs, although toxicant concentrations varied among species. Percent lipid was not related to organic contaminant concentrations. In general, Caspian terns (CATE) had the highest concentrations of all targeted toxicants while California least terns (CLTE) had the lowest, and PCBs and DDTs had the highest concentrations among species (Fig. 2). CATE and double-crested cormorants (DCCO) had similar ($p = 0.983$) and greater amounts of PCBs ($\chi^2(3) = 35.252$, $p \ll 0.001$) compared to western gulls (WEGU) and CLTE ($p = 0.983$). There was a similar pattern in DDTs ($\chi^2(3) = 51.813$, $p \ll 0.001$), where DCCO and CATE had the highest concentrations of DDTs ($p < 0.772$), but WEGU differed from CATE ($p \ll 0.001$), DCCO ($p < 0.001$), and CLTE ($p < 0.001$). DCCO had similar concentrations of PBDEs as CATE ($p < 0.084$), WEGU ($p < 0.879$), and CLTE ($p < 0.084$), but all other species were different from each other ($\chi^2(3) = 40.485$, $p \ll 0.001$). CHLs also differed among species ($\chi^2(2) = 37.329$, $p \ll 0.001$), with CHL concentrations higher in CATE than CLTE ($p < 0.006$) and WEGU ($p < 0.001$), and CHL concentrations higher in CLTE ($p < 0.001$) than WEGU. We did not include DCCO in CHL analyses because a high proportion (3/8) of samples were non-detects.

Two sites had sufficient sample size to examine differences in contaminant concentrations among species: Bolsa Chica and Salt Works. We sampled CATE and CLTE eggs at Bolsa Chica and CATE, CLTE, and DCCO eggs at Salt Works. At Bolsa Chica, PCB (Welch's t-test: $t_{6.66} = 10.474$, $p < 0.001$), PBDE ($t_{5.20} = 9.366$, $p < 0.001$), DDT ($t_{5.98} = 8.724$, $p < 0.001$), and CHL ($t_{6.11} = -5.278$, $p < 0.002$) concentrations were higher in CATE than CLTE (Fig. 3).

At Salt Works, DDT concentrations differed ($\chi^2(2) = 8.07$, $p < 0.018$) among species, where CATE ($p = 0.043$) and DCCO ($p = 0.043$) had higher concentrations than CLTE, but CATE and DCCO concentrations were similar ($p = 0.351$; Fig. 3). There were no observed differences in PCB ($\chi^2(2) = 5.66$, $p = 0.059$), PBDE ($\chi^2(2) = 4.17$, $p > 0.124$), or CHL ($t_{2.42} = 0.264$, $p > 0.812$) concentrations between species at Salt Works.

3.2. Trace elements: levels detected among species

We found some evidence of differences in trace element levels among species. Mercury concentrations significantly differed ($\chi^2(3) = 71.05$, $p \ll 0.001$) among species in a repeated pattern of concentrations ($p < 0.05$), with greatest to smallest found in CATE, CLTE, DCCO and WEGU in that order (Fig. 2). For other elements there were fewer obvious patterns, although DCCO samples were not analyzed for selenium or arsenic. Selenium concentrations were significantly ($\chi^2(2) = 26.412$, $p \ll 0.001$) greater in CLTE than WEGU, but CATE and WEGU ($p = 0.086$) and CATE and CLTE ($p = 0.884$) had similar selenium concentrations. CATE and WEGU had similar arsenic concentrations ($p = 0.075$), and both CATE ($p < 0.004$) and CLTE ($p \ll 0.001$) had higher arsenic concentrations than WEGU ($\chi^2(2) = 27.733$, $p \ll 0.001$). DCCO samples were not analyzed for selenium or arsenic.

There was also evidence for differences in element concentrations among species nesting at the same site that was similar to the overall patterns among species. At Bolsa Chica, CATE harbored significantly more mercury than CLTE ($t_{4.80} = 4.680$, $p < 0.006$; Fig. 3), but the two species had similar concentrations of selenium ($t_{4.54} = 0.656$ $p > 0.543$) and arsenic ($t_{6.62} = -0.928$, $p > 0.386$). At Salt Works, mercury concentrations differed ($\chi^2(2) = 27.733$, $p \ll 0.001$) and were higher in CATE than CLTE ($p < 0.029$) and DCCO ($p < 0.002$), whereas mercury concentrations were similar between CLTE and DCCO ($p > 0.125$, Fig. 3). Samples at Salt Works were not analyzed for selenium or arsenic.

3.3. Spatial patterns in toxicant concentration

To look for spatial patterns in toxicant concentrations, we evaluated toxicant levels across the region by class, investigated whether any of the available landscape predictors explained the detected variability, and looked for spatial differences in the concentrations of single POP compounds among the most urban sites. We had sufficient sample size and resolution to assess CLTE and WEGU toxicant levels across the region, and differences in concentrations of single POP compounds in CLTE eggs. AIC scores of regional comparisons and toxicants are in Table A.5. For CLTE, we found marine protected area status ($\chi^2(1) = 4.622$, $p < 0.032$) and latitude ($\chi^2(1) = 4.898$, $p < 0.005$) were significant and independent predictors of PBDE exposure; PBDE concentrations in CLTE samples decreased about 36% per degree of latitude and were 26% lower in sites located in MPAs (Fig. 4). Conversely, DDT concentrations in CLTE samples increased with latitude ($\chi^2(1) = 11.553$, $p < 0.001$) by about 45% per degree of latitude (Fig. 4).

Latitude was the strongest predictor for concentrations of PBDEs and DDTs (Table 2). DDT concentrations in CLTE were also significantly

Table 1
Screening values (NOAEC and LOAEC) for analyzed toxicants in ng/g fresh weight. No Observed Adverse Effect Concentration (NOAEC) are values below which no adverse effects are predicted. Lowest Observed Adverse Effect Concentration (LOAEC) are values at which eggshell thinning and/or reproductive success are impaired. NO and LO indicate the number of samples above NOAEC and LOAEC, respectively. Values between LOAEC and NOAEC may be of concern. NOAEC thresholds for DDTs are conservative estimates for all birds. No thresholds are available for CHL data.

Toxicant	NOAEC	LOAEC	Species (sample size)								Reference
			CATE (15)		CLTE (55)		DCCO (8)		WEGU (24)		
			NO	LO	NO	LO	NO	LO	NO	LO	
PCB	2600	23,000	0	0	0	0	0	0	0	0	Harris and Elliott, 2011
PBDE	200	1000	10	0	0	0	1	0	8	0	Rattner et al., 2011; Harris and Elliott, 2011
DDT[a]	200	10,000	15	0	21	0	8	0	19	0	DOI 1998
DDT[b]	1000	5000	12	2	1	0	2	0	3	0	DOI 1998
Mercury	500	800	4	2	0[c]	0[c]	0	0	0	0	Burger and Gochfeld, 1997; Henny et al., 2002
Selenium	900	3000	1[d]	0[d]	0[e]	0[e]	–	–	0[f]	0[f]	Ohlendorf and Heinz, 2011
Arsenic	910	>910	0[d]	0[d]	0[e]	0[e]	–	–	0[f]	0[f]	DOI 1998

[a] Thresholds for observed eggshell thinning in seabird species.
[b] Thresholds for reduced reproductive activity in seabird species.
[c] Sample size is 52.
[d] Sample size is 5.
[e] Sample size is 29.
[f] Sample size is 15.

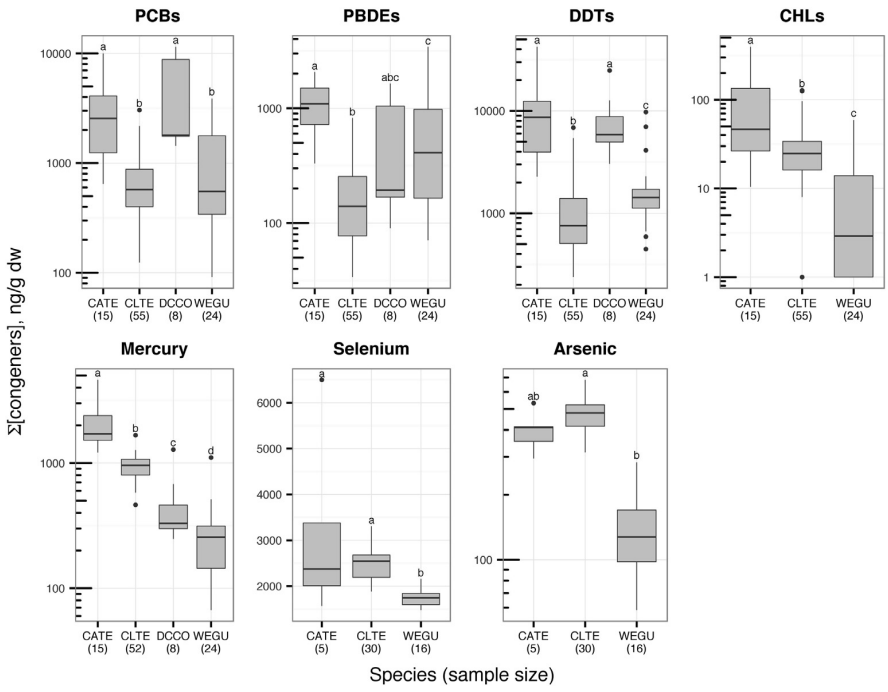

Fig. 2. Sum toxicant concentrations by species. The concentrations of congeners within organic contaminant classes are summed by sample. Each boxplot indicates the median (horizontal line), 25%–75% interquartile range (box), and 1.5 times the interquartile range (error bars). Letters represent similarities in sum toxicant concentration within each toxicant class among species.

related to distance between sites (Mantel test: $r = 0.764$, $p = 0.004$), with a similar, but less robust pattern for PBDE ($r = 0.329$, $p = 0.055$). No model adequately explained the spatial variation of PCB or CHL concentrations in CLTE. Additionally, no toxicant groups other than DDTs were significantly related by distance between sites (Mantel test, $p > 0.05$). Principle Components Analysis demonstrated spatial differences in congener profiles among CLTE in urban regions (Fig. 5). CLTE nesting in LA Harbor clustered negatively on PC1, which was dominated by DDT congener *p,p*-DDE followed by *p,p*-DDMU. Congener profiles of CLTE in San Diego Bay were dominated by PCB-138, −153, and −187, which loaded positively on PC1, whereas Tijuana River Estuary CLTE clustered positively on PC2 which indicated these samples have proportionally more PBDE-47 and, to a lesser degree, PBDE-99 and -100.

In WEGU, we found a significant relationship between PCB concentrations and marine protected area status where PCB concentrations were significantly lower ($\chi^2(1) = 5.106$, $p < 0.024$) by about 250% for WEGU nesting in the protected Channel Islands (Fig. A.1), although relative importance of MPAs was equivocal ($w+ = 0.66$, Table 2). Similarly, PCA showed the POP loads of WEGU from the Channel Islands contained proportionally less PCB-138 and -153 compared to WEGU nesting at NAS North Island in San Diego Bay (Fig. A.2). No predictors or their interactions significantly predicted PBDE, DDT, or CHL concentrations in WEGU, and no predictor was relatively more important than others (Table 2).

Though spatial patterns were evident for some POPs, likelihood ratio tests showed that no fixed effect significantly predicted mercury, selenium, or arsenic concentrations in regional comparisons of CLTE or WEGU samples. Similarly, no predictor had high relative importance (Table 2) and trace element concentrations were not related by distance (Mantel test, $p > 0.05$) in the CLTE model set. We did not conduct regional comparisons of selenium and arsenic in WEGU because samples from NAS North Island were not tested for these toxicants.

3.4. Potential biological responses

Regressions between CLTE eggshell thickness and PBDE and DDT concentrations explained very little of the observed variability in the eggshell data (PBDEs: $F_{1,52} = 2.02$, $R^2 = 0.037$, $p = 0.16$; DDTs: $F_{1,52} = 3.40$, $R^2 = 0.06$, $p = 0.07$, Fig. A.3). For WEGU, PBDE concentrations were not significantly related to eggshell thickness ($F_{1,21} < 0.003$, $R^2 < 0.0002$, $p = 0.961$, Fig. A.4). There was a significant but weak relationship between WEGU DDT concentrations and eggshell thickness ($F_{1,52} = 5.11$, $R^2 = 0.20$, $p = 0.034$, Fig. S2), which suggests DDT concentration may be one of many factors contributing to variation in WEGU eggshell thickness. The relationship between PBDE and DDT concentrations and Ratcliffe's index also explained little variability in the data for CLTE (PBDE: $F_{1,51} = 1.16$, $R^2 = 0.02$, $p = 0.29$; DDT: $F_{1,21} = 2.53$, $R^2 = 0.05$, $p = 0.12$, Fig. A.3) and WEGU (PBDE: $F_{1,21} = 0.10$, $R^2 = 0.004$, $p = 0.75$; DDT: $F_{1,21} = 0.45$, $R^2 = 0.02$, $p = 0.51$, Fig. A.4).

Across the region, no species exceeded the LOAEC-based thresholds for the legacy toxicants measured on a fresh weight basis (Table 1). However, DDT concentrations were above the NOAEC threshold for eggshell thinning for the majority of individuals in all species except CLTE (Table 1). Of all species, CATE had the highest proportion of individuals above NOAEC thresholds for multiple toxicants (Table 1). Effect thresholds were not available for CHLs.

4. Discussion

Regional contaminant monitoring in the SCB has been ongoing since 1994 and represents coordinated agency efforts to enhance the understanding of local and non-local pollutants in a regional marine environment (Cross and Weisberg, 1995). Environmental monitoring efforts of Southern California's coastal ocean typically focus on environmental

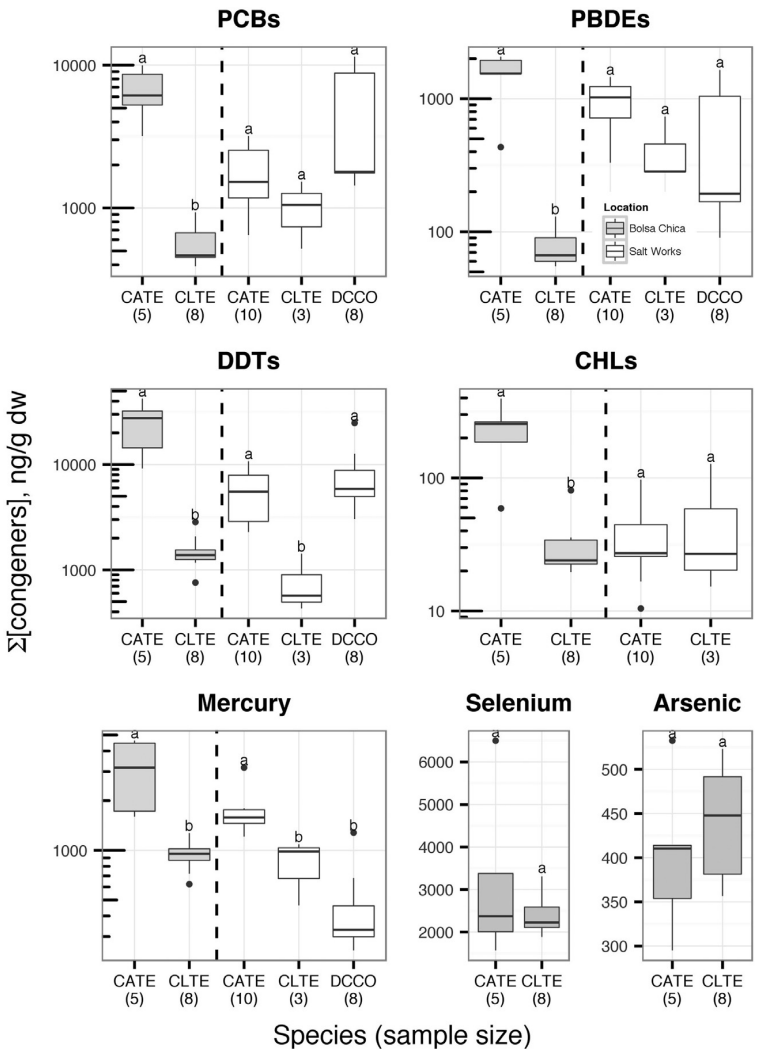

Fig. 3. Sum toxicant concentrations in Bolsa Chica (grey) and Salt Works (white) by species. Letters represent similarities in sum toxicant concentration within each toxicant class among species, but within site.

(water, sediment) or lower order taxa (bivalves) monitoring and are not designed to describe large-scale changes or to assess cumulative impacts from multiple compounds or monitor upper trophic level species. Results from this study, and other published research (Braune et al., 2002; Blasius and Goodmanlowe, 2008; Maruya and Schiff, 2009; Mallory and Braune, 2012), confirm the importance of coordinated regional monitoring efforts and demonstrate that levels of banned or highly regulated toxicants of interest are present but decreasing in the animals at the top of the SCB food webs. Our research also highlights exposure patterns of toxicants of interest among seabird species and across sites within the SCB and confirms that salvaged seabird eggs can be used to monitor larger regions (>100 km) of the coastal and marine environment, in support of restoration and protection of vulnerable species in this region (Braune et al., 2002; Elliott and Elliott, 2013).

4.1. Seabird toxicant exposure: differences among species

Every sample across each of 13 sites (Fig. 1) contained congeners from each class of pollutants assessed with the exception of CHLs. Among species, we found clear differences, i.e. up to an order of magnitude difference, in toxicant concentrations (Fig. 2). In general, we found larger, piscivorous species (CATE and DCCO) had higher organic contaminant levels than the generalist (WEGU) and smaller (CLTE) species (Figs. 2–3), a finding common with previous published research (Burger and Gochfeld, 1997; Braune et al., 2005). While all species in this study are piscivorous, there are likely differences in the trophic position and size of prey among the species we sampled. DCCO and CATE diets likely comprise larger and older fish due to a larger gape size and may consume higher proportions of higher trophic level fish in their diet versus other marine species like krill. The differences in contaminant levels we detected may also be driven by the extent or range of movement during breeding and non-breeding periods.

In contrast to the patterns in POP exposure among species, we found that CLTE had higher mercury concentrations (Fig. 2) than expected given their size and trophic level (Burger, 2002). Like POPs, mercury is both a point and non-point source pollutant, with mercury levels in top predators varying based on local anthropogenic activity at smaller temporal and spatial scales and the amount of sulfate and sulfate-reducing bacteria at the base of the food web that methylates elemental mercury (Elliott and Elliott, 2016). Increased mercury concentrations in

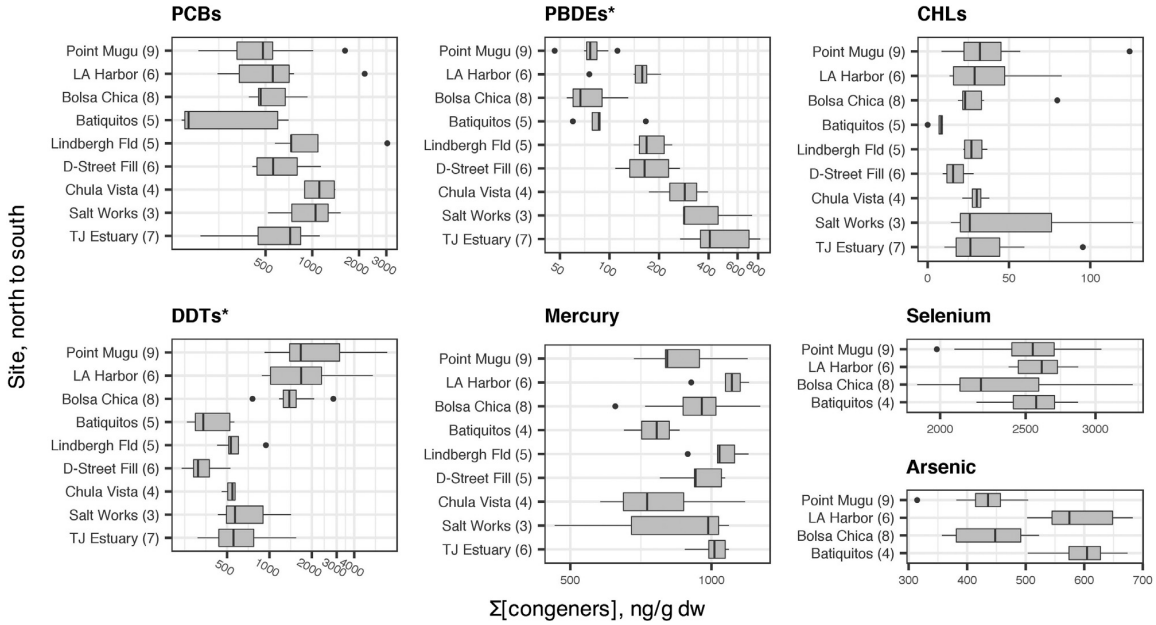

Fig. 4. Latitudinal comparisons of sum toxicant concentrations in California least terns. Parentheses indicate sample size by site. Asterisks represent plots where a significant latitudinal trend is present.

