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EVALUATION OF TRACE ELEMENT CONCENTRATIONS IN THE SERUM AND VIBRISSAE OF PERUVIAN PINNIPEDS (*ARCTOCEPHALUS AUSTRALIS* AND *OTARIA BYRONIA*)

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ABSTRACT: Concentrations of 15 trace elements (aluminum, arsenic, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, tin, vanadium, and zinc) were determined in vibrissae (whiskers) and serum of two sympatric pinniped species, the Peruvian fur seal population (PFS; *Arctocephalus australis* Peruvian subpopulation) and South American sea lion (SASL; *Otaria byronia*) at Punta San Juan, Peru during 2011–19 sampling events. Element concentrations were 2–20 times higher in vibrissae than in serum. Vibrissae and serum concentrations of several elements, including aluminum, arsenic, and lead, suggest that environmental contaminants may affect the health of pinnipeds at Punta San Juan. Although toxicity thresholds are unknown in pinnipeds, high concentrations of some elements (especially aluminum, arsenic, and lead) may have adverse impacts on their health such as immunosuppression and impaired reproduction. Arsenic was the only element that increased in mean vibrissae concentration throughout the study period. Female SASL vibrissae contained a mean arsenic concentration three times higher than the male SASL vibrissae mean arsenic concentration, and twice as high as the arsenic mean for all PFS vibrissae. The mean male SASL vibrissae cadmium concentration was five times higher than the vibrissae cadmium mean for both PFS males and females and nearly three times higher than the vibrissae cadmium mean for SASL females. Serum concentrations of aluminum, arsenic, copper, and manganese were significantly higher during moderate to extreme El Niño years compared to La Niña years. With stronger and more frequent El Niño-Southern Oscillation events predicted in the future, it is vital to understand how these trace elements may affect pinniped population health.

Key words: Arsenic, Peru, pinnipeds, SECLER, serum, trace elements, vibrissae.

INTRODUCTION

The Punta San Juan (PSJ) marine protected area (15°22′S, 75°11′W; Fig. 1) in southern Peru protects important rookeries for two sympatric pinniped species, the Peruvian fur seal population (PFS; *Arctocephalus australis* Peruvian subpopulation; Cárdenas-Alayza and Oliveira 2016) and South American sea lion (SASL; *Otaria byronia*). In 2000, PFS and SASL were protected under Peruvian law due to depressed population sizes, and PFS was classified as Vulnerable by the International Union for Conservation of Nature (Cárdenas-Alayza and Oliveira 2016). Peruvian pinniped populations have struggled over the last century from the effects of commercial harvesting, competition with commercial fisheries, and decreased prey availability during El Niño-Southern Oscillation (ENSO) events (Cárdenas-Alayza 2012). Peruvian pinniped population health has been assessed at PSJ for over a decade, but effects of environmental contaminants have not been evaluated. Both PFS and SASL populations are currently declining at PSJ, and it is vital to understand how environmental contaminants may be affecting pinniped population health as Peru's industrial activities continue to increase (Cárdenas-Alayza et al. 2021).

The Humboldt Current large marine ecosystem extends along the coasts of Chile and Peru, supporting numerous ecologically and economically important marine species. Approximately every 2–7 yr, this highly productive ecosystem is affected by El Niño phases

