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Effects of Nesting Yellow-legged Gulls (*Larus cachinnans* Pallas) on the Heavy Metal Content of Soils in the Cies Islands (Galicia, North-west Spain)

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Cd, Cr, Cu, Pb and Zn levels were determined in faeces of the yellow-legged gull *Larus cachinnans* in Galicia (NW Spain), and in soils from three breeding and one reference site. The levels of Cd, Cu, Zn and Pb in the soil were significantly higher at the site with highest gull density and with the longest history of use as a breeding site (Percha) than at the reference site. Zn levels were higher than levels of the other metals in all soil and faeces samples. Mean levels of metals in faeces were 305 mg kg^{-1} (Zn), 60 mg kg^{-1} (Cu), 40 mg kg^{-1} (Pb), 9.8 mg kg^{-1} (Cr) and 5.8 mg kg^{-1} (Cd).

Many seabird species breed in colonies on coastal sites, often at very high densities. At such sites, the organic input to the soil (due to faeces, regurgitated pellets, corpses etc.) is generally considerable, and the resulting changes in soil properties typically affect vegetation (Gillham, 1953, 1956; Sobey, 1976; Sobey and Kenworthy, 1979; Hogg and Morton, 1983;, Bukacinski *et al.*, 1994). These previous studies have focused on the effects of seabird colonies on soil fertility. Recently, however, Headley (1996) has reported that seabird faeces are the principal source of heavy metal input to Arctic soils.

In the present study, Cd, Cr, Cu, Pb and Zn levels were determined in soils from three breeding colonies of the yellow-legged gull (*Larus cachinnans*) in the Cies Islands Natural Park in Galicia (NW Spain), with the aim of evaluating whether heavy metal levels are correlated with pair density. In addition, levels of these metals were determined in samples of *L. cachinnans* faeces collected at fishing ports throughout the region.

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Materials and Methods

Study Area

The Cies Islands are located at the mouth of the Ria de Vigo in Galicia (NW Spain), at 42°15′04″N and 8°53′30″E (Fig. 1). This archipelago is one of the most important breeding sites of the species *Larus cachinnans* with more than 22 000 pairs (Munilla, 1997), which preferentially colonize the cliffs on the islands. The cliffs are characterized by slopes with gradients greater than 55%. The soils on these sites are shallow (generally less than 30 cm deep) and stony, and can be classified as lithic or umbric lithosols (FAO–UNESCO, 1990). The geological substrate is two-mica granite (IGME, 1981). The average annual precipitation is 877 mm, and the average annual temperature is 13.8°C (Carballeira *et al.*, 1983).

Soil Sampling

Soil samples were collected from four sites (Fig. 1). Three of these sites (Percha, Campana and Figueiras) are *L. cachinnans* breeding colonies. Pair densities at these sites were estimated on the basis of a census performed in 1991 (Alonso *et al.*, 1991). These authors divided the breeding areas into sectors and estimated the number of breeding pairs of *L. cachinnans* in each sector. In the present study, the area of each sector was estimated from a map (1:10 000), with the aid of a Placom KP-90 planimeter. The resulting density estimates (pairs ha^{-1}) were 553 (Percha), 272 (Campana) and 123 (Figueiras) (Table 1). Reference soil samples were collected from a fourth site (Cabo Home, 2.6 km away on the adjacent mainland) with very similar geological and environmental characteristics but without nesting birds. At each site, a total of 15 soil samples were collected from 15 randomly

