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Phosphorus in seagull colonies and the effect on the habitats. The case of yellow-legged gulls (*Larus michahellis*) in the Atlantic Islands National Park (Galicia-NW Spain)

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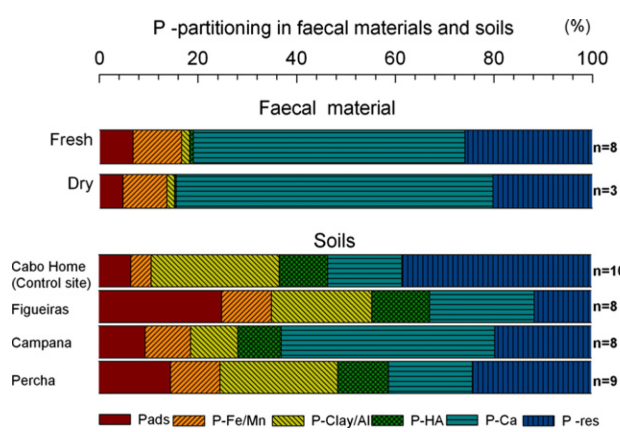
HIGHLIGHTS

- P concentration in soils did not vary in either the short or long term.
- Sandy soils of the seagull colonies in the Cies Islands are saturated with P
- Increased P concentration in soil colonies is an irreversible process
- New seagull colonies can cause negative effects on already threatened habitats

GRAPHICAL ABSTRACT



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ABSTRACT

During the period 1980–2000, the yellow-legged gull population underwent exponential growth due to an increase in the availability of anthropogenic food resources. The aim of this study was to highlight the effect of the gull colonies on the P soil cycle and the associated effects on coastal ecosystems. Samples of soil, water and faecal material were collected in a colony of yellow-legged gulls (Cíes Islands) and in a control area. Four sampling plots were installed in the study areas, and samples were collected in summer and winter in 1997 and 2011. Sample analysis included soil characterization and determination of the total P content (TP), bioavailable-P and fractionated-P forms in the soils and faecal material. The ^{31}P NMR technique was also used to determine organic P forms. Clear differences between the gull colony soils and the control soil were observed. The TP was 3 times higher in the gull colony soil, and the bioavailable P was 30 times higher than in the control soil. The P forms present at highest concentrations in the faecal material (P-apatite, P-residual and P-humic acid) were also present at high concentrations in the colony soil. The absence of any seasonal or annual differences in P concentration indicates that the P has remained stable in the soil over time, regardless of the changes in the gull population density. The degree of P saturation indicated that soils are saturated with P due to the low

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concentration of Fe/Al-hydroxides, which is consistent with a high P concentration in the run-off from the colonies. The P output from the colony soils to coastal waters may cause eutrophication of a nearby lagoon and the disappearance of a *Zostera marina* seagrass meadow. Similarly, the enrichment of P concentration in dune system of Muxieiro may induce irreversible changes in the plant communities.

1. Introduction

Phosphorus deficiency occurs in almost all surface biogeochemical systems and limits ecosystem productivity (Bashkin, 2002). Seabird colonies comprise one of the rare exceptions of habitats where high concentrations of biolimiting elements (i.e., P and N) occur as a result of the biodeposits generated during the birds' breeding season (e.g., faecal material, bird pellets, dead animals) (Gillham, 1956; Sobey and Kenworthy, 1979; Hogg and Morton, 1983; Portnoy, 1990; Buckacinski et al., 1994; García et al., 2002; Ligeza and Smal, 2003; Signa et al, 2012.; Gagnon et al., 2013). This geochemical anomaly leads to huge environmental differences relative to the patterns observed in coastal zones not inhabited by seabirds. Biodeposits may generate eutrophic soils and surface waters (Loder et al., 1996; Ligeza and Smal, 2003; Hobara et al., 2005; Liu et al., 2006; Brimble et al., 2009; Litaor et al., 2014). Furthermore, seabird colonies are considered an important worldwide source of ammonia (NH_3) (Blackall et al., 2008; Riddick et al., 2012) and can thus induce significant changes in the floristic composition (e.g., the emergence of nitrophilous species to the detriment of rare or threatened species) as well as in the distribution of plant communities (Sobey and Kenworthy, 1979; Hogg and Morton, 1983; Portnoy, 1990; Vidal et al., 1998; García et al., 2002; Ellis, 2005). Paradoxically, detailed long-term studies of the spatio-temporal distribution of P in soils are rare. Most studies have focused on the variation in the total contents or on the analysis of labile forms (soluble in weak acid or a salt extract) within short periods, typically less than 2 years (Buckacinski et al., 1994; García et al., 2002; Signa et al., 2012; Litaor et al, 2014).

Although generation of biodeposits by seabirds may be considered a natural process, this is not so for the yellow-legged gull: populations of this bird increased exponentially during the period 1980–2000 due to an increase in the availability of anthropogenic food resources such as trawling discards and domestic refuse in landfill sites (e.g.,Chudzik et al., 1994; Duhem et al., 2008). For this reason, several authors consider that the population increase has had a negative effect on the conservation of flora and they have related the loss of plant diversity in forests, grasslands and islands to N enrichment (Guitián and Guitián, 1989; Vidal et al, 1998; Stevens et al., 2004). However, more recent studies indicate that P may have a similar effect on the conservation of plant diversity (Wassen et al., 2005; Condit et al, 2013). Thus, an understanding of how the soil biogeochemical P cycle may be affected by seabird colonies in the mid to long term is important in an area such as the Atlantic Islands National Park, where a large number of rare or threatened endemic species have been recorded (Fernández et al., 2011) and the conservation of which may be threatened by the expansion of the colony.

The main aim of this study was to obtain further knowledge about how these yellow-legged gull colonies are affecting the spatio-temporal dynamics of the P in soil and water. The underlying study hypothesis is that P is one of the key elements involved in the environmental eutrophication and that an increase in P bioavailability may represent a threat to the conservation of certain plants and habitats (e.g., grey dunes). The behaviour of P in soils is complex as this element may occur in different chemical species and be precipitated, adsorbed, occluded or present as a component of soil organic matter. Because of the importance of P for plant growth, several methods of determining bioavailable P have been developed (see Kuo, 1996). However, few studies concerning soils affected by seabird colonies have considered the geochemical behaviour of P in response to different population densities, soil properties or time intervals (short or long term). Most studies of seabird colony soils have involved total P extraction (extracted with strong acids) and/or extraction of labile/available fractions with neutral salts or dilute acids (see e.g.,Hogg and Morton, 1983; Anderson and Polis, 1999; Sobey and Kenworthy, 1979; Ligeza and Smal, 2003; Maron et al, 2006).

The soils were sampled in 1997, coinciding with the end of the period of maximum density of the gull colony on the Cíes Island (1992–97), and also in 2011. In both years, the samples were collected in February (before the arrival of gulls in the colony) and in August (at the end of the reproductive period). The analyses included general characterization of the soil properties, determination of the total and available P and also sequential extraction of P forms from soils and faecal material: six operationally defined fractions were differentiated (loosely sorbed P, P associated with Fe and Mn oxides, P associated with clay and Al hydroxides, P associated with humic substances, P bound to Ca, and refractory organic P). Finally, and on the basis of previous studies demonstrating that organic P represents one of the most important types of P in faecal material and in soil (Tejada, 2012), the ^{31}P Nuclear Magnetic Resonance (NMR) technique was also used to obtain supplementary information about organic P forms.

2. Material and methods

2.1. Study area

The Atlantic Islands of Galicia National Park (NW Iberian Peninsula) consists of several of the islands that form the Cíes Islands (Fig. 1A,B). This National Park is home to the largest colony of the yellow-legged gull (*Larus michahellis*) in the world, with more than 30,000 bird pairs, more than 60% of which are concentrated on the cliffs of the Cíes Islands (Bermejo and Mouriño, 2004). This yellow-legged gull colony was chosen for study because it is one of the best studied in the National Park and one of those about which most information is available regarding evolution of the species (Otero, 1998; Bermejo and Mouriño, 2004; Pérez et al., 2012, Table 1).

The breeding population of the yellow-legged gull in the islands increased significantly between 1975 and 1991, from approximately 4000 pairs in the mid-1970s to 22,000 pairs in 1991 (Table 1). However, since 1997, the population has undergone a sharp decline, with the lowest numbers, 7465 pairs, reached in 2011 (Table 1). This decline in the breeding population appears to be related to a reduction in food resources as a result of landfill practices and the reduction in fishing discards (Oro et al., 1995; Bermejo and Mouriño, 2004; Pérez et al, 2012).

The most densely inhabited cliffs are characterized by a steep slope (>55%) and stony, shallow soils, generally of less than 25 cm in depth (Fig. 1). The lithological substrate mainly comprises two-mica granite coated by a sandy layer, which generates sandy soils (IGME, 1981; Otero and Pérez, 2009). The climate is classified as temperate with an average temperature of 13.8 °C and an average annual rainfall of 877 mm; 70% of the precipitation occurs between October and March (Carballeira et al., 1983).

