Impact of Seabirds on Soil

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Abstract

Colonial seabirds ingest food that contains oligoelements that accumulate in their tissues, from their feeding area to the soil depositing in the feces and food lying on the ground. This general pattern was observed for selected oligoelements, as well as persistent inorganic and organic pollutants in seabird colonies, in polar areas and in some tropical locations, but have not yet been demonstrated in Portugal. Consumers are known to bioaccumulate and biomagnify marine food networks, mainly cadmium (Cd), mercury (Hg), selenium (Se), copper (Cu), zinc (Zn) and strontium (Sr). Assuming that this pattern has existed for centuries, we also predict that, when analyzing soil samples in the colonies, we will see variation, but high levels compared to nearby soils but no colony of seabirds.
In analyzing the samples, we will analyze how accumulation may have differed over time, and assessments, if the patterns correlate with known climactic cycles, such as a North Atlantic Oscillation.
From your perspective, we expected the soils to be contaminated by various elements because of biotransport by birds feeding in a contaminated marine environment [1]. However, based on the analyses that I ran, I did not see this at all – in fact, there was no difference in concentrations of several elements which often are higher at colonies of seabirds in other studies.

Key words — Seabirds, trace elements, isotopes, techniques, samples, digestion, contaminants.

1. INTRODUCTION

For seabirds, defined as birds that spend a significant proportion of their life in coastal or marine environments, food intake (including fake foods such as plastic items) and water are the major routes of exposure to pollutants. Seabirds are susceptible to bioaccumulate a wide range of chemicals because they are large predators in marine food webs. This vulnerability, especially for lipophilic substances, makes these birds potentially indicators of changes in the environment and can be used to monitor pollutants that bioaccumulate and / or enlarge in concentrations at trophic levels. To verify these events we will have as study basis the island of Berlengas located near Peniche. The main objective of this dissertation is to evaluate the impact that seabirds have on the soil. When collecting and analyzing the samples we obtained, we can see if the presence of seabirds indicates any type of contamination, evaluating the presence of trace elements in them. To arrive at any kind of conclusion it is necessary to carry out several laboratory methods that are described in detail later in the dissertation.

2. SEABIRDS

Seabirds are an important vector between their marine feeding grounds and their terrestrial breeding environments [2]. These organisms transport nutrients and contaminants derived from the sea and then depositing them on land through manure [3]. As with nutrients, seabirds are also a significant source of contaminants to the terrestrial environment, as they are at the top of the food chain soon accumulate many contaminants, which enter the body and through manure, excretion, mortality, contaminate for example the nesting sites [3]. Every year, billions of migratory animals cross the globe in search of greater opportunities for security and reproductive production. In doing so, these migrants carry nutrients, energy and other organisms (including seeds, molluscs, parasites and pathogens) between different sites[4]. Seabirds are among the top predators in the marine ecosystem, and because of their relatively high trophic position, are at risk from the bioaccumulation of toxic chemicals from both natural and anthropogenic

Figure 1: Typical Island Seabird

sources. Mercury (Hg), lead (Pb), arsenic (As) and cadmium (Cd) are non-essential elements that are distributed globally and transported atmospherically [5]. Feathers often contain the biologically active form of metal contaminants [6] and feather replacement is a major pathway for the elimination of contaminants from a body burden [7].

2.1 Contaminants Analysed

There are several metals present in the collected samples, but for this case study we only want to analyze the As, Cr, Ni, Cu, Zn, Sr, Cd, Pb, which are pollutants that affect the area inhabited by seabirds [4]. Marine organisms often have elevated concentrations of As because of their acquisition of As via seawater [8]. While as has been measured in a variety of seabird studies, its toxicology and chemistry in marine birds is poorly known as compared with elements such as Hg or Pb [9]. In general, less than 30% of birds cadmium body burden is in feathers [9], much less than for Hg or Pb. Cd levels in feathers are often low, but concentrations that are observed are likely endogenous in origin [9]. Pb is an anthropogenic contaminant that has no biological function and can be transported great distances atmospherically [9]. In general, feather Pb levels above 4000 ppb are thought to cause sublethal effects in marine birds [9]. Knowledge of contaminant loads in adult seabirds does not normally allow to identify the exact location of point-source pollution [10] even though some species maybe useful as bioindicators at the regional scale. In general, chicks and fledglings are more suitable to investigate local pollution, especially through feather analysis [11].