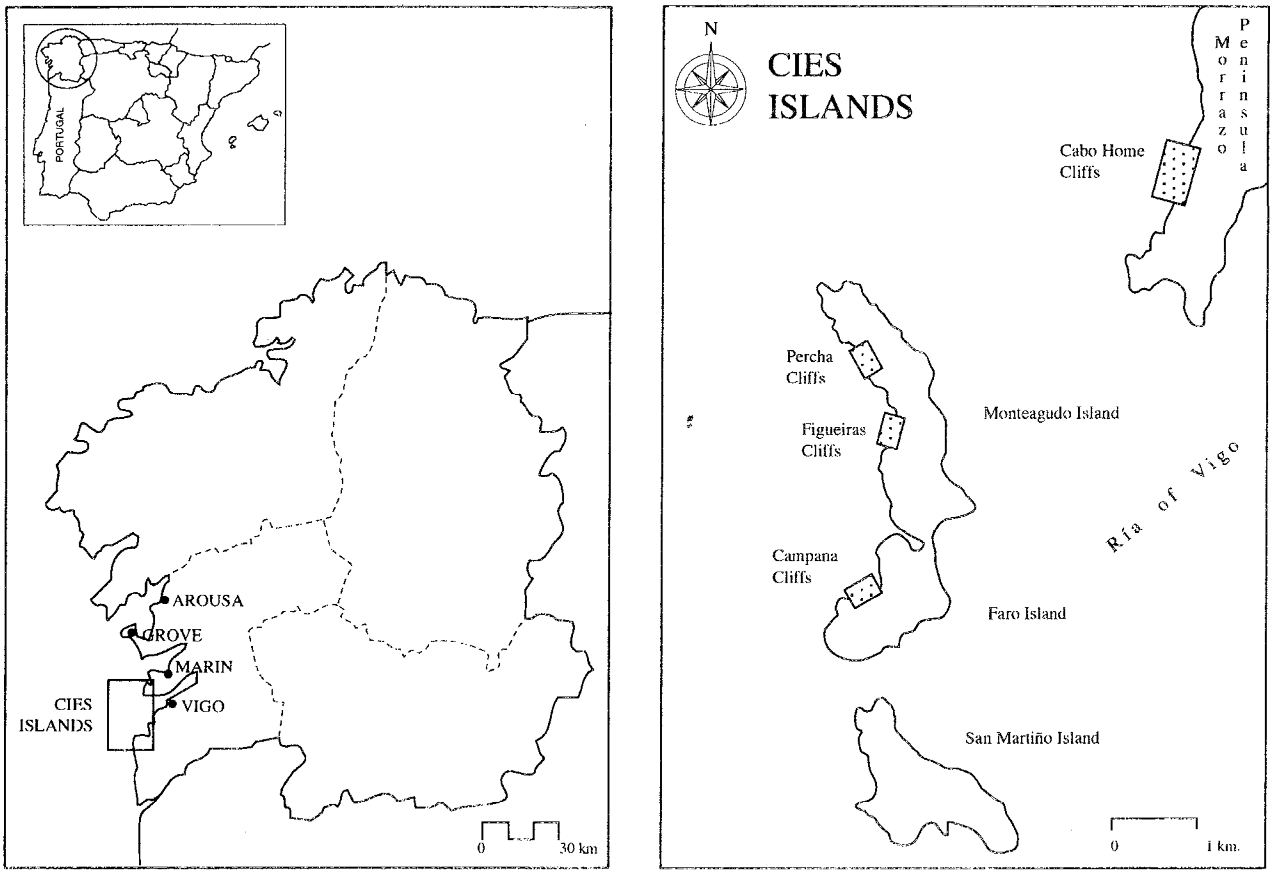

Fig. 1 Maps showing the location of the Cies Islands, the four faeces sampling areas, and the four soil sampling sites.

selected points in August 1996. All samples were taken from the top 20 cm of the soil.

Soil Analysis

Samples were air dried, then sieved to obtain the <63 μm fraction, which was digested with 1 M HCl (20 ml per g of sample, with continuous shaking for 2 h; Bryan *et al.*, 1985). Such digestion solubilizes the most labile, and thus most readily bioavailable, metal fraction (Luoma *et al.*, 1981; Tessier and Campbell, 1987). Metal contents in the extract were determined by atomic absorption spectrometry in a Perkin–Elmer 1100B apparatus, after membrane filtration (0.45 μm pore size).