2.2. Sampling of soils, water and faecal material

The study of the effects of the yellow-legged gull colonies on soil P contents and forms was carried out in four areas (Fig. 1A, B): three of the areas are included in the breeding zone of the yellow-legged gull in

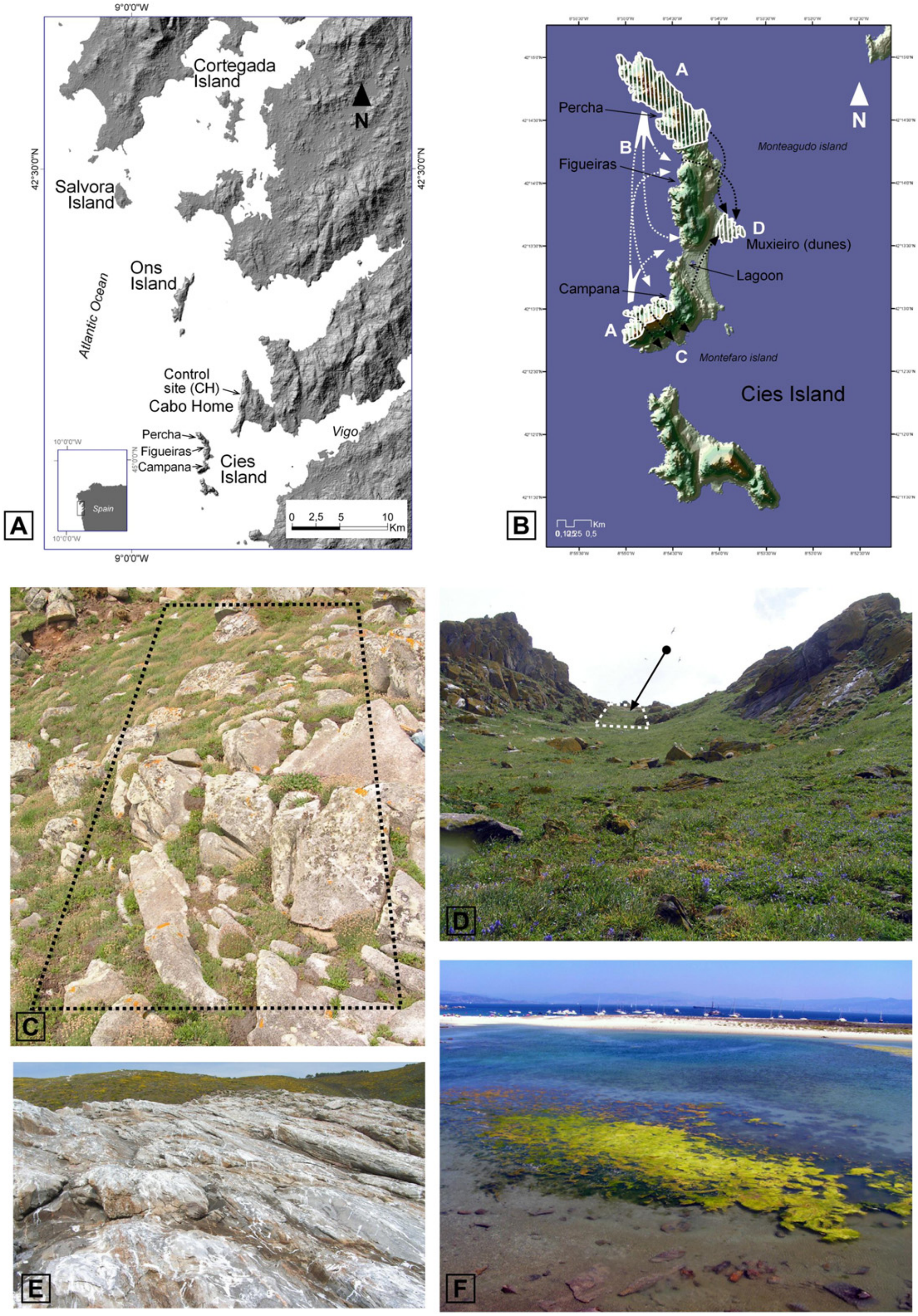

Fig. 1. A) Location of the Atlantic Islands of Galicia National Park. B) Sampling site location and dynamics of expansion of yellow-legged seagulls in the Cíes Islands: A) Main breeding sites during the 1960s and 1970s, B) Expansion of colonies on the cliffs during 1970–1980s, C) Breeding zones created after the 1990s on the east of the Cíes Island, and d) New breeding zone colonized after 2000 in the dune system of Punta Muxieiro. C) Overall view of the control site at Cape Home (CH), D) Overall view of the Percha cliffs, with predominance of *Dactylis glomerata* subsp. *maritima*. E) Seagull faecal material on the coastal rocks, E) Green algae bloom (*Enteromorpha* sp.) in the Cíes lagoon.

the Cíes Islands archipelago: Percha (PER), Campana (CAM) and Figueiras (FIG) and one area, considered as the control zone (no gulls), is situated on the cliffs of Cape Home (CH) (Fig. 1A). The study areas were selected on the basis of the density of gulls (past and present): Percha was considered as a high-density area, Campana as a medium density and Figueiras as a medium to low density area (see e.g., Otero, 1998).

The sampling plots on the cliffs were of area 35 m^2 (7×5 m) (Fig. 1C,D). Samples collected in 1997 and in 2011 were analyzed to determine the long-term effect of the yellow-legged gull colony on the P cycling in each plot. The samples collected in 1997 were used in a previous study (Otero, 1998) and correspond to the period of highest density of gulls in the colony (Table 1), whereas the samples collected in 2011

Table 1
Number of breeding pairs of yellow-legged gulls per study area. The densities of pairs (pairs/ha) estimated in the 1991 and 2011 censuses are shown in brackets.

	Seagulls cliffs			Total seagulls	
Year	Percha	Campana	Figueiras	Cíes islands	Reference
1976	260	30	45	4236	Barcena (1977)
1981	1575	489	300	11,441	Barcena et al. (1987)
1991	1572 (553)	526 (271)	447 (123)	22,098	Munilla (1997), Otero (1998)
1996	–	–	–	19,388	Arcea (1999)
2004	–	–	–	15,654	Bermejo and Mouriño (2004)
2011	558	289	85	7485	Pérez et al. (2012)

represent a period of sharp decline in the population. To determine the short term (seasonal) effects, samples were collected in February (before the arrival of gulls) and in August (at the end of the reproductive period) of each year. Eight soil samples were collected at random points in each plot, with the aid of a 50 × 50 cm sampling quadrat. Soil samples, 0–10 cm depth, were collected with a trowel (length 20 cm) and stored in plastic bags. During the breeding season, samples of faecal material (dried and fresh faeces) were collected from the rocks surrounding of study plots, taking care to include only faecal material and not to remove substrate material. Each sample consisted of 5–10 droppings, which were homogenized before analysis. Finally, between October and March, after periods of heavy rainfall, run-off water samples were collected at Percha. These samples were collected in Teflon bottles, filtered through 0.45 μm nylon filters and stored at 4 °C until analysis.

2.3. Chemical analysis of soil, water and faecal material

Soil analysis included pH in water, pH in KCl, pH in NaF, grain size composition, electrical conductivity, oxides and hydroxides of Al and Fe and Total Fe and Al. The grain size composition was determined by the Robinson pipette method (Buurman et al., 1996). The pH was analyzed in water (pH_{H2O}) and in 0.01 M KCl (pH_{KCl}) at a soil-to-water ratio of 1:2.5 (Buurman et al., 1996). The pH in 1 M NaF (pH_{NaF}) was determined to detect the presence of poorly crystalline Fe and Al oxides and hydroxides in the soil, which may exert an effect on the P adsorption (see Fieldes and Perrot, 1996). For this purpose, 1 g of dried soil sample was added to 50 ml of 1 M NaF solution (pH 7.1–8.2) and the mixture was stirred and left for 2 min before pH measurement; pH values above 10 are considered indicative of the presence of low crystallinity Al forms (Fieldes and Perrot, 1996).

The total organic carbon (TOC) and total nitrogen (TN) were determined in previously ground samples, in a Leco CNS1000 auto analyzer. Exchangeable cations were extracted with 1 M NH_4Cl (Peech et al., 1947), while Al was extracted with 1 M KCl (Buurman et al., 1996) and analyzed by flame atomic absorption spectroscopy (AAS) (Perkin-Elmer model 1100B).

Amorphous Fe (Fe_{Ox}) and Al (Al_{Ox}) oxides and hydroxides and associated P (P_{Ox}) were extracted with an ammonium oxalate solution (0.2 M; pH 3) (Blakemore, 1978). Crystalline Fe oxyhydroxides (Fe_D) were determined by subtracting the amount of Fe_{Ox} from the amount of Fe extracted with a sodium dithionite-citrate solution (0.5 M) (Holmgren, 1967) (for further information on these methods, see e.g.,Kuo, 1996). The degree of P saturation (DPS) was calculated according to Eq. (1), to determine the ability of the soil to adsorb the P from the gull faecal material:

$$DPS(\%) = \left(\frac{[P_{ox}]}{\alpha([Al_{ox}] + [Fe_{ox}])}\right) * 100 \qquad (1)$$

where P_{Ox}, Fe_{Ox} and Al_{Ox} represent, respectively the P, Fe and Al contents (in mmol kg^{-1}) extracted with ammonium oxalate, and α is an empirical parameter with a value of 0.5 for sandy soils (Sims et al., 2002). Total Fe, Al and P contents were determined by microwave-assisted triacid digestion (HCl/HNO3/HF; ratio 5:8:2). Bioavailable P was determined by the Mehlich 3 method (Mehlich, 1984).

Subsamples (2 g) of dried, ground soil samples and of faecal material obtained from each sampling site each year were subjected to sequential extraction to yield the following P fractions (for further details, see Ruttenberg, 1992; Jiménez-Cárceles and Álvarez-Rogel, 2008):

- F1-P: (P_{Ads}), i.e., weakly adsorbed and soluble phosphorus. The sample was extracted with 20 ml of 1 M $MgCl_2$ solution, with continuous stirring for 30 m. Samples were centrifuged at 10,000 rpm and filtered through Albet filter paper, and the extract thus obtained was stored at 3 °C until analysis. The residue was washed twice with Milli-Q water (18 Ω) before starting the next extraction. The centrifugation, filtration and washing procedures were repeated at the end of each of the extraction steps.
- F2-P ($P_{Fe/Mn}$), i.e., P adsorbed to Fe and Mn oxides and oxyhydroxides. Twenty ml of a sodium bicarbonate-dithionite solution ($Na_2S_2O_4$ 0.11 M + 0.11 M $NaHCO_3$; pH 7) was added to the residue from the prior extraction, and the mixture was stirred continuously for 1 h.
- F3-P ($P_{Clay/Al}$), i.e., P bound to Al hydroxides and clay. The samples were shaken for 18 h with 20 ml of sodium hydroxide (0.1 M NaOH).
- F3b-P (P_{HA}), i.e., P associated with soil humic substances. The extract obtained in step F3 was dark brown (almost black) in colour due to the dissolution of humic acids in alkaline conditions (Jiménez-Cárceles and Álvarez-Rogel, 2008). To avoid interference in the colorimetric quantification and for simultaneous quantification of the concentration of P associated with these soil components, the extract was acidified with 2.5 ml of concentrated sulphuric acid (H_2SO_4) and allowed to stand overnight. The organic flocs were allowed to settle at the bottom of the container and were then separated by filtration. The filter with the retained material was dried (45 °C) and subsequently calcined at 520 °C for 2 h in a muffle furnace. The ashes were dissolved in 5 ml of 1 M HCl by boiling the mixture for 30 min, and the extract was made up to 50 ml with Milli-Q water.
- F4-P (P_{Ca}), i.e., P bound to Ca phosphates. The samples were shaken for 1 h with 20 ml of 0.5 M HCl.
- F5-P (P_{Res}), i.e., P mainly associated with refractory organic matter (Schlichting et al., 2002; Largeau, 2004). The material remaining after the above extractions was calcined and processed as described in step F3b-P (P_{HA}).

