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Geographic and trophic patterns of OCs in pelagic seabirds from the NE Atlantic and the Mediterranean: A multi-species/multi-locality approach

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ABSTRACT

Trophic ecology and geographic location are crucial factors explaining OC levels in marine vertebrates, but these factors are often difficult to disentangle. To examine their relative influence, we analyzed PCBs, DDTs and stable-nitrogen isotope signatures ($\delta^{15}N$) in the blood of 10 pelagic seabird species across 7 breeding localities from the northeast Atlantic and western Mediterranean. Large scale geographic patterns emerged due to the confined character and greater historical OC inputs in the Mediterranean compared to the Atlantic basin. Spatial patterns also emerged at the regional scale within the Atlantic basin, probably associated with long-range pollutant transport. Trophic ecology, however, was also a major factor explaining OC levels. We found clear and consistent OC differences among species regardless of the sampled locality. However, species $\delta^{15}N$ and blood OC levels were not correlated within most breeding localities. Petrel species showed significantly greater OC burdens than most shearwater species but similar trophic positions, as indicated by their similar $\delta^{15}N$ signatures. This pattern probably results from Petrel species feeding on mesopelagic fish and squid that migrate close to the sea surface at night, whereas shearwater species mainly feed on epipelagic diurnal prey. In sum, this study illustrates the lasting and unequal influence of past human activities such as PCB and DDT usage across different marine regions. In addition, our results suggest that multi-species designs are powerful tools to monitor geographic patterns of OCs and potentially useful to assess their vertical dynamics in the marine environment.

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1. Introduction

Organochlorine contaminants (OCs), such as polychlorinated biphenyls (PCBs) and dichlorodiphenil trichloroethane (DDT), are globally found in marine food chains and are known to have a wide array of adverse effects (Walker and Livingstone, 1992). These contaminants bioaccumulate and biomagnify throughout marine food webs due to their persistent and lipophilic properties (Hop et al., 2002). As a result, significant concentrations of OCs have been reported among marine organisms at high trophic positions, potentially resulting in toxicological effects, but also providing opportunities for monitoring marine pollution (Walker, 1992; Jones and Voogt, 1999). Among marine predators, seabirds have been proposed as useful bioindicators for OCs, mainly because many of them are placed at high trophic positions, breed at specific locations and show large-scale distributions (Burger and Gochfeld, 2004). Despite the potential of seabirds to monitor contamination from different ocean habitats, most studies concerning OC levels in seabirds focus on coastal species, and few of them have dealt with species from pelagic ecosystems. This is unfortunate because pelagic seabirds can integrate contaminant levels of areas relatively unexploited by fisheries (Karpouzi et al., 2007), and therefore, poorly explored and difficult to monitor for contaminants.

The limited data on OCs with respect to pelagic seabirds is probably related to the ethical and technical limitations of the sampling strategies (Elliott, 2005; Yamashita et al., 2007), because common tissues for OC analysis (e.g., fat, liver or muscle) involve animal killing or unpractical sampling procedures, such as carcass collection. Nevertheless, thanks to the improvements in analytical skills, we can now survey a wide array of organic contaminants using small blood quantities obtained with negligible impact on the birds. Previous studies have validated the use of blood to evaluate OC levels in seabirds and have successfully used this tissue to evaluate recent exposure to marine contamination (Bustnes et al., 2005b; Finkelstein et al., 2006; Yamashita et al., 2007). In addition, blood can also be used to decipher seabird trophic ecology by means of stable isotope analysis. Specifically, the stable-nitrogen isotope ratio ($^{15}N/^{14}N$; $\delta^{15}N$) has been widely used to delineate the trophic position of seabirds (Kelly, 2000) and previous studies have

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reported significant positive relationships between blood OC levels and δ^{15}N, reflecting the biomagnification processes (Elliott et al., 2009; Roscales et al., 2010). However, because the accumulation of OCs is not determined by trophic level alone, partial upsets between δ^{15}N and OC levels in seabirds have been reported, suggesting that migratory movements, specific dietary habits or metabolic capabilities can also play a significant role in seabird pollution burdens (Fisk et al., 2001; Elliott, 2005; Ricca et al., 2008). In this regard, multi-species and multi-locality approaches can help to better understand the different contributions of the trophic level compared to other factors on OC burdens.

The present study focuses on OCs in pelagic seabirds (O. Procellariiformes) breeding across the northeast Atlantic and the Mediterranean Sea. Some seabirds are considered vulnerable or threatened, and previous studies have pointed out the need to improve our knowledge about their ecology and contaminant status in these regions (Monteiro and Furness, 1997; Forero and Hobson, 2003). Moreover, several species feed mostly on prey that are also consumed by humans, such as several epipelagic fish and squid species, which makes them potentially useful as sentinels of marine contamination. However, few studies dealing with organochlorine contamination in pelagic vertebrates have been conducted within these regions, even when the Mediterranean basin is known to be strongly affected by marine pollution (Jiménez et al., 2000; Albaigés, 2005). In this study, organochlorine levels and stable isotope signatures of nitrogen were analyzed in blood from 10 species of pelagic seabirds at seven breeding localities across the NE Atlantic and W Mediterranean archipelagos. We aimed (1) to evaluate the relative influence of geographic location and feeding ecology over OCs in pelagic seabirds; (2) to validate OC geographic patterns and sources previously assessed through a single-species approach (Roscales et al., 2010); (3) to understand the biomagnification process of OCs by relating PCB and DDT levels from different species to their feeding ecology.

2. Material and methods

2.1. Species, study area and sampling procedure

We sampled most petrels and shearwaters (10 species) breeding in the NE Atlantic Ocean and the west Mediterranean archipelagos (Fig. 1). Some groups of species included in this study are parapatric species. That is, their range does not significantly overlap, but are immediately adjacent to each other and show similar morphology and ecology (Table 1). This is the case with three superspecies of shearwaters, each including several paraspecies: the Cory's shearwater (*Calonectris diomedea*, *Calonectris borealis* and *Calonectris edwardsii*), the little shearwater (*Puffinus baroli* and *Puffinus boydi*, among others) and the Manx shearwater (*Puffinus yelkouan* and *Puffinus mauretanicus*, among others) superspecies. These species are closely related forms, and until recently, long considered subspecies of the same species and in some cases their taxonomic status is still being debated (e.g., *Calonectris* shearwaters) (Heidrich et al., 1998; Austin, 2004; Gómez-Díaz et al., 2009). Therefore, regarding contamination, we will consider each superspecies as a single statistical unit and not a different species.

Adult seabirds were sampled during their breeding season from 2003 to 2006 (Fig. 1), particularly during incubation and chick rearing periods. Species from the same breeding locality were sampled within a single year. Previous analysis on Cory's shearwater species complex suggested a negligible influence of sex as well as sampling year (period 2003–2006) over shearwater OC levels (Roscales et al., 2010). Depending on the size of the species, about 0.2–0.5 mL of blood was sampled from the brachial vein. Blood was transferred into vials with 1 mL of absolute ethanol and preserved at −24 °C until analysis.