Sampling and Analysis of Faeces

Fresh *L. cachinnans* faeces were collected from fishing ports in southern Galicia (Fig. 1), the main feeding site of the yellow-legged gulls which breed on the Cies Islands. Each sample comprised five separate droppings, which were pooled, dried at 80°C and powdered. The powdered samples were then digested with concentrated HNO_3 (10 ml per 0.5 g of sample) in Kjeldahl flasks, with evaporation to dryness at 100°C (Jackson *et al.*, 1993); the resulting residue was then dissolved in 15 ml of 1 M HCl. Metal contents in the extract were again determined by atomic absorption spectrometry in a Perkin–Elmer 1100B apparatus, after membrane filtration (0.45 μm pore size).

TABLE 1

Results of censuses of breeding *Larus cachinnans* (number of pairs) at the Percha, Campana and Figueiras sites. Estimated pair densities (pairs ha^{-1}) in 1991 are shown in brackets.

Year/Site	Percha	Campana	Figueiras	Reference
1976	260	30	45	Bárcena, 1977
1981	1575	489	300	Bárcena *et al.*, 1987
1991	4592	1712	554	Alonso *et al.*, 1991
	(553.3)	(271.7)	(123.1)	

General Analytical Procedures

For analysis of both soils and faeces, the acids used were *Suprapur* grade. Extracts and standards were, in all cases, stored at 4°C before analysis. All materials were carefully cleaned with 20% v/v HCl and Milli-Q water before use. The efficiency of extraction of each metal was evaluated by parallel analysis of certified reference material (*Platihypnidium riparioides*, BCR 61); recovery (mean of three replicates) was 99.3% for Zn, 99.5% for Cr, 92.5% for Cu, 97.8% for Pb and 95.7% for Cd.

Data Analysis

Variation in metal levels in soils between locations was assessed by analysis of variance followed by Tukey tests. For each metal, data normality was confirmed by

Kolmogorov–Smirnov tests; data whose distribution could not be assumed to be normal were subjected to appropriate transformations. Pearson correlation coefficients were used to find the relation between the different heavy metals. All analyses were performed with the aid of the SYSTAT 5.0 package (SYSTAT, 1992). Unless otherwise stated, statistical significance was taken to be indicated by p values of less than 5%.

Results

Heavy Metal Levels in Soil

Levels of all five metals were highest in soil samples from Percha, which is the site with the highest *L. cachinnans* pair density (Table 1, Fig. 2). At this site, mean metal levels were 64.8 mg kg^{-1} for Zn, 41.0 mg kg^{-1} for Pb, 12.5 mg kg^{-1} for Cu, 6.1 mg kg^{-1} for Cr and 1.8 mg kg^{-1} for Cd. The lowest levels of all metals except Cu were those in soils from the reference site (Cabo Home); mean levels at this site were 11.8 mg kg^{-1} for Zn, 9.5 mg kg^{-1} for Pb, 2.3 mg kg^{-1} for Cr and 0.5 mg kg^{-1} for Cd. The lowest mean level of Cu (3.0 mg kg^{-1}) was that obtained in soil samples from Campana. Tukey tests following analysis of variance indicated that mean levels of Cd, Cu, Pb and Zn were significantly higher in Percha soils than in soils from Cabo Home, the reference site (Fig. 2). There was no clear pattern of differences between mean levels in soils from the sites with intermediate nesting density (Campana, Figueiras) and soils from the reference site (Fig. 2). Nevertheless, Cd, Cr and Zn levels all showed the ranking expected on the basis of pair density.

