RECENT CHANGES IN HCB AND PCB LEVELS IN HERRING GULL (*LARUS ARGENTATUS*) AND AUDOUIN'S GULL (*LARUS AUDOUINII*) EGGS FROM THE NORTH WESTERN MEDITERRANEAN

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Introduction

During the last decades, considerable amounts of organic compounds, such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), have released into the environment as a consequence of agricultural and industrial development. Seabirds and their eggs have been proved suitable tools for monitoring environmental contamination, occupying high trophic levels.[1,2] Concentrations of chemicals in eggs tend to reflect pollutants uptake of female foraging in the few days prior to egg laying. In fact organochlorine compounds are conveyed from mother to eggs via lipids in varying quantities depending on the bird species (in Herring gulls the 24% of maternal PCBs are transferred to eggs).[3]

In this study levels of polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) were measured in eggs of Herring gull (*Larus argentatus*) and Audouin's gull (*Larus audouinii*) breeding in the Mediterranean Sea, in order to compare the accumulation of these compounds in two species of gulls with different ecological niches. The Herring gull is a scavenger species that feeds mainly at garbage dumps and/or on products derived from human activity, while the Audouin's gull often inhabits areas which are distant from human habitation and feeds mainly on fish and marine items.[4] Since 1970s several studies have been carried out to determine the levels of PCBs and OCPs in seabird eggs in the Mediterranean Sea and in other areas of the world.[4,5]A further aim of this study was to evaluate a possible temporal change in OC levels found in gull eggs since similar studies were conducted on egg samples collected from Capraia Island in the Tuscan Archipelago from 1981 to 1986.[4,5]

Materials and Methods

Collection of Samples. Unhatched eggs of Herring gull and Audouin's gull (n = 20 and n = 13, respectively) were collected during bird census under licence from two islands in the Tuscan Archipelago (Giannutri Island and Pianosa Island, respectively) between the years 2004-2005. The eggs were wrapped in aluminium foil, placed on a cotton-spread carton and brought to the laboratory in Siena, where they were kept frozen (-20°C) until freeze-dried and homogenized (shell excluded) prior to start the analysis.

Analysis of chlorinated compounds. PCB congeners and HCB were analyzed following the method described elsewhere, with some modifications.[6,7] These chemicals were identified and quantified using a gas chromatograph (Perkin Elmer mod. Autosystem) equipped with ^{63}Ni electron capture detector (GC-ECD); capillary column coated with DB-5 (Supelco Inc.). Blanks were analyzed throughout the analytical procedure to check for interference and laboratory contamination. Recoveries and detection limits were previously described and validated.[6] PCB congeners are represented by their IUPAC numbers throughout the text. ∑PCBs were calculated as the sum of the principal congeners identified (43 congeners). Results are given on a dry weight basis (dry wt).

Results and Discussion

PCBs and HCB levels. Results are showed in Table 1. ΣPCB average concentrations were five time higher in Audouin's gull than in Herring gull (4805.7 ng/g dry wt and 927.3 ng/g dry wt, respectively). In the Mediterranean Sea fish-eating birds exhibit higher amounts of total PCBs than scavenger species, [5,8] because an additional trophic level transfer increases the bioaccumulation. Moreover the enzymatic detoxifying systems in the fish-eating birds seem to be deficiently developed.[9,10]

The PCB class of isomers composition was similar in the two species (Figure 2) and the isomer specific pattern was: hexa-CBs > hepta-CBs > octa-CBs > penta-CBs > tetra-CBs > nona-CBs in both species. Hexa- and hepta-CBs account for over 70% of the total PCB residue in eggs of both species. Their concentrations were 383.2 ng/g dry wt and 367.5 ng/g dry wt, respectively, in Herring gull eggs, and 2260.1 ng/g dry wt and 1904.7 ng/g dry wt in Audouin's gull eggs.

PCB fingerprints were similar in the two species (Figure 1). The most abundant PCB congeners were the IUPAC numbers 153 > 180 > 138 > 170 and collectively they accounted for 56-61% of the total content of PCBs in Herring gull and Audouin's gull eggs. These congeners were found in highest levels in seabird eggs from the Mediterranean Sea[1,8,11,12] and worldwide[13,14]. This fact seems to be due to the persistency and bioaccumulative properties of these congeners. In fact PCB congeners with no adjacent unsubstituted *meta* and *para* positions on the biphenyl ring are eliminated very slowly.[3,9,12]

HCB levels were slightly more elevated in Herring gull than in Audouin's gull eggs (28.0 ng/g dry wt and 21.6 ng/g dry wt, respectively). HCB concentrations were lower than those found in eggs of *L. argentatus* and other species of birds from the Barents Sea.[15] HCB concentrations were lower than those of PCBs, one order of magnitude in Herring gull and two order of magnitude in Audouin's gull eggs. This organochlorine accumulation pattern is similar to that found in seabirds eggs from other areas of the world.[2,14]