The concentrations of total P (TP), bioavailable P (P Mehlich 3; Tran et al., 1990) in soils and in run-off water samples were determined colorimetrically, by the molybdenum blue method (Bowman, 1988). The concentrations of Fe and Al and P extracted in each step of the sequential extraction, oxalic acid and ammonium oxalate were determined in an ICP-OES spectrometer (Perkin Elmer Optima 4300 DV). Reference material (NIST2782 and industrial sludge, and SO_2, soil sample) was used to determine the accuracy of the P extraction processes. The mean percentage recovery of total P was 91 ± 2% (n = 6) and the sum of all fractions yielded by sequential extraction was 88.6 ± 4% (n = 3).

All equipment used during the extraction of the different forms of P was washed thoroughly with HCl (5%), for at least 48 h, and then with ultrapure water (Milli Q).

2.4. Nuclear magnetic resonance study

Four samples were selected for NMR analysis to study the P forms they contained: a) soil sampled in 1997 from Percha, where the density of gulls is highest; b) gull faecal material (faecal material), c) soil from the control area (CH-soil) and d) run-off water samples from Pecha (Pecha run-off). Organic molecules were extracted with NaOH/EDTA obtained from soil samples following the method proposed by Turner et al. (2003). Each sample was prepared by the addition of 550 μl of the extract to an NMR tube and addition of 50 μl of D_2O as the deuterium lock solvent. The NMR spectra were acquired at 25 °C in a Varian Inova 17.6 T spectrometer (750 MHz proton resonance) equipped with an inverse detection triple resonance probe $^{1}H/^{13}C/^{31}P$, and triple axis shielded PFG gradients for use with conventional 5 mm NMR tubes. NMR data processing and analysis software were performed with MestreNova software v. 9.1 (Mestrelab Research Inc.).

A 1D phosphorus NMR spectrum was measured for each sample by using the one pulse excitation–detection sequence under continuous broadband proton decoupling (1D $^{31}P\{^{1}H\}$ experiment). The inter-scan relaxation delay (d_1) was set to 2 s and the FID acquisition time was 0.54 s. To improve the quantitative resolution of the spectrum, a low angle of 45° was used for the ^{31}P excitation pulse. For consistency with previous ^{31}P signal assignment of analogue samples reported in the literature (Cade-Menum, 2005), the most intense peak in the ^{31}P spectrum corresponding to orthophosphate was referenced to 6.30 ppm. The spectrum was acquired with 16,384 scans in 11 h 37 min. The spectrum was processed with a line broadening of 5 Hz.

2.5. Data analysis

One-way ANOVA and a post hoc U Mann–Whitney test were used to test for any differences between the bioavailable P in dry and fresh faecal material from sites with and without gulls. The differences between sites and seasons were determined by two-way ANOVA, with *site* (control, colony) and *season* (February and August) as fixed factors and the soil properties as variable factors. Prior to ANOVA, all variables were checked for normality and homoscedasticity. Non-normally distributed data were transformed to natural logarithms, except for the percentage data for total C, N, and S contents, which were subjected to an arcsine transformation (Zar, 1996). The relationships between the different variables were tested using Spearman's correlation coefficient (rs). All statistical analyses were carried out using SigmaStat 2.0 software.

3. Results

3.1. Concentration of phosphorus in gull faecal material

The mean TP concentration in the seagull droppings was 26,623 mg kg^{-1} ($n = 42$); there were no significant differences ($p > 0.05$) in TP between dry (33,927 mg kg^{-1}) and fresh faeces (24,340 mg kg^{-1}) (Table 2). The sequential extraction of the P forms showed the same pattern for fresh and dry material: $P_{Ca} \gg P_{Res} \gg P_{Fe/Mn} > P_{Ads} > P_{Clay/Al} > P_{HA}$ (Table 2, Fig. 2). The concentrations of P_{Ca} and P_{Res} ranged from 9000 to 55,000 mg kg^{-1} and 687 to 15,732 mg kg^{-1}, respectively (Table 2, Fig. 2), while those of more labile forms such as P_{Ads} and $P_{Fe/Mn}$ were intermediate (P_{Ads} 235–4250 mg kg^{-1}; $P_{Fe/Mn}$ 579–6107 mg kg^{-1}) and those of P_{AH} were the lowest (27–308 mg kg^{-1}).

3.2. General characterization of the cliff soils

Most soils on the Cíes island cliffs are poorly developed (Fig. 1C) and the bedrock is usually within the first 15–25 cm of depth. The grain size composition is clearly dominated by the sand fraction, with mean values higher than 78%, followed by silt and clay, with mean values ranging from 8–13% (Table 3), indicating a loamy sand texture. The sand contents of the control soils were lower (70 ± 3%, $n = 5$) and the clay contents were higher (12 ± 4%) than in the colony soils and the texture was fine sandy loam. The organic C contents were high in all study sites, with values usually exceeding 7%, particularly in the soils from Percha where the breeding season lasts longest and the population density is highest (Table 1). The pH_{H2O} was acidic in all sites (varying between 5.1 and 5.9), while the pH_{KCl} was 0.8 units lower than the pH_{H2O}, indicating a negative charge balance in the soil. Calcium (5–13 $cmol_{(+)}$ kg^{-1}) was the dominant cation in the effective cation exchange capacity (ECEC), followed by Mg (3–12 $cmol_{(+)}$ kg^{-1}), Na (1.7–9.4 $cmol_{(+)}$ kg^{-1}) and K (0.7–1.3 $cmol_{(+)}$ kg^{-1}); the concentrations of Al were much lower (mean values < 0.20 $cmol_{(+)}$ kg^{-1}) possibly because the pH was close to 5.5, which limits the solubility of Al, particularly in quartzite soils with few alterable minerals (Table 3). The pH_{NaF} did not vary between sites, with mean values of 7.5 indicating the low participation of poorly crystalline compounds in these soils, which is consistent with the sandy texture (see below). The soil electrical conductivity indicated a slight marine influence, taking into consideration the values obtained for dissolution of Galician granite soils (Eh 130–200 mS cm^{-1}; Alvarez et al., 1992). The mean concentrations were significantly higher in the soils from the gull colony in comparison with the control site (Table 3), ranging from 1134 μS cm^{-1} in the cliffs to 268 μS cm^{-1} in the control site (Table 3).

3.3. Drivers of P adsorption: Al and Fe forms

The concentration of the main parameters and components controlling the P retention in soils (see Pierzynski et al., 2000) are shown in Table 4, for different areas and seasons. The total Fe (TFe) concentration was significantly higher (1.30 ± 0.04%) in the control site than in soils from the Cíes island cliffs (TFe: 0.58 ± 0.02%), due to the influence of a colluvium from a shale rock with higher Fe contents than granites. The total aluminium (TAl) concentrations in the soils of the Cíes cliffs (1.28 ± 0.08%) were similar to those in the control sites (1.03 ± 0.13%). Neither TAl nor TFe showed any clear pattern of variation (Table 4).

Concentrations of amorphous Fe oxides and oxyhydroxides (Fe_{Ox}) were very low and similar in soils from both gull colonies and the control area (mean values < 0.1%; Table 4). The concentrations of crystalline Fe oxides and oxyhydroxides (Fe_D) were significantly higher in the control soil than in the colony soils (mean value for control: 0.33 ± 0.03%; colony soils: 0.11 ± 0.05%) (Table 4); however, the values were much lower than those reported for soils developed from granitic rocks in Galicia (0.40–0.50%) (Taboada and García, 1997). Moreover, the results show that the crystalline forms are dominant and may represent between 60% and 80% of all free Fe (Fe not associated with silicates).

Table 2
Total phosphorus and P fractions (mean ± SD) in faecal material of yellow-legged gulls. Concentrations are expressed in mg kg^{-1} (dry weight). Minimum and maximum values are shown in brackets.

Sample	Total P	P_{ads}	$P_{Fe/Mn}$	P_{Al}	P_{HA}	P_{Ca}	P_{Res}
Dry faeces	33,927 ± 29,150 (4880–96,800) n = 10	1449 ± 429 (1034–1892) n = 3	2080 ± 1256 (120–1833)	349 ± 236 (120–591)	156 ± 88 (42–327)	11,699 ± 3596 (9076–15,798)	5497 ± 2662 (2919–8237)
Fresh faeces	24,340 ± 17,175 (3200–78,115) n = 32	1521 ± 1458 (235–4249) n = 8	2759 ± 2104 (578–6107)	529 ± 305 (50–1493)	122 ± 92 (87–303)	21,657 ± 17,804 (2708–54,776)	6216 ± 4690 (687–15,632)
Total	26,623 ± 20,400 (3200–96,800) n = 42	1511 ± 1318 (235–4249) n = 11	2768 ± 1862 (579–6107)	474–523 (51–1493)	111 ± 86 (27–308)	20,085 ± 16,352 (2708–54,776)	6319 ± 4250 (687–15,632)

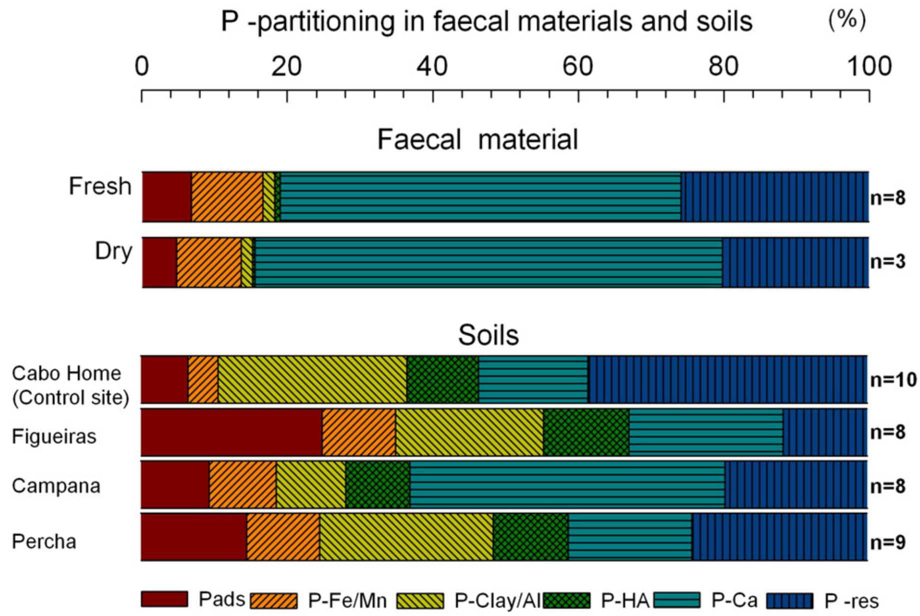

Fig. 2. Phosphorus fractions in faecal material and soils. Pads: weakly adsorbed and soluble phosphorus; P-Fe/Mn: P adsorbed to Fe and Mn oxides and oxyhydroxides; P-Clay/Al: P bound to Al hydroxides and clay; P-HA: P associated with soil humic substances; P-Ca: P bound to Ca phosphates; Pres: P mainly associated with refractory organic matter.