CLTE versus the larger species in this study, CATE and DCCO, may be due to differences in diet or foraging location. Other studies have also found higher mercury concentration in smaller seabirds (auklets and murrelets) versus piscivorous species that feed at a higher trophic level (e.g., herons, Elliott and Elliott, 2016). The relatively high mercury concentrations in CLTE could also reflect conditions at their overwintering area, as has been shown in some migratory populations of CATE and DCCO in the central US and Canada (Lavoie et al., 2015). Because mercury is not lipophilic like POPs (Ackerman et al., 2013), seabirds may have limited capacity to excrete body-bound mercury via burning adipose tissue, a decretion pathway that has been suggested for POPs.

4.2. Detecting toxicant trends in space and time

Based on the data from the two species for which samples were available across the study area, CLTE and WEGU, we also found evidence of significant distribution patterns of organic contaminant exposure. For CLTE, DDTs were highest near Los Angeles (Pt. Mugu south to Bolsa Chica) and PBDEs were highest in sites in and near San Diego Bay (Lindbergh Field south to Tijuana River Estuary, Fig. 4). The observed pattern for DDTs is likely explained by the location of the Palos Verdes Shelf Superfund Site, which lies ~23 km west of Bolsa Chica in the northern area of the SCB (Fry, 1994; Schiff and Allen, 2000; Zeng et al., 2005). While many seabird populations have recovered as contaminant exposure has declined, DDT levels remain detectable in coastal wildlife in the SCB (Macintosh et al., 2016). Although we found that across all colonies, DDT exposure was most similar at colonies in close proximity, the highest DDT concentrations were found in CLTE nesting north of Batiquitos (Fig. 4).

Table 2
Relative importance (w+) and rank of each variable for CLTE and WEGU model sets (Table A.5). Bold indicates w+ > 0.75.

	Latitude		MPA		UrbanDist	
	w+	Rank	w+	Rank	w+	Rank
CLTE						
PCB	0.31	2	0.70	1	0.09	3
PBDE	**0.88**	1	0.43	2	0.04	3
DDT	**0.98**	1	0.20	2	0.03	3
CHL	0.24	2	**0.81**	1	0.09	3
Mercury	0.30	2	0.60	2	0.12	3
Selenium	0.46	2	0.49	1	0.08	3
Arsenic	0.65	1	0.29	2	0.18	3
WEGU						
PCB	0.51	2	0.66	1	0.01	3
PBDE	0.52	2	**0.75**	1	0.01	3
DDT	0.54	2	0.58	1	0.01	3
CHL	0.57	2	0.59	1	0.01	3
Mercury	0.49	2	0.59	1	0.01	3

The spatial pattern in PBDEs also appears to be largely a geographic pattern rather than site-specific differences as the highest levels of PBDEs were detected in the CLTE colonies in and near San Diego Bay, a regional finding that has not been documented previously in seabirds. However, sediments in San Diego Bay and Los Angeles Harbor contain the highest concentrations of PBDEs in the SCB, likely from stormwater runoff (Dodder et al., 2012). Additionally, PCA revealed that the composition of POP congeners was significantly different among CLTE nesting sites in Los Angeles Harbor, San Diego Bay and Tijuana River Estuary (Fig. 5). These patterns suggest regional differences in contamination among contaminant class and individual congener profiles. The observed toxicant patterns also suggest CLTE may be a strong candidate for future regional monitoring in this area. The lack of spatial patterns for other toxicants (e.g., CHLs, trace elements) in this study suggests that exposure to these toxicants does not vary in the seabird species we sampled substantially across the region.

In WEGU, PCB concentrations increased from north to south and WEGU from the southern site, NAS North Island, had congener profiles containing greater proportions of PCBs than other WEGU (Fig. A.1). This finding reflects known patterns of PCB contamination in the SCB, where sediments in embayments harbored greater PCB concentrations than offshore areas (Maruya and Schiff, 2009). However, interpretation of spatial differences in WEGU contamination should be approached with caution because gulls feed omnivorously and opportunistically on marine and terrestrial resources.

Because there has been contaminant monitoring at specific sites and species within the SCB, we can also consider trends in toxicant levels

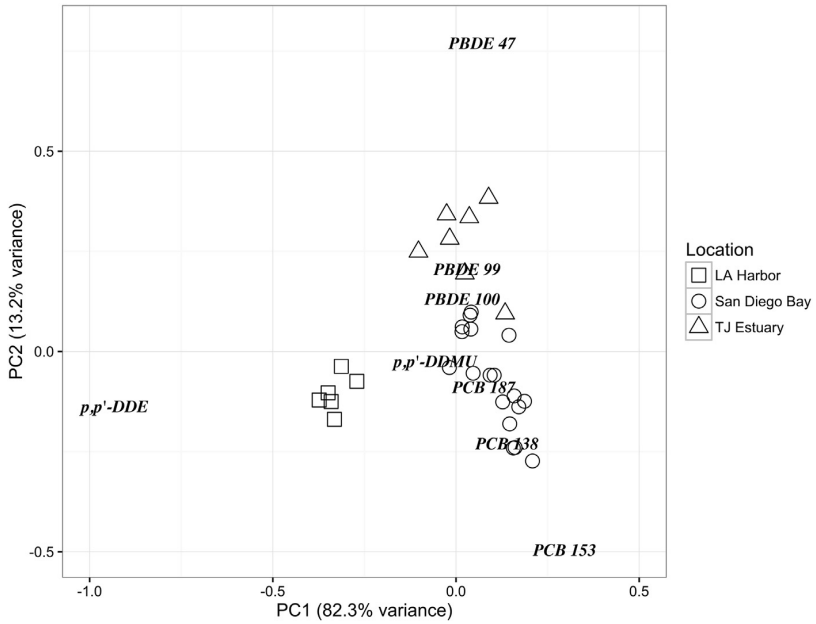

Fig. 5. PCA biplot of organic contaminant congeners among California least terns nesting at urban sites. Single congener concentrations within individual samples were converted to a percentage of the total organic contaminant concentration prior to analysis. Congeners are plotted according to their loadings.

detected over time. Our findings confirm that there is a continued decline in many POPs in the SCB (Maruya et al., 2015), yet many legacy toxicants persist in the SCB. On average, POPs were detected in lower concentrations in this study than those found in the recent past in seabird eggs in the SCB, including DDTs in WEGU nesting at NAS North Island (Jimenez-Castro et al., 1995), PCBs, PBDEs, and DDTs in nesting CATE at Salt Works (Zeeman et al., 2008), PBDEs in nesting CLTE at Salt Works (Zeeman et al., 2008), and PCBs and DDTs in nesting CLTE at the Tijuana River Estuary (Hotham and Powell, 2000). However, mean DDT concentrations in CLTE (764 ng/g ww) nesting at Salt Works were higher by about 400 ng/g ww on average, and above the maximum value of DDT concentrations in 2008 (Zeeman et al., 2008).

For trace elements, there are fewer data points to identify temporal trends as selenium and arsenic exposure were not available for our focal species. Identification of a temporal trend is also complicated because of temporal variability among studies, particularly in mercury concentrations. For example, mean mercury concentrations in our study are lower than those reported at the D-Street Fill CLTE colony in the 1980's (Hotham and Zador, 1995) but higher than mean concentration values reported from CLTE nesting at Tijuana River Estuary from 1994 to 1996 by ~300 ng/g dw (Hotham and Powell, 2000). The mechanism causing this variation merits further investigation (see Section 4.1, Elliott and Elliott, 2016).

Overall, these spatial and temporal trends suggest that concentrations of many legacy toxicants are steady or decreasing in seabirds in the SCB. Though the spatial trends in contamination we identified confirm findings from previous research on contamination in the SCB, we also identified important differences in contaminant profiles among seabird colonies that can inform local and regional management of SCB waters.

4.3. Biological response to toxicants

Regulated environmental monitoring is typically required to examine the potential biological effects of toxicant exposure, based on known thresholds which can help contextualize how toxins detected compare with known levels at which adverse effects take place. Eggshell thinning, which can lead to non-viable eggs and reproductive failure, is another commonly used metric in combination with identified thresholds to contextualize potential biological responses of toxicant exposure. All four monitored species exceeded the DDT NOAEC threshold for eggshell thinning. While there is historical precedence of eggshell thinning in the SCB associated with exposure to *p,p*-DDE, we did not find a relationship between DDT or PBDE contamination and eggshell thickness or Ratcliffe's index in CLTE or WEGU (Hickey and Anderson, 1968, Fig. A.3 and A.4). Although shell thickness in these species is approaching pre-1945 levels, neither CLTE or WEGU shell thickness has returned to values observed before DDT was in widespread use (Kiff, 1994; Jimenez-Castro et al., 1995; Zeeman et al., 2008).

When considering the adverse effects thresholds (NOAEC, LOAEC) independently, the evidence was equivocal. No species, on average, exceeded the adverse effects threshold, though a few individuals harbored contaminants at or above the LOAEC (Table 1). We found that some species exceeded the NOAEC for a compound class, but information on the effects of toxicants at these low concentrations and among species with varying sensitivities to toxicants is limited. Even larger data gaps exist regarding the additive or synergistic effects of contaminants and their interaction with other stressors, such as low food availability or changes in ocean climatic regimes (e.g., Noyes and Lema, 2015).

4.4. Seabirds as regional biomonitors

Monitoring contaminants at the regional scale is essential to aid in early detection of contaminant trends and adverse effects, and also to inform marine environmental policy with important implications for species and ocean health. Seabirds are considered effective monitors of marine ecosystem health (Mallory et al., 2006; Elliott and Elliott, 2013), but few large-scale toxicant monitoring efforts include seabirds as biomonitors. Here, we demonstrated that seabird biomonitoring can detect not only expected spatial and temporal patterns of contamination, but also reveal undescribed patterns in contaminant exposure both among species and across a nesting region (see Section 4.2).

There are advantages to using seabird tissues to examine regional contamination patterns. Abandoned and fail-to-hatch eggs are easily sampled at low cost on seabird colonies, compared to effort needed

for sampling marine sediments, macrofauna, and fish. Seabird eggs are often large enough to test for multiple contaminant classes, or can be combined within site to give site-specific parameters. Seabird tissues are also easily archived and are used to describe temporal differences in toxicant values among species, sites, and regions (Braune et al., 2002; Mallory and Braune, 2012; Bond et al., 2015). However, tissues from migratory seabirds may have toxicants incorporated from both breeding and overwintering foraging areas, which hinders tracing the source of toxicants (Braune et al., 2002; Bond and Diamond, 2010). Additional samples from tissues formed at different times within the life cycle, such as feathers or otoliths formed overwinter outside of the breeding season, can further clarify geographic sources of contamination (Ramos and González-Solís, 2012; Lavoie et al., 2015).

Another important comparison to contextualize detected contaminant levels in seabirds at the regional scale is to analyze concentrations among sample types, e.g. sediment, bivalves, invertebrates, fish, and water to provide greater understanding of the pathway by which seabirds are exposed to toxicants in a food web. Identification of the exposure pathways may be supported using seabird diet, stable isotope, and telemetry data (Braune et al., 2002; Ramos and González-Solís, 2012). Additional efforts are needed to compare the contaminant levels in the SCB across these sample types. Nevertheless, the detected values in our study can be used to address region-wide questions of pollutant sources and potential impacts, and have conservation relevance, as one of our study species, California least tern, is a federally and state-listed Endangered species. The findings from this study serve as a baseline for regional contaminant assessment, and can be used to direct future studies of contamination sources to support research on biomagnification, and food web ecology in coastal and marine regions, as well as inform management efforts for vulnerable species in the SCB.

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Appendix A & B

Appendices to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.11.057.

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APPENDIX A: Supplementary Data

Seabirds as regional biomonitors of legacy toxicants on an urbanized coastline

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	California least tern	Caspian tern	Double-crested cormorant	Western gull
Anacapa Island*				5
Batiquitos Lagoon*	5			
Bolsa Chica Reserve*	8	5		
Chula Vista Reserve	4			
D-Street Fill	6			
LA Harbor				
Lindbergh Field	5			
NAS North Island				8
Pismo Beach				1
Point Mugu	9			
Salt Works	3	10	8	
Santa Barbara Island*				9
Tijuana Estuary	7			
Vandenberg	2			1
SUM:	**55**	**15**	**8**	**24**

Table A1. Number of egg samples collected from each species by site. Asterisks indicate sites within a Marine Protected Area (MPA).

Toxicant class	Statistic	CATE	CLTE	DCCO	WEGU
PCBs	Mean (Geom Mean)	3413[a] (2509)	709[b] (563)	4795[a] (3284)	1235[b] (713)
	Median	2550	574	1791	556
	Range	645 - 9967	124 - 3042	1436 - 11448	91 - 3863
	N	15	55	8	24
PBDEs	Mean (Geom Mean)	1131[a] (989)	198[b] (146)	574[a,b,c] (339)	676[c] (410)
	Median	1093	140	194	410
	Range	330 - 2070	34 - 824	90 - 1645	71 - 3421
	N	15	55	8	24
DDTs	Mean (Geom Mean)	12150[a] (8071)	1185[b] (841)	8683[a] (6966)	2043[c] (1527)
	Median	8684	758	5883	1424
	Range	2282-42230	238-6866	3036-24830	447-9749
	N	15	55	8	24
CHLs	Mean (Geom Mean)	101[a] (56)	31[b] (0)	9 (0)	8[c] (0)
	Median	46	24	6	2
	Range	9-394	ND-127	ND-24	ND-58
	N (no. of non-detects)	15 (0)	55 (1)	8 (3)	24 (8)
Mercury	Mean (Geom Mean)	2184[a] (1983)	949[b] (927)	482[c] (411)	277[d] (224)
	Median	1710	958	330	256
	Range	1210 - 4617	462 - 1667	247 - 1280	67 - 1105
	N	15	55	8	24
Selenium	Mean (Geom Mean)	3165[a] (2773)	2495[a] (2474)	NA	1752[b] (1742)
	Median	2373	2547	NA	1747
	Range	1566 - 6500	1883 - 3307	NA	1480 - 2160
	N	5	29	0	16
Arsenic	Mean (Geom Mean)	401[a,b] (394)	494[a] (485)	NA	160[b] (136)
	Median	410	481	NA	131
	Range	295 - 532	315 - 683	NA	58 - 566
	N	5	29	0	16
Shell Thickness	Mean	0.3413	0.145	0.4096	0.371
	Range	0.3 - 0.371	0.123 - 0.169	0.328 - 0.466	0.331 - 0.442
Ratcliffe Index	Mean	1.529	0.666	1.986	1.804
	Range	1.279-1.682	0.573-0.804	1.773-2.123	1.567-1.954
Percent Lipid	Mean	9.42	10.33	4.525	10.01
	Range	5.01 - 12.3	4.08 - 24.8	0.77 - 6.58	6.75 - 13.6

Table A2. Summary statistics of egg toxicant data in ng/g (ppb) dry weight basis. Shell thickness data is in mm. Letters indicate significant differences between species within toxicant class. Geometric means for CHL data were 0 if the sample set contained a non-detect.

Toxicant class	Statistic	CATE	CLTE	DCCO	WEGU
PCBs	Mean (Geom Mean)	802 (627)	187 (143)	849 (527)	315 (188)
	Median	734	145	303	163
	Range	141 - 2163	33 - 833	207 - 2255	24 - 1089
	N	15	55	8	24
PBDEs	Mean (Geom Mean)	278 (247)	52 (37)	104 (54)	549 (108)
	Median	286	37	33	101
	Range	87 - 449	9 - 274	11 - 324	18 - 2749
	N	15	55	8	24
DDTs	Mean (Geom Mean)	2797 (2017)	290 (213)	1481 (1118)	547 (402)
	Median	2160	206	944	403
	Range	534 - 9164	54 - 1607	355 - 4394	123 - 2749
	N	15	55	8	24
CHLs	Mean (Geom Mean)	23 (14)	8 (0)	2 (0)	2 (0)
	Median	13	6	1	<1
	Range	2 - 71	ND - 30	ND - 4	ND - 17
	N (no. of non-detects)	15 (0)	55 (1)	8 (3)	24 (8)
Mercury	Mean (Geom Mean)	537 (495)	243 (236)	82 (66)	74 (59)
	Median	431	242	55	65
	Range	322 - 1100	142 - 401	35 - 228	17 - 274
	N	15	55	8	24
Selenium	Mean (Geom Mean)	642 (587)	609 (605)	NA	496 (490)
	Median	477	597	NA	468
	Range	368 - 1170	460 - 774	NA	367 - 656
	N	5	29	0	16
Arsenic	Mean (Geom Mean)	86 (83)	122 (119)	NA	45 (38)
	Median	94	117	NA	367 - 656
	Range	53 - 107	68 - 191	NA	15 - 155
	N	5	29	0	16

Table A3. Summary statistics of egg toxicant data in ng/g (ppb) wet weight basis. Geometric means for CHL data were 0 if the sample set contained a non-detect.

Toxicant class	Statistic	CATE	CLTE	DCCO	WEGU
PCBs	Mean (Geom Mean)	9305 (6844)	1819 (1388)	18266 (14033)	3369 (1906)
	Median	6673	1529	20100	1504
	Range	1953 - 30987	172 - 7741	4855 - 34274	246 - 10895
	N	15	55	8	24
PBDEs	Mean (Geom Mean)	3064 (2696)	544 (359)	1983 (1450)	1778 (1095)
	Median	2906	326	1312	1184
	Range	1063 - 6987	42 - 3148	548 - 4925	193 - 8215
	N	15	55	8	24
DDTs	Mean (Geom Mean)	33160 (22014)	3072 (2076)	34590 (29767)	5559 (4083)
	Median	21880	1973	29260	3967
	Range	5668 - 116000	160 - 17930	13080 - 68020	1201 - 27490
	N	15	55	8	24
CHLs	Mean (Geom Mean)	281 (153)	83 (0)	28 (0)	21 (0)
	Median	121	61	17	5
	Range	23 - 1414	ND - 439	ND - 76	ND - 139
	N (no. of non-detects)	15 (0)	55 (1)	8 (3)	24 (8)
Mercury	Mean (Geom Mean)	6083 (5408)	2437 (2268)	2169 (1757)	742 (599)
	Median	4626	2471	1581	673
	Range	3381 - 16587	309 - 5388	835 - 4938	182 - 2988
	N	15	55	8	24
Selenium	Mean (Geom Mean)	9243 (7403)	6321 (6171)	NA	4655 (4597)
	Median	6787	6018	NA	4696
	Range	3728 - 23353	3914 - 10813	NA	3311 - 6090
	N	5	29	0	16
Arsenic	Mean (Geom Mean)	1083 (1051)	1237 (1209)	NA	427 (359)
	Median	1060	1246	NA	339
	Range	711 - 1537	821 - 1761	NA	159 - 1520
	N	5	29	0	16

Table A4. Summary statistics of egg toxicant data in ng/g (ppb) lipid weight basis. Geometric means for CHL data were 0 if the sample set contained a non-detect.

