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Although seabirds have been proposed as useful biomonitors for organochlorine contaminants (OCs) in marine environments, their suitability is still unclear. To understand the geographic variability and the influence of seabird trophic ecology in OC levels, we analyzed PCBs, DDTs, $\delta^{13}C$, and $\delta^{15}N$ in the blood of adult *Calonectris* shearwaters throughout a vast geographic range within the northeast Atlantic Ocean (from Cape Verde to Azores) and the Mediterranean Sea (from the Alboran Sea to Crete). OC concentrations were greater in birds from the Mediterranean than in those from the Atlantic colonies, showing higher and lower chlorinated PCB profiles, respectively. This large-scale pattern may reflect the influence of historical European runoffs in the Mediterranean basin and diffused sources for OCs in remote Atlantic islands. Spatial patterns also emerged within the Atlantic basin, probably associated with pollutant long-range transport and recent inputs of DDT in the food webs of shearwaters from Cape Verde and the Canary islands. Moreover, a positive association of OC concentrations with $\delta^{15}N$ within each locality points out diet specialization as a major factor explaining differences in OCs at the intraspecific level. Overall, this study highlights wide range breeding seabirds, such as *Calonectris* shearwaters, as suitable organisms for biomonitoring large geographic trends of organochlorine contamination in the marine environment.

Introduction

Oceans act as a final repository for many land-based source contaminants. Among them, organochlorine contaminants (OCs), such as polychlorinated biphenyls (PCBs), dichlorodiphenyl ethane (DDT), and its main metabolites, have attracted much scientific interest due to their global distribution and wide array of adverse effects (*1, 2*). Although banned in most parts of the world since the 1970s, OCs still constitute an element of concern, because they are easily transported through air and water currents. Furthermore, their persistence and lipophilicity cause them to bioaccu-

mulate and biomagnify through marine food webs worldwide (*3, 4*). Therefore, the spatial distribution of OCs and their possible sources in the marine environment have been the subject of extensive research (*5– 7*).

Seabirds have been suggested among marine biota as useful biomonitors for OCs as a result of specific advantages that they have in comparison to other marine organisms (*8*). Most seabird species are placed at high trophic positions within marine food webs, and, thus, high contamination levels can be expected. Moreover seabirds show vast breeding ranges, allowing comparisons in pollutant levels across large geographic scales. Within a specific region, however, seabirds can forage up to several hundreds of km from their breeding colonies (*9*) integrating the chronic baseline levels of that region. To decipher the dynamics of OCs in the marine environment, several studies have combined OC analyses with spatial and trophic information using several approaches (*10, 11*). Among them, isotopic analyses are particularly valuable, because they provide information on the feeding ecology, while minimizing some of the common biases of the conventional diet studies (*12*). Nitrogen isotope ratios ($^{15}N/^{14}N$; $\delta^{15}N$) can be used to infer trophic position, whereas stable-carbon isotope analysis ($^{13}C/^{12}C$; $\delta^{13}C$) can indicate inshore or benthic compared to offshore or more pelagic feeding (*13*). In addition to geography or feeding ecology, further factors, such as sex, marked dietary switches, or specific excretion routes (e.g., egg laying), can also play a role in determining seabird OC levels (*10, 14, 15*).

Most seabird studies have revealed marked spatial patterns in OC concentrations and profiles (*6, 10, 11, 16*). These spatial differences have been commonly associated with different sources for these pollutants. For example, PCB profiles dominated by high chlorinated compounds have been widely related to specific point sources, such as direct industrial runoffs, while low chlorinated compounds, which are commonly associated with pollutant transport by atmospheric or oceanic currents, are related to diffuse sources (*16*). Large-scale geographic studies have been conducted mainly using seabird eggs (*10, 17*). However, this approach can be obscured by migratory movements and capital-income breeding strategies (*18*). Alternatively, minimally invasive procedures, such as blood sampling, could better reflect recent OC exposure (*19*). Previous studies have validated the suitability of blood to evaluate PCB and DDT burdens in seabirds (*20, 21*) and have reported significant relationships between blood OC levels and stable isotope signatures (*11, 22*). In fact, some studies have found that under stable environmental conditions, including stable food sources, OC concentrations seem to be stable in the blood not only for short-term periods (e.g., within the incubation period) but also over long-term periods (e.g., between breeding seasons) (*20, 23*).