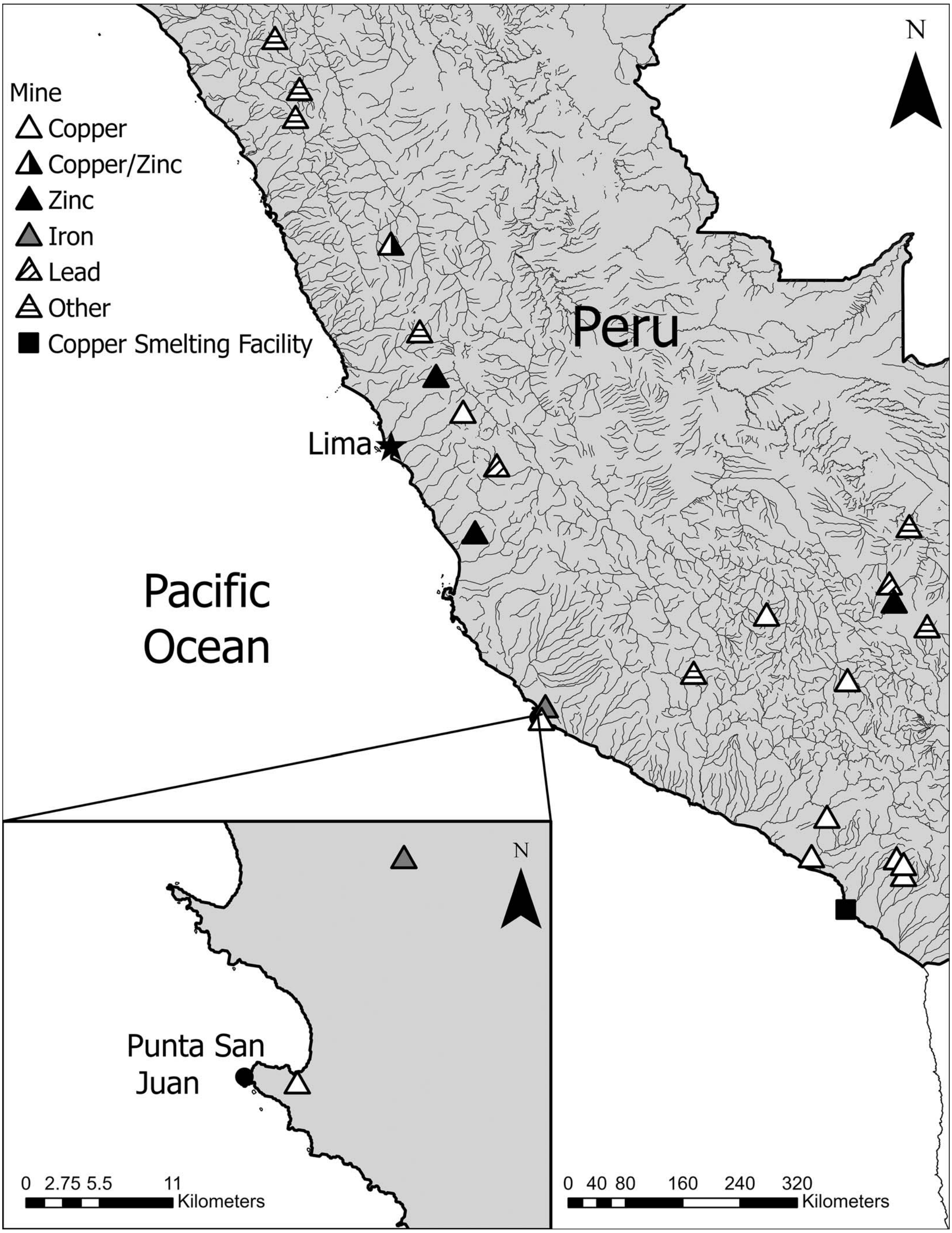

FIGURE 1. Map of Peru showing river systems, several major mine locations, and a copper smelting facility. The dot indicates our study site, the Punta San Juan marine protected area.

that last up to 18 mo (Taylor et al. 2008). The trophic dynamics of the ecosystem from the base of the food web to apex predators are greatly impacted by ENSO events, which can result in drastic decreases in pinniped populations (Taylor et al. 2008). Climate change models predict stronger and more frequent El Niño events in the future, highlighting the need to understand how these events impact the health of marine ecosystems (Wang et al. 2017).

Peru is among the world's largest producers of copper, lead, tin, and zinc. The nation's largest open-pit iron mine is located 20 km upstream from PSJ and a growing copper mine is within 6 km of PSJ (Fig. 1). Mine waste and sewage are discarded along the coast, including a dumping site within 4 km of PSJ (Adkesson et al. 2018). Elemental contamination from agriculture and mining can seriously impact ecosystem health. Tests of fluvial water, sediments, and human blood in the population of Paragsha, downriver from an open-pit mining area in the Peruvian Andes, have shown elevated levels of elements, particularly aluminum and lead (Bianchini et al. 2015).

Uptake of trace elements by animals occurs mainly through ingestion and digestion of food (Das et al. 2003). Peruvian anchoveta (*Engraulis ringens*) are a key prey for both PFS and SASL. While PFS tend to forage on pelagic schooling fishes and cephalopods, SASL are more generalist foragers and prey upon demersal fishes, crustaceans, and cephalopods (Arias-Schreiber 2000; Sarmiento-Devia et al. 2020). Female PFS have significantly lower $\delta^{13}C$ and $\delta^{15}N$ than do males, suggesting that they feed at a lower trophic level and possibly in different foraging locations (Edwards et al. 2021). Differences in contaminant concentrations among species, possibly linked to foraging differences, may help us better understand pinniped exposure.

Vibrissae (whiskers) are metabolically inert tissues that incorporate nutritional information as they grow, providing a noninvasive way to obtain contaminant concentrations (Hirons 2001; Andrade et al. 2007; Castellini et al. 2012; Ferdinando 2019). While vibrissae can reflect multiple years of trophic data (Hirons et al. 2001), serum reflects contaminants currently circulating through the body, either from recent exposure or remobilization from tissues such as blubber (Laker 1982; Gray et al. 2008; Yordy et al. 2010; Kooyomjian 2021).

Our study aimed to analyze 15 elements in vibrissae and serum samples from PFS and SASL collected between 2011–19. This would enable evaluation of concentrations between tissues, species, and sex, as well as the influence of ENSO events.