The Al_{Ox} content was very low ($Al_{Ox} < 0.2\%$) in comparison with previously reported values for granitic soil, of around ~0.35% (Macias et al., 1982). This value is consistent with the negative response to pH_{NaF} and sandy nature of the substrate, which indicates a low concentration of active Al forms (poorly crystalline). There were no significant seasonal differences in Fe and Al oxides and oxyhydroxides.

3.4. Total and bioavailable P in soils

The mean TP concentration of soils from the control site was 290 ± 90 mg kg^{-1}, with a significant increase in the soils in the yellow-legged gull colonies (918 ± 259 mg kg^{-1}) (Table 4). The highest TP content was recorded at Percha cliffs (Fig. 3), with mean values ranging from 962 to 1302 mg kg^{-1}. Similar values were obtained in the samples from Campana (923–1010 mg kg^{-1}) followed by Figueiras (501–692 mg kg^{-1}). There were no seasonal differences or differences between the years (1997 and 2011), despite the apparent decline in the TP content in 2011 (Table 4 and Fig. 3).

The mean concentrations of bioavailable P were significantly higher in the soils from the gull colonies, exceeding the concentrations in the control soil by 30 times (Table 4, Fig. 3). Considering the gull colony soils, the P content was highest in Figueiras in March 1997 (83 ± 104 mg kg^{-1}), while in Campana the P content was highest in August 1997 (514 ± 104 mg kg^{-1}) and in Percha in March 1997 (579 ± 176 mg kg^{-1}). These results show a general decline in bioavailable P in the gull colony soils during 2011 (Fig. 3).

Table 3
General characteristics of the soils (n = 5) in the study area. The samples were collected in August 1997.

	Control site	Seagulls colony		
Parameter	Cabo home	Figueiras	Campana	Percha
Sand (%)	70 ± 3	79 ± 2	81 ± 4	78 ± 4
Silt (%)	16 ± 1	13 ± 2	9 ± 2	12 ± 3
Clay (%)	14 ± 4	8 ± 2	10 ± 3	9 ± 5
pH_{H2O}	5.8 ± 0.6	5.0 ± 0.4	5.7 ± 0.5	5.1 ± 0.3
pH_{KCl}	4.4 ± 0.1	4.2 ± 0.1	4.9 ± 0.6	4.2 ± 0.2
pH_{NaF}	7.5 ± 0.01	7.5 ± 0.02	7.5 ± 0.04	7.5 ± 0.07
EC (μS cm^{-1})	268 ± 137	791 ± 618	1134 ± 627	575 ± 434
TOC (%)	9.3 ± 2.0	7.2 ± 1.5	7.8 ± 1.6	14.3 ± 6.9
Ca (cmol$_{(+)}$ kg^{-1})	5.40 ± 2.7	9.40 ± 5.6	12.03 ± 5.9	12.17 ± 6.9
Mg (cmol$_{(+)}$ kg^{-1})	3.48 ± 1.9	9.11 ± 4.7	12.34 ± 3.9	7.20 ± 6.5
Na (cmol$_{(+)}$ kg^{-1})	1.76 ± 0.6	4.70 ± 1.2	9.40 ± 4.2	2.51 ± 1.7
K (cmol$_{(+)}$ kg^{-1})	0.71 ± 0.5	0.90 ± 0.5	1.29 ± 0.6	0.70 ± 0.4
Al (cmol$_{(+)}$ kg^{-1})	0.05 ± 0.02	0.04 ± 0.01	0.03 ± 0.01	0.20 ± 0.08

3.5. Partitioning of soil phosphorus

The dominant P form in the control area was P_{Res} (Tables 4, 5Fig. 2), representing 44% of the TP (Fig. 2), followed in abundance by $P_{Clay/Al}$ (28.8 ± 3.69 mg kg^{-1}), P_{Ca} (17.7 ± 3.20 mg kg^{-1}) and finally P_{Ads} and $P_{Fe/Mn}$. No seasonal differences were observed in the P forms. The P concentrations (all fractions) were significantly higher in the gull colony soils than in the control soil (Tables 3, 4).

Different patterns were observed in the colony soils. However, considering the three sites together, the dominant forms were P_{Ca} and P_{Res}, which represent 28 and 20% of all the fractions, respectively. The P adsorbed to the Fe and Mn oxyhydroxides represented a minor fraction (~12%; Table 4 and Fig. 2). Furthermore, the concentrations of all fractions, except P_{Res}, were much lower in 2011 (in both February and August) (Table 5).

3.6. ^{31}P NMR study

The concentration of soluble P in the run-off water was high (9.25 ± 0.78 mg l^{-1}; n = 8) and therefore was considered for further analysis by ^{31}P NMR. The ^{31}P NMR signal spectrum of the four samples is shown in Fig. 4. The most abundant types of phosphorylated species in the Percha soil samples were orthophosphate (6.3 ppm), orthophosphate monoesters (6 to 3 ppm) and pyrophosphates (4.15 ppm) (Fig. 4A). These three types of signals were also abundant in the samples of faecal material (Fig. 4B), together with phosphonate species (20.7 ppm) (Fig. 4B). In contrast, the most abundant species in the control site (CH-soil) (Fig. 1C) was orthophosphate, followed by the phosphate monoesters. The proportion of the latter group was much smaller proportion in the CH-soil than in the Percha-soil and seagull excrement samples. The ^{31}P spectrum of run-off (Percha run-off) only showed the strong orthophosphate peak (Fig. 1D). Integration of the area under the

Table 4
Spatial and seasonal variations in pH, E.C. and concentrations (mean ± SD) of P, Fe and Al fractions in soils and ANOVA results. Two-way ANOVA results for site, season and site ∗ season. Statistically significant effect is found for site on most of the dependent variables. The season has a statistically significant effect only for the E.C. The interaction between site and season shows no statistically significant effect, which indicates that the effect of one factor does not depend on the status of the other factor. Bold numbers indicate significant differences (p < 0,05)

	Site		Season		*P*		
	Control (n = 10)	Colony (n = 60)	Summer (n = 39)	Winter (n = 31)	Site	Season	Site ∗ season
pH	5.6 ± 0.1	4.9 ± 0.1	5.3 ± 0.1	5.2 ± 0.1	<**0.001**	0.818	0.059
E.C. (dS cm^{-1})	297 ± 65	543 ± 39	337 ± 54	502 ± 54	**0.002**	**0.033**	0.540
Total P (mg kg^{-1})	290 ± 90	918 ± 259	815 ± 189	1133 ± 194	**0.001**	0.245	0.177
Mehlich-P (mg kg^{-1})	12.31 ± 3.59	380 ± 179	223 ± 50	133 ± 55	<**0.001**	0.228	0.323
P_{ads} (mg kg^{-1})	7.89 ± 2.89	60.0 ± 11	36.69 ± 12	47.50 ± 12	**0.014**	0.544	0.497
$P_{Fe/Mn}$ (mg kg^{-1})	3.68 ± 1.72	49.1 ± 6.6	32.0 ± 7.1	39.2 ± 6.8	**0.011**	0.468	0.625
$P_{Clay/Al}$ (mg kg^{-1})	28.8 ± 3.68	97.0 ± 14	87.2 ± 18	119 ± 17	<**0.001**	0.197	0.257
P_{HA} (mg kg^{-1})	12.1 ± 7.70	75.0 ± 6	46.8 ± 8	43.1 ± 7.1	<**0.001**	0.725	0.946
P_{Ca} (mg kg^{-1})	17.7 ± 3.20	149 ± 35	148 ± 44	189 ± 42	<**0.001**	0.519	0.766
P_{res} (mg kg^{-1})	55.1 ± 9.20	104 ± 13	89 ± 17	50.3 ± 24	**0.005**	0.110	0.265
Fe-Ox (%)	0.086 ± 0.02	0.091 ± 0.01	0.089 ± 0.01	0.090 ± 0.01	0.802	0.939	0.346
FeD (%)	0.30 ± 0.03	0.11 ± 0.05	0.18 ± 0.05	0.16 ± 0.05	**0.001**	0.130	0.179
Al-Ox (%)	0.05 ± 0.07	0.12 ± 0.09	0.13 ± 0.10	0.07 ± 0.02	0.122	0.343	0.397
Total Fe (%)	1.30 ± 0.04	0.58 ± 0.02	0.97 ± 0.04	0.88 ± 0.04	<**0.001**	0.100	0.419
Total-Al (%)	1.03 ± 0.13	1.28 ± 0.08	1.25 ± 0.11	1.06 ± 0.11	0.106	0.229	0.046

peaks in the $^{31}P\{^{1}H$ decoupled$\}$ spectra of Fig. 4 yielded the relative percentages of the four types of phosphorylated species (Table 6).

A detailed view of the ^{31}P spectrum of the Percha-soil and seagull faecal material samples in the region of the phosphate monoesters is shown in Fig. 5. No attempt was made to identify these phosphorylated species on the basis of only the 1D ^{31}P spectrum. However, the ^{31}P spectrum of the Percha-soil samples and faecal material (Fig. 5) showed a very characteristic peak at 6.07 ppm together with other three peaks that have been described for myo-inositol hexakisphosphate (Turner et al., 2003; Cade-Menum, 2005).

