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Elemental Distribution and Offloading in Peruvian Pinnipeds

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Abstract

Two sympatric pinniped species, Peruvian fur seals (PFS; *Arctocephalus australis* unnamed ssp.) and South American sea lions (SASL; *Otaria byronia*), reside in highly productive waters off the coast of Peru. These apex predators have experienced dramatic population fluctuations linked to both natural and anthropogenic events. As Peru's mining and agriculture industry increase, it is important to monitor potential effects on the vulnerable ecosystem. Fifteen trace elements in PFS and SASL vibrissae (whiskers), serum, and milk collected between 2009 and 2019 were analyzed via inductively coupled plasma mass spectroscopy (ICP-MS): aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se), tin (Sn), vanadium (V), zinc (Zn). Vibrissae contained the highest average concentrations of every element except As. Milk had the highest mean As concentration (0.41 µg/g) and overall, As concentrations increased from 2011 to 2019 in vibrissae and milk. Male SASL were younger than PFS males and expected to have lower element concentrations; however, SASL male vibrissae contained average Cd concentrations almost 5x higher than PFS males (1.31, 0.27 µg/g, respectively; $p<0.001$) indicating a diet of high Cd-containing prey. All elements analyzed were detected in PFS milk and pup vibrissae suggesting maternal transfer and a potential offloading pathway for dams. These results indicate accumulation and maternal transfer of trace elements and highlight the need for continued ecosystem monitoring as Peru's human population and industrial activities continue to grow.

Keywords: Trace elements, Peruvian fur seal, South American sea lion, Vibrissae, Serum, Milk, Maternal transfer.

1. Introduction

1.1. Preface

The coast of Peru is home to two sympatric pinniped species, the Peruvian fur seal and South American sea lion. These apex predators have experienced dramatic population fluctuations over the past century linked to both natural and anthropogenic events (Oliveira, 2011; Cárdenas-Alayza and Oliveira, 2016). Peruvian pinnipeds continue to struggle to recover from the effects of commercial harvesting, competition with commercial fisheries, and decreased prey availability during El Niño-Southern Oscillation events (IMARPE, 2006; Cárdenas-Alayza, 2012). The effects of environmental contaminants such as trace elements are poorly characterized in many marine mammals but may be linked to adverse health effects such as immunosuppression and impaired reproduction (Hyvärinen and Sipilä, 1984; De Guise et al., 1995; Das et al., 2003).

Trace elements associated with natural and anthropogenic events can accumulate and biomagnify in the marine food web concentrating in the tissues of top predators, mainly through ingestion/digestion. High concentrations of certain trace elements can have detrimental effects on the health of high trophic level species (Jakimska et al., 2011b; Tchounwou et al., 2012). Peruvian pinnipeds from Punta San Juan, Peru may be at an increased risk of exposure to contaminants due to large-scale industrial mining operations in the region and population growth in the adjacent town of San Juan de Marcona (Adkesson et al., 2018). This study examined fifteen trace element concentrations (aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se), tin (Sn), vanadium (V), zinc (Zn)) in Peruvian fur seal and South American sea lion vibrissae (whiskers; n=121) and serum (n=166) between 2009 and 2019 to determine their concentrations and examine any differences among species, sex, and year. Peruvian fur seal dam/pup paired vibrissae (n=22), serum (n=40), and milk samples (n=30) were analyzed to determine if mothers offload trace elements to their pups via gestation and/or lactation.

1.2. Peruvian marine environment

The Humboldt Current Large Marine Ecosystem (LME) supports numerous ecologically and economically important marine species, including these two sympatric pinniped species. The Humboldt Current LME extends along the coast of Chile and Peru, encompassing the largest eastern boundary upwelling system (EBUS) (Heileman et al., 2009). The strongest upwelling core in the Humboldt Current LME is located at Punta San Juan, Peru (PSJ; 15°22' S, 75°11' W; Figure 1) which is home to important Peruvian fur seal and South American sea lion rookeries (Majluf and Trillmich, 1981; Bakun and Weeks, 2008). The narrow continental shelf and strong local winds contribute to the PSJ upwelling core (Villanueva et al., 1969). The periodic, intense upwelling of cold, nutrient-rich water at PSJ correlates to the highest primary productivity in this ecosystem (Zuta et al., 1978). Located on a small peninsula in southern Peru, PSJ supports large colonies of marine mammals and seabirds. The PSJ reserve is a 133-acre peninsula separated from the town of San Juan de Marcona by a concrete wall. Originally established to protect nesting seabird populations to bolster commercial harvesting of guano, the presence of the reserve has indirectly protected important rookeries for both the fur seals and sea lions (Majluf and Trillmich, 1981; Majluf, 1991). Today, the reserve is part of a marine protected area network managed by the National Service of Protected Natural Areas of Peru (Cárdenas-Alayza & Cardeña-Mormontoy 2012).

The coastal waters of Peru are more productive than any other EBUS, resulting in large phytoplankton blooms that sustain productive zooplankton communities (Barth et al., 2007; Bakun et al., 2015). These zooplankton communities in turn support small, pelagic fish populations, including the largest single-species fishery in the world, the Peruvian anchoveta (*Engraulis ringens*) fishery (Chavez et al., 2003; Bakun and Weeks, 2008; Bakun et al., 2015). In addition to being an important economic resource, anchoveta is a key prey item that greatly influences seabird and marine mammal populations along the coast of Peru (Bakun et al., 2015). The Humboldt Current usually provides abundant prey for these pinniped species, but dramatic food web changes, including the collapse of the anchoveta fishery, occur during periodic El Niño-Southern Oscillation (ENSO) events (Taylor et al., 2008).

Approximately every 2-7 years, the highly productive Humboldt Current LME is affected by El Niño phases that last up to 18 months (Barber and Kogelschatz, 1990; Taylor et al., 2008). El Niño-Southern Oscillation events are characterized by alternating periods of warm and cold sea surface temperature (SST) in low latitudes of the central and eastern Pacific Ocean; the warm SST phase is referred to as El Niño and the cold SST phase is referred to as La Niña (Barber and Kogelschatz, 1990). During El Niño, there is a reduction in the upwelling of cold, nutrient-rich waters which leads to dramatic decreases in production (Pennington et al., 2006; Oliveira, 2011).

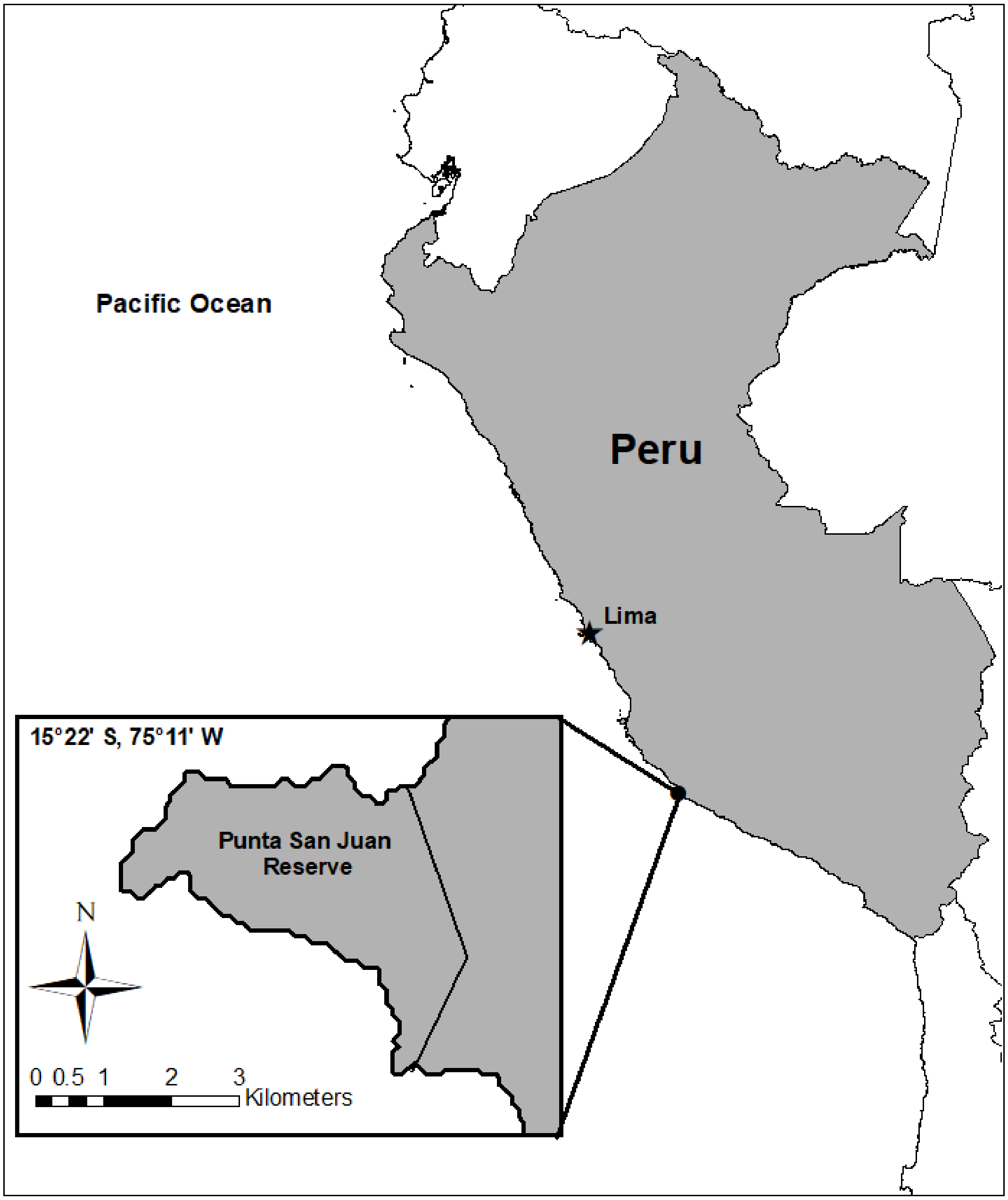

Figure 1. Map of Peru showing Punta San Juan Reserve, the study site location.

ENSO events change the trophic dynamics of the ecosystem from the base of the food web, primary producers, all the way to apex predators (Taylor et al., 2008). The Peruvian fishery accounts for nearly 10% of the world's industrial fishing landings (FAO, 2020). Anchoveta is highly abundant during normal conditions, but during El Niño, the anchoveta regime is shifted to a sardine dominated regime (Chavez et al., 2003). The effects on higher trophic level species were examined by Edwards (2018) who correlated stable isotope changes in Peruvian fur seal and South American sea lion vibrissae to fluctuations in SST. Edwards found that foraging strategies of Peruvian pinnipeds may be altered significantly during ENSO events, with foraging at lower trophic levels during El Niño years. Decreased foraging success and foraging on lower quality prey during El Niño has contributed to declines in Peruvian pinniped populations. The strongest recorded El Niño events occurred in 1982/83 and 1997/98 with a record-breaking event in 2015/16 (Jacox et al., 2016; Espinoza-Morriberón et al., 2017). Climate change models predict stronger and more frequent ENSO events in the future and understanding their effect is vital to help protect Peru's marine species (Oliveira, 2011).

Peru's marine environment may also be affected by coastal human population growth and increasing mining and agricultural operations. A leading mining nation, Peru is the third largest producer of copper and zinc as well as a major leader in silver and gold metal (Molina et al., 2016). The largest open-pit iron ore mine is located within 20 km of PSJ, the study site, with a growing copper mine located within 6 km of PSJ (Figure 2). Mine waste and sewage from the associated community are discarded in multiple locations along the Peruvian coast, including one site 4 km from PSJ (Adkesson et al., 2018). The dumping of untreated waste into the marine environment has been linked to decreased biodiversity and decreased abundance of benthic organisms (Castilla and Correa, 1997; Ramirez et al., 2005). Mining and the related activities can lead to enrichment of bioavailable metals in seawater and sediments causing negative impacts on coastal marine community structure, including high trophic level consumers (Wagemann, 1989; Ramirez et al., 2005; Stauber et al., 2005). As Peru's industrial activity and human population continue to increase, local, anthropogenic activities will continue to influence the coastal marine environment.

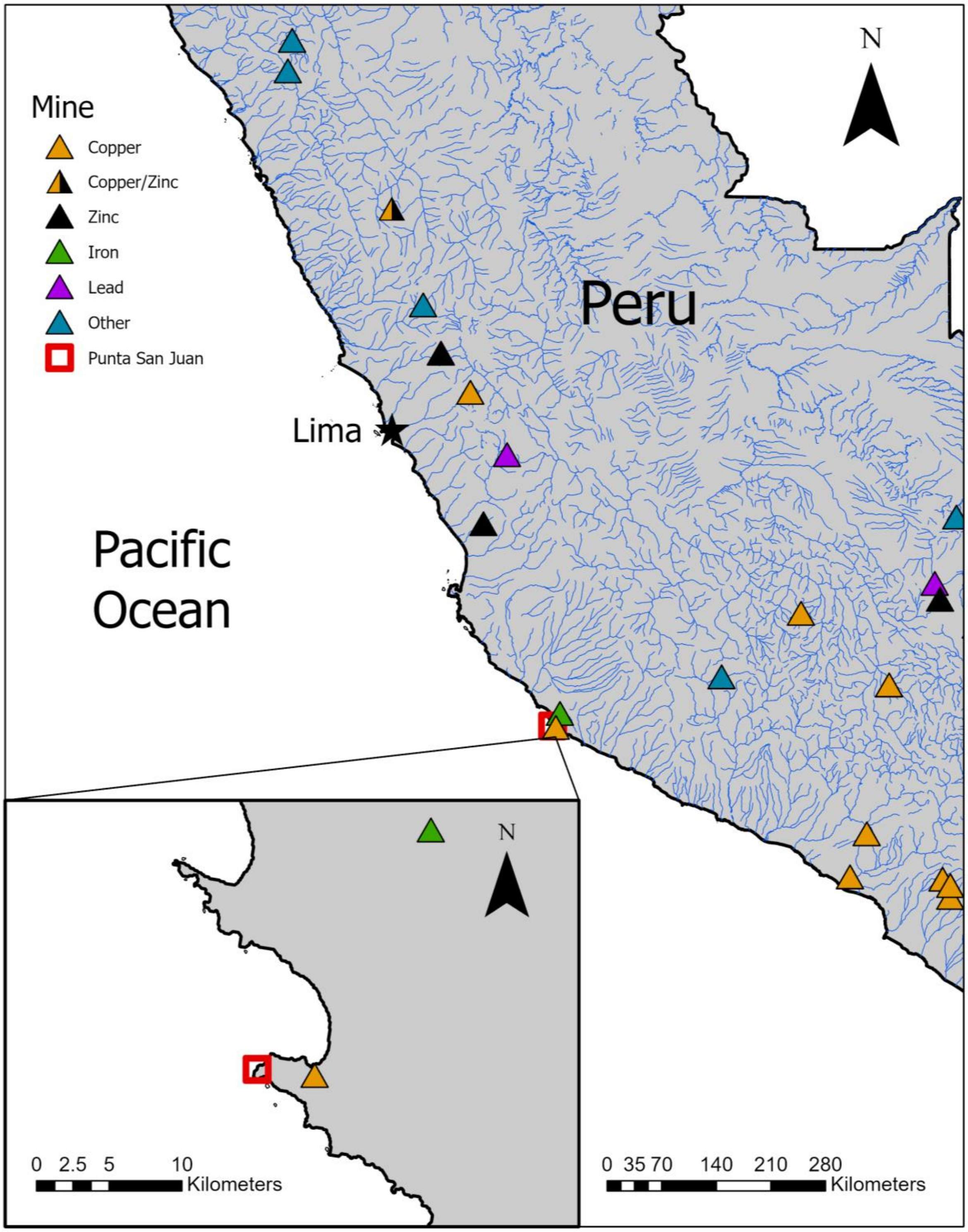

Figure 2. Map of Peru showing river systems and several major mine locations. The red box indicates the study site, the Punta San Juan reserve.

1.3. Peruvian fur seals

South American fur seals (*Arctocephalus australis*) are distributed along the coast of South America from southern Brazil to Peru, including the Falkland Islands (Jefferson et al., 1993). An isolated population of South American fur seals found in Peru and northern Chile is recognized as a genetically distinct subspecies, the Peruvian fur seal (*Arctocephalus australis* unnamed ssp.; PFS) (Berta and Churchill, 2012; Committee on Taxonomy, 2014; Oliveira and Brownell, 2014). Currently, the PFS is listed as Vulnerable according to the IUCN Red List, with population trends unknown (Cárdenas-Alayza and Oliveira, 2016).

Peruvian fur seals can be found year-round at haul-outs and rookeries along the Peruvian coast as they exhibit high site-fidelity (Majluf, 1987). The majority of the PFS population is found in Peru, and over 50% of the total population are found at just five sites which includes the Punta San Juan reserve (Cárdenas-Alayza and Oliveira, 2016). The total South American fur seal population is estimated to be around 219,000 individuals, while the Peruvian fur seal population is estimated at 21,000 individuals (IMARPE, 2014; Cárdenas-Alayza et al., 2016b).

Sexual dimorphism occurs in PFS with adult males reaching 1.7 m and 90–140 kg; while females reach approximately 1.3 m in length and 30-90 kg (Cárdenas-Alayza and Oliveira, 2016). Females achieve sexual maturity and give birth to their first pup at 3-4 years old. Females return to the rookery annually between October and December, about 1-4 days before giving birth to one pup (Majluf, 1987). Pups are born between 50-65 cm and 3.5-7.5 kg (Cárdenas-Alayza and Oliveira, 2016). Mothers (dams) suckle their pups daily for the first 8-12 days before entering estrus and mating. Dams nurse their pups for at least six months before the pup is weaned. Depending on the amount of food available, dams can nurse their pup for up to three years (Majluf, 1987). If a yearling is still dependent on the dam when the dam gives birth again, there can be competition between the two offspring for milk, which usually results in the death of the newborn. Bulls (adult males) return to the rookery from October to December to defend their breeding territory until after copulation. During the breeding season, the average ratio of adult females to males is 16:1 (Majluf, 1987). After the breeding season, dams continue to alternate between foraging trips and suckling their pup on land until the pup is weaned, while bulls do not return to the rookery until the following breeding season (Majluf, 1987; Trillmich, 1990).