CLTE

Model (**Toxicant class)**	df	AICc	ΔAICc	weight	logLik
PCBs					
MPA + (1 | Site)	4	27.59	0	0.603	-9.38
Lat + (1 | Site)	4	29.51	1.917	0.231	-10.34
Lat + MPA + (1 | Site)	5	31.84	4.251	0.072	-10.28
UrbanDist + (1 | Site)	4	32.34	4.742	0.056	-11.75
MPA + UrbanDist + (1 | Site)	5	33.87	6.277	0.026	-11.3
Lat + UrbanDist + (1 | Site)	5	36.19	8.599	0.008	-12.46
Lat + MPA + UrbanDist + (1 | Site)	6	38.56	10.965	0.003	-12.37
PBDEs					
Lat + (1 | Site)	4	-17.4	0	0.532	13.1
Lat + MPA + (1 | Site)	5	-16.3	1.046	0.315	13.79
MPA + (1 | Site)	4	-14.1	3.312	0.101	11.44
Lat + UrbanDist + (1 | Site)	5	-11.1	6.292	0.023	11.17
UrbanDist + (1 | Site)	4	-9.54	7.823	0.011	9.18
Lat + MPA + UrbanDist + (1 | Site)	6	-9.47	7.888	0.01	11.65
MPA + UrbanDist + (1 | Site)	5	-9	8.356	0.008	10.14
DDTs					
Lat + (1 | Site)	4	11.3	0	0.764	-1.23
Lat + MPA + (1 | Site)	5	14.13	2.829	0.186	-1.43
Lat + UrbanDist + (1 | Site)	5	18.2	6.901	0.024	-3.46
MPA + (1 | Site)	4	19.81	8.512	0.011	-5.49
UrbanDist + (1 | Site)	4	20.19	8.888	0.009	-5.68
Lat + MPA + UrbanDist + (1 | Site)	6	21.2	9.902	0.005	-3.69
MPA + UrbanDist + (1 | Site)	5	23.81	12.507	0.001	-6.26
CHLs					
MPA + (1 | Site)	4	42.6	0	0.676	-16.871
Lat + (1 | Site)	4	45.9	3.29	0.13	-18.517
Lat + MPA + (1 | Site)	5	46.4	3.79	0.102	-17.542
UrbanDist + (1 | Site)	4	47.8	5.22	0.05	-19.479
MPA + UrbanDist + (1 | Site)	5	48.8	6.26	0.03	-18.778
Lat + UrbanDist + (1 | Site)	5	51.6	9.04	0.007	-20.168
Lat + MPA + UrbanDist + (1 | Site)	6	52.6	10.02	0.005	-19.384
Mercury					
MPA + (1 | Site)	4	-80.3	0	0.578	44.58
Lat + (1 | Site)	4	-78.8	1.438	0.281	43.86
UrbanDist + (1 | Site)	4	-77	3.263	0.113	42.95
Lat + MPA + (1 | Site)	5	-73.2	7.052	0.017	42.3
MPA + UrbanDist + (1 | Site)	5	-71	9.252	0.006	41.2
Lat + UrbanDist + (1 | Site)	5	-70.7	9.547	0.005	41.05
Lat + MPA + UrbanDist + (1 | Site)	6	-65.3	14.97	0	39.63
Selenium					
MPA + (1 | Site)	4	-55.4	0	0.465	32.61
Lat + (1 | Site)	4	-55.3	0.142	0.433	32.54
UrbanDist + (1 | Site)	4	-51.8	3.614	0.076	30.81
Lat + MPA + (1 | Site)	5	-49.3	6.117	0.022	31.08
Lat + UrbanDist + (1 | Site)	5	-45	10.459	0.002	28.9
MPA + UrbanDist + (1 | Site)	5	-44.5	10.91	0.002	28.68
Lat + MPA + UrbanDist + (1 | Site)	6	-38.4	17.054	0	27.28
Arsenic					
Lat + (1 | Site)	4	-51	0	0.544	30.41
MPA + (1 | Site)	4	-48.9	2.124	0.188	29.35
UrbanDist + (1 | Site)	4	-48.5	2.461	0.159	29.18
Lat + MPA + (1 | Site)	5	-47.4	3.573	0.091	30.14
Lat + UrbanDist + (1 | Site)	5	-43.3	7.749	0.011	28.06
MPA + UrbanDist + (1 | Site)	5	-42	8.986	0.006	27.44
Lat + MPA + UrbanDist + (1 | Site)	6	-38.3	12.746	0.001	27.23

WEGU

Model (**Toxicant class)**	df	AICc	ΔAICc	weight	logLik
PCBs					
MPA + (1 | Site)	4	33.7	0	0.481	-11.69
Lat + (1 | Site)	4	34.5	0.75	0.331	-12.07
Lat + MPA + (1 | Site)	5	35.7	2	0.177	-10.99
UrbanDist + (1 | Site)	4	43.3	9.59	0.004	-16.48
MPA + UrbanDist + (1 | Site)	5	43.6	9.88	0.003	-14.93
Lat + MPA + UrbanDist + (1 | Site)	6	44.7	10.92	0.002	-13.53
Lat + UrbanDist + (1 | Site)	5	45.5	11.74	0.001	-15.86
PBDEs					
MPA + (1 | Site)	4	40.4	0	0.47	-15.04
Lat + MPA + (1 | Site)	5	41.5	1.05	0.278	-13.87
Lat + (1 | Site)	4	41.8	1.37	0.237	-15.72
UrbanDist + (1 | Site)	4	48.4	8.01	0.009	-19.04
Lat + MPA + UrbanDist + (1 | Site)	6	51.1	10.72	0.002	-16.77
MPA + UrbanDist + (1 | Site)	5	51.9	11.46	0.002	-19.07
Lat + UrbanDist + (1 | Site)	5	51.9	11.48	0.002	-19.08
DDTs					
MPA + (1 | Site)	4	25.8	0	0.448	-7.748
Lat + (1 | Site)	4	26	0.18	0.409	-7.838
Lat + MPA + (1 | Site)	5	28.3	2.49	0.129	-7.295
UrbanDist + (1 | Site)	4	33.7	7.88	0.009	-11.69
MPA + UrbanDist + (1 | Site)	5	36.3	10.45	0.002	-11.27
Lat + UrbanDist + (1 | Site)	5	37.5	11.66	0.001	-11.88
Lat + MPA + UrbanDist + (1 | Site)	6	37.7	11.9	0.001	-10.07
CHLs					
MPA + (1 | Site)	4	53.1	0	0.425	-21.4
Lat + (1 | Site)	4	53.3	0.13	0.399	-21.46
Lat + MPA + (1 | Site)	5	55	1.89	0.165	-20.64
UrbanDist + (1 | Site)	4	61.3	8.17	0.007	-25.48
MPA + UrbanDist + (1 | Site)	5	64.2	11.08	0.002	-25.24
Lat + MPA + UrbanDist + (1 | Site)	6	64.8	11.69	0.001	-23.62
Lat + UrbanDist + (1 | Site)	5	65	11.84	0.001	-25.62
Mercury					
MPA + (1 | Site)	4	11.1	0	0.495	-0.384
Lat + (1 | Site)	4	11.6	0.43	0.399	-0.599
Lat + MPA + (1 | Site)	5	14.5	3.39	0.091	-0.382
UrbanDist + (1 | Site)	4	19.1	7.98	0.009	-4.371
MPA + UrbanDist + (1 | Site)	5	21	9.92	0.003	-3.645
Lat + UrbanDist + (1 | Site)	5	23	11.89	0.001	-4.629
Lat + MPA + UrbanDist + (1 | Site)	6	24.5	13.35	0.001	-3.438

Table A5. Model selection tables for CLTE and WEGU spatial data.

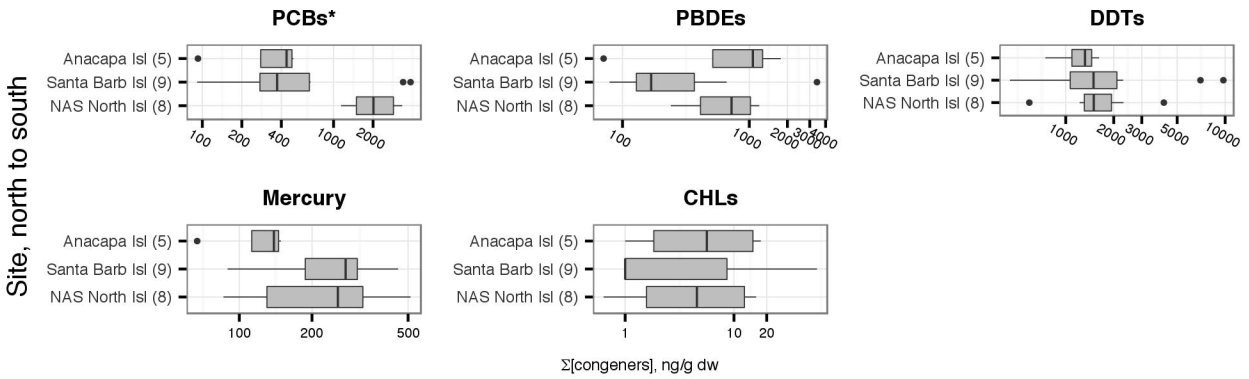

Figure A1. Latitudinal comparisons of toxicant concentrations in western gulls. Parentheses indicate sample size by site. Asterisks represent plots where a significant latitudinal trend is present.

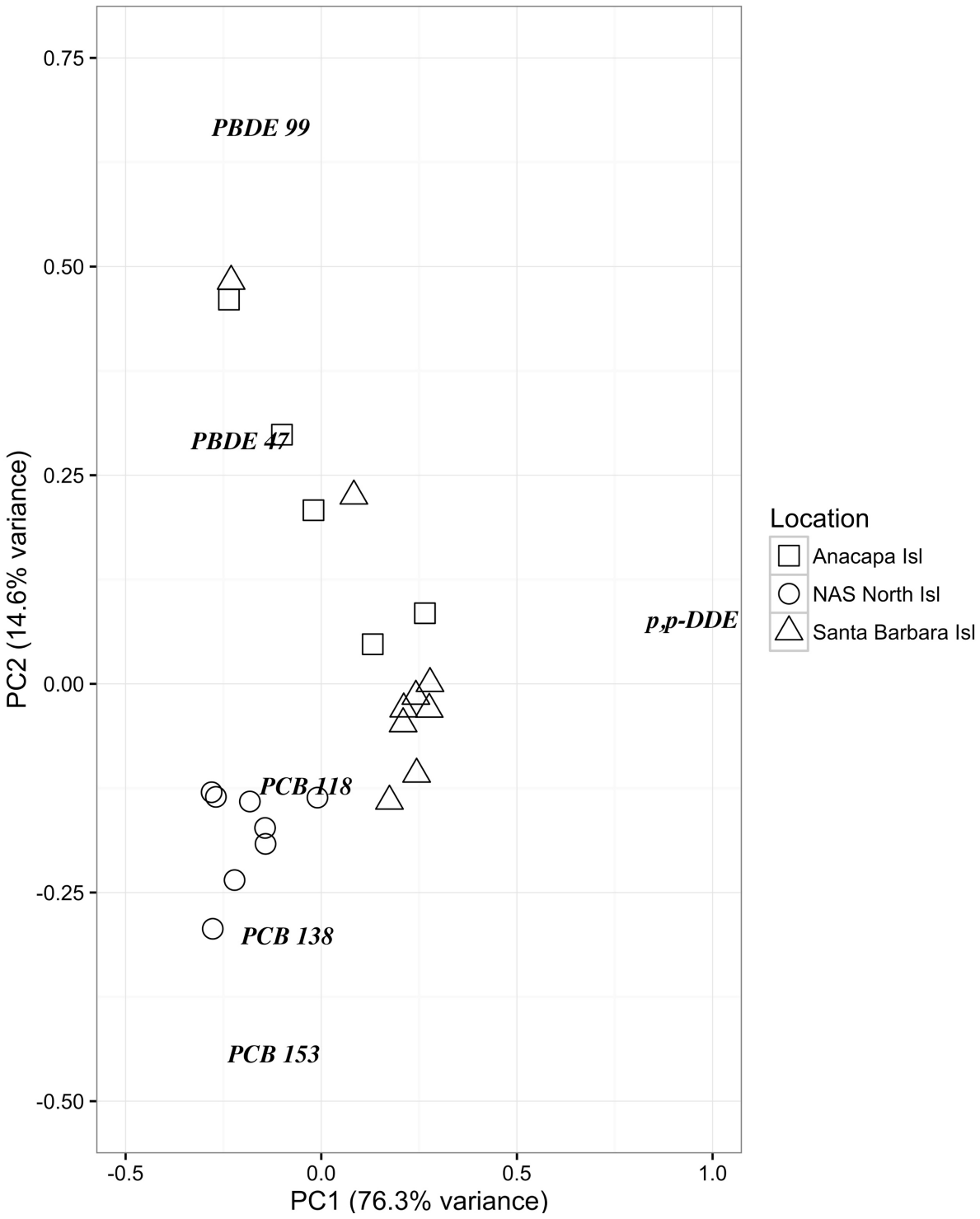

Figure A2. PCA biplot of organic contaminant congeners among western gulls. Single congener concentrations within individual samples were converted to a percentage of the total organic contaminant concentration prior to analysis. Congeners are plotted according to their loadings.

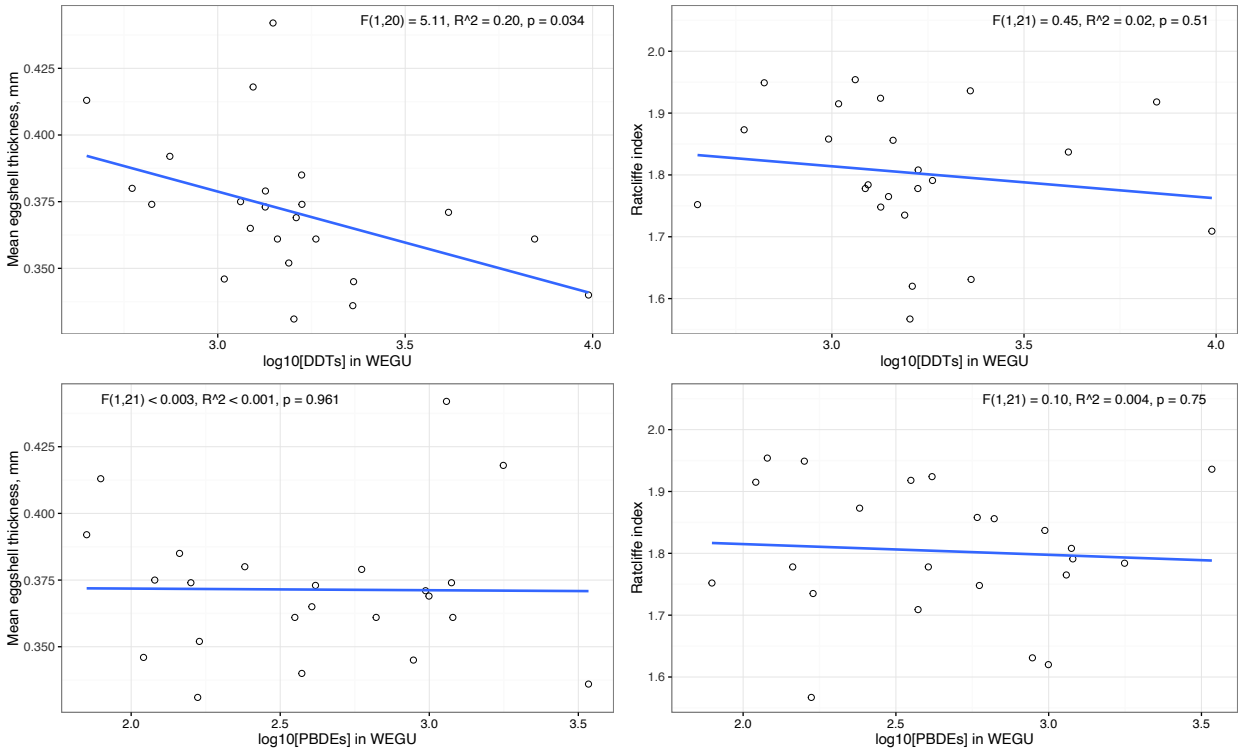

Figure A3. Linear regressions of sum $\log_{10}$DDT and PBDE concentrations versus mean eggshell thickness and Ratcliffe's Index in western gulls (WEGU).

APPENDIX B: Supplementary Methods

Seabirds as regional biomonitors of legacy toxicants on an urbanized coastline

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Methods

Eggs were cleaned with distilled water, weighed, and measured for maximum length and width to the nearest 0.1mm using a analog dial caliper. We measured volume as the weight of water displaced by the egg. For cracked eggs, we estimated volume using the generic approach by Hoyt (1979). Afterwards, we sliced eggs through the equator using a pre-sanitized scalpel, examined egg contents for approximate embryo age and malposition, placed contents into a kilned glass jar, and stored in a -20°C freezer until subsequent chemical analysis.

We let eggshells dry at room temperature for 30 days before measuring eggshell thickness at 4 separate points on the eggshell and shell membrane using a dial

micrometer. We averaged the 4 eggshell thickness measurements for each sample to derive one thickness measurement per sample. To account for errors in measuring thinner eggshells, we also calculated Ratcliffe's index, $RI = \frac{S}{L \cdot W}$, where L is the maximum shell length (mm), W is the maximum shell width (mm), and S is the weight of the dry shell (g) (Ratcliffe 1970).

The individual analytes and reporting levels are provided in Table B.1. POPs and selenium were measured by Physis Environmental Laboratories (PEL; in Anaheim, CA). Mercury was measured by the Sanitation Districts of Los Angeles County (LACSD; in Whittier, CA), and the City of San Diego, CA (CSD). Selenium and arsenic were measured by LACSD only.

An elemental inter-laboratory comparison was performed prior to the analysis of field samples. A single lab performed POP analyses, so no interlab comparisons took place. Two reference materials were used: National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1946: Lake Superior Fish Tissue, and a chicken egg homogenate containing spiked concentrations of the target elements. For both materials, all laboratories were within ± 30% of the mean value for each element.

The toxicants examined, their method detection limits, and reporting limits are available in Table S1. Each lab used established EPA methods or machinery to perform toxicant and egg content analysis (Table B.2). Laboratories ran a set of QC materials with the field samples, including method blanks, spiked blanks (elements only), reference materials, matrix spikes, and laboratory sample duplicates. Each QC material

had associated criteria for analytical frequency and accuracy (Table B.3). The success of meeting these criteria was evaluated for each contaminant class (Table B.4). In all cases, the frequency success was 100%. The accuracy success was generally between 84% and 100%, except as noted (Table B.4).

Due to the variety of reported contaminant concentrations in the literature, we used the R package "OrgMassSpecR" to convert contaminant concentrations to a standardized reporting metric, ng/g fresh weight (fw) (Dodder and Mullen 2014). To obtain fw-based values, wet weight-based (ww) contaminant levels reported by each laboratory were adjusted according to methods by Stickel et al. (1973), using an adjustment factor equal to the ratio of the egg volume to the egg weight for each egg that was sampled. Mean adjustment factors were calculated for those samples that were composites of multiple eggs (i.e., least terns). The extent of moisture loss from individual eggs was variable, such that unadjusted wet weight-based concentrations in some eggs would be over-reported by as much as nearly four-fold.

Current methods for PCB screening measures PCB congeners, whereas historic data and screening levels used Aroclor mixtures to examine sum PCB concentrations. To relate the total PCB contaminants of past studies (>90 PCB congeners) to the 41 congeners measured in this study, we adjust the total PCB levels in the study using a least squares linear regression method from Zeeman et al. (2008):

$$\text{Total PCBs (ng/g fw)} = 75.2 \text{ ng/g fw} + 1.17 \left(\sum \text{lab-reported PCB concentrations ng/g fw}\right)$$

This method is only used for comparisons with previous studies discussed in section 4.3.

PCBs	% detect	MDL	RL	PBDEs	% detect	MDL	RL	OCs	% detect	MDL	RL
PCB 018	0%	0.0125	0.025	PBDE 017	1%	0.0125	0.025	Chlordane, cis-	51%	0.0125	0.025
PCB 028	33%	0.0125	0.025	PBDE 028	74%	0.0125	0.025	Chlordane, trans-	6%	0.0125	0.025
PCB 037	23%	0.0125	0.025	PBDE 047	100%	0.0125	0.025	DDD(o,p)	100%	0.0125	0.025
PCB 044	11%	0.0125	0.025	PBDE 049	68%	0.0125	0.025	DDD(p,p)	24%	0.0125	0.025
PCB 049	41%	0.0125	0.025	PBDE 066	73%	0.0125	0.025	DDE(o,p)	35%	0.0125	0.025
PCB 052	84%	0.0125	0.025	PBDE 071	6%	0.0125	0.025	DDE(p,p)	100%	0.0125	0.025
PCB 066	92%	0.0125	0.025	PBDE 085	7%	0.0125	0.025	DDMU(p,p)	88%	0.0125	0.025
PCB 070	71%	0.0125	0.025	PBDE 099	95%	0.0125	0.025	DDT(o,p)	13%	0.0125	0.025
PCB 074	85%	0.0125	0.025	PBDE 100	98%	0.0125	0.025	DDT(p,p)	19%	0.0125	0.025
PCB 077	56%	0.0125	0.025	PBDE 138	9%	0.0125	0.025	Nonachlor, cis-	65%	0.0125	0.025
PCB 081	3%	0.0125	0.025	PBDE 153	76%	0.0125	0.025	Nonachlor, trans-	80%	0.0125	0.025
PCB 087	72%	0.0125	0.025	PBDE 154	75%	0.0125	0.025	Oxychlordane	1%	0.0125	0.025
PCB 099	98%	0.0125	0.025	PBDE 183	9%	0.0125	0.025				
PCB 101	84%	0.0125	0.025	PBDE 190	2%	0.0125	0.025				
PCB 105	89%	0.0125	0.025	PBDE 209	10%	0.0125	0.025				
PCB 110	96%	0.0125	0.025					**Metals**	**% detect**	**MDL**	**RL**
PCB 114	26%	0.0125	0.025					Mercury (CVAA)	100%	0.25	5
PCB 118	99%	0.0125	0.025					Mercury (EPA7473)	100%	2	2
PCB 119	0%	0.0125	0.025					Selenium	100%	0.25	12.5
PCB 123	12%	0.0125	0.025					Arsenic	100%	2.5	25
PCB 126	6%	0.0125	0.025								
PCB 128	87%	0.0125	0.025								
PCB 138	100%	0.0125	0.025								
PCB 149	87%	0.0125	0.025								
PCB 151	54%	0.0125	0.025								
PCB 153	100%	0.0125	0.025								
PCB 156	72%	0.0125	0.025								
PCB 157	31%	0.0125	0.025								
PCB 158	97%	0.0125	0.025								
PCB 167	65%	0.0125	0.025								
PCB 168	86%	0.025	0.05								
PCB 169	5%	0.0125	0.025								
PCB 170	66%	0.0125	0.025								
PCB 177	54%	0.0125	0.025								
PCB 180	99%	0.0125	0.025								
PCB 183	88%	0.0125	0.025								
PCB 187	93%	0.0125	0.025								
PCB 189	11%	0.0125	0.025								
PCB 194	56%	0.0125	0.025								
PCB 201	67%	0.0125	0.025								
PCB 206	25%	0.0125	0.025								

Table B1. Analyte list, method detection level (MDL), and reporting level (RL) for egg samples. MDL and RL were converted from wet weight basis to ng/g dry weight assuming 75% moisture. % detect refers to the percentage of samples in which each analyte was detected.