4. Discussion

4.1. Phosphorus dynamics in ornithogenic soils

The P content of soils is considered one of the most potentially limiting plant nutrients (Sposito, 1989; Soon, 2008) because most of the P occurs in soil as rather insoluble forms. In acidic and/or strongly weathered soils inorganic P forms are strongly adsorbed to amorphous Fe and Al oxides and oxyhydroxides, whereas in calcareous soils P is precipitated as calcium phosphate (Kuo, 1996; Jalali and Hemali, 2013). In this

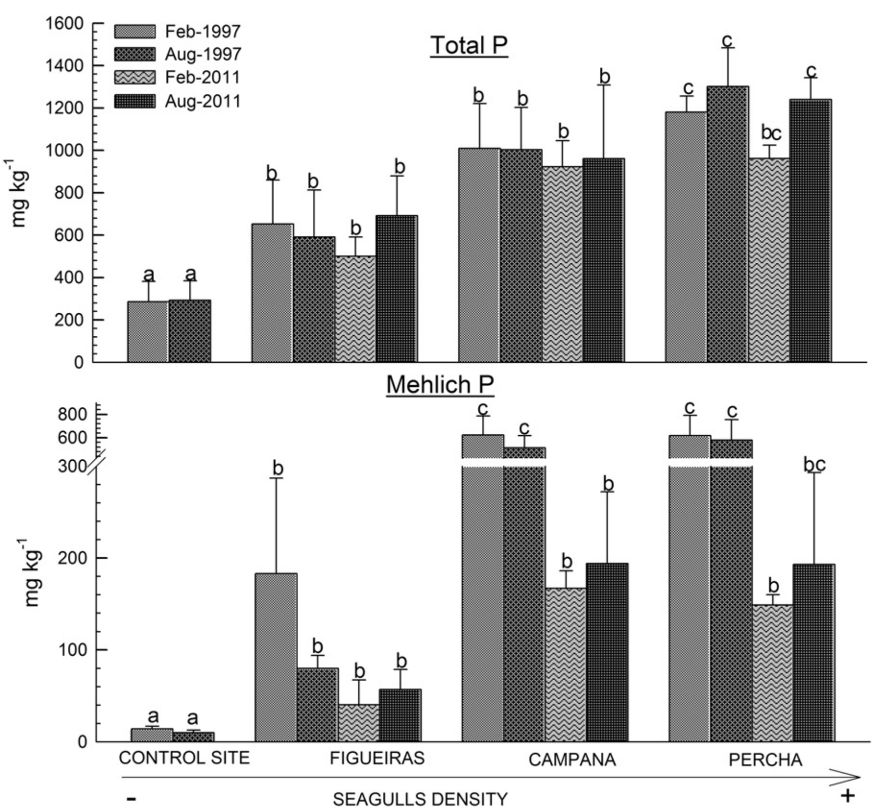

Fig. 3. Total phosphorus (TP) and bioavailable P ($P_{mehlich}$) contents (mean ± SD) of the control soil (CH) and seagull colony soils.

Table 5
Phosphorus partitioning in control and colony soils (mean ± SD).

Cliff name		Date	P_{ads}	$P_{Fe/Mn}$	P_{ClayAl}	P_{HA}	P_{Ca}	P_{Res}
			mg kg^{-1}					
Control site	Cabo Home	Feb-97	7.82 ± 3.15	2.5 ± 0.8	26.1 ± 3.06	14.2 ± 3.00	37.2 ± 5.04	29.3 ± 6.12
		Aug-97	7.97 ± 3.88	3.5 ± 0.5	31.5 ± 2.00	11.9 ± 12.00	38.2 ± 3.40	26.7 ± 2.60
Seagull colony	Figueiras	Feb-97	59.1 ± 36.7	35.8 ± 19.0	59.8 ± 11.0	53.6 ± 53.0	40.8 ± 20.0	53.3 ± 2.47
		Aug-97	115 ± 67.6	32.4 ± 10.0	27.4 ± 3.60	30.4 ± 1.00	40.5 ± 12.0	58.3 ± 9.13
		Feb-11	31.3 ± 6.0	26.6 ± 4.00	26.9 ± 8.20	35.6 ± 15.7	15.1 ± 6.04	57.5 ± 10.2
		Aug-11	22.8 ± 5.0	39.1 ± 11.3	168 ± 43.3	34.8 ± 10.0	238 ± 33.0	22.0 ± 5.23
	Campana	Feb-97	100 ± 7.00	85.1 ± 18.3	82.9 ± 21.2	65.4 ± 5.00	483 ± 167	207 ± 13.1
		Aug-97	69.6 ± 32.0	69.1 ± 33.0	56.3 ± 2.00	57.0 ± 2.00	295 ± 116	39.9 ± 11.1
		Aug-11	19.4 ± 3.00	29.4 ± 3.00	51.1 ± 10.2	53.7 ± 12.0	87.5 ± 42.9	144 ± 2.45
	Percha	Feb-97	60.5 ± 17.0	44.9 ± 5.00	129 ± 54.0	49.1 ± 8.05	71.0 ± 7.05	106 ± 9.34
		Aug-97	183 ± 55.0	114 ± 13.0	155 ± 50.4	62.1 ± 24.0	199 ± 91.0	129 ± 23.3
		Feb-11	35.7 ± 3.08	32.9 ± 5.70	169 ± 44.0	84.6 ± 39.0	54.3 ± 20.1	225 ± 59.4

sense, the seabird colonies represent a positive geochemical anomaly as the P is found in high concentrations and forming more soluble and bioavailable forms (see Cushman, 2013; Fig. 2).

During the breeding season, seabirds can form dense colonies, sometimes exceeding one million individuals (Mataloni et al., 2010). The high bird densities on costal cliffs generate significant changes in soil composition and properties which, in turn, may affect plant species composition and vegetation structure: "*Wherever a large bird colony exists, the birds may be regarded as dominant in the sense that … they determine the nature of community*" (Hutchinson, 1950, cited by Anderson and Pollis, 1999). The role of seabirds in transporting marine nutrients to terrestrial environments has long been considered important (Hutchinson, 1950; Gillham, 1953) and has recently been the subject of particular attention (see e.g.,Portnoy, 1990; Polis and Hurd, 1996; Hobara et al., 2005; Anderson and Polis, 1999; Liu et al., 2006; Gagnon et al, 2013; Slawomir and Halina, 2003; Simas et al., 2007; Maron et al., 2006; Mataloni et al., 2010; Vidal et al., 1998).

Nitrogen and phosphorus are the elements that have received most attention in studies regarding the effects of seabird colonies on terrestrial soils. Most of these studies have shown that the soils from marine bird colonies are enriched in N, P and other macronutrients such as K, Ca and Mg (Lindeboom, 1984; Anderson and Polis, 1999; Loder et al., 1996; Wainright et al., 1998). Thus, some authors have proposed that, from an edaphic perspective, the term *ornithogenic soils* should be used for the soils associated with penguin colonies in Antarctica (Ugolini, 1972; Campbell and Claridge, 1987). More recently, the soil classification

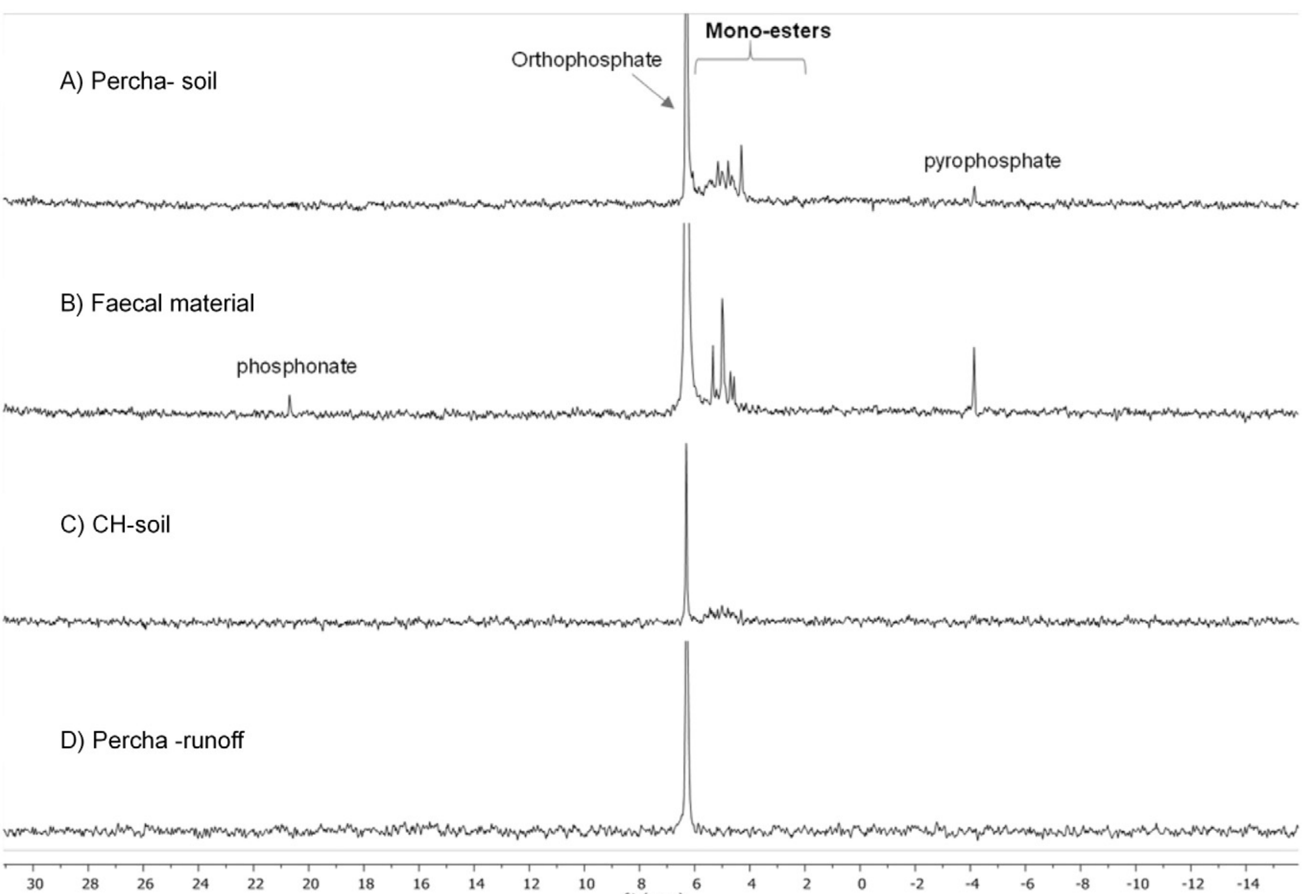

Fig. 4. 1D ^{31}P {^{1}H decoupled} spectrum of NaOH/EDTA extracts in soils (A, C), faecal material (B) and run-off (D). The spectra are referenced to the orthophosphate peak (6.3 ppm). Assignment of the peaks types is based on reports for similar samples (Cade-Menum, 2005).

Table 6
Relative percentages of phosphorylated species obtained by integration of the 1D ^{31}P {^{1}H decoupled} spectrum of the NaOH/EDTA extracts.