The diet of Peruvian fur seals consists mainly of anchoveta (*Engraulis ringens*), cephalopods, and lanternfish species (*Myctophidae*) with red squat lobster (*Pleuroncodes monodon*), sardines (*Sardinops sagax*), mote sculpin (*Normanichthys crockeri*), chub mackerel (*Scomber japonicus*), and Pacific jack mackerel (*Trachurus symmetricus*) preyed upon to a lesser extent (Arias-Schreiber, 2000; 2003; Cárdenas-Alayza pers. com.). Female foraging trips last approximately 1-8 days, traveling between 70 to 150 km on the continental shelf, remaining close to their rookery as they must return to nurse their pup. Males can forage longer, and average trip distances may extend to 200 km (Cárdenas-Alayza and Oliveira, 2016).

South American fur seal population declines have been caused by both natural and anthropogenic effects. Fur seals were targeted for their blubber and fur and were hunted heavily in Peru in the early 1900s. Peru banned sealing in 1959 but the PFS population still struggles to recover fully; it is estimated to be at only 33% of the historical estimated abundance (Majluf, 1984; Cárdenas-Alayza, 2012). From 2000 to 2015 the PFS population at PSJ increased from a few hundred individuals to nearly 4,500 individuals. Since the extreme El Niño in 2015, PFS populations at PSJ appear to be declining (PSJ Annual Report, 2020). The effects of ENSO events and commercial fishery operations that target forage fish have adversely impacted PFS recovery compared to Atlantic populations of South American fur seals. ENSO events are known to cause severe declines in population sizes, and these events are becoming more intense and frequent (Soto et al., 2004). Assessments of PFS population health at Punta San Juan are ongoing (Jankowski et al., 2015; Fire et al., 2016), but environmental contaminants in the context of population health have only been assessed in seabird populations at PSJ (Adkesson et al., 2018; Adkesson et al., 2019) Contaminants such as non-essential elements may have health or reproductive impacts that are further limiting PFS population recovery. Non-essential trace elements, including Cd, Pb, and Hg, have been found in muscle, liver, kidney, and heart tissues of South American fur seals in Brazil and Argentina (Marcovecchio et al., 1991, 1994; Baraj et al., 2009).

1.4. South American sea lions

South American sea lions (*Otaria byronia*; SASL) are distributed from Brazil to Peru (Jefferson et al., 1993). Sea lions along the Pacific coast show significant genetic differences from the Atlantic coast populations (Gehara, 2009). Currently, these populations are monitored as a single species and are listed as Least Concern on the IUCN Red List (Gehara, 2009;

Cárdenas-Alayza et al., 2016a). However, unlike the Atlantic population, the Pacific population is exposed directly to ENSO events that can cause dramatic declines, similar to PFS populations. After the 1997/98 El Niño that resulted in 100% pup mortality, the Peruvian government classified sea lions along the Peruvian coast as "Vulnerable" (Decreto Supremo No. 013- 99-AG; Oliveira, 2011). Globally, South American sea lion (SASL) populations are estimated to be about 445,000 individuals with 105,000 individuals in Peru (Cárdenas-Alayza et al., 2016a).

Sexual dimorphism is also seen in SASL with males reaching 3 m in length and up to 350 kg while females only reach about 2 m and 170 kg. Females are sexually mature by 4 years old, but males do not reach maturity until 5 or 6 years old (Vaz-Ferreira, 1982). Adults return to rookeries for breeding and pupping between mid-December and early February (Campagna, 1985). After giving birth to one pup, dams nurse their pups for approximately one week before copulating and returning to the sea to feed (Campagna and Le Boeuf, 1988). Dams alternate between foraging and nursing their pup for 8-10 months until the pup is weaned (Drago et al., 2009). Lactation may be extended for up to three years for SASL, forcing a mother to nurse multiple pups; however, this is rarely observed (Campagna and Le Boeuf, 1988).

Prey varies with location for South American sea lions, but the pinnipeds are considered to be generalists with common prey types consisting of benthic and pelagic fish, squid, crustaceans, birds, and occasionally marine mammals (Harcourt, 1993; Keon Alonso et al., 2000; Soto et al., 2006; Cappozzo and Perrin, 2009). Along the productive Pacific coast, sea lions are known to feed mainly on red squat lobster and Peruvian anchoveta, as well as mote sculpin, lumptail searobin (*Prionotus stephanophrys*), Peruvian hake (*Merluccius gayi peruanus*), and cephalopods (Paredas and Arias-Schreiber, 1999; Sarmiento-Devia et al., 2020; Cárdenas-Alayza pers. com.). During El Niño, when target prey are less abundant, sea lions modify their diet and forage on an even wider variety of prey (Soto et al., 2006; Sepúlveda et al., 2014). Length and distance of foraging trips vary between male and female sea lions. Males tend to have longer foraging trips lasting 4-9 days versus 1-4 days and travel further, up to 300 km versus 200 km for females (Campagna et al., 2001). Females tend to feed in shallower, coastal waters, while males feed on more pelagic species (Koen Alonso et al., 2000; Campagna et al., 2001).

Populations of SASL have faced many of the same adversities as PFS. During ENSO events, when there are food shortages, females spend more time foraging and less time suckling their pups. This leads to increased pup mortality during El Niño (Soto et al., 2006). The 1987/88

El Niño caused an 81% decrease in the SASL Peruvian population. By 2006, this Peruvian population saw a recovery of 76%; however, more frequent El Niño events may prevent the SASL Peruvian population from fully recovering (IMARPE, 2006; Oliveira et al., 2012). Similar to PFS, the impact of harmful concentrations of elements on population health has not been well studied and may be affecting the ability of SASL populations to recover fully. In Argentina, Cd, Pb, and Hg have been found in SASL liver, muscle, kidney, and blubber (Peña et al., 1988; Gerpe et al., 2007). The presence of these contaminants may affect the overall health of SASL and prevent populations from fully recovering.

1.5. Pinniped tissues

Serum is the component of whole blood that does not contain blood cells or clotting factors (Ehresman et al., 2007). Serum samples provide information on nutrients currently circulating through the body, as well as recent exposure and remobilization of contaminants (Laker, 1982, Habran et al., 2011). Contaminant concentrations in blood depend on current diet, as well as body condition. Blood mercury levels in northern elephant seals were shown to increase during fasting as adipose stores are metabolized and decrease when foraging resumed and body mass increased (Peterson et al., 2018). Metabolically taxing events such as gestation and lactation also appear to increase blood contaminant concentrations (Habran et al., 2011). Circulating serum levels of contaminants reflect a short time frame of days to months, but a tissue such as vibrissae can provide contaminant information for much longer time periods (Laker, 1982; Habran et al., 2011).

Vibrissae, also known as whiskers, are structures composed of proteinaceous keratin. They grow continuously from a highly innervated base for one year or longer. Metabolically inert tissues like vibrissae incorporate information about nutrition from the moment they begin to grow. This allows vibrissae to be used as a noninvasive way to obtain chronological nutrient and contaminant concentrations (Hirons et al., 2001; Darimont et al., 2002; Bearhop et al., 2004; Edwards, 2018; Rosas-Hernández et al., 2018). The lengths of vibrissae are used to determine the period of exposure represented in each vibrissa. Trace element analysis has been successful in keratinous pinniped tissues such as vibrissae (Wenzel et al., 1993; Andrade et al., 2007; Elorriaga-Verplancken and Aurioles-Gamboa, 2008; Castellini et al., 2012; Habran et al., 2013; Ferdinando, 2019). Vibrissae begin to grow in utero and can be analyzed to determine what elements were transferred from the dam to the pup through the placenta (Elorriaga-Verplancken and Aurioles-Gamboa 2008; Castellini et al., 2012; Habran et al., 2013).

Milk is a nutrient-rich solution secreted by the mammary gland in females to nourish their newborn. Milk samples also show what dams are potentially offloading to their pup. Milk content is dependent on the dam's successful foraging and body condition. In subantarctic fur seals (*Arctocephalus tropicalis*), mothers with good body conditions produced milk with higher lipid and energy content (Georges et al. 2001). Average milk content has been measured in otariid species to contain about 40% lipid, 12% protein, and 40% water (Arnould and Hindell, 1999; Georges et al., 2001). In South American fur seals, milk is composed of 28.3 to 57.1% lipids (Ponce de León and Pin, 2006). The high lipid and protein content in pinniped milk may contribute to the transfer of contaminants from dam to pup since many contaminants and trace elements bind to lipids and proteins. Milk composition changes throughout the lactation period which may affect the concentrations transferred throughout these different stages (Arnould and Hindell, 1999; Habran et al., 2013). Contaminants such as trace elements have been detected in marine mammal milk, but varying techniques and small sample sizes make comparing values difficult (Wagemann et al., 1988). Assessment of multiple body tissues, including those that are shed or excreted, will help determine potential paths of trace element offloading in Peruvian pinnipeds.

1.6. Maternal transfer

Nutrients, hormones, and contaminants are transferred from mother to offspring during gestation and lactation. Research on the transport of various contaminants, such as trace elements, has increased to determine if contaminants are being transferred, when they are being transferred, and the rate of transfer at various developmental stages (Beckmen et al., 2002; Habran et al., 2011; 2013). Maternal transfer of contaminants causes females to offload at much higher rates than males, generally resulting in lower concentrations of certain contaminants in sexually mature females than males of the same age class (Borrell et al., 1995; Ross et al., 2000; Barbosa et al., 2018; Lehnert et al., 2018). Prior to weaning, young marine mammals acquire all their nutrition from their mothers; therefore, during the neonatal period, elements found in pups were acquired from the dam either in utero via the placenta or through lactation. Many recent studies have focused on contaminants, but few have examined how trace elements can be harmful to marine mammals (Borrell, 1993; Borrell et al., 1995; Ridgway and Reddy, 1995; Ross et al., 2000; Greig et al., 2007; Gabrielsen et al., 2011; Brown et al., 2016; Grønnestad et al., 2017; Barbosa et al., 2018).

The maternal transfer of trace elements is documented in marine mammals, with most studies focusing on small whales and pinnipeds because they are easier to locate and handle. Since pinnipeds must breed on land, they are generally easier to capture and handle than fully aquatic marine mammals (Beckmen et al., 2002; Endo et al., 2006; Habran et al., 2011; Hoguet et al., 2013). Maternal transfer of trace elements has been demonstrated in both phocid and otariid species, with many studies focused on Hg levels. Maternal transfer of Hg in marine mammals appears to occur mainly during gestation with a moderate transfer occurring subsequently through lactation (Wagemann et al., 1988; Habran et al., 2011; Castellini et al., 2012; Habran et al., 2013; Rea et al., 2013). Habran et al. (2013) studied elements in milk, blood, blubber, and fur collected from gray seals (*Halichoerus grypus*) during early and late lactation. Of the eleven elements analyzed (Ca, Cd, Cr, Cu, Fe, Pb, Hg, Ni, Se, V, and Zn), all except Cd were above the detection limit in milk samples. However, Cd was detected in dam and pup gray seal fur samples and the liver of Juan Fernández fur seal (*Arctocephalus philippii*) pups, suggesting that Cd may be mainly transferred during gestation (Sepúlveda et al. 1997, Habran et al., 2013). The maternal transfer of some contaminants varies during different stages of gestation and lactation. For example, in gray seals, the level of Se in milk decreased from early to late lactation while Hg levels increased (Habran et al. 2013). Understanding maternal transfer is essential as exposure to contaminants, such as trace elements at a young age can negatively affect the growth and development of offspring.

1.7. Trace elements

Trace elements have both natural and anthropogenic sources. Most trace elements are present in the Earth's crust and enter the environment through erosion, volcanic eruptions, and other natural processes. However, many elements are now also introduced into the environment through anthropogenic activities, such as the burning of fossil fuels and mining (Nriagu, 1989; Visschedijk et al., 2004). The distribution of trace elements is widespread as they are commonly used in industrial, agricultural, pharmaceutical, and technological applications (Tchounwou et al., 2012).

Trace elements are classified as either essential or non-essential. Essential elements have biochemical and physiological functions, while non-essential elements do not have a biological function in the body (Tchounwou et al., 2012). In mammals, essential elements include, among others, Cr, Co, Cu, Fe, Mn, Ni, Se, V, and Zn. Elements such as Al, As, Cd, Pb, Hg, and Sn traditionally have been defined as non-essential (Das et al., 2003; Tchounwou et al., 2012), although some debate exists on whether trace levels of As should be considered essential (Mayer et al., 1993; Nielsen, 2000; Hunter, 2008). Essential elements can be harmful at high levels, but non-essential elements may be toxic even at low concentrations. Once contaminant concentrations exceed natural background levels, they are considered toxicants and may cause negative effects. Trace elements of concern for public health include As, Cd, Cr, Pb, and Hg due to their high risk of toxicity (Tchounwou et al., 2012).

Bioaccumulation of contaminants occurs when the uptake rate is higher than the excretion rate. Bioaccumulation in individuals is influenced by factors such as age, genetics, and physiological conditions (Jakimska et al., 2011b). Biomagnification of contaminants refers to an increase in contaminant concentration with an increase in trophic level. This process makes high trophic level animals, such as pinnipeds, more vulnerable to environmental contaminants and good indicator species for the health of the ecosystem (Das et al., 2003).

Mining and its associated activities, including smelting and shipping, release trace elements and byproducts directly to the environment (Valdés and Castillo, 2014). For example, Hg is released as a byproduct of the smelting process for Cu, Zn, Pb, Ni, and Au (Pirrone et al., 2010). Selenium is an essential element, but environmental levels can become elevated through the burning of coal and fossil fuels. Arsenic is introduced anthropogenically through use in herbicides, pesticides, wood preservatives, and industrial sources (Rosen and Liu, 2010). These anthropogenic activities increase bioavailable trace element concentrations in the local marine environment through runoff and discharge, where they can then be incorporated into the food web (Volesky, 1990; Valdés and Castillo, 2014). Once contaminants are released in the environment either naturally or anthropogenically, they can be absorbed by plants and animals.

1.8. Trace elements in mammals

The uptake of trace elements by organisms occurs through different routes of entry: uptake from the atmosphere through the lungs, absorption through the skin, but mainly through the ingestion of seawater and food (Das et al. 2003; Tchounwou et al. 2012). Some contaminants, including trace elements, can be accumulated in newborns through placental transfer and lactation (Das et al., 2003). The accumulation of elements in tissues depends on many factors, including the sex, size, and age of individuals (Das et al., 2003; Jakimska et al., 2011b). The chemical state of the element and environmental factors such as salinity, pH, and temperature also contribute to the accumulation in organisms (Irwandi, 2009). Body condition can play an important role in the storage and mobilization of contaminants. The body condition of an individual is based on mass relative to physical size, reflecting the amount of adipose tissue present relative to lean muscle and organ mass. As body condition decreases and adipose tissue is absorbed, sequestered trace elements may be remobilized into the circulation or distributed to other tissues (Peterson et al., 2018). The toxicity of an element depends on several factors, including the concentration, route of exposure, and oxidation state (Tchounwou et al., 2012). Trace element toxicity can lead to hepatotoxicity, neurotoxicity, genotoxicity, and nephrotoxicity depending on the element (Flora et al., 2008; Sharma, 2014).

Aluminum is the third most abundant element in the earth's crust and the most abundant metal (ATSDR, 2008; Gupta et al., 2013). Aluminum is a non-essential element that occurs naturally in air, water, and soil, but can be introduced into the environment anthropogenically through the mining and processing of Al ores or the production of Al metal, alloys, and compounds (ATSDR, 2008). Aluminum is generally stable, but as the pH of the environment decreases, Al bioavailability and toxicity increase (Gupta et al., 2013). Aluminum only occurs in one oxidative state, Al^{3+}, and can replace Mg^{2+} and Fe^{3+} in humans. This can lead to disruptions in intercellular communication, cellular growth, and secretory functions. Aluminum toxicity in humans causes neurotoxicity, as well as affecting bone growth and development (Jaishankar et al., 2014).

Arsenic is highly toxic and carcinogenic to organisms at low concentrations. Arsenic can be released into the environment naturally through volcanic eruption and erosion (Tchounwou et al., 2012). Copper smelting and coal combustion accounts for 60% of anthropogenic As emissions (Matschullat, 2000). Other anthropogenic sources of As include the manufacturing of several agricultural and medical products, wood preservation, and Pb and Zn smelting (Matschullat, 2000; Tchounwou et al., 2012). In its inorganic form, As is lethal to the environment and organisms (Jaishankar et al., 2014). Inorganic As can be distributed to organs quickly by binding to hemoglobin and traveling through the blood system (Guillamet et al., 2004). However, As can be detoxified by a biomethylation process and excreted through urine.

In pregnant humans, chronic exposure to As can lead to stillbirth and infant mortality (Singh et al., 2007; Jaishankar et al., 2014).

Cadmium is a by-product of Zn mining and smelting operations. It is often found in the soil, where it is absorbed and accumulated in plants (Irfan et al., 2013; Jaishankar et al., 2014). Cadmium has a similar structure to Zn and can replace Zn in metallothionein, thereby inhibiting it. Cadmium can also lead to Fe deficiency by binding with cysteine, glutamate, histidine, and aspartate ligands (Jaishankar et al., 2014). In humans, Cd toxicity causes skeletal deformities, kidney lesions, lung damage, and dysfunction of the cardiovascular system. Although high levels of Cd have been measured in marine mammals, signs of toxicity have not been documented, suggesting they can withstand high concentrations without adverse effects (Das et al., 2003). Ikemoto et al. (2004a) have suggested that Cd is detoxified mainly by metallothionein in the liver in high trophic level marine animals.

Chromium is introduced to the marine environment both naturally and anthropogenically through industrial activities including metal processing, tannery facilities, stainless steel welding, and chrome pigment production (Tchounwou et al., 2012; Jaishankar et al., 2014). Chromium is present in many oxidative states, with the most common forms of Cr being Cr(III) and Cr(VI). While Cr(III) is generally harmless and essential for proper insulin function, Cr(VI) is highly toxic and carcinogenic in mammals (Krejpcio, 2001; Jaishankar et al., 2014). Chromium (VI) is more permeable than Cr(III) and can easily cross cell membranes. When Cr(VI) reacts with biological reductants, it leads to oxidative stress in the cell and causes damage to DNA and proteins (Jaishankar et al., 2014). Excess Cr is excreted through urine, feces, hair, sweat, and bile. The excretion of Cr through urine is a good indicator of ingestion, but not of body stores (Krejpcio, 2001).

