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Influence of trophic ecology on the accumulation of dioxins and furans (PCDD/Fs), non-*ortho* polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) in Mediterranean gulls (*Larus michahellis and L. audouinii*): A three-isotope approach☆

Jose L. Roscales [a, *], Alba Vicente [a], Juan Muñoz-Arnanz [a], Laura Morales [b], Esteban Abad [b], Jose I. Aguirre [c], Begoña Jiménez [a]

[a] *Department of Instrumental Analysis and Environmental Chemistry, Institute of Organic Chemistry, IQOG-CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*
[b] *Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain*
[c] *Department of Zoology and Physic Anthropology, Faculty of Biology, University Complutense of Madrid, José Antonio Novais 2, Ciudad Universitaria, 28040 Madrid, Spain*

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ABSTRACT

The impact of pollution caused by severe anthropogenic pressure in the Mediterranean Sea, an important biodiversity hotspot, requires continuous research efforts. Sources of highly toxic chemicals such as Persistent Organic Pollutants (POPs) are misunderstood in representative Mediterranean species, which limits our capability to establish proper conservation strategies. In the present study, eggs of Audouin's and yellow-legged gulls (*Larus audouinii* and *L. michahellis*) were used to investigate the trophic sources, as measured by $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$, of legacy POPs, in particular, polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) and non-*ortho* polychlorinated biphenyls (no-PCBs), as well as recently-regulated POPs, e.g., polybrominated diphenyl ethers (PBDEs). Special attention was paid to the usefulness of rarely-explored $\delta^{34}S$ ratios in explaining POP exposure in wildlife, and $\delta^{34}S$ was the isotopic ratio that best explained POP variations among gulls in most cases, thus demonstrating its usefulness for understanding POP exposure in wildlife. Significant relationships between stable isotope signatures and POP concentrations revealed increasing levels of no-PCBs and low halogenated PCDD/Fs and PBDEs in Mediterranean gulls as the consumption of marine resources increases. In contrast, highly chlorinated and brominated congeners appeared to preferentially accumulate in gulls feeding primarily on refuse from dump sites and terrestrial food webs. The use of suitable dietary tracers in the study of POPs in yellow-legged gulls revealed the importance of dump sites as a source of POPs in Mediterranean seabirds, which has not previously been reported. In contrast, the preferential accumulation through marine food webs of low chlorinated PCCD/Fs and no-PCBs, which show the highest toxic equivalents factors (TEFs), led to a significantly greater toxicological concern in Audouin's as compared to yellow-legged gulls. Audouin's gull exposure to POPs appears primarily related to the pelagic food webs commonly exploited by fisheries, highlighting the need for further research given the potential impact on human consumption.

1. Introduction

Severe impacts of marine pollution have been identified within the Mediterranean basin (Danovaro, 2003; Albaigés, 2005; Zorita et al. 2007; Coll et al. 2010). Persistent organic pollutants (POPs) in particular have been recognized for many years as a significant threat to Mediterranean wildlife, especially for top predators, given that POPs biomagnify through food webs (Jiménez et al. 2000; Albaigés, 2005; Roscales et al. 2010; Fossi et al. 2013). Among

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* Corresponding author. Dept. of Instrumental Analysis and Environmental Chemistry, Institute of Organic Chemistry, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain.
E-mail address: jlroscales@iqog.csic.es (J.L. Roscales).

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them, 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are ranked among the most toxic POPs, along with the non-*ortho* substituted polychlorinated biphenyls (no-PCBs). Several studies have shown that PCDD/F and PCB levels in the environment have declined since the 1980's in several developed regions (Alcock and Jones, 1996; Srogi, 2008) including the Mediterranean basin (Munschy et al. 2008; Augusto et al. 2015). However, significant levels, probably resulting from chronic exposure, are still reported in some Mediterranean regions, and this justifies continuous research on these pollutants (e.g. Di Leo et al. 2014; Storelli and Zizzo, 2014).

In contrast to legacy organochlorines, regulations on the use of emerging POPs, such as polybrominated diphenyl ethers (PBDEs), are more recent (Stockholm Convention, 2006), and research on their environmental presence is still imperative (Law et al. 2014). PBDEs were widely applied as flame retardants until *penta*- and *octa*-PBDE formulations were banned in most industrialized countries as of 2004 (Jinhui et al. 2015). Although several studies have related this ban with decreasing temporal trends in the presence of PBDEs associated with these formulations (e.g., Miller et al. 2014), general global temporal trends cannot be assumed. During the last decade, both increasing and decreasing temporal patterns have been described in wildlife and other environmental matrixes in developed regions such as Europe and North America (Chen and Hale, 2010; Law et al. 2014; Miller et al. 2015). Although PBDE-209, the main component of *deca*-PBDE formulation, is not yet included in the POPs list under the Stockholm Convention, bans on *deca*-PBDE production have recently been placed in developed countries (Jinhui et al. 2015). However, levels of PBDE-209, are thought to have been generally increasing in the environment during the last decade (Law et al. 2014). In agreement with those findings, studies on air and wildlife suggest that levels of PBDE-209 are increasing in the Mediterranean region (Muñoz-Arnanz et al. 2011; Roscales et al. 2013).

