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Historic variation of trace elements in pinnipeds with spatially segregated trophic habits reveals differences in exposure to pollution

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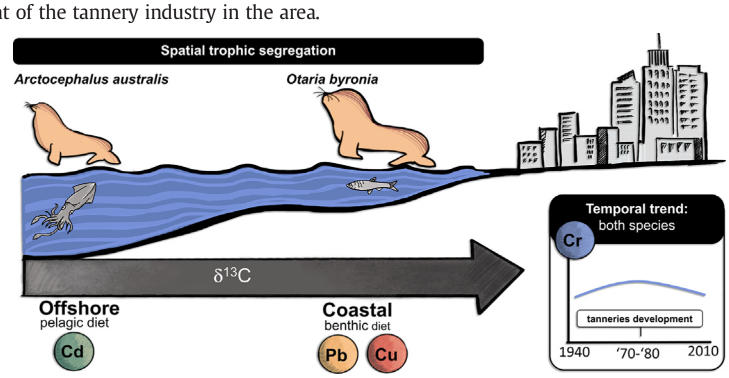
HIGHLIGHTS

- 70-year analysis of exposure to trace elements in two pinniped species.
- Both species had a higher concentration of Cr during '70–'80s, related to industry development.
- *O. byronia* with a costal-benthic diet had higher exposure to Pb and Cu
- *A. australis* have been more exposed to Cd, associated to their pelagic diet.
- Dentin is a reliable matrix to analyze trace element concentration in pinnipeds.

GRAPHICAL ABSTRACT

Spatial trophic segregation determines differential exposure to trace elements in two species of pinnipeds. *Arctocephalus australis* was more exposed to cadmium due to their offshore pelagic diet (based on squid), while *Otaria byronia* has been more exposed to lead and cooper associated to their coastal and benthic diet during the 20th century. Both species showed an increase of chromium exposure in the '70–'80s that coincides with the development of the tannery industry in the area.



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ABSTRACT

Marine mammals and the ecological functions they provide to coastal and pelagic ecosystems are increasingly threatened by the intensification of anthropogenic impacts. The Uruguayan coastline throughout the 20th century, like other coastal environments worldwide, has been the sink of a variety of trace metals derived from the rapid urbanization and industrialization of related land areas. This coastline is inhabited by two species of pinnipeds trophically and spatially segregated. *Otaria byronia* feeds in coastal environments while *Arctocephalus australis* preys mainly offshore. The present study aimed to analyze historic changes in concentrations of trace elements in teeth of both species from 1941 to the present day. We analyzed the dentin of 94 canine teeth using stable isotope analysis ($\delta^{13}C$) and ICP-MS to determine their feeding areas and the concentration of 10 trace elements (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) respectively. The concentration of Cr was significantly higher during '70–'80s, in both species coinciding with tannery industry development. Both species of pinnipeds have been differentially exposed to trace elements depending on their feeding area. A pelagic diet, possibly based on squid, increased the concentration of Cd in *A. australis*, while *O. byronia* has been more exposed to

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anthropogenic Pb and Cu associated to a costal and more benthic diet. Our results highlight dentin as a reliable matrix for historic studies on the exposure to trace elements. In light of our results, the *O. byronia*'s declining population could be the result of the synergistic effects of trace elements together with other ecological pressures faced in their environment.

1. Introduction

Marine mammals play a key role in the structure and dynamic of the communities because of their large body size and abundance (Bowen, 1997; Gotelli and Ellison, 2006; Weise et al., 2010). Their longevity, late sexual maturity and low reproductive rate make them extremely sensitive to anthropogenic impacts (Fair and Becker, 2000). More than 80% of humanity lives in coastal environments and our dependence on its services and resources are even larger (Lotze et al., 2006; Worm et al., 2006). Coastal environments are vulnerable to the input of trace elements (Fowler, 1990; Habran et al., 2012) from rivers as dissolved or particulate matter or as the result of burning fossil fuels (Libes, 2009). The major route of trace elements to top predators such as marine mammals is through their diet (Das et al., 2003), which makes them vulnerable to the bioaccumulation of these substances in their tissues if the rate of uptake is greater than the one excretion (Gray, 2002; Reinfelder et al., 1998).

Trace elements are classified depending on their biological functionality in organisms as essential or non-essential (Förstner and Salomons, 1983). Essential elements have a key role in the metabolism but if concentrations are higher than a certain threshold they can become toxic (e.g. cobalt, manganese, selenium, and zinc; Ando et al., 2005). Non-essential elements do not have a biological role and are toxic even at low concentrations (e.g. arsenic, cadmium, lead and mercury). Their presence in the tissues of organisms can indicate an environmental exposure due to natural or anthropic causes (Förstner and Salomons, 1983).

The Uruguayan coastline and the associated Rio de la Plata estuary have been classified as medium-high impacted areas (Halpern et al., 2007) threatened by costal urbanization, intensive agricultural activities, maritime transport and dredging (García-Alonso et al., 2019). Previous research has found high concentrations of trace elements in water and sediments of the region, with historical increases associated with industrialization and urbanization processes of two important capitals, Montevideo (Uruguay) and Buenos Aires (Argentina) (Carsen et al., 2003; García-Rodríguez et al., 2010; Gil et al., 1999; Marcovecchio and Ferrer, 2005; Viana et al., 2005). Even more selective metals are bioaccumulated in polychaetes in urban coastal areas, which can be the entrance of bioavailable metals to coastal trophic networks (Castiglioni et al., 2018).

The coastal area of Uruguay is inhabited by two sympatric pinnipeds species with clear spatial segregation of their trophic habits, *Otaria byronia* (de Blainville, 1820) (South American sea lion) and *Arctocephalus australis* (South American fur seal) (Zimmermann, 1783). *O. byronia* feeds on coastal areas (Franco-Trecu et al., 2014b; Riet Sapriza et al., 2013; Szteren et al., 2018; Vaz-Ferreira and Ponce de León, 1982; Zenteno et al., 2013) while *A. australis* preys mainly outside the continental shelf, although, it can feed in shallow coastal waters within the Rio de la Plata estuary (Franco-Trecu et al., 2014a; Szteren et al., 2018; Vales et al., 2013). Both species prey mainly on fish, while *A. australis* also includes pelagic cephalopods as one of the most important dietary items (Franco-Trecu et al., 2012; Naya et al., 2002). Both species have contrasting population trends since 1950, where both species had approximately 30,000 individuals (Vaz-Ferreira, 1976; Vaz-Ferreira and Ponce de León, 1982). The population size of *O. byronia* decreased 2% annually over the last 60 years to 10,000–12,000 individuals currently (Franco-Trecu et al., 2014b; Páez, 2006), while *A. australis* official survey estimates the population size to be 300,000 individuals with an annual growth rate of 1% (Páez, 2006).

