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RESEARCH ARTICLE

Metals as chemical tracers to discriminate ecological populations of threatened Franciscana dolphins (*Pontoporia blainvillei*) from Argentina

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Abstract Franciscana dolphins are the most impacted small cetacean in the Southwestern Atlantic Ocean, classified as Vulnerable A3d by IUCN. Essential (Fe, Mo, Mn, Cr, Ni, Co) and non-essential (Ag, Pb, Sn) trace elements (TEs) were measured in liver, kidney, and brain samples of by-catch Franciscana dolphins that were living in estuarine ($n = 21$) and marine ($n = 21$) habitats (1) to assess whether TEs posed a threat and (2) to evaluate the suitability of TEs for discriminating ecological populations of this species in Argentinean waters. Essential TEs showed little variation in tissues from both groups in agreement with levels reported for other cetaceans and suggesting that these concentrations correspond to normal physiological levels. Non-essential TEs were higher in estuarine juveniles and adults dolphins than in marine specimens. These results suggest anthropogenic sources associated with estuarine area and that Franciscana dolphins are good sentinels of the impact of the environment. The difference in the concentrations of TEs beetwen ecological populations appeared to be related to distinct exposures in both geographical areas, and it is suggested that Ag and Sn concentrations in adults are good chemical tracers of anthropogenic input of TEs. These results provide additional information for improved management and regulatory policy.

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Introduction

An understanding of population and stock structure is important for effective management and protection of cetaceans. Genetic studies provide information that can be used to discriminate among stocks but not variation due to anthropogenic impacts on local habitats and their effects on health. As a result, chemical tracers, such as carbon and nitrogen stable isotopes, trace elements, fatty acids, and organic pollutants are increasingly used in ecological studies to examine trophic relationships, habitat use, and migratory patterns of wildlife (Bustamante et al. 2006; Crawford et al. 2008; Lailson-Brito et al. 2011; Alonso et al. 2012).

Trace elements (TEs) may enter into the environment from both natural and anthropogenic sources (Zhou et al. 2001), and cetaceans are considered good sentinels of environmental contamination of these elements due to their long lifespan and their position at the top of the marine trophic webs (Moore 2008; Lailson-Brito et al. 2009; Aubail et al. 2013). The major source of TEs for cetaceans is through their diet (Bilandzic et al. 2012; Aubail et al. 2013) including both essential (with biological function and homeostatic regulation) and non-essential (with unknown physiologic function and toxic) TEs (O'Hara and O'Shea 2001). Therefore, TEs may be potential "chemical tracers" of the habitat or of the feeding zone of predators. However, other biological factors such as sex and age (Vanderklift and Ponsard 2003) should be considered when comparing different stocks or populations.

Franciscana dolphin (*Pontoporia blainvillei*) (Gervais and d'Orbigny 1844) is a small, endemic marine mammal that inhabits the Southwestern Atlantic Ocean. Its geographical distribution ranges from Itaúnas (18° 25′ S, 30° 42′ W, Brazil; Siciliano 1994) to Golfo Nuevo (42° 35′ S, 64° 48′ W, Argentina; Bastida et al. 2007). The International Union for Conservation of Nature (IUCN) has classified the species as Vulnerable A3d throughout its geographical range (Reeves et al. 2012), being the most anthropogenically impacted small cetacean in the Southwestern Atlantic Ocean (Secchi and Wang 2002). Due to their coastal and estuarine habitats, Franciscana dolphins inhabit areas with intense human activity, which poses several threats to their conservation.

The range for this species was divided into four Franciscana Management Areas (FMAs): two in southeastern Brazil (FMA I and II), one in southern Brazil and Uruguay (FMA III), and the other one in Argentina (FMA IV) (Secchi et al. 2003; Fig. 1). This species does not migrate long distances and presents site fidelity (Bordino et al. 2008; Cremer and Simoes-Lopes 2008). Recently, information has been obtained on home range (Bordino et al. 2008), population genetics (Mendez et al. 2008; 2010; Cunha et al. 2014; Gariboldi et al. 2015; Negri et al. 2016) and toxicology (Polizzi et al. 2013) indicating at least three different stocks within FMA IV. In this area, two main ecosystems occur the La Plata River estuary and the marine coast (Fig. 1). The estuarine area is influenced by urban and industrial activities in Argentina and Uruguay, and effluents are discharged into the river with little or no treatment (Carsen et al. 2003). In contrast, the marine coastal area is little by the contaminated estuarine waters, and although many tourist resorts are located in this area, they produce a minor environmental impact on the coast. The goals of this study were (1) to investigate if TEs pose a health threat assess to Franciscana dolphins and (2) to evaluate the suitability of TEs for differentiating ecological populations of this species in Argentinean waters.