MATERIALS AND METHODS

Sample collection

We used archival paired vibrissae and serum samples from 69 PFS (50 females and 19 males; one female only had serum) and 31 SASL (14 females and 17 males). All individuals were reproductively mature adults. Samples were collected under direct veterinary supervision from 2011–19 from pinnipeds that were anesthetized as part of an ongoing population health monitoring program at PSJ, performed during the breeding season (November for PFS, February for SASL), except that 2018 samples were collected in April. All collections were authorized under Peruvian permit numbers RJ no. 09-2010-, 23-2011-, 022-2012-, 09-2013-, 024-2014, 008-2015-, 019-2016-SERNANP-RNSIIPG. Sample importation was authorized by the United States National Marine Fisheries Service under Marine Mammal Protection Act permits 15471 and 19669. Vibrissae, including the root, were plucked and stored in plastic bags. Blood was collected from the jugular vein, stored in trace element tubes (no additive; Vacutainer, BD, Franklin Lakes, New Jersey, USA), and kept on ice for $\leq$8 h until centrifugation (1,132 $\times$ G for 10 min). Serum was separated and stored at –80 C until analysis.

Sample preparation and analysis

Vibrissae were cleaned using ultrapure deionized water (18.2 Mohm) from a Barnstead water purification system and high performance liquid chromatography-grade acetone before drying in a Fisher Scientific (Waltham, Massachusetts, USA) isotemp vacuum oven model 282A at 60 C at 10^{-2} torr using a 14008-01 model Welch 1400 DuoSeal vacuum pump (Welch, Mt. Prospect, Illinois, USA). Whole vibrissae were digested in Teflon polytetrafluoroethylene tubes using 5:1 trace metal basis nitric acid (Sigma Aldrich, St. Louis, Missouri, USA) and 30% hydrogen peroxide (Sigma Aldrich). Vibrissae samples were digested at 60 C for 24 h using a ModBlock and diluted to 25 mL in ultrapure deionized water (Ferdinando 2019; Shore 2020). Approximately 0.5 g of serum was mixed with 4 mL of trace metal basis nitric acid, 1 mL of 30% hydrogen peroxide, and 1 mL of ultrapure water and digested via microwave digestion system (Multiwave 5000, Anton Paar, Graz, Austria) using the following program: room temperature to 200 C with a ramp time of 15 min

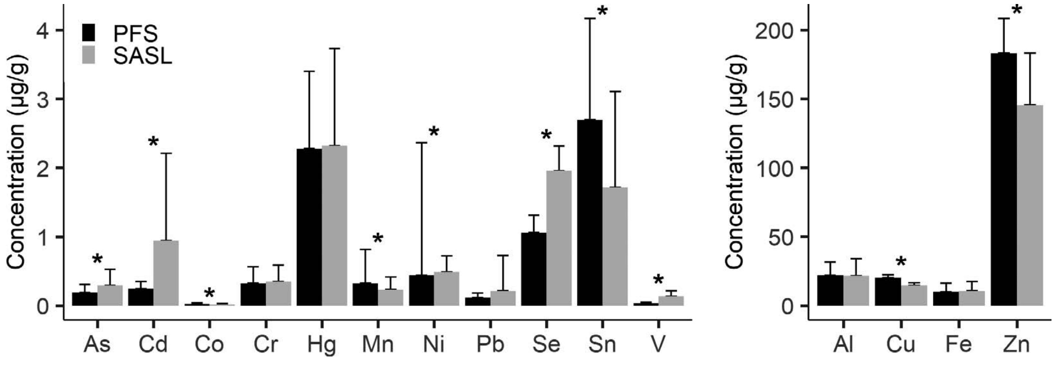

FIGURE 2. Mean element concentrations in the vibrissae from 68 Peruvian fur seals (PFS; *Arctocephalus australis* Peruvian subpopulation; black) and 31 South American sea lions (SASL; *Otaria byronia*; gray) from Punta San Juan, Peru, 2011–19. Error bars represent standard deviation. Asterisks indicate significant difference between species.

and a hold at 200 C for 15 min (Rey-Crespo et al. 2013). Samples were diluted to 25 mL with ultrapure deionized water.

The concentrations of 15 elements—aluminum, arsenic, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, tin, vanadium, and zinc (Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn, V, and Zn, respectively)—were analyzed at the University of Southern Mississippi's Center for Trace Analysis using an inductively coupled plasma mass spectrometer (ICP-MS, ThermoFisher Element XR, Waltham, Massachusetts, USA). The ICP-MS detection limits of each element are provided in Supplementary Material Table S1. Blanks of ultrapure deionized water and trace metal basis nitric acid (3%, 4%, 5%) were used for quality control. External and internal standards were used for standardization and calibration (Shore 2020). A certified reference material was not used to test recoveries due to limited access of the microwave digestion system.

All statistical analyses were conducted in R program version 3.6.0 (R Development Core Team 2019). The Shapiro-Wilk test was used to test for normality of data and the Bartlett test verified homogeneity of variances. Statistical significance was considered when $P<0.05$. Differences in element concentrations between species, sex, and ENSO events were tested using t-tests and Mann-Whitney Wilcoxon tests. Tin was not analyzed for serum samples and Hg was not analyzed for female serum samples for both species due to an insufficient number of samples. Trace element concentrations were reported as micrograms/gram (µg/g) dry weight for vibrissae and µg/g wet weight for serum.