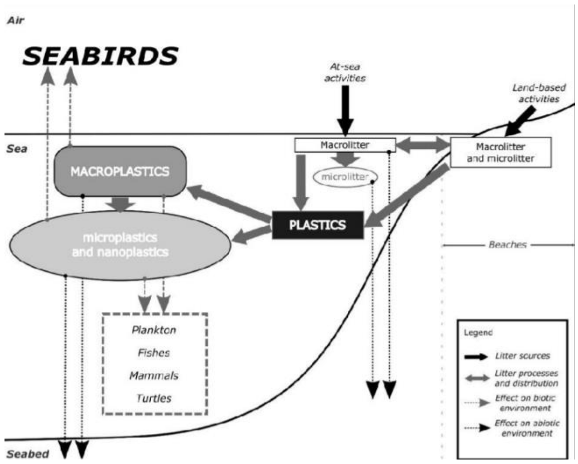

Figure 2: A schematic cycle of litter at sea focused on plastics and seabirds

3. STUDY AREA AND SAMPLING

The study site consisted of two nearby locations: Berlengas, a nature reserve consisting of an Island offshore where the seabirds nested; as well as the área surrounding, Peniche, the community on the peninsula which is closest to the island.

Figure 3: Berlengas Island

On November 16, 2017, different samplings were carried out along Berlengas Island, and soil samples were collected at various depths, collected from 0 cm to > 10 cm. A total of 64 samples were collected, including soil samples taken from Berlengas Island, collected in Peniche, and samples of stomach contents and guano of birds. Also, Vegetation was also collected, in which it was concluded that it would be the same both in the island of the Berlengas as in the Baleal. The collected samples will be studied in ICP-MS to observe if they contain elements like As, Cd, Cu, Cr, Ni, Pb, Zn and Sr in their constitution to determine if the seabirds, through their guano, have affected the concentrations of these elements in the soil [12]. The 64 samples were collected and stored in plastic bags. The samples were then oven dried at 40 ° C overnight to avoid loss of volatile compounds. Subsequently, they were disintegrated in powder through an agate mortar and stored in polyethylene tubes, after which the process of digestion of the samples was started. After all the samples had passed through the digestion process, they were taken to the C2TN laboratory where the ICP-MS is located, and it was possible to evaluate the concentration of isotopes present in each sample. As a sampling method, we use a clean steel corer, 2 cm in diameter, and pushed it and twisted it into the soil to get as deep as possible. Once we removed it, we carefully extracted the core and cut 1 cm sections and placed each one in a separate bag, labeled "0-1" to the top, "1-2" to the next cm, to the end of the corer.

4. ANALYTICAL METHODS

4.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

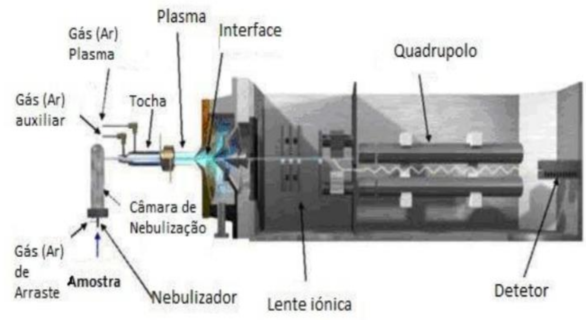

Figure 5: Main elements of ICP-MS

This technique is based on the use of the energy supplied by the plasma for the ionization of the sample, where later the ions that have been separated according to their mass / charge ratio are converted into a measurable electric signal under the action of electromagnetic fields.