Heavy Metal Levels in Faeces

Mean heavy metal levels in samples of faeces are listed in Table 2. The rankings of metal contents are the same for all four sites (except O Grove, for which Pb and Cu are switched). The metal present at highest concentration was Zn (166–398 mg kg^{-1}, global mean 305.1 $\pm$ 158 mg kg^{-1}). The remaining metals were present at lower concentrations (global means: Cu 60.1 $\pm$ 33.3 mg kg^{-1}, Pb 39.9 $\pm$ 5.8 mg kg^{-1}, Cr 9.8 $\pm$ 5.1 mg kg^{-1}, Cd 5.8 $\pm$ 2.6 mg kg^{-1}). The only positive correlations found were between Zn and Cd ($r = 0.56$, $p = 0.049$) and between Zn and Cu ($r = 0.58$, $p = 0.043$) (Table 3).

One estimate of the total input of heavy metals by the yellow-legged gull in the three colonies studied (without considering the contribution of the chicks) is shown in Table 4. The values have been calculated from the amount of faeces (3.1 faeces h^{-1}) and their mean dry weight (0.529 g) obtained for herring gulls (*Larus argentatus*) by Portnoy (1990), and assuming that each bird stays in the colony 18 h a day for 122 days in the year (Munilla, 1997). Taking these data into account, notably high levels of heavy metals were obtained for the Percha colony, where (using the 1991 density data, Table 1) the total inputs via excrement calculated were: 1.22 kg ha^{-1} of Zn, 0.24 kg ha^{-1} of Cu, 0.16 kg ha^{-1} Pb and 0.02 kg ha^{-1} Cd.

Discussion

Headley (1996) found considerable heavy metal contents in the faeces of seabirds in an Arctic region, and suggested that the faeces of nesting seabirds constitute the principal input of heavy metals to the soil in such regions. In the present study, heavy metal contents in yellow-legged gull faeces were higher than those reported for larids by Headley. Metal concentrations in the tissues of seabirds are affected by factors including diet, feeding behaviour and a variety of physiological features (Joseph *et al.*, 1982; Di Giulio and Scalon, 1984; Goede and Voogt, 1985; Honda *et al.*, 1986; Norheim, 1987; Elliot *et al.*, 1992). The faeces contain non-biologically available heavy metals present in the gut contents and those accumulated in different organs of the body and which are excreted via different physiological routes (Rainbow, 1990). According to this, the results obtained for the faeces seem to indicate that the diet of the yellow-legged gull has a higher heavy metal content than the species studied by Headley (1996), possibly because 40% of their diet in Galicia is composed of municipal rubbish tips (Munilla, 1997).

With regard to the heavy metal content of the soils, mean levels of all those considered were markedly higher in soils from Percha than in soils from the other two nesting sites and from the reference site (Fig. 2). It seems likely that the higher levels in Percha soils can be attributed to greater faecal input, because of the higher *L. cachinnans* pair density at the Percha site and/or because this site has been used for longer (Tables 1 and 4). The breeding population of *L. cachinnans* on the Cies Islands has increased dramatically over the last 20 years (Table 1); up to the 1970s, breeding occurred only on the northern part of Monteagudo Island (i.e. the area of the Percha Cliffs), since the more accessible sites (such as Figueiroa and Campana) were used for goat and sheep grazing, and as the local people collected eggs and chicks wherever possible (Bárcena, 1977; Otero *et al.*, 1994). The recent population explosion can be attributed both to a reduction in human pressure on the islands themselves, and to increased availability of food in the region as a whole (notably because of the expansion of Vigo as a fishing port, and the spread of municipal rubbish tips) (Bárcena *et al.*, 1987).