The quantification of trace elements in organisms' tissues provides information about their bioavailability, distribution and fate in the marine ecosystem (Kurucz et al., 1998). Bioaccumulation and chronic exposure to trace elements could affect the health and survival of marine mammals (Fair and Becker, 2000) and result in the decline of their populations (Barron et al., 2003; Becker and Krahn, 2000). To understand the fate of contaminants and trace elements in marine ecosystems, it is necessary to analyze them in the context of the trophic network (Van de Vijver et al., 2003). For this purpose, stable isotope analysis has proven to be a useful tool to reconstruct the diet of organisms (Boecklen et al., 2011; Dehn et al., 2006). Particularly, $\delta^{15}N$ and $\delta^{13}C$ provide relevant information on the trophic position and the origin of organic matter in the ecosystem (Fry, 2006; Kelly, 2000; Post, 2002).

Lead, Hg, Cd, Cu, Zn and Cr (among others elements) have been quantified in tissues of marine mammal from the Southwest Atlantic Ocean (Kunito et al., 2004; Lemos et al., 2013; Panebianco et al., 2012). Different tissues provide information regarding the diet of the organism and exposure to contaminants across different time scales depending on their turnover rate (Hobson and Sease, 1998; Vander Zanden and W. Fetzer, 2007). The low turnover rate of calcified matrixes, such as teeth and bone, makes them excellent long-term sampling tissues that integrate isotopic relationships and trace element concentrations throughout the life of organisms (Evans et al., 1995; Hirons et al., 2001). In particular, the yearly generation of a new growth layer in teeth allows for reliable reconstructions across the organisms lifetime (Hobson and Sease, 1998; Klevezal, 1996). In this context, bone and teeth have been used to assess the environmental exposure to trace elements in marine mammals (Yamamoto et al., 1987; Outridge and Stewart, 1999). Teeth incorporate trace elements during their formation by three possible mechanisms of deposition (Levine, 2011). The first mechanism is the incorporation of trace elements by isomorphic substitution (Farlay and Boivin, 2012). Divalent ions substitute calcium (Ca^{2+}) while trivalent ions can substitute the phosphate group (PO_4^{3-}) (Wakamura et al., 2000). Secondly, trace elements may co-precipitate with calcium in the formation sites and be incorporated into the hydroxyapatite crystals (Blumenthal, 1990). Lastly, trace elements could be bound to the organic components of the calcified matrixes such as proteins (Triffitt, 1985). For example, Pb and Cd can be incorporated into the skeleton, because of its similarity to calcium (Bronner and Stein, 1992) and it contains 90% of the body burden in seals (Kakuschke et al., 2006). Cadmium is also present in calcified matrices as part of the organic portion (osteoblasts and osteoclasts) bound to metallothionines as a detoxification mechanism (Sogawa et al., 2001). Zinc concentration in human teeth has been considered as a possible indicator of environmental exposure to this trace element (Tvinnereim et al., 1999).

The aim of the present study is to analyze historic changes in concentrations of trace elements in teeth of *O. byronia* and *A. australis* in the Uruguayan coastline from 1941 until 2010. Our working hypothesis is that the concentration of trace elements will increase in the last 7 decades accompanying the urbanization and industrialization of the areas and that the concentration of trace elements will be associated with the feeding area of both species of pinnipeds. We predict higher concentration of non-essential trace elements (such as Pb and Cr) in coastal diets, more common in *O. byronia* than in *A. australis*.

2. Materials and methods

We sampled canine teeth of *A. australis* and *O. byronia* from to two scientific skull collections: Facultad de Ciencias, Universidad de la República (Montevideo, Uruguay) and the Museo Nacional de Historia Natural (Montevideo, Uruguay). We used teeth because the yearly deposition of dentin growth layers allows for lifetime reconstructions (Hobson and Sease, 1998; Klevezal, 1996). In addition, the dentin, is much less affected by post-mortem decomposition processes driven both by physical-chemical and biological factors due to its hardness, avascular and largely acellular nature (Turner-Walker, 2008). In the particular case of Uruguay, teeth are the only structures with historic records besides skulls for historic reconstructions as the one presented here. We sampled 94 teeth, 33 from *O. byronia* and 61 from *A. australis*. Teeth belonged to animals stranded along the Uruguayan coastline or collected during controlled harvest at the breeding colonies from 1944 to 2013. Thirty-nine canine teeth were collected in the Department of Rocha, 49 in Maldonado, 3 in Canelones, 1 in Montevideo and 2 in San José (Fig. 1). Sex was determined, whenever it was not present in the collection records, using teeth measurements of crown and root. For this, we used the method suggested by Lowry and Folk (1990) for sea lions and chosen by Molina-Schiller and Pinnedo (2004) as the most accurate for *A. australis*. To age all individuals, an upper canine tooth was cut longitudinally with a diamond wire-saw (Isomet), from root to crown, then one half was placed in formic acid 10% for one-two hours, and annual growth layers were counted (Szteren et al., 2018).

2.1. Stable isotope analysis

Dentin samples were collected from every growth layer except from the fetal one as described in Szteren et al. (2018). This procedure was performed with a high precision Micro Mill drill (New Wave Research), which extracted a 300 μm wide and 500 μm deep sample from each growth layer. Afterward, dental collagen was extracted by demineralization with 3 washes of hydrochloric acid (10%) and a final rinse with distilled water. Then, 1 mg was weighed into tin capsules and kept dry until analysis. Finally, the samples were sent to the University of California Davis for carbon and nitrogen analysis with an isotope ratio mass spectrometer.

Stable isotope abundances were expressed in delta notation as the variation of stable isotope ratios from international standards. This delta notation was expressed in per mil (‰) and calculated as:

$$\delta^{15}N \text{ or } \delta^{13}C = \left(\left(R_{sample}/R_{standard}\right)-1\right) * 1000‰$$

where R_{sample} and $R_{standard}$ are the corresponding stable isotope ratio between $^{13}C/^{12}C$ or $^{15}N/^{14}N$. The international standard references were