In eggs of Audouin's gull (n = 11) collected along the western coast of Sardinia in 2004, ΣPCB and HCB average concentrations were 5845.9 ng/g dry wt and 44.1 ng/g dry wt, respectively (data not published). These values were higher than those found in this study and probably due to differences in the foraging grounds of colonies. PCB levels in eggs of Audouin's gull reported by Goutner *et al.* for birds breeding in the Eastern Mediterranean were lower than those of this study. Also OC levels recorded in birds from Danube Delta were lower than those found in Audouin's gull eggs.[14] However it is difficult to compare our results with those given by other authors who have analysed OC pollutants in eggs of seabirds, since units are reported sometimes on wet and sometimes on dry weight basis. Moreover sample size, sampling procedures (as the collection of first or second egg laid) and the number of PCB congeners identified may impede comparisons.[16]

Temporal changes. ΣPCB average concentrations ranged from 56100 ng/g dry wt (1983) to 30400 ng/g dry wt (1981) in Herring gull eggs collected at Capraia Island in 1981 – 1986, and HCB levels varied from 260 ng/g dry wt (1983) to 100 ng/g dry wt (1986).[5] In Audouin's gull eggs collected at Capraia Island in the same period, ΣPCB average concentrations ranged from 45190 ng/g dry wt (1984) to 28640 ng/g dry wt (1986) and HCB levels varied from 80 ng/g dry wt (1984) to 20 ng/g dry wt (1986).[4] In those previous studies, ΣPCB average concentration was given by a minor number of PCB congeners identified. To compare PCB levels found in this study to those recorded in 1980s, we recalculated the ΣPCB average concentrations considering only the PCB congeners detected in the samples collected in 1980s and thus the PCB concentrations resulted 819.3 ng/g dry wt in eggs of *L. argentatus* and 4385.4. ng/g dry wt in eggs of *L. audouinii*. In general, the organochlorine levels were higher in samples of 1980s than those detected in this study, with the exception of HCB concentration in Audouin's gull eggs that was similar. The decline in OC levels in the last 20 years seems confirmed by data reported by Barrett *et al.* for Herring gull eggs collected from the Barents Sea in 1990s.[15] In fact these Authors found lower PCB and HCB levels of than those found in 1980s but higher than those of this study. A decline in the PCB concentrations in recent years was found also in Herring gull eggs from the Great Lakes[13] and the Lake Ontario.[17]

PCB congener profiles in Herring gull eggs collected in 1980s and 2000s were similar (Figure 2). PCB congeners 153, 180 and 138 were highest in both study, but in recent years an increase of PCB 170 concentrations has been observed (from 4.4% in 1985 to 11.4% in 2004-2005). The isomer specific pattern in Herring gull eggs collected in 1985 was: hexa-CBs > hepta-CBs > penta-CBs > octa-CBs > tetra-CBs. The main differences between 1985 and 2004-05 were the increase of hepta-CBs and octa-CBs (from 26.9% to 39.7% and from 3.5% to 10.0%, respectively) and the decrease of hexa-CBs (from 55.8% to 44.3). In Audouin's gull eggs PCB congener profile was dominated by PCBs 153, 180, 138 and 170 in both studies (Figure 3). In 1980s the isomer specific pattern in Audouin's gull eggs was hepta-CBs > hexa-CBs > octa-CBs > penta-CBs > tetra-CBs. In Audouin's gull eggs the percentage of hexa-CBs increased from 37.3% in 1980s to 47.2% in 2004-05, whereas the amount of hepta-CBs was similar (38.9% in 1980s and 38.8% in 2004-05). Moreover, octa-CBs and penta-CBs decreased from 13% to 5.9% and from 11.9% to 7.1%, in the 1980s sampling and this study respectively. This shift in the PCB congener patterns over time agrees with data reported for other seabird eggs worldwide.[18,19]

Declines in PCB and pesticide concentrations were reported for seabirds from Europe[14] and from different areas of the world.[13,17,18] In most cases, decreasing concentrations in eggs over time reflect declines associated with restriction on the use of these compounds. In fact, a lot of chlorinated hydrocarbons have been banned by many

European and other countries since 1970s.[15,20] Herring gull egg organochlorine concentrations are influenced by birds diet and migratory behaviour in response to weather and/or may reflect the ecological, physiological and behavioural adaptation of the birds to the environment.[17,21] However much of the existing data on OC contamination temporal trends are difficult to understand because samples have been analysed over a long period of time with developments in techniques and instrumentation.[22]

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Table 1. HCB and ΣPCB average concentrations (X±SD), minimum and maximum values (min-max) in Herring gull and Audouin's gull eggs (ng/g dry wt).

	Herring gull		Audouin's gull	
n	20		13	
	X±SD	min-max	X±SD	min-max
HCB	28.0±16.5	2.4-67.1	21.6±7.6	12.0-34.9
ΣPCBs	927.3±395.2	214.5-2054.4	4805.7±2209.1	1726.6-9465.5

Table 2: Class of isomer concentrations (ng/g dry wt) and percentage (in brackets) in Herring gull and Audouin's gull eggs.