Zinc, which was present in soils at much higher levels than the other metals considered, is an essential element typically present in bird tissues at higher levels than other essential metals (such as Mn and Cu) and toxic metals (such as Pb and Cd); generally, only Fe levels are higher (Norheim, 1987; Thompson, 1990; Kim *et al.*, 1996). Zinc levels are typically highest in the liver and kidneys (Kim *et al.*, 1996). In accordance with this general rule, Zn was the second most abundant metal after Fe in the faeces of the Arctic larids analysed by Headley (1996), and the most abundant metal in the *L. cachinnans* faeces analysed in the present study (Table 2). The high concentrations of Zn in faeces may reflect mechanisms for reducing body levels of other heavy metals. Regarding this, Kim *et al.*

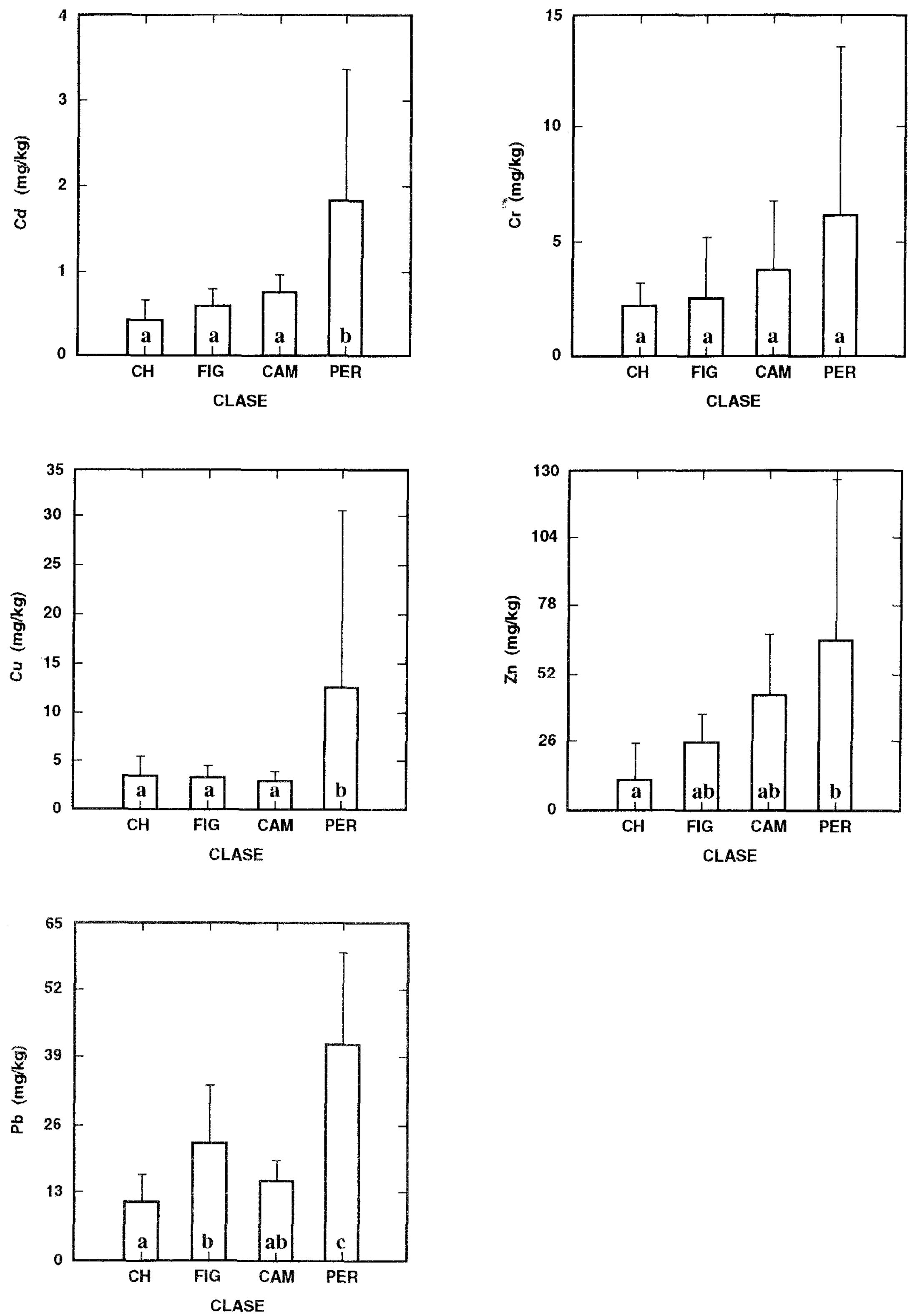

Fig. 2 Mean concentrations of Zn, Cu, Cd, Pb and Cr in soils from the four sampling sites. Vertical lines show standard errors. For each metal, bars with the same letter represent means that do not differ significantly at the 5% level. CH = Cabo Home, FIG = Figueiras, CAM = Campana, PER = Percha.

TABLE 2

Heavy metal concentrations (mg kg^{-1} dry weight, means ± SD) in faeces of *Larus cachinnans* collected from fishing ports in four areas on the Galician coast (see Fig. 1).

Site	n	Cr	Zn	Pb	Cd	Cu
Vigo	6	8.6 ± 5.5	397.9 ± 174.5	47.9 ± 20.5	6.7 ± 7.7	73.9 ± 37.7
Marin	2	19.5 ± 5.3	171.8 ± 66.5	26.2 ± 16.6	2.1 ± 0.9	60.9 ± 53.8
Arousa	3	8.9 ± 8.2	301.2 ± 110.8	22.9 ± 5.2	7.7 ± 2.5	51.7+3.3
O Grove	2	5.3 ± 0.6	165.9 ± 54.2	55.1 ± 41.8	3.8 ± 1.5	30.4 ± 18.3
Mean	13	9.8 ± 5.1	305.1 ± 158.6	39.9+5.8	5.8 ± 2.6	60.1 ± 33.3

