

The Kelp Gull as bioindicator of environmental chemicals in the Magellan region. A comparison with other coastal sites in Chile*

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SUMMARY: During the breeding seasons 1994/5 and 1995/6 we collected Kelp Gull (*Larus dominicanus*) eggs from five locations in central to south Chile to study the contamination with mercury and organochlorine compounds. The sites were Algarrobo, Concepción, Maiquillahue Bay, Doña Sebastiana Island (Chalcao channel at Chiloé) and Magdalena Island (Straits of Magellan). We found differences among the sites: Kelp Gull eggs from Chiloé and Algarrobo had the greatest concentrations of mercury (about 170 ng g⁻¹ fresh weight). Residues of DDT were greatest in eggs from Algarrobo and Maiquillahue Bay, those of PCBs (polychlorinated biphenyls) greatest at Algarrobo and Concepción. HCB had highest levels at Concepción. Considering all organochlorines, samples from Algarrobo had the highest concentrations, those from Chiloé the lowest. In consequence we found a geographical pattern from north to south, i.e., from areas with greater to lesser human impact. In comparison with other studies, the levels of environmental chemicals found in Kelp Gulls from Chile are much lower than those known to cause adverse effects on reproductive success.

Key words: Environmental chemicals, Kelp Gull, *Larus dominicanus*, eggs, Chile, mercury, organochlorines, PCBs

RESUMEN: LA GAVIOTA DOMINICANA COMO BIOINDICADOR DE LOS PRODUCTOS QUÍMICOS AMBIENTALES EN LA REGIÓN DE MAGALLANES. UNA COMPARACIÓN CON OTRAS LOCALIDADES COSTERAS EN CHILE. – Durante las estaciones reproductoras de los años 1994/5 y 1995/6 recolectamos huevos de la gaviota dominicana (*Larus dominicanus*) en cinco localidades ubicadas entre el centro y sur de Chile para el estudio de la contaminación por mercurio y compuestos organohalogenados. Dichas localidades fueron Algarrobo, Concepción, Bahía de Maiquillahue, Isla Doña Sebastiana (Canal de Chacao-Chiloé) e Isla Magdalena (Estrecho de Magallanes). Los huevos de la gaviota dominicana provenientes de la Isla Doña Sebastiana y Algarrobo presentaron las mayores concentraciones de mercurio (170 ng g⁻¹ peso fresco). Los mayores niveles de residuos de DDT fueron detectados en las muestras procedentes de Algarrobo y de Bahía de Maiquillahue, los mayores niveles de residuos de PCBs (bifenilos policlorinados) en las muestras de Algarrobo y de Concepción. Los mayores valores de HCB se hallaron en Concepción. Considerando la suma de todos los compuestos organoclorados, los huevos provenientes de Algarrobo presentaron las mayores concentraciones y los de la Isla Doña Sebastiana las menores. En consecuencia, se encuentra un patrón de variación geográfica de norte a sur y de mayor a menor impacto. En comparación con otros estudios, los niveles de los productos químicos ambientales encontrados en los huevos de gaviota dominicana en Chile pueden considerarse muy bajos como para provocar efectos adversos sobre el éxito reproductor.

Palabras clave: Productos químicos ambientales, *Larus dominicanus*, huevos, Chile, mercurio, organoclorados, PCB

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INTRODUCTION

Coastal ecosystems are often very vulnerable and exposed because of their proximity to pollution sources, such as industrial emissions, municipal discharges containing chemical products, and biocides used in agriculture. The pollutants are transported by the rivers and /or atmosphere or are directly discharged into the sea. In aquatic environments, many chemicals are accumulated by organisms and biomagnified via the food chains to high levels in the tissues of top-predators like fish-eating birds. Persistent organochlorines are very lipophilic, and during the breeding season they are mobilized and deposited into the eggs bound to the yolk-fat (e.g. Furness, 1993, Henriksen *et al.*, 1996). In this way, the eggs of seabirds can be used as bioindicators of contamination in coastal and marine environments (e.g. Nisbet and Reynolds, 1984; Becker, 1989, 1991; Becker *et al.*, 1992; Tillitt *et al.*, 1992; Furness, 1993). The Kelp Gull (*Larus dominicanus*, Lichtenstein 1823) has a wide distribution and eats a

wide variety of food (Hoyo *et al.*, 1996) ; hence the eggs of this species may be good indicators of the chemical pollution of the environment (like eggs of Herring Gulls *Larus argentatus*, Pontoppidan 1763: Weseloh *et al.*, 1990).