In the present study, PCB and DDT levels and $\delta^{15}N$ and $\delta^{13}C$ signatures were analyzed in blood of three closely related taxa of shearwaters, which were, until recently, considered a single species: the Scopoli's (*Calonectris diomedea*), the Cory's (*C.borealis*), and the Cape Verde (*C.edwardsii*) shearwaters. Shearwaters are at the top of the food webs, mostly feeding on species that are also consumed by humans, such as several epipelagic fish and squid species, thus making shearwaters potentially useful as sentinels of marine contamination. Moreover, their wide distribution offers an excellent opportunity to investigate biogeographic patterns of OCs across a vast geographic area. In this context, we aimed (1) to explore the geographic patterns in PCB and DDT levels of shearwaters throughout the NE Atlantic Ocean

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and the Mediterranean Sea; (2) to examine profiles of PCBs and DDTs in shearwaters in order to assess their potential sources and (3) to understand the effects of the trophic ecology on PCB and DDT levels, as shown by stable isotope signatures of carbon and nitrogen, potentially influenced by sexual, intercolony, and individual variations in the trophic ecology of *Calonectris* shearwaters.

Material and Methods

Species, Study Area, and Sampling Procedure. The three shearwater taxa included in the present study, the Scopoli's, the Cory's, and the Cape Verde shearwaters, have mostly disjointed distributions across the Mediterranean Sea, the NE Atlantic (except Cape Verde), and the Cape Verde archipelago, respectively. Although their taxonomic status is still being debated, recent studies suggest that the three taxa should be regarded as separate rather than as a single species (*24*). However, since the three taxa show very similar morphology, ecology, and physiology (*9, 25*), we will consider them as a single statistical unit.

This study was conducted covering the whole breeding range of the three shearwater taxa. Adult shearwater sampling was carried out during their breeding season, concretely among incubation and chick rearing periods, from 2003 to 2006 (Table 1). Each breeding colony was sampled within a single year. The study covers 9 breeding colonies (Supporting Information; Figure S1): 5 throughout the northeast Atlantic Ocean including, from south to north, Cape Verde, Canary, Madeira, Azores, and the Berlengas islands, and 4 among the Mediterranean including, from west to east, the Terreros, Balearic, Hyeres, and Crete islands. Blood (0.5 mL) from the brachial vein was sampled and transferred into a vial with 1 mL of absolute ethanol and preserved at −24 °C until analysis. Bill depth, bill depth at the nostril, and maximum head length to the nearest ±0.1 mm were measured using a digital caliper in all individuals except on Hyeres islands. Biometrical measurements were used to sex shearwaters by means of a discriminant analysis (further details are described in the Supporting Information).

Chemical Analysis

A subsample from the blood fixed with absolute ethanol was used for stable isotope analysis. Once subsamples were dried, we placed from 0.36 to 0.40 mg of blood (weighed to the nearest μg) into tin buckets for combustion. Isotopic analyses were carried out by elemental analysis-isotope ratio mass spectrometry (EA-IRMS), and stable isotope ratios were expressed in conventional notation as parts per thousand (‰).

The following organochlorine compounds were analyzed: *ortho* PCB congeners #28, #52, #95, #101, #123, #149, #118, #114, #153, #132, #105, #138, #167, #156, #157, #180, #183, #170, #189, and #194, and DDTs, including *p,p'*-DDT and its two main metabolites, *p,p'*-DDD and *p,p'*-DDE. OC concentrations were determined following the procedure described by Otero et al. (*26*) with some modifications. From 0.2 to 0.1 g of dried blood was used for OC determination. Sample treatment consisted basically of 3 successive extraction steps with hexane and concentrated sulfuric purification. PCB and DDT concentrations were determined by high-resolution gas chromatography with microelectron capture detection. Further details of the analytical procedure for the determination of stable isotope ratios and OC concentrations are described in the Supporting Information.