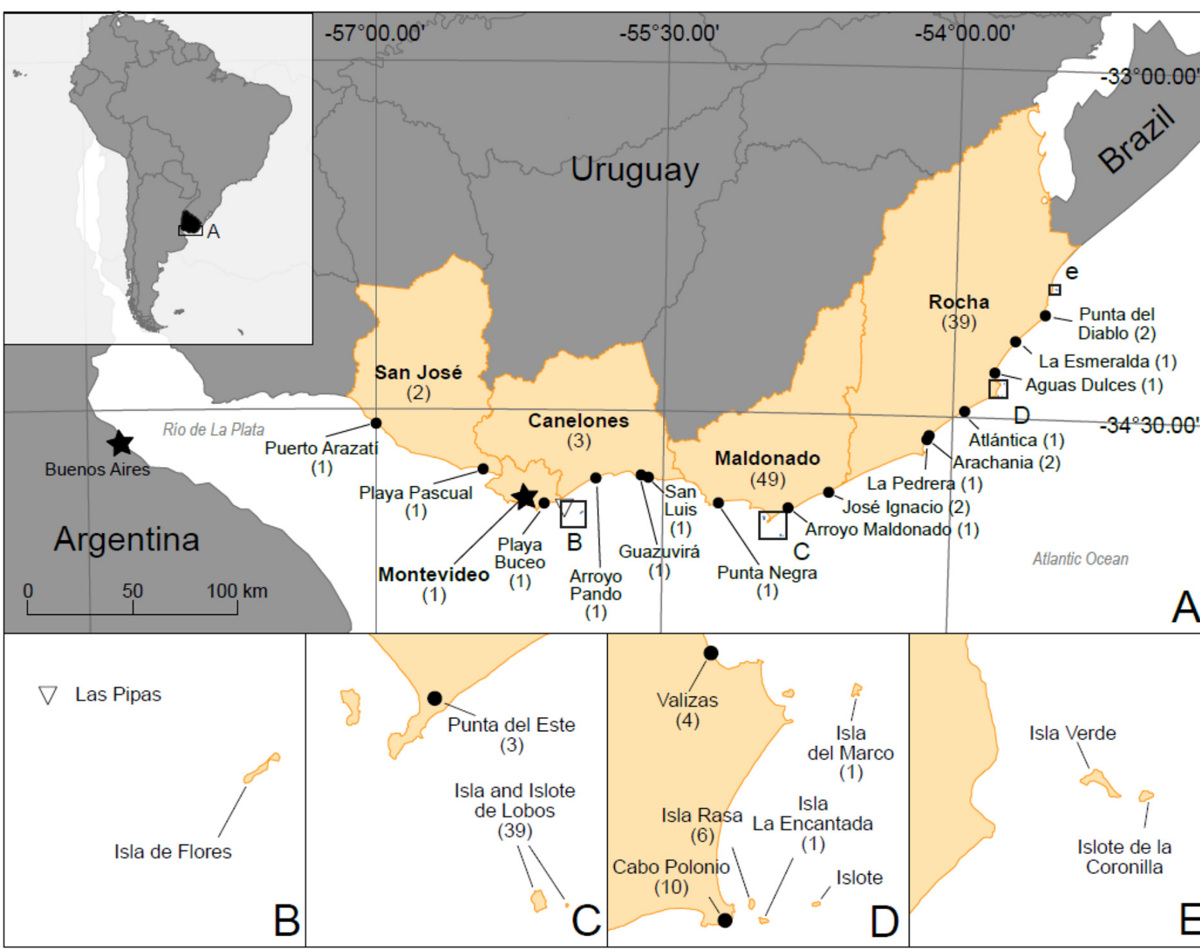

Fig. 1. Map showing the sites where the 94 teeth from *Otaria byronia* and *Arctocephalus australis* where collected along the Uruguayan coastline. In bold are shown the name of the Departments and between brackets the total number of teeth collected in each of them. Dots and lines indicate the exact sampling location in each Department, for those cases where this information was available (for some samples only the Department information was provided in the consulted collections). Here too, the number of collected teeth is presented between brackets. Capital cities in the area are shown with a star (Montevideo and Buenos Aires) (A). Insets B, C, D and E show breeding and non-breeding colonies for both species of pinnipeds along the Uruguayan coastline. Las Pipas and Isla de Flores are the westernmost non-breeding colonies in the Rio de la Plata estuary (Szteren, 2015) (B), Isla and Islote de Lobos are breeding colonies in the Department of Maldonado (C), Isla Rasa, Isla La Encantada, Islote, and Isla del Marco (D), and Isla Verde and Islote de la Coronilla (E) are breeding colonies in the Department of Rocha (Vaz-Ferreira, 1960) (E).

Pee Dee Belemnite calcium carbonate for $\delta^{13}C$ and atmospheric Nitrogen (Air, N_2) for $\delta^{15}N$. Based on the difference in $\delta^{13}C$, it is possible to distinguish between carbon sources from pelagic and oceanic, or benthic and nearshore feeding areas (Hobson et al., 1996). Coastal and nearshore environments are enriched in ^{13}C and, therefore, their signal is higher than in pelagic environments (Burton and Koch, 1999). Stable isotopes are useful tools for the interpretation of trace element accumulation in the context of differences in feeding areas, trophic position and prey (Habran et al., 2012; Jakimska et al., 2011; Marcovecchio et al., 1994).

2.2. Trace elements analysis

For trace element analysis, the other half tooth was carefully cleaned up to avoid possible contamination due to storage. A sequential leaching protocol was followed according to Shafer et al. (2008) with hydroxide peroxide (50%), acetone and lastly with nitric acid (0.1 M) wash. The first wash was meant to eliminate general contamination, acetone for organic contaminants and nitric acid for inorganic contaminants in general. After every wash, the tooth-half was rinsed with Milli-Q® water. All laboratory materials were acid washed, and the tooth-half was manipulated with Teflon forceps. Each sample was dried at 60 °C for 1 h and 200 mg of dentin was sampled with a diamond handpiece on a manual low-speed drill (Saeyang Marathon®). All growth layers, except the fetal one, where sampled homogeneously. Lastly, samples were digested overnight in 2 mL of supra pure nitric acid. The concentrations of As, Al, Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn were determined considering that these elements are frequently found in urbanized areas (Poleto et al., 2009). Trace element concentrations were determined using a multi-element inductively coupled plasma mass spectrometry (ICP-MS, 7500 CX Agilent Technologies Tokyo, Japan) at the Chemistry Department of the Pontifícia Universidade Católica do Rio de Janeiro (Brazil). One of the main advantages of ICP-MS is the high sensitivity compared with other analytical methods, making it an ideal tool for analyzing accumulation in organisms, as previously shown for teeth samples (Webb et al., 2005). Quality assurance was done through analysis of standard reference bone ash (NIST 1400) provided by the National Institute of Standards & Technology. The ICP-MS operating conditions and measurement parameters are shown in Supplementary Table 1. The recovery was between 94% and 100% for all trace elements, except for Cr and Ni that are not present in the standard reference. Detection limits, in $\mu g\ g^{-1}$ by dry weight, were: As 0.002, Al 0.095, Cd 0.0005, Cr 0.005, Cu 0.055, Fe 38.4, Mn 0.005, Ni 0.020, Pb 0.001, and Zn 0.008. Concentrations were calculated using blank subtraction and linear fit standardization of Rhodium (^{103}Rh). To determine the concentration of Fe, each sample needed to be diluted (1:101). To perform the statistical analysis in case samples exhibited concentrations below the detection limit, half of this value was considered. A maximum of 2 observations under the detection limit was registered for each element, except for As where 60 out of 94 samples were below the detection limit.