2.2. Chemical analysis

A sub-sample of the blood fixed with absolute ethanol was used for stable isotope analysis. About 0.36–0.40 mg of dried blood (weighed to the nearest µg) were placed 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 (‰).

From 0.02 to 0.2 g (depending on the species) of dried blood was used for OC determination. High-resolution gas chromatography coupled to micro-electron capture detection was used for the analysis of organochlorinated compounds: *ortho* PCB congeners #28, #52, #95, #101, #123, #149, #118, #114, #153, #132, #105, #138, #167, #156, #157, #180, #183, #170, #189, #194 and DDTs, including *p,p′*-DDT and its two main metabolites, *p,p′*-DDD and *p,p′*-DDE. Further details of the sample treatment and

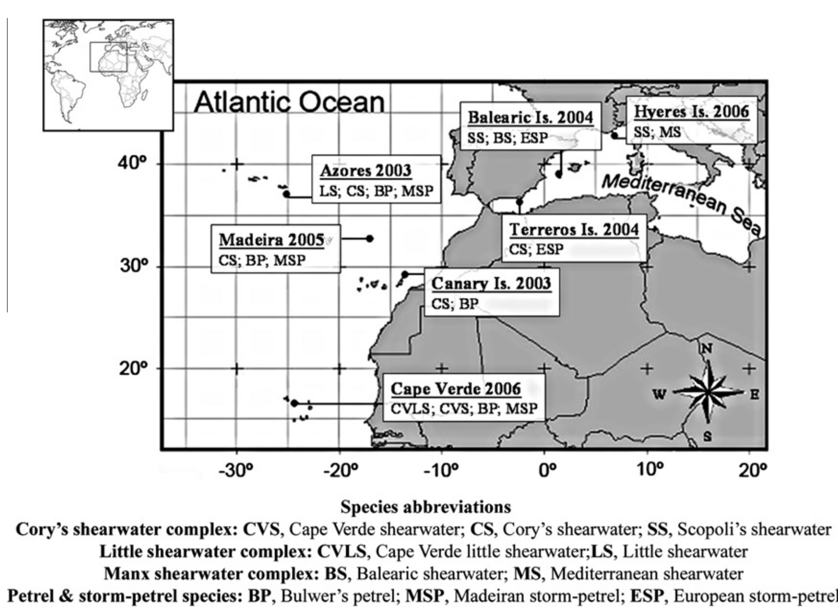

Fig. 1. Geographic distribution of the studied seabirds. Black points indicate the localities where seabirds were sampled, including the species and the sampling year.

Table 1
Biological characteristics of pelagic seabirds (O. Procellariiformes) breeding across the NE Atlantic and the Mediterranean.

Superspecies species	n[a]	Weight (g) mean ± SD	Diet	Winter habitat	Breeding areas within the study range	References[d]
Cory's shearwaters						
Cory's shearwater	40	839 ± 70[b]	Epipelagic fish/squid	Canary, Benguela, and Agulhas currents and Brazil-Falklands currents confluence	NE Atlantic and Alboran Sea	*1*, *2*
Scopoli's shearwater	18	654 ± 62[b]	Epipelagic fish/squid	Canary and north Benguela Currents	Western Mediterranean	*2*, *3*
Cape Verde shearwater	10	431 ± 55[c]	Epipelagic fish/squid	Brazil-Falklands currents confluence	Cape Verde	*4*, *5*
Little shearwaters						
Little shearwater	8	156 ± 11[b]	Epielagic fish/squid/zooplankton	No migratory	Macaronesia	*6*, *7*
Cape Verde little shearwater	9	162 ± 14[c]	Epielagic fish/squid/zooplankton	Tropical North Atlantic	Cape Verde	*8*, *9*
Manx shearwaters						
Mediterranean shearwater	7	416 ± 29[b]	Pelagic and demersal fish/squid	Mediterranean basin and Black Sea	Western Mediterranean	*3*, *4*, *10*
Balearic shearwater	6	522 ± 25[b]	Demersal and pelagic fish/fishery discards	NE Atlantic	Balearic Is.	*11*, *12*
Petrel species						
Bulwer's petrel	39	104 ± 11[b]	Mesopelagic fish/squid/zooplankton	Southern tropical and subtropical Atlantic	Macaronesia	*4*, *9*, *13*
Madeiran storm-petrel	22	49 ± 4[b]	Mesopelagic fish/squid/zooplankton	Dispersion tropical and subtropical Atlantic	Macaronesia	*4*, *8*, *13*, *14*
European storm-petrel	15	20 ± 1[b]	Fish/squid/plankton and carrion/fatty droplets	Southern Atlantic	Western Mediterranean	*4*, *15*, *16*

[a] Number of individuals included in this study.
[b] Brooke (2004) and Cramp and Simmons (1977).
[c] González-Solís unpublished (*C. edwardsii* n = 80; *P. boydi* n = 57).
[d] *1*, Granadeiro et al. (1998); *2*, González-Solís et al. (2007); 3, Karen et al. (2009); *4*, Brooke (2004); *5*, González-Solís et al. (2009); *6*, Neves et al. (in preparation); *7*, Monteiro et al. (1996); *8*, Roscales et al. (2011); *9*, J. González-Solís unpublished; *10*, Karen and Vidal (2008); *11*, Navarro et al. (2009); *12*, Mouriño et al. (2003); *13*, Monteiro et al. (1998); *14*, Bolton et al. (2008); *15*, D'Elbée and Hémery (1997); *16* Valeiras (2003).

the analytical procedure including QA/QC procedures for the determination of stable isotope ratios and OC concentrations are extensively described in our previous work (Roscales et al., 2010).

2.3. Data analysis

SPSS 15.0 for Windows was used for all of the statistical analysis. Distributions of PCB, DDT and δ^{15}N levels were inspected for normality. Values under the detection limit were set to zero (Supplementary data, Table S1). Total contaminant concentrations ($\sum_{23}$OCs, $\sum_{20}$PCBs and $\sum_{3}$DDTs) were log transformed (using base 10 logarithms) in order to satisfy a normal distribution and the homogeneity of variance. The Shapiro–Wilk test and Q–Q plots revealed a normal distribution for pollutant concentrations (after log transformation) and δ^{15}N (all $P > 0.05$). The relationship between total PCBs and DDTs was evaluated by means of Pearson correlation analysis. Levels of both organochlorine families were strongly correlated ($r = 0.92$, $P < 0.001$) and thus, we evaluated seabird contaminant burden variability using the total amount of organochlorine contaminants. Because the sampling design in this study was unbalanced (all sampled species do not breed in all localities), the analysis of variability of organochlorine contaminants was performed by applying a Generalized Linear Model analysis (SPSS v.15, GLM, Type IV SS for unbalanced designs) using $\sum$OCs as the response variable. We tested the main effects and interactions of the superspecies, breeding colony and δ^{15}N. The final selected model was built following a forward stepwise procedure, which included only the significant effects retained. Because species and locality interacted significantly, we checked interspecies differences in OC levels within each breeding locality separately using one-way ANOVA tests. To evaluate the relationship of [OCs]-δ^{15}N among seabird species within each breeding locality, we applied ANCOVA analysis over the mean $\sum$OC and δ^{15}N levels of seabird species using breeding locality as a fixed factor and δ^{15}N as a covariable.

