



Occurrence of rare earth elements in fledgelings of *Thalasseus sandvicensis*

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ABSTRACT

Rare Earth Elements (REEs) are increasingly exploited for crucial new technologies, and their massive use in the past decades has significantly increased their environmental concentrations. Although their effects have been extensively studied in vitro and in vivo in model species, little is known of their accumulation and potential toxic effects in wildlife, including waterbirds. In the present work, we measured the concentrations of REEs in feathers of young Sandwich tern (*Thalasseus sandvicensis*) about 16–20 days old to assess whether the accumulation of these elements may be a concern in Venice's Lagoon, one of the most important wetlands of the Mediterranean area for breeding and migrating birds. The REE concentrations detected in the Sandwich tern were the highest among those reported in the literature for bird's feathers ($940.9 \pm 223.0 \text{ ng g}^{-1}$), although in the study area industrial activities related to REEs mining, processing and disposal are absent. In particular, Lanthanum (La) was more abundant in the feathers than other REEs and accounted for 73–97% of total REEs detected. Analysis of bird's food indicated that diet is a relevant route of exposure to REEs for young terns; however, concentration in fishes are relevantly higher than in the feathers for all REEs other than La. The study evidenced the need to collect more information concerning the occurrence of REEs both in the abiotic matrices (i.e. water and sediments) and in living organisms of different trophic levels to improve the general knowledge concerning the fate of REEs in the aquatic ecosystems.

1. Introduction

Anthropogenic activities release continuously trace elements in the environment and are one of the main threats to the biodiversity and the conservation of wildlife (Tovar-Sánchez et al., 2018). Accumulation and effects of non-essential and toxic elements were extensively studied in past decades (Scheuhammer and Norris, 1996; Vizueté et al., 2018; Wolfe et al., 1998). In contrast, rare earth elements (REEs) such as yttrium (Yt), scandium (Sc) and lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) have received the attention of the scientific community more recently, due to their increasing concentrations in aquatic and terrestrial ecosystems (Adeel et al., 2019; Khan et al., 2017; Kulaksiz and Bau, 2011).

Even if their abundance in the Earth's crust is significantly higher than other commonly exploited elements (Gupta and Krishnamurthy, 2004), REEs are never found as pure elements, and they occur naturally only as minor/major components in a wide range of mineral types, in-

cluding halides, carbonates, oxides, phosphates and silicates (Dostal, 2017). Moreover, REEs are non-essential elements for the biota (Leal Filho, 2016), and their occurrence in tissues of plants and animals can be ascribed almost exclusively to anthropogenic sources, including active and abandoned mines, discharges/effluents from industries processing REEs, disposal of consumer and industrial products containing REEs, electronic wastes recycling plants (Gwenzi et al., 2018). REEs' peculiar physical and chemical properties make them crucial for many critical technologies, including high-performance permanent magnets, high-efficiency batteries for electric and hybrid-electric cars, x-ray and other medical imaging, fluoresce light production, aircraft engines manufacturing, glass and ceramic industry (Adeel et al., 2019; Balaram, 2019; Charalampides et al., 2015; Jordens et al., 2013). In addition, fluid catalytic cracking catalysts, industrial residues (red muds and phosphogypsum), application in agricultural soils and uses as additives in growth promoters for livestock are also possible sources of environ-

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mental contamination (Abdelnour et al., 2019; Binnemans et al., 2013; Thomas et al., 2014).

Toxic effects of REEs have been studied in vitro for decades to address effects on humans and model vertebrate species (Haley et al., 1961; Pałasz and Czekaj, 2000; Rim et al., 2013; U.S. EPA, 2012 and citations therein; Wang et al., 2017), plants (Wang et al., 2019; Xu et al., 2016) and invertebrates models (Oral et al., 2017; Trifuoggi et al., 2017; U.S. EPA, 2012 and citations therein). However, few ecotoxicological studies on REEs bioaccumulation and transfer in food webs have been performed (Amyot et al., 2017; Mayfield and Fairbrother, 2015; Squadrone et al., 2019b).

Although birds are particularly vulnerable to element pollution (Burger and Gochfeld, 2002), effects of REEs on birds were poorly studied, and most of the available studies dealt primarily with effects caused on poultry, broilers and laying hens by REEs used as feed additives (Abdelnour et al., 2019, and citation therein). As concern bioaccumulation also, the literature on REEs' tissue concentrations in wild birds is scant, and data are available only for a restricted number of species, including the ring-billed gull (*Larus delawarensis*) (Brown et al., 2019), the common eider (*Somateria mollissima*) and the willow ptarmigan (*Lagopus lagopus*) (MacMillan et al., 2017). These studies recognised the liver as the organ accumulating more REEs in vertebrates, including birds; nevertheless, a recent study performed on Humboldt penguins (*Spheniscus humboldti*) evidenced that also feathers may serve as a reliable indicator of REEs exposure and accumulation in birds (Squadrone et al., 2019a).

Feather analysis is an ethically superior technique as compared with organ and tissue analysis since feather collection is a non-invasive, harmless procedure and can be repeated on the same individual to study the accumulation of trace elements without affecting its welfare or survival (Adout et al., 2007; Rutkowska et al., 2018). Furthermore, accumulation in feathers may be associated with a particular timespan, which can be inferred through ptilochronology in adult birds (Grubb, 2006; Picone et al., 2019) or from the date since hatching for nestlings.