	Herring gull		Audouin's gull	
n	20		13	
Tetra-CBs	24.9	(2.7%)	24.3	(0.5%)
Penta-CBs	49.1	(5.3%)	232.7	(4.8%)
Hexa-CBs	383.2	(41.3%)	2260.1	(47.0%)
Hepta-CBs	367.5	(39.6%)	1904.7	(39.6%)
Octa-CBs	91.7	(9.9%)	370.3	(7.7%)
Nona-CBs	10.9	(1.2%)	13.7	(0.3%)

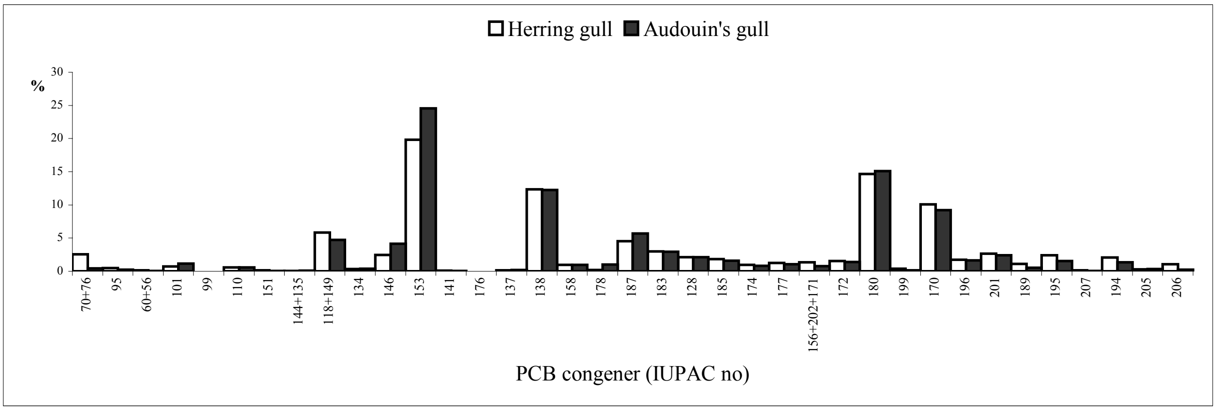

Figure 1: PCB fingerprints of Herring gull and Audouin's gull eggs.

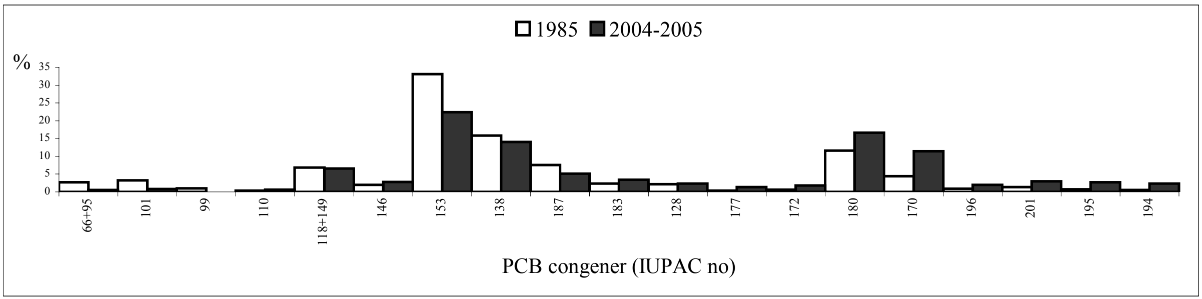

Figure 2: PCB fingerprints in Herring gull eggs collected in 1985 and in 2004-2005.

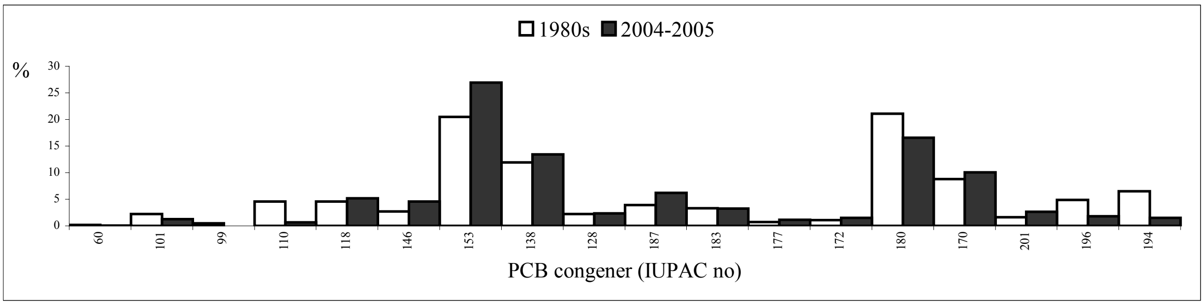

Figure 3: PCB fingerprints in Audouin's gull eggs collected in 1980s and in 2004-2005.

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