2.3. Statistical analysis

Each individual sample was assigned to a particular year of the considered time frame (1941–2010) which corresponded with half of their lifespan. This year was calculated based on the year of death and age of individuals as: $yearofdeath-\frac{age}{2}$. In case the individual had lived an odd number of years, the year was determined by rounding the obtained result to the nearest unit. Therefore, samples were collected from 1944 to 2013 but our individuals were assigned to the time frame 1941–2010. For each animal, stable isotope values were calculated as the average of all growth layers ($\delta^{13}C$ and $\delta^{15}N$). The carbon values were corrected considering the Suess effect using the same methodology as in Szteren et al. (2018). This effect is an environmental change in the proportion of ^{13}C and ^{12}C due to the release of CO_2 from fossil fuel burning, which produces a systematic and constant decrease of $\delta^{13}C$ (Cullen et al., 2001; Francey et al., 2002; Hanson et al., 2009). This is why, to compare trace element concentrations considering $\delta^{13}C$ from animals that have lived in different periods during the last 70 years, carbon values were corrected as follows:

for animals that lived before 1960,

$$\delta^{13}C_{corrected} = \delta^{13}C - 0.005 \text{ x } (\text{Numbers of years to 1960}) - 0.022 \text{ x } (53)$$

for animals that lived after 1960,

$$\delta^{13}C_{corrected} = \delta^{13}C - 0.022 \text{ x } (\text{Numbers of years to 2013})$$

Trace element concentrations were analyzed with generalized linear models (GLM), adjusted using the function *glm* from the R package *stats* (R Core Team, 2019). Age, $\delta^{13}C$, sex and year were considered explanatory variables. Given the normal or log-normal distributions that characterize element concentrations, the Gaussian distribution and identity link function were used for fitting GLM, applying a logarithmic transformation when required. The identity link function was used in all fitted models. Models derived from all possible combinations of candidate explanatory variables were automatically generated and ranked based on the Akaike's Information Criterion (AIC) using the function *dredge* from the package *MuMIn* (Barton, 2019) (Supplementary Table 2). Models with the lowest AIC values were retained as the best ones.

The identity of species was not considered as an explanatory variable in the GLM because *A. australis* and *O. byronia* exhibit spatial trophic segregation and this was already represented in the models by $\delta^{13}C$. Trophic segregation has been determined through different methods, including stable isotope analysis (see further evidence in Drago et al., 2015; Franco-Trecu et al., 2014a, Franco-Trecu et al., 2012; Szteren et al., 2018). The carbon and nitrogen isotope values of both species of pinniped showed a high and significant correlation over the 70 years considered in the study (Pearson's correlation, $R = 0.58$, $p < 0.001$) (Supplementary Fig. 1). This association is due to the fact that coastal prey not only have higher values of $\delta^{13}C$ but also higher $\delta^{15}N$ that is reflected in their predators (Franco-Trecu et al., 2012). Therefore, to avoid collinearity only one variable could be included in the models and we chose $\delta^{13}C$ for three reasons. 1) Both species of pinnipeds showed a stronger segregation in relation to $\delta^{13}C$ than $\delta^{15}N$ (Drago et al., 2017; Szteren et al., 2018), and the difference in $\delta^{15}N$ was less than 3–5‰, values used to determine if species belong or not to different trophic levels (Deniro and Epstein, 1981; Michner and Kaufman, 2007). 2) None of the analyzed trace elements bioaccumulate with the increase in trophic position (Won et al., 2018). 3). We analyzed the concentration of trace elements associated to anthropogenic activities (Poleto et al., 2009) which are mainly transported from the land, particularly from cities and industries, by rivers and atmospheric fluxes into the estuaries and, then, into the oceans (Libes, 2009). In this context, the spatial information provided by $\delta^{13}C$ on the origin of organic matter results particularly explanatory.

The adequacy of fitted models was evaluated through a detailed visual inspection of residual plots. In case the explanatory variables, $\delta^{15}N$, Sex, age and year were not retained as relevant explanatory variables in the modeling process, the residuals of the selected model were analyzed against these variables to evaluate potential trends not detected (Supplementary Figs. 2, 3, 4 and 5).

3. Results

3.1. Profile of trace elements in the dentin of *Otaria byronia* and *Arctocephalus australis*

Both species had very similar trace element relative concentrations, with Fe as the element with the greatest concentration, followed by Zn, Al and Ni (Table 1). In decreasing order, *A. australis* had Fe > > Zn > Al > Ni > Mn > Cu > Cr > Pb > Cd, while in *O. byronia* Cu and Mn had similar concentrations and Pb values were higher than those for Cr (Table 2). Arsenic was detected only in 34 samples. When it was detected, the mean concentration was 0.01 ± 0.03 (standard deviation) μg g^{-1} dry weight for *A. australis* and for *O. byronia* was 0.009 ± 0.02 μg g^{-1} dry weight.

3.2. Concentration of trace elements according to year, δ^{13}C, sex and age

None of the included explanatory variables statistically contributed to explaining Fe, Ni, Mn, Zn and Al concentrations. The concentration of these elements in the dentin of *A. australis* and *O. byronia* has remained almost the same for 70 years considered in the study, despite δ^{13}C, age and sex.

Chromium concentrations changed from 1941 to 2010 following a second-order polynomial function for both species with a maximum concentration during 1970–1980, being significantly higher in males than females during the entire study period (Table 2, Fig. 2). The explained deviance of the model was 16% (Supplementary Table 2). In the case of Cd, Cu and Pb, the concentration varied significantly with δ^{13}C for both species of pinnipeds, not showing temporal trends (Table 2, Fig. 3). Cadmium concentration decreased linearly with δ^{13}C, and males had significantly higher concentration than females (Fig. 3A, Table 2), explaining 33.1% of the deviance (Supplementary Table 2). Higher concentrations of Cd were found in individuals with lower δ^{13}C, i.e., those particularly observed in *A. australis*. In the case of Cu, concentrations increased linearly with δ^{13}C, but no significant differences were observed between sexes (Fig. 3B, Table 2). The model for Cu explained 11% of the deviance (Supplementary Table 2). Lead concentrations increased linearly with δ^{13}C and males had higher concentrations than females for the 70 years of analysis (Fig. 3C, Table 2). For Pb, the model explained 20% of the deviance (Supplementary Table 2). The concentration of Cu and Pb increased towards higher values of δ^{13}C, i.e., those particularly observed in *O. byronia*.