Venice's Lagoon is one of Italy's primary breeding areas for marine birds (Scarton, 2017). Although the level of contamination in the area is low to moderate (Apitz et al., 2007a, 2007b; Picone et al., 2016), recent studies on breeding birds reported that exposure to trace elements (e.g. Hg, Pb, Cd) in the Lagoon is consistent with possible detrimental effects on species conservation (Picone et al., 2019). Conversely, information on REEs inputs and concentrations in water and sediment of Venice's Lagoon are lacking, despite potential sources of REEs contamination for the Lagoon are known, including runoff from agricultural areas, industrial sewage (i.e. from glass manufacturing and petroleum refining), hospital wastewaters and the occurrence of phosphogypsum landfills (Critto et al., 2003; Spagnolo et al., 2018; Zonta et al., 2005). Then, although not monitored to date, REEs may have undergone a transfer from abiotic matrices to the biota, possibly up to apical consumers, posing a risk for the wildlife, including birds breeding or overwintering in the lagoon. To assess whether birds breeding in the Venice Lagoon are critically exposed also to REEs, we measured the accumulation of Y, Sc and 15 lanthanides in contour feathers collected from fledgelings of the sandwich tern *Thalasseus sandvicensis* reared in natural and reconstructed salt-marshes within the Lagoon. This species is included in the IUCN Italian Red List as a vulnerable (VU) species due to its restricted distribution (criterion D2) (Rondinini et al., 2013). It was chosen as a biomonitor for REEs because it is a top predator in the aquatic food web and parents feed developing chicks and fledgelings with prey caught from within a few kilometres of the breeding colony (Fasola and Bogliani, 1990; Fijn et al., 2017; Perrow et al., 2011), allowing for the spatial integration of the accumulation. Flightless chicks were preferred since young birds obtain all their body burdens from their parents through food and via the egg. Since maternal transfer via egg is a small part of the total biomass of the fledging chick, given the rapid growth of young birds (Ackerman et al., 2011), trace element levels in feathers of

young birds at the time of fledgeling reflect almost entirely the local exposure in breeding grounds (Burger and Gochfeld, 1997).

Since we expected that food items might serve as one of the primary sources of contaminants for the fledgelings, we also measured REEs burdens in prey items spontaneously regurgitated by chicks during the ringing procedures to assess whether the transfer through food ingestion may be of concern for the Sandwich tern.

2. Materials and methods

2.1. Study area and sampling

The Lagoon of Venice is one of the largest coastal-transitional ecosystems of the Mediterranean sea (Tagliapietra et al., 2009), with a surface of about 540 km². Salt marshes occupy 36 km² of the whole Lagoon, islands approximately 30 km², while canals and shallows occupy the remaining 474 km². Three inlets (Lido, Malamocco and Chioggia) allow connection with the Adriatic Sea and tidal flushing twice a day (microtidal and predominantly semidiurnal tides) (Tagliapietra and Volpi Ghirardini, 2006). The catchment area of the Lagoon has a total surface of about 1850 km². It includes relevant urban centres, several industrial districts (including the main industrial area of Porto Marghera), zootechnical activities, but most of its surface (about 70%) is occupied by cultivated soil (Zonta et al., 2005).

The inputs of REEs into the Lagoon are actually not known. Industrial activities related to REEs mining, REEs processing and disposal of wastes containing REEs are absent in the study area and its surrounding mainland. Nevertheless, point and non-point sources such as agricultural runoff from the catchment area, industrial discharges, hospital wastewaters and phosphogypsum landfills may contribute, or have contributed in the past, to REEs' input in water and sediments of the Lagoon (Critto et al., 2003; Spagnolo et al., 2018; Zonta et al., 2005). However, no data are available for REEs in surface waters, sediments, and biota of the Venice Lagoon to date.

Feathers from Sandwich terns in Venice Lagoon were collected in colonies settled in Palude Fondello and Barena Celestia. Palude Fondello (45°15'9.66"N, 12°14'4.28"E) is a natural salt marsh characterised by dense halophilous vegetation, dominated by *Atriplex latifolia*, *Halimione* sp. and *Arthrocnemum* sp., and bare soil strips along its margins. Feathers of Sandwich tern were collected here only in 2017, because since 2018 Palude Fondello was not colonised by *T. sandvicensis*, probably due to a flooding event during adults' early settling. The colony then moved permanently to Barena Celestia (45°26'29.64"N, 12°21'26.27"E), a reconstructed salt marsh located 22 km NE, characterised by bare soil, high shell coverage, and sparse halophilous vegetation, mostly *Atriplex latifolia* and marginally *Spartina* sp. Since the foraging area of the Sandwich tern averages 27 km (Fijn et al., 2017), it covers the entire basin of Venice's Lagoon and its coastal area both for the colony settled in Palude Fondello and in Barena Celestia. Therefore, bioaccumulation data obtained from feathers collected in both salt marshes may represent the exposure on the whole study area.

Fledgelings about 16–20 days old were hand-collected by authorised operators (Veneto Region, decrees nr. 18/2015, 14/2018, and 142/2018) and deployed into large plastic tanks covered with jute sheets to minimise stress. Metal and colour rings (yellow) with 3-digit alphanumeric code were applied on the left and right tarsus, respectively, to univocally identify the birds and avoid duplicate sampling. A clump of contour feathers was retrieved from the rump of each bird. Fledgelings were kept for no longer than 60 min in the tanks. Once collected, feathers were placed in paper envelopes labelled with the date, ring codes and sampling location and stored at room temperature until chemical analyses (Jaspers et al., 2007; Picone et al., 2019). Removal of the feather caused no visible trauma to birds and did not affect their fledgeling period. REEs were determined in 10 feather samples col-

lected in Palude Fondello (2017) and 25 samples collected in Barena Celestia (2018, n = 10; 2019, n = 15).