As in other countries, in Chile mercury and organochlorine compounds have been used in industry and agriculture, but the knowledge of Chilean marine pollution is poor. Recently, Focardi *et al.* (1996) analysed organochlorine residues in fish and birds at the Biobio river; the animals contained high concentrations of PCBs at the river's mouth. Although some environmental chemicals are prohibited in Chile since 1981 (e.g. historical pesticides like DDT, Aldrin, Endrin, Dieldrin), we expect them still to exist in the environment owing to their persistence. But nowadays also a large number of various insecticides, fungicides and herbicides are in use in Chile (Barra *et al.*, 1995).

The objective of this study is to determine spatial trends in contamination of Kelp Gulls along the Chilean coast, from areas with varying human

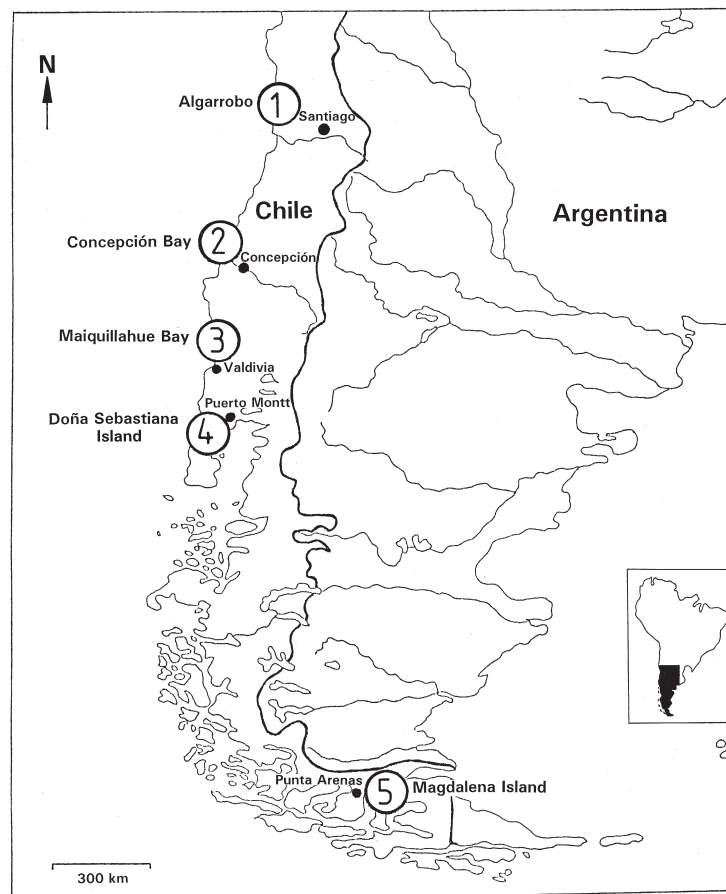


FIG. 1. – Sampling sites for Kelp Gull eggs in Chile. 1: Algarrobo, 2: Concepción, 3: Maiquillahue Bay, 4: Doña Sebastiana Island (Chacao channel at Chiloé, and 5: Magdalena Island (Strait of Magellan). Eggs were taken in the breeding seasons 1994/5 or 1995/6.

impact. We analyze mercury and organochlorinated compounds in eggs collected in the Magellan region for comparison with that of other sites in Chile, to evaluate the pollution of the Magellan area.

MATERIAL AND METHODS

During the breeding seasons 1994/5 and 1995/6 samples of Kelp Gull eggs ($n=7-20$) were collected from each of five sites along the Chilean coast. The sites (Fig. 1) and sampling dates were Algarrobo ($33^{\circ}30' S 71^{\circ}48' W$, 26 November 1995), Concepción (Faro Hualpen $36^{\circ}40' S 73^{\circ}26' W$, 11 January 1995, Isla Quiriquina $36^{\circ}37' S 73^{\circ}03' W$, 10 December 1995), Maiquillahue Bay ($39^{\circ}30' S 73^{\circ}36' W$, 19 November – 17 December 1995), Doña Sebastiana Island (Chacao channel at Chiloé, $41^{\circ}40' S 73^{\circ}48' W$, 31 January 1995) and Magdalena Island (Straits of Magellan, $53^{\circ}05' S 71^{\circ}00' W$, December 1995, Fig. 1).