Sample	Phosphonate (%)	Orthophosphate (%)	Orthophosphate mono-esters (%)	Pyrophosphate (%)
Percha-soil	0	58.9	39.5	1.6
Seagulls-exc	0.05	88.75	9.9	1.3
CH-soil	0	50.0	45.7	4.3
Runoff	0	100.0	0	0

system World Reference Base for Soil Resources (IUSS Group, 2007) has also included the more generic term *ornithogenic material* as diagnostic material. This type of material is mainly characterized by the presence of matter generated by bird activity (bones, feathers, droppings) and by high P concentrations (~0.25% P_2O_3, extracted with a 1% citric acid solution). More recently, the term "*phosphatization*" has been proposed to describe the soil-forming process in seabird colonies (Simas et al., 2007).

The high P and N concentrations in the seabird droppings are derived from a diet rich in squid, fish and crabs, which yields a guano containing high amounts of nutrients (Hutchinson, 1950). However, information about the total P contents of the seabird faecal material is scant as most studies have analyzed soil or guano (aged dropping material including several types of seabird material and sometimes mixed with seal faeces). The highest P concentrations reported in the literature correspond to the droppings of the red-footed booby (*Sula sula*), with TP contents ranging from 14 to 17% (Liu et al., 2006; Table 7). Lower concentrations were reported for different species of penguins (0.96–4.6%), gulls (0.12–4.42%), cormorants (5.95%) and fulmars (0.12–2.74%; Table 7). In this context, the TP concentration of the yellow-legged seagull droppings on the islands were relatively high (mean 2.6 ± 2.0%; Table 1 and 7) and even higher than those obtained for the same species in the Mediterranean (see Signa et al., 2012; Table 7). In the latter case, the TP may have been overestimated because the authors sieved (200 μm) the faecal material to remove coarse (sand and shell fragments) fragments that are usually abundant for this species. Furthermore, although a large fraction of the P in faeces is associated with refractory or poorly soluble forms, such as P_{Res} and P_{Ca} (Table 2, Fig. 2), and the most labile fraction (P_{Ads}) is present in a much lower proportion (generally < 10% of total P, Fig. 2), the P_{Ads} in the faeces is 3400 times higher than the P_{Ads} obtained in the soils from the control site (Table 2 and 5). Therefore, in addition to poorly soluble P forms, which may remain in the soil for long periods of time (from hundreds to thousands of years; see below), the seagulls may also incorporate substantial amounts of weakly adsorbed P.

The TP concentration in soils under the seabird colonies reached extremely high, although very variable, values (Table 7). Thus, the TP of the ornithogenic soils ranged from 1.0–5.4%. Taking these results into account, the concentrations of TP in the soils of the islands would be one of the lowest (Table 7), while the P bioavailability would be slightly higher. This may be related to the density of birds, which is generally much higher in other seabird colonies where thousands and sometimes millions of birds are concentrated (i.e., on the coast of Antarctica). Nevertheless, in soils from former seabird colonies, abandoned for hundreds or even thousands of years (Moor et al., 1988; Hawke et al., 1999; Sun et al., 2000; Table 7), the TP contents are still much higher than those

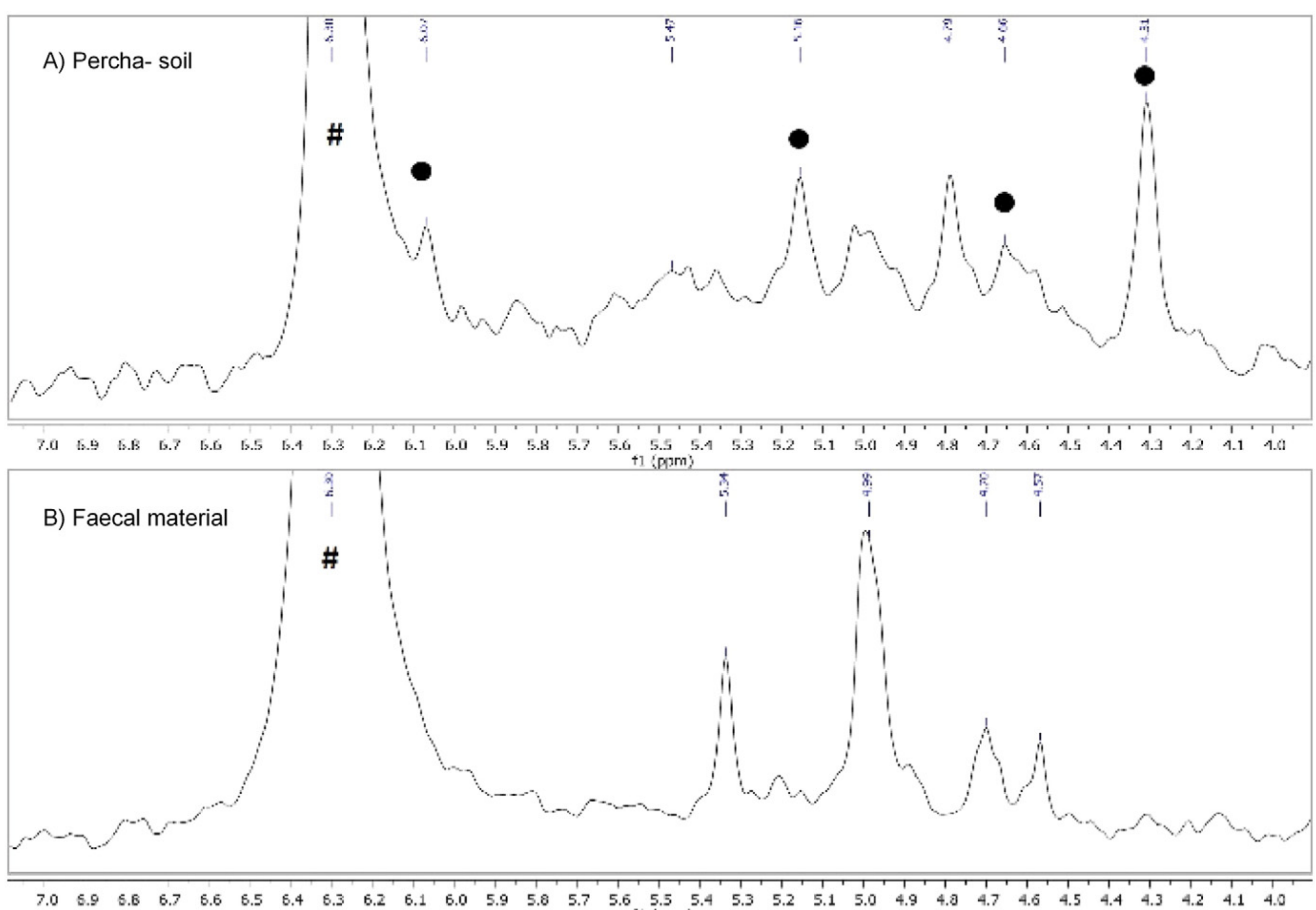

Fig. 5. Region of the phosphate monoesters in the 1D ^{31}P {^{1}H decoupled} spectrum of NaOH/EDTA extracts for (A) the Percha soil and (B) faecal material. The signal indicated by hashtag symbol corresponds to orthophosphate. In A) the peaks indicated by black circles are consistent with myo-inositol hexakisphosphate (Cade-Menum, 2005).

Table 7
Total P and available P (extracted with neutral salts or diluted acids) in faecal material and ornithogenic soils from present and previous gull colonies.

Site	Seabird species	Material	P forms	Reference
Cies islands (NW Spain)	Yellow-legged gulls (*Larus michaellis*)	Excreta Ornitogenic soil Control soil	TP: 0.32–9.68% TP: 0.09 ± 0.02% Pav: 0.03 ± 0.02% TP: 0.030 ± 0.009% Pav: 0.001 ± 0.003%	This study
Marinello coastal, Sicilia (Italy)	Yellow-legged gulls (*Larus michaellis*)	Excreta	TP[a]: 0.73 ± 0.25%	Signa et al. (2012)
Isla of May (Scotland)	Herring gulls (*Larus argentatus*)	Excreta	TP_{adults}: 0.12 ± 0.04% TP_{chikcs}: 2.78 ± 1.73%	Sobey and Kenworthy (1979)
Cape Vera (N Devon island, Canadian territory of Nunavut)	Fulmar (*Fulmarus glaciaris*)	Excreta	TP: 0.95 ± 0.20%	Brimble et al. (2009)
Fildes peninsula (W of Antarctica)	Gull guano (*Larus dominicanus*) Penguin Guano (*Aptenodytes forsteri*) Skua guano (*Catharacta maccormicki*)	Guano Ornitogenic soil	TP: 5.48% TP: 1.65% TP: 0.96% TP: 0.97–1.26%	Zhu et al. (2009)
Dongdao island (China)	Red-footed booby (*Sula sula*)	Excreta Ornitogenic soil Control soil	TP: 14.4–16.7% TP: 0.35–3.95% TP: 0.04–0.33%	Liu et al. (2006)
Marion island (Antarctica)	Macaroni penguin (*Eudyptes chrysolopus*) King penguin (*Aptenodotys patagonicus*)	Excreta	PT: 42,7 mg P/day bird PT: 13.0 mg P/day bird	Lindeboom (1984)
Livingston island (Antarctica)	Getoo penguin (*Pygoscelis papua ellsworthii*)	Excreta	TP: 4.6 ± 0.20%	Metcheva et al. (2011)
Bahia de los Angeles-Golf of California (Mexico)	Seabirds	Ornitogenic soils	TP: 1.30 ± 0.24%	Anderson and Polis (1999)
Katy Ryvackie, Dobskie lake, Golab at Deblin (Poland)	Black cormorant (*Phalacrocorax carbo sinensis*) Grey heron (*Ardea cinerea*)	Ornitogenic soil Control soil	Pav.: 0.016–0.084% Pav.: 0.008–0.033	Ligeza and Smal (2003)
New Zealand	Pre-Europeans seabird colonies of Petrels	Ornitogenic paleosoils Control soil	TP: 0.22–0.51% TP: 0.05 ± 0.005%	Hawke et al. (1999)
Campbell Island (New Zeland)	Penguin breeding sites abandoned over 30 y	Ornitogenic soils	TP: 2–3.6%	Moors et al. (1988)
Marion Island (Antarctica)	Blue petrel (*Halobaena caerulea*) Soft-plumaged petrel (*Pterodroma mollis*) Grey petrel (*Procellaria cinerea*) White-chinned petrel (*Procellaria aequinoctialis*) Great-winged petrel (*Pterodroma macroptera*)	Excreta Excreta Excreta Excreta Excreta	TP: 2.1 ± 1.25% TP: 1.1 ± 0.48% TP: 1.8 ± 0.81% TP: 1.4 ± 0.55% TP: 2.6 ± 1.47%	Fugler (1985)
Rottnest Island (Western Australia)	*Puffinus pacificus*	Excreta	TP: 1.54%	Bancroft et al. (2005)
Isla Norte de Nueva Zelanda, 21 Islas	*Pelecanoides urinatrix*; *Puffinus bulleri*; *Pterodroma macroptera*; *Pelagodroma marina* y otros.	Ornitogenic soils	TP: 0.56% POlsen: 237%	Mulder et al. (2009)
New Zealand, South Island	*Procellaria westlandica*	Ornitogenic soils	TP: 0.10 ± 0.05%	Hawke and Wu (2012)
Japón, Isaki Headland y Isla Chikubu	*Phalacrocorax carbo*	Suelo forestal (capa Oe y Oa) Suelo mineral (0–5 cm)	TP: 0.21 ± 0.12% TP: 0.23 ± 0.17% Porg: 0.10 ± 0.08% Pinorg: 0.13 ± 0.10%	Hobara et al. (2005)
North-western part of Wedel Jarlsberg, western Spitsbergen	Black-legged kittiwake (*Rissa tridactyla*)	Transecto (m a colonia; profundidad en cm) 0; 0–10 25; 0–10 50; 0–10 75; 0–10	(%) TP: 1.6; Porg: 0.12 Pinorg: 1.49 TP: 1.0; Porg: 0.16 Pinorg: 0.83 TP: 0.5; Porg: 0.13 Pinorg: 0.38 TP: 0.2; Porg: 0.12 Pinorg: 0.10	Ziolek and Melke (2014)
Horsens Fjord in Eastern Jutland, Denmark	*Phalacrocorax carbo sinensis*	Ornitogenic soils A1 (0–5) A2 (5–15)	TP: 5.95 ± 6.50% POlsen: 0.71 ± 0.85% Pox:1.25 ± 1.32% TP: 0.64 ± 0.29% POlsen: 0.10 ± 0.03% Pox: 0.22 ± 0.10%	Breuning-Madsen et al. (2008)
Ardley Island, Antarctica	Adélie penguin (*Pygoscelis adelie*)	Excreta	TP: 6.08 ± 0.19%	Xianyan et al. (2014)
Vestfold Hills, Antarctica	Adélie penguin (*Pygoscelis adelie*)	Excreta	TP: 2.76 ± 0.10%	
Cape Crozier (Ross Island, Antarctica)	Adélie penguin (*Pygoscelis adelie*)	Excreta	TP: 2.29 ± 0.05%	
Ardley Island, Antarctica	Gentoo penguin (*Pygoscelis papua*)	Excreta	TP: 10.28 ± 0.31%	