4. Discussion

The dentin of both species of pinnipeds showed quantifiable concentrations of trace elements. Concentrations of Fe, Al, Mn, Ni, and Zn did not show significant changes over the last 70 years, regardless of the age of individuals and the differences in feeding areas between species of pinnipeds. Therefore, the concentrations of these elements could be used as a reference for analyses of dentin trace element composition in *A. australis* and *O. byronia* in the study area. Iron was the most abundant trace element in both species, coinciding with previous analysis of calcified matrixes in marine mammals (Ando et al., 2005; Edmonds et al., 1997; Fujise et al., 1988; Honda et al., 1986; Yamamoto et al., 1987). However, the concentration of Fe did vary between species (Table 1). The presence of Fe in the dentin may be associated with physiological processes in the odontoblastic cells in charge of the synthesis and maturation of the matrix (Piesco, 1994; Tjäderhane et al., 2012) more than an environmental exposure. In comparison with other species, *A. australis* and *O. byronia* showed high Fe concentrations than, e.g., *Leptonychotes weddellii* in the Antarctic (Table 1, Yamamoto et al., 1987). This could be related to the high bioavailability of this element in the Uruguayan coastline where it can present concentrations between 2 and 12 mg g^{-1} dry weight (García-Alonso et al., 2017).

Zinc was the second most abundant element present in the dentin of both species of pinnipeds and the concentrations found were very similar to those observed in *L. weddellii* (Table 1, Yamamoto et al., 1987). In human bone, the concentration of Zn varied from 60 to 310 μg g^{-1} dry weight between and is considered to have a strong physiological regulation (Shafer et al., 2008). Thus, the concentration range found in our study could be considered normal in the dentin of pinnipeds despite the presence of Zn enrichment in Montevideo sediments, where this element can reach concentrations 8 times higher than the earth's crust average (García-Alonso et al., 2017). Aluminum is the third most abundant element in the Earth's crust (Martin, 2006) and the main form of uptake by mammals is through the diet. Previous studies have reported the Al concentrations in total and the reactive fractions of sediments as well as in organisms of the Uruguayan coastline (García-Alonso et al., 2017) and, therefore, are likely to be incorporated into the bone (Priest, 1993) and dentin of pinnipeds. The range of Mn concentrations in both species of pinnipeds was similar to that found in other calcified matrixes of marine mammals (Table 1) (Agusa et al., 2011; Honda et al., 1986; Yamamoto et al., 1987). The presence of Mn in dentin could be a common metabolic requirement as suggested by previous studies (Arora et al., 2012).

Non-essential trace elements in *A. australis* and *O. byronia*, such as Cd, Cr and Pb; and Cu, showed either temporal or spatial trends in the last 70 years.

4.1. Temporal trend

Chromium was the only trace element that significantly changed over the last 70 years in pinnipeds dentin. Recent evidence shows that Cr cannot be considered an essential trace element because there is no data, up to our knowledge, on the biological effects of its deficiency or that its supplementation relieves symptoms (Vincent, 2013). Trivalent Cr is associated with glucose metabolism and rarely produces toxicity, while hexavalent Cr is toxic, and its compounds are irritant and corrosive. Unfortunately, the valence of Cr measured in the present and previous studies cannot be identified. Chromium is used as a dye for textiles, particularly for tanning leather (Covington et al., 2001). Because of its capacity to bind collagen, Cr can be easily analyzed in the dentin as shown in our research, in which collagen is the main protein (Butler, 1995; Silvestre et al., 1994). Argentina and Brazil are among the largest producers of leather in the world (FAO, 2013). Marine mammals rarely have Cr exposure, even when analyzing liver concentrations (Stockin et al., 2007; Szefer et al., 1994; Zhou et al., 2001), however, it has been detected in all dolphin samples from the South of Brazil, and Argentina (Kunito et al., 2004; Panebianco et al., 2012). Leather industries have pushed Uruguay's economy during the studied period (Instituto Cuesta Duarte, 2005). Chromium is the main effluent of tanneries located very close to the Pantanoso river that flows to Montevideo Bay in the Rio de la Plata estuary (Feola et al., 2013; Muniz et al., 2004a). Leather manufacturing in Uruguay increased during the 20th century, in the '70–'80s reached its maximum production, followed by a reduction during the '90s (Instituto Cuesta Duarte, 2005). The increase in Cr concentrations in dentin from 1941 until 1980 correlates with the increase of this element concentration in Montevideo Bay sediments for the same period (Burone et al., 2013; García-Rodríguez et al., 2010). Since 1993, the Cr effluent from tanneries has decreased to only 2% of the historic loads in rivers (Feola et al., 2013; Rafaelle, 2012) after wastewater treatment systems were installed (Lacerda et al., 1998). The concentration found in dentin of pinnipeds is below what is considered the average for environmentally exposed humans (50 ± 22 μg g^{-1}) (Nowak and Chmielnicka, 2000), despite the fact that the enrichment factor for Uruguayan coastline sediments could reach values up to 4.6 times when compared to the average concentration in the Earth's crust (García-Alonso et al., 2017).

4.2. Spatial segregation of trophic habits and differential exposure

In the last 70 years, the concentration of Cd, Cu and Pb in the dentin of both species of pinnipeds significantly changed depending on their feeding areas. The concentration of Cd in both species of pinnipeds decreases towards higher values of δ^{13}C, i.e., coastal feeding areas and/or benthic prey. More negative values of δ^{13}C, corresponding to a more pelagic diet, and higher Cd concentration were more common in *A. australis* than *O. byronia* (although some individuals of *O. byronia*

Table 1
Literature review on the concentration of trace elements in calcified matrices in marine mammals, including the results of this publication (bold). For each study mean and standard deviation (SD) are shown (μg g^{-1}). * indicates wet weight.

