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Influence of diet in the accumulation of organochlorine compounds in herons breeding in remote riverine environments

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HIGHLIGHTS

- Organochlorine compounds (OCs) accumulate more in egrets feeding on aquatic preys.
- Lower OC accumulation is found in egrets that feed on aquatic and terrestrial preys.
- OCs of low biomagnification potential do not show selective accumulation in egrets.
- The diet differences between species are confirmed with the $\delta^{13}C$ and $\delta^{15}N$ ratios.
- p,p'-DDT in cattle egret is maybe still showing influences of past agriculture use.

GRAPHICAL ABSTRACT

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ABSTRACT

The composition of organochlorine compounds (OCs), pentachlorobenzene (PeCB), hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), DDTs and polychlorobiphenyls (PCBs), has been analyzed in eggs from cattle egret (*Bubulcus ibis*) and little egret (*Egretta garzetta*), two species of herons (family *Ardeidae*), nesting at the same remote riverine environment (Aiguabarreig, Ebro River). These two species were selected to evaluate the importance of diet in the accumulation of OCs. Cattle egret essentially feeds on dry grassy habitats and follow cattle or other large animals whereas little egret feeds on fish, amphibians and crustaceans captured in shallow waters. The $\delta^{15}N$ and $\delta^{13}C$ isotopic composition of the sampled eggs was studied and the results were consistent with these species feeding habits. In both species, the compounds accumulated the most were the less volatile and more lipophilic, e.g. PCB congeners of higher chlorination, DDT and metabolites. The distinct foraging species preferences were reflected in significant higher concentrations in little egret than cattle egret of all pollutant groups analysed. These differences were statistically significant for DDTs and PCBs ($p < 0.015$ and $p < 0.047$, respectively), e.g. the p,p'-DDE and PCB concentrations were 6 and 4.5 times higher, respectively, in the former than the latter. This strong contrast indicates that in remote environments aquatic riverine ecosystems are more efficient OC reservoirs than the terrestrial ecosystem.

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1. Introduction

Aquatic ecosystems are crucial environments during the breeding season of a great number of birds which obtain protection and feeding opportunities between reedbeds, bushes, trees or mangroves. Unfortunately, birds living in these environments accumulate organochlorine compounds (OCs) which may compromise reproduction and species survival. Thus, p,p'-DDE has been described to generate deleterious effects such as low eggshell thickness, embryo mortality and chick malformations (Aurigi et al., 2000; De Luca-Abbot et al., 2001). In birds of prey, decreases in eggshell thickness and reproduction impairment have been observed for p,p'-DDE egg concentrations above 2 μg/g ww (Pain et al., 1999).

In some species of herons, reproduction disturbances, mainly non-viable eggs, and chick mortality have been observed for 2 and 3.5 μg/g ww (Thomas and Anthony, 1999; McEwen et al., 1984). The effects of polychlorobiphenyls (PCBs) and other organochlorine compounds are difficult to assess independently from those of DDTs. The lowest observable effect concentration (LOEC) for total PCBs in cormorants for reproductive success was observed to be 3.5 μg/g ww (Tillitt et al., 1992) and 30 μg/g ww were correlated with embryo mortality (Sakellarides et al., 2006; Verreault et al., 2006; Erikstad et al., 2011).

The specific properties of these pollutants, namely their chemical stability and lipophilicity, has led to their widespread occurrence in all continental ecosystems, including the most remote sites (Grimalt et al., 2001). These properties also involve increasing accumulation along the food chain and highest concentrations in the high predators (Catalan et al., 2004). Bird predators may therefore be used as sentinel organisms of the pollution burden of the food webs that sustain them. Attempts to identify specific food web effects have been rarely addressed. Comparison of concentrations of OCs between top bird predators may be confounded by metabolic differences between species or differences in the concentrations of OCs in the environments where they live, among other aspects.

This topic has been addressed in the present study by comparison of the OC concentrations in cattle egret (*Bulbucus ibis*) and little egret (*Egretta garsetta*), two species of herons (family *Ardeaide*), living in one remote riverine site, Aiguabarreig (Ebro River, 41°23′59″N, 0°19′38″E). This site is a freshwater swamp containing shallow waters and has a high ecological value as breeding zone for migratory species. The location is full of islands surrounded by slow waters and extended riparian forests that make it especially suitable for waterbirds that nest in aquatic environments. It is formed at the confluence of Segre and Cinca, two tributaries of the Ebro River (Fig. 1). The river discharges into the Mediterranean Sea forming a large Delta that has been catalogued as an UNESCO wildlife and bird reserve (Pastor et al., 2004). Fig. 1 shows some key areas from the Ebro River containing heron colonies.