To assess the relative exposure to PCB and DDT congeners among seabirds, we examined their profiles at each breeding place (calculated as the average percent of each PCB or DDT related to $\sum_{20}$PCBs and $\sum_{3}$DDTs, respectively). Concerning PCBs, we grouped congeners depending on their chlorination degree ($\leqslant$tetra-, penta-, hexa- and $\geqslant$hepta-chlorinated PCBs). Moreover, a principal component analysis (PCA) was applied to the normalized contributions (%) of all PCBs analyzed to check whether PCB profiles segregated seabirds depending on their breeding locality or their taxonomic status. In the case of DDTs, we calculated DDE/DDT ratios to check seabird profile differences and to detect possible recent inputs of this pesticide (Springer et al., 1984; Mora, 1997).

3. Results

3.1. Influence of species, δN^{15} and breeding locality on OC levels

Considering the levels of $\sum$OCs (Table 2), the GLM explained up to 91.5% of the initial variance and included five explanatory variables: breeding locality ($F_{6,174} = 3.56$, $P = 0.003$), superspecies ($F_{5,174} = 111.39$, $P < 0.001$), δN^{15} ($F_{1,174} = 5.69$, $P = 0.017$) and the interactions breeding locality $*$ species ($F_{8,174} = 4.92$, $P < 0.001$) and breeding locality $*$ δN^{15} ($F_{6,174} = 4.11$, $P = 0.001$). The significant effect of interactions indicated that interspecies differences of OC levels as well as the relationship [OCs]-δN^{15} vary depending on the breeding locality.

The GLM showed the significant effect of breeding locality on seabird OC levels. In fact, at intraspecific levels or within each superspecies group, seabirds showed consistent spatial patterns in their PCB and DDT burdens (Fig. 2). Generally, storm-petrels and shearwaters from the Mediterranean showed respectively greater OC

Table 2
Arithmetic and Geometric mean (AM and GM), standard error (SE) and range of $\sum_{20}$PCBs and $\sum_3$DDTs concentrations (ng g^{-1} d.w.) in blood from pelagic seabird species depending on their breeding locality.

Breeding colony			∑PCBs			∑DDTs		
Species[a]	*n*	Year	AM ± SE	Range	GM	AM ± SE	Range	GM
Atlantic								
Cape Verde		2006						
CVLS	9		39.40 ± 7.06	21.12–92.68	35.94	7.201 ± 1.232	3.162–14.90	6.478
CVS	10		43.25 ± 7.31	17.74–97.35	38.42	7.691 ± 3.594	1.852–39.80	4.891
BP	10		65.22 ± 7.41	32.97–120.6	61.75	14.72 ± 1.71	5.866–23.80	13.74
MSP	9		115.1 ± 9.4	75.33–161.3	118.9	35.81 ± 7.43	16.08–82.46	30.80
Canary Is.		2003						
CS	10		59.22 ± 9.37	30.94–114.8	53.93	13.13 ± 4.43	2.91–42.59	8.384
BP	9		122.3 ± 14.4	72.00–193.1	115.5	33.50 ± 6.48	15.40–68.46	29.28
Madeira		2005						
CS	10		125.3 ± 40.9	51.40–488.9	98.34	38.18 ± 19.28	11.03–208.7	22.06
BP	10		311.0 ± 24.5	200.2–442.2	302.4	89.43 ± 13.77	40.67–171.4	80.86
MSP	8		419.9 ± 84.0	186.5–784.2	361.4	172.1 ± 41.29	27.78–329.8	128.4
Azores Is.		2003						
LS	8		57.43 ± 6.49	26.66–79.80	54.52	12.52 ± 2.18	5.026–24.19	11.25
CS	10		99.33 ± 14.84	41.22–217.8	91.21	42.09 ± 21.48	12.49–234.3	25.13
BP	10		262.1 ± 17.5	185.7–337.7	256.8	58.99 ± 11.73	23.13–146.8	50.77
MSP	5		1073 ± 206	441.7–1726.7	982.3	319.1 ± 85.07	88.69–546.9	264.1
Mediterranean								
Terreros Is.		2004						
CS	10		212.72 ± 34.54	91.68–463.6	191.5	100.1 ± 24.91	25.50–248.2	76.98
ESP	5		6843 ± 1213	3186–10 495	6362	5816 ± 1500	2971–11 561	5204
Balearic Is.		2004						
BS	6		53.99 ± 11.24	27.34–105.8	49.24	16.25 ± 8.80	4.724–59.93	10.08
SS	10		158.24 ± 13.38	102.1–227.7	153.3	69.57 ± 14.96	30.98–191.9	59.61
ESP	10		4504 ± 1022	1645–12 298	3739	2781.5 ± 599.3	883.4–6266	2254
Hyeres Is.		2006						
SS	8		510.7 ± 107.8	216.2–1189	448.5	303.3 ± 96.81	96.26–911.7	233.58
MS	7		229.0 ± 16.1	155.95–283.12	225.3	81.03 ± 11.22	48.94–133.1	76.84

[a] CVLS, Cape Verde little shearwater; CVS, Cape Verde shearwater; BP, Bulwer's petrel; MSP, Madeiran storm-petrel; LS Little shearwater; CS, Cory's shearwater; SS, Scopoli's shearwater; BS, Balearic shearwater; MS, Mediterranean shearwater.

levels than those from the Atlantic. Moreover, within the Atlantic basin, PCB and DDT burdens increased from southern to northern breeding localities regardless of the species. Inter-species differences of ∑OCs at each breeding locality (Fig. 2) were significant in all breeding localities (Cape Verde, $F_{3,38} = 17.71$; Canary, $F_{1,19} = 16.85$; Madeira, $F_{2,28} = 17.60$; Azores, $F_{3,33} = 56.25$; Terreros, $F_{1,15} = 171.01$; Balearic, $F_{2,26} = 179.35$; Hyeres, $F_{1,15} = 12.60$; All $P < 0.001$ except Hyeres with $P = 0.007$). In general, PCB and DDT levels in seabird blood showed consistent inter-species patterns in all of the breeding localities (Fig. 2). Within the Atlantic basin, little shearwater species showed the lowest mean values of both ∑PCBs and ∑DDTs, followed by Cory's shearwater species, Bulwer's petrel and Madeiran storm-petrel. Post hoc tests revealed that differences in ∑OCs were significant for all pair comparisons with the exception of Bulwer's petrel *vs.* Madeiran storm-petrel and Cory's *vs.* little shearwater species. Among Mediterranean breeders, the Balearic shearwater showed the lowest amount of PCBs and DDTs, followed by the Mediterranean and Cory's shearwater species. The European storm-petrel showed the greatest ∑PCBs and ∑DDTs values in all of the breeding localities. All pair comparisons between species were significant. However, within both Atlantic and Mediterranean breeding localities, most seabirds showed δ^{15}N values that were strongly overlapped and did not follow the contamination level patterns (Fig. 2).