Trace element	Species	Matrix	Mean	SD	Reference
Fe	***Atrocephalus australis***	**Teeth**	**4.85 (mg g^{-1})**	**1.81**	**This study**
	Otaria byronia	**Teeth**	**4.88 (mg g^{-1})**	**1.80**	**This study**
	Dugong dugon	Teeth	6.4 (mg g^{-1})	3.2	(Edmonds et al., 1997)
	Leptonychotes weddellii	Teeth	17.9*	–	(Yamamoto et al., 1987)
	Phocoenoides dalli	Bone	281	–	(Fujise et al., 1988)
	Stenella coeruleoalba	Bone	101*	12.9	(Honda et al., 1986)
	Zalophus californianus	Bone	58.81	–	(Szteren and Aurioles-Gamboa, 2013)
Zn	***Arctocephalus australis***	**Teeth**	**105.4**	**46.0**	**This study**
	Otaria byronia	**Teeth**	**81.8**	**24.8**	**This study**
	Leptonychotes weddellii	Teeth	101*	–	(Yamamoto et al., 1987)
		Bone	87.8	–	(Yamamoto et al., 1987)
	Stenella coeruleoalba	Bone	409*	39	(Honda et al., 1986)
	Phoca vitulina	Bone	98.0	–	(Agusa et al., 2011)
	Phocoenoides dalli	Bone	296*	–	(Fujise et al., 1988)
	Zalophus californianus	Bone	60.78*	–	(Szteren and Aurioles-Gamboa, 2013)
Al	***Arctocephalus australis***	**Teeth**	**29.6**	**42.6**	**This study**
	Otaria byronia	**Teeth**	**18.6**	**24.8**	**This study**
	Zalophus californianus	Bone	73.70	–	(Szteren and Aurioles-Gamboa, 2013)
Ni	***Arctocephalus australis***	**Teeth**	**4.06**	**1.87**	**This study**
	Otaria byronia	**Teeth**	**3.67**	**1.36**	**This study**
	Stenella coeruleoalba	Bone	0.08*	0.05	(Honda et al., 1986)
	Phocoenoides dalli	Bone	0.22	–	(Fujise et al., 1988)
Mn	***Arctocephalus australis***	**Teeth**	**1.07**	**0.39**	**This study**
	Otaria byronia	**Teeth**	**0.96**	**0.26**	**This study**
	Stenella coeruleoalba	Bone	0.82*	0.22	(Honda et al., 1986)
	Leptonychotes weddellii	Teeth	1.35*	–	(Yamamoto et al., 1987)
	Phoca vitulina	Bone	0.67	–	(Agusa et al., 2011)
	Phocoenoides dalli	Bone	0.55	–	(Fujise et al., 1988)
	Obdobenus rosmarus rosmarus	Teeth	–	0.17 (min) – 1.24 (max)	(Outridge and Stewart, 1999)
Cu	***Arctocephalus australis***	**Teeth**	**0.83**	**0.85**	**This study**
	Otaria byronia	**Teeth**	**1.39**	**1.10**	**This study**
	Delphinapterus leucas	Teeth	0.17*	–	(Outridge et al., 1997)
	Leptonychotes weddellii	Teeth	0.42*	–	(Yamamoto et al., 1987)
		Bone	0.77*	–	(Yamamoto et al., 1987)
	Odobenus rosrnams	Teeth	0.44*	–	(Outridge et al., 1997)
	Stenella coeruleoalba	Bone	0.48*	0.01	(Honda et al., 1986)
Cr	***Arctocephalus australis***	**Teeth**	**0.17**	**0.17**	**This study**
	Otaria byronia	**Teeth**	**0.14**	**0.09**	**This study**
	Phoca vitulina	Bone	0.093	–	(Agusa et al., 2011)
Pb	***Arctocephalus australis***	**Teeth**	**0.17**	**0.12**	**This study**
	Otaria byronia	**Teeth**	**0.42**	**0.41**	**This study**
		Bone	1.6*	0.2	(Peña et al., 1988)
	Delphinus leucas	Teeth	0.16	0.04	(Kinghorn et al., 2008)
	Delphinapterus leucas	Teeth	0.2*	–	(Outridge et al., 1997)
	Eumetopias jubatus	Teeth	10.04	11.6	(Ando et al., 2005)
	Leptonychotes weddellii	Bone	0.48*	–	(Yamamoto et al., 1987)
		Teeth	0.48*	–	(Yamamoto et al., 1987)
	Stenella coeruleoalba	Bone	0.39	0.08	(Honda et al., 1986)
	Odobenus rosrnams	Teeth	2.0*	–	(Outridge et al., 1997)
	Phoca vitulina	Bone	0.11	–	(Agusa et al., 2011)
	Phocoenoides dalli	Bone	0.15*	–	(Fujise et al., 1988)
	Trusiops aduncus	Bone	2.78*	3.07	(Lavery et al., 2008)
	Tursiops truncatus	Bone	0.85*	0.19	(Lavery et al., 2008)
	Delphinus delphis	Bone	1.03*	0.55	(Lavery et al., 2008)
Cd	***Arctocephalus australis***	**Teeth**	**0.08**	**0.07**	**This study**
	Otaria byronia	**Teeth**	**0.01**	**0.01**	**This study**
	Delphinapterus leucas	Teeth	0.029	–	(Outridge et al., 1997)
	Leptonychotes weddellii	Bone	0.02*	–	(Yamamoto et al., 1987)
		Teeth	0.02*	–	(Yamamoto et al., 1987)
	Odobenus rosrnams	Teeth	0.05*	–	(Outridge et al., 1997)
	Stenella coeruleoalba	Bone	0.18*	0.05	(Honda et al., 1986)
	Phoca vitulina	Bone	0.003	–	(Agusa et al., 2011)
	Phocoenoides dalli	Bone	0.23*	–	(Fujise et al., 1988)
	Trusiops aduncus	Bone	0.047*	0.81	(Lavery et al., 2008)
	Tursiops truncatus	Bone	–	–	(Lavery et al., 2008)
	Delphinus delphis	Bone	–	–	(Lavery et al., 2008)
	Zalophus californianus	Bone	2.99*	–	(Szteren and Aurioles-Gamboa, 2013)

showed low values of δ^{13}C and matching high Cd concentration). These pinniped species are trophically segregated since the last century (Drago et al., 2017; Szteren et al., 2018). *A. australis* feeds more on pelagic preys, particularly on squid which make up 40% of their diet along with anchovies (*Engraulis anchoita*) (Franco-Trecu et al., 2013, 2014a; Szteren et al., 2004). Squid accumulate Cd bound to cytosolic proteins in their digestive gland, favoring its transference through the trophic web (Bustamante and Bertrand, 2006). The Argentine shortfin squid (*Illex argentines*) in the Southwest Atlantic can accumulate up to 485 μg g^{-1} (wet weight) of Cd (Gerpe et al., 2000). *E. anchoita*

Table 2
Significant estimates for the corresponding models for trace element concentration. Model coefficients are expressed in R syntax. * *p*-value <0.05, ** *p*-value <0.01 and *** *p*-value <0.001.

Model	Coefficient	Estimate	p-value
Ln (Cadmium)	Intercept	−9.95	<0.001***
	Sex-Male	1.52	<0.001***
	$\delta^{13}C$	−0.39	0.012**
Ln (Chromium)	Intercept	−2.43	<0.001***
	Poly(Year,2) 1	−0.98	0.24
	Poly(Year,2) 2	−2.26	0.0078**
	Sex-Male	0.41	0.029*
Ln (Copper)	Intercept	3.30	0.0054**
	$\delta^{13}C$	0.27	0.0017**
Ln (Lead)	Estimate	2.00	0.039*
	Sex-Male	0.38	0.031*
	$\delta^{13}C$	0.30	<0.001***

could also transfer Cd to both species of pinnipeds, particularly to *A. australis*. The concentration of Cd in visceral tissue of anchovies can be as high as 3.32 μg g^{-1} (Polizzi et al., 2017). Therefore, our results support previous findings in which *A. australis* had a higher concentration of Cd than *O. byronia*, in other tissues such as in kidney and liver (Marcovecchio et al., 1994; Tagliamonte, 2009).