Food items were collected in 2019 in Barena Celestia. Regurgitated fishes were hand collected from the plastic tanks used to hold fledgelings before ringing and sampling the feathers. Field-operators monitored the bird continuously to collect the regurgitations as soon as possible and avoid that chicks could pick up or damage the samples.

Only whole prey or prey missing only the head were collected, placed individually in a plastic bag and then stored in a portable refrigerator until the laboratory's arrival. The prey items were rinsed with deionised water, classified using appropriate identification keys and then frozen at $-20\text{ }^{\circ}\text{C}$ (Fischer et al., 1987). A total of 25 prey items were identified and analysed: 6 European anchovies (*Engraulis encrasicolus*), 6 European pilchards (*Sardina pilchardus*), 7 European sprats (*Sprattus sprattus*), 1 Sand smelt (*Atherina boyeri*) and 5 indetermined *Clupeidae*.

2.2. Chemical analyses

Feathers were analysed according to the procedure reported in Picone et al. (2019). Briefly, each clump of feathers was washed using alternately ultrapure water (Elga) and acetone (UpS, Romil Chemical Ltd., Cambridge, UK) 2% solution to remove the external deposition of dust and sediment particles (Borghesi et al., 2016; Fritsch et al., 2019; Jaspers et al., 2004; Mikoni et al., 2017; Vidal et al., 2021). Then, it was dried overnight under a laminar flow fume hood and weighed as a whole before microwave digestion. All the instruments and glassware used for handling the feathers were decontaminated, rinsed with ultrapure water (Elga) and dried before use. The vessel-inside-vessel technology was employed to mineralise the feathers (Milestone, Ethos 1). The secondary quartz vessels contained feathers and digestion reagents HNO_3 (69%, Plasma Pure Plus, with trace metal impurity levels <10 ppt, SCP Science, Baie d'Urfè, Quebec, Canada), and H_2O_2 (30–32% Ultrapure, Romil, Cambridge, UK) at a ratio 4:1, while the primary TFMTM vessel contained the solution required to accomplish accurate temperature monitoring (ultrapure water, Elga, and H_2O_2 Ultrapure Romil; ratio 4.5:1). Reagent blanks were similarly prepared and placed in the vessels randomly to assess background concentrations and check for possible contamination during sample preparation. Microwave digestions were performed at a controlled temperature using a high-pressure rotor. Once completed the mineralisation, every digested sample was recovered, weighed, diluted 1:2 with ultrapure water (in triplicate) and stored frozen at $-20\text{ }^{\circ}\text{C}$ until the analysis in inductively coupled plasma-mass spectrometry (ICP-MS).

Primary and secondary vessels were cleaned after every digestion: quartz vessels were thoroughly rinsed with ultrapure water and then filled with HNO_3 , while primary vessels were filled with the above-described mix. After appropriate microwave digestion, all vessels were thoroughly rinsed with ultrapure water and left to dry. All the steps were performed under a cleaned fume hood to minimise any contamination.

Frozen fish samples were freeze-dried for 24-h and then shredded using a mortar to obtain a homogeneous powder. The samples (50 mg) were then digested with HNO_3 in the primary TFMTM vessels. Microwave digestion and sample recovery were performed as described above for the feather samples.

The following elements were measured in all samples: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Promethium (Pm) was not included in the study as it does not occur naturally in the environment. Rhodium (Rh) was used as an internal standard to test for any matrix effect and check for interferences.

Mean measurement error, expressed as the percentage of the relative standard deviation (σ^* , RSD) was $<10\%$ for all elements of interest, both in feathers and fishes; the measure of uncertainty expressed as

the percentage of the standard error (SEM) was $<5\%$ for all elements studied, and the confidence interval was $\geq 95\%$.

A Certified Reference Material (CRM) for REEs, BCR-668 "Mussel tissue" (Joint Research Centre Institute for Reference Materials and Measurements, Geel, Belgium), was analysed to check for the procedure's accuracy. Results obtained showed good recoveries for all REEs analysed in the CRM ($>90\%$), then the procedure was considered accurate.

2.3. Data handling and analysis

Arithmetic means (AM) were used to calculate average element concentrations in both feathers and food items and standard error (SE) as a data dispersion measure. Concentrations were reported both for the pooled dataset (2017–2019) and the single year as:

- Individual lanthanides, Sc and Y concentration in ng g^{-1} dw;
- Total concentrations (ΣREEs), calculated as the sum of individual lanthanides, Sc and Y in ng g^{-1} dw;
- The sum of light REEs (LREE) and heavy REEs (HREE), where LREE includes Sc and lanthanides La, Ce, Pr, Nd, Sm, Eu, and Gd, while HREE includes Y and lanthanides Tb, Dy, Ho, Er, Tm, Yb and Lu, according to Brown et al. (2019).

Individual lanthanides, Sc and Y concentrations in feathers were also shale-normalised to geological abundances using the improved Post-Archean Australian Shale (PAAS) and European Shale (EUS) data set, in order to eliminate the Oddo-Harkins effect and facilitate the identification of possible anomalies (Bau et al., 2018; Pourmand et al., 2012). Normalisation to shales (both PAAS and EUS) is obtained by dividing the REE concentration in biological samples by the corresponding REE concentration in the reference shale. After normalisation to PAAS and EUS, deviation of REEs from the smooth trend may indicate a possible anthropogenic enrichment in individual REEs (Bau et al., 2018; MacMillan et al., 2017).

