Comunicaciones

IV REUNIÓN NACIONAL DE DIOXINAS, FURANOS Y COMPUESTOS ORGÁNICOS PERSISTENTES RELACIONADOS

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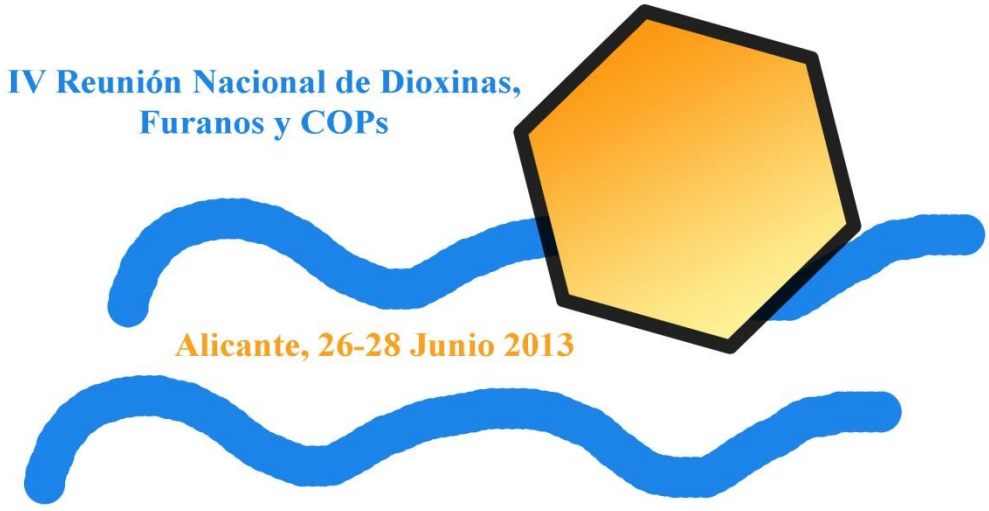

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POLYCHLORINATED DIBENZO-p-DIOXINS, DIBENZOFURANS ANDBIPHENYLS, AND CHLORINATED PARAFFINS IN GULL EGGS (*Laurus*michahellis)FROM SPANISH NATIONAL PARKS

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Introduction

In recent years there has been a growing concern about the risks associated with the presence of persistent organic pollutants (POPs) in marine-terrestrial ecosystems. These compounds are toxics and ubiquitous pollutants in the environment and tend to be bioaccumulated into the fat tissues of living beings, and to be biomagnified through the food web.[1]

Seabirds have been commonly used as sentinel species for monitoring the levels of POPs in the marine environment because they are very widespread and are sensitive to the environmental changes.Thus, they may be exposed to relatively high concentrations of these environmental contaminants and are able to integrate pollutant levels over a large area by bioaccumulation.Studies in bird-breeding areas of special protection have reported unexpected high levels of polychlorinated byphenyls (PCBs), several organochlorine pesticides (e.g., DDTs, DDE and hexachlorocyclohexane isomers), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), dioxin-like PCBs (dl-PCBs) and flame retardants.[2-5]These findings reinforce the necessity of a better knowledge of the presence of halogenated compounds on sensitive areas which are refuges for numerous wildlife bird species.To assess the levels and trends of POPs, bird eggs have been proposed to assess the levels ofPOPs.At least within species, POP levels in eggs reflect the contaminant burden of the female at the time of egg laying, especially the uptake of contaminants from food recently ingested around the colony, although some contaminants may derive from the previously accumulated levelsin the adipose tissue.[5]

The aim of this study was to evaluate the occurrence of several POP families in gull eggs (*L. michaellis)* from three Spanish gull colonies located in Atlantic Islands of Galicia National Park, the Cabrera Archipelago National Park and the National Hunting Refuge of Chafarinas Islands, as part of an ongoing monitoring project devoted to evaluate the presence of these pollutants in areas of special protection. The POPs considered in this study include priority contaminants, such as PCDD/Fs, dioxin-like PCBs and marker PCBs, and other emerging pollutants, such as short-chain chlorinated paraffins (SCCPs), recently listed by the Stockholm Convention as candidate to a new persistent organic pollutant. The results and conclusions of this study are presented here.

Materials and Methods

Analytical method

Analysis of PCDD/Fs and dl-PCBs was performed following the USEPA 1613 and 1688 methods, respectively. After addition of the $^{13}C_{12}$-PCDD/Fs$^{13}C_{12}$-dl-PCBs to the sample, ten grams of freeze-dried sample were Soxhlet extracted using a toluene:cyclohexane solvent mixture (1:1) and the purification of the extracts was accomplished using the automated clean-up Power-Prep™ System (FMS, Waltham, M.A., USA)based on the use of multilayer silica, basic alumina and PX-21 carbon sorbents. For SCCP and marker PCB analyses, a simultaneous extraction and clean-up method based on selective pressurized liquid extraction (sPLE), using acidic silica (20%, w/w) as fat retainer was applied.

Samples
Eggs of yellow-legged gull (*L. michahellis)* were collected at the beginning of the breeding season from three colonies located atthe Atlantic Islands of Galicia National Park (Galicia, north-west of Spain), the Cabrera Archipelago National Park (Balearic Islands, east of Spain) and the National Hunting Refuge of Chafarinas Islands (south of Spain), during the time period 2010-2012. For each colony and year, 12 eggs were randomly collected from three sub-colonies (36 eggsin total per colony and year). To ensure that the reproductive potential of each nest was maintained, only the first egg of each nest was sampled. The eggs were transported to the laboratory in a cool box and the eggs of each sub-colony were then pooled, freeze-dried and stored at -20ºC before analysis.