Cobalt is a relatively rare metal that is essential for the formation of vitamin B_{12} in mammals. Anthropogenic sources of Co include fossil fuel burning, engine emissions, sewage sludge, and processing of cobalt-containing alloys. Exposure to Co is mainly a concern for industrial workers, but the public consumes trace amounts of Co through fish and vegetables (Barceloux and Barceloux, 1999). In humans, mild levels of Co exposure reversibly affect the hematologic and endocrine systems, but exposure to high concentrations can lead to neurologic and cardiac problems (Leyssens et al., 2017). The mechanism of Co toxicity is not fully understood, but it appears to damage calcium ion pumps (Simonsen et al., 2012). Cobalt toxicity interferes with the homeostasis of calcium and Fe which can lead to the disruption of many body functions (Leyssens et al., 2017).

Copper is biologically available and essential for the proper growth of animals (Flemming and Trevors, 1989; Ikemoto et al., 2004b). Anthropogenic inputs of Cu include mining, smelting, metal and electrical manufacturing, fertilizers, and pesticides. Copper exists in three forms: Cu, Cu(I), and Cu(II). Zinc and Fe interfere with the absorption of copper in the intestinal mucosa which leads to low Cu levels in the liver. Although Cu is relatively nontoxic in mammals, it can be harmful to certain marine species, particularly invertebrates. Copper has been shown to cause alterations in growth, reproduction, and behavior in high trophic level aquatic organisms (Flemming and Trevors, 1989). Anan et al. (2002) suggested that increased Zn and decreased Cu led to immune suppression in diseased Caspian seals (*Pusa capsica*).

Iron, an essential element, is the second most abundant metal in the Earth's crust (Jaishankar et al., 2014). Anthropogenic sources of Fe include the combustion of fossil fuels, construction, and the production and use of Fe and steel goods (Wang et al., 2007). Iron has two common oxidative states: Fe(II) and Fe(III). While Fe(II) is more soluble, Fe(III) is more common in most aquatic environments. Phytoplankton are highly dependent on bioavailable Fe for photosynthesis. Due to high demand, primary production is limited by Fe availability in one-third of oceans (Schoffman et al., 2016). In animals Fe is a critical component in hemoglobin and myoglobin proteins, which transport and stores oxygen throughout the body (Jaishankar et al., 2014). A deficiency in Fe can lead to anemia as well as improper growth in children. Iron toxicity in humans has been linked to liver and heart disease, cancer, diabetes, and immune system abnormalities (Valko et al., 2005).

Lead is a highly toxic, non-essential element that is often taken up by mammals through food or drinking water. Lead is anthropogenically released through fossil fuel burning, mining, and manufacturing with many uses in agricultural and industrial processes (Tchounwou et al., 2012). Lead is absorbed by plants where it causes damage to chlorophyll and photosynthetic processes and suppresses the overall growth (Jaishankar et al., 2014; Najeeb et al., 2014). In humans acute Pb exposure is known to cause loss of appetite, headache, renal dysfunction, and fatigue. Chronic exposure or exposure to high levels of Pb can result in more serious problems, such as miscarriages, brain and kidney damage, and death (Martin and Griswold, 2009).

Manganese is the fifth most common metal in the Earth's crust and is essential in humans for proper bone development and metabolism. Approximately 95% of Mn is used for the manufacturing of steel (Trumbo et al., 2001; Levy and Nassetta, 2013). Manganese is important in enzyme composition and activation (Trumbo et al., 2001). High levels of Mn can be extremely harmful, especially in fetuses. Manganese toxicity in pregnant women can lead to a decrease in fetal weight and delays in the development of the skeleton and internal organs. In adults, toxicity causes neurological symptoms as Mn accumulates in regions of the brain (Grazuleviciene et al., 2009). Manganese deficiency in animals is proposed to cause skeletal deformities and reproductive issues in both males and females (Finley and Davis, 1999).

Mercury is a very well-studied trace element due to its extreme toxicity and high concentrations in the environment (Jaishankar et al., 2014). Anthropogenic sources of Hg are coal and oil combustion; smelting Cu, Zn, Pb, Ni, and Au; cement production; and waste incineration. Approximately 30% of global Hg emissions are produced by anthropogenic sources (Pirrone et al., 2010). Mercury exists in three forms that vary in bioavailability and toxicity: the metallic element, inorganic salts, and organomercury compounds. These forms of Hg are taken up by microorganisms and methylated to produce the bioaccumulating methylmercury (Das et al., 2003; Jaishankar et al., 2014). Methylmercury is an organic form of Hg that is lipid-soluble and highly toxic (Das et al., 2003). Methylmercury is a neurotoxin that is responsible for mitochondrial damage, lipid peroxidation, and the accumulation of neurotoxic molecules. Mercury toxicity is known to damage the central nervous system and cause behavioral and sensory impairments (Patrick, 2002). Although the brain is the main target for Hg, any organ can be compromised, leading to the malfunctioning of nerves, kidneys, and muscles. Tertiary and quaternary protein structures can be damaged by Hg, altering cell function (Jaishankar et al., 2014). In marine animals, muscle Hg levels over 5 μg/g can lead to exhaustion, impaired coordination, loss of appetite, and even death (Eisler, 1987). Peterson et al. (2018) showed Hg levels decreased in muscle tissue and increased in the blood during prolonged fasting in northern elephant seals (*Mirounga angustirostris*). Marine mammals possess a limited ability to detoxify certain elements, such as Hg. Selenium is known to act as an antagonist to Hg by demethylating and thereby detoxifying it (Ikemoto et al., 2004b). The formation of a Se-Hg complex during the detoxifying process causes a roughly 1:1 Se to Hg molar ratio (Das et al., 2003).

Nickel is considered an essential element for many organisms. Anthropogenic inputs of Ni include the combustion of coal, diesel oil, the incineration of waste and sewage, and tobacco. Nickel is generally nontoxic in humans due to its slow uptake in the gastrointestinal tract. The absorption of Ni is dependent on many factors, including gut acidity, the presence of phosphate, metal ion binding components, and pH. Skin sensitivity to Ni is the most common negative effect, but the respiratory system and kidneys can also be affected by inhalation and ingestion of Ni (Cempel and Nikel, 2006). Hyvärinen and Sipilä (1984) correlated high Ni concentrations in the air to stillbirths in ringed seals, but an exact cause of the stillbirths remains unclear.

Selenium is essential in mammals for proper growth and development. It is released into the environment anthropogenically mainly through coal and petroleum fuel combustion, but is also a byproduct of mining Cu, Zn, and Pb (Fernández-Martínez and Charlet, 2009). Selenium has mainly been studied for its role in selenoproteins and detoxification of trace elements. Selenium is involved in the detoxification of Cd, Cu, and Hg (Ikemoto et al., 2004b; Zhang et al., 2014). In humans the margin for proper Se levels is narrow while deficiencies and toxicity can cause major health issues (Papp et al., 2007; Zhang et al., 2014). Deficiencies in Se can lead to decreased immune and thyroid function as well as neurologic disorders (Papp et al., 2007). However, high concentrations of Se can cause loss of keratinous tissues such as hair and nails as well as skin lesions, nervous system disorders, and cancer (Sun et al., 2014; Zhang et al., 2014). Selenium may also have adverse effects on reproduction in mammals. Marine mammals may be more equipped to handle higher Se levels, but more research is needed on the toxicity of Se in marine mammals (Dietz et al., 2000).

There is some debate on the essentiality of tin in mammals, but due to a lack of data and no known biological function, Sn is still considered non-essential in humans (Nielsen and Sandstead, 1974; Nielsen, 1998; ATSDR, 2005). Tin is anthropogenically introduced mainly through incinerating waste, burning of fossil fuels, smelting processes, and metal production (Byrd and Andreae, 1986; ATSDR, 2005). Although inorganic Sn is generally nontoxic, organic Sn compounds can be highly toxic. Organotin compounds such as tributyltin (TBT) are mainly used as antifouling agents in marine paints and nets as well as in agrochemicals (Tanabe, 1999; Hoch, 2001). Although the use of TBT has been banned or restricted in many countries, organotin compounds continue to pose a threat to aquatic organisms in some regions. Organotin compounds have been detected in many marine mammal species with higher concentrations found in coastal species compared to offshore species (Hoch, 2001). In Steller sea lions (*Eumetopias jubatus*), the highest butyltin levels were found in fur which suggests that molting may be important for excreting butyltin in pinnipeds (Kim et al., 1996). Organotin compounds can lead to immunosuppression, growth and reproductive defects, and neurotoxicity in mammals (Kannan et al., 1997; 1998; Olushola Sunday et al., 2012).

Vanadium is one of the lesser studied trace elements. It may be essential in mammals but since the biological pathway is not well-known, there is still some debate (Mackey et al., 1996; Schlesinger et al., 2017). Vanadium is released into the environment anthropogenically, mainly through the extraction and combustion of heavy crude oils and petroleum coke and mining of V ores (Schlesinger et al., 2017). The biological pathway of V is not well-known, but most of the metal seems to be excreted through urine. Bioaccumulation of V has been recorded for marine mammals, with liver, bone, and fur showing the highest concentrations (Mackey et al., 1996; Saeki et al., 1999). In some animals, V can negatively affect bone development and growth rate (Mackey et al., 1996). Although the effects of V are poorly understood in humans, high concentrations of V in freshwater phytoplankton and zooplankton were found to have lethal effects (Schiffer and Liber, 2017; Schlesinger et al., 2017).

Zinc is an essential element that aids in proper immune, sexual, and neurosensory functions. It is a major component of many proteins, enzymes, and transcription factors (Trumbo et al., 2001). The main anthropogenic sources of Zn include fossil fuel combustion, Cu and Zn mining, cement and fertilizer production, and waste incineration (Councell et al., 2004). The amount of Zn in the body is controlled by decreasing absorption and increasing excretion when levels are too high (Trumbo et al., 2001; Nriagu, 2007). Similar to other essential elements, Zn can be harmful at concentrations above or below levels of homeostasis. Deficiencies can lead to erosion of the gastrointestinal tract, skin lesions, cardiac failure, and malformations of the brain in humans (Kozlowski et al., 2009). In people exposed to extremely high levels of Zn, toxicity symptoms of nausea, vomiting, epigastric pain, lethargy, and fatigue may arise. Increased Zn uptake can interfere with Cu absorption and lead to Cu deficiency (Fosmire, 1990). Free ionic Zn may also promote the death of neurons, glia, and other cell types (Nriagu, 2007).

2. Materials and Methods

2.1. Sample collection

Vibrissae, serum, and milk were collected from PFS and SASL between the years 2009 and 2019 as part of a population health monitoring program at the Punta San Juan reserve in southern Peru. All collection was authorized under Peruvian permits (RJ No. 09-2010-, 23-2011-, 022-2012-, 09-2013-, 024-2014, 008-2015-, 019-2016-SERNANP-RNSIIPG). Procedures and importation were further approved by the United States National Marine Fisheries Service under Marine Mammal Protection Act permits 15471 and 19669. This reserve is one of the largest rookeries in Peru for both PFS and SASL, making it an ideal location to assess both species. Individuals were anesthetized for sample collection under the supervision and direction of Dr. M. Adkesson, Chicago Zoological Society. All samples were collected from live individuals during the breeding season (November for PFS, February for SASL) except for 2018 samples which were collected in April. Samples labeled as adult indicate reproductively mature individuals. Vibrissae (including the follicle) were removed from individuals and stored in plastic bags at room temperature. Blood samples were collected from the jugular vein and placed in royal blue trace element tubes (no additive; Vacutainer, BD, Franklin Lakes, New Jersey, USA) for serum analysis. Milk samples were manually collected through manual expression or use of gentle suction from a syringe. Samples were maintained on ice packs in the field and then stored at -80^{o} C until analysis. Vibrissae and serum were available from all individuals except 2009 and 2010 when only serum was available for adult female PFS and their corresponding pup. Milk was available from 2011 (n=16), 2015 (n=3), and 2019 (n=11) PFS dams. The dam and pup vibrissae (n=22 pairs) and serum (n=40 pairs) samples were used to determine the maternal transfer of trace elements. There were no available milk or corresponding pup samples for SASL females. To compare species and sex, male and female PFS (n=19, n=76, respectively) and SASL (n=17, n=14, respectively) were sampled (Table 1).

2.2. Trace element analysis

Trace element analysis was performed on up to fifteen elements: Al, As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Ni, Se, Sn, V, and Zn. Vibrissae were cleaned using a series of baths with ultrapure deionized water (18.2 megohms) from a Barnstead water purification system and HPLC grade acetone. Vibrissae were then dried for at least two hours in a Fisher Scientific isotemp vacuum oven model 282A at 60^{o} C and pressure below 10^{-2} torr using a 14008-01 model

Table 1. Total number of pinniped tissues analyzed in this study, including year, species, sex, age class, and tissue type. PFS = Peruvian fur seal, SASL = South American sea lion.

Year	Species	Sex	Age Class	Tissue	N
2009	PFS	Female	Adults	Serum	11
			Pups	Serum	11
2010	PFS	Female	Adults	Serum	15
			Pups	Serum	15
2011	PFS	Female	Adults	Vibrissae	12
				Milk	16
				Serum	13
		Male	Adults	Vibrissae	4
				Serum	4
2012	PFS	Female	Adults	Vibrissae	15
				Serum	15
		Male	Adults	Vibrissae	5
				Serum	5
2013	SASL	Male	Adults	Vibrissae	4
				Serum	4
2014	SASL	Male	Adults	Vibrissae	4
				Serum	4
	PFS	Male	Adults	Vibrissae	4
				Serum	4
2015	PFS	Female	Adults	Vibrissae	6
				Milk	3
				Serum	6
			Pups	Vibrissae	6
	SASL	Male	Adults	Vibrissae	9
				Serum	9
2016	PFS	Male	Adults	Vibrissae	6
				Serum	6
2017	SASL	Female	Adults	Vibrissae	6
				Serum	6
2018	SASL	Female	Adults	Vibrissae	8
				Serum	8
2019	PFS	Female	Adults	Vibrissae	16
				Serum	16
				Milk	11
			Pups	Vibrissae	16
				Serum	14

Welch 1400 DuoSeal vacuum pump. The length and dry weight of each vibrissa was recorded (Table 2).

Vibrissae were digested in 100 mL Teflon PTFE tubes using 5:1 trace metal basis nitric acid (Sigma Aldrich CAS Number 7697-37-2) and 30% hydrogen peroxide (Sigma Aldrich CAS Number 7722-84-1). Samples were placed in a ModBlock block digester at 60^{o} C for a minimum of 24 hours, or until full digestion was complete. Most vibrissae had dried weights over 0.1 g, but some vibrissae, such as pup vibrissae only weighed 0.01 g. Lighter vibrissae were digested with less nitric acid and hydrogen peroxide, but with the same 5:1 ratio. All vibrissae samples were then diluted to 10% nitric acid using ultrapure deionized water. Serum and milk samples were thawed and homogenized before digestion. Approximately 0.5 g of sample was combined with 4 mL of trace metal basis nitric acid, 1 mL of 30% hydrogen peroxide, and 1 mL of ultrapure water. Serum and milk were digested using a microwave digestion system (Multiwave 5000, Anton Paar). The two-step microwave program was as follows: room temperature to 200^{o} C, ramp time 15 minutes and hold at 200^{o} C for 15 minutes (Rey-Crespo et al., 2013). Serum and milk samples were transferred to 50 mL Teflon PTFE tubes by rinsing the microwave digestion tubes with ultrapure water to ensure that no sample was left behind. Since additional ultrapure water was added to the samples, the samples were placed on the ModBlock at 60^{o} C to allow excess solution to evaporate. Once serum and milk samples reached 2.5 mL, they were diluted to 25 mL with ultrapure deionized water.

Samples were analyzed using a sector-field inductively coupled plasma mass spectrometer (ThermoFisher Element XR) with a Peltier-cooler spray chamber (PC-3; Elemental Scientific, Inc.). Prior to analysis, digested samples were diluted 5-fold in 0.64 M ultrapure nitric acid (Seastar Baseline) containing 2 ppb indium as an internal standard. Diluted samples were held in acid-washed Teflon autosampler vials. Mass spectrometer scans were performed in low (Cd-111, Hg-199,200,201,202, Pb-208), medium (Al-27, V-51, Cr-52, Mn-55, Fe-56, Co-59, Ni-60, Cu-63, Zn-66), and high (As-75, Se-77,82) resolution, depending on the isotope. Mo-98 was monitored to correct for MoO^{+} interference on Cd. Standardization was by use of external standards, with a high standard and a blank re-run every eight samples. For the elements (Hg, Se) where multiple isotopes were determined, no significant analytical differences were noted between the isotopes. Two USGS reference water concentrations were also assessed as part of each analytical run to verify the standardization. In several cases sample calibration was also

Table 2. Total number of vibrissae analyzed, including species, year, number of associated sex (adults) mean ± standard deviation (SD) of lengths and weights. PFS = Peruvian fur seal, SASL = South American sea lion.

Species	**Year**	**Total N**	**Female N**	**Male N**	**Pup N**	**Length ± SD (cm)**	**Weight ± SD (g)**
PFS	2011	16	12	4	-	12.23 ± 2.29	0.13 ± 0.04
	2012	20	15	5	-	11.44 ± 2.57	0.12 ± 0.04
	2014	4	-	4	-	15.14 ± 2.05	0.17 ± 0.03
	2015	12	6	-	-	11.46 ± 1.42	0.12 ± 0.02
			-	-	6	7.21 ± 0.29	0.01 ± 0.002
	2016	6	-	6	-	12.88 ± 1.19	0.14 ± 0.03
	2019	32	16	-	-	12.48 ± 1.71	0.12 ± 0.03
			-	-	16	7.35 ± 0.73	0.01 ± 0.001
SASL	2013	4	-	4	-	26.21 ± 6.50	0.27 ± 0.05
	2014	4	-	4	-	18.31 ± 5.31	0.21 ± 0.11
	2015	9	-	9	-	17.49 ± 3.89	0.14 ± 0.07
	2017	6	6	-	-	15.58 ± 2.52	0.10 ± 0.02
	2018	8	8	-	-	16.00 ± 2.33	0.12 ± 0.03

verified by standard additions. Blanks of ultrapure deionized water, hydrogen peroxide, and trace metal basis nitric acid (10%) were used for quality control purposes. Detection limits are presented in Table 3.