One egg per completed clutch was taken at random (see Table 1 for n). The eggs were stored frozen ($-18^{\circ}C$). Some eggs contained embryos (max two weeks old). As we found no significant correlation of egg weight and embryo age ($r_s = -0.096$, $n=39$) and as egg mass loss should only be up to 6.7 % during the first two weeks of incubation (Herring Gull, Drent, 1970), we analysed each homogenized egg individually on fresh weight basis.

For determination of organochlorine compounds 2 g of the egg homogenate were dried with sodium sulfate, cleaned by a column filled with silica gel, eluted with *n*-hexane:dichloromethane (8:2), evaporated and taken up in 250 μ l toluene. A gas chromatograph HP 5890, series II, coupled with a mass selective detector HP 5971 was used, with electron impact ionization and measure in SIM-mode. Two HT-5- columns with an overall length of 50 m were utilized for the separation. See Sommer *et al.* (1997) for details and for the quantification of pesticides and CB congeners. For mercury determination 100 μ g egg homogenate were prepared with a mixture of nitric acid, chloric acid and perchloric acid in partly closed test tube. An atomic absorption spectrometer (FIMS-400, Perkin Elmer) with an integrated flow injection module of the FIAS series was used for the measurement. Detection limits were 0.1 μ g g^{-1} fresh egg for mercury, and 0.3-0.9 μ g g^{-1} for all examined organochlorines. Concentrations are given in μ g g^{-1} egg fresh weight.

The organochlorine compounds analyzed were hexachlorobenzene (HCB), three isomers of hexachlorocyclohexane (α -, β - and γ -HCH) and also their sum (SHCH), DDT (expressed as SDDT including six metabolites: *op'*-DDT, *op'*-DDE, *op'*-DDD, *pp'*-DDT, *pp'*-DDE, *pp'*-DDD), and polychlorinated biphenyls (PCBs). We analyzed 62 congeners of PCBs (expressed as the sum, SPCB), 41 of them were recorded individually. For comparison with other studies we also calculated the sum of six "indicator congeners" (PCB6CONG; Bundesminister für Umwelt, 1988; referred to by the IUPAC-numbers, Ballschmiter and Zell, 1980), PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180. Moreover toxic PCB congeners were grouped to non- (PCB 126, PCB 169), mono- (PCB 105, PCB114, PCB 118, PCB 123, PCB 156, PCB 157, PCB 167, PCB 189), and di-ortho congeners (PCB 128, PCB 138, PCB 158/129, PCB 196, PCB 170; Safe *et al.*, 1985). As the toxicity depends on both the quantity and position of the chlorine-atoms, we considered also the degree of chlorination (PCB3Cl to PCB8Cl, Table 2). Concentrations of all organochlorines were summed up per egg as total organochlorine concentration (SORGANOCHLORINE).

SPSS/PC+ was used for statistical analyses. For statistical comparisons among sites, means were compared by analysis of variance. The data were log-transformed ($\log x + 1$) prior to analyses. Statistical significance of differences was determined using Scheffé-tests and $p < 0.05$ chosen as significance level.

RESULTS

In most chemicals analyzed we found significant spatial variation (Fig. 2, Table 1, 2).

The samples from Algarrobo site (5) and Doña Sebastiana Island (4) had the highest levels of the heavy metal mercury (Fig. 2, Table 1), those from Concepción (2) the lowest.

The concentrations of DDT and metabolites were significantly higher at Algarrobo (1) and Maiquillahue Bay (3) than at the other sites (Fig. 2, Table 1). In all locations, without exception, *pp'*-DDE was the most concentrated metabolite (*pp'*-DDE/SDDT ratio upper 0.9); the *op'*-metabolites of DDE, DDD and DDT were not detected. The concentrations of *pp'*-DDT and of SHCH were very low and not significantly different between sites (Table 1, Fig. 2).