Because Pb has a high affinity for red blood cells, studies report whole blood Pb concentrations (DeSilva 1981). We estimated whole blood Pb concentrations from serum Pb concentrations using the linear relationship described by Manton et al. (2001):

$$\text{Serum Pb} = 0.0003 + 0.00241(\text{whole blood Pb}).$$

RESULTS

Vibrissae

Summary statistics for PFS and SASL vibrissae are displayed in Supplementary Tables S2 and S3. All vibrissae (n=99) contained detectable amounts for 13/15 analyzed elements; 83% of vibrissae contained As and 82% contained Sn. Only mean As concentrations increased from 2011 to 2019 (R^2=0.607). Element concentrations for PFS vibrissae (n=68) were significantly different than SASL (n=31) for 10/15 elements analyzed (Fig. 2). Concentrations in PFS vibrissae were significantly higher than in SASL vibrissae for Co (P=0.03), Cu ($P<0.001$), Mn ($P<0.001$), Sn (P=0.006), and Zn ($P<0.001$) and significantly lower than SASL vibrissae for As (P=0.03), Cd ($P<0.001$), Ni ($P<0.001$), Se ($P<0.001$), and V ($P<0.001$). Vibrissae concentration variations between females and males were similar for both species for Al, Cd, Cu, Hg, Mn, Sn, V, and Zn. Female vibrissae had higher concentrations of Al, Cu, Mn, Sn, and Zn, and lower concentrations of Cd and Hg, than did male vibrissae (Figs. 3, 4 and Supplementary Tables S2, S3).

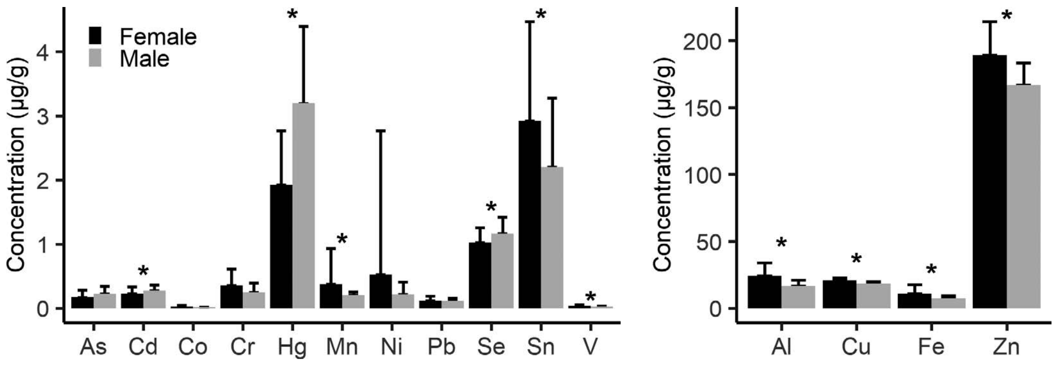

FIGURE 3. Mean element concentrations in the vibrissae from Peruvian fur seal (*Arctocephalus australis* Peruvian subpopulation) females (n=49; black) and males (n=19; gray) from Punta San Juan, Peru, 2011–19. Error bars represent SD. Asterisks indicate significant difference between sex.

Serum

Summary statistics for PFS and SASL serum are displayed in Supplementary Tables S4 and S5. All serum samples (n=100) contained detectable amounts of 12/15 elements; 96% of serum samples contained V, 35% contained Hg, and only 6% contained Sn. Serum concentrations between PFS (n=69) and SASL (n=31) differed significantly for 5/15 elements analyzed (Fig. 5). Serum As concentrations were significantly higher in PFS than in SASL ($P<0.001$), while Co ($P<0.001$), Fe ($P<0.001$), Se ($P<0.001$), and V (P=0.006) serum concentrations were significantly higher in SASL compared to PFS. Serum As concentrations were significantly higher in males than in females. Cobalt and Cu concentrations were also significantly higher in PFS male serum compared to female serum, while Cd and Se concentrations were higher in SASL male serum than in female (Figs. 6, 7).

El Niño

Sea surface temperature anomalies from the 1+2 Niño Index were used to define sampling periods within 2011 to 2019 as either El Niño or La Niña (Edwards et al. 2021; Supplementary Fig. S1). Only serum collected during moderate to extreme ENSO events (SSTA>±1 C; El Niño n=16; La Niña n=12) were included for analysis because serum reflects recent exposure or remobilization from tissues (Yordy et al. 2010) while vibrissae reflect exposure over multiple years and ENSO events (Edwards et al. 2021). Serum