Data were measured in μg/L and converted to μg/g, or parts per million (ppm), to correct for dilution and mass through the following equation:

$$\frac{Solution\ Concentration\left(\frac{\mu g}{L}\right) * \ Total\ Solution\ Volume\ (L)}{Solid\ Sample\ Mass\ (g)}$$

2.3. Statistical analysis

Descriptive statistics for all trace element concentrations, including range, mean, and standard deviation, were calculated using Excel (v. 2012; Microsoft Corporation). The statistical program R-Studio (v. 3.6.0) was used to calculate 95% mean confidence intervals and examine relationships between elements concentrations and species, sex, years, and sample type. To determine the differences among trace element concentrations, both parametric and non-parametric analyses were utilized. The Shapiro-Wilk test was used to determine if the data were normally distributed, and Bartlett's test was used to determine homogeneity of variances. Differences in trace element concentrations between species and sex were tested using t-tests and Mann-Whitney Wilcoxon tests. For species and sex analyses, Sn was not analyzed for serum samples and Hg was not analyzed for female serum samples of both species due to an insufficient number of samples above the detection limit. Analysis of Variance (ANOVA) and Kruskal-Wallis tests along with post-hoc tests were performed to determine if concentrations varied among years and degree of hemolysis. For variations among years, Sn was not analyzed for male vibrissae (both species) and Cd, Hg, and Sn were not analyzed for milk samples due to insufficient sample size above the detection limit. Peruvian fur seal dam and corresponding pup vibrissae, serum, and milk were studied using paired t-tests and Spearman rank correlation ($n \leq 30$) or Kendall's tau correlation ($n > 30$). Due to insufficient sample size, Hg and Sn were not analyzed for pup serum and milk. Correlations were also used to investigate the relationship among trace element concentrations in vibrissae, serum, and milk samples. A positive correlation indicates that as one variable increases, the other variable increases and vice versa; a negative correlation indicates that as one variable increases the other variable decreases. The correlation

Table 3. Inductively coupled plasma mass spectrometer (ICP-MS) detection limits (µg/g) for all 15 elements tested.

Element	**Detection Limit**
Al	0.1
As	0.00003
Cd	0.00001
Cr	0.0001
Co	0.00002
Cu	0.005
Fe	0.004
Pb	0.0004
Mn	0.00008
Hg	<0.00001
Ni	0.0005
Se	0.00003
Sn	0.001
V	0.00004
Zn	0.02

coefficient shows the strength of the correlation so that the closer the coefficient is to one, the stronger the correlation. Analyses were conducted on adults only unless otherwise noted.

To express the proportions of Se and Hg more accurately, the molar ratio was calculated instead of the concentration ratios. The molar ratio of Se to Hg was calculated for each individual via:

$$\frac{Se}{Hg} = (\frac{Se/78.96}{Hg/200.59})$$

where 78.96 g/mol and 200.59 g/mol are the atomic masses of Se and Hg, respectively. Correlations determined the strength of the statistical relationship between Se and Hg concentrations.

3. Results and Discussion

3.1. Metal Concentrations

The mean, median, and standard deviation for each element in vibrissae and serum are presented by species in Table 4. Summary statistics for milk concentrations, including if data were normally distributed, are presented in Table 5. All vibrissae, serum, and milk samples (n= 317) contained detectable values of 9 of the 15 elements - Al, Cr, Co, Cu, Fe, Pb, Mn, Se, and Zn. All vibrissae samples (n=121) contained detectable amounts of 12 of the 15 elements - Al, Cr, Co, Cu, Fe, Pb, Mn, Hg, Ni, Se, V, and Zn. Of the remaining 3 elements, 99% of vibrissae contained Cd, 86% contained As, and 84% contained Sn. Keratinous tissues, such as vibrissae, are high in sulfur containing thiols which binds many elements including Al, As, Cd, Cr, Co, Cu, Pb, Hg, Ni, and Zn (Rubino, 2015).

All serum samples (n=166) contained detectable amounts of 10 of the 15 elements - Al, As, Cr, Co, Cu, Fe, Pb, Mn, Se, and Zn. Of the remaining 5 elements, 98% of serum samples contained V, 96% contained Cd, 94% contained Ni, 26% contained Hg, and only 5% contained Sn. Since serum does not include red blood cells, it is not a good indicator of elements that bind to red blood cells such as Hg and Sn (ATSDR 2005; Berglund et al., 2005).

All milk samples (n=30) contained detectable amounts of 11 of the 15 elements - Al, As, Cr, Co, Cu, Fe, Pb, Mn, Se, V, and Zn. Of the remaining 4 elements, 83% of milk samples contained Ni, 50% contained Cd, 47% contained Hg, and 33% contained Sn. Although Cd was detected in half of our milk samples, the average concentration (0.025 µg/g) was less than half of

Table 4. Trace element concentrations for vibrissae and serum in adult Peruvian pinnipeds. Data presented as mean (median) ± standard deviation (μg/g). PFS = Peruvian fur seal, SASL = South American sea lion, N/A = not available.

Element	Species	Vibrissae	Serum
Al	PFS	22.08 (19.88) ± 9.294	5.186 (3.747) ± 4.242
	SASL	21.80 (19.85) ± 12.26	4.211 (3.462) ± 2.100
As	PFS	0.186 (0.193) ± 0.120	0.069 (0.065) ± 0.028
	SASL	0.294 (0.239) ± 0.228	0.041 (0.034) ± 0.039
Cd	PFS	0.242 (0.209) ± 0.103	0.008 (0.002) ± 0.034
	SASL	0.945 (0.708) ± 1.267	0.003 (0.002) ± 0.005
Cr	PFS	0.323 (0.275) ± 0.236	0.035 (0.029) ± 0.027
	SASL	0.350 (0.283) ± 0.239	0.034 (0.029) ± 0.023
Co	PFS	0.021 (0.015) ± 0.020	0.002 (0.001) ± 0.002
	SASL	0.017 (0.013) ± 0.011	0.003 (0.002) ± 0.005
Cu	PFS	20.03 (20.01) ± 2.174	0.911 (0.872) ± 0.300
	SASL	14.60 (14.72) ± 1.735	0.862 (0.811) ± 0.239
Fe	PFS	9.899 (8.765) ± 6.139	5.640 (4.641) ± 3.945
	SASL	10.58 (8.548) ± 6.725	6.901 (5.571) ± 3.632
Pb	PFS	0.116 (0.100) ± 0.064	0.082 (0.024) ± 0.178
	SASL	0.215 (0.093) ± 0.514	0.039 (0.023) ± 0.055
Mn	PFS	0.325 (0.249) ± 0.488	0.032 (0.014) ± 0.092
	SASL	0.231 (0.164) ± 0.186	0.028 (0.016) ± 0.057
Hg	PFS	2.281 (2.112) ± 1.119	0.003 (0.003) ± 0.003
	SASL	2.322 (2.061) ± 1.409	0.002 (0.001) ± 0.003
Ni	PFS	0.438 (0.169) ± 1.927	0.015 (0.008) ± 0.020
	SASL	0.488 (0.434) ± 0.231	0.019 (0.009) ± 0.020
Se	PFS	1.060 (1.035) ± 0.248	0.317 (0.316) ± 0.053
	SASL	1.951 (1.898) ± 0.365	0.357 (0.344) ± 0.050
Sn	PFS	2.697 (2.871) ± 1.471	0.405 (0.166) ± 0.496
	SASL	1.713 (2.277) ± 1.394	N/A
V	PFS	0.033 (0.033) ± 0.012	0.003 (0.002) ± 0.003
	SASL	0.134 (0.106) ± 0.079	0.003 (0.003) ± 0.002
Zn	PFS	183.0 (181.0) ± 25.31	7.926 (1.336) ± 36.01
	SASL	145.4 (147.2) ± 37.69	6.196 (1.445) ± 26.16

Table 5. Summary statistics for Peruvian fur seal milk (n=30). Concentrations in µg/g. 95% CI = 95% Confidence Interval of the mean, N/D = not detected.

Peruvian fur seal milk						
Element	**Mean**	**Standard Deviation**	**Median**	**95% CI**	**Range**	**Normal Distribution**
Al	5.05	3.44	3.95	3.69-4.93	2.45-18.59	No
As	0.41	0.15	0.40	0.35-0.47	0.17-0.83	Yes
Cd	0.025	0.075	0.005	0.004-0.009	N/D-0.306	No
Cr	0.07	0.09	0.04	0.03-0.07	0.01-0.38	No
Co	0.003	0.002	0.003	0.002-0.004	0.001-0.008	No
Cu	2.24	0.97	2.23	1.88-2.50	0.99-5.78	No
Fe	3.63	2.71	2.70	2.31-4.31	0.75-11.64	No
Pb	0.05	0.05	0.03	0.03-0.05	0.01-0.25	No
Mn	0.05	0.04	0.04	0.03-0.06	0.002-0.16	No
Hg	0.129	0.409	0.004	0.002-0.120	N/D-1.700	No
Ni	0.04	0.06	0.02	0.02-0.04	N/D-0.30	No
Se	0.35	0.13	0.35	0.31-0.40	0.11-0.55	Yes
Sn	0.05	0.02	0.05	0.03-0.07	N/D-0.10	Yes
V	0.0037	0.0030	0.0028	0.0023-0.0045	0.0004-0.0127	No
Zn	10.30	10.69	8.10	7.43-9.75	3.18-65.09	No

what was found in harp seals from the Gulf of Saint Lawrence (0.057 µg/g; Wagemann et al., 1988). Cadmium was the only element out of 11 below the detection limit in gray seal milk from Scotland (instrumental quantification limit of Cd was 0.002 ppb compared to the detection limit of 0.01 ppb in this study; Habran et al., 2013). Mercury was found in 47% of our PFS milk samples, with Hg concentrations ranging from not detected (N/D) - 1.700 µg/g, which is a much wider range than results from other studies (0.006 - 0.022 µg/g, Scotland gray seals, Habran et al., 2013; 0.0037 - 0.01 µg/g, Gulf of Saint Lawrence harp seals, Wagemann et al., 1988).

On average, vibrissae had the highest concentrations of all elements compared to serum and milk except As. Similarly, Gray et al. (2008) found that for all 14 trace elements analyzed in leopard and Weddell seals, fur concentrations were higher than serum concentrations. Otariids retain their vibrissae for multiple years and therefore reflect several years of data compared to serum and milk, which reflect only days to months of exposure or metabolism, respectively (Laker, 1982; Hirons et al., 2001; Darimont et al., 2002; Bearhop et al., 2004; Edwards, 2018; Rosas-Hernández et al., 2018). Kelleher's (2016) northern fur seal vibrissae growth rate of 0.09 mm/day was used to determine the approximate time scale represented in each vibrissa. Adult PFS vibrissae averaged 12.22 ± 2.21 cm in length, each vibrissa represented an average of 45.25 ± 8.2 months (3.8 ± 0.7 years). Adult SASL vibrissae were longer than PFS with an average length of 17.97 ± 4.89 cm, each vibrissa represented an average of 66.55 ± 18.1 months (5.5 ± 1.5 years). Milk samples contained the highest average As levels; the average As concentration was more than twice as high in PFS dam milk (0.410 µg/g) than dam vibrissae (0.166 µg/g).

Correlation tests were performed for each element, but significant correlations between sample types were only found for As, Se, and V. Arsenic concentrations were significantly negatively correlated between vibrissae and serum samples ($Z = -2.788$, $\tau = -0.194$, $p = 0.005$). Selenium concentrations were significantly positively correlated between milk and serum samples ($S = 1866$, $\rho = 0.430$, $p = 0.03$) and between vibrissae and milk samples ($S = 1752$, $\rho = 0.401$, $p = 0.04$), but not between vibrissae and serum ($Z = -0.344$, $\tau = -0.022$, $p = 0.73$). Vanadium concentrations were significantly positively correlated between milk and serum samples ($S = 1716$, $\rho = 0.476$, $p = 0.01$) and vibrissae and serum samples ($Z = 3.292$, $\tau = 0.216$, $p = 0.001$), but not milk and vibrissae ($S = 2734$, $\rho = 0.065$, $p = 0.75$).

The ratio of Se:Hg was examined to determine potential mercury toxicity (Table 6). A molar ratio greater than 1 indicates that Se may be bound to all Hg, protecting against Hg toxicity (Berry and Ralston 2008). Less than 7% of all vibrissae samples had a molar ratio under one suggesting low concern for Hg toxicity. The range for Se:Hg molar ratio for vibrissae was 0.44 – 11.25, with an average of 2.91. Male SASL vibrissae showed a significant positive correlation between Se and Hg ($S = 314$, $\rho = 0.615$, $p = 0.01$) with an average molar ratio of 1.71. There was no significant correlation between Se and Hg for SASL females or PFS. Mercury was either not detected or very low in serum and milk samples causing extremely high average Se:Hg molar ratios of 4663.3 and 459.2, respectively.

The occurrence of hemolysis in serum can significantly influence concentrations of various analytes, including trace elements. Hemolysis occurs when red blood cells rupture, releasing their contents into the surrounding plasma which can lead to the dilution or enrichment of certain trace elements in serum (Lippi et al., 2006). To examine the potential effects of hemolysis in this study, an ANOVA was used to determine if element concentrations differed with degree of hemolysis in serum. Hemolysis of serum samples was rated on a visual scale from 1 to 4 with 1 being a clear sample and no indication of hemolysis to category 4 being a bright red sample indicating a high degree of hemolysis. Out of the 166 serum samples, approximately 15% were categorized as 1, 40% were categorized as 2, 30% were categorized as 3, and 15% were categorized as 4. Element concentrations decreased as degree of hemolysis increased for As, Cd, and Cu. Element concentrations increased as degree of hemolysis increased for Fe. For As, concentrations for category 1 samples (0.074 μg/g) were significantly higher than concentrations for category 3 samples (0.055 μg/g) and category 4 samples (0.048 μg/g; $F(3) = 3.774$, $p=0.01$). For Cd, concentrations for category 1 samples (0.006 μg/g) were significantly higher than concentrations for category 3 samples (0.003 μg/g; $X^2(3) = 10.364$, $p=0.02$). For Cu, concentrations for category 1 samples (0.902 μg/g) were significantly higher than category 3 samples (0.742 μg/g; $X^2(3) = 12.333$, $p=0.006$). For Fe, concentrations of category 1, 2, and 3 samples (4.293 μg/g, 5.423 μg/g, 5.969 μg/g, respectively) were significantly lower than category 4 samples (9.848 μg/g; $X^2(3) = 33.525$, $p<0.001$). This indicates a potential overcalculation of Fe and undercalculation of As, Cd, and Cu in serum samples.

3.2. Effects of sea surface temperature

To determine potential effects of SST on element concentrations, a t-test was used to compare serum concentrations during El Niño (warm) and La Niña (cold) years. Sea surface temperature anomalies from the 1+2 Niño Index were used to define sampling periods as either

Table 6. Vibrissae, serum, and milk Se and Hg concentrations (µg/g), molar Se and Hg concentrations (µg/g), and the molar ratio of Se to Hg for each sample. N/D = not detected.

Sample ID	Se	Hg	Molar Se	Molar Hg	Molar Ratio Se:Hg
Vibrissae					
AA-1111W	1.35	4.69	0.0170	0.0234	0.730
AA-1112W	1.17	5.43	0.0149	0.0271	0.549
AA-1113W	0.79	4.60	0.0100	0.0229	0.436
AA-1114W	1.10	4.98	0.0139	0.0248	0.561
AA-1115W	0.80	1.92	0.0101	0.0096	1.054
AA-1116W	0.95	1.58	0.0121	0.0079	1.530
AA-1118W	0.81	2.76	0.0103	0.0138	0.745
AA-1119W	0.96	4.65	0.0121	0.0232	0.522
AA-1122W	0.91	3.24	0.0116	0.0161	0.716
AA-1124W	0.97	2.24	0.0122	0.0112	1.095
AA-1125W	1.08	2.08	0.0137	0.0103	1.325
AA-1126W	1.16	2.11	0.0147	0.0105	1.394
AA-1127W	0.78	1.46	0.0098	0.0073	1.352
AA-1129W	0.95	2.23	0.0120	0.0111	1.081
AA-1132W	1.08	3.76	0.0136	0.0188	0.726
AA-1133W	1.54	0.95	0.0195	0.0048	4.090
AA-1201W	0.92	1.89	0.0117	0.0094	1.241
AA-1202W	1.16	1.55	0.0147	0.0077	1.902
AA-1203W	0.91	2.72	0.0115	0.0136	0.848
AA-1204W	1.23	3.16	0.0155	0.0158	0.985
AA-1205W	1.99	0.94	0.0252	0.0047	5.391
AA-1206W	0.97	1.33	0.0123	0.0066	1.868
AA-1208W	0.89	0.68	0.0112	0.0034	3.295
AA-1210W	0.83	3.15	0.0106	0.0157	0.674
AA-1212W	0.81	0.66	0.0103	0.0033	3.120
AA-1214W	0.83	0.71	0.0105	0.0036	2.966
AA-1216W	0.75	0.95	0.0095	0.0047	2.021
AA-1220W	0.76	2.41	0.0097	0.0120	0.807
AA-1222W	0.80	0.58	0.0101	0.0029	3.498
AA-1226W	1.09	0.88	0.0138	0.0044	3.123
AA-1228W	0.95	0.92	0.0120	0.0046	2.628
AA-1230W	0.90	2.21	0.0115	0.0110	1.042

