



## Presence and impact of Stockholm Convention POPs in gull eggs from Spanish and Portuguese natural and national parks

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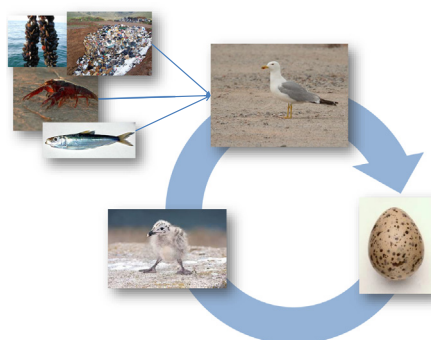
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### HIGHLIGHTS

- POPs were detected in gull eggs from 10 colonies in the Iberian Peninsula.
- The protected species *L. audouinii* had higher levels of POPs than *L. michahellis*.
- Differences in eggshell parameters were found among colonies.
- No correlation was found between eggshell parameters and POPs levels.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The aim of the present work was to comparatively assess the occurrence and impact of persistent organic pollutants (POPs) in nine natural and national parks from Spain and Portugal using gull eggs (*Larus michahellis* and *L. audouinii*) as bioindicators of environmental contamination. Sampling was performed during the breeding season of 2016. Compounds studied include polychlorinated biphenyls (PCBs), organochlorinated pesticides (OC pesticides), perfluorooctane sulfonic acid (PFOS) and polybrominated diphenyl ethers (PBDEs), and were analyzed using mass spectrometric based techniques. The results showed a high contamination by PCBs in all colonies, with total levels ranging from 59 to 1278 ng/g wet weight (ww), despite their use is not currently authorized. OC pesticides were also present in all colonies, with a high incidence of 4,4'-DDE in gull eggs at levels up to  $218 \pm 50$  ng/g ww in *L. michahellis* and  $760 \pm 412$  ng/g ww in *L. audouinii* from the Ebro Delta natural park. PBDEs and PFOS were also detected at levels up to  $91.7 \pm 21.3$  ng/g ww, which can be attributed to a more recent use. Except for PBDEs, the POP levels in eggs from *L. audouinii* were higher than in *L. michahellis*, presumably associated to the fish-based diet of the former. Finally, the effect of POP levels on eggshell parameters (volume, eggshell thickness and desiccation index) were investigated for each colony and gull species in order to evaluate the egg viability and, therefore, the reproduction success.

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## 1. Introduction

Nowadays many habitats are strongly affected by anthropogenic and environmental pressures which can affect the wellbeing of many species. National and natural parks are protected spaces meant to maintain the functioning of the natural ecosystems and act as refuge for many species, as a migratory reserve for numerous birds and as breeding areas. These spaces have a high degree of protection in order, among others, to avoid and minimize any anthropogenic activity that can alter the landscape, the integrity and the evolution of their natural systems, as well as to prevent the impact of pollution. However, these habitats are strongly affected by environmental pollution caused by different families of persistent organic pollutants (POPs) (Vicente et al., 2012; Morales et al., 2016).

Seabirds are commonly used as sentinel species for monitoring POP levels in the marine environment since they are widespread and sensitive to environmental changes. Among birds, gulls have been reported as excellent bioindicators of POPs (OSPAR, 2000; Fliedner et al., 2012) as they reflect the contamination pattern of an area. Gull species have the following characteristics: (i) they have a long lifespan (up to 20 years) and accumulate the contaminants through food which are thereafter transferred to the eggs; (ii) gulls are secondary consumers and apex organisms, and are able to biomagnify the POPs of the sea-shore food chain; (iii) they are colonial breeders and exhibit high levels of breeding philopatry, so they reflect the contamination of a given area; (iv) they are widespread around the world and are able to reflect geographical distribution of POPs; (v) many gull species, especially *Larus michahellis*, are non-protected species whose eggs represent a non-invasive and simple sampling protocol due to the large colonies settled in many coastal areas.

Spain and Portugal host several maritime-terrestrial natural and national parks along the Atlantic and Mediterranean shores, where birds have an important ecological role. These locations are considered by the Directive 2009/147/EC on the conservation of wild birds (European Community Commission, 2009) as Special Protection Areas (SPAs), Sites of Community Importance (SCIs) and/or Special Areas of Conservation (SACs), which host a large number of bird species and a huge biodiversity. Despite the high degree of protection of natural and national parks, they are often affected by human activities related to tourism, harbor and maritime activities, agriculture and hunting, and even industries are emplaced in the surroundings. This results in the input of contaminants via pesticide treatments, discharges of wastewater treatment plant effluents, marine outfalls or run-off. Over the years, the different degrees of anthropogenic pressures have posed these rich ecosystems at risk and this may affect the bird populations. In Spain, birds have been exposed to chemicals used in the past by the industry (e.g., PCBs or perfluorinated compounds) (Gonzalez et al., 1991; Vicente et al., 2012) and agriculture (e.g., organochlorine pesticides) (Jiménez et al., 2007; Merino et al., 2005; Muñoz-Arnanz and Jiménez, 2011). Their presence at relatively high concentrations in the environment can impair neurodevelopment, endocrine, reproductive and survival effects (Gonzalez, 1988; Iwaniuk et al., 2006; Ortiz Martinez and Martinez-Conde, 1995), and in extreme cases, mortality. These findings reinforce the necessity of a better knowledge on the presence of POPs in sensitive areas which are refuges for numerous bird species.