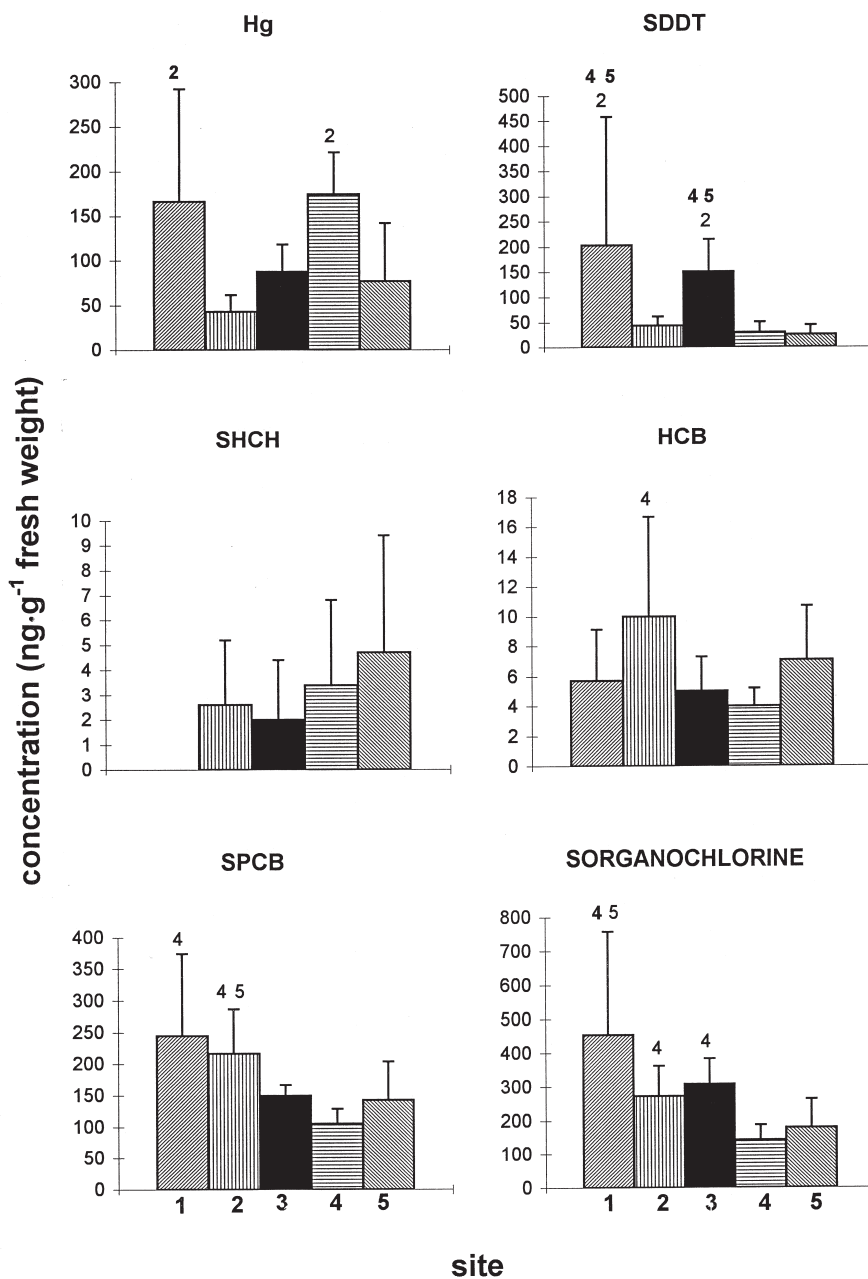


FIG. 2. – Concentrations of environmental chemicals in Kelp Gull eggs from 5 locations on the Chilean coast (see Fig. 1): 1: Algarrobo, 2: Concepción, 3: Maiquillahue Bay, 4: Doña Sebastiana Island (Chacao channel at Chiloé), and 5: Magdalena Island (Strait of Magellan). Concentration of all organochlorines investigated: SORGANOCHLORINE. Means + 1 s.d. Significant intersite differences are indicated by the site number at the top of the column with the significant higher value ($p < 0.05$; bold numbers $p < 0.001$).

α -HCH was not detected in any eggs, β -HCH occurred only at Concepción (2) and Magdalena Island (site 5; Table 1). Only in eggs from the Magellan region, was the concentration of β -HCH higher than that of γ -HCH. The concentrations of HCB were greatest in eggs from Concepción (2), but significantly different only between Concepción and Doña Sebastiana Island (site 4; Table 1, Fig. 2).