Anomalies of Ce (∂Ce) and Eu (∂Eu) as compared with the geological abundance were quantified according to MacMillan et al. (2017):

$$\partial\text{Ce} = \frac{Ce_N}{(La_N \cdot Pr_N)^{0.5}}$$

$$\partial\text{Eu} = \frac{Eu_N}{(Sm_N \cdot Gd_N)^{0.5}}$$

where the subscript "N" indicates the shale-normalised feather concentrations. Positive anomalies (namely values >1) designate possible increased uptake of the element relative to other REEs, while negative anomalies (namely values <1) indicate decreased uptake of the element relative to other REEs.

Kruskal-Wallis ANOVA followed by Dunn's multiple comparisons test was used to check for possible differences in REEs concentrations in feathers among years. Spearman's non-parametric correlation was used to assess possible correlations in feathers among elements. Measurements below limits of quantification (LoQ) were estimated one half of the LoQ value for all analyses, except when applying normalisation to shales (MacMillan et al., 2017). All the statistical analyses were performed using the software StatSoft Statistica v. 7.0.

3. Results

3.1. REEs concentrations in feathers

All REEs were quantified in feathers, but only Ce and Ho occurred at concentrations above LoQs in all samples. Scandium, Eu, Gd, Dy, Er, Tm and Lu were below their respective LoQ in almost all the samples collected in 2018 (n = 9), while they were detected in all feather's sam-

ples collected both in 2017 and 2019. Quantification rates for each REE are reported in Supplementary Material, Table SM-1.

Fig. 1 shows the trends obtained for each REE in feathers of Sandwich tern during the three years of sampling. Significant differences among sampling years were observed for all the elements. In general, the highest REE concentrations were measured in 2019, but the differences with 2017 data were significant only for Y, Tb, Ho and Lu. Conversely, La concentrations were significantly higher in 2017 than in 2019. For most of the REEs, the lowest concentrations were detected in samples collected in 2018, but only for Sc, Ce, Sm, Eu, Gd, Dy, Er, Tm,

Yb and Lu, there was a statistically relevant difference as compared with 2017 and 2019.

Total REEs concentrations varied significantly among years (Kruskal-Wallis ANOVA: $H_{2,35} = 12.5$, $p = 0.002$), with samples collected in 2017 ($2151 \pm 570 \text{ ng g}^{-1}$) differing significantly from feathers collected in 2018 ($293 \pm 141 \text{ ng g}^{-1}$; Dunn's multiple comparisons test: $Z = 3.51$, $p = 0.001$), but not from feathers collected in 2019.

The elements deposited at higher concentrations in all years were La and Ce, followed by Nd (2019, 2017) and Y (2018). Heavy REEs accounted for a minor fraction of the total accumulated rare elements;