Target class	Method or instrument	Labs performed
PCBs	EPA8270Cm	PEL[a]
PBDEs	EPA8270Cm	PEL
OCs	EPA8270Cm	PEL
Mercury	EPA7473	CSD[b]
Mercury	CVAA[c]	LACSD[d]
Selenium	ICPMS[e]	LACSD
Arsenic	ICPMS	LACSD
Lipid	EPA160.3	PEL
Solids	SM2540D	PEL

[a]PEL = Physis Environmental Labs

[b]CSD = City of San Diego

[c]CVAA = Cold vapor atomic absorption

[d]LACSD = Los Angeles County Sanitation District

[e]ICPMS = Inductively coupled plasma mass spectroscopy

Table B2. Standard methods and instruments used to quantify each target class.

QC Material	Objective	Metal Criteria	Organics Criteria
Method Blank	Frequency	1/batch	1/batch
Method Blank	Accuracy	blank < 5 times MDL or blank < 5 times the minimum field concentration	blank < 10 times MDL
Spiked Blank	Frequency	1/batch	Not required
Spiked Blank	Accuracy	+/- 25% of spike value	NA
Reference Material	Frequency	1/batch	1/batch
Reference Material	Accuracy	+/- 20% of true value	+/- 30% of true value for 70% of compounds
Matrix Spike	Frequency	>= 10% of field samples	1/batch
Matrix Spike	Accuracy	+/- 25% of true value	+/- 50% of true value
Sample Duplicate	Frequency	>= 10% of field samples	1/batch
Sample Duplicate	Accuracy	< 25% RPD	< 25% RPD

Table B3. Quality control data quality objectives. A batch was defined as not more than 20 samples. Metals include mercury, arsenic, and selenium. For the organics, the accuracy was evaluated by individual contaminant (not the class sum). The reference material was either rNIST SRM 1946: Lake Superior Fish Tissue, or a custom laboratory control material made from bird eggs. MDL = method detection limit and RPD = relative percent difference.

QC Material	Objective	PCB Success	OC Success	PBDE Success	Metal Success
Method Blank	Frequency	100%	100%	100%	100%
Method Blank	Accuracy	100%	100%	100%	85%
Spiked Blank	Frequency	NA	NA	NA	100%
Spiked Blank	Accuracy	NA	NA	NA	84%
Reference Material	Frequency	100%	100%	100%	100%
Reference Material	Accuracy	50%[1]	100%	92%	93%
Matrix Spike	Frequency	100%	100%	100%	100%
Matrix Spike	Accuracy	86%	91%	89%	86%
Sample Duplicate	Frequency	92%	92%	92%	100%
Sample Duplicate	Accuracy	82%	84%	75%[2]	94%

[1]Accuracy success was 100% if +/- 40% of the true value for 70% of the compounds, instead of +/- 30% of the true value for 70% of the compounds.

[2]Accuracy success was 82% if the RPD was < 30%, instead of < 25%.

Table B4. Data quality objective success rates for each contaminant class. Metals include mercury, arsenic, and selenium. For the organics, the accuracy was evaluated by individual contaminant (not the class sum).

CHAPTER 2

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Foraging in marine habitats increases mercury concentrations in a generalist seabird

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HIGHLIGHTS

- Mercury (Hg) contamination in western gulls varies among habitat types.
- Foraging plasticity in generalists like gulls may reflect different exposure to Hg.
- Gulls foraging in ocean habitats had 55% higher blood Hg concentrations.
- Blood Hg concentrations were unrelated to colony, foraging fidelity and sex.
- Differential foraging habitat use may have implications for gull health.

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ABSTRACT

Methylmercury concentrations vary widely across geographic space and among habitat types, with marine and aquatic-feeding organisms typically exhibiting higher mercury concentrations than terrestrial-feeding organisms. However, there are few model organisms to directly compare mercury concentrations as a result of foraging in marine, estuarine, or terrestrial food webs. The ecological impacts of differential foraging may be especially important for generalist species that exhibit high plasticity in foraging habitats, locations, or diet. Here, we investigate whether foraging habitat, sex, or fidelity to a foraging area impact blood mercury concentrations in western gulls (*Larus occidentalis*) from three colonies on the US west coast. Cluster analyses showed that nearly 70% of western gulls foraged primarily in ocean or coastal habitats, whereas the remaining gulls foraged in terrestrial and freshwater habitats. Gulls that foraged in ocean or coastal habitats for half or more of their foraging locations had 55% higher mercury concentrations than gulls that forage in freshwater and terrestrial habitats. Ocean-foraging gulls also had lower fidelity to a specific foraging area than freshwater and terrestrial-foraging gulls, but fidelity and sex were unrelated to gull blood mercury concentrations in all models. These findings support existing research that has described elevated mercury levels in species using aquatic habitats. Our analyses also demonstrate that gulls can be used to detect differences in contaminant exposure over broad geographic scales and across coarse habitat types, a factor that may influence gull health and persistence of other populations that forage across the land-sea gradient.

1. Introduction

Contaminants are commonly used as indicators of environmental quality for wildlife species and systems (Buck 1979; Fairbrother et al., 2019). Because a primary pathway of contaminant exposure is through diet, contaminant levels are also used to

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describe the foraging ecology of terrestrial and marine wildlife species (Finkelstein et al., 2006; Ramos and Gonzalez-Solis 2012; Jackson et al., 2015). However, understanding the dietary, trophic, and geographic contributions to contaminant concentration can be complex, as the amount of contaminants present can vary across species ranges from local to global scales (Sunderland et al., 2009; Driscoll et al., 2013). Contaminants have been used to describe foraging habitat conditions and characterize foraging at known point sources of contamination (Anderson et al., 1975) or describe potential contaminant exposure from urban areas (Herman et al., 2005; Clatterbuck et al., 2018). Contaminant exposure has also been used to distinguish marine and terrestrial dietary sources within a population, leveraging the broad differences in potential food sources and contaminant types between marine and terrestrial foodwebs (Post 2002; McGrew et al., 2014; Kurle et al., 2016; Peterson et al., 2017). Unlike other tracers of foraging ecology, contaminant analyses can also provide information on potential downstream effects on organismal health and reproduction (Ramos and Gonzalez-Solis 2012; Kurle et al., 2016).

Mercury (Hg) is a metal that is converted to bioavailable methylmercury through biogeochemical processes largely occurring in aquatic environments, making it a potential tracer of animal foraging across the land-sea gradient (Thompson et al., 1998; Elliott and Elliott 2016; Peterson et al., 2015). As methylmercury is also bioaccumulative and biomagnified, its impacts are largely seen in high trophic organisms, like seabirds, where elevated methylmercury concentrations are associated with impaired endocrine, immune, and general physiological responses (Finkelstein et al., 2006; Goutte et al. 2014, 2015; Tartu et al., 2016). Negative impacts on breeding ecology in seabird species have been linked to elevated methylmercury concentrations, including decreased likelihood of breeding (Tartu et al., 2013; Goutte et al., 2015), lower egg hatchability (Goutte et al., 2014), and fewer fledged chicks per breeding pair (Evers et al., 2008; Goutte et al., 2014), even at methylmercury levels below those known to cause adverse effects (Tartu et al., 2013; Provencher et al., 2016). Thus differences in body burdens of methylmercury within a species or population may differentially impact animal reproduction and survival (Croxall et al., 2012; Goutte et al. 2014, 2015). However, assessment of contaminant body burdens is complex as animals integrate and offload chemical signatures over varying temporal scales due to differences in turnover rates among tissues. For example, avian blood integrates methylmercury from the diet over days and weeks, whereas avian feathers contain Hg accumulated over months and deposited during molt (Furness et al., 1986; Kahle and Becker 1999). Therefore, appropriate environmental and life history context are needed to understand variation in contaminant concentrations as a function of foraging habitat use (Bond 2010). Although previous assessments indicate that mercury concentrations are elevated in species that use marine and freshwater habitats as compared to terrestrial habitats (Evers et al., 2005; Jackson et al., 2015; Davis et al., 2016; Ackerman et al., 2016), there are still limited opportunities to document variation in mercury concentrations across populations that forage differentially along the land-sea gradient.

Developments in spatial analyses and modeling paired with improved telemetry devices have also provided an opportunity to pair movement and chemical tracing to define where animals are exposed to harmful contaminants while also providing important information on foraging locations. Combining contaminant and movement data sources may be particularly useful to characterize the foraging ecology of species that consume a variety of prey items and, therefore, may have highly integrated chemical signals (Finkelstein et al., 2006; Peterson et al., 2017). Gulls (*Larus* spp.) are opportunistic foragers known to shift foraging across a land-sea habitat gradient in response to the annual cycle or external factors including food availability and weather patterns (Isaksson et al., 2016; Spelt et al., 2019), although there is recent evidence that some gull populations may have individual foraging specialists (Bolnick et al., 2003; Masello et al., 2013; Navarro et al., 2017). In the absence of direct observations of on what and where birds are foraging, data on foraging locations is a useful alternative to understanding how food web-based contaminants vary across the landscape (Annett and Pierotti 1999; Weiser and Powell 2010). Multiple tracers, including bulk and compound-specific stable isotopes (Masello et al., 2013; Hobson et al., 2015; Corman et al., 2016; Sánchez-Fortún et al., 2020), organic contaminants (Gentes et al., 2015), telemetry (Masello et al., 2013; Camphuysen et al., 2015; Corman et al., 2016; Isaksson et al., 2016; Spelt et al., 2019), and diet samples (Annett and Pierotti 1999; Weiser and Powell 2010; Corman et al., 2016) have been used to understand changes in gull foraging activity over time and space, and in many cases, to explore potential links to observed productivity or population declines.

In this study, we examined the relationship between mercury concentrations and foraging habitat of western gulls (*Larus occidentalis*), a coastal gull native to the western United States that is known to feed on land and at sea (Annett and Pierotti 1999; Shaffer et al., 2017). We tracked movement and tested whole blood for total mercury in western gulls at three colonies, including a colony where gull population and productivity have exhibited a long-term decline (Southeast Farallon Island; Johns and Warzybok 2018). We combined movement data with blood Hg concentrations of breeding gulls to assess whether land cover features where gulls forage, foraging site fidelity, or sex may be associated with elevated mercury concentrations. Specifically, we compared data on foraging locations and fidelity based on GPS locations with Hg levels, as mercury becomes more bioavailable in aquatic systems, to explore how Hg is related to the relative use of oceanic versus terrestrial foraging areas. By pairing movement data with contaminant tracer, we identify gull foraging patterns across a large ocean area and consider how current patterns in habitat use are linked to potential exposure to contaminants and ultimately to population dynamics.

2. Methods

2.1. Field collection & lab analyses

From 2015 to 2017, we captured actively incubating western gulls (n = 59) at three colonies on the west coast of the United States: Cleft-of-the-Rock (n = 19) and Hunters Island (n = 11), off the Oregon coast and Southeast Farallon Island in California (n = 29; Fig. 1). Whereas Cleft-of-the-Rock and Hunters Island are located near rural human development on or near the Oregon mainland (respectively, human population <24,000 within ca. 60 km), Southeast Farallon Island lies ~60 km east of the urbanized San Francisco Bay Area (human population ca. ~7.6 million). Gulls were captured using a mixture of noose carpet and noose traps surrounding the nest. On the first capture, we attached one of three waterproofed GPS units: iGot-U (GT-series; www.i-gotu.com), Mr. Lee (CatLog; www.mr-lee.com), or Ornitela (Ornitrack; www.ornitela.com) to gull back or tail feathers using Tesa tape (Beiersdorf AG GmbH, Hamburg, Germany) or using a Teflon™ leg loop harness (Mallory and Gilbert 2008). All units weighed 15–25 g, which corresponded to 1.6–3.0% of body mass (mean ± SD 1060 ± 117 g) on deployment. We programmed a regular sampling rate ranging from 120s to 600 s for all GPS units. Before release, we banded unmarked gulls using steel U.S. Geological Survey (USGS) leg bands.

On re-capture, we retrieved the GPS unit and collected gull

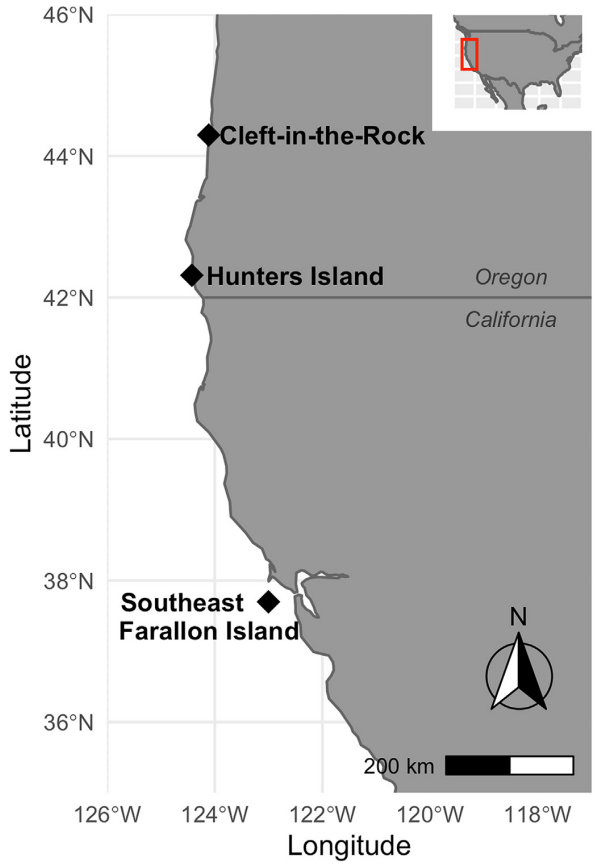

Fig. 1. Western gull colonies where gulls were trapped and sampled over the study period.

morphometric data and blood. Gull morphometrics, including culmen, skull, and tarsus length, were measured to the nearest 0.5 mm using a dial caliper. We measured gull mass using a Pesola® spring scale to the nearest 10 g during both capture and recapture when possible and collected up to 1.5 mL of gull whole blood from the tarsal or brachial vein using 24–26 gauge needles and 2 mL syringes. Birds equipped with Ornitela tags (n = 7) were not recaptured and blood samples and morphometrics were taken at first capture.

After collection, we put gull blood in vacutainers containing K_2EDTA and when possible stored the vacutainers on ice in the field and in −20 °C freezers in the lab. Due to conditions in the field, almost all gull blood samples were congealed and desiccated upon arrival for Hg analysis. Gull blood samples were analyzed wet for total mercury (THg) using a Nippon MA-3000 Direct Mercury Analyzer (Nippon Instruments North America, College Station, Texas, USA) following Environmental Protection Agency Method 7473 (U.S. Environmental Protection Agency, 2000) at the U.S. Geological Survey, Dixon Field Station Environmental Mercury Laboratory (Dixon, California; Ackerman et al., 2020). Blood samples were defrosted and allowed to warm to room temperature before weighed and analyzed for THg. THg is a suitable proxy for MeHg, as MeHg accounts for >90% of THg concentrations in avian whole blood (Rimmer et al., 2005; Renedo et al., 2021). Quality assurance measures included analysis of a certified reference material (either dogfish muscle tissue [DORM-4] or lobster hepatopancreas [TORT-3] certified by the National Research Council of Canada, Ottawa, Canada), system blank, method blank, continuing calibration verification, and duplicate with each set of about 10 samples. Quality assurance measures included machine blanks with each run (n = 28), continuing calibration verification (mean ± SD percent recovery = 99.3 ± 1.2%, n = 13), and certified reference materials (mean ± SD percent recovery = 99.5 ± 1.7%, n = 17). We were concerned that the congealed nature of the blood samples could result in high within-sample variation in Hg. However, duplicate samples indicated similarity in THg concentrations (mean ± SD relative percent difference = 2.4 ± 2.2%, n = 15) (Ackerman et al., 2016; Peterson et al., 2017). Blood Hg concentrations were non-normally distributed, so we used Tukey's ladder of powers to find the transformation that best met the assumption of normality for linear modeling: transformed THg = $-1 * [\text{THg}]^{-0.15}$. All blood Hg concentrations are reported as $\mu g\ g^{-1}$ wet weight and are publicly available in (Ackerman et al., 2021).

All data was processed for further analysis using R software (R Core Team 2020). We determined sex based on these measurements using linear discriminant analysis, which was trained using a dataset of gulls where sex was known (Shaffer, unpublished data). Data were scaled and normalized using the "caret" package (Kuhn 2019) before predicting sex using the lda() function in the "MASS" package (Venables and Ripley 2002). Cross-validation suggested the model error rate when using the training dataset was 7.4%. We accepted the model's predictions for sex if the posteriors for either sex was 95% or greater.

2.2. Identifying putative foraging locations

We analyzed GPS data from tagged gulls to determine where gulls foraged. We retained all GPS location data points (~99.9%) that connected to three or more satellites and interpolated this data to 600 s intervals, the longest sampling rate, to ensure foraging data was comparable among individuals. For individuals equipped with Ornitela satellite tags that were not recaptured, we analyzed GPS data taken within the first 10 days after deployment. Because potential feeding areas were local to gull breeding colonies, we defined trips as any departure and return beyond a 1 km radius of the colony that lasted over 90 min using the package "trakR" (Fleishman et al., 2019). To identify locations where gulls foraged, we applied a behavioral classification system – Residence in Space and Time (RST) – with a dynamic scaling radius identified for each bird (mean ± SD radius = 1.7 ± 1.3 km) (Torres et al., 2017). RST calculates the difference of the normalized residence in time and distance to define each location as one of three potential behavioral states – rest, area-restricted search, or transit – and has been effective at defining behavior states using GPS tracks from a variety of taxa including surface foraging seabirds (Torres et al., 2017). We further split rest locations into those at the colony and included roosting movement behavior as part of the foraging classification when birds were away from the colony. Gulls are known to employ sit-and-wait foraging strategies and may remain relatively stationary when hunting in the intertidal. We then interpreted these behavioral states as the gull was either at the colony, foraging, and transit. Finally, we determined individual foraging fidelity to a geographic location by comparing maximum displacement values between foraging trips (Hazen et al., 2016; Shaffer et al., 2017), where negative values indicate low fidelity and positive values indicate high fidelity (Fleishman et al., 2019).

2.3. Classifying foraging habitat types

We conducted a cluster analysis to classify individuals based on primary foraging habitat type at putative foraging locations. To characterize the habitat type at a foraging location, we overlaid locations in the foraging (area-restricted search) state with available geographic state boundary and waterbody data, which categorized each location as either land, ocean, or freshwater (including brackish bays and estuaries; California Department of Forestry and Fire Protection 2015; Oregon Water Resources Department 2005). To normalize foraging effort among individuals, we calculated the proportion of land cover type for all foraging locations within an individual. Once all foraging locations were classified, we then considered whether there was evidence of clustering of gulls in foraging habitat categories based on the proportions of foraging locations in one of the three land cover categories using non-metric multidimensional scaling (nMDS, R package "vegan") with Bray-Curtis distances to account for zeroes in the proportional data (Oksanen et al., 2019). We used model-based clustering to confirm observed foraging habitat clusters from nMDS ordination using the R package "mclust" (Scrucca et al., 2016), where individuals were probabilistically assigned to a single cluster. We tested models of 2–4 clusters and used Bayesian Information Criterion (BIC) and similarity metrics to determine the most likely number of foraging habitat clusters. We further confirmed that these clusters separated habitat types by grouping consecutive foraging points in time as a foraging event. Like foraging locations, foraging events were also characterized by land cover, but each event consists of multiple foraging locations and potentially multiple land cover types. Therefore, foraging events were characterized as either coastal (consisting of a combination of land and ocean points), inland (land and freshwater points), mixed tidal (ocean and freshwater points), completely land, ocean, or freshwater, or all (land, ocean and freshwater). We then used pairwise t-tests and Wilcoxon rank-sum tests, depending on whether or not data were normally distributed, to examine cluster-based differences of land cover for foraging locations and foraging events, separately.

2.4. Links to THg exposure

We first asked whether differences in THg exposure were related to colony using a one-way ANOVA. We then asked whether foraging habitat type, fidelity to a foraging area, or sex were related to THg concentration. Because fidelity index was correlated with foraging habitat types (point biserial correlation, $t = -3.64$, df = 49, $p < 0.001$), we ran two separate regression models: One with foraging cluster and sex as potential independent variables and another with fidelity index and sex as potential independent variables. We were unable to test for an interaction between colony and foraging habitat type because only one individual from each Cleft-in-the-Rock and Hunters Island clustered separately from the other individuals in those colonies, which violated the assumption of independence between colony and foraging cluster (Chi-square test of independence, $\chi^2 = 18.28$, $p < 0.001$). To further explore this potential interaction, we analyzed ocean foragers alone by colony using a non-parametric ANOVA and conducted pairwise comparisons of THg for ocean foragers between each colony using t-tests. We could not perform the same analysis for inland foragers due to inadequate sample sizes from Cleft-in-the-Rock and Hunters Island. Significance was evaluated at $p < 0.05$.