The levels of PCBs are shown in Fig. 2 and Table 2. The samples from Algarrobo (1) showed higher

concentrations of SPCB and of the six “indicator congeners” (PCB6CONG), but the intersite differences were significant only compared to the eggs from Doña Sebastiana Island (4) or to Magdalena Island (5). The non-ortho congeners were not detected in any samples. Also the mono- and di-ortho congeners had highest levels at Algarrobo (1) and Concepción (2). The PCBs with three, four and five chlorine-atoms showed no differences among sites (Table 2). In general, the PCBs with six, seven and

TABLE 1. – Levels of mercury and organochlorines in eggs of Kelp Gulls from five locations in Chile in ng · g⁻¹ fresh weight (means ± sd). See Table 2 for PCBs. α-HCH, op'-DDD, op'-DDE, op'-DDT were not detected. Significant intersite differences are indicated by the location numbers (at least p ≤ 0.05).

	1 Algarrobo (n=10)	2 Concepción (n=20)	3 Maiquillahue Bay (n=7)	4 Doña Sebastiana Island (n=8)	5 Magdalena Island (n=10)
mercury	166.7 ± 125.7 ²	43.5 ± 18.3 ^{1,4}	88.0 ± 30.8	175.0 ± 46.2 ²	77.0 ± 65.3
HCB	5.7 ± 3.4	9.9 ± 6.7 ⁴	5.0 ± 2.3	4.0 ± 1.2 ²	7.1 ± 3.6
β-HCH	0.0	0.6 ± 1.8	0.0	0.0	2.7 ± 3.1
γ-HCH	0.0 ⁴	2.0 ± 2.3	2.0 ± 2.4	3.4 ± 2.1 ¹	2.0 ± 2.1
SHCH	0.0 ⁵	2.6 ± 3.6 ⁵	2.0 ± 2.4 ⁵	3.4 ± 2.1 ⁵	4.7 ± 5.1 ¹⁻⁴
pp'-DDD	5.8 ± 5.0 ⁵	2.3 ± 3.6	5.5 ± 3.3 ⁵	1.6 ± 3.0	0.0 ^{1,3}
pp'-DDE	191.9 ± 243.8 ^{2,4,5}	40.2 ± 17.0 ^{1,3}	138.8 ± 57.2 ^{2,4,5}	28.0 ± 20.2 ^{1,3}	23.8 ± 19.0 ^{1,3}
pp'-DDT	5.3 ± 8.7	0.6 ± 2.8	6.8 ± 8.8	0.0	1.3 ± 4.1
SDDT	203.0 ± 255.2 ^{2,4,5}	43.2 ± 18.7 ^{1,3}	151.0 ± 63.9 ^{2,4,5}	29.6 ± 21.6 ^{1,3}	25.1 ± 19.2 ^{1,3}
SORGANOCHLOR	454.0 ± 304.2 ^{4,5}	272.8 ± 88.8 ⁴	307.9 ± 75.6 ⁴	142.7 ± 44.4 ¹⁻³	179.5 ± 83.3 ¹

TABLE 2. – Levels of PCBs in eggs of Kelp Gulls from five locations in Chile in ng · g⁻¹ fresh weight (means ± sd). Non-ortho PCBs were not detected. See text for details. Significant intersite differences are indicated by the location numbers (at least p ≤ 0.05).