Data Analysis

SPSS 15.0 for Windows was used for statistical analysis. We validated the normal distribution of $\delta^{15}N$, $\delta^{13}C$, and pollutant levels (previously log transformed) among breeding colonies

TABLE 1. Concentrations of Σ_{20}PCBs and Σ_3DDTs (ng g^{-1} d.w.), Stable Isotope Signatures of Carbon and Nitrogen (‰), and Linear Regression Analysis Statistics in *Calonectris* Shearwater Blood

breeding colony	year	n	ΣPCBs		ΣDDTs		δ¹⁵N	δ¹³C	[ΣOCs] − δ¹⁵N
			AM^a ± SE (min − max)	GM^b	AM ± SE (min − max)	GM	AM ± SE (min − max)	AM ± SE (min − max)	R², P
Atlantic									
Cape Verde	2006	10	43.25 ± 7.31 (17.74 − 97.35)	38.42	7.691 ± 3.595 (1.85 − 39.80)	4.89	12.2 ± 0.4 (10.2 − 13.2)	−16.8 ± 0.2 (−17.9 − −16.2)	R² = 0.02, P = 0.96
Canary Is.	2003	10	59.22 ± 9.37 (40.94 − 114.8)	53.93	13.13 ± 4.43 (2.906 − 42.59)	8.38	12.1 ± 0.2 (11.0 − 12.8)	−16.9 ± 0.2 (−17.9 − −16.0)	R² = 0.40, P < 0.05
Madeira Is.	2005	10	125.3 ± 41.0 (51.40 − 488.9)	98.34	38.18 ± 19.28 (11.03 − 208.7)	22.06	11.2 ± 0.1 (10.9 − 11.9)	−18.8 ± 0.2 (−19.4 − −17.7)	R² = 0.53, P < 0.05
Azores Is.	2003	10	99.33 ± 46.93 (41.22 − 217.7)	91.21	42.09 ± 21.48 (12.49 − 234.2)	25.13	9.97 ± 0.16 (9.21 − 10.9)	−18.9 ± 0.1 (−19.4 − −18.5)	R² = 0.51, P < 0.05
Berlengas Is.	2004	10	119.4 ± 11.9 (69.98 − 175.4)	113.9	25.29 ± 3.66 (10.17 − 49.33)	22.97	13.0 ± 0.1 (12.6 − 13.4)	−18.0 ± 0.1 (−18.2 − −17.2)	R² = 0.34, P = 0.06
total			89.31 ± 71.34	73.31	25.28 ± 42.42	13.91	11.7 ± 1.2	−17.9 ± 1.0	
Mediterranean									
Terreros Is.	2004	10	212.7 ± 34.5 (91.68 − 463.5)	191.5	100.1 ± 24.9 (25.50 − 248.1)	76.98	12.0 ± 0.1 (11.4 − 12.3)	−18.2 ± 0.1 (−18.5 − −18.0)	R² = 0.67, P < 0.05
Balearic Is.	2004	10	158.2 ± 13.4 (102.1 − 227.7)	153.3	69.57 ± 14.96 (30.98 − 191.8)	59.61	10.8 ± 0.1 (10.3 − 11.3)	−18.5 ± 0.1 (−18.7 − −18.3)	R² = 0.52, P < 0.05
Hyeres Is.	2006	8	510.6 ± 107.8 (216.2 − 1189)	448.5	303.2 ± 96.8 (96.26 − 911.6)	233.6	10.0 ± 0.1 (9.50 − 10.4)	−18.1 ± 0.1 (−18.3 − −17.8)	R² = 0.24, P = 0.24
Crete	2005	9	678.9 ± 102.5 (145.1 − 1124)	593.0	895.3 ± 203.6 (89.45 − 1720)	641.4	9.99 ± 0.13 (9.47 − 10.5)	−17.7 ± 0.2 (−18.3 − −16.6)	R² = 0.34, P = 0.07
total			375.8 ± 300.1	285.3	329.2 ± 461.7	152.0	10.8 ± 0.9	−18.1 ± 0.4	

^{a} Arithmetic mean. ^{b} Geometric mean.