The low potential of δ^{15}N to predict ∑OC concentrations in seabird species was evident when evaluating the relationship between these variables (Fig. 3). Breeding locality, δ^{15}N and their interaction did not show a significant effect (ANCOVA test, all $P \geqslant 0.1$), which indicates a lack of correlation between species OC levels and δ^{15}N. In fact, the regression analysis between OC levels and δ^{15}N was only significant within seabirds from the Azores ($r^2 = 0.87$, $P = 0.007$) due to the smaller overlap in Azorean seabird nitrogen signatures compared to the rest of breeding localities.

3.2. PCB and DDT profiles

Overall, among the analyzed PCB congeners, # 153, 138 and 180 were the most abundant in seabird blood samples. Although the relative contribution of ⩽tetra-, penta-, hexa- and ⩾heptachlorinated PCBs (Fig. 4) varied among species and localities, in general, petrel species showed a greater presence of hexa- and heptachlorinated PCBs than shearwaters within each breeding locality. Similarly, PCBs of high chlorination degree were more abundant in Mediterranean than in Atlantic seabird populations.

Hexachlorinated PCBs accounted for the greatest contributions (Fig. 4) and concentrations (Supplementary data, Table S2) in most seabird species. Only the Cape Verde and the little shearwaters showed PCB profiles dominated by low chlorinated PCBs (⩽tetra- or penta-PCBs). Generally, Mediterranean breeders showed a large proportion of higher chlorinated congeners (hexa- and ⩾hepta-chlorinated PCBs) with two exceptions: (1) Madeiran storm-petrels from the Azores and Madeira whose PCB profiles were clearly dominated by higher chlorinated PCBs, and (2) Balearic shearwaters from the Balearic Islands, which showed a larger amount of lower chlorinated PCBs compared to the rest of the Mediterranean breeders. Furthermore, the principal component analysis (PCA) performed with the relative abundance (% related to the total amount of PCBs) of all analyzed congeners (Fig. 5) segregated most Mediterranean breeders (with the exception of the Balearic shearwater) and Madeiran storm-petrels from the rest of the seabirds

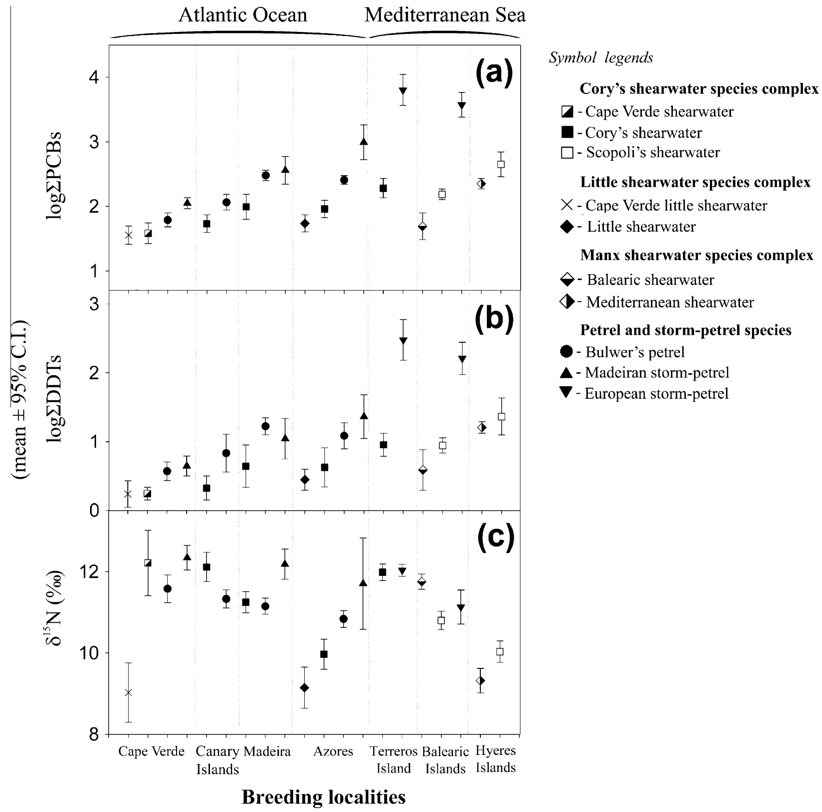

Fig. 2. Mean and 95% intervals of confidence (IC) of PCBs (a), DDTs (b) and $\delta^{15}N$ (c) among breeding localities of pelagic seabirds from the NE Atlantic Ocean and the Mediterranean Sea.

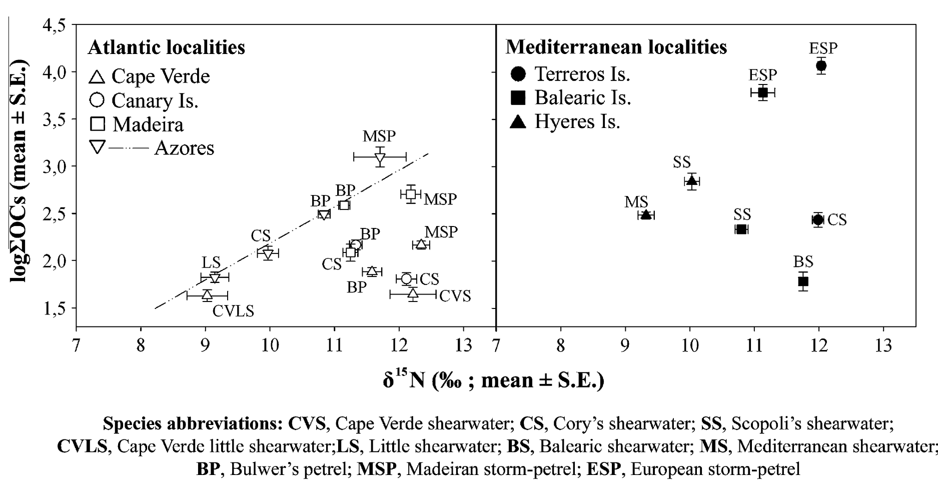

Fig. 3. Relationship between seabird blood $\delta^{15}N$ signatures and $\sum$OC concentrations within each breeding locality. Only significant regression lines are shown. Mediterranean and Atlantic seabird populations appear separately for clarity purposes.

due to the major presence of high chlorinated PCB congeners in these groups. Two principal components explained 50.59% of the total variance. The component matrix indicated that PC1 was mostly positively associated with the relative abundance of higher chlorinated PCBs and mainly negatively related to lower chlorinated congeners (factor loadings included in the Supplementary data, Table S3). PC2 did not show marked differences in its association with PCB congeners. Therefore, PC1 mostly represented a gradient of congener chlorination, and PC2, a general measure of PCB contamination.