Materials and methods

Study area and sampling

Franciscana dolphins were collected from two coastal areas of Buenos Aires Province between 2008 and 2011 (Fig. 1):

(1) The estuarine area, which is formed by the estuary of the La Plata river, being an environment with great impact (Carsen et al. 2003, Schenone et al. 2007). The cities where estuarine dolphins (n = 21) were collected were Río Salado and San Clemente del Tuyú.

(2) The marine coastal area, which represents a low impacted environment to the south of the estuarine zone. Marine dolphins (n = 21) were collected from different cities along the coast: Mar de Ajó, Mar Chiquita, Mar del Plata, Necochea, and Claromecó.

Fig. 1 Marine and estuarine geographic areas in Argentinean continental shelf and the management areas of the whole geographic distribution of Franciscana dolphin (*Pontoporia blainvillei*) in South America

Dolphins were incidentally captured in artisanal fishing nets, being entangled for a period less than 10 h before sampling. The quality of the carcass was evaluated according to Geraci and Lounsbury (2005). Total length, weight, and sex were determined for the specimen. Samples of the liver, kidney and brain were collected, immediately frozen in liquid nitrogen and stored at −80 °C until analysis.

Body condition index, age determination, and fine scale adjustments

All analyses were performed with specimens caught incidentally by the artisanal fishery, so it was started with the premise that individuals were healthy and with normal body condition (Rodríguez et al. 2002; Denuncio 2012). To assess the body condition, the Relative Index of Body Condition (Kn = recorded body weight/estimated body weight) of Le Cren (1951) was calculated. The estimated weight was obtained from the length vs weight curve of this species in Argentinean waters, using the following equation previously reported by Rodríguez et al. (2002). The fat index was determined by Denuncio (2012) in the same specimens analyzed here, indicating a normal body condition (average: 31.87 ± 6.24 %).

Age was determined by Denuncio et al. (2013) using dentine and cementum dental layers to determine growth layer groups (GLGs). Each GLG was considered 1 year (Pinedo and Hohn 2000). Kasuya and Brownell (1979) and Harrison et al. (1981) found that peak calving for Franciscana dolphins in Uruguay occurs during November. In Argentinean waters, calving occurs from early October to early February with a peak in November (Denuncio et al. 2013). On the basis of this information, we used mid-November as the mean birth date for calves to estimate the fine scale age (by month).

Franciscana dolphins were divided into four age classes:

(1) Fetus: dolphins found in the womb
(2) Calves: suckling (only milk in stomachs), mix diet (milk and solid prey), and weaned (only solid prey) dolphins with age less than 1 year (Kasuya and Brownell 1979, Rodríguez et al. 2002; Denuncio et al. 2013)
(3) Juveniles (sexually immature): 1–3.5 years old (Kasuya and Brownell 1979, Panebianco et al. 2012a)
(4) Adults (sexually mature): 3.5 years onwards (Kasuya and Brownell 1979)

Trace element determination

Lyophilized liver, kidney, and brain triplicate samples were weighed to the nearest 0.1 mg and subjected to microwave-assisted digestion in Teflon™ vessels with 2 ml HNO_3 (65 %), 1 ml H_2O_2 (30 %), and 5 ml of 18.2 MΩ cm deionized water. After cooling, samples were diluted to 50 ml with deionized water in a volumetric flask. Fe, Cr, Mn, Co, Ni, Mo, Ag, Sn, and Pb levels were determined by inductively coupled plasma mass spectroscopy (ICP-MS, PerkinElmer, Sciex, DCR 2). An internal standard (^{103}Rh, CertiPUR®, Merck) was added to each sample and calibration standard solutions were used. Quality control and quality assurance included field blanks, method blanks, and certified reference materials (CRMs: NIST 1566b, NIST 2976, DOLT-3, and NIST 1577c). Measured CRMs and the instrumental detection limits for each element are listed in Table 1. Average recovery of CRMs for each element was 90 ± 5 % (range 85–100 %). The concentrations (μg g^{-1} dry weight) of elements were expressed as the median ± standard error. However, for comparison with concentrations of TEs previously reported and expressed in wet weight, conversion factors were used based on Yang and Miyazaki (2003).

Statistical analysis

In previous reports for Franciscana dolphins (Lailson-Brito et al. 2002; Kunito et al. 2004; Dorneles et al. 2007; Seixas et al. 2009a; Panebianco et al. 2011, 2012b), no significant differences in concentrations of TEs were found between male and female dolphins; therefore, the data was analyzed together without differentiation of sex. Data were tested for a normal distribution using Kolmogorov-Smirnov's test, and homoscedasticity of data was checked by Levene's test. After that, differences between groups in juveniles and adult dolphins were performed using Mann-Whitney test. Correlations between TEs and estimated age were carried out using the non-parametric Spearman test. Level of significance was set at $p < 0.05$. Statistical analysis in the fetus and calf age classes were not statistical analyzed due to the small sample size. TEs data were subjected to principal component analysis (PCA) to evaluate the suitability of TEs for discriminating ecological populations. All analyses were conducted using STATISTICA® 6.0 (Statsoft, Inc.).