and sexes by checking Q-Q plots and by the Shapiro-Wilk test (all $P > 0.05$). In the case of values under the detection limit, they were set to zero. Analysis of the variability of PCBs and DDTs was performed applying generalized linear models (GLM) using total PCBs (Σ_{20}PCBs, the sum of the 20 individual PCBs) and total DDTs (Σ_3DDTs, the sum p,p'-DDT, and metabolites) as response variables. We tested the main effects and interactions of breeding colony, sex, and stable isotopes for both classes of pollutants. The initial model included all the breeding colonies except Hyeres, since in this case shearwater sex was unknown. The final selected model was built following a forward stepwise procedure, which included only the significant effects retained. We found that sex was a nonsignificant factor in the model, and, thus, we conducted the GLM procedure again including Hyeres breeding colony but not shearwater sex factor. Differences among breeding colonies were examined using posthoc pair-comparisons (Bonferroni adjustment). The relationship between OC levels and δ^{15}N was further examined within each breeding locality by means of linear regression analysis. To assess the relative exposure to PCBs among the breeding range of Cory's shearwater, we grouped PCB concentrations depending on their chlorination degree ($\leq$tetra-, penta-, hexa-, and $\geq$heptachlorinated PCBs) and compared their concentrations among breeding colonies using one-way ANOVA. Moreover, we examined fingerprints of shearwaters (calculated as the average percent of each PCB or DDT in respect to Σ_{20}PCBs and Σ_3DDTs, respectively) to assess the geographic patterns and sources of these pollutants. In the case of DDTs we also explored the relationship p,p'-DDE/p,p'-DDT to decipher a possible recent use of DDT in the studied area (27, 28). Finally, a principal component analysis (PCA) was applied to the normalized contributions of all PCBs and DDTs to check whether OC profiles segregate shearwaters depending on their breeding locality or other possible factors. Concentrations are expressed in ng.g^{-1} on a dry weight basis (d.w.).

Results

Considering ΣPCB and ΣDDT levels (Table 1), the GLM analysis explained up to 77.1% and 65.7%, respectively, of the initial variance and included two main explanatory variables for both contaminant families: breeding colony ($F_{7,79}$ = 29.60 for ΣPCBs; $F_{7,79}$ = 12.76 for ΣDDTs; both $P < 0.0001$) and δ^{15}N ($F_{1,79}$ = 8.44, $F_{1,79}$ = 8.26 for ΣPCBs and ΣDDTs, respectively; $P < 0.01$). Seabird sex ($F_{1,79}$ = 0.01 and $P = 0.95$ for ΣPCBs; $F_{1,79}$ = 0.07 and $P = 0.79$ for ΣDDTs) and δ^{13}C ($F_{1,79}$ = 0.49, $P = 0.48$; $F_{1,79}$ = 2.87, $P = 0.10$; for ΣPCBs and ΣDDTs, respectively) did not show a significant effect explaining both PCB and DDT levels within *Calonectris* shearwaters. Since sex was not significant, we conducted the GLM analysis again including the breeding colony of Hyeres (France), where the sex of shearwaters was unknown. The resulting models explained up to 79.4% and 65.7% of the total variance of ΣPCBs and ΣDDTs, respectively. Breeding colony ($F_{8,87}$ = 29.87 for ΣPCBs, $F_{8,87}$ = 14.37 for ΣDDTs: both $P < 0.0001$) and δ^{15}N ($F_{1,87}$ = 9.51 and $P = 0.003$, $F_{1,87}$ = 6.79 and $P = 0.011$ for ΣPCBs and ΣDDTs, respectively) showed again a significant effect. Differences among colonies were due to the greater PCB and DDT levels found in the Mediterranean compared to the Atlantic colonies (Figure 1). Specifically, posthoc pair comparisons revealed that Crete and Hyeres, showing the greatest ΣPCB (Figure 1a) and ΣDDT (Figure 1b) concentrations, differed significantly for all pair comparisons. Conversely, Canary Is. and Cape Verde showed the lowest concentrations and also differed significantly from most breeding colonies. Stable isotope signatures of carbon and nitrogen also showed spatial differences (Table 1). Regarding stable-carbon isotope signatures, shearwaters from Cape Verde plus Canary Is. showed marked enriched signatures compared with the rest of shearwater colonies, and those