Concerning DDTs, although *p,p′*-DDE, followed by *p,p′*-DDT and *p,p′*-DDD, showed the relative largest contributions in most seabirds (Supplementary data, Table S4), DDT profiles varied among species and breeding localities (Fig. 4). *p,p′*-DDE/*p,p′*-DDT ratios reflected these differences, showing mean values markedly lower in seabirds from Cape Verde and the Canary Islands (Table S4) compared to the rest of the breeding colonies. Specifically, *p,p′*-DDE/*p,p′*-DDT ratios in Cape Verde seabirds were lower than 1 in 44.7% of the cases and reached values between 1 and 2 in 21.1% of them. In the case of the Canary Islands, 31.6% and 15.9% of the

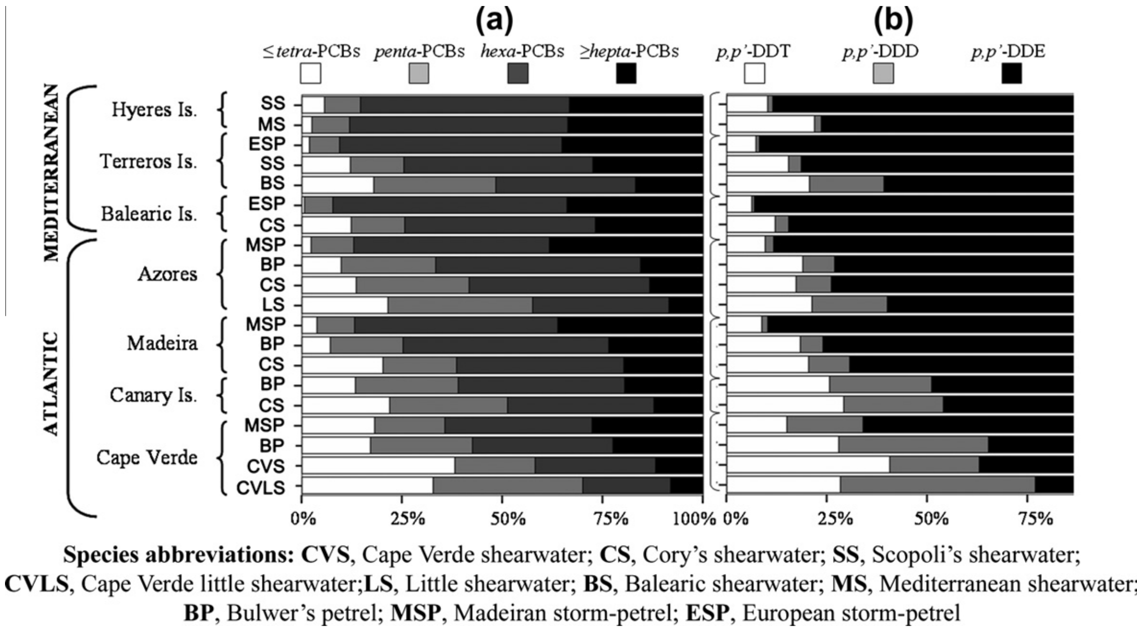

Fig. 4. PCB and DDT profiles in the blood of pelagic seabirds depending on their breeding localities.

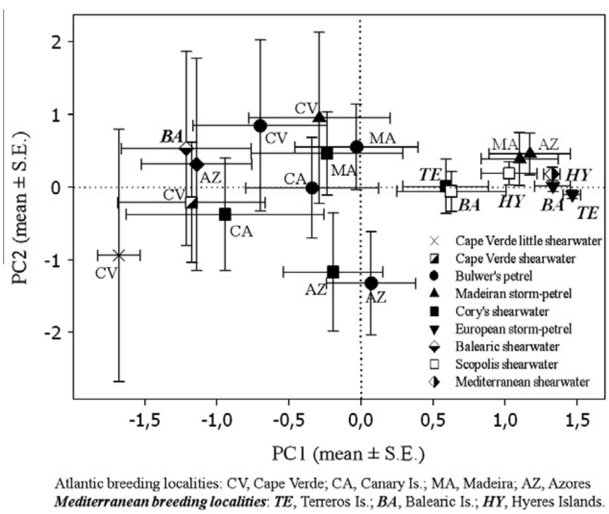

Fig. 5. Principal components (PC1–PC2) performed with the relative normalized contributions of all PCBs analyzed in pelagic seabird blood. Breeding localities from the Mediterranean Sea are indicated in bold plus italic type.

seabirds also showed a DDE/DDT ratio lower than 1 and between 1 and 2, respectively. The rest of the seabirds from this study showed DDE/DDT ratios greater than two. These differences in the DDE/DDT ratios reflected a major abundance of *p,p′*-DDT in DDT blood profiles from seabirds breeding in the southern Macaronesian archipelagos compared to the rest of the sampled localities.

4. Discussion

To the best of our knowledge, this is the first large-scale study reporting persistent organic pollutant levels in several pelagic seabird species over multiple localities from the NE Atlantic and the Mediterranean Sea. Overall, our results show that both breeding locality and species have a marked influence on seabird organochlorine contamination. Further evidence of this combined influence was supported by a PCA analysis, which did not allow grouping seabirds by species or breeding locality alone. Despite that, DDT and PCB levels in seabird blood showed similar spatial trends regardless of the species and greater burdens in petrels than in shearwaters within all the breeding locations. Moreover, previous studies based on the usage of tracking devices have shown the foraging areas of the seabird populations studied here (Paiva et al., 2010; Roscales et al., 2011), which provides useful knowledge to understand OC differences across separated seabird populations.

Our results revealed a large homogeneity in the spatial patterns of OCs in pelagic seabirds regardless of the species. On the whole, the geographic patterns of OCs reported in this study across the Atlantic and Mediterranean basins through a multi-specific approach validate and give more consistence to those reported previously at intraspecific level in the Cory's shearwater complex (Renzoni et al., 1986; Roscales et al., 2010). Within the Atlantic seabird populations, OC levels increased from the southern to the northern archipelagos. This latitudinal pattern is likely associated with the influence of North American coastal waters and pollution sources above the central-north Atlantic (including the Azorean region) (Santos et al., 1995; Stohl et al., 2002). Moreover, most seabirds breeding in the southern Macaronesian archipelagos (Cape Verde and Canary Islands) showed DDE/DDT ratios that suggest recent inputs of DDT into their food webs. The nearby Sub-Saharan African countries, where DDT is still in use to control malaria outbreaks, represent the most probable source of these contaminants (Walker et al., 2003; Roscales et al., 2010). Since a fresh source of DDT is an unexpected finding in the marine environment, our results may indicate that the use of DDT on human health issues is detectable not only in terrestrial but also in marine food webs.