Pav: P bioavailability.
[a] Fraction sieved at 200 μm to eliminate sand and coarse materials (i.e., shells).

found in the soils associated with the gull colonies on the Cíes Islands (Table 7).

Other factors must be taken into account. For example, the environmental conditions may play a crucial role in the retention or leaching of soil P (Sposito, 1989; Sims and Pierzynski, 2005). Physical factors such as low rainfall and gentle slope favour retention of P in the soil, as they reduce soil drainage (Hawke et al., 1999). By contrast, soil chemical factors such as high concentrations of Ca or very high Fe_{Ox} contents and acidic pH will lead to the formation of a positive charge in the Fe/Al oxyhydroxides, according to reactions 2 and 3, allowing adsorption of phosphate and/or precipitation of Fe/Al phosphates (Wild, 1993).

$$Me - OH + H^{+} \rightarrow Me - OH_2^{+} (Me = Al \text{ or } Fe) \quad (2)$$

$$Me - OH_2^{+} + H_2PO_4^{-} \rightarrow Me - O\text{–}PO_3H_2 + H_2O \quad (3)$$

The degree of P saturation (DPS) in soil from the control site was less than 20%, indicating that this soil is undersaturated with respect to P (Fig. 6) (Kröger and Moore, 2011; Breuning-Madsen et al., 2008). On the contrary, the DPS of the gulls colony soils ranged from 52% in Figueiras to 90% in Pecha (Fig. 6), values that are extremely high considering that a DSP > 40% is the threshold from which the soil stops adsorbing P and starts to lose it by leaching and/or run-off (Sallade and Sims, 1997; Sims et al., 2002; Kröger and Moore, 2011). Despite the low P concentrations in the soil associated with the yellow-legged gull colonies, relative to those found in other seabird colonies in the world, the DPS is high because of the characteristics of the soils on the islands. The extremely sandy texture and the low concentration of amorphous Fe/Al oxyhydroxides reduce the P adsorption capacity of the soils.

The between year comparison (1997 and 2011) did not show significant changes for the TP concentration, and the P bioavailability ($P_{Mehlich}$, Fig. 3) tended to decrease due to soil P saturation, leading to loss of P by leaching/run-off, accompanied by a reduction in the number of pairs of gulls (Table 1).

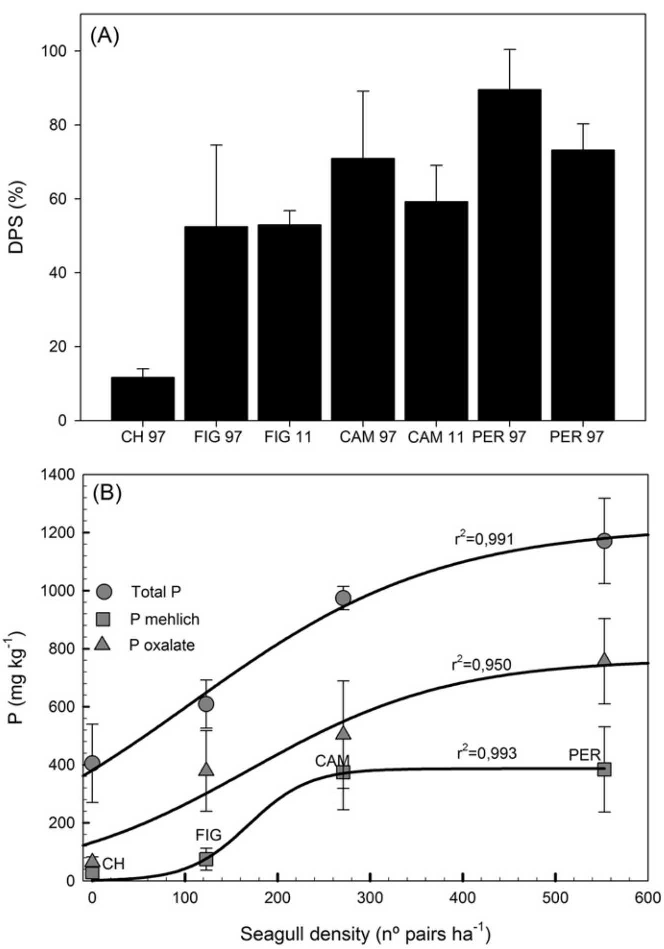

Fig. 6. A) Degree of P saturation (DPS), B) Relation between the total P, P soluble in oxalate and $P_{mehlich}$ in soils and gull density. CH: Cape Home (control site); FIG: Figueiras cliffs; CAM: Campana cliffs; PER: Percha cliffs.

Moreover, plots of labile P forms (P_{Ox} and $P_{mehlich}$) in 1997 against the density of gulls clearly show the P saturation of the soils affected by the gull colonies: the sigmoidal curve is characteristic of highly saturated systems (Fig. 6). This was not as obvious for the TP, as the difference between the years was not obvious (Fig. 3), probably because the main forms of P (P_{Res}, P_{Ca}, $P_{Clay/Al}$) are not adsorbed P forms but are precipitated, occluded or included in the structure of organic macromolecules. The labile P forms (primarily monodentate P_{Ads} and P_{AH}) may be quickly lost washed into coastal waters or reorganized in the soil through more refractory fractions, as may be the bidentate or binuclear P sorption, precipitated P or organic P associated with the P_{Res} fraction (Sims and Pierzynski, 2005).

Leaching of P from the colony soils to coastal waters was revealed by analysis of the run-off water samples obtained after heavy rainfall during the months of November to January of 2011–2012 and by the ^{31}P NMR analysis (Table 6, Fig. 4). The run-off analysis revealed high concentrations of soluble P (9.25 ± 0.78 mg l^{-1}; n = 8), while in the control area and small streams outside the gull colonies, the concentration of soluble P was always below the detection limit (<0.05 mg l^{-1}) (Tejada, 2012). Therefore seabird colonies may be an important source of nutrients to freshwater and coastal waters and/or lead to eutrophication of shallow water aquatic environments, such as ponds or lagoons (García et al., 2002; Ellis et al., 2006; Keatley et al., 2009; Signa et al., 2012). In fact, phosphorus has been recognized as the main limiting nutrient regulating total ocean productivity (Tyrrel, 1999). On the other hand, eutrophication produced by increased phosphorus (P) concentrations may trigger several known deleterious effects to water bodies (i.e., intensive growth of benthic organisms, decreased concentrations of dissolved oxygen, sharp changes in pH and release toxins (Tappin, 2002; Smith, 2003; Deng et al., 2010)).

4.2. Phosphorus distribution in soils under gull colonies

All P forms were positively and highly significantly correlated (Table 8), which is unusual due to the competition of the different soil components for the phosphate ion (see e.g.,Jiménez-Cárceres and Alvarez-Rogel, 2008) but is consistent with the fact that most of the P forms have a common origin; the faecal material produced by gulls.

Moreover, the distribution of the P forms in the cliff soil differed from that observed in other soils. The dominant P forms in acidic soils usually include P bound to Fe and Al oxy-hydroxides (Wild, 1993; Sims and Pierzynski, 2005; Rengel and Marschner, 2005). However, due to the low concentration of amorphous Fe and Al oxides and hydroxides (Fe_{Ox} and Al_{Ox}), the $P_{Fe/Mn}$ and $P_{Clay/Al}$ were minor fractions and the P_{Ca} was the main fraction. High P_{Ca} contents are typical of alkaline soils, not acidic soils such as those in the study area (Sims and Pierzynski, 2005). In this study, the P_{Ca} (the dominant P form) appears to have originated from seagull droppings (Table 2). Similar results were found in soils under other seabird colonies (see e.g.,Ziólek and Melke, 2014). Another possible source of the P_{Ca} may be the weathering products of apatite, an accessory mineral in local granites. This would explain the relatively high presence of this P fraction in the control area.

The P_{Res} was also an important fraction in the colony soils and the concentrations were much higher than in the control area soils. High P_{Res} contents may also be derived from faecal material in which it represents the most abundant P form, although part of the P_{Ads} in the soil may join the residual fraction over time (Tiessen et al., 1994; Pierzynski et al., 2000). This may occur through association with alkyl or aromatic groups in the humified organic matter (Hamdan et al., 2012). This is consistent with the highly significant correlation between the P_{Res} and organic C (rs = 0.785; p < 0.001, n = 10).