Our results show an increase in the concentration of Cu towards higher $\delta^{13}C$ values, corresponding to a more coastal and/or benthic diet for both species of pinnipeds, being more common in *O. byronia*. A higher concentration of Cu can be found in lakes, rivers and estuaries than in the ocean (Georgopoulos et al., 2001). Sediments with up to 135 μg g^{-1} dry weight concentrations of Cu in Montevideo Bay are considered to be highly polluted (Muniz et al., 2004a), and Cu was also found in the intertidal sediments (Castiglioni et al., 2018; García-Alonso et al., 2017). The external area of Rio de la Plata estuary also has levels of Cu that could toxic for the resident biota (Carsen et al., 2003). *O. byronia* uses more coastal and benthic areas than *A. australis* and, therefore, has a higher concentration of Cu. These trends have reminded similar for the last 70 years, despite that Montevideo Bay sediments showed a sharp increase in concentrations of Cu before 1940 and another one during the '90s (García-Rodríguez et al., 2010).

The concentration of Cu in both species of pinnipeds prey has not been studied in detail. Mullet (*Mugil platanus*) is the most abundant coastal fish species in Uruguay with a high concentration of Cu (up to

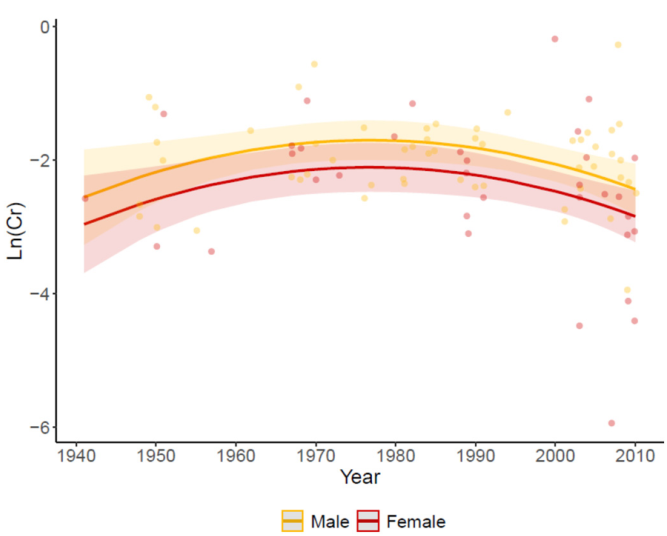

Fig. 2. Temporal trends in the concentration of Chromium (μg g^{-1} dry weight) for males (red) and females (yellow) of *Arctocephalus australis* and *Otaria byronia* during the last 70 years. Solid lines represent mean trends and shaded areas 95% confidence intervals.

493 μg g^{-1} dry weight in liver) (Viana et al., 2005). It has not been reported as a common species in the scats of *O. byronia*, but this species of pinniped has been seen eating mullet during the interaction with coastal fisheries (observed by the authors), making it a possible source of Cu (De María et al., 2014a, 2014b). The Whitemouth croaker (*Micropogonias furnieri*), Stripped weakfish (*Cynoscion guatucupa*) and Brazilian codling (*Urophyscis brasiliensis*) are better represented in *O. byronia*'s diet (Franco-Trecu et al., 2013) and have approximately 50 μg g^{-1} dry weight of Cu in their livers (Viana et al., 2005). Future research should quantify the concentration of these metals in pelagic fish such as *E. anchoita* and cephalopods to confirm the possible differential trophic transfer of Cu from benthic and pelagic preys found in this study. The concentrations of Cu in *O. byronia* and *A. australis* individuals that prey in coastal environments are above those found in calcified matrixes of other marine mammals from around the world (Table 1). Future studies should address the association between the concentration of Cu in teeth and other tissues to completely understand its physiological consequences.

The concentrations of Pb were higher in individuals preying in benthic and coastal environments (i.e. particularly in *O. byronia*) than those feeding in pelagic areas. Higher concentrations of Pb occur in coastal environments because of the anthropic input associated with cities and burn of fossil fuels (Libes, 2009) as well as several studies indicate that about 82 to 90% of the organic and inorganic suspended particulate material is retained in the continental shelf and deltas region (Hedges, 1992; Hedges and Keil, 1995). Until 2000, Pb was used as a gasoline additive in Uruguay and Argentina (ANCAP, 2020; MECON, 1998) and it still used in car batteries, paint pigments and ammunition (International Lead and Zinc Study Group, 2020). In Uruguay, there is still recycling and smelting of batteries that are responsible for human exposure to Pb (Burger and Pose Roman, 2010). Lead has toxic effects in humans, causing central nervous system problems, hypertension and kidney failure (Fowler et al., 2015). The concentration of Pb in Montevideo Bay sediments is higher than in the adjacent Southwest Atlantic (Muniz et al., 2004b). Moreover, rivers that flow to the Rio de la Plata in Uruguay and Argentina have sediment concentrations that could be toxic for biological communities (Carsen et al., 2003; Feola et al., 2013). Teeth are a trustworthy source of environmental exposure to Pb in humans (Karahalil et al., 2007) and concentrations over 4 μg g^{-1} dry weight suggests lead intoxication (Al-Mahroos and Al-Saleh, 1997). The concentration of Pb in both species of pinnipeds did not reach this threshold and, therefore, seem not to be intoxicated with Pb. Based on this threshold for humans, observed concentrations of Pb in both species of pinnipeds seem not to reach toxic levels. However, studies on the specific-sensitivity of pinnipeds to Pb are still missing and the definition of critical levels should be addressed in future studies. The concentration of Pb in *Eumetopias jubatus* in Asia was higher than in *O. byronia* and *A. australis* (Table 1, Ando et al., 2005). This could be due to the large differences in Pb contamination between regions, being much higher in Asia than in South America (Shahidul Islam and Tanaka, 2004). However, the concentration of Pb found in other marine mammal species in calcified matrixes in the Antarctic and Arctic are similar to the ones found in the present study (less than 2.0 μg g^{-1}; Outridge et al., 1997; Outridge and Stewart, 1999; Yamamoto et al., 1987) (Table 1).