On a large scale, spatial patterns in seabird OCs emerged between the Mediterranean and the Atlantic. Most Mediterranean seabird populations showed greater concentrations of OCs and a major presence of high chlorinated PCBs compared to their Atlantic counterparts. Although this general pattern is consistent with the historically great input of OCs and the confined character of the Mediterranean basin, we found one exception to this geographic trend. Balearic shearwaters showed lower OC levels than the rest of Mediterranean species and PCB profiles similar to those found in the case of the Atlantic populations. This unexpected result could be related to the migratory movements of Balearic shearwaters since this species spends the non-breeding period in the NE Atlantic. Migratory movements of seabirds to less or more polluted regions can shift the OC levels expected from their breeding grounds (Buckman et al., 2004). Although blood has been suggested to reflect mainly recent OC exposition, lipid mobilization can release pollutants accumulated in adipose tissues over past periods into the bloodstream. This may explain the contaminant pattern found in Balearic shearwaters. However, in spite of this exception, our results showed a marked relationship between breeding places and OCs in the rest of seabird species which in general suggests a lesser influence of the species migratory movements. For example, other Mediterranean seabirds wintering in Atlantic waters (i.e. Scopoli's shearwater and European storm-petrel) showed OC levels and profiles clearly different from Atlantic species. Similarly, Atlantic species with similar migratory movements showed significantly different OC levels (i.e. Bulwer's petrel and Cory's shearwaters) and non-migratory species did not show significant differences in OCs compared to transequatorial migrants (i.e. Cory's and little shearwater species).

OC levels differed significantly among seabird species within all the breeding localities. Among the studied seabirds, little shearwaters showed the lowest OC burdens and the lowest stable-nitrogen signatures. This result agrees with previous studies of heavy metals suggesting a relatively lower trophic position for these species (Monteiro et al., 1995). Cory's shearwaters showed greater amounts of OCs related to the rest of shearwater species, but significantly lower levels than petrels (Fig. 2). In contrast, blood δ^{15}N signatures showed a great overlap among petrels and Cory's shearwater species and this intrinsic marker was not a good estimator of species OC levels. The small differences in blood stable-nitrogen signatures between these groups of species suggest no marked differences in their trophic position, which agrees with previous studies (Monteiro et al., 1995; Monteiro et al., 1998; Roscales et al., 2011). However, similar isotopic values among species or individuals cannot necessarily be interpreted as evidence of similar diets (Hobson et al., 1994). Therefore, the greater levels found in petrels could be related to different exposure through their diet, but also to different metabolic capacities or energetic requirements among species.

The energetic requirements per unit mass, and hence the feeding rate, is proportionally greater in smaller species, which gives them a greater exposure rate to contaminants. The petrel species included here are smaller than the Cory's shearwaters (Table 1). Similarly, little shearwater is about 73% lighter than Cory's shearwaters and for example, only 27% heavier than Bulwer's petrel. However, in spite of being within the smallest seabird species, little shearwater species showed significantly lower OC levels than those from the Cory's shearwater complex. Moreover, all the analyzed species are phylogenetically close (O. Procellariformes) and biologically and ecologically similar compared to other seabird groups. Therefore, although we cannot completely exclude some differences in OC levels associated with the energetic requirements of the species, it seems to be a minor factor influencing seabird OC levels. Concerning the metabolic capabilities of seabirds, previous studies about Mixed-Function Oxidase (MFO) activity revealed a slightly greater activity for some enzymes in storm-petrels (*Oceanodroma leucorhoa*) compared to shearwaters (*Puffinus puffinus*) (Knight and Walker, 1982; Peakall et al., 1987). These small differences in MFO activity between storm-petrels and shearwaters could be related to the lower presence of low chlorinated PCBs that we found in petrel species. Nonetheless, it could not explain the large difference in OC levels between these groups.

Although most petrel and shearwater species included in this study feed mainly on pelagic resources, they exploit different prey types (Table 1). The diet described for the European storm-petrel could explain the great OC levels compared to δ^{15}N signatures found in this species. Resources such as fatty droplets can contribute to increase OC burdens in this storm-petrel but not their nitrogen signatures since OCs are lipophilic compounds but droplets lack protein content. In addition, previous studies have shown that seabird scavenging events also can contribute to upsetting the relationship between OC levels and δ^{15}N (Fisk et al., 2001; Elliott, 2005). Similarly, dietary habits of Atlantic seabirds can explain inter-species differences in OC levels. Madeiran storm-petrels and Bulwer's petrels are mainly nocturnal feeders specialized in exploiting daily vertical mesopelagic (from 200 to 1000 m of depth) migratory fishes, such as myctophids (Monteiro et al., 1996, 1998; Bolton et al., 2008). In fact, these seabird species have been pointed out as excellent indicators of mercury levels from mesopelagic environments (Thompson et al., 1998). In contrast, Cory's shearwater species are mainly epipelagic (0–200 m) diurnal feeders. Dietary differences between petrels and shearwaters are probably associated with their OC levels. Previous studies in the Atlantic and Pacific oceans have reported higher burdens of OCs in mesopelagic and deep sea fishes compared to those from the upper water layers (Ballschmiter et al., 1997; Froescheis et al., 2000; De Brito et al., 2002; Mormede and Davies, 2003). Specifically, studies on Pacific mesopelagic fishes have revealed significantly greater burdens of organic pollutants in some daily vertical migrant and semi-migrant myctophid species in comparison to other mesopelagic fishes (Takahashi et al., 2000). Therefore, seabirds feeding on these resources are probably exposed to greater OC burdens than those of similar trophic position but feeding on epipelagic prey. Therefore, our findings suggest that multi-species strategies in marine monitoring could be used to assess not only regional differences of OCs, but are also potentially useful to study the vertical distribution of these contaminants. Further studies on the OC levels of Atlantic mesopelagic fish species and the relationship between predator and prey OC burdens are necessary to confirm this hypothesis.

The multi-species approach over different breeding localities included in this study showed a broader interval of risk levels than single species based strategies. The former represents a more comprehensive evaluation of marine pollution. Previous studies on seabirds have reported adverse ecological effects on the reproductive performance and behavior of gulls related to their whole blood OC burdens (Bustnes et al., 2001, 2005a; Helberg et al., 2005). The mean $\sum$PCB levels reported in the present study were generally lower than those reported for gulls (i.e., mean concentrations in Glaucous gull blood from Bear Is. ranged from 325.8 to 431.1 ng g^{-1} w.w.) (Bustnes et al., 2005a). However, most Mediterranean seabird populations and some Atlantic petrel species showed greater mean PCB levels or a range of PCB levels strongly overlapped with those reported for gulls. In addition, previous studies of albatross species from the Pacific have documented plasma organochlorine levels that are believed to be of toxicological concern (Auman et al., 1997; Guruge et al., 2001; Finkelstein et al., 2006). However, our results are not directly comparable since we used whole blood and thus, we cannot assess the possible effects of OCs over pelagic seabird populations. Nevertheless, the greater levels found in the Mediterranean compared to the Atlantic shearwaters as well as the high PCB levels found in storm-petrels probably represent an extra stressor element for these populations. This highlights the lasting and unequal impacts of past human activities in the marine environment, especially in confined regions such as the Mediterranean Sea. Therefore, monitoring OCs in pelagic seabird from the northeast Atlantic and the Mediterranean as well as further evaluations of possible adverse effects derived from these pollutants seems appropriate in order to anticipate and prevent possible impacts on their populations.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.07.070.