FIGURE 1. PCB (a) and DDT (b) levels in Scopoli's, Cory's, and Cape Verde shearwaters at different localities. Asterisks and dots indicate mean values of males and females, respectively.
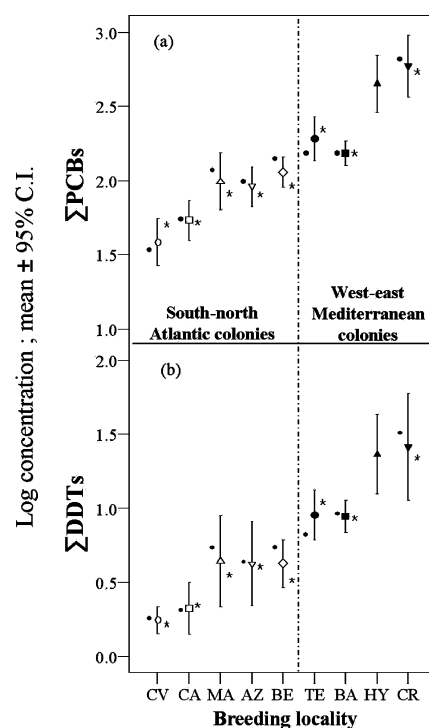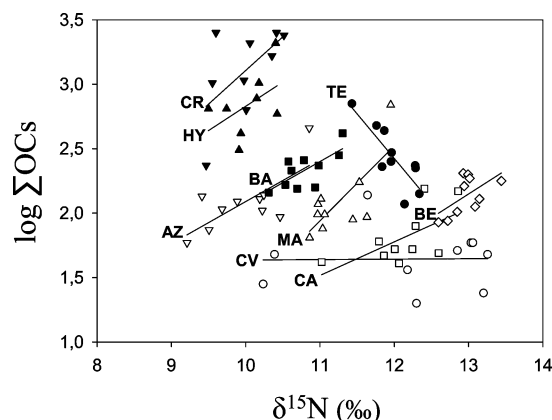
Atlantic: **CV**,O - Cape Verde; **CA**,□ - Canary Is.; **MA**,△ - Madeira; **AZ**,▽- Azores; **BE**,◇ - Berlengas Is.; Mediterranean: **TE**,● - Terreros Is.; **BA**,■ - Balearic Is.; **HY**,▲ - Hyeres Is.; **CR**,▼ - Crete

FIGURE 2. Relationship between δ^{15}N signatures and ΣOC levels (ΣOCs = Σ_{20}PCBs + Σ_3DDTs) in *Calonectris* shearwaters. Linear regressions are shown for each breeding colony separately and identified with the abbreviations of the locality. Symbol and abbreviation legends are included in Figure 1.

from Madeira and Azores showed the lowest mean δ^{13}C values, reflecting different food sources among shearwater colonies. The mean δ^{15}N values ranged from 13.0 ± 0.2‰ in shearwaters from Berlengas to 10.0 ± 0.5‰ in those from Azores. Moreover, δ^{15}N values in shearwater blood were significantly correlated with total OC levels within most breeding colonies (Table 1) but not among the whole data set (R^2 = 0.16, P = 0.06). The relationships between [ΣOCs]-δ^{15}N (Figure 2) were positive in all the breeding localities except within Terreros Is. and Cape Verde, where we found a negative and flat relationship, respectively.

PCB congeners differed significantly among breeding colonies (Table S1). Hexachlorinated PCBs accounted for
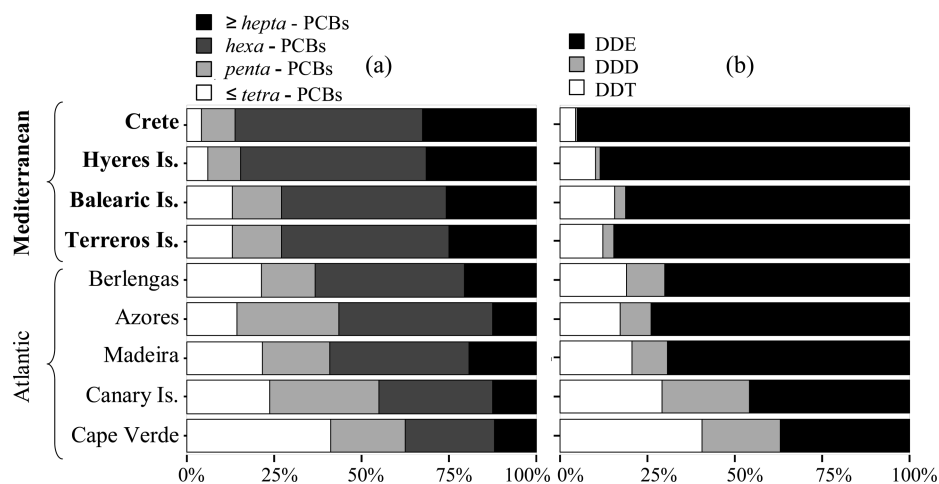
FIGURE 3. Fingerprints of PCBs and DDTs in the blood of *Calonectris* shearwaters among their breeding colonies.