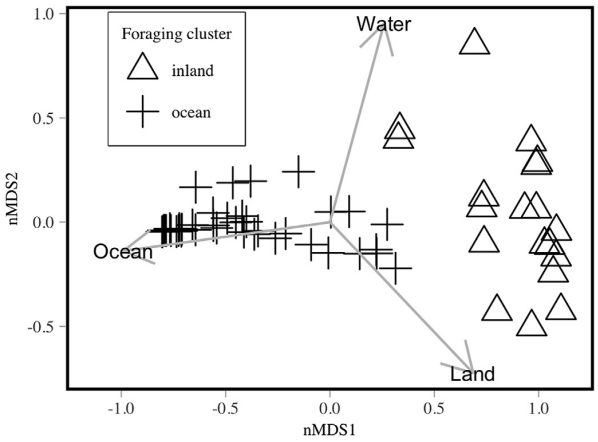

Fig. 2. Gull clusters based on nMDS ordination and model-based clustering. Loadings indicate land cover for foraging location data. Model-based clustering defined three total clusters, two of which exhibited similar mean proportions of ocean foraging. These were combined into a single ocean foraging cluster for further analysis. The final cluster identified by both nMDS ordination and model-based clustering, the inland foraging cluster, was retained for analysis.

3. Results

Using the 59 western gulls from Cleft-in-the-Rock (n = 19), Hunters Island (n = 11), and Southeast Farallon Island (n = 29), we performed linear discriminant analysis using gull body measurements to further classified these individuals as 22 males and 33 females, with four gulls (6.8%) where sex remained unknown. Gulls took a total of 584 trips away from colonies over a sum of 381 days where GPS units were deployed. Gulls generally returned to a similar geographic area (mean fidelity index = 0.49) and had a total of 14,599 GPS points classified as foraging. On average, total blood Hg concentration for all gulls was 0.637 μg g^{-1} wet weight (geometric mean; range 0.150–3.278), and we detected Hg in every individual gull.

3.1. Foraging habitat clusters

Using foraging locations, we identified two habitat type clusters using nMDS ordination – ocean and inland (Fig. 2). However, model-based clustering identified three habitat type clusters. Model-based clusters a and b were dominated by ocean foraging (mean of 97% and 71%, respectively) and cluster c that contained the same individuals as the inland habitat type cluster from nMDS ordination (Figure S1; Table S1). Because two of the three model-based clusters were dominated by ocean foraging activity and did not differ in THg concentration (Kruskal-Wallis ANOVA, $p = 0.07$; TukeyHSD, $p = 0.998$), we collapsed them into a single ocean habitat cluster that resembled the ocean habitat type cluster identified using nMDS ordination for further analysis (Figs. 2 and 3).

3.2. Foraging habitat types

Our clustering algorithms classified each gull as an ocean or inland forager based on the proportions of each habitat type at all foraging locations for that gull. Of 59 total gulls, 40 were identified

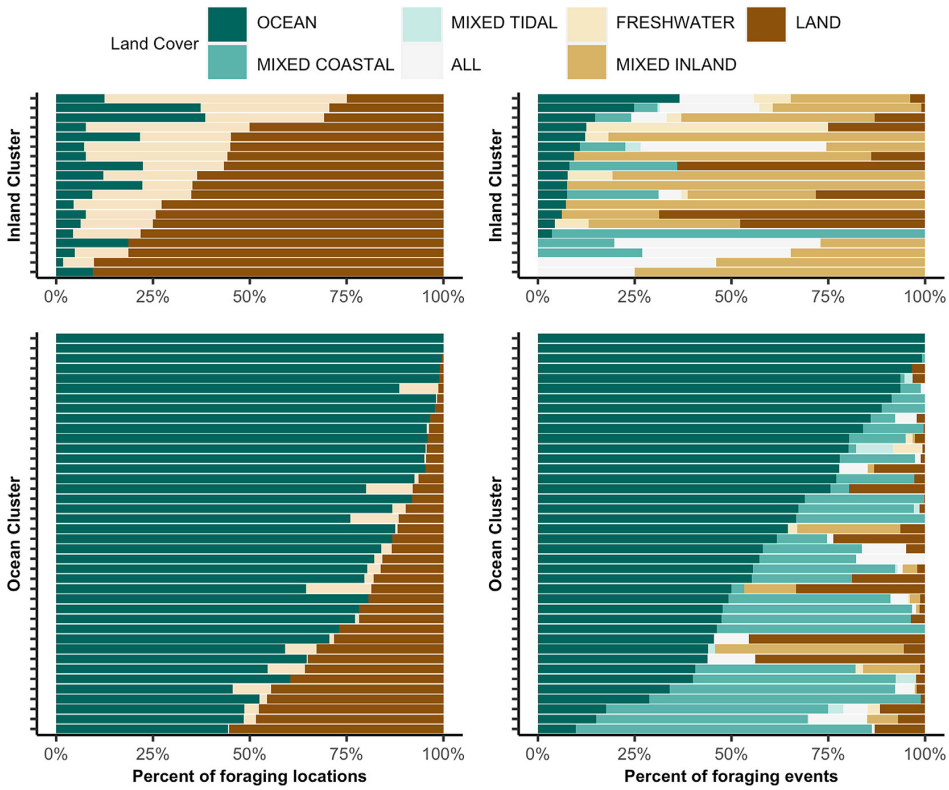

Fig. 3. Percentage land cover of gull foraging locations (left) and foraging events (right) separate by foraging cluster. Because foraging events are combinations of foraging locations, events may have mixed land cover types or all land cover types in addition to the ocean, freshwater, and land classes.

as ocean foragers while 19 were classified as inland foragers. Almost all gulls from Cleft-in-the-Rock and Hunters Island were classified as ocean-foraging gulls, while 17 of 19 inland-foraging gulls nested at Southeast Farallon Island. Gulls differed in their proportion of ocean, land, and water locations, where gulls in the ocean cluster generally had greater than 50% ocean locations and fewer land and water locations than the inland cluster (*t*-test, all $p < 0.001$, Fig. 3a). These differences were also reflected in proportions of foraging events, where gulls in the ocean cluster had greater proportions of ocean and coastal foraging events and fewer inland and water foraging events than inland gulls (Wilcoxon rank-sum tests, $p < 0.05$, Fig. 3b). Ocean-foraging gulls also exhibited significantly less fidelity (0.40 ± 0.37) to a geographic area than inland-foraging gulls (0.85 ± 0.37; Wilcoxon rank-sum test, $W = 381$, $p < 0.001$) and had higher variability in trip direction (mean azimuth = 208 ± 107°) than inland-foraging gulls (mean azimuth = 143 ± 66°), though not significantly so (Watson-Wheeler test, $W = 4.74$, df = 2, $p = 0.09$). Trip duration and normalized trip frequency also did not differ between habitat types (t-tests, $p > 0.05$, Table 1).

3.3. Links to THg exposure

We found no difference in THg among colonies ($F_{2,56} = 0.88$, $p = 0.42$). Using multiple regression analysis, we found that THg differed among gulls that foraged in ocean versus inland habitat (Fig. 4). Linear regression demonstrated that ocean foraging gulls had on average 55% higher blood THg concentrations than inland foraging gulls ($F_{2,54} = 3.91$, $p = 0.026$, adjusted $R^2 = 0.13$; $t = 2.21$, $p = 0.032$), although foraging habitat used only explained ~13% of the observed variation in THg concentrations. Sex was not significantly related to THg ($t = 1.50$, $p = 0.14$). As there was no interactive effect of sex with foraging cluster ($t = 0.27$, $p = 0.79$), we report the model without this interaction as a predictor. However, the model

Table 1
Summary statistics for gull foraging clusters. Ranges are given as standard deviations except for THg.

Cluster	N	Sex (N)			THg[a]	Mean land cover (%)			fidelity index[b]	trips per day	trip duration[c]	trip azimuth
		♀	♂	unk		ocean	water	land				
inland	19	12	6	1	0.47 ± 2.07	13 ± 11	24 ± 15	63 ± 19	0.85 ± 0.31	1.9 ± 1.3	574 ± 379	143 ± 66°
ocean	40	21	16	3	0.73 ± 1.94	80 ± 17	3 ± 4	17 ± 16	0.40 ± 0.37	1.6 ± 0.6	406 ± 239	208 ± 107°

[a] Values are the geometric mean and geometric standard deviation in μg g-1 wet weight.
[b] Values range from −1 (most dissimilar) to 1 (most similar).
[c] Values are in minutes.

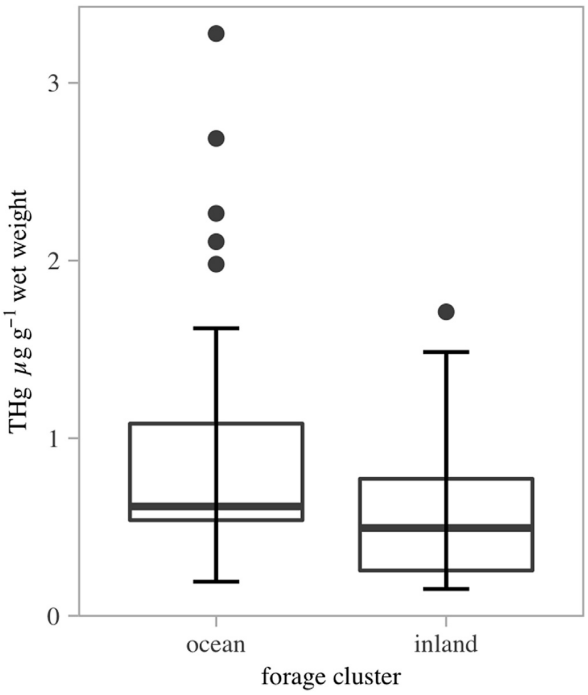

Fig. 4. Total mercury concentrations of western gulls grouped by foraging cluster. The boxplot represents the 25–75% quartile range and the median bar.

that included fidelity index and sex as predictor variables was not significantly different from the null model ($F_{2,49} = 1.51$, $p = 0.231$, $R^2 = 0.031$). Though fidelity was strongly related to foraging cluster, it was unrelated to THg ($t = -0.045$, $p = 0.964$) and there was no interactive effect of fidelity index with sex ($t = 1.13$, $p = 0.265$). Exploring the potential interaction between foraging cluster and colony, we found ocean foraging gulls had similar THg regardless of colony ($F_{2,37} = 1.02$, $p = 0.38$). Pairwise comparisons among ocean foragers from all colony combinations were not significant (Cleft-in-the-Rock and Hunters Island, $t = -1.43$, df = 16.49, $p = 0.17$; Cleft-in-the-Rock and Southeast Farallon Island ($t = -0.51$, df = 14.02, $p = 0.62$; Hunters Island and Southeast Farallon Island $t = 0.38$, df = 17.14, $p = 0.71$).

4. Discussion

Because the primary pathway for body burdens of contaminants is through diet, variables that impact diet, including geographic location, foraging habitat, and physiology are expected to influence contaminant concentrations (Finkelstein et al. 2006, 2007; Robinson et al., 2011; Ramos and Gonzalez-Solis 2012; Jackson et al., 2015). While wildlife biomonitoring efforts commonly uses these relationships to identify point sources of chemical pollution, relatively fewer studies have examined broad-scale differences in contaminant concentrations in coastal and marine waters off the urbanized west coast of the United States. Our analyses demonstrate that western gulls – generalist, avian foragers – had higher total blood Hg concentrations when foraging over ocean habitat compared to inland habitat across three geographically distinct colonies in the Northeast Pacific and that relative to colony, fidelity to foraging areas and sex, the type of foraging habitat used has the largest effect on gull Hg exposure. While there are no doubt other differences among these three colonies, our finding emphasizes the ubiquity of Hg exposure across multiple food webs (Post 2002; Kurle et al., 2016). This finding is particularly important for generalists that exploit multiple habitat types, shift foraging strategies according to food availability, or exhibit individual specialization (Annett and Pierotti 1999; Hobson et al., 2015; Bolnick et al., 2003). Our research also affirms that the use of chemical tracers can be an effective tool to identify animal foraging habitat and organismal and environmental health (Peterson et al., 2017).

Using GPS foraging locations to identify foraging habitat type, we found gulls across the three colonies fell into one of two categories: ocean-foraging gulls that foraged over ocean or coastal habitat, or inland-foraging gulls that foraged in terrestrial and freshwater habitats (Fig. 3). We detected significant differences in THg concentrations in ocean-foraging versus inland-foraging gulls (Fig. 4), a finding supported by a number of studies which also found differential Hg exposure across the land-sea foraging gradient, associated directly with the food consumed (McGrew et al., 2014; Kurle et al., 2016) and differences in foraging locations within or among colonies (Peterson et al., 2017; Sánchez-Fortún et al., 2020; Thorne et al., 2021). The differences we identified in Hg concentration based on foraging habitat have been linked to differences in methylmercury bioaccumulation between terrestrial and marine food webs (Ackerman et al., 2016). Additionally, more recent studies show Hg concentrations are predictive of foraging habitat use in other species of gulls using GPS locations or stable isotope analysis, respectively (Peterson et al., 2017; Sánchez-Fortún et al., 2020; Thorne et al., 2021). Our study supports these findings and also highlights some important areas for future research. Compared to published studies, the blood Hg values we observed in western gulls were variable, which may reflect wide variation in methylmercury exposure found in gull species (Ackerman et al., 2016). The relative importance of foraging habitat used, as compared to colony, site fidelity and sex, further support the use of Hg as a tracer of foraging ecology (Kurle et al., 2016; Peterson et al., 2017; Chételat et al., 2020).

Our findings suggest a significant link between foraging habitat and THg exposure, foraging habitat used only explained ~13% of the observed variation in THg concentrations. This is unsurprising as many other factors are known to influence methylmercury concentrations in wild birds, including biogeochemical processes that make elemental Hg bioavailable, body condition, and physiological storage and excretion mechanisms (Eagles-Smith et al., 2009; Elliott and Elliott 2016; Chételat et al., 2020). THg in avian blood represents mobilization of mercury both through the diet and from internal body tissues (Evers et al., 2005; Chételat et al., 2020). Controlled studies of seabirds that were dosed with methylmercury suggest methylmercury in whole blood has a rapid half-life of 24 h, followed by a slower half-life of 30–60 days (Monteiro and Furness 2001). Additionally, western gulls are omnivorous and their diet includes a variety of prey representing different foraging habitats and trophic levels (Annett and Pierotti 1999). In this context, it is probable that the THg concentrations we measured also assess accumulation prior to the time periods captured by the GPS tracks. Dietary shifts can occur in western gulls at the time of chick-hatching, where gulls tended to consume more marine prey; however, our study did not sample gulls over this time period (Annett and Pierotti 1989). As opportunistic foragers, gulls may exploit multiple foraging sources depending on forage availability. Longer GPS deployments or including another indicator of foraging habitat, such as sulfur stable isotopes or compound-specific stable isotopes, may strengthen the relationships we observed (Peterson et al., 2017; Sanchez-Fortun et al., 2020; Binkowski et al., 2021). Despite these complexities, a significant link between THg concentrations and oceanic versus inland foraging was detectable

(Peterson et al., 2017; Thorne et al., 2021; Chételat et al., 2020).

Previous work has suggested that western gulls that forage in terrestrial habitats have greater fidelity to a geographic foraging area than ocean foraging gulls, in part because prey distribution at sea is ephemeral whereas terrestrial food availability may be reliable and uniformly distributed (Corman et al., 2016; Shaffer et al., 2017). Our findings support these conclusions, although fidelity to a geographic foraging area was unrelated to THg concentrations. That foraging cluster, but not geographic foraging fidelity, is linked to THg concentration further suggests that methylmercury contamination in western gulls reflects broad differences in methylmercury contamination across habitat types, rather than specific geographic sources of Hg (Ackerman et al., 2016). Recent studies of gull habitat use have utilized fine-scale geographic attributes to describe gull foraging (Isaksson et al., 2016; Navarro et al., 2017; Shaffer et al., 2017; Spelt et al., 2019). While fine-scale measurements of gull habitat may be helpful to understand of local contamination for urban or point-source sites (Ricca et al., 2008; Gentes et al., 2015), our work suggests that even with coarser resolution habitat information, we can contextualize Hg concentrations with gull foraging ecology.

Despite being separated by hundreds of miles along coastlines with vastly different degrees of development, we did not detect significant differences in THg concentration among the three colonies we sampled and found that ocean-foraging gulls had similar THg concentrations regardless of colony. This aligns with other studies of seabird foraging that associate contaminant concentrations with foraging habitat used rather than site-specific signals (Soldatini et al., 2020; Thorne et al., 2021), and suggests that tracers of foraging ecology are useful because they can distinguish between multiple potential foraging strategies in and among populations (Ramos et al., 2013). Still, the possibility for an interaction between foraging habitat and colony still exists and may be easier to detect for known Hg hotspots. For example, San Francisco Bay is a well-documented area of elevated methylmercury exposure, and California gulls (*Larus californicus*) that used the estuarine waters of the bay had elevated Hg concentrations compared to terrestrial-feeding conspecifics (Peterson et al., 2017). The blood Hg values we observed in inland-foraging western gulls aligned with the range of blood Hg values found in California gulls in San Francisco Bay (Fig. 4, Peterson et al., 2017). While our cluster analysis did not distinguish between estuarine and terrestrial foraging, an interaction may be more obvious between inland foraging gulls nesting at each colony. Unfortunately, the low sample size of inland foraging gulls from the Oregon colonies did not allow us to make this comparison. Future studies may consider how variation in gull foraging strategies, likely driven by ecological pressures including intra- or interspecific competition, levels of nearby marine food resources, and fisheries activity, may influence contaminant concentrations in these populations (Hobson et al., 2015; Corman et al., 2016; Garthe et al., 2016).

5. Conclusions

Widespread production and deposition of anthropogenic compounds is expected to continue to impact seabirds and other top predators, including gulls. While the use of contaminants to identify potential point sources of pollution is needed, contaminant tracers can also inform our understanding of multi-colony or regional impacts of large-scale production and deposition of manmade compounds (Gentes et al., 2015; Peterson et al., 2017). With continued research into potential pathways for contaminant deposition and availability across the land-sea gradient, studies of contaminants and habitat use can be used to assess exposure to a wide range of contaminants (Ramos et al., 2013; Gilmour et al., 2019). Our results show that contaminant exposure is different in terrestrial, estuarine, or marine forage foods, which for a generalist species like the western gull may impact breeding, recruitment and population trajectories (Annett and Pierotti 1999; Duhem et al., 2008; Weiser and Powell 2010). With differential habitat use and thus exposure to contaminants, the adverse impacts of contaminant-associated diet may be an important consequence of foraging plasticity in gull populations. Future studies can determine how Hg and other contaminants can be used as chemical tracers to understand the ecological consequences of diet-mediated contaminant exposure for gull populations.

Author contribution

Corey Clatterbuck: Conceptualization, Methodology, Validation, Formal analysis, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Funding acquisition. **Rebecca Lewison**: Methodology, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration. **Rachael Orben**: Software, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing, Funding acquisition. **Joshua Ackerman**: Validation, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Funding acquisition. **Leigh Torres**: Software, Resources, Writing – original draft, Writing – review & editing, Funding acquisition. **Robert Suryan**: Resources, Writing – original draft, Writing – review & editing, Funding acquisition. **Pete Warzybok**: Investigation, Writing – original draft, Writing – review & editing, Funding acquisition, Project administration. **Jaime Jahncke**: Writing – original draft, Writing – review & editing, Funding acquisition, Project administration. **Scott Shaffer**: Conceptualization, Investigation, Resources, Writing – original draft, Writing – review & editing, Project administration, Funding acquisition

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2021.130470.

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Supporting Information

No. clusters	BIC	wss	avg silhouette width
2	-1514	76724	0.319
3[a]	-1426	26387	0.429
4	-1429	18006	0.391

[a] combined two of the clusters in from this model into one for final analysis

Table S1. Model-based clustering parameters based on foraging location.

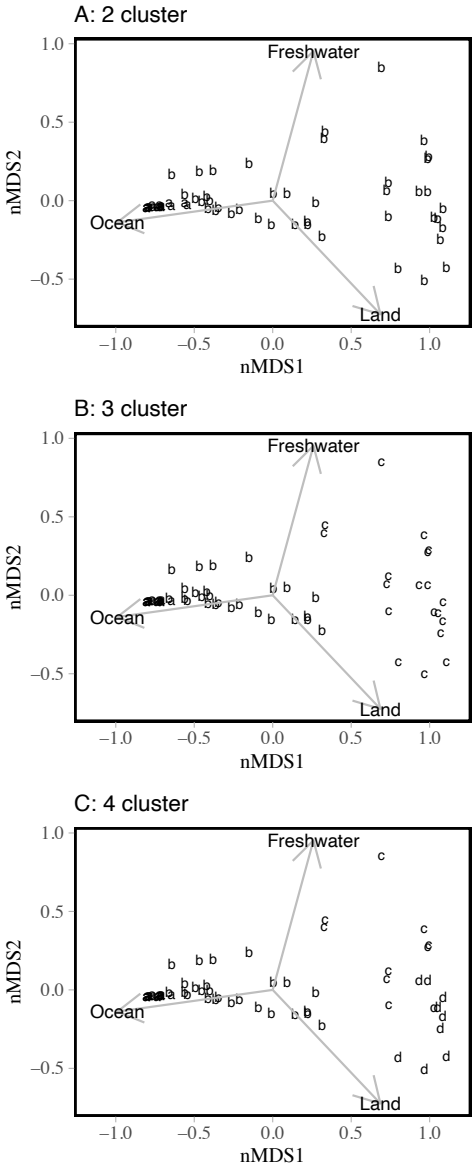

Figure S1. Gull clusters derived from model-based clustering on foraging locations. Each panel corresponds to model-based clustering with 2-4 defined clusters. We combined clusters a and b in the 3-cluster panel (ocean) and retained cluster c (inland) for further analysis. Loadings indicate land cover for foraging location data.