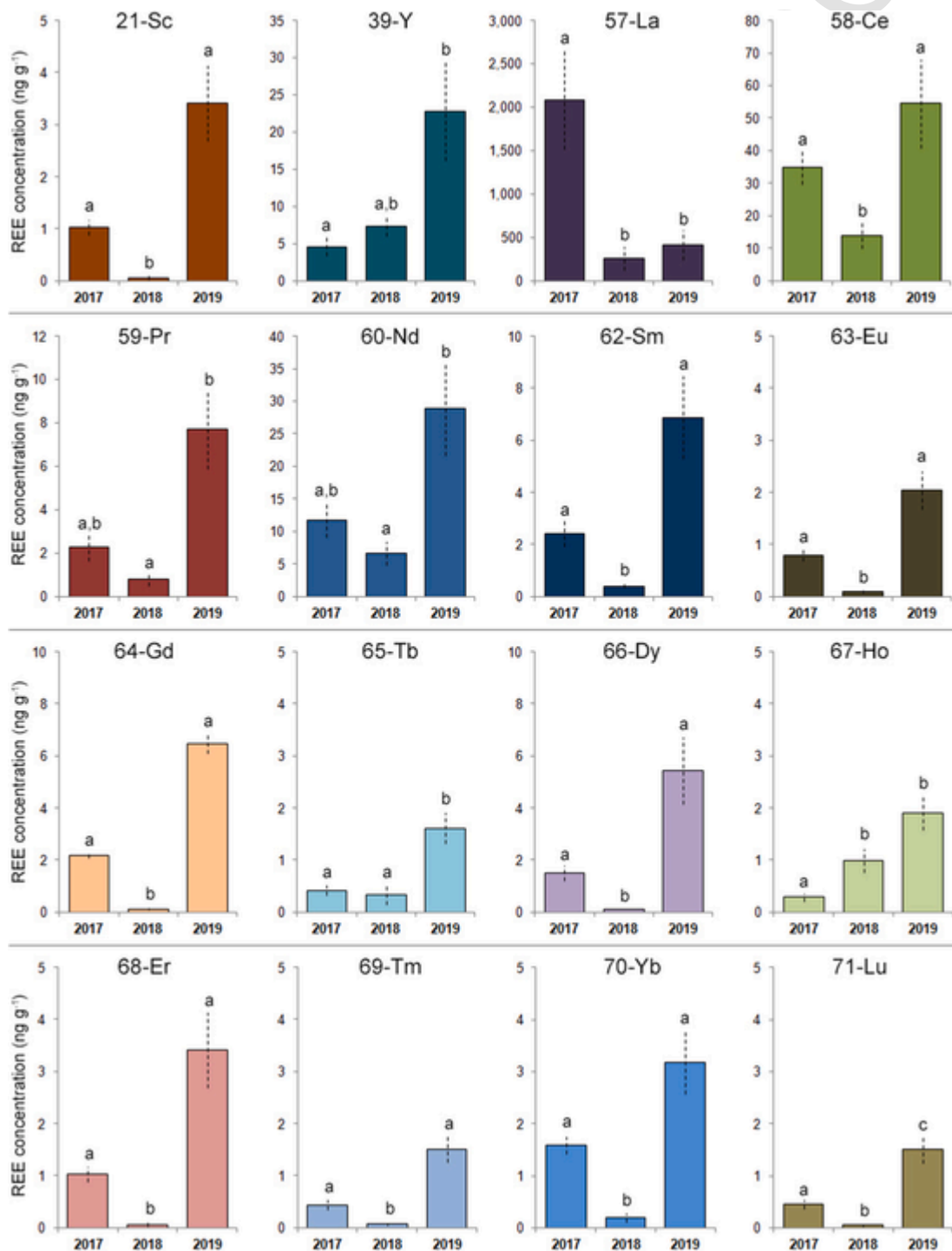


Fig. 1. REE concentrations measured in feathers of Sandwich tern chicks during the three sampling seasons. Bars indicate arithmetic means (AM), while whiskers indicate standard errors (SE). Letters indicate homogeneous groups after Kruskal-Wallis ANOVA and Dunn's multiple comparisons test (different letters indicate significant differences between samples at $\alpha = 0.05$).

mean ΣREEs for the pooled data were $940.9 \pm 223.0 \text{ ng g}^{-1}$, with LREEs contributing 97% to total REEs concentration. Similarly, LREEs contributed to 99%, 97% and 92% of ΣREEs in 2017, 2018 and 2019, respectively (Supplementary Material, Table SM-2). Lanthanum accounted for 90% of mean ΣREEs for pooled data, and its contribution ranged from 73% in 2019 up to 97% in 2017 (Fig. 2).

Plotting the pooled mean concentrations of lanthanides versus atomic numbers evidenced a log-linear or saw-tooth pattern decreasing with atomic number, according to the Oddo-Harkins' rule (Fig. 3, panel A).

Normalisation to the EUS data set provided a smoothing of patterns only for LREEs, evidencing a positive anomaly for La, and showed a persisting saw-tooth pattern for elements from Gd to Lu (Fig. 3, panel B). A very similar trend was obtained after normalisation to PAAS (Supplementary Material, Figure SM-1). Quantification of anomalies compared to EUS confirmed an enrichment for Eu ($\delta\text{Eu} = 1.77 \pm 0.10$) and a negative anomaly for Ce ($\delta\text{Ce} = 0.61 \pm 0.18$) compared with crustal abundance. However, the Ce anomaly's calculation is severely affected by the very high La concentration measured in the feathers and may be



Fig. 2. REEs' profile in feather's samples.

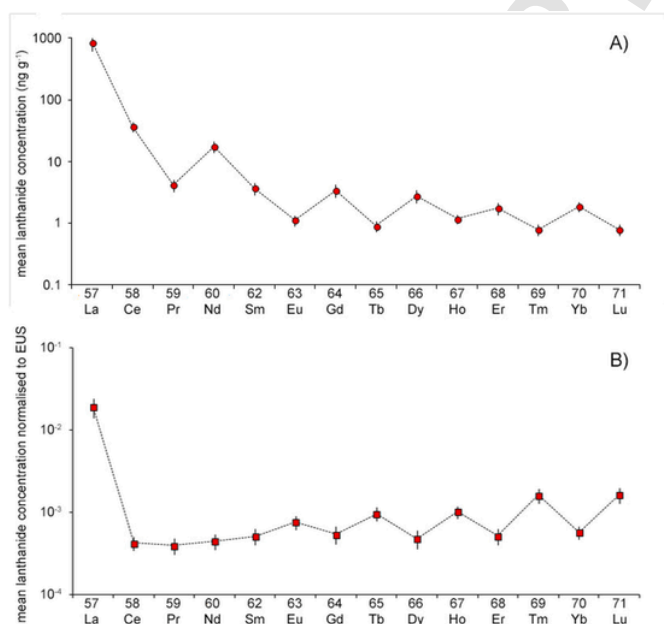


Fig. 3. Concentration of lanthanides in Sandwich tern versus atomic number. Panel A shows the trend for the pooled mean concentrations of lanthanides, while panel B shows the trend for the European Shale (EUS) normalised concentrations.

biased. Normalisation to PAAS produced comparable outcomes (Supplementary Material, Table SM-3).

Spearman's correlation confirmed that REEs are positively and firmly intercorrelated (Spearman's $R > 0.39$), except for La that does not correlate with any of the other elements (Supplementary Material, Table SM-4).

3.2. REEs concentrations in prey items

Mean, minimum and maximum concentrations obtained for each fish species are summarised in Supplementary Material, Table SM-5. *Sprattus sprattus* ($4587 \pm 347 \text{ ng g}^{-1}$) and *S. pilchardus* ($4067 \pm 477 \text{ ng g}^{-1}$) were the species with the highest ΣREEs concentrations while *E. encrasicolus* ($2042 \pm 700 \text{ ng g}^{-1}$) and *A. boyeri* (1403 ng g^{-1}) showed the lowest concentrations. However, statistical analysis did not evidence any significant difference among the species (Kruskal-Wallis ANOVA: $H_{3,24} = 6.0$, $p = 0.112$). As in feathers, LREEs accounted for the major fraction of ΣREEs, while HREEs constitutes less than 27% of ΣREEs in all analysed samples. The elements deposited at higher concentrations in all species were Ce ($312.8\text{--}1468.2 \text{ ng g}^{-1}$), La ($199.9\text{--}793.9 \text{ ng g}^{-1}$) and Nd ($180.8\text{--}727.5 \text{ ng g}^{-1}$), in decreasing order. La accounts on average for less than 20% of ΣREEs, and it is not dominant as in the feathers. All species also presented high concentrations of Sc and Y.