AA-1232W	0.76	0.94	0.0097	0.0047	2.054
AA-1236W	1.06	1.08	0.0134	0.0054	2.480
AA-1238W	1.09	0.82	0.0138	0.0041	3.380
AA-1240W	0.86	1.25	0.0108	0.0062	1.735
13-05W	2.09	5.35	0.0264	0.0267	0.990
13-06W	2.59	4.31	0.0328	0.0215	1.525
13-07W	2.78	5.28	0.0352	0.0263	1.340
13-12W	2.38	3.48	0.0302	0.0173	1.742
14-01W	2.35	5.46	0.0298	0.0272	1.094
14-02W	2.00	3.78	0.0253	0.0188	1.343
14-03W	1.94	2.96	0.0246	0.0148	1.667
14-05W	1.91	1.94	0.0242	0.0097	2.499
14-08W	1.21	3.74	0.0154	0.0186	0.825
14-09W	1.31	2.95	0.0166	0.0147	1.131
14-11W	1.16	4.15	0.0147	0.0207	0.714
14-13W	1.36	2.75	0.0172	0.0137	1.257
15-01W	1.76	2.18	0.0223	0.0109	2.057
15-02W	1.71	2.32	0.0217	0.0116	1.871
15-03W	1.79	2.29	0.0226	0.0114	1.985
15-04W	2.37	2.33	0.0300	0.0116	2.579
15-05W	2.21	2.65	0.0279	0.0132	2.112
15-06W	1.67	2.81	0.0212	0.0140	1.514
15-07W	1.90	4.03	0.0240	0.0201	1.198
15-08W	1.30	1.64	0.0165	0.0082	2.009
15-09W	1.69	2.66	0.0214	0.0133	1.616
15-12PW	3.53	1.08	0.0447	0.0054	8.333
15-12W	1.10	1.97	0.0139	0.0098	1.415
15-13PW	3.06	1.34	0.0388	0.0067	5.812
15-13W	0.80	2.95	0.0102	0.0147	0.691
15-15PW	2.33	0.92	0.0295	0.0046	6.426
15-15W	0.95	1.74	0.0120	0.0087	1.386
15-16PW	3.06	0.81	0.0388	0.0040	9.612
15-16W	2.03	2.05	0.0256	0.0102	2.510
15-17PW	2.70	1.15	0.0342	0.0058	5.940
15-17W	0.87	1.79	0.0110	0.0089	1.227
15-18PW	2.88	0.71	0.0365	0.0035	10.352
15-18W	1.05	2.47	0.0134	0.0123	1.083

AA16-01W	1.34	3.17	0.0169	0.0158	1.073
AA16-02W	1.02	2.51	0.0129	0.0125	1.027
AA16-03W	1.10	2.07	0.0139	0.0103	1.349
AA16-04W	0.89	3.14	0.0113	0.0156	0.721
AA16-05W	0.98	2.13	0.0124	0.0106	1.171
AA16-06W	1.08	4.16	0.0137	0.0207	0.663
17-01W	1.84	1.36	0.0233	0.0068	3.442
17-02W	1.35	0.98	0.0171	0.0049	3.502
17-03W	1.73	1.13	0.0220	0.0056	3.903
17-04W	2.36	1.01	0.0299	0.0050	5.929
17-05W	1.81	2.06	0.0229	0.0103	2.228
17-08W	2.02	1.35	0.0256	0.0068	3.787
18-01W	1.86	1.08	0.0236	0.0054	4.386
18-02W	2.16	0.93	0.0273	0.0046	5.922
18-03W	1.66	1.03	0.0210	0.0051	4.102
18-04W	2.43	0.55	0.0308	0.0027	11.245
18-05W	1.53	1.59	0.0194	0.0079	2.453
18-06W	2.15	1.27	0.0272	0.0063	4.318
18-07W	1.80	0.93	0.0227	0.0046	4.902
18-08W	1.33	1.25	0.0169	0.0062	2.712
19-01W	0.75	1.56	0.0096	0.0078	1.229
19-02W	1.01	2.16	0.0128	0.0108	1.189
19-03W	1.28	1.92	0.0162	0.0096	1.695
19-04W	0.85	2.10	0.0107	0.0105	1.024
19-05W	1.27	1.73	0.0161	0.0086	1.868
19-06W	1.18	2.11	0.0150	0.0105	1.424
19-07W	1.09	2.56	0.0138	0.0128	1.080
19-08W	1.21	2.28	0.0153	0.0114	1.350
19-09W	1.11	2.01	0.0141	0.0100	1.408
19-10W	1.38	3.21	0.0175	0.0160	1.092
19-11W	0.92	2.11	0.0117	0.0105	1.110
19-12W	1.22	2.02	0.0155	0.0101	1.535
19-13W	1.01	2.13	0.0128	0.0106	1.203
19-14W	1.08	1.51	0.0136	0.0075	1.810
19-15W	1.26	1.76	0.0159	0.0088	1.819
19-16W	1.24	2.65	0.0158	0.0132	1.192
19-201W	3.13	0.92	0.0396	0.0046	8.642

19-202W	4.48	1.26	0.0567	0.0063	9.046
19-203W	4.13	1.65	0.0523	0.0082	6.365
19-204W	3.95	1.33	0.0500	0.0066	7.561
19-205W	6.06	2.16	0.0768	0.0108	7.140
19-206W	5.64	1.82	0.0714	0.0091	7.875
19-207W	4.02	1.58	0.0509	0.0079	6.465
19-208W	4.37	1.78	0.0553	0.0089	6.224
19-209W	3.67	1.61	0.0465	0.0080	5.809
19-210W	3.87	1.82	0.0490	0.0091	5.396
19-211W	3.33	1.80	0.0422	0.0090	4.700
19-212W	4.70	1.51	0.0595	0.0075	7.906
19-213W	3.00	1.83	0.0380	0.0091	4.170
19-214W	5.33	1.82	0.0675	0.0091	7.453
19-215W	4.82	1.80	0.0611	0.0090	6.809
19-216W	5.35	1.54	0.0678	0.0077	8.813
Serum					
AA-007S	0.18	N/D	0.0022	N/D	N/D
AA-009S	0.35	N/D	0.0044	N/D	N/D
AA-011S	0.33	N/D	0.0042	N/D	N/D
AA-015S	0.26	N/D	0.0032	N/D	N/D
AA-017S	0.30	N/D	0.0037	N/D	N/D
AA-019S	0.31	N/D	0.0039	N/D	N/D
AA-021S	0.35	N/D	0.0045	N/D	N/D
AA-023S	0.30	N/D	0.0038	N/D	N/D
AA-025S	0.26	N/D	0.0033	N/D	N/D
AA-027S	0.23	0.0126	0.0029	0.0001	47.02
AA-029S	0.28	N/D	0.0035	N/D	N/D
AA-1002S	0.37	0.00001	0.0047	0.0000001	88803.04
AA-1003S	0.32	N/D	0.0041	N/D	N/D
AA-1006S	0.49	0.0036	0.0063	0.00002	347.42
AA-1008S	0.33	N/D	0.0041	N/D	N/D
AA-1010S	0.35	N/D	0.0044	N/D	N/D
AA-1012S	0.30	N/D	0.0038	N/D	N/D
AA-1014S	0.32	N/D	0.0040	N/D	N/D
AA-1016S	0.34	N/D	0.0043	N/D	N/D
AA-1018S	0.39	N/D	0.0049	N/D	N/D
AA-1020S	0.36	N/D	0.0046	N/D	N/D

AA-1022S	0.35	0.0001	0.0044	0.000001	7297.90
AA-1024S	0.28	N/D	0.0035	N/D	N/D
AA-1026S	0.42	0.0009	0.0053	0.000004	1222.10
AA-1028S	0.33	N/D	0.0042	N/D	N/D
AA-1030S	0.31	N/D	0.0039	N/D	N/D
AA-1111S	0.45	0.0061	0.0057	0.00003	188.67
AA-1112S	0.26	N/D	0.0033	N/D	N/D
AA-1113S	0.26	0.0057	0.0033	0.00003	116.35
AA-1114S	0.24	0.0027	0.0030	0.00001	223.49
AA-1115S	0.24	N/D	0.0030	N/D	N/D
AA-1116S	0.30	N/D	0.0038	N/D	N/D
AA-1120S	0.31	N/D	0.0039	N/D	N/D
AA-1121S	0.28	N/D	0.0035	N/D	N/D
AA-1122S	0.32	N/D	0.0040	N/D	N/D
AA-1123S	0.26	N/D	0.0033	N/D	N/D
AA-1124S	0.25	0.00001	0.0032	0.0000001	54215.33
AA-1125S	0.30	N/D	0.0038	N/D	N/D
AA-1126S	0.31	N/D	0.0039	N/D	N/D
AA-1127S	0.33	N/D	0.0042	N/D	N/D
AA-1129S	0.23	0.0081	0.0029	0.00004	72.49
AA-1132S	0.37	0.0035	0.0047	0.00002	274.14
AA-1133S	0.28	N/D	0.0035	N/D	N/D
AA-1201S	0.33	0.0029	0.0042	0.00001	285.18
AA-1202S	0.32	0.0034	0.0041	0.00002	243.50
AA-1203S	0.34	0.0020	0.0043	0.00001	423.06
AA-1204S	0.23	0.0030	0.0029	0.00001	194.56
AA-1205S	0.32	0.0050	0.0040	0.00003	159.80
AA-1206S	0.34	N/D	0.0043	N/D	N/D
AA-1208S	0.28	N/D	0.0036	N/D	N/D
AA-1210S	0.31	N/D	0.0040	N/D	N/D
AA-1212S	0.31	N/D	0.0040	N/D	N/D
AA-1214S	0.27	N/D	0.0035	N/D	N/D
AA-1216S	0.32	N/D	0.0041	N/D	N/D
AA-1220S	0.34	N/D	0.0043	N/D	N/D
AA-1222S	0.36	N/D	0.0046	N/D	N/D
AA-1226S	0.33	0.0003	0.0042	0.000002	2488.19
AA-1228S	0.33	N/D	0.0041	N/D	N/D

AA-1230S	0.32	N/D	0.0040	N/D	N/D
AA-1232S	0.31	N/D	0.0039	N/D	N/D
AA-1236S	0.35	N/D	0.0044	N/D	N/D
AA-1238S	0.32	N/D	0.0040	N/D	N/D
AA-1240S	0.33	N/D	0.0042	N/D	N/D
13-05S	0.38	0.0003	0.0049	0.000002	3059.01
13-06S	0.44	0.0008	0.0055	0.000004	1307.68
13-07S	0.41	0.0108	0.0052	0.0001	97.07
13-12S	0.38	0.0046	0.0048	0.00002	208.22
14-01S	0.44	N/D	0.0056	N/D	N/D
14-02S	0.37	N/D	0.0047	N/D	N/D
14-03S	0.34	0.0021	0.0044	0.00001	420.15
14-05S	0.42	N/D	0.0053	N/D	N/D
14-08S	0.34	0.0054	0.0044	0.00003	163.38
14-09S	0.45	0.0013	0.0058	0.00001	922.02
14-11S	0.37	0.0017	0.0047	0.00001	568.13
14-13S	0.30	0.0027	0.0038	0.00001	284.25
15-01S	0.33	N/D	0.0041	N/D	N/D
15-02S	0.31	0.0024	0.0040	0.00001	330.61
15-03S	0.43	0.0007	0.0055	0.000004	1510.13
15-04S	0.43	0.0007	0.0054	0.000004	1469.65
15-05S	0.33	0.0001	0.0041	0.000001	5838.10
15-06S	0.43	0.0038	0.0055	0.00002	285.49
15-07S	0.40	0.0011	0.0051	0.00001	940.38
15-08S	0.33	N/D	0.0042	N/D	N/D
15-09S	0.39	0.0002	0.0049	0.000001	4334.20
15-12S	0.27	0.0002	0.0034	0.000001	2827.20
15-13S	0.32	0.0008	0.0040	0.000004	1039.52
15-15S	0.34	N/D	0.0043	N/D	N/D
15-16S	0.34	N/D	0.0044	N/D	N/D
15-17S	0.27	N/D	0.0034	N/D	N/D
15-18S	0.26	N/D	0.0033	N/D	N/D
AA 16-01S	0.34	N/D	0.0043	N/D	N/D
AA 16-02S	0.29	0.0003	0.0036	0.000002	2275.08
AA 16-03S	0.26	N/D	0.0033	N/D	N/D
AA 16-04S	0.51	0.0020	0.0065	0.00001	646.87
AA 16-05S	0.33	0.0027	0.0042	0.00001	313.42

AA 16-06S	0.29	0.0009	0.0037	0.000005	820.19
17-01S	0.35	N/D	0.0044	N/D	N/D
17-02S	0.25	N/D	0.0032	N/D	N/D
17-03S	0.37	N/D	0.0047	N/D	N/D
17-04S	0.35	N/D	0.0045	N/D	N/D
17-05S	0.33	N/D	0.0042	N/D	N/D
17-08S	0.34	N/D	0.0043	N/D	N/D
18-01S	0.33	N/D	0.0042	N/D	N/D
18-02S	0.30	N/D	0.0038	N/D	N/D
18-03S	0.32	N/D	0.0040	N/D	N/D
18-04S	0.31	N/D	0.0040	N/D	N/D
18-05S	0.29	N/D	0.0036	N/D	N/D
18-06S	0.33	N/D	0.0042	N/D	N/D
18-07S	0.30	N/D	0.0038	N/D	N/D
18-08S	0.34	N/D	0.0044	N/D	N/D
19-01S	0.28	N/D	0.0035	N/D	N/D
19-02S	0.33	N/D	0.0042	N/D	N/D
19-03S	0.31	N/D	0.0039	N/D	N/D
19-04S	0.30	N/D	0.0038	N/D	N/D
19-05S	0.36	N/D	0.0045	N/D	N/D
19-06S	0.28	N/D	0.0035	N/D	N/D
19-07S	0.33	N/D	0.0042	N/D	N/D
19-08S	0.35	N/D	0.0045	N/D	N/D
19-09S	0.28	N/D	0.0036	N/D	N/D
19-10S	0.31	N/D	0.0040	N/D	N/D
19-11S	0.35	N/D	0.0044	N/D	N/D
19-12S	0.31	N/D	0.0039	N/D	N/D
19-13S	0.28	N/D	0.0036	N/D	N/D
19-14S	0.41	N/D	0.0052	N/D	N/D
19-15S	0.37	N/D	0.0047	N/D	N/D
19-16S	0.27	0.0026	0.0035	0.00001	267.64
Milk					
AA-1115M	0.13	N/D	0.002	N/D	N/D
AA-1116M	0.18	0.0015	0.002	0.00001	301.46
AA-1117M	0.32	N/D	0.004	N/D	N/D
AA-1118M	0.21	0.0026	0.003	0.00001	209.52
AA-1119M	0.42	0.0052	0.005	0.00003	206.19

AA-1120M	0.29	N/D	0.004	N/D	N/D
AA-1121M	0.35	N/D	0.004	N/D	N/D
AA-1122M	0.33	N/D	0.004	N/D	N/D
AA-1123M	0.29	N/D	0.004	N/D	N/D
AA-1124M	0.21	N/D	0.003	N/D	N/D
AA-1125M	0.35	N/D	0.004	N/D	N/D
AA-1126M	0.34	N/D	0.004	N/D	N/D
AA-1127M	0.35	0.0008	0.004	0.000004	1093.81
AA-1129M	0.17	N/D	0.002	N/D	N/D
AA-1132M	0.11	0.0004	0.001	0.00000	756.22
AA-1133M	0.23	0.0021	0.003	0.00001	284.77
15-13M	0.33	1.70	0.004	0.008	0.49
15-15M	0.34	N/D	0.004	N/D	N/D
15-16M	0.51	0.0005	0.006	0.000003	2528.75
19-01M	0.39	N/D	0.005	N/D	N/D
19-02M	0.38	0.0038	0.005	0.00002	256.47
19-04M	0.37	0.0249	0.005	0.00012	37.71
19-06M	0.53	0.0011	0.007	0.00001	1184.74
19-07M	0.55	0.0142	0.007	0.00007	98.70
19-08M	0.47	0.0289	0.006	0.00014	41.20
19-09M	0.39	0.2389	0.005	0.00119	4.16
19-10M	0.51	0.0372	0.006	0.00019	34.58
19-11M	0.54	0.0044	0.007	0.00002	308.24
19-12M	0.49	N/D	0.006	N/D	N/D
19-14M	0.55	N/D	0.007	N/D	N/D

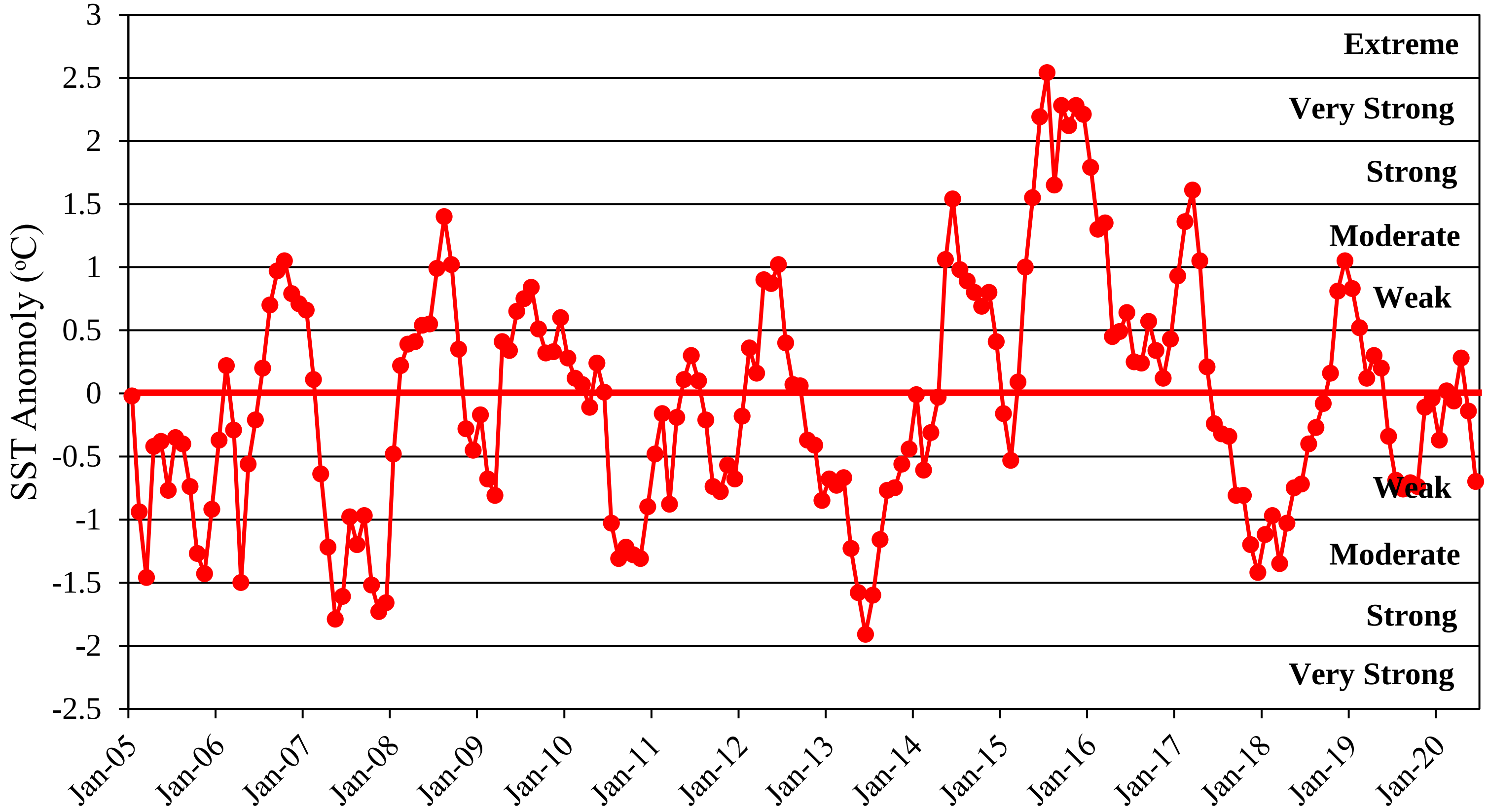

Figure 3. Sea surface temperature anomaly (SSTA) time series for Nino index 1+2 from 2005-2020 (NOAA_ERSST_V5 data provided by the NOAA/OAR/ESRL PSD). Positive anomalies represent warm periods (El Niño), and negative anomalies represent cold periods (La Niña). Modified from Edwards (2018).