Results

Biometric measurements of the specimens and TE concentrations in the differents tissues are presented on Tables 2 and 3, respectively. All carcass were in good condition (code 2) and the Kn value for estuarine dolphins was 0.91 ± 0.15, while for marine dolphins it was 1.03 ± 0.14. These values were not statistically different ($p = 0.94$).

Table 1 Precision and accuracy measured on certified reference materials and instrumental detection limits (IDL) for each trace element. Data are expressed in μg g^{-1} dry weight

Element	IDL	NIST 1566b		NIST 2976		DOLT-3		NIST 1577c	
		Certified value	Measured value	Certified value	Measured value	Certified value	Measured value	Certified value	Measured value
Fe	0.04	205.8 ± 6.8	193.5 ± 0.2	171.0 ± 4.9	190.4 ± 2.9	1484 ± 57	1558 ± 48	197.9 ± 0.65	196.5 ± 0.52
Cr	0.02	–	–	0.50 ± 0.16	0.37 ± 0.007	3.5	2.0 ± 0.1	53 ± 0.014	67 ± 3.5
Mn	0.02	18.5 ± 0.2	18.4 ± 0.7	33 ± 2	40.5 ± 0.7	–	–	10.46 ± 0.47	10.4 ± 0.01
Co	0.01	0.371 ± 0.009	0.378 ± 0.0	0.61 ± 0.02	0.71 ± 0.02	–	–	300 ± 0.018	313 ± 4.24
Ni	0.08	1.04 ± 0.09	0.95 ± 0.01	0.93 ± 0.12	0.89 ± 0.06	2.72 ± 0.35	3.31 ± 1.69	0.04 ± 0.009	0.06 ± 0.001
Mo	0.01	–	–	–	–	–	–	3.30 ± 0.13	3.60 ± 0.07
Ag	0.01	0.666 ± 0.009	0.656 ± 0.006	11 ± 5	22 ± 4	1.20 ± 0.07	1.30 ± 0.04	0.006 ± 0.002	0.01 ± 0.001
Sn	0.02	0.031 ± 0.008	0.021 ± 0.004	96 ± 39	269 ± 1	0.4	0.5 ± 0.00	–	–
Pb	0.008	0.308 ± 0.009	0.336 ± 0.006	1.19 ± 0.18	1.27 ± 0.00	319 ± 0.05	320 ± 12	0.063 ± 0.001	0.062 ± 0.002

Table 2 Estimated fine scale age, total weight, and length range of *Pontoporia blainvillei* from marine and estuarine groups. *n* = number of dolphins

	Estuarine dolphins				Marine dolphins			
	n	Estimated age (year)	Weight (kg)	Total length (cm)	*n*	Estimated age (year)	Weight (kg)	Total length (cm)
Fetus	1	–	1.9	60	1	–	2.4	51
Calves	7	0.1–0.4	4.6–13.5	75–97	2	0.1	4.1–15.9	74–108
Juveniles	8	1.1–3.4	11.5–19.3	91–120	14	1.0–3.3	13.6–23.0	98–129
Adults	5	3.5–10.5	16.4–29.0	114–140	4	4.0–9.0	22.5–31.1	120–136

Hepatic Cr, Ni, Sn, and Pb concentrations were higher in the estuarine fetus compared to those from the marine dolphin. Silver, Fe, Mn, Co, and Mo concentrations were similar in fetus of both groups. Hepatic Sn and Pb were sixfold higher in estuarine calves, while Fe, Cr, Co, Ni, Mo, Mn, and Ag were similar for both groups. This similarity between groups in calves was also found for renal TEs concentration.

Iron, Mn, Co, Ni, Pb, Ag, and Cr concentrations in liver were similar ($p > 0.05$) between juveniles from both geographical groups. However, hepatic Sn ($p = 0{,}007$) and Mo ($p = 0{,}034$)

Table 3 Trace element concentrations (median ± SE, μg g^{-1}, dry weight) in the liver, kidney, and brain in age classes and groups of *Pontoporia blainvillei*. The average value is calculated from the samples which concentrations were detectable