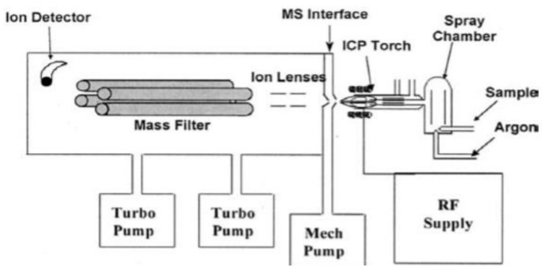

Figure 4: Illustration of how ICP-MS works

The ICP-MS system is usually composed by: Sample introduction system, that contains a nebulizer and a spray chamber; ICP torch and RF (radiofrequency) coil, responsible for the generation of argon plasma; Interface, the connection between the system; Vacuum System; Collision/reaction cell eliminates the possible interferences, before the sample reaches the mass spectrometer; Ion optics conduct the desired ions to the quadrupole; Mass spectrometer; Detector, responsible to the count of the individual ions; Data handling and system controller. The process begins with the input of the sample into the nebulizer, as an aerosol gas with argon plasma [13]. This plasma has the functions of dry the aerosol, dissociate the molecules and removing the electrons. The resulting aerosol is sprayed into the mass spectrometer where the ions will be divided accordingly to their mass-to-charge ratio. At the end, the ions are converted into an electrical signal and a software compares the pulses from the electrical signal with standards, creating a calibration curve. Is through this calibration curve that is determine the concentration of the elements [14].

4.2 Laboratory Methods

The determination of the concentrations of the total elements in ICP-MS is performed with liquid samples, so that the collected soil samples and sediments must be digested with acid. Approximately 0.150 g of each sample (weighing the balance accurately) was placed in Teflon pumps. This procedure involves the mixing of regal water, which is obtained by mixing 65% (v / v) bi-distilled HNO 3 and 35% (v / v) distilled HCl twice. As the objective was to put 1 ml of this water in each sample, 7.5 ml of nitric acid and 22.5 ml of hydrochloric acid were measured, after the measurements the mixture was added to this sample and then 6 ml of 40% (v/v) HF. At the end of this step, the next step was to put all the pumps in the oven and wait until it reached the temperature of 100 ° C, when it arrived it was expected 1h for the samples to heat up. After the time was up, the samples were opened with the lid open in the sandbath in order to evaporate the contents (ie all the liquid left and only dried). Then, after the samples had evaporated, 1 mL of 1M HNO 3 (1 mL of HNO 3 and 5 mL of H 2 O) was added to the resulting residue and allowed to stand for twenty minutes. Then each liquid of each sample was passed into each well-identified test tube and filled with Milli-Q water (pure water) until it reached 30 ml, and the digestion process was completed 4 times, 16 samples at a time. At C2TN a semi-quantitative analysis was started in the laboratories, to know for sure what to dilute, after that it was placed 9ml of HNO3 at 5% and 1ml of each sample in each tube. The next step was to shake the samples on the shaker and placed the 1 μl sample in ICP-MS. As mentioned above the ICP-MS is an apparatus that reads the concentrations of several metals present in the samples, for my case study the metals that are important are Cr; Ni; Ass; Zn; At; Sr; Cd and Pb. In this apparatus for the reading to be viable the concentration of metals must vary between 3-200 ppm for Cr; 0,2-200 ppm for Ni and Cu; 6-200 ppm for Zn; 0,3-200 ppm for As; 0,14-200 ppm for Sr; 0,03-200 ppm for Cd and finally 2-200 ppm for Pb.

4.3 Quality Control and Errors

To evaluate the recovery and quality control of the process, a certificate reference material (CRM) was used. The reference material used was MESS-3 (estuarine sediment) from the NRC (National Research Council of Canada). To guarantee the quality and representativeness of the samples, 2 repeated samples were used in each digestion to minimize measurement errors, thus 16 samples were digested, 2 replicates the reference material and the blank.