References

Albaigés, J., 2005. Persitent organic pollutants in the Mediterranean Sea. In: Saliot, A. (Ed.), The Mediterranean Sea. Springer, Berlin, pp. 89–149.
Auman, H.J., Ludwig, J.P., Summer, C.L., Verbrugge, D.A., Froesen, K.L., Colborn, T., et al., 1997. PCBs, DDE, DDT and TCDD-EQ in two species of albatross on Sand Island, Midway atoll, North Pacific Ocean. Environ. Toxicol. Chem. 16, 489–504.
Austin, J.J., 2004. A global molecular phylogeny of the small *Puffinus* shearwaters and implications for systematics of the Little-Audubon's shearwater complex. Auk 121, 847–864.
Ballschmiter, K.H., Froescheis, O., Jarman, W.M., Cailliet, G.M., 1997. Contamination of the Deep-Sea. Mar. Pollut. Bull. 34, 288–289.
Bolton, M., Smith, A.L., Gómez-Díaz, E., Friesen, V.L., Madeiros, R., Bried, J., et al., 2008. Monteiro's storm-petrel *Oceanodroma monteiroi*: a new species from the Azores. Ibis 150, 717–727.
Brooke, M., 2004. Albatrosses and Petrels Across the World. Oxford University Press, Oxford.
Buckman, A.H., Norstrom, R.J., Hobson, K.A., Karnovsky, N.J., Duffe, J., Fisk, A.T., 2004. Organochlorine contaminants in seven species of Arctic seabirds from northern Baffin Bay. Environ. Pollut. 128, 327–338.
Burger, J., Gochfeld, M., 2004. Marine birds as sentinels of environmental pollution. Ecohealth 1, 263–274.
Bustnes, J.O., Bakken, V., Erikstad, K.E., Mehlum, F., Skaare, J.U., 2001. Patterns of incubation and nest-site attentiveness in relation to organochlorine (PCB) contamination in Glaucous gulls. J. Appl. Ecol. 38, 791–801.
Bustnes, J.O., Miland, O., Fjeld, M., Erikstad, K.E., Skaare, J.U., 2005a. Relationship between ecological variables and four organochlorine pollutants in an artic glaucous gull (*Larus hyperboreus*) population. Environ. Pollut. 136, 175–185.
Bustnes, J.O., Skaare, J.U., Berg, V., Tveraa, T., 2005b. Interseasonal variation in blood concentrations of organochlorines in Great black-backed gulls (*Larus marinus*). Environ. Toxicol. Chem. 24, 1801–1806.
Cramp, S., Simmons, K.E.L., 1977. The Birds of the Western Palearctic, vol. I. Oxford University Press, Oxford.
D'Elbée, J., Hémery, G., 1997. Diet and foraging behaviour of the British storm petrel *Hydrobates pelagicus* in the bay of Biscay during summer. Ardea 85, 1–10.
De Brito, A.P.X., Takahashi, S., Ueno, D., Iwata, H., Tanabe, S., Kubodera, T., 2002. Organochlorine and butyltin residues in deep-sea organisms collected from the western North Pacific, off-Tohoku, Japan. Mar. Pollut. Bull. 45, 348–361.
Elliott, J.E., 2005. Chlorinated hydrocarbon contaminants and stable isotope ratios in pelagic seabirds from the north Pacific Ocean. Arch. Environ. Contam. Toxicol. 49, 89–96.
Elliott, K.H., Cesh, L.S., Dooley, J.A., Letcher, R.J., Elliott, J.E., 2009. PCBs and DDE, but not PBDEs, increase with trophic level and marine input in nestling bald eagles. Sci. Total Environ. 407, 3867–3875.
Finkelstein, M., Keitt, B.S., Croll, D.A., Tershy, B., Jarman, W.M., Rodriguez-Pastor, S., et al., 2006. Albatross species demonstrate regional differences in north Pacific marine contamination. Ecol. Appl. 16, 678–686.
Fisk, A.T., Hobson, K.A., Norstrom, R.J., 2001. Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the Northwater Polynya marine food web. Environ. Sci. Technol. 35, 732–738.
Forero, M.G., Hobson, K.A., 2003. Using stable isotopes of Nitrogen and Carbon to study seabird ecology: applications in the Mediterranean seabird community. Sci. Mar. 67, 23–32.
Froescheis, O., Looser, R., Cailliet, G.M., Jarman, W.M., Ballschmiter, K., 2000. The deep-sea as a final global sink of semivolatile persitent organic pollutants? Part I: PCBs in surface and deep-sea dwelling of fish of the North and South and the Monterey Bay Canyon (California). Chemosphere 40, 651–660.
Gómez-Díaz, E., González-Solís, J., Peinado, M.A., 2009. Population structure in a highly pelagic seabird, the Cory's shearwater *Calonectris diomedea*: an examination of genetics, morphology and ecology. Mar. Ecol. Prog. Ser. 382, 197–209.
González-Solís, J., Croxall, J.P., Oro, D., Ruiz, X., 2007. Transequatorial migration and mixing in the wintering areas in a pelagic seabird. Front. Ecol. Environ. 5, 297–301.
González-Solís, J., Felicísimo, A., Fox, J.W., Afanasyev, V., Kolbeinsson, Y., Muñoz, J., 2009. Influence of sea surface winds on shearwater migration detours. Mar. Ecol. Prog. Ser. 391, 221–230.
Granadeiro, J.P., Monteiro, L.R., Furness, R.W., 1998. Diet and feeding ecology of Cory's shearwater *Calonectris diomedea* in the Azores, north-east Atlantic. Mar. Ecol. Prog. Ser. 166, 267–276.
Guruge, K.S., Tanaka, H., Tanabe, S., 2001. Concentration and toxic potential of polychlorinated biphenyl congeners in migratory oceanic birds from the North Pacific and the Southern Ocean. Mar. Environ. Res. 52, 271–288.
Heidrich, P., Amengual, J., Wink, M., 1998. Phylogenetic relationships in Mediterranean and north Atlantic shearwaters (Aves: Procellariidae) based on nucleotide sequences of mtDNA. Biochem. Syst. Ecol. 26, 145–170.
Helberg, M., Bustnes, J.O., Erikstad, K.E., Kristiansen, K.O., Skaare, J.U., 2005. Relationships between reproductive performance and organochlorine contaminants in great black-backed gulls (*Larus marinus*). Environ. Pollut. 134, 475–483.
Hobson, K.A., Piatt, J.F., Pitocchelli, J., 1994. Using stable isotopes to determine seabird trophic relationships. J. Anim. Ecol. 63, 786–798.
Hop, H., Borga, K., Gabrielsen, G.W., Kleivane, L., Skaare, J.U., 2002. Food web magnification of persistent organic pollutants in poikilotherms and homeotherms from the Barents Sea food web. Environ. Sci. Technol. 36, 2589–2597.
Jiménez, B., González, M.J., Jimenez, O., Reich, S., Eljarrat, E., Rivera, J., 2000. Evaluation of 2, 3, 7, 8 specific congener and toxic potency of persistent polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in cetaceans from the Mediterranean Sea, Italy. Environ. Sci. Technol. 34, 756–763.
Jones, K.C., Voogt, P., 1999. Persistent organic pollutants (POPs): state of the science. Environ. Pollut. 100, 209–221.
Karen, B., Vidal, E., 2008. The endemic Mediterranean yelkouan shearwater *Puffinus yelkouan*: distribution, threats and a plea for more data. Oryx 42, 187–194.
Karen, B., Vorenger, J., Vidal, E., Faulquier, L., Legran, J., 2009. Diet and contamination of an endemic shearwater confined to the enclosed Mediterranean basin. In: Eric, S., Ratcliffe, N., Seys, J., Tack, J., Mees, J., Dobbelaere, I. (Eds.), Seeabird Group 10th International Conference. Conference Proceeding, Brugge, Belgium, 27–30 March 2009, pp. 11–12.
Karpouzi, V.S., Watson, R., Pauly, D., 2007. Modelling and mapping resource overlap between seabirds and fisheries on a global scale: a preliminary assessment. Mar. Ecol. Prog. Ser. 343, 87–99.
Kelly, J.F., 2000. Stable isotopes of carbon and nitrogen in the study of avian and mammalian trophic ecology. Can. J. Zool. 78, 1–27.
Knight, G.C., Walker, C.H., 1982. A study of the hepatic microsomal monogenase of sea birds and its relationships to organochlorine pollutants. Comp. Biochem. Physiol. 73C, 211–221.
Monteiro, L.R., Furness, R.W., 1997. Accelerated increase in mercury contamination in north Atlantic mesopelagic food chains as indicated by time series of seabirds feathers. Environ. Toxicol. Chem. 16, 2489–2493.
Monteiro, L.R., Furness, R.W., Del Nevo, A.J., 1995. Mercury levels in seabirds from Azores, Mid-North Atlantic Ocean. Arch. Environ. Contam. Toxicol. 28, 304–309.
Monteiro, L.R., Granadeiro, J.P., Furness, R.W., 1998. Relationship between mercury levels and diet in Azores seabirds. Mar. Ecol. Prog. Ser. 166, 259–265.
Monteiro, L.R., Ramos, J.A., Furness, R.W., Del Nevo, A.J., 1996. Movements, morphology, breeding, moult, diet and feeding of seabirds in the Azores. Col. Wat. 19, 82–97.
Mora, M.A., 1997. Transboundary pollution: persistent organochlorine pesticides in migrant birds of the southwestern United Sates and Mexico. Environ. Toxicol. Chem. 16, 3–11.
Mormede, S., Davies, I.M., 2003. Horizontal and vertical distribution of organic contaminants in deep-sea fish species. Chemosphere 50, 563–574.
Mouriño, J., Arcos, F., Salvadores, R., Sandoval, A., Vidal, C., 2003. Status of the Balearic shearwater (*Puffinus mauretanicus*) on the Galician coast (NW Iberian Peninsula). Sci. Mar. 67, 135–142.
Navarro, J., Louzao, M., Igual, J.M., Oro, D., Delgado, A., Arcos, J.M., Genovart, M., Hobson, K.A., Forero, M.G., 2009. Seasonal changes in the diet of a critically endangered seabird and the importance of trawling discards. Mar. Biol. 156, 2571–2578.
Neves, C.V., Bried, J., González-Solís, J., Roscales, J.L., Clark, M.R., in preparation. Feeding ecology and movements of the Macaronesian shearwater *Puffinus baroli baroli* in the Azores, NE Atlantic. Mar. Ecol. Prog. Ser.
Paiva, V.H., Xavire, J., Geraldes, P., Ramirez, I., Garthe, S., Ramos, J.A., 2010. Foraging ecology of Cory's shearwaters in different oceanic environments of the North Atlantic. Mar. Ecol. Prog. Ser. 410, 257–268.
Peakall, D.B., Jeffrey, D.A., Boersma, D., 1987. Mixed-function oxidase activity in seabirds and its relationship to oil pollution. Comp. Biochem. Physiol. 88C, 151–154.
Renzoni, A., Focardi, S., Fossi, C., Leonzio, C., Mayol, J., 1986. Comparison between concentrations of mercury and other contaminants in eggs and tissues of Cory's Shearwater *Calonectris diomedea* collected on Atlantic and Mediterranean islands. Environ. Pollut. (Ser. A) 40, 17–35.