		Fetus		Calf		Juvenile		Adult	
	Group Tissue	Estuarine	Marine	Estuarine	Marine	Estuarine	Marine	Estuarine	Marine
Fe	Liver	691	1860	1289 ± 277	1240–1590	1232 ± 327	1337 ± 203	1397 ± 468	1597 ± 454
	Kidney	572	559	653 ± 133	705–940	816 ± 128	714 ± 116	973 ± 301	728 ± 131
	Brain	na	126	143 ± 33.5	187	170 ± 57	132 ± 37	79–230	138 ± 41
Cr	Liver	0.149	0.037	0.06 ± 0.034	0.065–0.081	0.131 ± 0.159	0.074 ± 0.035	0.065 ± 0.015*	0.113 ± 0.032*
	Kidney	0.369	0.386	0.231 ± 0.218	0.070–0.160	0.123 ± 0.085	0.123 ± 0.084	0.173 ± 0.142	0.084 ± 0.040
	Brain	na	0.329	0.125 ± 0.088	0.138	0.131 ± 0.067	0.159 ± 0.082	0.041–0.057	0.154 ± 0.064
Mn	Liver	2.7	5.43	17.21 ± 6.11	8.23–16.20	13.15 ± 2.24	13.61 ± 2.25	12.70 ± 4.41	11.58 ± 2.83
	Kidney	2.25	2.15	6.43 ± 3.84	3.62–3.69	3.65 ± 2.10	3.96 ± 1.13	3.88 ± 1.35	3.88 ± 0.41
	Brain	na	3.25	3.06 ± 0.71	2.02	2.43 ± 0.39	2.22 ± 0.26	2.52–2.58	2.37 ± 0.35
Co	Liver	nd	0.046	0.035 ± 0.011	0.041–0.053	0.061 ± 0.017	0.061 ± 0.017	0.067 ± 0.016	0.072 ± 0.019
	Kidney	0.018	0.022	0.035 ± 0.018	0.027–0.085	0.076 ± 0.013	0.063 ± 0.018	0.089 ± 0032	0.067 ± 0.010
	Brain	na	0.037	0.026 ± 0.002	0.036	0.04 ± 0.007	0.031 ± 0.006	0.027–0.045	0.039 ± 0.01
Ni	Liver	0.084	0.038	0.048 ± 0.011	0.037	0.049 ± 0.022	0.056 ± 0.016	0.067 ± 0.015	0.051 ± 0.010
	Kidney	0.087	0.174	0.120 ± 0.106	0.037–0.041	0.064 ± 0.026	0.058 ± 0.019	0.101 ± 0.028	0.278 ± 0.361
	Brain	na	0.244	0.179 ± 0.141	0.058	0.173 ± 0.134	0.148 ± 0.107	0.195–0.256	0.093 ± 0.042
Mo	Liver	0.74	0.54	1.15 ± 0.29	0.70–1.66	2.81 ± 0.95*	2.11 ± 0.29*	4.58 ± 0.94*	2.98 ± 1.2*
	Kidney	0.68	0.59	0.62 ± 0.11	0.75–0.77	0.94 ± 0.11	0.88 ± 0.12	0.88 ± 0.12	0.98 ± 0.20
	Brain	na	0.372	0.271 ± 0.019	0.352	0.287 ± 0.061	0.276 ± 0.022	0.201–0.307	0.284 ± 0.035
Ag	Liver	0.42	0.35	0.63 ± 0.29	0.43–0.49	0.65 ± 0.47	1.76 ± 1.47	4.96 ± 4.02*	1.54 ± 0.94*
	Kidney	0.030	0.010	0.030 ± 0.010	0.010–0.040	0.020 ± 0.010	0.020 ± 0.010	0.030 ± 0.010	0.010 ± 0.005
	Brain	na	0.021	0.042 ± 0.007	0.067	0.272 ± 0.108	0.138 ± 0.043	0.231–0.258	0.075 ± 0.032
Sn	Liver	0.093	0.017	0.087 ± 0.025	0.014–0.069	0.425 ± 0.123*	0.162 ± 0.253*	0.755 ± 0.253*	0.067 ± 0.023*
	Kidney	0.037	0.037	0.034 ± 0.030	0.014–0.097	0.038 ± 0.009	0.016 ± 0.004	0.039 ± 0.005	0.015 ± 0.001
	Brain	na	0.024	0.012 ± 0.002	0.016	0.033 ± 0.01	0.014 ± 0.002	0.017–0.402	0.06 ± 0.083
Pb	Liver	0.057	nd	0.088 ± 0.052	nd	0.070 ± 0.031	0.054 ± 0.011	0.055 ± 0.003	0.059 ± 0.01
	Kidney	0.058	0.056	0.079 ± 0.027	0.058	0.056 ± 0.003	0.054 ± 0.004	0.054 ± 0.006	0.036 ± 0.026
	Brain	na	nd	0.02 ± 0.01	0.041	0.023 ± 0.023	0.026 ± 0.027	nd	0.043 ± 0.035

*Significant difference between groups ($p < 0.05$)

na not analyzed, *nd* not detectable

levels were significantly higher in estuarine juveniles. Most of the analyzed TEs showed no differences between groups in the kidney, with the exception of Sn which showed higher concentrations in estuarine juveniles compared to those from the marine area ($p < 0.0001$). Estuarine juveniles presented higher brain Ag ($p = 0.011$), Sn ($p = 0.001$), and Co ($p = 0.028$) concentrations than marine dolphins. In adult dolphins, only hepatic concentrations of Sn ($p = 0.014$) and Cr ($p = 0.019$) and renal Sn levels ($p = 0.034$) were higher in estuarine specimens.