Instrumental Analysis
PCDD/F and dl-PCB analyses were performed on a Trace GC Ultra gas chromatograph (Thermo Fisher Scientific, Milan, IT) coupled to a DFS(Thermo Fisher Scientific, Bremen, Germany) high resolution mass spectrometer controlled by a Xcalibur data system and operating in selected ion monitoring (SIM) mode at resolving power of 10,000 (10% valley definition). Separation was accomplished using a DB-5ms (Agilent, Palo Alto, CA, USA) fused-silica capillary column (60 m x 0.25 mm I.D., 0.25 µm film thickness). Quantification of PCDD/Fs and dl-PCBs was carried out using isotopic dilution method. Short-chain chlorinated paraffins (SCCPs) and marker PCBs were analysed on a Trace GC 2000 series gas chromatograph coupled with a DSQIIquadrupole mas spectrometer (Thermo Fisher Scientific, Milan, IT) operating in negative ion chemical ionisation (methane as moderating gas) and electron ionisation, respectively. Chromatographic separation of SCCPs and marker PCBs was performed using a 15 m and 60 m x 0.25 mm I.D., 0.25 µm of film thickness DB-5 ms capillary column (Agilent), respectively. Quantification of marker PCBs was performed by isotopic dilution, while for SCCPs internal standard method was selected, using $^{13}C_6$-hexachlorobenzene as surrogate standard.

Results and Discussion

PCDD/Fs, dl-PCBs, SCCPs and marker PCBs were determined in all yellow-legged gull eggs collected in the three colonies studied. Among them, marker PCBs were the compounds found at the highest concentrations, with a contribution to the total contaminants of 91% in Chafarinas Islands, 78% in Atlantic Islands of Galician and 83% in the Archipelago of Cabrera. Total PCB concentrations, expressed as sum of six marker PCBs, ranged from 171.8 ng/g wet weight (ww) (Galician Atlantic Islands in 2011) to 1405 ng/g ww (Chafarinas Islands in 2011). Comparing these results with those reported for similar samples collected in 1995, a slightly decreasing on the PCB levels can be observed, as occur with PCDD/Fs and dl-PCBs. Among marker PCBs, CB-153 was the most predominant congener, followed by CB-180 and CB-138. These results may suggest a contamination produced by a PCB formulation of high chlorinated degree.

Regarding PCDD/Fs and dl-PCBs, concentration levels ranging from0.197 to 1.30 pg WHO-TEQ/g wwfor PCDD/Fs and between 3.16 and 10.2 pgWHO-TEQ /g wwfor dl-PCBs were determined. For all egg samples, OCDD was the most predominant congener among PCDD/Fsdetected at concentrations ranging from 0.87 to 26.5 pg/g ww, while for dl-PCBs, a clear predominance of CB-118 (5.01-23.9 ng/g ww), followed by CB 156, 105 and 167,was observed, suggesting that Aroclor 1260 was the main PCB mixture responsible of the contamination.For SCCPs, they were almost detected in all samples at concentrations ranging from 4.52 to 16.7 ng/g ww and it is the first time these compounds are identified in seagull eggs from the Iberian Peninsula. Comparing with the results obtained in the three colonies, the highest concentrations of the target compounds were detected in eggs collected in Cabrera Archipelago, mainly due to the high contribution of PCBs, followed byChafarinas and Atlantic Islands. During the period of the study (2010-2012), a low temporal variation on the concentrationsof POPs studied was observed, indicating a diffuse contamination but also constant produced by the effect of anthropogenic activities developed near of these protected areas.

Conclusions

Generally, the POP levels found in egg samples collected at the three gull colonies are relatively high, especially for PCBs, and their presence may pose a risk to the development of the eggs, the chicks or of the colony survival. The variability of concentrations within one species or among species can probably be attributed to different feeding habits, seasonal variation of food composition, age and condition of the birds. Gull eggs have shown to be a suitable matrix for

the biomonitoring of POPs and they permit to evaluate the contamination impact of a local area.In addition, collection of eggs is a relatively non-invasive technique that can minimize the adverse effects on the bird community. It is early to evaluate the effects that these contaminants may produce to the gulls, but considering the neurotoxicity, carcinogenicity and endocrine disruption effects of detected POPs, additional studies should be launched to assess the sources and fate of these pollutants and to take actions to minimize their impact upon birds, especially for protected species.

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References

1. Fries GF. *Journal of Animal Science,* 1995; 73:1639.
2. Gómara B, González MJ, Bao R, Hiraldo F, Abad E, Rivera J, Jiménez B. *Environmental*International, 2008; 34:73-78.
3. Bordajandi R, Abad E, Rivera J, Jiménez B. *EnvironmentalToxicology and Chemistry*, 2005; 24: 2088-2093.
4. Muñoz-Arnanz J, Sáez M, Aguirre JI, Hiraldo F, Baos R, Pacepavicius G, Alaee M, Jiménez B. *Environmental International*, 2011; 37:572-576.
5. Jiménez B, Merino R, Abad E, Rivera J, Olie K. *EnvironmentalScience and PollutionResearch*, 2007; 14:61-68.
6. Antoniadou V, Konstantinou K, Gouther V, Sakellarides, TM, Albanis, TA, Bintoudi E. *Archive Environmental Contamination and Toxicology*, 2007; 53:249-260.