El Niño or La Niña (Figure 3). Serum samples from adults of both species were used for moderate to extreme events (SSTA> ±1^{o} C). El Niño samples included 2014 (PFS only), 2015 (PFS only), and 2017 serum samples, while La Niña samples included 2010, 2014 (SASL only), and 2018 serum samples. Arsenic and Mn serum concentrations were significantly higher during El Niño than La Niña (As: 0.07, 0.03 µg/g, respectively; p = 0.002, Mn: 0.05, 0.04 µg/g, respectively; p = 0.009) Arsenic is likely released into the environment from agricultural contamination and Cu smelting. Increased rain and runoff in Peru during El Niño may lead to increased As in the marine environment, where is it taken up into the food web and bioaccumulates in Peruvian pinnipeds (Holmgren et al., 2001). During normal and La Niña years in Peru, dissolved Mn is higher offshore than in the upwelling along the coast (Vedamati et al., 2015). Increased Mn concentrations may be due to less oxidizing conditions caused by El Niño. Warm waters decrease oxygen levels and increase the solubility of Mn allowing it to enter the food web more readily during El Niño years (Vedamati et al., 2015). Godwin et al. (2020) found lower Mn oxidation rates in less productive waters in Lake Erie, suggesting increased soluble Mn during El Niño may also be due to decreased productivity.

Since vibrissae reflect exposure over several years and length varies for each individual, it is difficult to determine variations among years. Seasonal and annual fluctuations likely occur, but these variations cannot be seen when analyzing whole vibrissae. Milk samples were collected in 2011, 2015, and 2019. Both 2011 and 2019 were cold SST years. There was an extreme El Niño in 2015, but only three milk samples were collected making it difficult to compare warm and cold years. Cadmium and Hg appear to be elevated in 2015 milk samples, but Cd was only detected in one sample (0.31 µg/g) and Hg was only detected in two samples (1.70, 0.001 µg/g). Average element and SST anomaly (SSTA) by year is presented in Tables 7 (vibrissae), 8 (serum), and 9 (milk).

3.3. Peruvian fur seals

Summary statistics for PFS vibrissae and serum concentrations, including if data were normally distributed, are presented in Tables 10 and 11. Two-sample t-tests and Mann-Whitney Wilcoxon tests determined differences in vibrissae and serum values between adult female and male PFS. Tin was not analyzed for PFS serum or male vibrissae and Hg was not analyzed for female serum due to insufficient sample size. Element concentrations in vibrissae were significantly different between PFS females (n=49) and males (n=19) for Al, Cd, Cu, Fe, Mn,

Table 7. Mean vibrissae element concentrations for adult Peruvian fur seals and South American sea lions by year (µg/g). Sea surface temperature anomaly (SSTA) is the Niño 1+2 index for June of the corresponding year (NOAA_ERSST_V5 data provided by the NOAA/OAR/ESRL PSD). A positive SSTA indicates above average temperatures (El Niño) and a negative SSTA indicates below average temperatures (La Niña).

Year	**SSTA**	**Al**	**As**	**Cd**	**Cr**	**Co**	**Cu**	**Fe**	**Pb**	**Mn**	**Hg**	**Ni**	**Se**	**Sn**	**V**	**Zn**
2011	0.30	21.18	0.10	0.30	0.32	0.02	20.29	9.19	0.13	0.27	3.04	0.26	1.02	2.82	0.03	189.9
2012	1.02	27.25	0.07	0.24	0.44	0.02	19.74	10.76	0.11	0.28	1.44	1.03	0.98	3.39	0.04	179.1
2013	-1.91	12.16	0.09	1.28	0.15	0.02	15.47	7.86	0.08	0.15	4.61	0.64	2.46	0.01	0.19	115.7
2014	1.54	13.92	0.25	0.48	0.22	0.01	16.33	6.85	0.13	0.15	3.47	0.21	1.66	1.81	0.06	158.8
2015	2.19	23.38	0.13	1.05	0.41	0.03	15.84	12.04	0.13	0.56	2.39	0.38	1.55	1.26	0.12	149.1
2016	0.64	17.73	0.32	0.24	0.30	0.02	17.45	7.86	0.08	0.17	2.86	0.20	1.07	2.44	0.03	160.8
2017	-0.24	28.22	0.37	0.68	0.48	0.02	14.72	12.68	0.57	0.28	1.32	0.49	1.85	2.79	0.12	171.0
2018	-0.72	22.49	0.54	0.38	0.32	0.02	15.57	9.04	0.12	0.23	1.08	0.52	1.87	2.78	0.09	166.4
2019	-0.34	20.40	0.26	0.19	0.20	0.02	21.69	11.02	0.12	0.29	2.12	0.13	1.12	0.02	0.04	189.4

Table 8. Mean serum element concentrations for adult Peruvian fur seals and South American sea lions by year (µg/g). Sea surface temperature anomaly (SSTA) is the Niño 1+2 index for June of the corresponding year (NOAA_ERSST_V5 data provided by the NOAA/OAR/ESRL PSD). A positive SSTA indicates above average temperatures (El Niño) and a negative SSTA indicates below average temperatures (La Niña). N/D = not detected.

Year	**SSTA**	**Al**	**As**	**Cd**	**Cr**	**Co**	**Cu**	**Fe**	**Pb**	**Mn**	**Hg**	**Ni**	**Se**	**Sn**	**V**	**Zn**
2009	0.65	4.67	0.06	0.004	0.02	0.001	0.75	7.77	0.02	0.01	0.013	0.01	0.29	N/D	0.004	1.89
2010	0.01	5.46	0.06	0.004	0.05	0.002	1.04	7.50	0.06	0.07	0.001	0.01	0.35	0.70	0.004	14.22
2011	0.30	5.93	0.06	0.002	0.04	0.001	0.85	4.82	0.09	0.02	0.004	0.01	0.29	0.09	0.002	1.72
2012	1.02	3.86	0.09	0.006	0.03	0.001	0.96	5.54	0.15	0.03	0.003	0.02	0.32	0.12	0.002	7.67
2013	-1.91	2.90	0.03	0.006	0.02	0.002	0.84	4.86	0.02	0.02	0.004	0.02	0.40	N/D	0.002	1.49
2014	1.54	4.93	0.07	0.005	0.04	0.004	0.95	7.27	0.07	0.08	0.003	0.04	0.38	1.29	0.004	37.9
2015	2.19	5.59	0.08	0.004	0.04	0.002	0.84	5.84	0.05	0.04	0.001	0.01	0.35	0.37	0.003	11.11
2016	0.64	4.81	0.08	0.002	0.02	0.001	1.06	4.87	0.02	0.02	0.001	0.02	0.34	N/D	0.001	1.66
2017	-0.24	3.63	0.04	0.001	0.04	0.006	1.04	7.45	0.03	0.02	N/D	0.03	0.33	N/D	0.004	1.50
2018	-0.72	3.46	0.02	0.001	0.04	0.001	0.76	7.41	0.04	0.02	N/D	0.02	0.32	N/D	0.002	1.66
2019	-0.34	6.17	0.05	0.024	0.03	0.001	0.85	3.79	0.09	0.03	0.003	0.01	0.32	N/D	0.002	1.25

Table 9. Mean Peruvian fur seal milk element concentrations by year (µg/g). Sea surface temperature anomaly (SSTA) is the Niño 1+2 index for June of the corresponding year (NOAA_ERSST_V5 data provided by the NOAA/OAR/ESRL PSD). A positive SSTA indicates above average temperatures (El Niño) and a negative SSTA indicates below average temperatures (La Niña). N/D = not detected.

Year	SSTA	Al	As	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Ni	Se	Sn	V	Zn
2011	0.30	4.89	0.36	0.005	0.09	0.003	1.92	4.40	0.04	0.06	0.002	0.03	0.27	0.05	0.005	7.35
2015	2.19	6.35	0.40	0.305	0.05	0.002	2.41	2.78	0.03	0.03	0.850	0.01	0.39	N/D	0.002	10.78
2019	-0.34	4.95	0.48	0.001	0.06	0.003	2.67	2.73	0.06	0.05	0.044	0.07	0.47	N/D	0.002	14.47

Table 10. Summary statistics for Peruvian fur seal female (n=49) and male (n=19) vibrissae (µg/g). 95% CI = 95% Confidence Interval of the mean, N/D = not detected, NS = no significant difference between sexes.

Peruvian fur seal vibrissae								
Element	**Sex**	**Mean**	**Standard Deviation**	**Median**	**95% CI**	**Range**	**Normal Distribution**	**p-value**
Al	Female	24.25	9.65	22.84	20.74-25.13	13.55-70.30	No	<0.001
	Male	16.47	4.71	16.10	14.20-18.74	9.28-25.95	Yes	
As	NS	0.19	0.120	0.19	0.15-0.22	N/D-0.50	Yes	0.115
Cd	Female	0.23	0.10	0.19	0.18-0.25	0.11-0.67	No	0.006
	Male	0.27	0.09	0.23	0.22-0.32	0.18-0.50	No	
Cr	NS	0.32	0.24	0.27	0.25-0.34	0.05-1.52	No	0.099
Co	NS	0.021	0.020	0.015	0.015-0.018	0.008-0.130	No	0.498
Cu	Female	20.74	1.89	20.71	20.19-21.28	15.96-24.74	Yes	<0.001
	Male	18.20	1.73	18.80	17.52-19.13	13.21-20.22	No	
Fe	Female	10.91	6.80	9.41	8.82-10.79	5.31-51.05	No	<0.001
	Male	7.30	2.14	6.51	6.15-8.45	4.38-11.41	No	
Pb	NS	0.12	0.06	0.10	0.10-0.12	0.04-0.51	No	0.465
Mn	Female	0.37	0.56	0.27	0.26-0.31	0.13-4.20	No	<0.001
	Male	0.20	0.06	0.18	0.17-0.23	0.13-0.31	No	
Hg	Female	1.93	0.84	2.01	1.62-2.11	0.58-4.65	No	<0.001
	Male	3.20	1.23	3.14	2.60-3.79	0.94-5.43	Yes	
Ni	NS	0.44	1.93	0.17	0.16-0.21	0.06-16.05	No	0.524
Se	Female	1.02	0.23	0.97	0.94-1.06	0.75-2.03	No	0.006
	Male	1.16	0.26	1.16	1.04-1.24	0.79-1.99	No	
Sn	Female	2.93	1.55	3.20	2.50-3.49	N/D-6.17	No	0.006
	Male	2.20	1.12	2.11	1.62-2.77	N/D-4.68	Yes	
V	Female	0.037	0.01	0.036	0.034-0.039	0.02-0.07	No	<0.001
	Male	0.024	0.009	0.022	0.019-0.028	0012-0.047	Yes	
Zn	Female	189.1	25.22	187.6	181.8-196.4	140.9-246.6	Yes	<0.001
	Male	167.1	16.83	170.4	159.0-175.2	127.5-194.2	Yes	

Table 11. Summary statistics for Peruvian fur seal female (n=76) and male (n=19) serum (µg/g). 95% CI = 95% Confidence Interval of the mean, N/D = not detected, NS = no significant difference between sexes.

Peruvian fur seal serum								
Element	**Sex**	**Mean**	**Standard Deviation**	**Median**	**95% CI**	**Range**	**Normal Distribution**	**p-value**
Al	NS	5.19	4.24	3.75	3.69-4.67	2.22-33.00	No	0.632
As	Female	0.064	0.025	0.060	0.057-0.068	N/D-0.149	No	<0.001
	Male	0.09	0.03	0.08	0.08-0.10	0.03-0.17	Yes	
Cd	NS	0.008	0.034	0.002	0.002-0.004	N/D-0.332	No	0.763
Cr	NS	0.035	0.027	0.029	0.025-0.035	0.003-0.141	No	0.450
Co	NS	0.0016	0.0017	0.0012	0.0011-0.0015	0.0007-0.0154	No	0.095
Cu	Female	0.88	0.31	0.86	0.81-0.88	N/D-2.93	No	0.001
	Male	1.02	0.24	0.98	0.91-1.14	0.64-1.11	Yes	
Fe	NS	5.64	3.94	4.64	4.48-5.95	1.23-27.28	No	0.976
Pb	NS	0.08	0.18	0.02	0.03-0.06	0.003-1.32	No	0.159
Mn	NS	0.03	0.09	0.01	0.01-0.02	0.005-0.759	No	0.580
Hg	NS	0.0029	0.0028	0.0026	0.0016-0.0035	N/D-0.0126	No	0.159
Ni	NS	0.015	0.020	0.008	0.008-0.013	N/D-0.108	No	0.109
Se	NS	0.32	0.05	0.32	0.30-0.32	0.18-0.51	No	0.798
Sn	NS	0.40	0.50	0.17	0.05-1.29	N/D-1.29	No	N/A
V	Female	0.003	0.003	0.002	0.002-0.003	N/D-0.003	No	0.014
	Male	0.003	0.004	0.001	0.001-0.003	N/D-0.017	No	
Zn	NS	7.93	36.01	1.34	1.35-1.59	0.81-291.7	No	0.138

Hg, Se, Sn, V, and Zn (Figure 4). Female PFS vibrissae had significantly higher concentrations than males for Al (26.25, 16.47 μg/g, respectively; $p<0.001$), Cu (20.74, 18.20 μg/g, respectively; $p<0.001$), Fe (10.91, 7.30 μg/g, respectively; $p<0.001$), Mn (0.37, 0.20 μg/g, respectively; $p<0.001$), Sn (2.93, 2.20 μg/g, respectively; $p = 0.006$), V (0.04, 0.02 μg/g, respectively; $p<0.001$), and Zn (189.1, 167.1 μg/g, respectively; $p<0.001$). Females sampled were reproductively active adults and an increase of essential elements compared to adult males may be linked to the increased metabolic demand and mobilization of adipose stores needed for proper development of the fetus and lactation. Female vibrissae had significantly lower concentrations than male vibrissae for Cd (0.23, 0.27 μg/g, respectively; $p = 0.006$), Hg (1.93, 3.20 μg/g, respectively; $p<0.001$), and Se (1.02, 1.16 μg/g, respectively; $p = 0.006$). Some contaminants such as Cd and Hg are offloaded into keratinous tissues such as vibrissae (Habran et al., 2013). Since females have other offloading mechanisms via gestation and lactation, they may accumulate lower concentrations of non-essential elements in vibrissae than males. Higher fur concentrations of Hg, Cd, and Se in males compared to females was also found in harbor seals and leopard seals (Wenzel et al., 1993; Brookens et al., 2007; Gray et al., 2008). However, Gray et al. (2008) did find higher Mn concentrations in male leopard seals which contradicts our findings for vibrissae of PFS and SASL.

Element concentrations in PFS serum were significantly different between females (n=76) and males (n=19) for As, Cu, and V (Figure 5). Female PFS serum had significantly higher concentrations of V than males (0.0027, 0.0026 μg/g, respectively; $p = 0.01$). Female serum had significantly lower concentrations than males for As (0.06, 0.09 μg/g, respectively; $p<0.001$) and Cu (0.88, 1.02 μg/g, respectively; $p = 0.001$). Serum concentrations reflect recent exposure of days to months, while vibrissae reflect long-term exposure of up to 7 years. Less variation in the concentrations of elements in serum compared to vibrissae between sexes may indicate that at the time of sample collection, the uptake of elements did not vary significantly, but the overall accumulation of trace elements throughout the year does vary. Male and female PFS had some overlap for years of collection (2011 and 2012), but the difference in sampling years could have an impact on element concentrations since the Peruvian ecosystem can change drastically from year to year. Since serum samples indicate current circulation concentrations, they are more sensitive to environmental changes than vibrissae.