CHAPTER 3

Nontargeted screening of halogenated organic compounds in North Pacific albatrosses

Abstract

Detection and characterization of halogenated organic compounds (HOCs) remains an important goal of marine biomonitoring given the persistence of these compounds in the environment and their deleterious impacts on wildlife. Nontargeted analytical approaches allow for the broad detection of HOCs of interest, and, as such, provide a proactive approach to monitoring parent HOCs and their degradation products in the environment. To date, the majority of nontargeted analyses for ocean monitoring have focused on coastal marine mammals, which reflect coastal pollutants that may not be representative of HOCs in the open ocean. Here, we use a previously established nontargeted screening approach with a data reduction script to detect HOCs in the adipose tissues of three wide-ranging North Pacific albatross species incidentally caught in North Pacific fisheries. We found a total of 202 HOCs in albatross tissues, with 129 compounds not typically monitored and 74 compounds not detected previously in comparable analyses in marine mammals. The majority of compounds were of anthropogenic origin (n=159), with fewer compounds of natural (n=16) and unknown (n=27) origins. While DDT and PCB-related compounds remained in highest relative abundance, compounds of unknown and natural origin were found in similar abundances to other anthropogenic HOC classes. Anthropogenic HOC profiles in black-

footed albatrosses clustered separately from Laysan and short-tailed albatrosses, which is consistent with knowledge about the differences in foraging ranges and associated contaminant exposure of these species. However, albatross species were inseparable when clustering by HOCs of natural or unknown origin. These findings highlight the extent to which even remote ocean foragers are exposed to suites of HOCs including known harmful chemicals, the need for additional study of the transport and fate of these typically unmonitored HOCs, and the utility of conspecific seabirds for monitoring chemicals in large, oceanic basins.

Introduction

Biomonitoring, the measurement of compounds in living organisms, has become an important tool in determining the presence and distribution of potentially harmful compounds in the environment, which can inform environmental quality assessments and legislative and regulatory intervention (Elliott and Elliott 2013, Krowech et al. 2016). Biomonitoring has historically focused on manmade halogenated organic compounds (HOCs), compounds with covalently-bonded chlorine or bromine substituents, used in commercial, industrial, or agricultural applications (Stockholm Convention, 2001). HOCs are commonly detected in environmental matrices due to their persistence, semi volatility, and their tendency to bioaccumulate in food webs and biomagnify in long-lived wildlife species. Because HOCs have been linked to compromised individual survival, reproduction, and immune responses (Finkelstein et al. 2007, Erikstad et al. 2013,

Trego et al. 2018), they have been identified as key compounds of interest in wildlife and human health biomonitoring research (Stockholm Convention, 2001).

Targeted analytical approaches are routinely used in biomonitoring applications to identify previously defined and identified HOCs (Muir and Howard 2006). While informative, targeted approaches omit detection of HOCs which are not target analytes regardless of their abundance. These HOCs can include new, degraded, or metabolized HOCs with similar properties to legacy HOCs and may impact wildlife in ways similar to known HOCs. This gap has led to the development of nontargeted analytical approaches which can identify currently unmonitored as well as unknown and natural HOCs that have similar relative abundance to targeted, known HOCs of interest (Jobst et al. 2013, Shaul et al. 2015), even when there is incomplete information on their origin and chemical structure (Hoh et al. 2009, Hoh et al. 2012). Because nontargeted analytical approaches can identify emerging and potentially harmful compounds before they become widespread or identify previously unknown compounds, nontargeted analytical approaches are an intensive but valuable complement to targeted approaches for biomonitoring and health safety efforts (Hoh et al. 2012, Sobus et al. 2017) and represent a proactive biomonitoring tool to provide comprehensive information on the suite of potentially harmful HOCs present in an environment.

One of the limitations of using wildlife as biomonitors is the extent to which organisms are distributed across the landscape (Brown and Takada 2017). Nontargeted contaminant analyses of HOCs in wildlife are frequently implemented in species residing in a single geographic region (Shaul et al. 2015, Alonso et al. 2017, Fernando

et al. 2018, Rebryk and Haglund 2021) and often in a single sample (Vetter et al. 2018, Tue et al. 2021). These studies have been instrumental in establishing the presence of typically unmonitored HOCs (Shaul et al. 2015, Millow et al. 2015, Fernando et al. 2018) and identifying effective biomonitors for coastal pollution in some regions (Cossaboon et al. 2019). This research has also begun to identify the physiological impacts of both regularly monitored and currently unmonitored contaminants (Heffernan et al. 2017, Trego et al. 2018). This growing body of nontargeted HOC biomonitoring research has also highlighted gaps in how nontargeted screening of HOCs can characterize contaminant distributions and differences over larger spatial scales. Given the ability of many HOCs to be atmospherically transported and the recurring presence of unmonitored compounds in both the Atlantic and Pacific Oceans (Alonso et al. 2017, Cossaboon et al. 2019), establishing wide-ranging species with similar ecologies as monitors can expand biomonitoring efforts and interpretation at landscape and ocean-wide scales.

Albatrosses (Diomedeidae) are upper trophic level ocean wanderers that have documented threats from physical and chemical pollution (Elliott 2005, Wilcox et al. 2015, Connors et al. 2018). In the North Pacific, black-footed albatross (*Phoebastria nigripes*), Laysan albatross (*Phoebastria immutabilis*), and the endangered short-tailed albatross (*Phoebastria albatrus*) forage on oceanic scales across overlapping, but largely disparate oceanic areas (Shuntov 1972, Kappes et al. 2015, Suryan and Kuletz 2018). This spatial segregation has been suggested as a primary driver of differences in organic pollutant and trace metal concentrations among black-footed and Laysan

albatrosses (Muir et al. 2002, Finkelstein et al. 2006, Harwani et al. 2011). Diet may also contribute to observed differences in contaminant concentrations among species. These sympatric species are thought to have similar, squid-dominant diets during the breeding season despite spatial segregation in foraging habitat (Harrison et al. 1983, Finkelstein et al. 2006, Conners et al. 2018). During the non-breeding season, black-footed albatrosses feed on a slightly higher proportion of squid than fish-feeding Laysan albatrosses (Gould et al. 1997, Elliott 2005, Suryan and Fischer 2010). Additional differences in diets include increased prevalence of fish eggs and fisheries discards in black-footed albatrosses as well as differences in species consumed due to foraging area (e.g., differences in squid species in cool Alaskan vs. warmer temperate waters; Harrison et al. 1983, Conners et al. 2018). Dietary data are not available for short-tailed albatrosses but their diet is suspected to be similar to black-footed albatross diet, as both species frequently forage at shelf break regions (Suryan and Fischer 2010). Given their broad foraging ranges and trophic position, albatross tissues harbor bioaccumulating, biomagnifying, and possibly toxic, contaminants found across North Pacific waters, which suggests these species can serve as representative biomonitors for this large ocean area (Finkelstein et al. 2006). Indeed, a wide range of HOCs have already been detected in black-footed and Laysan albatrosses, including polychlorinated biphenyls (PCBs), DDT-related compounds including DDEs and DDMUs, mirex, heptachlors, chlordanes, polybrominated diphenyl ethers (PBDEs), drins, polychlorinated terphenyls (PCTs), and toxaphenes (Fisher 1973, Jones et al. 1996, Auman et al. 1997, Muir et al. 2002, Elliott 2005, Finkelstein et al. 2006, Harwani

et al. 2011). Tris(4-chlorophenyl)methane (TCPM) and it's presumed derivative, tris(4-chlorophenyl)methanol (TCPM-OH), are thought to be impurities of DDT and Dicofol production (Buser 1995, de Boer 1997) and have also been detected in black-footed albatross tissues (Muir et al. 2002). Many of the previously studied HOCs are legacy persistent organic pollutants, yet HOCs of natural origin as well as emerging contaminants of interest have not been assessed in these species (but see Tittlemier et al. 1999).

To better understand North Pacific albatross exposure to HOCs, we conducted a GC×GC/TOF-MS based nontargeted analysis (Hoh et al. 2012) to detect HOCs in the adipose tissues of three species of North Pacific albatrosses. The importance of the North Pacific extends beyond albatross, as it is one of the largest biomes on earth and supports multi-million dollar groundfish fisheries (Fissel et al. 2018). Using salvaged tissue from three, conspecific North Pacific albatross species, our aims were to confirm the presence of known HOCs, characterize newly described HOCs, and compare profiles of HOC diversity and abundance within and among species. In addition to providing an inventory of HOCs in the North Pacific and the associated fishery grounds, our research expands our understanding of contaminant loads in albatrosses, contributing to a greater understanding of the threats to Diomedeidae, the most threatened bird Family (Croxall et al. 2012).

Methods

Study species

All samples were obtained as a part of NOAA's seabird bycatch program and stored under San Diego State University's IACUC (APF# 15-05-003L). We sampled a maximum of 10g of subcutaneous adipose tissue from three species of albatross incidentally caught in Alaskan longline fisheries: Laysan albatross (n=4), black-footed albatross (n=4), and short-tailed albatross (n=3). Short-tailed albatross samples were specifically stored under USFWS scientific permit #13-076 and Migratory Bird Treaty Act #MB025076-0. Samples were collected during necropsy by the NGO Oikonos Ecosystem Knowledge and archived at -20°C upon collection. Age and sex of the salvaged individuals was not known.

Chemical analysis

We treated the albatross tissue samples following the method described in Shaul et al. 2015. Briefly, we extracted ~2g of adipose tissue using a Dionex Accelerated Solvent Extractor (Dionex ASE 350, ThermoFisher Scientific) using 4 cycles at 100°C, 1500 psi, 60% flush, and a 100s purge time. A procedural blank was included with each ASE extraction batch. After evaporation of the extract at 40°C, we combined ~1g of oil with 1:1 cyclohexane:ethyl acetate to 5mL total volume and spiked known amounts of 3 internal standards: $^{13}C_{12}$-PCB-169, ^{13}C-tris(4-chlorophenyl)methane (Wellington Laboratories, Guelph, Ontario, Canada), and 4'fluoro-2,3',4,6-tetrabromodiphenyl ether (Accustandard, New Haven, CT, USA). Ten percent of this extract was evaporated to determine lipid weight. We then removed lipids using 2 rounds of gel permeation chromatography (J2 Scientific, Columbia, MO). The GPC eluent was concentrated,

solvent exchanged in isooctane, and spiked with a recovery standard solution ($^{13}C_{12}$-PCB-189) to a final volume of 100 μL. Final extracts were injected into a LECO Pegasus 4D GC×GC/TOF-MS using the parameters for wildlife tissue samples described in Hoh et al. 2012.

Chemical identification

To identify halogenated mass spectra, we used an automated data handling procedure described in Cossaboon et al. 2019 based on the data reduction software by Pena-Abaurrea et al. 2014. These software routines identify spectra that are characteristic of halogenation based on ion intensity ratios for chlorines and bromines (Dodder et al. 2017). These routines identified an average of 368 potentially halogenated mass spectra from an average of 9424 chromatographic features per sample, which allowed for analysis in a timely manner. Resulting spectra were manually reviewed for halogenation, cross-checked to align compounds among samples, and identified against spectra from the NIST 2014 Electron Impact Mass Spectral Library and existing mass spectral libraries produced using the same nontargeted HOC screening approach (see Hoh et al. 2012, Shaul et al. 2015, Mackintosh et al. 2016, Alonso et al. 2017, Cossaboon et al. 2019, all available at https://orgmassspec.github.io/libraries.html). These libraries are comprised of HOCs found in a common dolphin (Delphinus delphis) in the northwestern Atlantic (Hoh et al. 2012); and bottlenose dolphins in the southeastern Atlantic (Alonzo et al. 2017); bottlenose dolphins (Tursiops truncatus; Shaul et al. 2015), black skimmers (Rynchops niger; Millow et al. 2015), long-beaked

common dolphins (Delphinus bairdii), short-beaked common dolphins (Delphinus delphis), Risso's dolphins (Grampus griseus), California sea lions (Zalophus californianus), and Pacific harbor seals (Phoca vitulina) in the Southern California Bight (Cossaboon et al. 2019). For PCBs, we selected the 15 largest peaks among samples and among them, we were able to identify twelve PCB congeners: PCB-52, -66, -101, -118, -153, -105, -138, -187, -128, -167, -180, and -170. Three PCB compounds, a 4Cl, 6Cl, and 8Cl-PCB, could not be identified to congener but are included in the final dataset. Because PCBs from technical mixtures are well-described in these taxa, and only a few PCB congeners comprise the majority (>70%) of PCB contamination in North Pacific albatrosses (Harwani et al. 2011), we retained these 15 PCB congeners present in PCB technical mixtures as a marker of their continued pervasiveness in marine wildlife. Additionally, frequently unmonitored PCB metabolites (e.g, methylsulfonyl-PCBs) were included in the final dataset. Detailed manual identification procedures for unknown compounds not found in other libraries are available in Hoh et al. 2012.

Data analysis

All data analysis was performed in R. Relative responses of each identified compound were calculated based on peak area against the internal standard $^{13}C_{12}$-PCB-169 and then divided by the lipid weight of each sample (g). We removed compounds detected in the blank that had a peak area relative to the internal standard less than 5 times higher than the relative peak area found in the blank. Based on this criterion, four compounds were removed from the analysis: a chlorinated benzene, 2

organophosphates, and 1 chlorophosphate. Five additional compounds, including 4 PCBs (PCB-118, -153, -138, -180) and p,p'-DDE were also determined in the procedural blank, but these compounds in experimental samples had a relative peak area 301-3406 times higher than the corresponding peak area found in the blank and were therefore retained for analysis.

Comparing profiles among species

One of our central research questions was whether the three albatross species harbored different contaminant profiles. To determine potential differences in chemical profiles among species, we performed three unsupervised learning methods -- hierarchical clustering, k-means clustering, and PCA clustering -- on log-transformed relative responses for each compound. We separated the compounds into separate datasets based on compound origin (anthropogenic, natural, and unknown), because previous work demonstrated potential differences in species profiles based on compound origin (Shaul et al. 2015). We tested clusters with 2 and 3 centers, reflecting the hypotheses that short-tailed albatross contaminant profiles are similar to Laysan albatross profiles and that all three species have different contaminant profiles, respectively.

Results

Profile of detected HOCs

We detected 202 unique HOCs (mean 166 ± 24, n = 11) among 25 structural classes. Of the HOCs where a chemical formula could be ascertained (n = 141), the majority (83%) of HOCs were chlorinated, 9% were brominated, and 8% contained chlorines and bromines. Compounds of unknown structure and origin comprised 13.4% (n=27) of the detected HOCs. We separated the unknown compound class into two categories based on whether the unknown compounds had similar halogenation patterns, but the majority of unknowns remained in a separate unknown class. Of the known HOCs, 159 were of anthropogenic origin and 16 of natural origin. Overall, 90 compounds were detected in every sample (~45% of all compounds). Only 36 compounds (22%) we detected are regularly screened in monitoring programs, and 36 of the detected compounds have been detected in North Pacific albatross in prior work.

Abundance of detected HOCs

We semi-quantitatively determined the abundance of each compound relative to the internal standard and used lipid weight to normalize these values (see Methods: Data Analysis for full protocol). In terms of relative abundance, PCBs and DDT-related compounds dominated sample profiles (Figure 1). Legacy compound classes, including mirex, chlordane, chlorinated benzenes, and toxaphene were found in similar abundances to each other. Dimethyl bipyrroles (DMBPs) and compounds of unknown structure and origin were found in similar or higher relative abundances to other anthropogenic compound classes including HCH-related, heptachlor-related, drins, polychlorinated terphenyls, and PBDEs.

DDT-related compounds: DDT is a chlorinated legacy pesticide consisting of multiple isomers which, in addition to its metabolites, are frequently detected in environmental matrices. We detected a total of 12 DDT-related compounds in albatrosses, including *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DBP, and 4 DDMU isomers. Three likely breakdown products of DDT were detected, including 4,4'-dichlorobenzophenone, which is also a likely breakdown product of dicofol and has not been detected in seabirds previously (Thiel et al. 2011). One of these breakdown products is also new to nontargeted analysis (DDT-related 1). We did not detect TCPM or its presumed metabolite TCPM-OH, which has previously been detected in a number of coastal and marine predators, including albatrosses (Muir et al. 2002, Shaul et al. 2015, Millow et al. 2015).

Mirex-related compounds: Mirex is a polychlorinated pesticide primarily used as an insecticide prior to its ban on production. Mirex is the only regularly monitored compound from this class and comprised the majority of mirex-related profiles in albatrosses (Figure S1). However, we detected a total of 13 mirex-related compounds, including 5 isomers of Mirex 2Cl, 3 isomers of mirex 1Cl, dechlorane 602, and 3 compounds previously unidentified in our reference libraries.

Chlordane-related compounds: Technical chlordane is a legacy organochlorine pesticide comprised of >100 compounds. In addition to the five regularly-monitored chlordane components (α-chlordane, γ-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane), we detected 25 additional components among all albatross species (Figure S2). Only 6 of these compounds (the 5 regularly monitored compounds and

U82, an octachloroisomer) have previously been detected in North Pacific albatrosses (Muir et al. 2002). Additionally, 10 of the 25 chlordane-related compounds are newly detected compared to our reference libraries.

Toxaphenes: Toxaphene is a neurotoxic legacy pesticide comprised of over 600 polychlorinated monoterpene compounds. Due to historical issues with analyzing toxaphene, we identified putative toxaphene compounds based on chlorination pattern. We detected 36 toxaphene congeners, making it the most diverse compound class we delineated (Figure S3). The majority (n = 23) of toxaphene compounds we found are newly detected.

Halogenated natural products: The halogenated natural products (HNPs) we found contained bromines, chlorines, or both halogens and are produced by a variety of coastal and marine invertebrates, algae, and bacteria (Blunt et al. 2009). Some HNPs have similar aqueous solubilities and octanol/water partition coefficients to other HOCs, suggesting high capacity for bioaccumulation and therefore potential for detrimental impacts on high trophic organisms (Tittlemier et al. 2004, Pangallo and Reddy 2010). We detected 16 HNPs, including 11 DMBPs, 2 methoxy-polybrominated diphenyl ethers (MeO-BDE), 1 methoxy-polybrominated biphenyl (MeO-PBB), 1 bromoindole (4,6'-dibromoindole), and 1 methyl bipyrrole (MBP-Cl_7, also known as Q1). DMBP-Br_4Cl_2 was the most abundant HNP among all species, similar to previous reports in dolphins and seabirds in the North Atlantic and North Pacific (Shaul et al. 2015, Mello et al. 2020). All of these compounds have been detected in marine biota previously, but only 2'-

MeOBDE-68, 6-MeOBDE-47, MBP-Cl_7, and DMBP Br_4Cl_2 have been identified or quantified in tandem in seabirds (Mello et al. 2020).

Additional compound classes: We also detected four additional classes of legacy pesticides that are either banned globally or highly regulated: 3 chlorinated benzenes, 4 hexachlorocyclohexane-related compounds, 5 heptachlor-related compounds, and 2 drins. These compounds were detected in lower abundances than the legacy pesticides described above and were generally less diverse (Figure 1, Table 1). We also detected three classes of compounds previously produced as flame retardants: 6 polybrominated diphenyl ethers (PBDEs), 4 polybrominated biphenyls (PBBs), and 13 polychlorinated terphenyls (PCTs), the last of which also had additional industrial uses similar to PCBs. All of the PBDEs and PBBs were previously detected in our reference libraries. The PCTs consisted of 1 tri-, 6 tetra-, 3 penta-, and 3 hexa- congeners and 7 of the PCTs were not previously reported in our reference libraries (coastal marine mammals and birds). We detected a single chlorinated cyclopentadiene in 9 of 11 samples that has not been detected previously in our reference libraries (Table 1). This compound is frequently listed as a reagent in Diels-Alder reactions, including the production of flame retardants for plastics (Schmerling 1975). We also detected 9 chlorinated styrenes that are likely byproducts of industrial chlorination processes (Kaminsky and Hites 1984).

Unknown compounds with halogenated patterns: We detected a total of 27 compounds that have ion clusters characteristic of halogenation but could not be identified. Less than one-third of these compounds (n = 8) were also detected in coastal dolphin blubber in the North Pacific and North and South Atlantic. We also detected 2 new compounds

in the unknown-4 compound class, which are hypothesized to be polychlorinated diphenyl ethers or hydroxy-PCBs (Shaul et al. 2015). Additionally, the unknown compounds in highest abundance are primarily comprised of newly-detected unknowns (Figure S4).