In fishes, the mean concentrations of lanthanides showed a saw-tooth pattern decreasing with atomic number, according to the Oddo-Harkins' rule (Fig. 4, panel A). However, food items' concentrations are considerably higher than in feathers collected in the same year, except for La, Tm and Lu (Fig. 4, panel A). As concern La, feather concentrations were higher than in *E. encrasicolus* (106%) and *A. boyeri* (208%), while averaged the 50% of the concentration measured in *S. sprattus* and *S. pilchardus*. As for Tm and Lu, there is an overlap between concen-

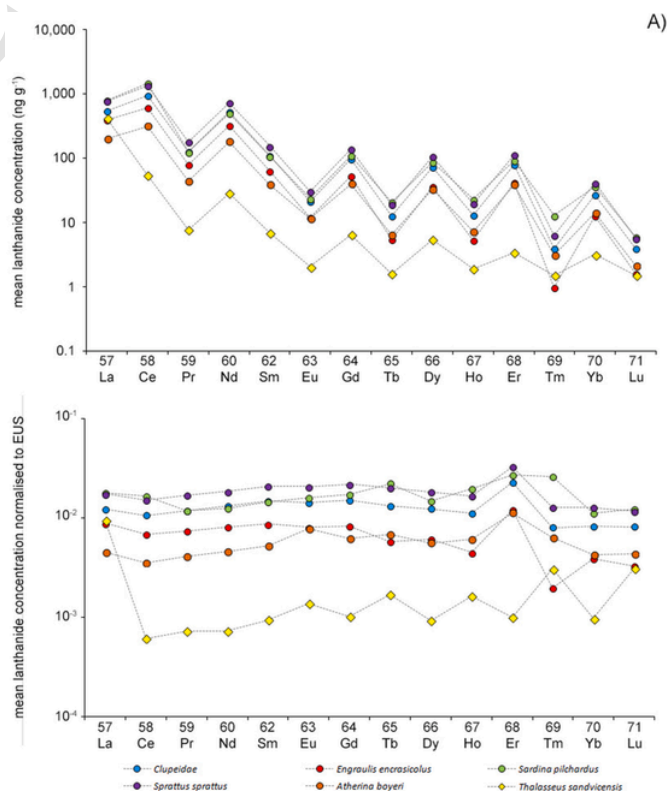


Fig. 4. Concentration of lanthanides in fishes and Sandwich tern versus atomic number. Only data collected in 2019 are reported. Panel A shows the trend for the mean concentrations of lanthanides, while panel B shows the trends for the European Shale (EUS) normalised concentrations.

trations measured in feathers and *E. encrasilocus*. For all the other elements, REE concentrations in feathers accounted for a minor fraction of the whole fish burdens (from 1% for Sc up to 36% for Ho).

Normalisation to EUS data set smoothed the patterns for all the fish species; apparent deviation from the smoothed trend concerned Er in all fish species, and Tm in *E. encrasilocus* (apparent negative anomaly) and *S. pilchardus* (apparent positive anomaly) (Fig. 4, panel B). Eu anomalies evidenced minor deviations from the unit (Supplementary Material, Table SM-3), except for *S. pilchardus* ($\partial\text{Eu}_{\text{EUS}} = 1.16 \pm 0.15$; $\partial\text{Eu}_{\text{PAAS}} = 1.34 \pm 0.17$). In contrast, negative Ce anomalies were calculated for all fish species except *S. pilchardus*, for which a positive anomaly was observed ($\partial\text{Ce}_{\text{EUS}} = 1.40 \pm 0.32$; $\partial\text{Ce}_{\text{PAAS}} = 1.38 \pm 0.31$).

4. Discussion

4.1. High concentrations of REEs measured in feathers and fishes

The accumulation of REEs at quantifiable levels in the analysed samples evidenced the bioaccessibility of REEs to breeding birds. Moreover, REEs concentrations detected in the Sandwich tern (940.9 ng g⁻¹) are the highest among those reported in the literature for bird's feathers. Squadrone et al. (2019a) found in adult Humboldt penguins (*Spheniscus humboldti*) housed in an aquarium a mean concentration of ΣREEs of 160 ng g⁻¹, while Borghesi et al. (2017) observed mean concentrations of ΣREEs in the range 202–565 ng g⁻¹ in chicks of wild Greater flamingo (*Phoenicopterus roseus*), and 173 ng g⁻¹ in adult flamingoes housed in a zoo. Also, the pattern of REEs observed in Sandwich tern is utterly different from those reported for penguins and flamingoes: in Sandwich terns, La is the dominant REE in feathers (73–99% of ΣREEs), while it accounts only for about 15–19% of ΣREEs in both flamingoes and penguins. Moreover, in Greater flamingoes and Humboldt penguins, the more abundant REEs are Ce (31–38% of ΣREEs in flamingoes; Borghesi et al., 2016), Sc and Y (15–22% of ΣREEs in penguins; Squadrone et al., 2019a), while all these elements account for a minor fraction of REEs detected in Sandwich terns.