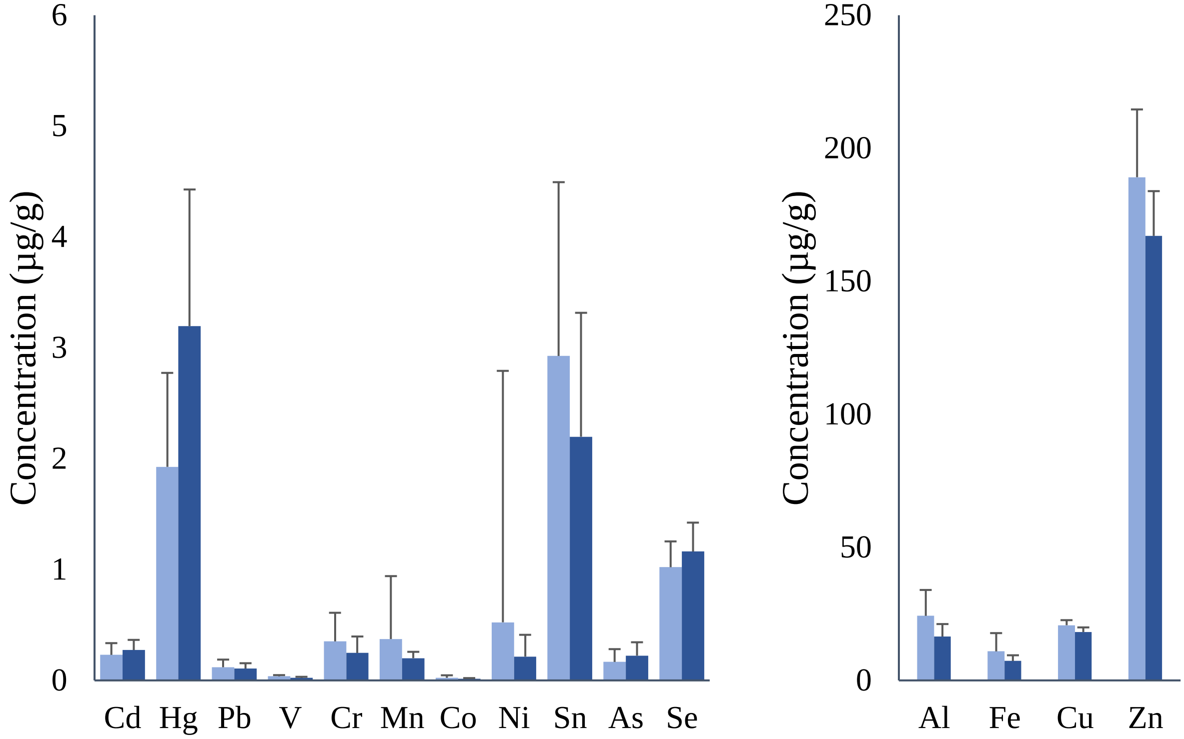

Figure 4. Mean vibrissae trace element concentrations (µg/g) for adult Peruvian fur seal females (light blue) and males (dark blue). Error bars correspond to standard deviation.

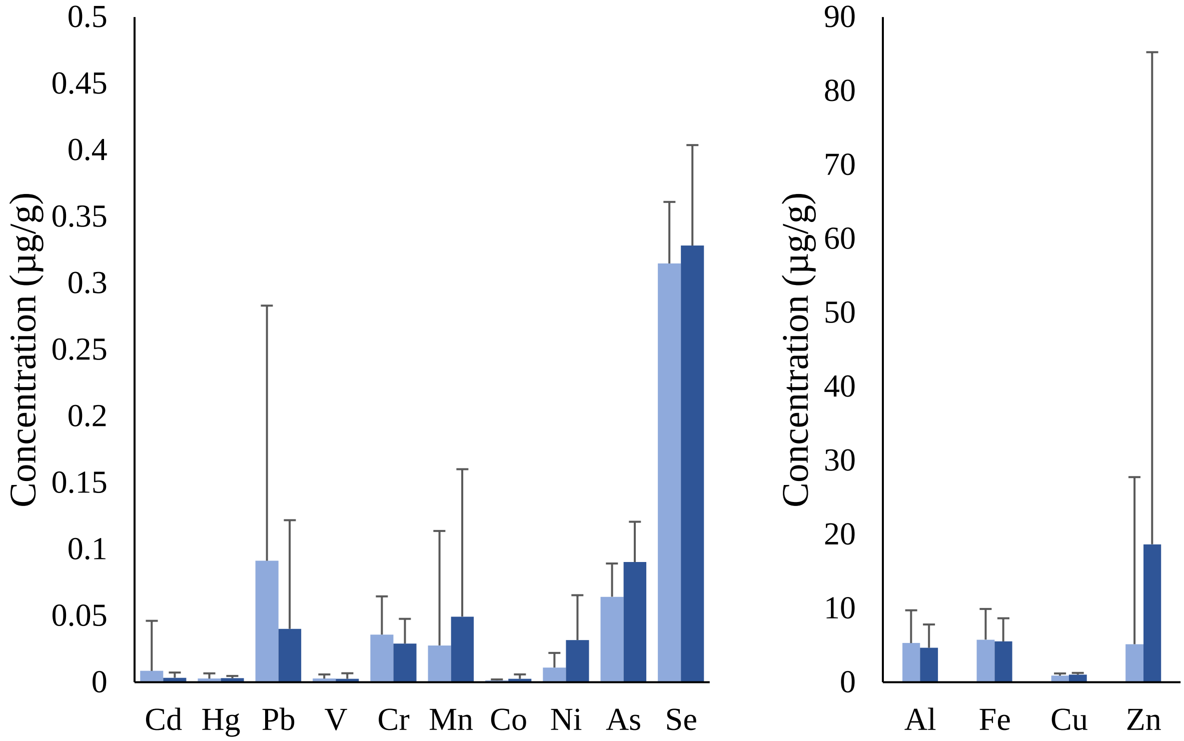

Figure 5. Mean serum trace element concentrations (µg/g) for adult Peruvian fur seal females (light blue) and males (dark blue). Error bars correspond to standard deviation. Tin was not analyzed.

Adult male PFS vibrissae and serum were collected in 2011 (n=4), 2012 (n=5), 2014 (n=4), and 2016 (n=6). Male vibrissae significantly differed between years for As, Cd, and Hg (Figure 6). Concentrations of Cd and Hg were significantly higher in 2011 than 2012, 2014, and 2016 (0.43, 0.25, 0.21, 0.24 μg/g, $F(3) = 15.467$, $p<0.001$; 4.93, 2.05, 3.40, 2.86 μg/g, $F(3) = 12.014$, $p<0.001$, respectively). Arsenic concentrations in vibrissae were significantly lower in 2012 (0.10 μg/g) than 2016 (0.31 μg/g; $F(3) = 4.575$, $p = 0.02$). Male PFS vibrissae represented approximately 4 years of growth. The effects of a strong La Niña from 2007 may be represented in 2011 vibrissae. A strong La Niña also occurred in 2013, but the strong and extreme El Niño in 2014 and 2015, respectively may be masking the La Niña in the 2014 and 2016 vibrissae. The high Cd and Hg in 2011 vibrissae may indicate higher accumulations of these elements during La Niña. Cadmium and Hg are mainly accumulated from prey such as squid and fish which is more abundant during La Niña (Gerpe et al., 2000).

Male serum samples only significantly differed between years for cobalt (Figure 7). Cobalt concentrations in 2014 (0.007 μg/g) were significantly higher than concentrations in 2011, 2012, and 2016 (0.001, 0.002, 0.001 μg/g, respectively; $F(3) = 8.069$, $p = 0.002$). The increase in serum Co levels in 2014 may be linked to the moderate to strong El Niño that year while in 2011, 2012, and 2016 when samples were collected (November) the sea surface temperature anomaly was within ±1^{o} C.

Adult female PFS serum was collected in 2009 (n=11) and 2010 (n=15), while both vibrissae and serum were collected in 2011 (vibrissae n=12, serum n=13), 2012 (n=15), 2015 (n=6), and 2019 (n=16). Female vibrissae element concentrations significantly differed between years for Al, As, Cr, Cu, Hg, Ni, Se, and Sn (Figure 8). Concentrations from 2012 were significantly higher than 2019 for Al (30.15, 20.40 μg/g, respectively; $F(3) = 3.798$, $p = 0.02$) and Cr (0.49, 0.20 μg/g, respectively; $F(3) = 6.295$, $p = 0.001$). Arsenic concentrations were significantly lower in 2011 (0.03 μg/g) and 2012 (0.06 μg/g) compared to 2019 (0.026 μg/g; $X^2(3) = 24.599$, $p<0.001$). The 2015 vibrissae samples (19.07 μg/g) had significantly lower Cu concentrations than 2019 (21.69 μg/g; $X^2(3) = 9.230$, $p = 0.03$), while Hg concentrations in 2011 (2.42 μg/g) and 2019 (2.11 μg/g) were significantly higher than 2012 samples (1.24 μg/g; $X^2(3) = 14.646$, $p = 0.002$). The antagonist effect of Se on Hg is reflected in the significantly lower concentrations in 2012 (0.89 μg/g) compared to 2019 concentrations (1.12 μg/g; $X^2(3) = 12.220$,

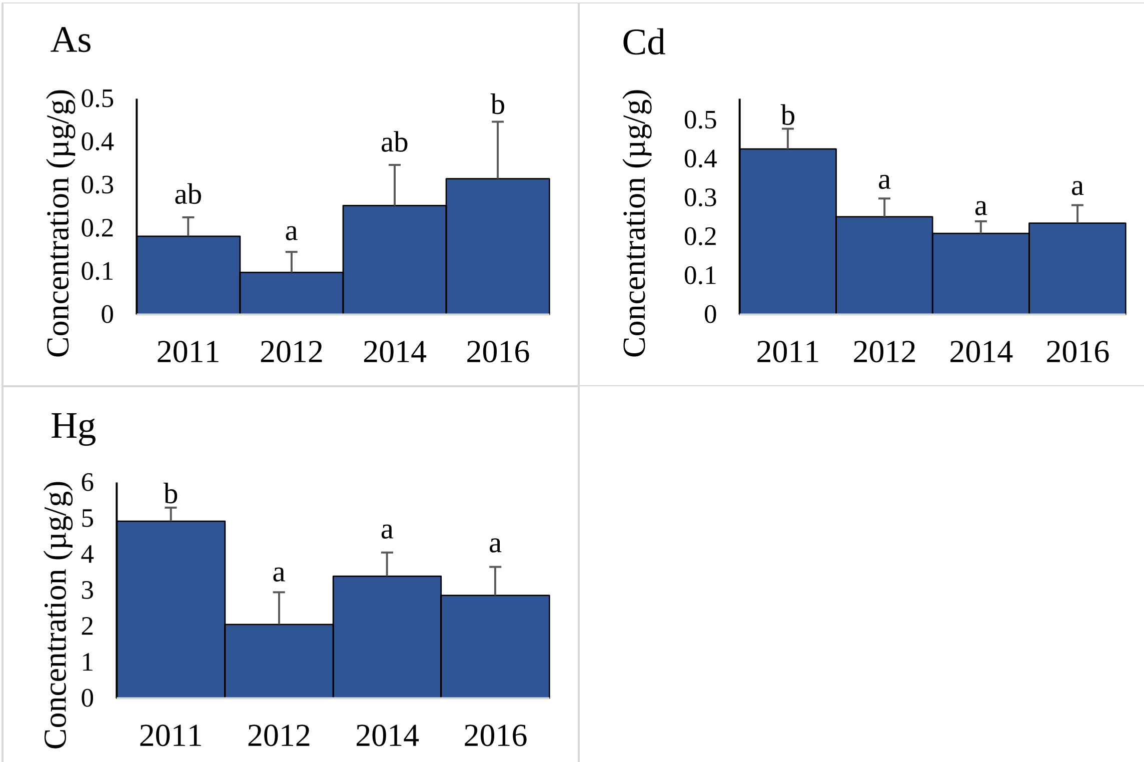

Figure 6. Mean vibrissae concentrations (µg/g) for trace elements that significantly differed between years in Peruvian fur seal males. For each element, years with the same letter are not significantly different from each other. Error bars correspond to standard deviation.

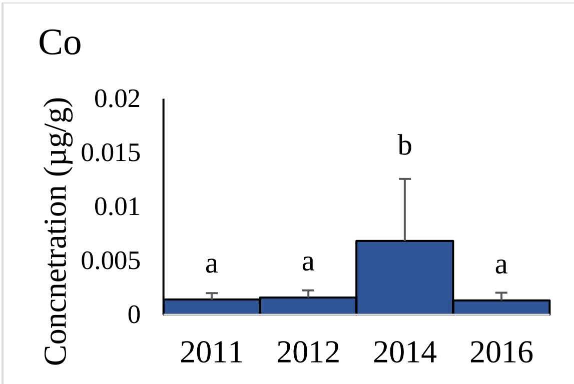

Figure 7. Mean serum concentrations (µg/g) for cobalt in Peruvian fur seal males by year. Cobalt was the only trace element that significantly differed between years. Years with the same letter are not significantly different from each other. Error bars correspond to standard deviation.

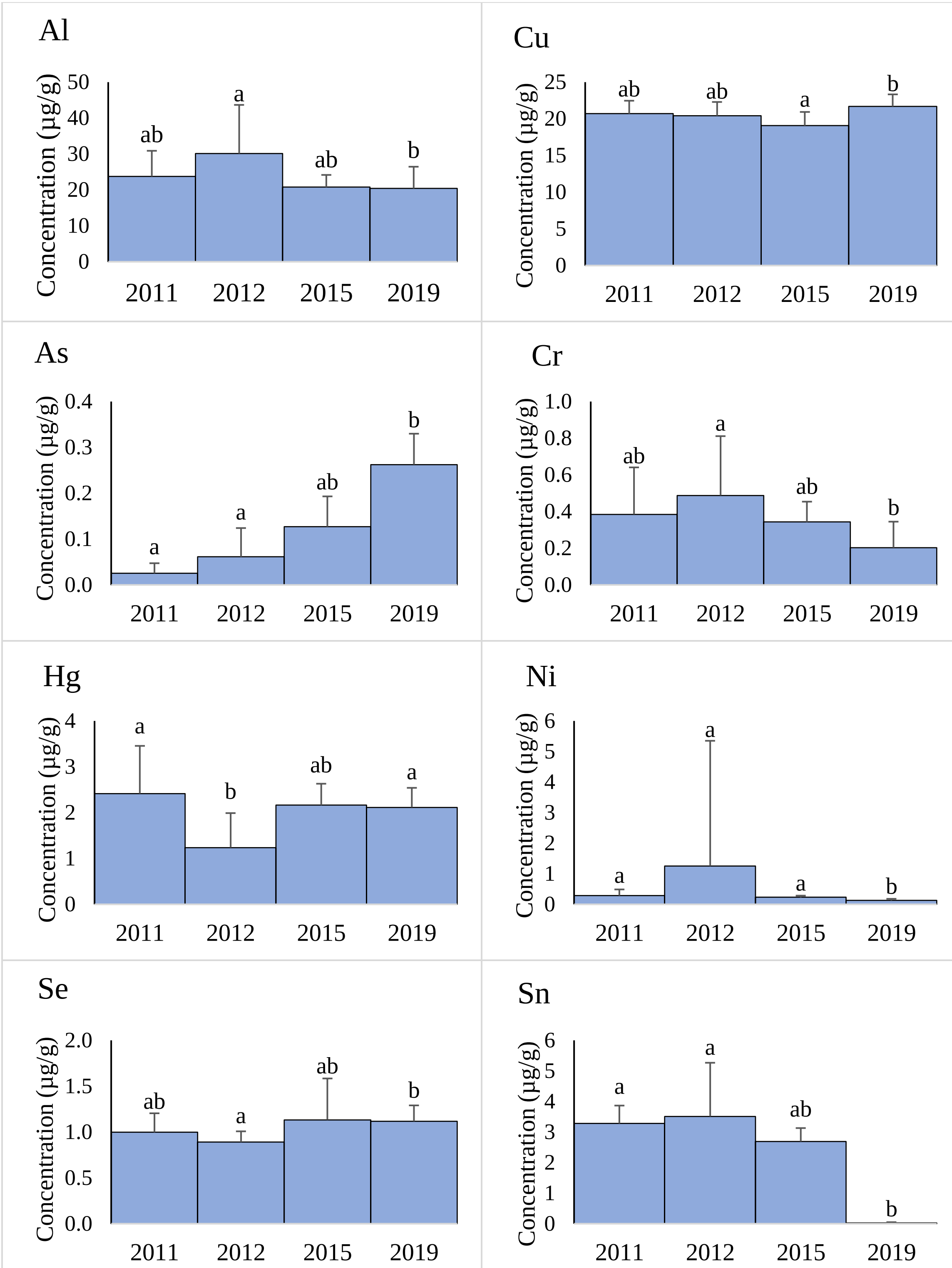

Figure 8. Mean vibrissae concentrations (µg/g) for trace elements that significantly differed between years in Peruvian fur seal females. For each element, years with the same letter are not significantly different from each other. Error bars correspond to standard deviation.

p = 0.007). Nickel concentrations in 2019 (0.13 μg/g) vibrissae were significantly lower than 2011, 2012, and 2015 (0.28, 1.26, 0.23 μg/g, respectively; $X^2(3) = 16.508$, $p<0.001$). Tin concentrations in 2011 (3.28 μg/g) and 2012 (3.51 μg/g) were significantly higher than 2019 (0.02 μg/g; $X^2(3) = 13.887$, $p = 0.003$).

Vibrissae As concentrations increased throughout the years sampled for both male and female PFS. The main source of As into the environment is through Cu smelting (Matschullat, 2000). There is a Cu smelting facility on the coast, south of PSJ in Ilo, Peru. Since the Humboldt current flows from south to north, contaminants from the smelting facility may travel north to Peruvian pinniped foraging grounds. The growing agricultural industry in Peru may also be a contributor to rising As concentrations through agricultural runoff (Tchounwou et al., 2012; Bedoya-Perales et al., 2018). Female PFS vibrissae represented an average of 3.5 years of growth. The 2015 vibrissae contain data from the middle of 2012 to 2015 which includes a moderate, strong, and extreme El Niño as well as a strong La Niña. The strong La Niña may be masking element concentration fluctuations from the strong and extreme El Niño years. In respect to SSTA, 2011 and 2012 vibrissae reflect very similar fluctuations, 2011 vibrissae include a moderate El Niño in 2008, but another moderate El Niño occurred in 2012. The variations in concentrations among years may be partially due to individual variations.

Female serum element concentrations significantly differed between years for As, Cu, Fe, Pb, Ni, Se, V, and Zn (Figure 9). Arsenic serum concentrations in 2010 (0.062 μg/g) were significantly higher than concentrations in 2011 (0.046 μg/g), and concentrations in 2012 (0.09 μg/g) and 2015 (0.09 μg/g) were significantly higher than 2009 (0.06 μg/g), 2010 (0.06 μg/g), 2011 (0.05 μg/g), and 2019 (0.05 μg/g; $F(5) = 11.847$, $p<0.001$). Copper serum concentrations in 2009 (0.75 μg/g) were significantly lower than concentrations in 2010 (1.04 μg/g) and 2012 (1.00 μg/g; $X^2(5) = 20.141$, $p = 0.001$). Iron concentrations were significantly higher in 2009 (7.77 μg/g) compared to 2019 (3.79 μg/g; $X^2(5) = 13.169$, $p = 0.02$). Lead concentrations in 2019 (0.09 μg/g) were significantly higher than 2009 (0.02 μg/g), 2011 (0.11 μg/g; without an outlier 0.01 μg/g), and 2015 (0.02 μg/g; $X^2(5) = 23.475$, $p<0.001$). Nickel concentrations in 2009 (0.005 μg/g) were significantly lower than 2019 (0.012 μg/g; $X^2(5) = 14.148$, $p = 0.01$). For Se, concentrations from 2010 (0.35 μg/g) were significantly higher than 2009 (0.28 μg/g) and 2011 (0.29 μg/g; $F(5) = 4.418$, $p = 0.001$). Vanadium concentrations from 2009 (0.004 μg/g) were significantly higher than 2012 (0.002 μg/g) and 2019 (0.002 μg/g; $X^2(5) = 20.229$, $p = 0.001$).