Species comparisons

Although every structural class and almost every compound was present in each albatross species, we did find differences across species. Overall, black-footed albatrosses exhibited higher mean abundances of compounds of anthropogenic origin by compound class than Laysan or short-tailed albatrosses (Figure 1). For anthropogenic HOCs, the cluster analyses grouped all but one of black-footed albatrosses as distinct from Laysan and short-tailed albatrosses (Figure 2). In addition to differences in compound abundance, individuals in the black-footed albatross cluster also harbored a greater variety of anthropogenic compounds drawing from multiple compound classes. However, this species clustering did not hold for natural or unknown compounds (Figures S5 and S6), where individuals from each species clustered independently.

Discussion

As the first nontargeted study in North Pacific waters to assess potential HOC exposure in marine predators in the North Pacific that range beyond coastal habitats, we found albatross species were effective biomonitors of a diverse array of HOCs. We identified

and semi-quantified 202 halogenated compounds from 25 structural classes present in the adipose tissues of long-lived, North Pacific albatrosses. The majority (78%) of these compounds are not regularly monitored in contaminant screening programs (Table 1), and the majority of unmonitored compounds were of anthropogenic origin (67%). Black-footed albatrosses generally exhibited higher compound abundances and clustered separately from Laysan and short-tailed albatrosses. A substantial proportion (37%) of the total compounds identified have not been detected previously in our reference libraries of HOCs in marine mammals and a coastal seabird (Figure 3, see Methods for libraries used). Our analysis demonstrates that the total HOC burden in albatrosses is high, posing a risk to North Pacific albatrosses, other resident marine organisms in this biodiversity hotspot, and to the economically important fishing grounds in this large marine ecosystem.

Occurrence of HOCs

The presence of a wide range of known HOCs reflects the persistence and distribution of these compounds throughout marine environments, particularly legacy anthropogenic compounds that remain detectable decades after bans on production and use. Many of the legacy anthropogenic compounds have been detected in albatross tissues since 1969, have been the primary focus of HOC studies on albatross tissues globally (Fisher 1973, Harwani et al. 2011, Goutte et al. 2014), and continue to be the most abundant compound classes in the albatrosses we analyzed (Figure 1). The commonly monitored compounds in these groups are often used to detect physiological and ecological

impacts of HOCs in seabirds. For example, commonly monitored HOCs including PCBs and organochlorine pesticides have been associated with reduced immune function in black-footed albatrosses and reduced fecundity and fledgling probability in less-exposed Southern Ocean albatrosses, contributing to potential demographic decline in these long-lived taxa (Finkelstein et al. 2007, Goutte et al. 2014). However, our work suggests that over 100 additional compounds contribute to the total known HOC profile in North Pacific albatrosses (Table 1, Figure 3). As mixtures of chemicals at low concentrations can lead to adverse effects, and mixtures of multiple chemicals is a more realistic characterization of environmental chemical exposure, gaining a deeper understanding of available chemical mixtures is important for ecosystem and human health (Kortenkamp 2007, Carlin et al. 2013). On an individual basis, some unmonitored compounds were more abundant than the currently monitored compounds in their respective compound class (Figures S1-S3). Because commonly monitored HOCs can impact albatross breeding and population growth and many detectable HOCs remain unmonitored yet are at similar abundances of some monitored HOC classes (Figure 1), our results suggest that the cumulative HOC exposure detected in North Pacific albatross could have individual and population-level impacts for this taxa.

One application of nontargeted analysis is to determine the presence of previously undetected compounds that may have similar properties as known compounds of concern that are potentially detrimental to wildlife and ecosystem health. We detected likely HOCs of unknown structure and origin at lower abundances than PCBs and DDT-related compounds but at similar abundances (e.g., within an order of

magnitude) as other known HOC compound classes (Figure 1). Unknown HOCs were detected in all three albatross species which suggests that, like known HOCs, these compounds are pervasive throughout North Pacific food webs (Figure S4). Additionally, the majority of unknown HOCs were not previously detected in our available reference libraries, which consisted of the same nontargeted methods for marine mammal tissues. Therefore, these compounds may have different sources, transport, or mechanisms of exposure. Given their abundance and frequency of detection, continued monitoring of unknown HOCs should remain a biomonitoring priority.

Comparisons among albatross species

Previous work found similarities in HOC presence among North Pacific albatross species (Muir et al. 2002). Similarly, we found that each HOC compound class was detectable in all three albatross species. However, our series of clustering methods based on anthropogenic HOC presence and abundance suggested two distinct clusters, where black-footed albatrosses clustered separately from Laysan and short-tailed albatrosses. Differences in anthropogenic HOC abundance between black-footed albatrosses and Laysan albatrosses have previously been attributed to potential differences in trophic level and, more recently, species-level differences in geographic foraging range (Elliott 2005, Finkelstein et al. 2006, Harwani et al. 2011). Although age and sex of the sampled individuals was not known, the single black-footed albatross that was grouped with the other species may represent a juvenile as differences in age has been found to impact HOC profiles (Trego et al. 2018). Available contaminant data

for short-tailed albatrosses is sparse, but isotopic profiles during the limited non-breeding season suggests this species occupies a similar trophic niche to black-footed albatrosses where they co-occur (Kunisue et al. 2006, Suryan and Fischer 2010). While short-tailed albatrosses may visit the shelf waters of the North American west coast, their primary breeding grounds are in the western North Pacific, where Laysan albatrosses tend to forage throughout the year (Shuntov 1972, Kappes et al. 2015, Suryan and Kuletz 2018). Given that the short-tailed and Laysan albatrosses clustered together (Figure 2) and appear to have similar compound abundances (Figure 1), our data support the hypothesis that differences in HOC abundance among North Pacific albatross species are due to broadscale differences in species foraging range. Furthermore, the differences we detected in known HOCs between black-footed albatross and short-tailed albatross despite the observed similarities in diet between the species during the non-breeding season (Suryan and Fischer 2010) suggests that distribution of prey and not just prey type itself may be an important factor in understanding HOC exposure. However, given our limited sample size, additional study of anthropogenic compounds in short-tailed and other albatrosses, potentially through collection of nonviable, salvaged eggs, warrants further investigation.

Unlike anthropogenic HOCs, compounds of natural origin are not well-studied in albatrosses, and, to our knowledge, only a single HNP, 1,1'-dimethyl-tetrabromo-dichloro-2,2'-bipyrrole (DMBP Br_4Cl_2), has been identified in North Pacific albatross tissues previously (Tittlemier et al. 1999). However, HNP profiles among marine mammals and ecotypes that share a region are often distinct, potentially due to

proximity to potential sources or ability to metabolize these compounds (Pangallo and Reddy 2010, Shaul et al. 2015, Cossaboon et al. 2019). However, our clustering analyses did not identify separation among albatross species based on natural or unknown HOC profiles. While potential marine sources of HNPs are diverse (Blunt et al. 2009), the transport and distribution of HNPs in marine environments are not well-known. Unlike anthropogenic HOCs, it is possible that natural and unknown HOCs may have similar geographic distribution or detectability in marine food webs throughout the North Pacific. Potential species-level differences due to physiological mechanisms are less likely, given that these species are closely related and share multiple life history strategies. Comparisons of HNP occurrence and abundance among seabirds are sparse, but as seabirds and their ecologies are frequently used to detect contaminants within and among food webs, continued study may elucidate potential exposure pathways for these compounds (Elliott and Elliott 2013, Mello et al. 2020).

Diet has been identified as a primary or key pathway for HOC exposure and contamination in upper-trophic species; however, albatrosses generally feed on similar food items throughout their range (Gould et al. 1997, Conners et al. 2018). However, North Pacific albatrosses also have high incidence of plastic consumption (Gray et al. 2012, Donnelly-Greenan et al. 2018) which may also serve as a pathway for HOC exposure as plastics can adsorb HOCs that could be deposited in wildlife tissues if ingested (Tanabe et al. 2004, Rochman et al. 2013). Procellariformes like albatrosses produce a lipid-rich stomach oil, which may act as a hydrophobic vector for transfer of HOCs and other plastic additives for albatrosses (Place et al. 1989, Tanaka et al. 2015).

Understanding the relative role of HOC transfer to avifauna via plastics is complex, as the direction of contaminant transfer can be bidirectional (Herzke et al. 2016, Thaysen et al. 2020). Additionally, albatrosses exhibit differences in plastics abundance (Young et al. 2009) and type (Blight and Burger 1997) dependent on regional foraging grounds, as well as species-specific differences in total plastics mass (Robards et al. 1997) and potentially diet thought to be associated with fish eggs (Gray et al. 2012). Like regional and species-specific differences in HOC exposure, differences in plastic consumption could influence the presence and abundance of HOCs described here. While diet remains the primary known contributor to HOC contamination in upper-trophic species, the environmental persistence of HOCs and high plastic exposure for albatrosses suggest plastic ingestion could be a potential long-term pathway of HOC exposure for albatrosses (Wilcox et al. 2015, Herzke et al. 2016).

Comparisons to nontargeted studies in other marine species

We compared our results to previously published research on nontargeted analysis of HOCs in blubber from cetaceans in the Northwest Atlantic Ocean, Southwest Atlantic Ocean, and the Southern California Bight (SCB) in the Eastern Pacific Ocean, as well as pinnipeds and a single coastal seabird in the SCB (Hoh et al. 2012, Shaul et al. 2015, Millow et al. 2015, Alonzo et al. 2017, Cossaboon et al. 2019). Compared to the SCB studies, albatrosses harbored more total HOCs on average (mean = 166, Figure 3) than long-beaked (mean = 89), short-beaked (mean = 89), and Risso's dolphins (mean = 90) as well as California sea lions (mean = 29) and Pacific harbor seals (mean = 22)

and black skimmers (Millow et al. 2015, Cossaboon et al. 2019). Though albatrosses may have similar or higher numbers of HOCs on average than the marine animals we referenced, the HOC profiles of albatrosses differed from those of cetaceans and pinnipeds. For example, albatrosses had a lower proportion of HOCs of natural and unknown origin in albatrosses compared to other marine species (Hoh et al. 2012, Alonso et al. 2017, Cossaboon et al. 2019).

We also detected a greater variety of chlordane-related, mirex-related, and toxaphenes in albatross tissues. Both prior use of these legacy organochlorine pesticides (OCPs) in Asia as well as long range atmospheric transport may contribute to the occurrence of these compounds in albatrosses. For example, chlordane and mirex were produced and used in China until 2009 (Wang et al. 2013). Typically monitored chlordanes were elevated compared to other OCPs in coastal birds in China (Lam et al. 2008) and Japan (Kunisue et al. 2003), with recent exposure suggested near Hong Kong (Wang et al. 2011), unlike coastal birds from the West Coast of the U.S. (Millow et al. 2015). Recently 128 chlordane-related compounds were detected in the livers of coastal and terrestrial birds in Japan, but these same samples yielded only 5 toxaphenes and 3 mirex-related compounds (Tue et al. 2021). Compared to chlordanes, data on toxaphenes and mirex in birds from the Asia-Pacific remains scarce (Wang et al. 2011, Abbasi et al. 2016). While toxaphene was used in a number of countries in continental Asia, and may still be used in some countries worldwide, the United States remains the highest known source (Voldner and Li 1993, de Geus et al. 1999). Because all of these OCPs may undergo long range atmospheric transport to higher latitudes,

such as where these albatrosses forage, albatross contaminant profiles may be more diverse than those of other temperate, coastal wildlife (Wania and Mackay 1996).

We also detected fewer DDT-related and brominated compounds compared to previously published studies on marine species in the Southern California Bight, an area where black-footed albatrosses, in particular, may forage during several months of the year (Table 1; Shaul et al. 2015, Millow et al. 2015). This observed difference in DDT may be because of the relatively limited about of time albatrosses forage in the SCB, which is a known location of DDT wastewater outfall and disposal into deep water basins (Stull et al. 1996, Kivenson et al. 2019). This hypothesis is supported by published nontargeted studies of dolphins in the North Atlantic and Brazil (Hoh et al. 2012, Alonzo et al. 2017), a sperm whale in the North Sea (Vetter et al. 2018), and a food web in the Baltic Sea (Rebryk and Haglund 2021) which were found to have lower diversity of DDT-related compounds compared to dolphins in the SCB. However, terrestrial and coastal birds in Japan had 2.5 times the number of DDT-related compounds compared to albatrosses (Tue et al. 2021), which may be due to closer proximity to the coastline or differences among coastal or pelagic food webs. We also detected 8 compounds of unknown structure or origin that were commonly found in marine mammals residing in both the Atlantic and Pacific. This frequency of detection suggests the widespread bioavailability of these compounds and highlights the need for ongoing attention to new pollutants that may be ubiquitous across oceans but are currently undetected in traditional biomonitoring schema.

Implications for future research

As the body of literature on comprehensive HOC screening expands, there is a greater opportunity for cross-study comparisons. However, there remain substantial challenges to these comparisons among taxa, i.e. marine mammal vs. seabird, and among large marine ecosystems, i.e. Atlantic vs. Pacific. As a result, it can be difficult to determine whether the differences of HOC profiles between this study and published literature are due to broadscale differences among species physiology and ecology or differences in study regions. For example, pinnipeds were found to harbor a less diverse suite of halogenated natural products than cetaceans despite residing in the same geographic region and likely foraging on similar prey (Cossaboon et al. 2019). Similarly, the HOC profiles found in urbanized, coastal areas may not be representative of exposure across more remote ocean areas where long-range transport far from potential emission sources may be an important exposure pathway (Wania & Mackay 1995, Kunisue et al. 2008). As such, we caution that the broad differences in libraries presented here warrant further investigation. Despite these complexities, it is clear that the suites of HOCs in North Pacific albatross differ considerably from those detected in coastal marine mammals even though two of our reference libraries originate from coastal Southern California where at least one albatross species, black-footed albatrosses, commonly forage. While sampling environmental media and organisms from open oceans is logistically difficult, it is vital to better understand the transport, fate, and risks associated with emerging HOCs of interest. High trophic feeding seabirds that depend on oceanic areas for foraging provide a strong opportunity for continued study

of the emerging contaminants present in open ocean environments (Elliott & Elliott 2013, Gilmour et al. 2019).

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Tables & Figures

Table 1. Characteristics and detection frequencies of HOCs by compound class in albatross tissues. UD refers to an undetermined number of bromines or chlorines. As toxaphene is typically difficult to resolve, its congeners are not determined as either typically or not-typically monitored (Muir et al. 2002). Class names, including the unknown compound classes, follow Shaul et al. 2015.

class	no. compounds	no. bromines	no. chlorines	source	no. not typically monitored	no. new to libraries
chlordane-related	30	0, UD	6,7,8,9,10,UD	anthropogenic	25	10
chlorinated benzenes	3	0	3,4,5,6	anthropogenic	3	0
chlorinated cyclopentadiene	1	0	4	anthropogenic	1	1
chlorinated styrenes	9	0	4,5,6,7,8	anthropogenic	9	1
drins	2	0	6	anthropogenic	0	1
DDT-related	12	0	2,3,4,6,7,UD	anthropogenic	8	3
hexachlorocyclohexane-related (HCH)	4	0	5,6	anthropogenic	2	2
heptachlor-related	5	0	6,7,8	anthropogenic	4	1
methylsulfonyl polychlorinated biphenyls (methylsulfonyl-PCBs)	6	0	5,6	anthropogenic	6	2
mirex-related	13	0	10,11,12,UD	anthropogenic	12	4
polybrominated biphenyls (PBBs)	4	4,5,6	0	anthropogenic	3	0
polychlorinated biphenyls (PCBs)	15	0	4,5,6,7,8	anthropogenic	0	0
polybrominated diphenyl ethers (PBDEs)	5	4,5,6	0	anthropogenic	0	0
polychlorinated terphenyls (PCTs)	13	0	3,4,5,6	anthropogenic	13	8
toxaphenes	36	0	5,6,7,8,9,UD	anthropogenic	NA	21
brominated indoles	1	2	0	natural	1	0
dimethyl bipyrroles (DMBPs)	11	0,2,3,4,5	1,2,3,4,6	natural	11	1
methoxy brominated diphenyl ether (MeO-BDEs)	2	4	0	natural	2	0
methoxy polybrominated biphenyl (MeO-PBB)	1	4	0	natural	1	0
methyl bipyrroles (MBPs)	1	0	7	natural	1	0
unknown-1	1	0	6	unknown	1	0
unknown-4	2	UD	UD	unknown	2	2
unknown-6	2	UD	UD	unknown	2	0
unknown-7	1	UD	UD	unknown	1	0

Figure 1: Normalized abundances of HOCs summed by compound class. Points represent the mean for each species, while bars represent the standard error. For acronyms, see Table 1.

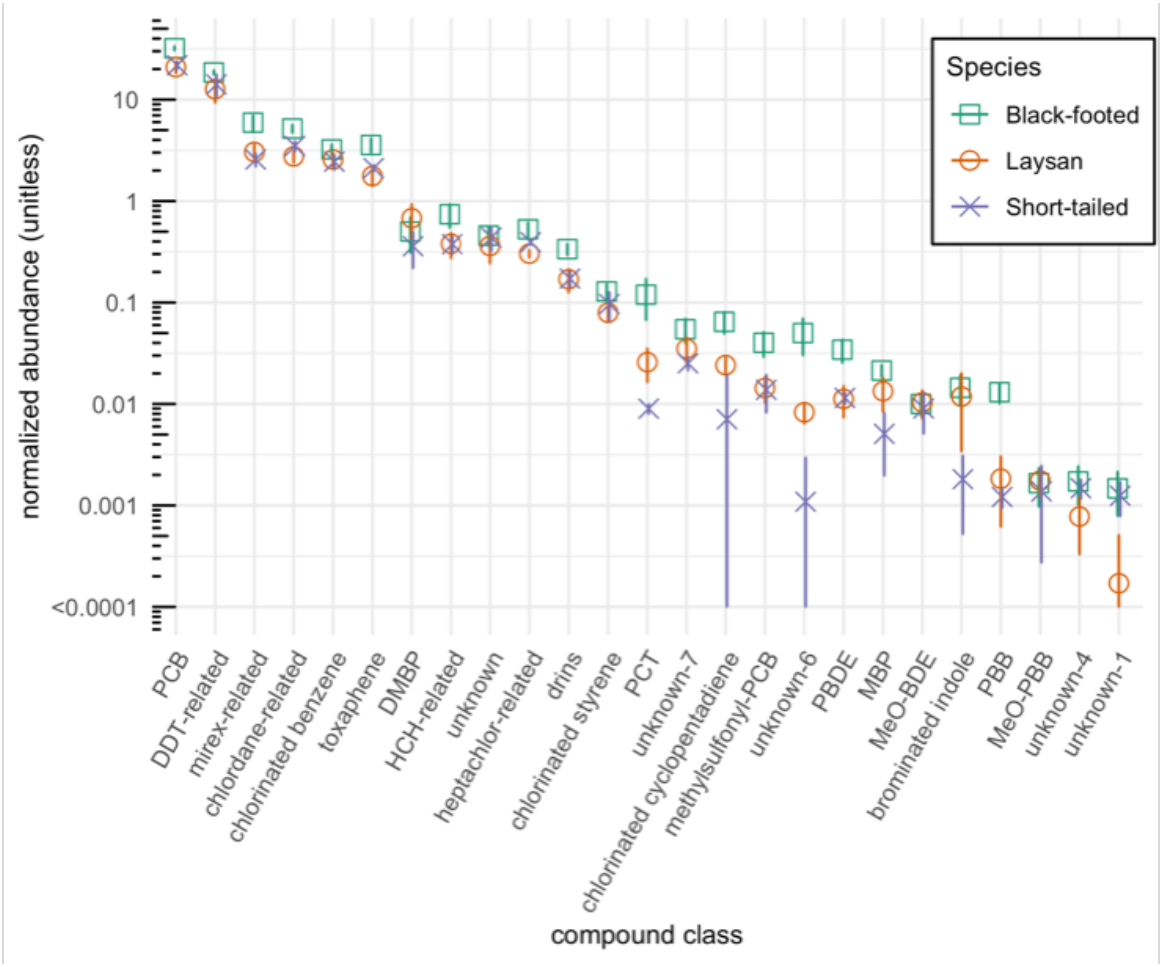


Figure 2. Hierarchical clustering of North Pacific albatross samples using anthropogenic HOCs. Non-detects appear as zeroes. Results using K-means and PCA clusters are available in the supplement.