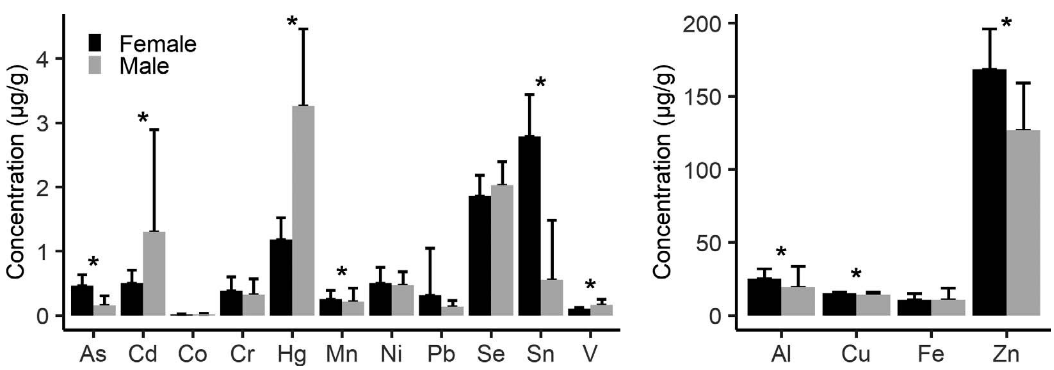

FIGURE 4. Mean element concentrations in the vibrissae from South American sea lion (*Otaria byronia*) females (n=14; black) and males (n=17; gray) from Punta San Juan, Peru, 2011–19. Error bars represent SD. Asterisks indicate significant difference between sexes.

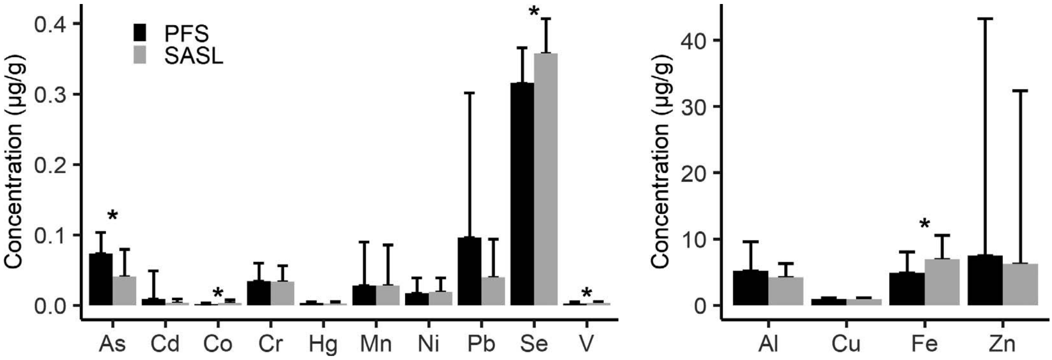

FIGURE 5. Mean element concentrations in serum from 69 Peruvian fur seals (PFS; *Arctocephalus australis* Peruvian subpopulation; black) and 31 South American sea lions (SASL; *Otaria byronia*; gray) from Punta San Juan, Peru, 2011–19. Error bars represent SD. Asterisks indicate significant difference between species. Tin was not analyzed.

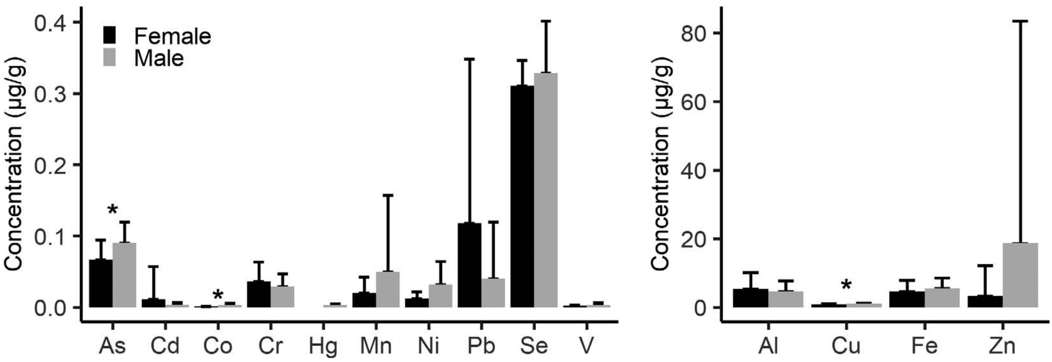

FIGURE 6. Mean element concentrations in the serum from Peruvian fur seal (*Arctocephalus australis* Peruvian subpopulation) females (n=50; black) and males (n=19; gray) from Punta San Juan, Peru, 2011–19. Error bars represent SD. Asterisks indicate significant difference between sexes.

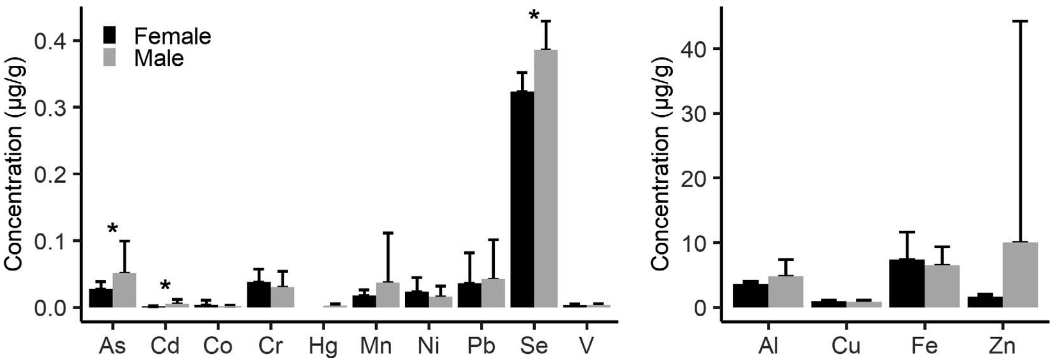

FIGURE 7. Mean element concentrations in the serum from South American sea lion (*Otaria byronia*) females (n=14; black) and males (n=17; gray) from Punta San Juan, Peru, 2011–19. Error bars represent SD. Asterisks indicate significant difference between sexes.