Thus, the aim of this study was to evaluate the occurrence of several families of POPs using gull eggs from the opportunistic *L. michahellis* as bioindicators of pollution and to compare the levels with the protected species *L. audouinii*. Studied areas include nine natural and national parks spread over Portugal and Spain. The POPs considered in this study include marker-PCBs, PBDEs, OC pesticides and PFOS, which are included in the Stockholm Convention (2009). The potential risks of POPs on eggshell thickness and egg size have also been evaluated.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Standard Pesticide Mix 1 containing aldrin,  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -hexachlorocyclohexane (HCH),  $\alpha$ - and  $\gamma$ -chlordane, 2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, dieldrin,  $\alpha$ - and  $\beta$ -endosulfan, endrin, heptachlor, heptachlor *exo*- and *endo*-epoxides, hexachlorobenzene (HCB), isodrin, methoxychlor, mirex, and oxychlordane, at a concentration of 10  $\mu$ g/mL and the PCB congeners: 28, 52, 101, 138, 153 and 180, at 1  $\mu$ g/mL in toluene, were purchased from AccuStandard (New Haven, CT, USA). Dicofol was also obtained from AccuStandard (New Haven, USA) at a concentration of 100  $\mu$ g/mL in methanol. Endosulfan sulphate (20  $\mu$ g/mL in methanol) was supplied by Supelco (Bellefonte, PA, USA), while hexachlorobutadiene (5000  $\mu$ g/mL in methanol) and pentachlorobenzene (solid, 98% purity) were acquired from Sigma-Aldrich (St. Louis, MO, USA). PBDE standard mixture containing the following congeners: PBDE 28, 47, 99, 100, 153, 154, 183 (1  $\mu$ g/mL), and PBDE 209 (10  $\mu$ g/mL) in nonane/toluene was purchased from Wellington Laboratories (Guelph, Canada). The surrogate standards used for quantification were:  $^{13}\text{C}_6$ -hexachlorobenzene (100  $\mu$ g/mL in acetone) and PCB 209 (10  $\mu$ g/mL in cyclohexane), both acquired from Dr. Ehrenstorfer (Augsburg, Germany),  $^{13}\text{C}_{12}$ -4,4'-DDE at a concentration of 100  $\mu$ g/mL in nonane,  $^{13}\text{C}_{12}$ -PBDE 77 (50  $\mu$ g/mL) supplied from Cambridge Isotope Laboratories (Andover, MA, USA), and PCB 65 (solid, 98% purity), purchased from AccuStandard. Sodium perfluorooctane sulfonate (PFOS) at a concentration of 2  $\mu$ g/mL in methanol as well as its labeled surrogate internal standard used for quantification, sodium perfluoro-1-(1,2,3,4- $^{13}\text{C}_4$ ) octane sulfonate (m-PFOS) at 50  $\mu$ g/mL in methanol, were supplied by Wellington Laboratories (Ontario, Canada).

For the clean-up of extracts, Strata FL-PR Florisil cartridges, 10 g/60 mL Giga tube (170  $\mu$ m particle diameter and 80 Å pore size), were supplied by Phenomenex (Torrance, CA, USA). Active charcoal (120–400 mesh) was from Supelco (Bellefonte, PA, USA). Dichloromethane, n-hexane and isooctane, for gas chromatography analysis, and water and acetonitrile of HPLC grade were purchased from Merck (Darmstadt, Germany). Glacial acetic acid was provided by Panreac (Barcelona, Spain). Nitrogen for the evaporation of the sample extracts (purity>99.995%), helium (purity>99.9995%) as carrier gas for GC separation, and ammonia (purity>99.995%) as moderate gas for gas chromatography-electron capture negative ionization-mass spectrometry (GC-ECNI-MS) determination, were supplied by Air Liquid (Barcelona, Spain).

### 2.2. Study areas

The natural and national parks studied host the main gull colonies of Spain and Portugal (Fig. 1). The sampling sites and their main characteristics are described from northern Atlantic colonies to northern Mediterranean.

The National Park of Atlantic Islands of Galicia (thereafter Atlantic Islands) is located in the north-west of Spain and is composed of three archipelagos (Ons, Cíes and Sálvora). Its environmental value lies on its geographical position, because it protects the Galician coast and its estuaries from the ocean's tides, creating a unique and rich ecosystem. Aquaculture activities represent a very important sector in the area with cultivation of shellfish and sea fish. Moreover, many industrial and transport activities are carried out in the surroundings, including a chlor-alkali industry that produced organochlorine pesticides until their ban around 1977. The yellow-legged gull (*Larus michahellis*) is the most abundant species with >15,000 pairs in Cíes Islands in 2004 (Molina and Bermejo, 2009).

Berlengas is a group of three islets located about 10–15 km away of Portugal coast, in front of Peniche town close to Lisbon. They were declared as Biosphere Reserve by UNESCO in 2011 and host around 8500 breeding pairs of yellow-legged gulls (Ceia et al., 2014).

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