Higher concentration and different REEs patterns in Sandwich terns compared with adult housed penguins and flamingoes were expected due to the different exposure pathways characterising natural environments and the different diets of wild birds compared with housed ones. Differences in accumulation may reflect heterogeneities of the diet since different prey items may contain distinct concentrations of REEs. In marine fishes, ΣREEs concentrations varied considerably among different case study, but occur at concentrations generally higher than in invertebrates and zooplankton, at least in the Mediterranean area (Squadrone et al., 2019b). The ΣREEs measured in the prey items of the Sandwich tern (1403–4579 ng g⁻¹) are distinctly higher than concentrations measured in capelins used to feed Humboldt penguins (5.7 ng g⁻¹; Squadrone et al., 2019a) and those observed in fishes from the Tyrrhenian sea (210 ± 20 ng g⁻¹ in dorsal muscle; Squadrone et al., 2019b), freshwater reservoirs (an average of 243 ng g⁻¹ in the whole body and muscle tissue; Mayfield and Fairbrother, 2015) and temperate lakes of North America (110–450 ng g⁻¹ in dorsal muscle; Amyot et al., 2017). However, the ΣREEs concentration we found in *S. sprattus*, *S. pilchardus* and *E. encrasilocus* are comparable with the values observed in muscle tissue of yellow (1796–2901 ng g⁻¹) and silver eels (4694–6203 ng g⁻¹) in the Loire estuary (Lortholary et al., 2020).

4.2. Internal and external sources of REEs for the sandwich tern

The high concentrations measured in fishes suggest the internal exposure through the diet as a primary source of REEs for the Sandwich tern. Other sources cannot be a priori excluded, but their contribution compared to diet appears to be of less concern.

The external contamination due to deposition of atmospheric dust, suspended particulate matter and sediment particles on feathers during preening is a possible source to consider when analysing trace elements in feathers (Dauwe et al., 2003; Jaspers et al., 2019). However, external contamination is a higher issue for adult birds than for nestlings and chicks (Jaspers et al., 2019), who had less time to accumulate dust and particles on feather's surfaces. In particular, Borghesi et al. (2016) pointed out the major contribution of sediment particles over other factors to external contamination in chicks reared in salt marshes, and observed that an appropriate washing procedure may remove most of the salts (>99%) and had a strong effect on major elements, including La. Consequently, external deposition due to atmospheric dust is expected to be minimal compared to food ingestion for the analysed samples due to: 1) age of the chicks (16–20 days), which allow for a short period of exposure to atmospheric dust; 2) sheltering provided by parents during the sunniest hours of the day, nights and rainy days in the first days of life of the chicks, which prevents chick's exposure to atmospheric dust; 3) absence of REEs mining areas, REEs processing plants and disposal of wastes containing REEs in the study area and its surrounding, which prevent from the formation of REE-enriched dust; 4) occurrence in the study area of potential sources of REEs affecting the aquatic compartment primarily.

Similarly, the contribution of maternal transfer via the egg is a possible way of exposure for the first days of life, but to a lesser extent than the diet due to the rapid growth undergone by chicks up to fledge (Ackerman et al., 2011; Burger and Gochfeld, 1997).

4.3. Anomalies of La, Eu and Ce and their possible sources

The pattern of REEs in feathers (except for La) and fishes displays a trend similar to that already observed in the biota by Weltje et al. (2002) and MacMillan et al. (2017), namely a log-linear decreasing pattern with atomic numbers, following the Oddo-Harkins' rule. According to MacMillan et al. (2017), this pattern indicates that REE accumulation mirrors their crustal abundances, strongly conserved in soils and sediments. After normalisation to shales, feathers showed an evident positive anomaly for La and a scattered trend for HREEs, including Tb, Ho, Tm and Lu, while in fishes lacks the La anomaly, and the trend is not scattered for HREEs.

The positive La anomaly in birds may be due to preferential deposition of La in feathers or different elimination pathways compared with other REEs. Feathers represent just one of the tissues where birds may store non-essential elements, and then it cannot be excluded that significant amounts of REEs are stored in other tissues and organs, such as the liver, kidneys and bones. Based on our data, we can hypothesise that Sandwich terns store a considerable amount of La in their feathers, while the other lanthanides, Y and Sc, are either eliminated more efficiently than La or deposited in other tissues.

Possible environmental sources of La include industrial wastewaters and runoff from agricultural land. For example, the La anomaly observed in shale-normalised patterns in Rhine River water and biota was considered as an anthropogenic anomaly due to industrial wastewaters, including discharges from a catalyst production plant (Kulaksiz and Bau, 2011, 2013; Merschel and Bau, 2015). Similarly, Brown et al. (2019) observed a positive La anomaly in the internal organs of the Ring-billed gull *Larus delawarensis* and related it with the application of REE enriched fertilisers in the foraging areas of the birds.

The particular dynamics of the Lagoon may also play a relevant role in the accumulation of La in the Sandwich tern and its preys: contaminants accumulated into surface sediments after wastewater discharges, runoff from the catchment basin, and other possible sources may undergo resuspension due to wind, tidal currents, clam fishing, boat traffic, and ship wakes (Scarpa et al., 2019; Sfriso et al., 1991; Zonta et al., 2020). Once transferred to the water column, the remobilised particles and associated pollutants may be taken up by the pelagic biota, includ-

ing Sandwich tern's prey items spending their life-cycle, or part of it, in the Lagoon. In particular, laboratory experiments showed that biota-to-sediment accumulation factors for La are significantly increased by resuspension compared with undisturbed conditions (Moermond et al., 2001). Resuspension may have also played a relevant role in determining the significantly different REEs (and especially La) concentrations observed in the feathers among the three years of monitoring.