concentrations for PFS and SASL were significantly higher during El Niño years for Al (4.73 μg/g and 3.36 μg/g, respectively, P=0.03), As (0.07 μg/g and 0.03 μg/g, respectively, P<0.001), Cu (0.96 μg/g and 0.75 μg/g, respectively, P=0.01), and Mn (0.05 μg/g and 0.01 μg/g, respectively, P=0.007).

DISCUSSION

Tissue comparison: vibrissae and serum

Vibrissae accumulate elements over multiple years of growth and provide an ideal offloading avenue, as they are not metabolically active and can store contaminants (Hirons 2001). Serum reflects recent elemental exposure and mobilization from body stores (Gray et al. 2008; Yordy et al. 2010).

Keratinous vibrissae elemental concentrations were 2–20 times higher than serum concentrations. Gray et al. (2008) found similar results for 14 elements in keratinous fur and serum from leopard (*Hydrurga leptonyx*) and Weddell seals (*Leptonychotes weddellii*). Adkesson et al. (2019) analyzed 14 elements in keratinous feather and serum from PSJ's Humboldt penguins (*Spheniscus humboldti*) at the same rookery as the pinnipeds in this study. Feather concentrations were higher than serum for all elements. Iron concentrations in both penguin feather and serum were 3–30 times higher than in pinniped tissues, while Zn concentrations in both pinniped vibrissae and serum were approximately 10 times greater than in penguin tissues. Additionally, Mn and As in the penguin feathers were nearly 20 times greater than in pinniped vibrissae (Supplementary Tables S6, S7).

Ikemoto et al. (2004) analyzed fur from Baikal (*Pusa sibirica*), Caspian (*Pusa caspica*), and northern fur seals (*Callorhinus ursinus*), and Habran et al. (2013) analyzed gray seal fur (*Halichoerus grypus*) all for eight elements. Lead concentrations in the Peruvian pinniped vibrissae were 10 times less than in fur, while Mn concentrations were six times lower and V 20 times lower compared to the Baikal and Caspian seal fur. The pinniped vibrissae Zn concentrations were 1–2 times higher than in fur and Cu was three times higher (Supplementary Tables S6, S7).

Sex

Vibrissae concentrations were variable between sexes in both otariid species (Figs. 3, 4), differing in 10 elements for PFS (Al, Cd, Cu, Fe, Hg, Mn, Se, Sn, V, and Zn) and nine elements for SASL (Al, As, Cd, Cu, Hg, Mn, Sn, V, and Zn). Female pinnipeds can offload trace elements during gestation and lactation, e.g., the mean As concentration in PFS dam vibrissae was 0.25 μg/g while dam milk and pup vibrissae were 0.56 μg/g and 0.41 μg/g, respectively (Kooyomjian 2021, table 14). Male pinnipeds do not offload elements through these routes, so they may accumulate higher elemental concentrations.

Each otariid vibrissa can reflect multiple years of dietary accumulation and growth (Hirons et al. 2001; Kelleher 2016) but mechanical abrasion, or wear, can also affect its length and its respective elemental loads. Each vibrissa reflects a different time frame across multiple years, and SASL vibrissae reflected nearly 2 yr more than PFS vibrissae (Edwards 2018). These cumulative vibrissae inconsistencies probably explain some of the variability exhibited in concentrations.

The mean As concentration in female SASL vibrissae (0.47 μg/g) was three times higher than in male vibrissae (0.15 μg/g) and more than twice as high as male and female PFS vibrissae (0.19 μg/g). At PSJ, female SASL forage closer to the coast compared to males and both PFS sexes; therefore, diet and runoff may contribute to these concentration differences (Cárdenas-Alayza et al. 2021). Male SASL vibrissae had mean Cd (1.31 μg/g) and Hg (3.26 μg/g) concentrations nearly three times higher than female vibrissae Cd (0.51 μg/g) and Hg (1.18 μg/g). Male and female PFS Cd vibrissae concentrations (0.27 μg/g and 0.23 μg/g, respectively) were almost five times lower compared to male SASL (Supplementary Tables S2, S3). Male SASL are probably foraging on Cd-rich prey such as squid at a higher rate than do the other otariids (Gerpe et al. 2000). This may also contribute to Sn concentration differences between the sexes of both pinniped species. Male SASL vibrissae had a mean Sn concentration (0.56 μg/g), nearly five times lower than female SASL (2.79 μg/g), five times lower than female PFS (2.93 μg/g), and four times lower than male PFS (2.2 μg/g) concentrations. Serum concentrations had much less variability for both species, differing among sexes for only three elements (As, Co, and Cu for PFS and As, Cd, and Se for SASL), suggesting similar elemental uptake rates in males and females for the specific tissue (Figs. 6, 7). While the serum turnover rate in pinnipeds is undetermined, elemental accumulation in human blood occurs in a relatively short amount of time compared to that of inert hair (Laker 1982). Therefore, we surmise a similar pattern occurs in analogous pinniped tissues.