Many studies have demonstrated the usefulness of seabirds as bioindicators of marine pollution (Burger and Gochfeld, 2004; Roscales et al. 2010). In particular, yellow-legged and Audouin's gulls (*Larus michahellis* and *L. audouinii*) have been widely used to monitor POPs in the Mediterranean Sea (Pastor et al. 1995; Morales et al. 2012; Lacorte et al. 2014). However, to our knowledge, no studies on the trophic factors driving POP exposure in these species have been conducted yet, and never on an individual-level basis. This is particularly relevant because diet constitutes the main source of POPs in birds, and dietary habits of yellow-legged and Audouin's gulls vary markedly between species as well as across their distribution (González-Solís et al. 1997a; Ramos et al. 2011). Trophodynamics of POPs in gulls can be addressed by using dietary tracers such as stable isotope ratios of carbon, nitrogen, and sulfur ($\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$), because ratios in consumers reflect those of their prey in a predictable manner (Kelly, 2000). $\delta^{15}N$ has commonly been used to delineate biomagnification and bioaccumulation of POPs (Hop et al. 2002). $\delta^{13}C$ provides information about the origin of resources exploited by consumers (e.g., $\delta^{13}C$-terrestrial < $\delta^{13}C$-marine ecosystems) and thus, the potential trophic sources of POPs (Chen et al. 2012). $\delta^{34}S$ has been proven to be very useful for addressing trophic preferences and pollutant sources in gulls, because sulfur ratios provide better discrimination than $\delta^{13}C$ when several land-based and aquatic resources, such as refuse, terrestrial, continental water, and marine items, are involved (Moreno et al. 2010; Ramos et al. 2013). Although relatively common in trophic studies, to our knowledge, $\delta^{34}S$ has not yet been evaluated to address trophodynamics of POPs in birds.

In the present study, stable isotope ratios of C, N, and S, and concentrations of PCDDs, PCDFs, no-PCBs, and PBDEs were measured in individual eggs of yellow-legged and Audouin's gulls breeding sympatrically in the Chafarinas Islands, SW Mediterranean. We aimed to investigate the influence of trophic ecology of gulls on their exposure to POPs, and to provide a more comprehensive view of their role as potential bioindicators in the Mediterranean basin than in previous studies. Because POP studies in seabirds have not previously explored the potential of $\delta^{34}S$, special attention was paid to the usefulness of adding S ratios to the commonly-used $\delta^{13}C$ and $\delta^{15}N$. In addition, temporal variations and potential toxicological implications related to POPs in Mediterranean gulls are evaluated.

2. Materials and methods

2.1. Sampling design and studied species

A total of 19 and 18 eggs from Audouin's and yellow-legged gulls, respectively, were analyzed in the present study. Samples were collected during the 2007 breeding season in the Chafarinas Islands (35°10′ − 35°11′N and 2°24′− 2°27′W), which are located close to the North African coast of Morocco within the Alboran Sea, SW Mediterranean (supplementary material, Fig. S1). The breeding season of these gulls spans about four months, and eggs were collected during the first days of the laying period, in early March and early April, for yellow-legged and Audouin's gulls, respectively. The collection of eggs used in this study was previously used to assess emerging contaminants such as Dechlorane plus and further details on sampling procedure can be found in Muñoz-Arnanz et al. (2012).

In the Mediterranean, the yellow-legged gull is considered a superabundant and highly-opportunistic predator that can feed on a wide array of terrestrial and marine resources, as well as on food items derived from human activities (Ramos et al. 2009). In contrast, Audouin's gull is a scarce and endemic Mediterranean species that mainly feeds on epipelagic fish prey and fishery discards (Arcos et al. 2001). Outside of the breeding season, the yellow-legged gull is considered to be a non-migratory and dispersive species (Sol et al. 1995). Audouin's gulls are known to visit NW Atlantic waters, although a portion of the population remains in the Mediterranean (Sanpera et al. 2007). Nonetheless, both species are considered income breeders (Ruiz et al. 1998; Ramírez et al. 2010). Therefore, isotope ratios and pollutant levels in eggs are expected to reflect gull diets and pollutant sources mainly from their breeding area.

2.2. Stable isotope analysis (SIA)

About 0.36 mg (weighed to the nearest μg) of dried lipid-free egg were placed into tin cups for $\delta^{15}N$ and $\delta^{13}C$ analysis (see further details on sample preparation in Muñoz-Arnanz et al. 2012). Additionally, 3.60 mg of sample were used to determine $\delta^{34}S$ values. Analyses were carried out in the Serveis Científico-Técnics of the University of Barcelona. Stable isotope ratios were determined by means of elemental analysis-isotope ratio mass spectrometry (EA-IRMS) using a Carlo-Erba Flash 1112 series elemental analyzer coupled to a Finnigan Delta C isotope ratio mass spectrometer by means of a Thermo Finnigan MAT ConFlo III interface. Stable isotope ratios were expressed as δ values in parts per thousand (‰) relative to atmospheric nitrogen (AIR; $\delta^{15}N$), Vienna Pee Dee Belemnite (VPDB; $\delta^{13}C$), and Vienna Cañon Diablo Troilite (VCDT; $\delta^{34}S$). Three reference materials (International Atomic Energy Agency, IAEA) were analyzed every 12 samples to calibrate the equipment and correct potential shifts over time (detailed data in the supporting information, Table S1).