Cadmium, Cr and Pb showed differences between sexes in both species of pinnipeds, being higher in males than in females. It is possible that larger organisms like males of both species, require a larger energy input (Segura et al., 2015) and this could increase the intake of trace elements. It is also probable that females could deposit less (or even remove) Cd and Cr in ossified matrixes during gestation and lactation as it occurs with Pb (Levine, 2011). Higher concentrations of Pb found in males than in females could be due to the maternal transference during pregnancy and lactation, as part of the Ca and Pb kinetics in the skeleton (Bronner, 2008; Ong et al., 1993; Téllez-Rojo et al., 2002). Particularly, in human studies, the concentration of Pb is higher in men than in women

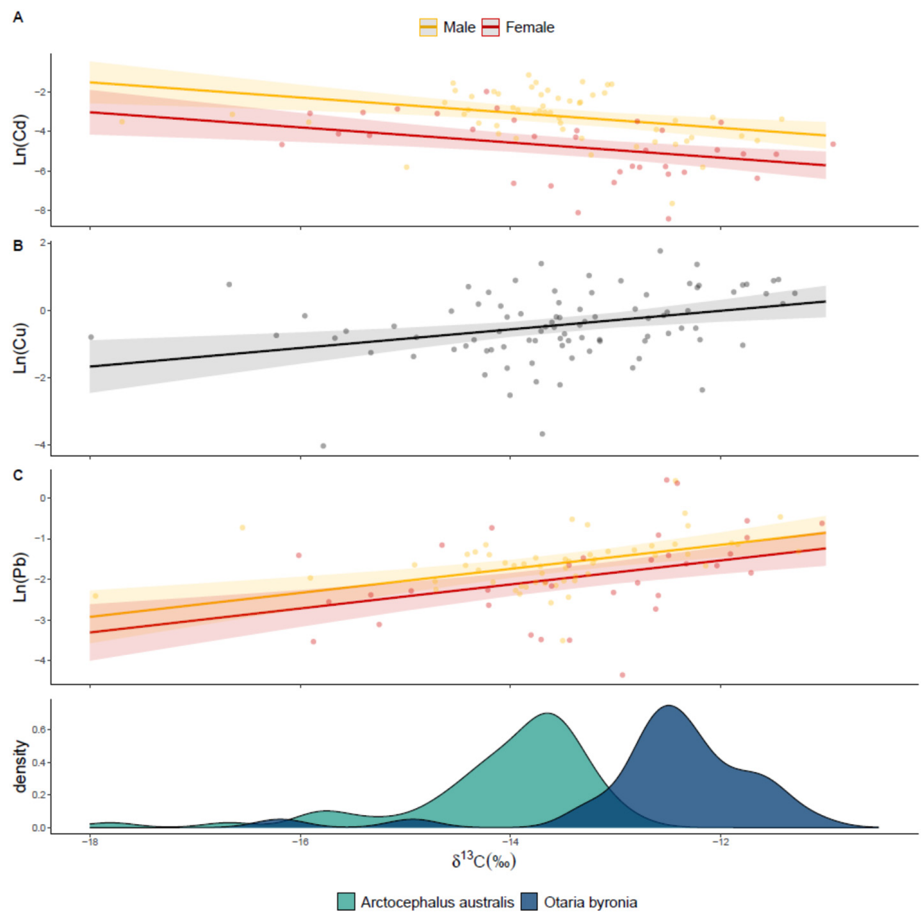

Fig. 3. Effect of $\delta^{13}C$ on the concentration of cadmium (A), copper (B) and lead (C) in *Arctocephalus australis* and *Otaria byronia* in the last 70 years. Concentrations (μg g^{-1} dry weight) are expressed in logarithmic scale. In A and C, the trends in red are for females and the ones yellow for males. In B, gray there is no differences between sexes. Solid lines represent mean trends and shaded areas 95% confidence intervals. Density plots represent the frequency of $\delta^{13}C$ values for *A. australis* (green) and *O. byronia* (blue).

(Alomary et al., 2006; Baranowska et al., 2004) and this mechanism of transference has been reported for pinnipeds, e.g. in *Halichoerus grypus* (Habran et al., 2012). In addition, *A. australis* females could receive less Pb through their diet because they consume more pelagic prey than males (Franco-Trecu et al., 2014a). In both species, females are smaller and feed from a lower trophic position than males (Arim et al., 2007; Segura et al., 2015; Szteren et al., 2018), likely reducing the transference of Pb. However, this relationship between trophic level and Pb has been inconclusive and previous studies have shown both positive and negative relationships between $\delta^{15}N$ and Pb in trophic networks including pinnipeds (Elorriaga-Verplancken and Aurioles-Gamboa, 2008; Sydeman and Jarman, 1998).

5. Conclusions

Our results show that dentin is a reliable matrix to analyze the environmental exposure to trace elements in marine mammals, particularly for Cr, Cu, Cd and Pb, when proper tools for analysis as ICP-MS are available (Borkowska-Burnecka et al., 2010). It is an available matrix that does not require the sacrifice of organisms, sampling is possible from dead animals and from scientific collections and requires no special storage conditions.

The use of Cr by industries during the twentieth century was reflected in *A. australis* and *O. byronia*. In addition, these species have been differentially exposed to trace elements depending on their feeding areas. A pelagic diet based on squid increased the concentration of Cd in *A. australis*, whereas a nearshore or benthic diet, more common in *O. byronia*, increased the concentration of Cu and Pb. *O. byronia* has been more exposed to anthropogenic sources of Pb and Cu and as result, could have experienced synergistic effects form the exposure to multiple trace elements (Aherne et al., 1990; Whittaker et al., 2011) particularly in the case of males. Future studies could address the relationship between the concentration of trace elements in the dentin and other organs to fully understand the physiological consequences of the exposure to trace elements in pinnipeds. The combined effects of exposure to trace element along with other ecological pressures such as the interaction with fisheries and, the reduction in the size of prey consumed (De María et al., 2014a, 2014b; Drago et al., 2010; Riet Sapriza et al., 2013) could result in a higher sensitivity of *O. byronia* to anthropogenic pressures.

CRediT authorship contribution statement

Maite De María: Conceptualization, Methodology, Software, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization, Project administration, Supervision, Funding acquisition. **Diana Szteren:** Funding acquisition, Methodology, Investigation, Resources, Writing - review & editing, Supervision. **Javier García-Alonso:** Methodology, Resources, Funding acquisition, Writing - review & editing, Supervision. **Carlos E. de Rezende:** Resources, Validation, Writing - review & editing. **Rodrigo Araújo Gonçalves:** Validation, Data curation. **José Marcus Godoy:** Resources, Writing - review & editing. **Francisco R. Barboza:** Methodology, Software, Formal analysis, Investigation, Data curation, Writing - review & editing, Visualization, Supervision.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.141296.

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