The amount of $P_{mehlich}$ indicates increased P bioavailability to plants in all soils affected by the yellow-legged gull colonies. This is evident on the Percha cliffs, where large, dense clumps of prairie grasses (*Dactilys glomerata* subsp. *maritima*) grow, in contrast to the rare occurrence of the plant in the control area (Fig. 1C, D). Plant growth leads to the

Table 8
Correlation coefficients among degree of P saturation (DPS), P mehlich and P total (TP) and different P forms.

	TP	$P_{mehlich}$	P_{Ads}	$P_{Fe/Mn}$	$P_{Clay/Al}$	P_{HA}	P_{Ca}	P_{Res}
DPS	0.809***	0.778***	0.792***	0.916***	0.756***	0.543**	0.752***	ns
TP		0.639***	0.527**	0.684***	0.446**	0.647***	0.543***	0.543**
$P_{mehlich}$			0.579***	0.596***	0.416*	0.395*	ns	ns
P_{Ads}				0.792***	ns	0.625***	ns	0.403*
$P_{Fe/Mn}$					0.436*	0.575***	0.564***	ns
$P_{Clay/Al}$						ns	0.539***	ns
P_{HA}							ns	0.574***
P_{Ca}								ns
P_{Res}								

ns: no significance.
*** $p < 0.001$.
** $p < 0.01$.
* $p <= 0.05$.

incorporation of P in plant biomass and therefore to an increase in the organic P that becomes part of the soil humic substances (Pierzynski et al., 2000). The present results clearly show P enrichment in both the P_{Res} and in the soil humic acid (P_{HA}) (Tables 4 and 5), a common minor P fraction in other soils (see e.g.,Jiménez-Cárceles and Álvarez-Rogel, 2008) but the fourth most abundant P fraction in the soils affected by the yellow-legged seagull colonies (Table 4). Organic P should also be considered as a bioavailable form because alkaline phosphatase, an enzyme produced by many microalgae, can hydrolyse phosphomonoesters (one of the most abundant organic P form in gulls colony soils, see below) for utilization as a potential source of P for phytoplankton growth (García et al., 1997) and thus may contribute to the eutrophication of coastal waters.

The ^{31}P NMR analysis revealed clear differences between the P contents of humic substances in the control area, colonies and faeces (Fig. 4). The spectrum of the colony soil (Soil-Percha) was more complex and similar to the spectrum obtained for the faecal material in comparison with the soil in the control area (Soil-CH). Pyrophosphate and orthophosphate monoesters (mainly myo-inositol hexakisphosphate) were also obtained along with the orthophosphate ion (Fig. 5, Table 6). Inositol phosphates are regarded as one of the most common and stable P forms in mineral soils (Stevenson, 1982), which explains its presence in the control site, although at much lower concentrations in the colony soils. On the other hand, inositol phosphates (phytate) can be hydrolyzed by phytase, an enzyme that is exuded in large amounts by several microorganisms (e.g.,*Aspergillus niger*), thus enabling plants to utilize phytate (Osborne and Regel, 2002; Rengel and Marschner, 2005). Pyrophosphate (although inorganic) can be considered functionally similar to organic phosphorous because it has a biological origin and requires hydrolysis by phosphatase enzymes (Turner and Engelbrecht, 2011).

4.3. Dynamics of the yellow-legged gull population and the effects on natural habitats of community interest (Directive 92/43/EEC)

The Percha cliffs, located in the northern part of Monteagudo Island (Fig. 1), are considered the cliff areas where the gulls exert the greatest influence on soils and vegetation. In the first census carried out, the highest densities of gulls were recorded on this side of the island (Table 1). The densities were lower in the other two selected areas (especially Figueiras) in the 1970s and early 1980s, presumably due to their greater accessibility, which probably caused a higher degree of human pressure (i.e., grazing and collection of eggs; Barcena, 1977). After the 1980s, due to a combination of several factors (cessation of the human impacts, increased environmental protection and increased food resources, such as fishery discards and urban landfills in Vigo and Pontevedra), the seagull colonies expanded, occupying all of the cliffs on the islands (Table 1; Munilla, 1997; Arcea, 1999). More recently, despite the dramatic decrease in the breeding population, the yellow-legged seagulls on Cíes Islands have begun to occupy the eastern slope of the islands, which is more protected from the wind and storms, and to nest in heavily humanized areas such as roads, lighthouses and wharfs. Similar behaviour has also been observed in other gull species such as Auduoin's gull (*Ichthyaetus audouinii*), which has abandoned the traditional breeding colonies located on small islands in the Mediterranean, and has begun to settle in strongly humanized areas, such as docks and roads (Jiménez, 2014).

In about 2008, the yellow-legged seagull began to colonize the most important dune system in the National Park, located in Punta Muxieiro (Fig. 1). Colonization of this new habitat by the yellow-legged gull has potentially negative effects on the grey dunes, a priority habitat (habitat 2130, Directive 43/92 / EEC) and on some of the rare or unique plant taxa from the NW of the Iberian Peninsula, such as *Corema album* and *Armeria pungens*. In the dune areas of the Sálvora archipelago (located on North of the National Park, Fig. 1), the vegetation has been greatly modified due to the nesting of yellow-legged gulls. In this case, ruderal species such as *Urtica membranacea*, *Erodium cicutarium*, *Echium rosulatum*, *Cistus salvifolia* and *Parietaria judaica* are common, and *Linaria arenaria*, which does not occur in other dune systems, is predominant during the summer. The results obtained for this dune system indicate a high P content in both summer ($P_{mehlich}$0–5 cm $= 80 \pm 23$ mg kg^{-1}) and winter ($P_{mehlich}$ 0–5 cm $= 57 \pm 28$ mg kg^{-1}), despite the sandy texture of the substrate. However, the concentrations of the N forms (N^-NO_3, $N–NH_4$), which are easily removed by leaching, were below the detection limit (<0.05 mg kg^{-1}; Tejada, 2012; Otero, 2014). Likewise, recent studies in the grey dune at Punta Muxierio, revealed significantly higher bioavailable P contents than in the dune systems without gulls (P Mehlich without gulls: 7.60 ± 3.0 mg kg^{-1}; with seagulls 63.2 ± 26.1 mg kg^{-1} n = 5; $p < 0.02$; Otero 2014). Therefore, because of the stability of certain P forms in the soil, enrichment of these elements should be considered a permanent, irreversible change, which may lead to changes in plant communities such as in former colonies of seabirds that disappeared hundreds or thousands of years ago (see Hawke et al., 1999; Sun et al., 2000; Huang et al., 2009).

On the other hand, the seagrass (*Zostera marina*) growing in the Lagoon "Lago dos Nenos" (Fig. 1), which is also considered a priority habitat (habitat 1150 coastal lagoons, Directive 43/92/EEC), disappeared during the occurrence of a summer green algae bloom (*Enteromorpha* sp.; Fig. 1F). Analysis of lagoon sediments indicated enrichment of P in the upper 5 cm (0–3 cm depth TP = 1215 mg kg^{-1}, Otero, 2014) relative to the deepest core layer (22 cm; TP = 274 mg kg^{-1}, Otero, 2014).

Study of the concentration of seagull droppings shows that between 5 and 15% of the P present is highly soluble and mobile. In addition, precipitation also incorporates high concentrations of N associated with the volatilization of NH_3 directly from the faeces (Riddick et al., 2012). This leads to an increased bioavailability of nutrients and to eutrophication of surface systems, which may gradually induce changes in plant communities (see e.g.,Vidal et al., 2000; Bowman et al., 2012; Wassen et al., 2005). Most terrestrial ecosystems of the temperate zone are considered to be N-limited; therefore, N-enrichment is seen as a major cause of the loss of plant diversity in forests, grasslands and islands (Vitousek and Howarh, 1991; Guitián and Guitián, 1989; Vidal et al., 1998, 2000; Sala et al., 2000; Stevens et al., 2004; Suding et al., 2005; Bobbink et al., 2010). However, recent studies indicate that P may play a similar or more important role than N in the conservation of plant diversity (Wassen et al., 2005; Condit et al., 2013).

However, in contrast to previous assertions (e.g.,Guitián and Guitián, 1989), the key element for the changes observed in plant communities in seabirds colonies may be P rather than N (Wassen et al., 2005). Previous studies have shown that in soils under the yellow-legged gull colony, the inorganic exchangeable N in the soil (NH_4^+ and NO_3^-) decreases to concentrations similar to those measured in the control region during the winter, even in cliffs with higher densities of seagulls (Otero and Sanjurjo, 2000; De La Peña, 2012). By contrast, the P concentration in soil colonies is not subject to seasonal changes and is present at much higher concentrations in the soil colonies than in the control area throughout the year (Table 4). Thus, despite the strong decline in the gull population that occurred between 1997 and 2011, the concentration of PT scarcely underwent changes and no clear pattern was observed in the bioavailable P concentrations. These findings are consistent with the behaviour of P in the soil and with the interactions with soil components. Large quantities of P can be stored in soils by chemical fixation processes involving soil constituents, such as Al, Ca, Fe, and organic matter, which prevents its loss via leaching, and at the same tine shows that enrichment of this element in the soil should be considered a permanent, irreversible process.

5. Conclusions

The faecal material generated by the yellow-legged gull in the Atlantic Islands of Galicia National Park contains high levels of phosphorus, similar or even higher than those observed in other seabird colonies. The high P contents have led to the accumulation of levels of total P and bioavailable P that are up to, respectively, 3 and 30 times higher than in the control site. The chemical fractionation and ^{31}P NMR spectra clearly showed the influence of faecal material on soils affected by seagull colonies. The major P forms in the faecal material and in the colony soils were apatite P and refractory organic P forms and, to a lesser extent, $P_{Clay/Al}$, P_{HA} and $P_{Fe/Mn}$.

The dominance of precipitated or occluded (in mineral phase) P forms in the faecal material and in the soil reduces the P loss through run-off. As a result, and despite the heavy rainfall and absence of gulls, the P contents were high in the colony soils during winter. However, refractory P forms can become bioavailable (Hawke and Comdron, 2014). In addition, the soluble P fraction present in the faecal material (P_{Ads}) will not be incorporated into the P-saturated colony soil and may be lost via run-off to coastal waters. The significant changes in the soil and water P cycles caused by seabird colonies must be considered as permanent and irreversible and the impacts on plant communities and habitats must also be assessed.

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