Ricca, M.A., Miles, A.K., Anthony, R.G., 2008. Sources of organochlorine contaminants and mercury in seabirds from the Aleutian archipelago of Alaska: inferences from spatial and trophic variation. Sci. Total Environ. 406, 308–323.

Roscales, J.L., Gómez-Díaz, E., Neves, V., González-Solís, J., 2011. Trophic versus geographic structure in stable isotope signatures of pelagic seabirds breeding in the northeast Atlantic. Mar. Ecol. Prog. Ser. 434, 1–13.

Roscales, J.L., Muñoz-Arnanz, J., González-Solís, J., Jiménez, B., 2010. Geographical PCB and DDT patterns in shearwaters (*Calonectris* sp.) breeding across the NE Atlantic and the Mediterranean archipelagos. Environ. Sci. Technol. 44, 2328–2334.

Santos, R.S., Hawkins, S., Monteiro, L.R., Alves, M., Isidro, E.J., 1995. Marine research, resources and conservation in the Azores. Aquat. Conserv. Mar. Freshw. Ecosys. 5, 311–354.

Springer, A.M., Walker II, W., Risebrough, R.W., Benfield, B., Ellis, D.H., Mattox, W.G., Mindell, D.P., 1984. Origins of organochlorines accumulated by peregrine falcons, *Falco peregrinus*, breeding in Alaska and Greenland. Can. Field-Nat. 98, 159–166.

Stohl, A., Eckhardt, S., Forster, C., James, P., Spichtinger, N., 2002. On the pathways and timescales of intercontinental air pollution transport. J. Geophys. Res. 107, 4684.

Takahashi, A., Tanabe, S., Kawaguchi, K., 2000. Organochlorine and butyltin residues in mesopelagic myctophid fishes from the Western North Pacific. Environ. Sci. Technol. 34, 5129–5136.

Thompson, D.R., Furness, R.W., Monteiro, L.R., 1998. Seabirds as biomonitors of mercury inputs to epipelagic and mesopelagic marine food chains. Sci. Total Environ. 213, 299–305.

Valeiras, J., 2003. Attendance of scavenging seabirds at trawler discards off Galicia, Spain. Sci. Mar. 67, 77–82.

Walker, C.H., 1992. The ecotoxicology of persitent pollutants in marine fish-eating birds. In: Walker, C.H., Livingstone, D.R. (Eds.), Persistent Pollutants in Marine Ecosystems. Pergamon Press, pp. 195–210.

Walker, C.H., Livingstone, D.R., 1992. Persistent Pollutants in Marine Ecosystems. Pergamon Press, Oxford.

Walker, K.R., Ricciardone, M.D., Jensen, J., 2003. Developing an international consensus on DDT: a balance of environmental and disease control. Int. J. Hyg. Environ. Health 206, 423–435.

Yamashita, R., Takada, H., Murakami, M., Fukuwaka, M., Watanuki, Y., 2007. Evaluation of noninvasive approach for monitoring PCB pollution of seabirds using preen gland oil. Environ. Sci. Technol. 41, 4901–4906.