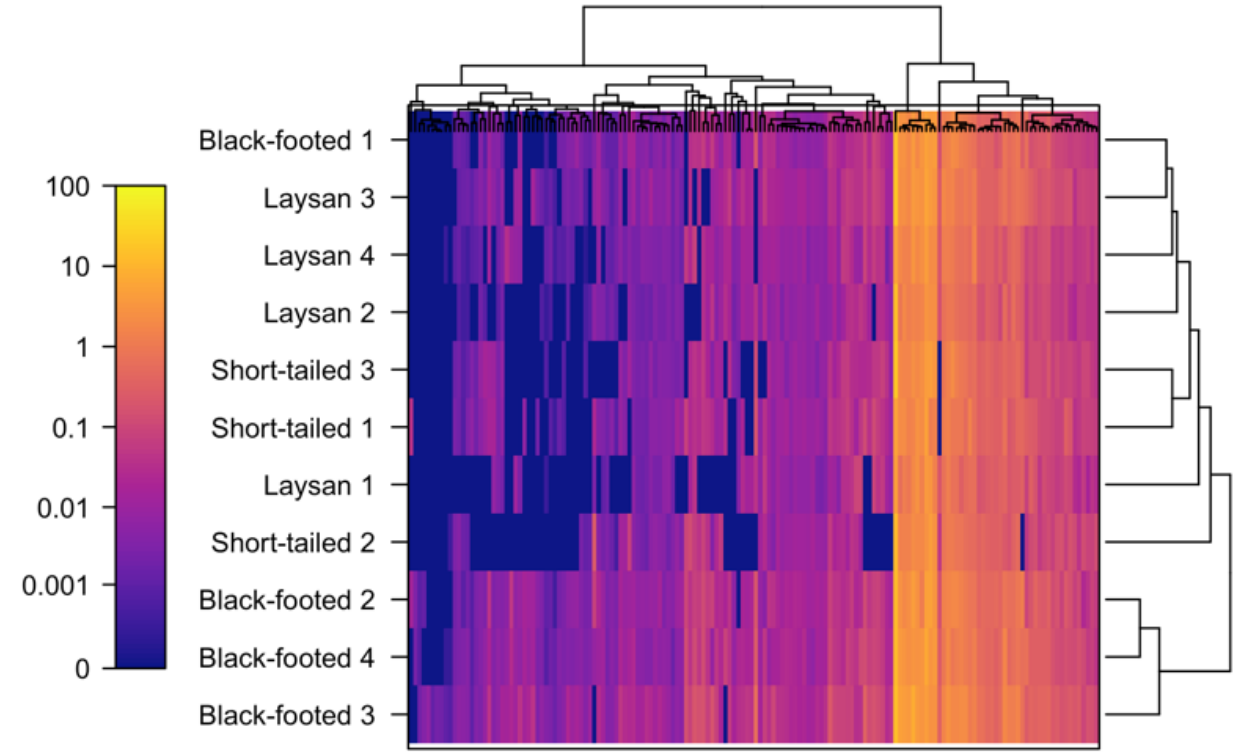
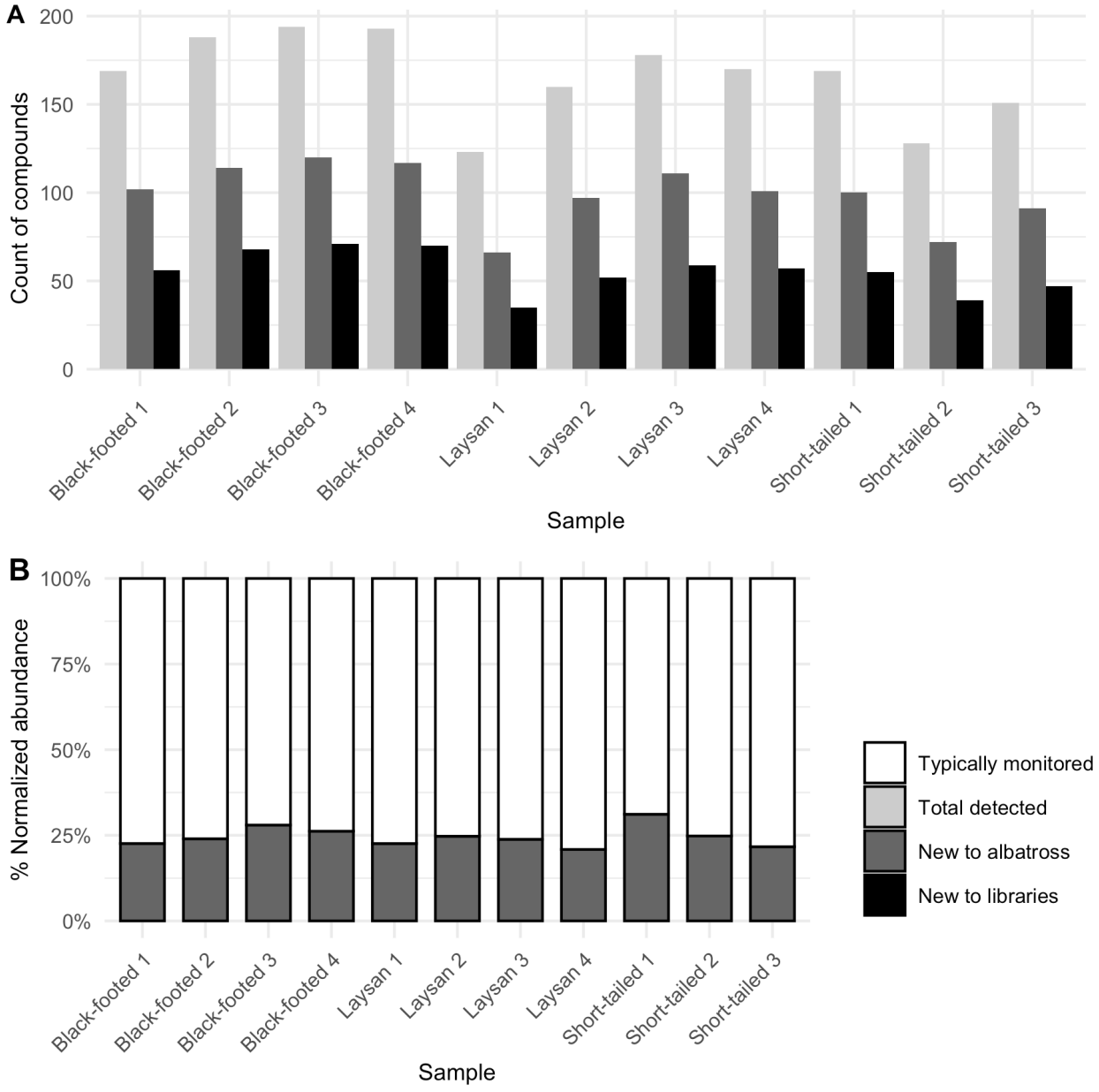


Figure 3. A. Summary of detected compounds, the detected compounds not found previously in North Pacific albatross, and the detected compounds that are new to our reference non-targeted libraries by albatross sample; B. Comparison of normalized abundance among typically monitored compounds and compounds not found previously in North Pacific albatrosses after removing PCBs and *p,p'*-DDE. Toxaphenes were not considered typically monitored or unmonitored as were thus removed from consideration in panel B.



Supporting information

Table S1. K-means clustering results for anthropogenic compounds (n = 158).

Sample	*2-cluster*	*3-cluster*
Laysan 1	1	1
Laysan 2	1	1
Laysan 3	1	1
Laysan 4	1	1
Black-footed 1	1	1
Black-footed 2	2	2
Black-footed 3	2	2
Black-footed 4	2	2
Short-tailed 1	1	1
Short-tailed 2	1	3
Short-tailed 3	1	1

Table S2. K-means clustering results for the natural compounds (n = 16).

Sample	*2-cluster*	*3-cluster*
Laysan 1	1	3
Laysan 2	2	2
Laysan 3	2	2
Laysan 4	2	1
Black-footed 1	1	1
Black-footed 2	1	1
Black-footed 3	2	1
Black-footed 4	2	1
Short-tailed 1	2	2
Short-tailed 2	1	3
Short-tailed 3	1	1

Table S3. K-means clustering results for the unknown compounds (n = 27).

Sample	*2-cluster*	*3-cluster*
Laysan 1	2	2
Laysan 2	1	3
Laysan 3	1	1
Laysan 4	1	3
Black-footed 1	1	3
Black-footed 2	1	1
Black-footed 3	1	1
Black-footed 4	1	1
Short-tailed 1	1	1
Short-tailed 2	2	2
Short-tailed 3	1	3

Figure S1. Mean abundance of mirex compounds by albatross species. Symbols indicate the mean, while the lines represent the standard error.

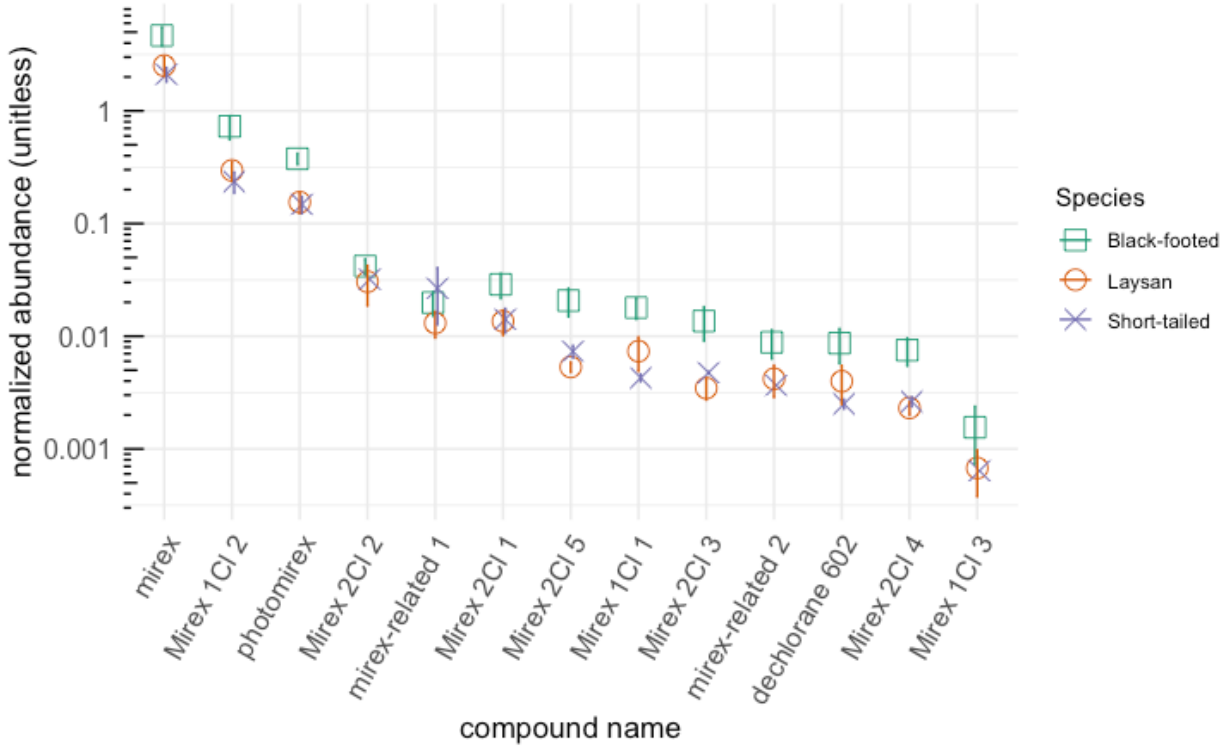


Figure S2. Mean abundance of chlordane-related compounds by albatross species. Symbols indicate the mean, while the lines represent the standard error.

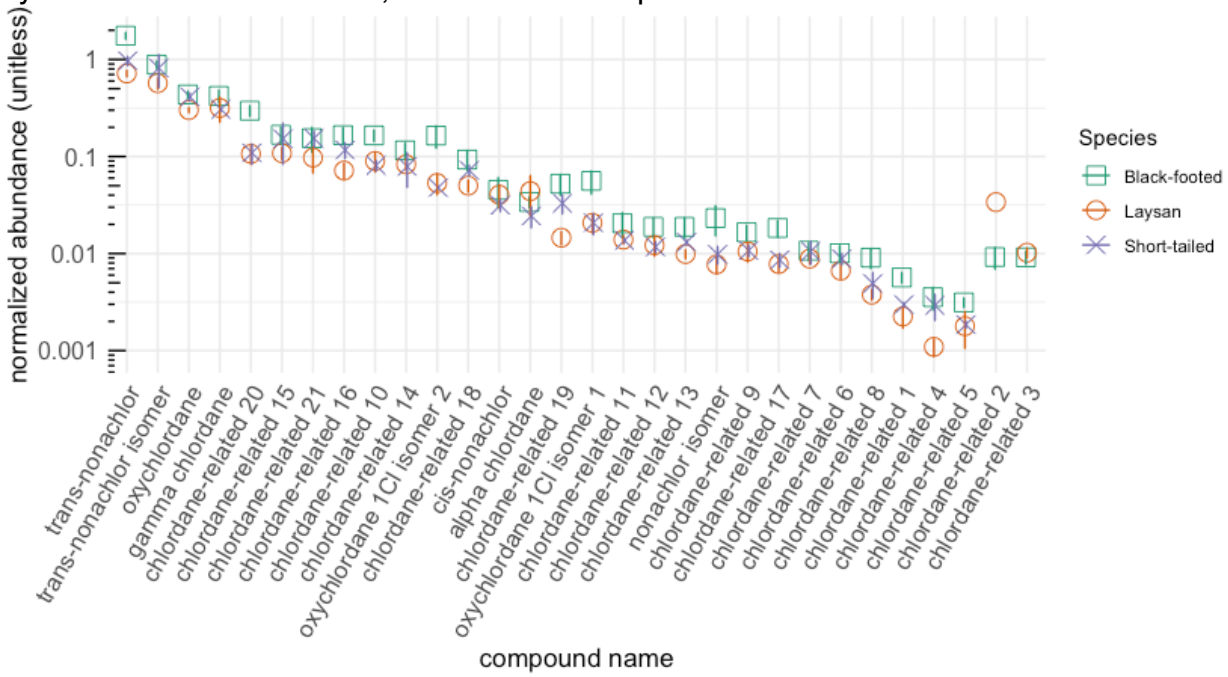


Figure S3. Mean abundance of toxaphene compounds by albatross species. Symbols indicate the mean, while the lines represent the standard error.

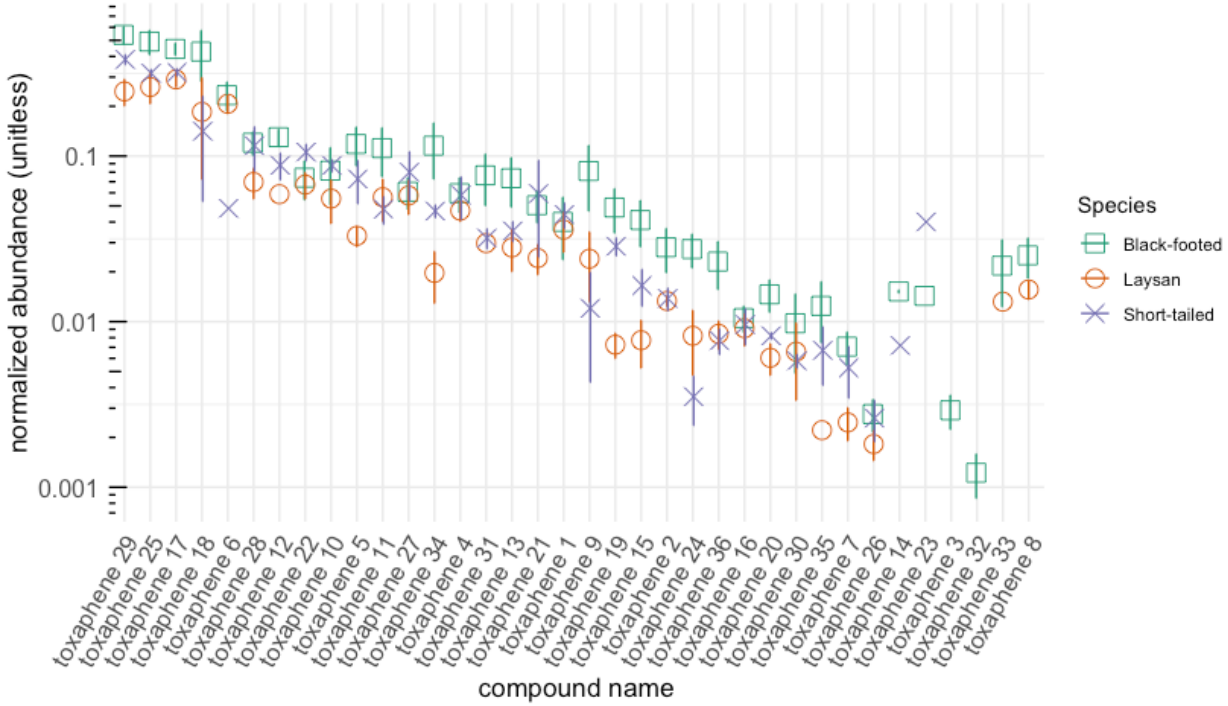


Figure S4. Mean abundance of unknown compounds by albatross species. Symbols indicate the mean, while the lines represent the standard error.

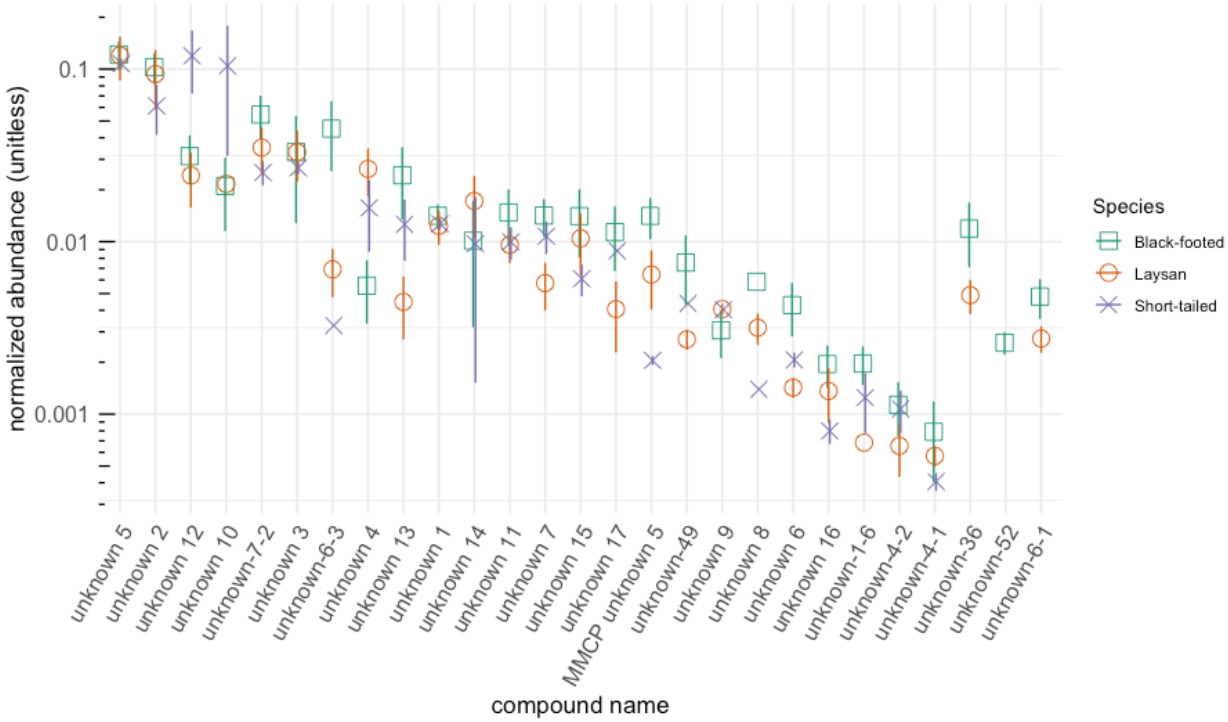


Figure S5. Hierarchical clustering of the relative abundance of halogenated natural products in albatross samples.

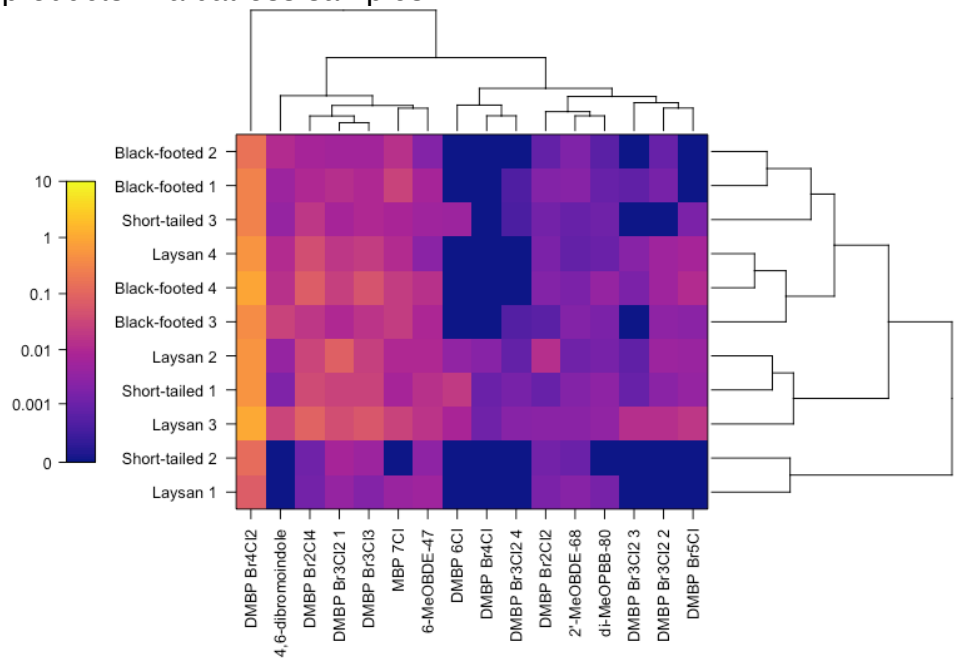


Figure S6. Hierarchical clustering of the relative abundance of unknown compounds in albatross samples.