the greatest mean concentrations (in all colonies except Cape Verde). Hexa- as well as penta- and ≥ heptachlorinated PCBs differed significantly among localities (statistics summarized in Table S1) due to the low levels in shearwaters breeding in the Atlantic compared to those breeding in the Mediterranean. Posthoc test comparisons revealed that significant differences arose mainly from the low values shown by shearwaters from Cape Verde and Canary Is. compared to the high concentrations from shearwaters breeding on Hyeres and Crete. Spatial differences in ≤ tetrachlorinated PCBs were marginally nonsignificant. PCB profiles (Figure 3a) in shearwaters were dominated by hexachlorinated PCBs (in all colonies except Cape Verde). The higher chlorinated congeners (hexa- and ≥ heptachlorinated PCBs) were more abundant in shearwaters from the Mediterranean than from the Atlantic colonies. Conversely, the low chlorinated congeners (≤tetra- and pentachlorinated PCBs) predominated in the profiles of Atlantic breeders. The presence of each PCB congener also varied among localities, but overall the most abundant congener in shearwater blood was CB153 (5.4 − 33.1%; average 22.54%) followed by CB180 (0.4 − 28.3%; average 12.0%).

Concerning DDTs, we also found significant differences among breeding colonies. Shearwaters from the Mediterranean showed significantly greater concentrations of p,p'-DDT, p,p'-DDE, and p,p'-DDD in the blood than those from the Atlantic (Table S1). Among DDTs, p,p'-DDE was the most abundant (Figure 3b) in all colonies except in Cape Verde, where p,p'-DDT (40.7%) was the predominant compound, and in the Canary Is., where the difference between p,p'-DDE (46.1%) and p,p'-DDT (30.0%) in shearwater blood was slight compared with the rest of the breeding colonies. In fact, shearwaters from Cape Verde and Canary Is. showed p,p'-DDE/p,p'-DDT ratios (2.0 and 2.8, respectively) markedly lower than the rest of shearwater colonies (Supporting Information; Table S1). The p,p'-DDD was the less abundant compound in all cases. The principal component analysis (PCA) on the relative abundance of all analyzed OCs (Figure 4) reflects the geographic differences of OCs among breeding colonies. PC1 and PC2 accounted for 42.7% and 13.5% of the variance, respectively. In the graphic representation of the two main principal components, Cory's, Scopoli's, and Cape Verde shearwaters appear mostly segregated. The component matrix indicated that PC1 was mainly negatively associated with higher chlorinated PCBs and p,p'-DDE and positively with lower chlorinated PCBs and p,p'-DDT. Therefore, PC1 represented a gradient of congener chlorination and an abundance of p,p'-DDT metabolite segregating between Atlantic and Mediterranean breeders. PC2 was dominated by CB114, CB153, CB194, CB180, and CB118, segregating
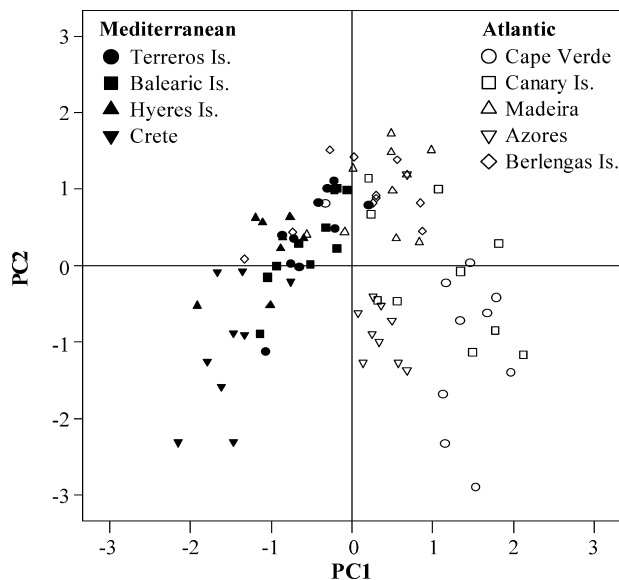

FIGURE 4. Principal components (PC1 and PC2) extracted from PCBs and DDTs in the blood from *Calonectris* shearwaters.

within Atlantic (Azores, Canary, and Cape Verde from Maderia and Berlengas) and within Mediterranean breeders (Crete from the rest of the localities).