Aluminum and lead

Concentrations of Al in PFS and SASL vibrissae (22.08 μg/g and 21.80 μg/g, respectively) were more than twice as high as leopard and Weddell seal fur (8.87 μg/g and 9.13 μg/g, respectively; Gray et al. 2008). However, PSJ Humboldt penguin feathers contained a mean Al concentration of 67 μg/g (Adkesson et al. 2019), suggesting elevated bioavailable Al near PSJ (Supplementary Table S6). In human hair, Al over 8 μg/g is linked to developmental disorders in children (Blaurock-Busch et al. 2012).

Aluminum in serum of Peruvian pinnipeds (PFS 5.21 μg/g, SASL 4.21 μg/g) and PSJ Humboldt penguins (2.14 μg/g) were one order of magnitude higher than in leopard seals (0.25 μg/g) and two orders of magnitude higher than in Weddell seals (0.08 μg/g; Gray et al. 2008; Adkesson et al. 2019; Supplementary Table S6), which indicates elevated bioavailable Al in this ecosystem. In human serum, Al is typically 0.001–0.003 μg/g (ATSDR 2008); levels above 0.1 μg/g are potentially toxic and above 0.2 μg/g are associated with clinical symptoms of toxicity (Ferrante 2007). Aluminum toxicity in mammals can result in impaired bone growth and development and inhibit Fe absorption (Jaishankar et al. 2014). Aluminum serum concentrations in PFS and SASL were higher (5.19 μg/g and 4.21 μg/g, respectively) than toxic levels in human serum, implying that Peruvian pinnipeds may be at risk of Al toxicity (Supplementary Table S8).

Because Al is the most abundant metal in the earth's crust, mining activities may release it into the environment at higher rates than would natural processes (ATSDR 2008). Acidic waste from mining activities may increase Al and other metal bioavailability in the environment, ground water, and surface water (Gupta et al. 2013; Bianchini et al. 2015; Stefanova and Todorova 2020; USGS 2021). Mining is a major economic activity in Peru; annual copper mining production has doubled from 2011 to 2019 and is projected to increase into 2025 (Ministry of Energy and Mines 2019, 2021). A new, open-pit magnetite mine located east of PSJ transports its product via a slurry pipeline to the coast near PSJ for dewatering and export (Strike Resources 2021). The Marcona, Peru district, which incorporates the PSJ reserve, also has additional iron and copper mines (Chen et al. 2010).

Vibrissae Pb concentrations (PFS 0.12 μg/g; SASL 0.22 μg/g) were more than one order of magnitude below Pb values for human hair (6.82 μg/g, Mortada et al. 2002). Lead serum concentrations in PFS and SASL (0.08 μg/g; 0.04 μg/g, respectively) were more than one order of magnitude higher than leopard and Weddell seal serum Pb concentrations (Gray et al. 2008; Supplementary Table S6). Human serum Pb concentrations represent 0.24–0.70% of whole blood Pb (DeSilva 1981; Hernández-Avila et al. 1998; Manton et al. 2001). Using the linear relationship described by Manton et al. (2001), whole blood Pb concentrations for Peruvian pinnipeds were estimated to be 33.07 μg/g for PFS and 16.47 μg/g for SASL. These estimates are two orders of magnitude higher than human toxicity thresholds (Supplementary Table S8). Whole blood Pb levels over 0.3 μg/g in mammals suggest Pb poisoning (Dalefield 2017). In humans, chronic exposure to Pb can lead to brain and kidney damage (Jaishankar et al. 2014). Although caution must be exercised when using pan-specific comparisons, evaluation of Peruvian pinniped whole blood samples should be prioritized and populations monitored for potential signs of Pb toxicity.

Arsenic

Arsenic vibrissae concentrations increased in samples from 2011 to 2019 (R^2=0.607). This finding is consistent with Loaiza et al. (2022) that As is of concern in Peruvian marine ecosystems. Concentrations of As in PFS and SASL vibrissae (0.19 μg/g; 0.29 μg/g, respectively) were one order of magnitude less than in leopard and Weddell seal fur (1.63 μg/g; 2.51 μg/g; Gray et al. 2008). However, Humboldt penguin feathers collected from PSJ contained a higher mean As concentration (5.0 μg/g; Adkesson et al. 2019).