	1 Algarrobo (n=10)	2 Concepción (n=20)	3 Maiquillahue Bay (n=7)	4 Doña Sebastiana Island (n=8)	5 Magdalena Island (n=10)
PCB28	4.1 ± 2.7	3.5 ± 0.7	3.5 ± 0.3	3.0 ± 0.2	2.8 ± 0.4
PCB52	3.5 ± 1.4	3.5 ± 0.7	4.1 ± 0.8	3.4 ± 0.4	2.8 ± 0.3
PCB101	6.6 ± 2.1	6.3 ± 1.9	7.8 ± 1.8	5.4 ± 0.9	6.7 ± 1.5
PCB118	9.8 ± 5.7 ^{4,5}	9.2 ± 3.6 ³⁻⁵	4.9 ± 0.9 ²	4.5 ± 0.9 ^{1,2}	4.9 ± 2.2 ^{1,2}
PCB138	17.1 ± 11.9 ⁴	14.4 ± 6.0 ³⁻⁵	7.2 ± 1.0 ²	5.2 ± 2.0 ^{1,2}	8.5 ± 4.6 ²
PCB153	35.8 ± 24.0 ³⁻⁵	27.6 ± 11.8 ^{3,4}	13.4 ± 2.4 ¹	9.5 ± 4.4 ^{1,2}	17.2 ± 10.7 ¹
PCB180	20.2 ± 17.9 ^{4,5}	16.3 ± 6.9 ^{3,4}	7.0 ± 1.3 ²	5.0 ± 2.0 ^{1,2}	11.0 ± 9.6
PCB6CONG	87.3 ± 56.4 ⁴	71.6 ± 25.4 ⁴	43.1 ± 6.1	31.4 ± 9.6 ^{1,2}	49.0 ± 24.7
MONORTHO	23.6 ± 14.2 ⁵	19.7 ± 8.8 ⁵	13.3 ± 4	9.7 ± 2.2	9.0 ± 4.1 ^{1,2}
DIORTHO	30.3 ± 20.6 ⁴	26.1 ± 9.9 ^{2,4}	15.4 ± 2.5	9.7 ± 4.3 ^{1,2}	15.7 ± 7.9 ²
PCB3Cl	4.1 ± 2.7	3.5 ± 0.7	3.5 ± 0.3	3.0 ± 0.2	2.8 ± 0.4
PCB4Cl	22.5 ± 8.5	21.7 ± 3.9	21.2 ± 1.3	19.9 ± 1.3	17.0 ± 1.7
PCB5Cl	50.0 ± 21.1	47.3 ± 12.4	44.2 ± 3.5	34.9 ± 4.4	34.8 ± 6.5
PCB6Cl	90.2 ± 52.2 ^{4,5}	74.2 ± 28.7 ⁴	47.1 ± 5.3	31.0 ± 11.4 ^{1,2}	47.5 ± 22.1 ¹
PCB7Cl	64.1 ± 44 ^{4,5}	54.3 ± 21 ⁴	30.6 ± 8.4	16.9 ± 6.3 ^{1,2}	32.8 ± 23 ¹
PCB8Cl	14.1 ± 11.9 ⁴	15.9 ± 6.9 ³⁻⁵	2.9 ± 3.2 ²	0.0 ^{1,2}	7.6 ± 12.9 ²
SPCB	245.2 ± 128.9 ⁴	216.8 ± 70 ^{4,5}	149.8 ± 16.9	105.7 ± 23 ^{1,2}	142.5 ± 61.1 ²

eight chlorine-atoms had highest concentrations at Algarrobo (1) and Concepción (2). The same trend was found in single PCB congeners (Table 2).

The total concentration of all organochlorine compounds (Fig. 2, Table 2) was greater in samples from Algarrobo (1), although only significantly different from those from Doña Sebastiana Island (4) and Strait of Magellan (5) (p < 0.05).

DISCUSSION

The existence of geographical patterns in the contamination of Kelp Gulls along the Chilean coast was confirmed for most chemical compounds, e.g. mercury, the higher chlorinated PCBs, and SDDT. Mercury occurred in highest concentrations in eggs

from Algarrobo and the Doña Sebastiana Island, where industrial activities are very low. Volcanic mercury input may be a possible pollution source in this area.

Among the pesticides, levels of DDT and metabolites were significantly higher in Algarrobo and Maiquillahue Bay in comparison with the other sites. This pattern may be caused by the highly developed agriculture in these regions (Algarrobo, region V: cultivation of fruits, vegetables; Maiquillahue Bay, region IX/X: grain- and corn-growing). The consumption of agrochemicals in region V and IX of Chile was much higher than in the VIII (Concepción) and X (Doña Sebastiana Island, Barra *et al.*, 1995), probably also during the 1970s, when DDT was still in use. The residues of pp'-DDT found in eggs of Kelp Gulls in 1994/5, however,

indicate a more recent application of DDT in both areas. SHCH and HCB had very low concentrations and did not show clear geographical variation. Nevertheless, the highest concentrations of lindane (γ -HCH) were found in eggs from Doña Sebastiana Island (region X), where lindane is more in use than in the other regions of Chile (Barra *et al.*, 1995).