Table 1: Concentration of the Blanks (μg/L)

	Blank 1	Blank 2	Blank 3	Blank 4
As	1,60	1,61	1,60	1,60
Cd	1,34	1,34	1,34	1,34
Ni	1,85	2,61	1,69	1,69
Cu	1,87	1,91	1,62	1,61
Cr	1,66	2,08	1,83	1,85
Pb	1,59	1,63	1,46	1,46
Sr	3,80	4,48	1,72	1,71
Zn	1,60	1,61	1,60	1,60

The validation of the accuracy of the process and the results were obtained by the blanks, the CRM and the random replicateThese samples were performed exactly like the regular samples in the methods. Errors were calculated by an appropriate formula and were added at the end to each respective concentration. I calculated the concentration for each of the 7 elements analyzed for each of the collected samples, below just a small example.

Table 2: Some of the samples and some of the metal concentration´s

Concentration/ Samples	As	Cd
Ber 1 0-1	8,9±0,79	4,41±3,19
Ber 1 3-4	6,9±0,76	3,45±3,07
Ber 2 0-2	6,6±0,77	4,06±3,13
Ber 2 2-3	7,4±0,72	4,09±2,93

5. RESULTS AND DISCUSSION

To make a comparison and comment the results I will divide this section into 2 parts, the soils, in which I analyze all the soil samples both on the island of Berlengas and in Peniche, the other part is only relative to feces, and in the end I compare the results obtained in the soils with the results obtained in the feces. Within this section my comparison parameters will be the depth at which each sample was taken and will be the location (on the island or continent). Analyzing the metal concentrations for each sample, (table that is present in Annex D), it is observed that the elements As, Cd, Cu, Zn were often present in lower concentrations as the depth increases, which does not happen for the zone 1, zone 3 and zone 6.

Table 3: Example showing concentration variation with depths

	As	**Cd**
Ber 1 0-1	9,00 ± 0,79	4,41±3,20
Ber 1 3-4	6,87 ± 0,76	3,45±3,07
Ber 3 0-1	13,51 ±0,78	7,67±3,17
Ber 3 2-3	12,38± 0,82	4,82±3,29
Ber 6 1-2	13,44 ±0,76	6,18±3,08
Ber 6 2-3	5,39 ±0,81	1,41±3,28
Ber 6 4-5	6,08 ±0,78	3,17±3,16
Ber 6 6-7	6,38±0,82	0,98±3,32

Because the deeper the soil the less contact the birds have with it, since at the top of the soil the birds deposit the feces, they make nests, they eat, and this can contaminate the soils if the birds are contaminated. When precipitation occurs, rainwater infiltration to the soil can occur, which may be why some of the metals are infiltrated in the soils [15], such as Ni, Cr, Pb and Sr and are present in higher concentrations in the deeper soils. Areas marked 1-4 are in rocky areas where there are not so many nesting birds formed, at least not as evident as in zones 5-7. In areas where nests predominate are areas where the concentration of most of the contaminants should be higher, as they are areas in which gulls drop their feathers, stand near their nest and spend more time, all of which is associated with defecation. Regarding the location, the samples taken from the soil of the continent have lower concentrations of As, Cd, than the samples taken from the Island, which was unexpected. This may be due to the fact that gulls carry mainly contaminant values in their feathers (mainly As through the sea), and then end up depositing them in the soil in various ways. We can also observe that the soil samples have a higher concentration of Pb, Sr and Zn in relation to the other samples. Zn is already present in birds alone [16]. So, it is enough for a bird to have landed on the ground or to have deposited a feze for this metal to be detected. Pb is rarely found in its elemental state, usually found in Zinc minerals.