The concentration of hepatic Mo in dolphins from both group were correlated with the age of the dolphins (Fig. 2A; estuarine, $p < 0.0001$; marine, $p = 0.001$). It was also observed a relationship with age in marine dolphins for hepatic Co (Fig. 2B; $p = 0.03$) and in estuarine specimens for Sn (Fig. 2C; $p < 0.0001$) and Ag (Fig. 2D; $p = 0.01$). Only a positive relationship between renal Co and age was observed in estuarine dolphins ($p = 0.012$).

Principal component analysis (PCA) was conducted considering all TEs in liver and brain, with exception of Pb due to the fact that more of 50 % on the individuals have undetectable levels in the tissues. In liver, the two principal components (PCs) represented 46.3 and 38.9% of the variance, respectively (Fig. 3), and their eigenvalues were greater than 1. The PC1 resulted from higher levels of Ni and Cr to the left of the origin, separating the estuarine fetus. PC2 resulted from the highest levels of Ag, Sn, and Mo in estuarine adult dolphins which differentiated it from the other groups that were greater than zero. In brain (Fig. 4), PC1 represented 39.1 % of the variance and, in liver, was associated with higher levels of Ag and Sn in estuarine adults and higher concentrations of Cr and Mo in marine fetuses. PC2 represented a 34.6 % of the total variance, and it resulted from higher levels Ni and Mn above the origin which separated estuarine calves and higher levels of Fe below zero associated with marine calves.

Discussion

The essential TEs are subject to regulatory mechanisms (Bowles 1999; Law 1996), and their physiology is evaluated by the "dose-response curve" where the two ends represent conditions of deficiency and toxicity, both incompatible with life (Minoia et al. 1990). Effects of nutritional deficiency of these elements include reduced body size, reduced birth rates, increased neonate, and juvenile mortality (Trites and Donnelly 2003). Nevertheless, the levels of essential elements higher