The positive anomaly observed for Eu ($\delta Eu > 1$) in Sandwich tern feathers and fishes is unresolved. Positive δEu was often observed in waters and biota, but Eu enrichment's possible causes are not yet fully recognised. Moermond et al. (2001) suggested that positive δEu may be due to Eu's specific redox behaviour, namely its reduction from Eu(III) to the more mobile and bioavailable Eu(II) under anoxic conditions. However, this condition is supposed to occur only in hydrothermal waters. MacMillan et al. (2017) agreed with the hypothesis of the reduction of Eu(III) to Eu(II) under anoxic conditions, since they observed positive δEu in surface water and benthic biota but not into sediments; moreover, the authors suggested that positive δEu may be analytical artefacts due to BaO interference on the ICP-MS. Finally, Censi et al. (2017) explained positive δEu in vascular plants with the similarity between Ca ions and Eu(III) in the aqueous phase, suggesting an Eu/Ca substitution during physiological processes enhancing the transport of Eu as compared with its neighbour REEs.

As concern Ce, negative anomalies are typical of surface waters, where Ce(III) is rapidly oxidised to the insoluble Ce(IV), which in turn tends to adhere to particulate matter and sink into sediments (MacMillan et al., 2017; Weltje et al., 2002). The negative anomalies we observed in pelagic fishes are then consistent with these findings; consequently, the negative anomalies in feathers are also consistent with a diet based on pelagic fishes. Nevertheless, since the negative δCe values in feathers may be a calculation artefact due to the high levels of La, further studies are needed to confirm the anomaly.

As concern the other REEs, the scattered trend observed for Tb, Ho, Tm and Lu in feathers seems to suggest an enrichment of these elements as compared with the other lanthanides; however, this trend should be interpreted with care because concentrations were very low, and in some cases (i.e. Tb, Tm and Lu) close to detection limits. Furthermore, the low concentrations measured in feathers compared with fishes may suggest the occurrence of trophic dilution for most of REEs, as already observed by other authors (Amyot et al., 2017; MacMillan et al., 2017; Squadrone et al., 2019b). Nevertheless, it cannot be excluded that a considerable amount of these elements may have been stored in other tissues and organs.

4.4. Ecotoxicological significance of REEs accumulation

Data collected for the Sandwich tern evidenced that REEs (especially La, followed by Ce, Y and Nd) are bioaccessible and bioavailable to birds breeding in the Venice Lagoon. Nevertheless, it is not possible to quantify the risk posed by the exposure to REEs due to the lack of dose-response studies and adverse-effect thresholds relating feathers' concentration with toxic effects.

However, literature data indicate that accumulation of REEs is of concern for vertebrates because some of them, including Y, La, Ce, and Nd, may induce oxidative stress (Pagano et al., 2015; Rim, 2016) and interfere with Ca metabolism at various levels (Redling, 2006).

Nevertheless, disruption of Ca metabolism is the mechanism of toxicity of primary concern for REEs. Alteration of Ca metabolism occurs mainly via competition for Ca-binding proteins and Ca-ion channels (Jakubek et al., 2009), interaction with membrane-associated enzymes and protein, and disruption of the neurotransmission (Buccigross and Nelson, 1986; Jakubek et al., 2009; Weiss, 1974). Brown et al. (2019) observed different accumulation patterns during nesting between females and males Ring-billed gulls; according to these authors, Y could

bind to albumin and other Ca-binding proteins in the plasma of females, leading to higher accumulation of Y in female liver relative to males during the incubation period.

REEs may also affect reproduction in birds. The deposition of plasma-circulating REEs into the developing egg provides a distinctive exposure pathway for embryos (Squadrone et al., 2019a). In particular, the deposition of Y in place of Ca may impair the calcification of the developing embryos' skeleton (Chien et al., 2009; Kaweewong et al., 2013).

5. Conclusion

This work was the first study to identify REEs' accumulation in wild piscivorous waterbirds. The analysis performed on contour feathers of fledgelings of Sandwich tern using a non-invasive approach evidenced that REEs are bioaccessible and bioavailable for birds, with La emerging as the element of primary concern. In particular, REEs concentrations measured in the Sandwich tern are the highest among those reported in the literature for bird's feathers.

High REE concentrations measured in fish samples indicate that internal exposure through diet is a relevant route of exposure to REEs for birds. The significant differences observed in REEs concentrations among years also evidenced that REE bioaccessibility and bioavailability changed over time.

Normalisation to EUS and PAAS shales evidenced a positive La anomaly in feathers not confirmed in fishes, suggesting that La was deposited in feathers more efficiently than other REEs.

Further studies on water, sediment and other biological matrices (including plasma and egg-shells as concern birds and different fish species) are necessary to fully understand the occurrence, fate and possible route of exposure to lanthanides for both adult birds and chicks, as well as other key components on the trophic web.

Author contributions

Marco Picone: Conceptualization, Methodology. Investigation. Data curation. Writing-Original draft preparation. **Gabriele Giuseppe Distefano:** Investigation. Resources. Formal analysis. Data curation. **Fabiana Corami:** Investigation. Resources. Formal analysis. Data curation. **Piero Franzoi:** Writing - Review & Editing. **Simone Redolfi Bristol:** Investigation. Resources. Writing - Review & Editing. **Marco Basso:** Investigation. Resources. **Lucio Panzarin:** Investigation. Resources. **Annamaria Volpi Ghirardini:** Supervision. Writing - Review & Editing. Funding acquisition.

Compliance with ethical standards

All applicable international, national, and/or institutional guidelines for the care and use of animals were followed. This article does not contain any studies with human participants performed by any of the authors.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envres.2021.112152>.

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