Table 4: Range of sample concentrations for soils

Elements /Locals	**Soil on the Island**	**Soil on Continent**
As	3,9 - 22	4,8 – 35
Cd	0,9 -9,1	2,9 -21
Ni	5,9 - 38	6,6 - 27
Cu	4,6 - 32	9,9 - 81
Cr	5,4 - 13	6,3 - 53
Pb	3,8 - 73	3,9 - 50
Sr	29 - 284	3 - 999
Zn	3,9 - 22	4,8 – 35

In general, contrary to what was expected, the concentrations of trace elements present in the Continent are greater than those present on the Island. Based on many other studies, I expected that the concentrations of elements would be higher in soils at the bird colony, as found in many other studies [1]. A recente study [17] found that gulls from Berlengas feed both on land but notably at sea, where they clearly feed high in the food chain and thus must acquire elements as at colonies to the north [1]. What this suggests to me is two possibilities. First, I noted that the "soil" from many of the sites at the Island was very coarse and rocky, with little organuc material. This may mean that the physical characteristics of the soil are unsuitable for trap much of the faeces – it may run off the island extensively with rainfall. Second, the mainland sites I sampled at were close to Peniche or agricultural areas. These would be areas that would receive considerable pollution from local industry and human activities. Biotransport by the birds, even to a site close by, is far less of an issue than local pollution. In relation to feces only samples were taken from the island, so I can not make a comparison with Peniche, just compare with the soils in general. When analyzing concentrations in the feces of birds, it is seen that concentrations of As, Cd and Ni predominate in this type of sample and are present in higher concentrations compared to the other samples. This may be due to, the fact that birds eat fish, which are contaminated with these metals, especially with As, since it is the most common metal present in the fish's organism, ie the birds ingest the fish become contaminated, and by defecating contaminate the soils in which they circulate [17]. Cd can be found in water, in small quantities, ingested by fish, which will affect seabirds again and subsequently soils [17].

Table 5: Range of sample concentrations for feces

Elements /Locals	Feces
As	19 - 69
Cd	4,5 - 73
Ni	9,2 - 112
Cu	7,6 - 133
Cr	5,8 - 7,6
Pb	3,7 - 4,9
Sr	77 - 569
Zn	19 - 69

The stool samples were taken from the same zone as the samples from zone 2 to zone 5. These zones are really the places where they have the highest concentration of metals and where there is the presence of gulls. I suspect that during the breeding season the gulls are feeding on fish (with high levels of elements) and defecating near their nesting areas.

5.1 Statistical Analysis

We want to verify if there are differences between the average responses of treatments; the procedure used to infer whether such differences actually exist is called Analysis of Variance (ANOVA). This statistical procedure consists of a type of data analysis made from the excell which gives us a value of p, that is, tests for statistical significance, or the likelihood of getting differences by chance. If the value of p for any comparison is less than 0.05, then it means that the probability of the two groups being different by chance is less than 5%, a small chance, and we consider this then to be statistically significant. For all of the comparisons except Cr, the F statistic is low and the p values are higher than 0.05, which means that the concentration of each element for the soils on the Island and for the soil in the Continent are statistically similar. Actually, looking at Table 8, the maximum concentrations for all of these elements were higher on the Continent than on the Island. For Cr, the Continental soil values were also higher than the Island values, and were statistically significant. This is not surprising because Cr does not biomagnify but it is a common industrial output from activities like tanning leather, textile preparation, wood preservation and welding [18]. Thus, with industrial activities around Peniche and on the mainland, higher Cr levels than on the island would be expected.

6. CONCLUSION

From your perspective, we expected the soils to be contaminated by various elements because of biotransport by birds feeding in a contaminated marine environment [1]. However, based on the analyses that I ran, I did not see this at all – in fact, there was no difference in concentrations of several elements which often are higher at colonies of seabirds in other studies. The suite of elements that I examined may not differ that much between mainland and offshore Island colony sites, but most of those elements do not biomagnify [19]. However, other chemicals (persistent organic pollutants, mercury) might because they biomagnify, attaining high concentrations in bird faeces, and thus they should be dramatically higher at the colony site. A follow up study focused on these biomagnifying chemicals would help shed light on whether the lack of significant diferences in chemical concentrations between the mainland and Island is due to the elements examined or represents na anomalous colony site where soils have not built up high levels of contamination from nesting birds.

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