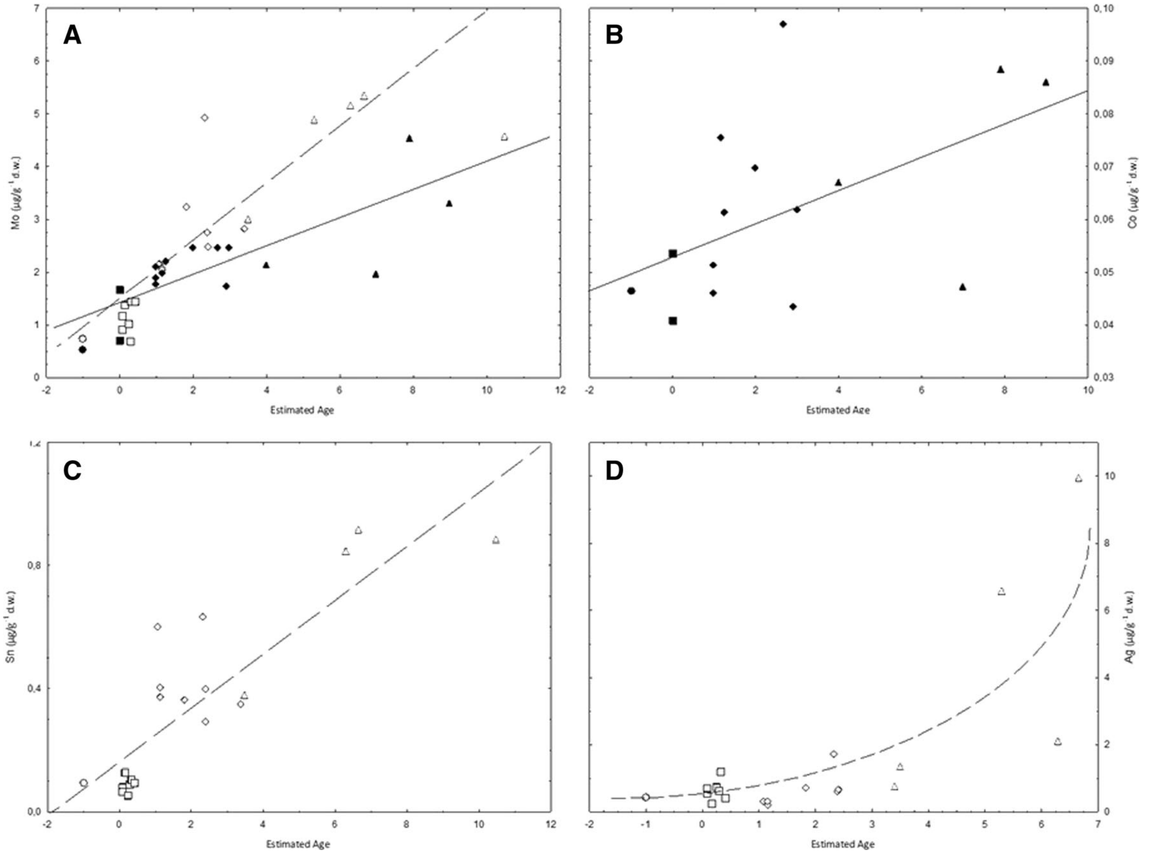

Fig. 2 Relationship of trace element concentration (µg g^{-1} d.w.) in liver of *Pontoporia blainvillei* and estimated age for marine (continuous line and filled symbols) and estuarine (cutline and open symbols) dolphins groups. *Circle*: fetus, *square*: calves, *diamond*: juveniles, *triangle*: adults. **a** Molybdenum, **b** cobalt, **c** tin, **d** silver

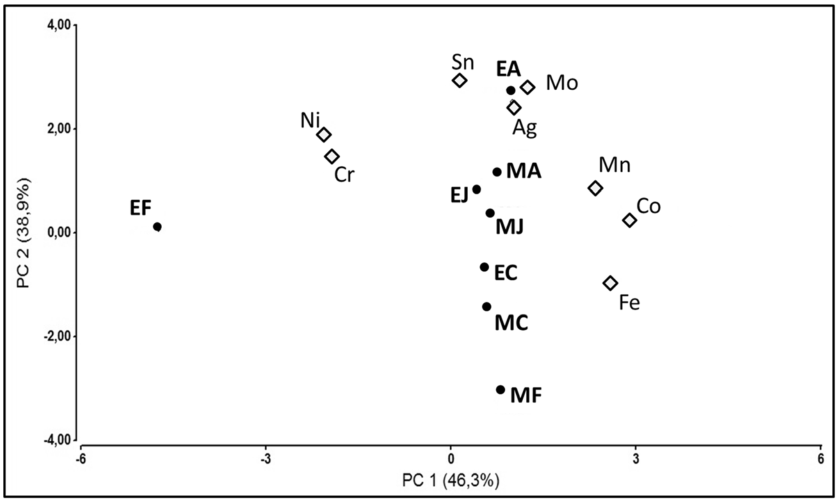

Fig. 3 Principal component analysis performed in the liver using trace elements as variables. *Diamond*: trace element; *circle*: group of dolphin; *E* estuarine, *M* marine, *A* adult, *J* juveniles, *C* calf, *F* fetus

than normal physiological levels may be toxic, and the toxicity depends on the particular element (O'Hara and O'Shea 2001). In contrast to essential TEs, those that are non-essential are potentially toxic even at low concentrations and have no known physiological function. Due to the longevity of cetaceans, long exposure times, and their upper trophic position, accumulation of these elements in tissues is common. Therefore, accumulation in the food web is considered the major risk for top predators (Das et al. 2003).

Fat index and Kn values from Franciscana dolphins indicated a good body condition of the specimens (Polizzi et al. 2014). Hepatic Fe, Mn, Co, and Mo levels in calves, juveniles, and adults were similar to values previously reported for Franciscana dolphins in Brazil (Kunito et al. 2004). Bioaccumulation of Co and Mo in liver was evident for Franciscana dolphins reported here as it was for dolphins from Brazil (Kunito et al. 2004). Iron is an essential nutritional element for all life-forms. Iron is stored as ferritin and hemosiderin in the liver of marine mammals (Denton et al. 1980). According to this, Fe hepatic levels in Franciscana dolphins were higher than in kidney; being consistent with other cetacean species (Capelli et al. 2000; Cardellicchio et al. 2002; Cáceres-Saez et al. 2012). The most commonly reported effect of Mn toxicity is a secondary iron deficiency, leading to an anemia (Keen et al. 2000). As it was mentioned, Franciscana dolphins had Fe levels similar to previous reports; this situation could be indicating that no signs of anemia are present in the studied dolphins. Furthermore, the present results were within the expected Mn concentrations in marine mammals, which are thought to be lower than 7 μg g^{-1} w.w. in all tissues (Thompson 1990).