Cattle egret is usually found in woodlands near lakes or rivers, in swamps or in small inlands, sharing space with other wetland birds. Unlike most other herons, it feeds in relatively dry grassy habitats, often accompanying cattle or other large mammals, since it catches insects, spiders, earthworms and small vertebrates disturbed by these animals (Telfair and Raymond, 2006). Little egret prefers platforms of sticks in trees or shrubs and sometimes reed beds or bamboo groves (BirdLife International, 2011). This species commonly share breeding zones with cattle egret but it preferably eats fish, amphibians and crustaceans which are captured in shallow waters nearby the nesting zone. In Catalonia, both species are found in irrigated herbaceous crops and wetlands located between 0 and 200 m above sea level (ICO, 2011a and b).

The stable isotope signatures of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) were studied to evaluate assimilated, and not only ingested, diet. These signatures have been extensively used in studies of waterbird communities (Hobson et al., 2000; Ramírez et al., 2011; Rodríguez et al., 2013). $\delta^{15}N$ reflects the trophic level, with consumer signatures being higher than in their prey whereas information on the carbon sources entering into the food webs can be obtained from $\delta^{13}C$ (Hobson, 1999).

The two selected heron species live in the same remote environment under the influence of long-range OC transport. Comparison of the OC concentrations in their eggs offers an opportunity for identification of specific food web effects on the accumulation of OCs in these top predators. This approach is particularly important in studies from southern Europe given the limited information on pesticide and PCB contamination of *Ardeidae* in this world region (Focardi et al., 1988; De Cruz et al., 1997; Sakellarides et al., 2006).

2. Material and methods

2.1. Sampling

Eighteen eggs were collected during the spring season of 2006 at Aiguabarreig. Half belonged to cattle egret and half to little egret. Eggs were collected in different nests in each colony. The smallest egg was selected in each laying. They were labelled and kept refrigerated during transport to the laboratory where they were stored frozen (−20 °C) until analysis. Egg content was separated from the eggshell, weighed, and placed into a glass container for freeze-drying. Freeze-dried samples were homogenized and two sample aliquots were used, one for OC analysis and the other for stable isotope determinations.

2.2. Isotope analysis

The samples for isotope analysis were extracted with methanol and chloroform. Lean sub-samples (ca. 0.36 mg) were placed in tin buckets and crimped for combustion. The instrumental determinations were carried out by elemental analysis-isotope ratio mass spectrometry using a Thermo Finnigan Flash 1112 elemental analyser coupled to a Delta isotope ratio mass spectrometer via a CONFLO III interface.

The stable isotope ratios were expressed in conventional notation as parts per thousand (‰) following the equation: $\delta X = [(R\ sample/R\ standard) - 1]^*1000$, where X is ^{15}N or ^{13}C and R is the corresponding $^{15}N/^{14}N$ or $^{13}C/^{12}C$ ratio. The standards for ^{15}N and ^{13}C were atmospheric nitrogen and Pee Dee Belemnite, respectively. Precision and accuracy for the $\delta^{13}C$ and $\delta^{15}N$ measurements were $\leq$0.1‰ and $\leq$0.3‰, respectively. The laboratory used the following international standards that were run every 12 samples: IAEA CH7 (87% of C), IAEA CH6 (42% of C) and USGS 24 (100% of C) for ^{13}C and IAEA N1 and IAEA N2 (with 21% of N) and IAEA NO3 (13.8% of N) for ^{15}N.

2.3. Sample preparation and clean up for OC analysis

The individual eggs samples (1.5 g) were ground with activated sodium sulphate until a fine powder was obtained. The powder mixtures were then introduced into previously cleaned cellulose cartridges (24 h in Soxhlet). These mixtures were Soxhlet-extracted with 100 mL of n-hexane–dichloromethane (4:1 v/v) for 18 h. At this step, 1,2,4,5-tetrabromobenzene (TBB) and PCB-200 were added as recovery standards. The lipid content of all samples was determined gravimetrically from an aliquot of the extract. The rest of the extract was concentrated under vacuum to 2 mL and 2 mL of sulphuric acid were added. After vigorous stirring in a Vortex-mixer