(1996) have suggested that the positive correlation observed between liver/kidney levels of Zn and Cd may result from the induction of metallothionein synthesis by high accumulation of Cd leading to greater binding of Zn uptake for essential functions. Moreover, George (1990) established that the heavy metals which are able to bind to the metallothioneins are Zn, Cu, Cd, Hg and Ag. The positive correlations between Cd and Zn as well as between Zn and Cu (Table 3) seem to indicate that this is the mechanism functioning in the area studied. George (1990) proposed that, once the metallothioneins bind the metal, they are directed to the lysosomes where they are immobilized and later excreted.

In the Percha soils, the concentration of bioavailable Zn is greater than the average total content found in either the surface horizons of granite soils in Galicia (Macías *et al.*, 1993) or in this kind of rock (Adriano, 1986). The high Zn content found in soils as well as in excrements seems to indicate that the excrements of this species are an important vector of heavy metal input in these cliffs, except for lead. Pb was the second most abundant metal in soils, but only the third most abundant (after Cu) in faeces (Table 2). This result may indicate that the soils studied have a major source of Pb other than gull faeces.

TABLE 3

Relationship between heavy metal concentrations in the faeces of yellow-legged gulls. n.s.: non-significant; *: $p < 0.05$.

	Cr	Zn	Ni	Pb	Cd	Fe
Zn	n.s.					
Ni	0.60*	n.s.				
Pb	n.s.	n.s.	0.54*			
Cd	n.s.	0.56*	n.s.	n.s.		
Fe	n.s.	n.s.	n.s.	n.s.	n.s.	
Cu	n.s.	0.58*	n.s.	n.s.	n.s.	n.s.

TABLE 4

Estimation of input of heavy metals to the three breeding colonies studied via the excrement of yellow-legged gulls (kg ha^{-1}) calculated from the 1991 density data.

Site	Fe	Zn	Pb	Ni (kg ha^{-1})	Cu	Cr	Cd
Percha	6.40	1.22	0.16	0.07	0.24	0.04	0.020
Campana	3.15	0.61	0.08	0.03	0.12	0.02	0.010
Figueiras	1.42	0.27	0.03	0.01	0.05	0.01	0.005

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