Hepatic levels of Ni in all age classes and both geographical groups are much lower than the toxic concentration reported for mammals (Denkhaus and Salnikow 2002) and below the maximum levels (2.1 mg kg^{-1} w.w.) found in the liver of sperm whales (*Physeter macrocephalus,* Law et al. 1996). Panebianco et al. (2011) reported undetectable renal concentrations (<0.05 μg g^{-1} w.w.) and apparently higher hepatic concentrations (Panebianco et al. 2012b) in Franciscana dolphins than those reported here. These levels (0.69 ± 0.88

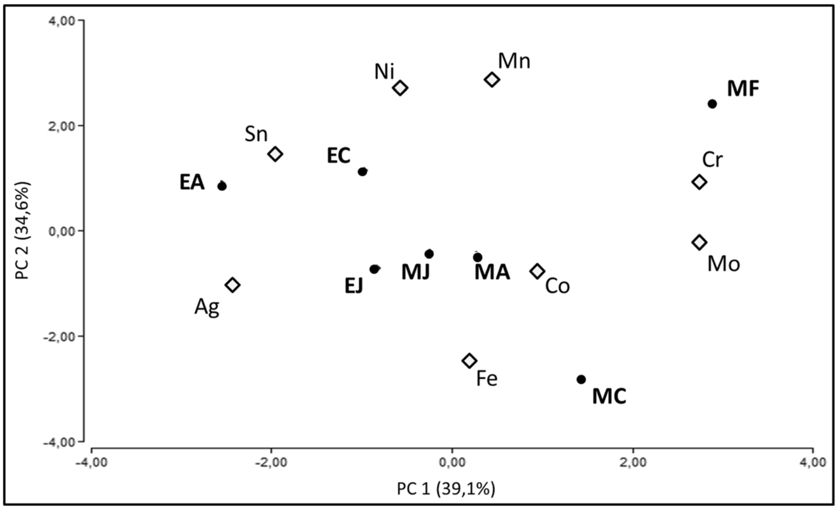

Fig. 4 Principal component analysis performed in the brain using trace elements as variables. *Diamond*: trace element; *circle*: group of dolphin; *E* estuarine, *M* marine, *A* adult, *J* juveniles, *C* calf, *F* fetus

μg g^{-1}w.w.) showed high variability suggesting that there was exogenous input of this metal in the south of Buenos Aires province.

The hazards associated with exposure to Cr are dependent on its oxidation state, Cr (III) is an essential nutrient for mammals involved in carbohydrates and lipid metabolism while Cr (VI) is highly toxic (Velma et al. 2009). Hepatic and renal Cr concentrations in both geographic groups of Franciscana dolphins were apparently lower than those reported by Kunito et al. (2004) in Brazil and are similar to levels reported previously for the species in Argentinean waters (Panebianco et al. 2011, 2012b). Although Cr valence was not determined in this study, even if were the toxic form, the low chromium concentrations found in Franciscana dolphins meant that it did not constitute a health risk to the species.

Despite the importance of essential TEs for normal development and function of the brain (Sandstead 1986), there is no information in the literature regarding these elements in Franciscana dolphins. Brain TE levels for this species were within the ranges previously reported for bottlenose dolphins (*Tursiops truncatus*, Capelli et al. 2008), striped dolphins (*Stenella coeruleoalba*, Cardellicchio et al. 2002, Capelli et al. 2008) and Risso's dolphin (*Grampus griseus*, Shoham-Frider et al. 2002, Capelli et al. 2008). Therefore, the levels of essential elements reported in this study suggests that they correspond to physiological levels.

The fetal period is characterized by a high metabolic rate, elevated development and growth, and the need for high amounts of nutrients (Mc Ardle and Ashworth 1999). Deficiencies and imbalances of essential elements have repercussions on the proper development of the fetuses. For this reason, it is relevant to assess the status of these TEs in this age class. There is little information about these elements in Franciscana dolphins with a few values for Cu and Zn levels (Gerpe et al. 2002; Polizzi et al. 2013, 2014). Therefore, the analysis reported here is the first information of Mn, Fe, Co, Cr, Mo, and Ni for the species.

Low variability is characteristic of essential elements, which are subject to regulation mechanisms (Law et al. 1991). Furthermore, our results are consistent with the variability reported in cetaceans (Ciesielski et al. 2006; Stavros et al. 2007), and since the dolphins in this study had good body condition, it is suggested that TEs concentrations in the Franciscana dolphins were at normal physiological levels.