Discussion

To our knowledge, this is the first study dealing with OC contaminants in seabirds covering an extensive area across the northeast Atlantic and the Mediterranean. Our results showed clear geographic gradients in PCB and DDT levels increasing from the southern to northern Atlantic and from the western to eastern Mediterranean colonies (Figure 1). Further, differences in OC profiles were so different among colonies that a PCA analysis segregated most colonies, showing a relatively small overlap among them (Figure 4). Moreover, we found a significant and positive relationship of ∑OC levels with $\delta^{15}N$ signatures within most breeding localities (Figure 2).

The broad geographic coverage of our sampling design offers the opportunity to compare contamination levels among distant localities, but it would have been difficult to carry it out in a single year. Therefore, different localities were sampled during the period of 2003−2006. Potential changes in contamination among years may interfere with comparisons among localities, but the main geographic patterns also emerged among samples collected in a single

year, suggesting that interyear differences in OCs were a minor source of variability in this study. In addition, temporal differences mainly emerge when comparing between distant time periods, such as interdecade comparisons, whereas interannual differences in OC levels are usually little or nonsignificant (7, 20, 29, 30). In fact, interannual coefficients of variation (CV) of PCB and DDT levels found in the literature were low compared to those obtained among localities in the present study, suggesting our differences can mainly be attributed to spatial variability in contamination rather than to the sampling year (this study CV PCBs = 0.99, CV DDTs = 1.74 among localities; Northern Atlantic fulmar: CV PCBs = 0.32, CV DDTs = 0.36 between 1998 and 2003 (31); Northern Atlantic gannets: CV PCBs = 0.08 between 1998 and 2004 (17); Mediterranean stripped dolphins: CV PCBs = 0.12, CV DDTs = 0.56 between 2000−2002 (7)).

Geographic differences in PCB and DDT levels mainly arose from the low OC levels found in the Atlantic compared to the Mediterranean shearwaters. Within each basin, ΣPCB and ΣDDT levels increased from the south to the north in the Atlantic shearwaters and from the west to the east in the Mediterranean ones (Figure 1). Several factors could be contributing to these patterns, but the two major factors are probably related to diet differences among colonies and to geographic differences in baseline levels. However, the diet of the Scopoli's, Cory's, and Cape Verde shearwaters is fairly homogeneous, mostly composed of epipelagic fish and, to a lesser extent, of cephalopods, crustaceans, and plankton (32, 33). Moreover, δ^{15}N was significantly correlated with ΣOC levels only after controlling for breeding colony, i.e., reflecting a relationship between OCs and trophic levels at the intralocality level but not among localities (Figure 2). The lack of correlation between ΣOC levels and δ^{15}N among the breeding localities suggests that differences in δ^{15}N among colonies do not arise from differences in trophic levels but from differences in baseline signatures among water masses (34). Therefore, intercolony differences in pollutant levels seem to reflect geographic differences in OC levels rather than differences in trophic ecology among localities. Our results are in line with other studies pointing out the Mediterranean Sea as a confined water mass, which results in greater levels of contamination compared to other oceanic waters (35).

Geographical differences in OCs among the Atlantic and Mediterranean waters are further supported by differences in PCB and DDT profiles. In the case of PCBs, highly chlorinated congeners (hexa-, $\geq$ heptachlorinated PCBs) were the most abundant in shearwaters breeding in the Mediterranean. Conversely, Atlantic PCB profiles were dominated by lower chlorinated congeners ($\leq$tetra- and pentachlorinated PCBs) (Figure 3). This result is probably related to a differential transport and persistence among congeners. Lower chlorinated PCBs are more volatile and easily transported to remote locations, whereas highly chlorinated congeners are more persistent and not easily metabolized by marine biota (36, 37). Therefore, assuming biotransformation efficiencies across *Calonectris* shearwaters do not change, their PCB profiles suggest that Atlantic shearwaters are mainly exposed to PCBs originating from distant sources, whereas in the case of Mediterranean breeders, higher chlorinated compounds serve as further evidence of point sources for PCBs. This pattern is consistent with a confined sea with historically greater inputs of PCBs from the highly industrialized countries of Europe, such as is the case for the Mediterranean Sea, compared to the more isolated oceanic archipelagos in the Atlantic Ocean. Within the Atlantic basin, differences in PCB levels and profiles among shearwater colonies from Macaronesian archipelagos could be related to the influence of pollutant sources and waters flowing from North America above the Central North Atlantic Ocean,

including the Azores region (38, 39), resulting in greater levels of pollutants in northern (Azores and Madeira) compared to southern Macaronesian colonies (Cape Verde and Canary Is.). In addition, greater OC levels in shearwater blood from Berlengas Is. could be related to the influence of Mediterranean waters along the southern Portuguese coast (40).