In humans, As hair concentrations 0.1–0.5 μg/g indicate chronic As exposure (Ratnaike 2003). All SASL female vibrissae contained As concentrations >0.1 μg/g, including 29% >0.5 μg/g. Overall, 59% of Peruvian pinniped vibrissae contained As concentrations >0.1 μg/g, and all vibrissae collected from 2016 to 2019 had As concentrations exceeding this threshold, indicating possible chronic As exposure in Peruvian pinnipeds (Supplementary Table S8).

Arsenic concentrations in serum of PFS (0.069 μg/g) and SASL (0.041 μg/g) from PSJ were relatively similar to leopard (0.07 μg/g) and Weddell seals (0.05 μg/g; Gray et al. 2008; Supplementary Table S6), but were more than one order of magnitude higher than human serum reference values (0.0035 μg/g; Iyengar and Woittiez 1988). Arsenic is a known carcinogen in humans that can cause cardiovascular and neurologic disorders (Hong et al. 2014) and can lead to stillbirth (von Ehrenstein et al. 2006). Because PSJ Peruvian pinniped populations are currently declining, it is important to determine potential effects of As toxicity on reproductive health (Cárdenas-Alayza et al. 2021).

Arsenic is often found in Cu ores, thus nearby Cu mines may be a source of environmental As. Globally, the main anthropogenic sources of As include Cu smelting, coal combustion, and herbicide use (Matschullat 2000). There is a Cu smelting facility south of PSJ in the coastal town of Ilo, Peru (Fig. 1). The Humboldt Current may carry As emissions north from this and other facilities into pinniped foraging grounds. The increasing agricultural activities in Peru and Chile, which use herbicides, probably contribute to bioavailable As (Bedoya-Perales et al. 2018).

Arsenic toxicity varies greatly with oxidation states and chemical forms, where inorganic is more toxic than organoarsenic species. In marine mammals, arsenic is thought to be mainly stored as lipid-soluble organoarsenics (Kubota et al. 2002; Kunito et al. 2008). We did not determine arsenic speciation.

Low concentration elements

Vibrissae concentrations in both Peruvian pinniped species for Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Se, V, and Zn (Supplementary Tables S2, S3) were the same order of magnitude or lower as values reported for human and domestic animal hair (Puls 1988; Schaefer et al. 2014; Liang et al. 2017; Rahimzadeh et al. 2017). Pinniped vibrissae contained a mean Fe concentration of approximately 10 μg/g. Hair concentrations of 20–40 μg/g indicate Fe deficiency in cattle (Puls 1988). Low Fe concentrations in Peruvian pinniped vibrissae may be worth investigating, as Fe deficiency can lead to improper growth and reduced immune response (Valko et al. 2005). However, no evidence of deficiency or associated anemia has been noted in published blood analyses. Mercury concentrations (0.97–3.90 μg/g) in Peruvian pinniped vibrissae were similar to total Hg concentrations detected in fur of Steller sea lion (*Eumetopias jubatus*) yearlings from the Gulf of Alaska (0.77–3.95 μg/g; Castellini et al. 2012). Although toxicity thresholds are not clear for pinniped species, Hg does not appear to be a major health concern for Peruvian pinnipeds.

Peruvian pinniped serum concentrations of Cu, Fe, Hg, Se, and Zn (Supplementary Tables S4, S5) were the same order of magnitude as published values for human and domestic animal serum (Iyengar and Woittiez 1988; Puls 1988). Serum concentrations of Co, Cr, and Mn were one order of magnitude higher than values reported for human serum and may be worth investigating (Iyengar and Woittiez 1988; Crossgrove and Zheng 2004).

El Niño

Serum Al, As, Cu, and Mn concentrations increased during El Niño years. During normal and La Niña years in Peru, dissolved Mn is higher offshore than in upwelled waters along the coast. Increased Mn concentrations may be due to less-oxidizing conditions caused by El Niño. Warm waters during El Niño years decrease oxygen levels and increase Mn solubility, allowing it to enter the food web more readily (Vedamati et al. 2015).

Increased runoff likely contributes to elevated elemental concentrations during El Niño, as freshwater discharge is a major source of dissolved trace elements in coastal waters (Brown et al. 2010). El Niño sharply increases river discharge rates due to high precipitation, which can cause higher elemental concentrations from mine and agricultural runoff (Holmgren et al. 2001). The Peruvian open-pit mines are located along major river systems that act as a transport mechanism for element-laden sediment erosion to the near coastal ecosystem (Rodbell et al 2014; Custodio et al. 2020; Ccanccapa-Cartagena et al. 2021). Increased rainfall has influenced uptake of arsenic and cadmium in shellfish along the Peruvian coast (Loaiza et al. 2018).

Punta San Juan, Peru is home to many economically and ecologically important species that are subject to natural and anthropogenic impacts. Increased mining activities in the region may contribute to elevated trace elemental concentrations through runoff, which is exacerbated by increasingly strong El Niño events. Our study has identified trace elements in vulnerable otariid species including toxic concentrations of Al, Pb, and increasing concentrations of As in vibrissae and serum relative to human thresholds. These data provide an important set of temporospatial reference data for continued monitoring of the health of the Peruvian marine ecosystem.

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SUPPLEMENTARY MATERIAL

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