Studies of health impacts of Ag in animals suggest that this metal may have effects on the brain, heart and reproductive system (ATSDR, Agency for Toxic Substances and Disease Registry 1990). Silver bioaccumulates in different tissues of cetaceans (Seixas et al. 2009a), and this is true for Franciscana dolphins (Kunito et al. 2004, Seixas et al. 2009b). Its accumulation in juvenile estuarine dolphins suggests a major input of this metal in the diet food. Moreover, hepatic levels of Ag observed in estuarine adults were significantly higher than those from the marine area. In general, concentrations of Ag in marine and estuarine waters are very low (0.1–0.3 ng l^{-1}); therefore, relatively small anthropogenic inputs result in environmental enrichment (Luoma et al. 1995). The higher concentrations found in estuarine dolphins could be related to the main urban and industrial centers of Argentina and Uruguay located along the La Plata River. Most urban and industrial waste and effluents are discharged into the river without or low-efficiency treatment (Carsen et al. 2003).

The toxic effects of Pb on mammals include anemia, renal damage, hypertension, cardiac disease, immuno-suppression (through antibody inhibition), and neurological damage (Mertz 1987). The La Plata River estuary has elevated levels of Pb in sediments and biota (Schenone et al. 2007; Beltrame et al. 2011). Marine fetuses and calves had no detectable Pb levels in liver. In contrast, estuarine fetuses showed evidence of anthropogenic sources of Pb. Juveniles and adults showed lower hepatic Pb levels than calves. Furthermore, Pb accumulation in bones is usually higher than in soft tissues of marine mammals (Caurant et al. 2006). Lead half-life varies from 5 to 20 years in the hard tissues of mammals, whereas it is only a few weeks or months in soft tissues (Ma 1996). Therefore, the levels presented in liver and kidney would indicate a recent input of Pb in the diet of Franciscana dolphins.

Elevated levels of Sn in the marine environment occurs in organic compounds which have been widely used as antifouling paints on ships and harbors (Almeida et al. 2007), and they have been shown to produce immunosuppressive effects in marine mammals (Kannan et al. 1996; Nakata et al. 2002). It is known that the gastrointestinal absorption of tin is poor (Hiles 1974), while the cetacean can accumulate large amounts of organic tin compounds (Tanabe et al. 1998). Therefore, elevated hepatic Sn in Franciscana dolphins probably resulted from exposure to organotin compounds. Estuarine dolphins had hepatic and renal concentrations higher than marine group, suggesting that the former group is more exposed to organotin compounds than the latter one. Although total concentration of Sn was determined here, studies in cetaceans confirmed that a great percentage of tissular Sn is present in an organic form reflecting the anthropogenic contribution (Le et al. 1999; Takahashi et al. 2000; Dorneles et al. 2008). Furthermore, its presence in fetuses suggests a placental pathway of organic Sn due to the transference of inorganic species had been not demonstrated in cetaceans (Dorneles et al. 2008), although it was for butyltins (Yang and Miyazaki 2006) and phenyltins (Yang et al. 2007).

Genetic (Mendez et al. 2008, 2010; Cunha et al. 2014; Gariboldi et al. 2015; Negri et al. 2016), homerange (Bordino et al. 2008) and toxicological studies (Polizzi et al. 2013) in the FMAIV suggested the presence of at least three ecological populations. The results obtained in this study on TE accumulation suggest the presence of at least two different ecological populations. Denuncio (2012) reported differences in both food items and size of the prey (higher in estuarine dolphins) of juveniles and adults Franciscana dolphins from both groups. This could be the cause of the differences found in non-essential TEs between marine and estuarine dolphins. Several factors can be used to evaluate the separation of stocks such as age, sex, body size, genetics, reproductive status, and nutritional condition (Aguilar et al. 2002; Verreault et al. 2009). In addition, some authors have proposed the assessment of pollutants to discriminate stocks (Kunito et al. 2002, Krahn et al. 2007, Praca et al. 2011). From the information obtained for Franciscana dolphins in the FMAIV, differences in TE concentrations among groups may be related to age and geographical area. Hence, the study of Ag and Sn concentrations in adults as chemical tracers may complement the proposal of at least two ecological populations in this area. The number of samples analyzed should be increased to differentiate other ecological populations in the marine area as were reported by Gariboldi et al. (2015) and Negri et al. (2016). In addition, our results suggest that Franciscana dolphins are good sentinels of environmental contamination by TEs.

Franciscana dolphins are listed by the IUCN as Vulnerable A3d due to population declines resulting from incidental mortality in gillnet fisheries (2900 animals per year in all four management areas; Reeves et al. 2012). Although by catch is a real and specific problem, other potential threats, such as degradation of habitats (impacts from contaminants; Alonso et al. 2012, 2015; Gago-Ferrero et al. 2013), can pose long-term risks that may contribute to population decline. It is therefore important to know the status of the pollutants (TEs) and their effects on different stocks for better management or regulatory actions.

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