Also the industrial PCBs showed a geographical trend, characterized by highest concentrations at Algarrobo (adjacent to the harbour of Valparaíso) and Concepción (industrial area); both areas are zones of major anthropogenic pollution. This decreasing trend from north to south in gull contamination with PCBs, and also with the organochlorine total, corresponds to a decrease in density of the human population from central Chile to the Magellanic area (region V, Algarrobo (1), Fig. 1: 84 inhabitants/km²; region VIII, Concepción (2): 47 inhabitants/km²; Maiquillahue Bay (3): between region IX, 25 inhabitants/km², and region X, 14 inhabitants/km², Doña Sebastiana Island, Chacao channel at Chiloé (4): region X (see above); region XII, Magdalena Island (5): 1 inhabitant/km²; Seeler 1994) and reflects the use or emission of these xenobiotics in the urban and industrial areas (see also Focardi *et al.*, 1996). According to Focardi *et al.* (1996), most PCB residues in fish and birds near Concepción consisted of congeners between penta- and heptachlorobiphenyls, which also showed significant spatial variation (Table 2).

That means that the relatively important oil and gas industry in the Magellan region (Punta Arenas) did not cause serious pollution problems by industrial chemicals for the seabirds (PCBs, mercury). But the pesticide levels in the eggs from that area were also low in comparison with northern sites of the Chilean coast. The Magellan area is characterized by extensive stock farming with the consequence of minimal pollution by pesticides. These compounds originate from the intensive agriculture and forestry concentrated in the central region of Chile and producing higher contamination of the environment, including seabirds.

Intersite differences in diet composition may be another source of variation in contaminant loads of the gulls. For example, benthic organisms are less contaminated by organochlorines than fish (e.g. Mattig *et al.*, 1997). In consequence, higher proportions of fish in the diet would lead to larger amounts of residues in the gulls. Food composition, however, was not investigated.

TABLE 3. – Comparison of egg contamination (ng/g, arithmetic means) of Kelp Gulls in Chile and Herring Gulls in North America (Weseloh pers. comm.) and Europa (Muñoz and Becker unpubl. data) in 1995

	Kelp Gull	Herring Gull	
	<i>Larus dominicanus</i> Algarrobo	Lake Ontario	German Wadden Sea
n	9	1 pooled sample	12
pp'-DDE	192	2590	62
β -HCH	0	0	5
HCB	6	22	11
SPCB	245	14800	1623
Hg	167	-	163

The Herring Gull is closely related to the Kelp Gull and very similar in feeding and reproductive ecology. In North America and Europe Herring Gulls have been widely used as bioindicator for chemical contamination of aquatic environments. Several studies have shown that the concentration of pollutants in their eggs reflect the female's contaminant load (Becker *et al.*, 1989; Lewis *et al.*, 1993) and that of their habitats (Becker *et al.*, 1985a,b, 1993a; Weseloh *et al.*, 1990; Koster *et al.*, 1996). In comparison with the published values of Herring Gull egg contamination, the eggs of Kelp Gulls in Chile showed much lower levels of most chemicals investigated, except for mercury (Table 3).

Various effects of chemical contaminants on the reproductive biology of birds are known (Ohlendorf *et al.*, 1978; Scheuhammer, 1987; Nisbet, 1994; Fry, 1995), but direct relationships between pollutant levels and reproductive success are difficult to establish. Egg concentrations of mercury higher than 0.5 $\mu\text{g g}^{-1}$ can have embryotoxic effects (Scheuhammer, 1987). We found lower mercury levels in the eggs of the Kelp Gull in Chile (Table 1). Also pp-DDE concentrations correlating negatively with eggshell thickness in Herring Gulls, were much higher (2.8 - 9.5 $\mu\text{g.g}^{-1}$, Weseloh *et al.*, 1990) than the values found in this study. PCB concentrations exceeding the range of 3 - 5 $\mu\text{g g}^{-1}$ can cause embryotoxicity in birds (Lorenz and Neumeier, 1982, Common Tern *Sterna hirundo*, Linné 1758; Becker *et al.*, 1993b). In general, the concentrations detected in this study are lower than levels known to cause biological effects in other gull species. None of the Kelp Gull eggs contained the extremely toxic non-ortho-PCBs, and mono- and di-ortho-PCBs were found only in low concentrations, probably not producing negative effects on reproduction (e.g. Bosveld *et al.*, 1995).

To conclude, this first study of the geographical variation in chemical pollution of seabirds in Chile showed that the contamination of Kelp Gulls along the Chilean coast is very low, both by pesticides and by industrial chemicals, not at a level that would threaten the health of the species. To verify this we are expanding our project to other seabird species and to other chemicals, as those investigated represent only a small section of all compounds used in Chile. PCP (pentachlorophenol), for example, is broadly applied in forestry and produces environmental problems in some areas (Barra *et al.*, 1995, Fossi *et al.*, 1995).

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