In this study, the high p,p'-DDE/p,p'-DDT ratios in shearwater from the Mediterranean indicate a major historical influence of DDTs in the Mediterranean countries. Although the mean ratio values were >1 in all sampled colonies (both Atlantic and Mediterranean), indicating a greater abundance of p,p'-DDE, this ratio was markedly lower in shearwaters from Canary Is. and Cape Verde. In fact, 7 out of 10 Cape Verde shearwaters and 5 out of 10 Cory's shearwaters from Canary Is. showed p,p'-DDE/p,p'-DDT ratios lower than 1. The remaining 67 shearwaters showed ratios far greater than 1, indicating that shearwaters from Canary Is. and Cape Verde have been more recently exposed to DDTs. This exposure is likely related to the location of the foraging grounds of the shearwaters breeding on these two southernmost Macaronesic archipelagos. This hypothesis is supported by the differences in *Calonectris* shearwater δ^{13}C signatures (Table 1), which, however, did not show a significant effect over OC levels, reflected the differential exploitation of inshore and offshore resources across their breeding range. That is, previous tracking studies showed that *Caloenctris* shearwaters from Cape Verde and Canary Is. feed mainly over the Sub-Saharan African shelf (41, 42), therefore showing greater δ^{13}C values typical of a neritic feeding habit. In contrast, *Calonectris* shearwaters breeding in Azores and Madeira showed the lowest mean δ^{13}C signatures, since they feed on pelagic waters that are far away from any coastal systems (42). Thus, unexpected shearwater DDT profiles from Cape Verde and Canary Is. colonies are probably related to their feeding habits over the African shelf, since Sub-Saharan countries still use DDT to control malaria outbreaks (43).

δ^{15}N showed a significant effect over PCB and DDT concentrations when controlling for the breeding locality. In fact, all the colonies showed a consistently positive relationship between δ^{15}N and OC levels, except Terreros Is. and Cape Verde. Since δ^{15}N signatures increase with trophic levels, relationships between δ^{15}N signatures and OCs probably reflect the well-known biomagnification properties of PCBs and DDTs. Exceptions, such as Terreros Is. and Cape Verde, are probably related to a differential use of feeding grounds with different baseline δ^{15}N levels, obscuring the bioaccumulation processes. For example, shearwaters from Terreros have been suggested to feed on both Mediterranean and Atlantic waters, with contrasting δ^{15}N baseline levels (44). The relationship between nitrogen signatures and OCs found in this study indicates that biomagnification processes not only become apparent across species but also can be detected at the intraspecific level, reflecting the relevance of dietary preferences among seabird individuals. Therefore, our results confirm the utility of combining stable isotope data with pollutant levels when evaluating the relative effect of feeding ecology over large regions in order to provide new insights into the dynamics of contaminants.

The present study emphasizes the suitability of seabirds with wide breeding ranges, such as the *Calonectris* shearwaters, as useful organisms to biomonitor the levels of OCs in pelagic ecosystems. As far as we know, no previous studies have related adverse effects to whole blood OC levels in Procellariiform species. Since species sensitivity to pollutants varies widely and stress factors do not impact upon different species equally, interspecific comparisons are difficult and scarcely representative (2, 45). Nonetheless, previous seabird studies have reported some evidence of adverse ecological effects associated to blood OC levels in gulls (46). Similarly,

studies of Albatross species have indicated possible toxic effects associated with elevated OC concentrations (*11*). In this context, although we cannot assess the possible effects of OCs in shearwater populations, the greater levels found in the Mediterranean compared to Atlantic shearwaters represent an extra stressor element for the Mediterranean populations. Therefore, continued monitoring of OCs in *Calonectris* shearwaters seems an appropriate research direction in order to evaluate their sources and trends across the North Atlantic and Mediterranean subtropical region and their possible impact on the populations.

Acknowledgments

Supporting Information Available

Details of analytical methods, sexual determination and its relevance in the present study, Figure S1 (breeding localities map), and Table S1 (PCB congener and DDT metabolites concentrations in Calonectris shearwaters). This material is available free of charge via the Internet at http://pubs.acs.org.

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