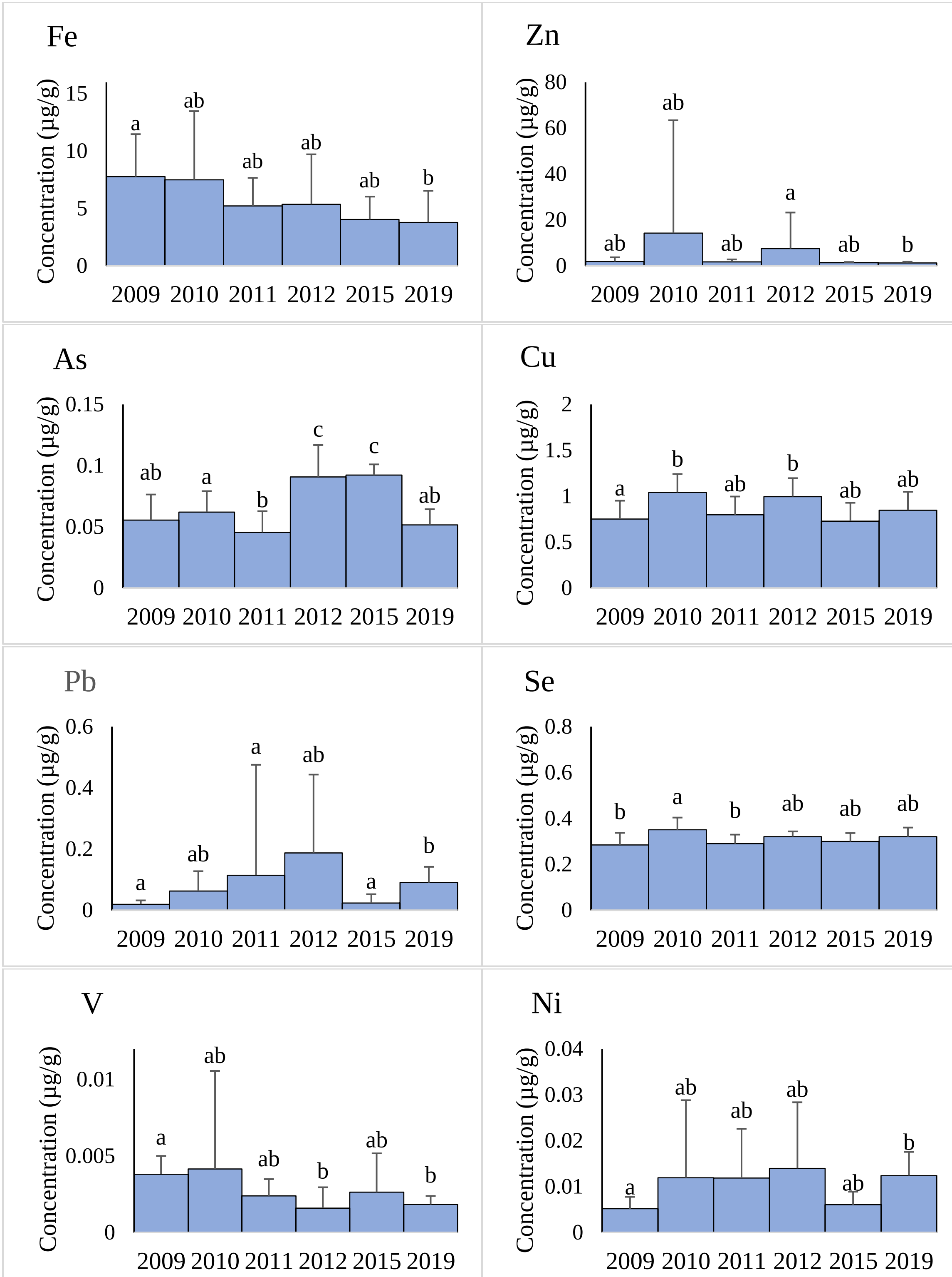

Figure 9. Mean serum concentrations (µg/g) for trace elements that significantly differed between years in Peruvian fur seal females. For each element, years with the same letter are not significantly different from each other. Error bars correspond to standard deviation.

Zinc concentrations from 2012 (7.53 μg/g) were significantly higher than 2019 concentrations (1.23 μg/g; $X^2(5) = 12.171$, $p = 0.03$).

Arsenic serum concentrations were significantly higher in 2012 and 2015 which correspond to a moderate and extreme El Niño, respectively. Increased rain and runoff during El Niño may increase As contamination throughout the food web, bioaccumulating in pinnipeds. Serum concentrations of Fe and V decreased from 2009 to 2019. The significant difference in Fe concentrations from 2009 to 2019 may be due to more highly hemolyzed serum samples in 2009 (6 of 11 samples categorized as 3 or 4) compared to 2019 (2 of 16 samples categorized as 3 or 4).

3.4. South American sea lions

Summary statistics for SASL vibrissae and serum concentrations, including if data were normally distributed, are presented in Tables 12 and 13. Two-sample t-tests and Mann-Whitney Wilcoxon tests determined differences between vibrissae and serum in adult female and male SASL. Mercury and Sn were not analyzed for serum and Sn was not analyzed for male vibrissae due to insufficient sample size. Vibrissae element concentrations were significantly different between females (n=14) and males (n=17) for Al, As, Cd, Cu, Mn, Hg, Sn, V, and Zn (Figure 10). Female SASL vibrissae concentrations were significantly higher than males for Al (24.95, 19.20 μg/g, respectively; $p = 0.002$), As (0.47, 0.15 μg/g, respectively; $p<0.001$), Cu (15.21, 14.10 μg/g, respectively; $p = 0.03$), Mn (0.25, 0.21 μg/g, respectively; $p = 0.04$), Sn (2.79, 0.56 μg/g, respectively; $p<0.001$), and Zn (168.4, 126.4 μg/g, respectively; $p<0.001$). Conversely, female vibrissae concentrations were significantly lower than males for Cd (0.51, 1.31 μg/g, respectively; $p<0.001$), Hg (1.18, 3.26 μg/g, respectively; $p<0.001$), and V (0.10, 0.16 μg/g, respectively; $p = 0.01$). SASL serum concentrations for females (n=14) were significantly lower than males (n=17) for As (0.03, 0.05 μg/g, respectively; $p = 0.01$), Cd (0.001, 0.005 μg/g, respectively; $p<0.001$), and Se (0.32, 0.39 μg/g, respectively; $p<0.001$; Figure 11).

Differences between sexes were similar for PFS and SASL with females of both species having higher vibrissae concentrations of Al, Cu, Mn, Sn, and Zn and lower vibrissae concentrations of Cd and Hg compared to males. In serum, As was lower in females than males for both species. However, SASL female vibrissae had As concentrations three times higher than males (more than 2x higher than PFS). Female SASL forage in very coastal, shallow water compared to PFS males and females and SASL males (Cárdenas-Alayza pers. com.). This may increase year-round exposure to agricultural runoff, a major contributor of As to the

Table 12. Summary statistics for South American sea lion female (n=14) and male (n=17) vibrissae (µg/g). 95% CI = 95% Confidence Interval of the mean, N/D = not detected, NS = no significant difference between sexes.

South American sea lion vibrissae								
Element	**Sex**	**Mean**	**Standard Deviation**	**Median**	**95% CI**	**Range**	**Normal Distribution**	**p-value**
Al	Female	24.95	7.19	23.54	20.79-29.10	13.66-40.00	Yes	0.002
	Male	19.20	14.96	15.84	13.26-20.35	4.69-72.90	No	
As	Female	0.47	0.18	0.42	0.36-0.57	0.21-0.81	Yes	<0.001
	Male	0.15	0.16	0.10	0.08-0.18	0.03-0.70	No	
Cd	Female	0.51	0.21	0.43	0.35-0.61	0.27-0.85	No	<0.001
	Male	1.31	1.63	0.79	0.70-1.32	0.22-7.34	No	
Cr	NS	0.35	0.24	0.28	0.23-0.43	0.05-0.97	No	0.276
Co	NS	0.017	0.011	0.013	0.012-0.016	0.009-0.063	No	0.922
Cu	Female	15.21	0.79	15.12	14.75-15.67	14.24-16.97	Yes	0.032
	Male	14.10	2.13	14.25	13.01-15.20	9.45-17.95	Yes	
Fe	NS	10.58	6.72	8.55	8.10-11.05	4.31-40.10	No	0.530
Pb	NS	0.22	0.51	0.09	0.08-0.14	0.03-2.93	No	0.570
Mn	Female	0.25	0.15	0.21	0.17-0.30	0.11-0.69	No	0.018
	Male	0.21	0.22	0.14	0.12-0.24	0.08-099	No	
Hg	Female	1.18	0.36	1.10	0.97-1.38	0.55-2.06	Yes	<0.001
	Male	3.26	1.24	2.81	2.63-3.90	1.64-5.46	Yes	
Ni	NS	0.49	0.23	0.43	0.38-0.57	0.16-1.08	No	0.661
Se	NS	1.95	0.37	1.90	1.82-2.08	1.30-2.78	Yes	0.208
Sn	Female	2.79	0.68	2.89	2.39-3.18	1.24-3.71	Yes	<0.001
	Male	0.56	0.96	0.04	0.02-1.21	N/D-2.65	No	
V	Female	0.103	0.024	0.095	0.089-0117	0.074-0.162	Yes	0.015
	Male	0.16	0.10	0.13	0.08-0.47	0.08-0.47	No	
Zn	Female	168.4	28.82	169.0	151.8-185.1	110.7-228.0	Yes	<0.001
	Male	126.5	33.80	128.8	109.1-143.8	66.22-183.4	Yes	

Table 13. Summary statistics for South American sea lion female (n=14) and male (n=17) serum (µg/g). 95% CI = 95% Confidence Interval of the mean, N/D = not detected, NS = no significant difference between sexes.

South American sea lion serum								
Element	**Sex**	**Mean**	**Standard Deviation**	**Median**	**95% CI**	**Range**	**Normal Distribution**	**p-value**
Al	NS	4.21	2.10	3.46	3.32-4.31	2.65-11.82	No	0.544
As	Female	0.03	0.01	0.03	0.02-0.03	0.01-0.05	Yes	0.010
	Male	0.05	0.05	0.04	0.03-0.05	0.02-0.23	No	
Cd	Female	0.0013	0.0009	0.0011	0.0008-0.0019	0.0004-0.0033	No	<0.001
	Male	0.0051	0.0069	0.0029	0.0022-0.0058	0.0007-0.0302	No	
Cr	NS	0.034	0.023	0.029	0.024-0.040	0.007-0.105	No	0.179
Co	NS	0.0027	0.0049	0.0017	0.0015-0.0021	0.0007-0.0286	No	0.444
Cu	NS	0.86	0.24	0.81	0.78-0.91	0.31-1.58	No	0.670
Fe	NS	6.90	3.63	5.57	5.18-8.21	1.64-14.99	No	0.875
Pb	NS	0.039	0.055	0.023	0.017-0.033	0.005-0.240	No	0.774
Mn	NS	0.028	0.057	0.016	0.015-0.021	0.009-0.335	No	0.421
Hg*	Male	0.002	0.003	0.001	0.001-0.004	N/D-0.011	No	N/A
Ni	NS	0.019	0.020	0.009	0.007-0.026	0.002-0.071	No	0.053
Se	Female	0.32	0.03	0.33	0.31-0.34	0.25-0.37	Yes	<0.001
	Male	0.39	0.04	0.39	0.36-0.41	0.31-0.44	Yes	
V	NS	0.0029	0.0025	0.0027	0.0020-0.0030	0.0009-0.0137	No	0.569
Zn	NS	6.20	26.15	1.44	1.36-1.56	0.92-147.1	No	0.444

*Mercury was only detected in South American sea lion males.

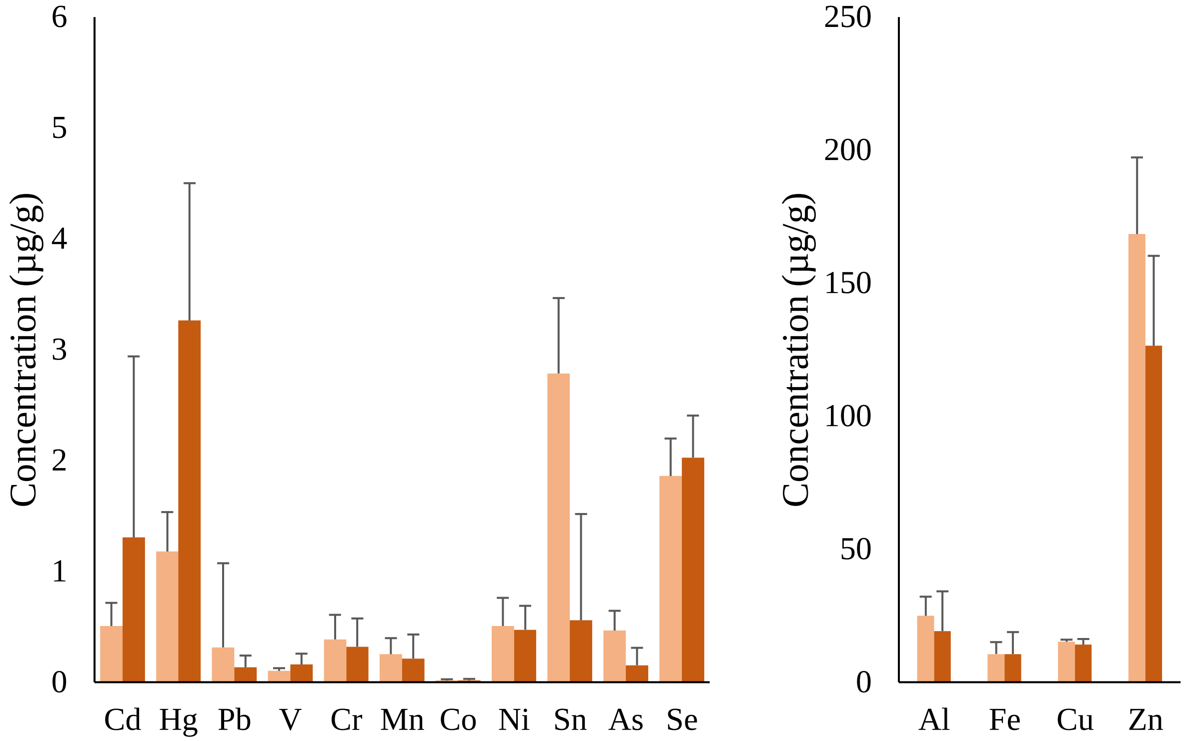

Figure 10. Mean vibrissae trace element concentrations (µg/g) for South American sea lion females (light orange) and males (dark orange). Error bars correspond to standard deviation.

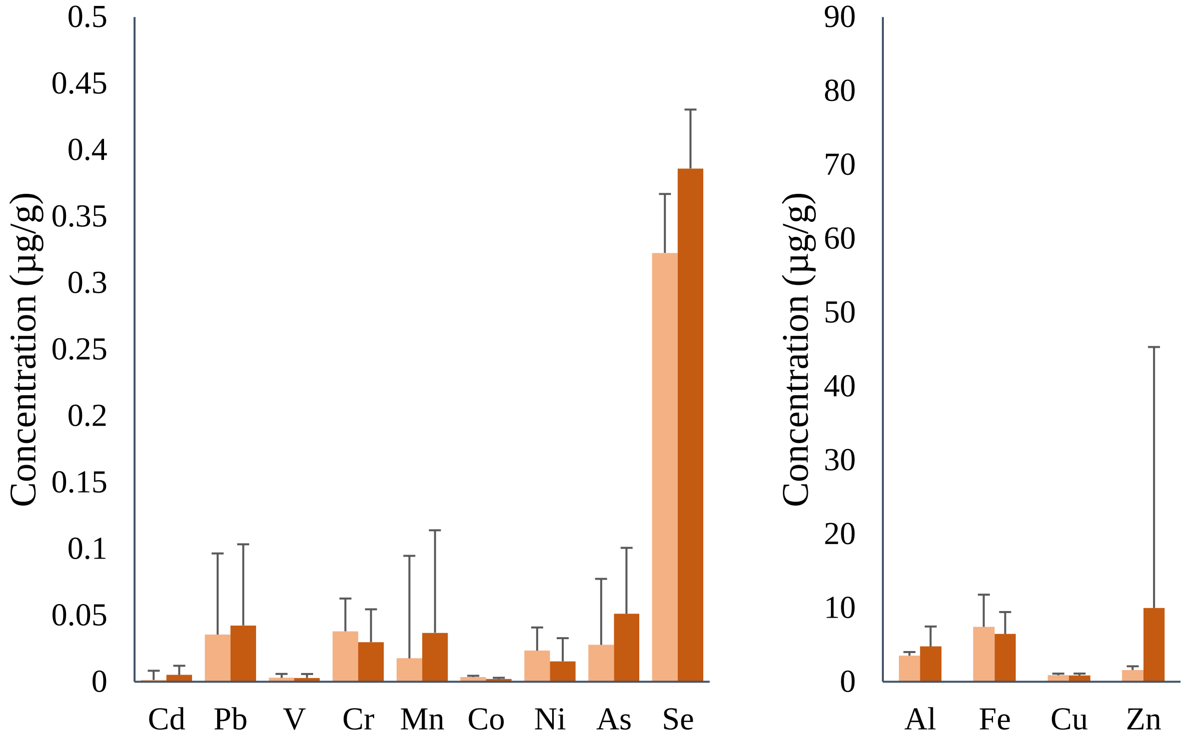

Figure 11. Mean serum trace element concentrations (µg/g) for South American sea lion females (light orange) and males (dark orange). Error bars correspond to standard deviation. Mercury and tin were not analyzed.

environment for SASL females, leading to higher accumulation of As in vibrissae. Female SASL had higher vibrissae As concentrations but lower serum As concentrations compared to males. High levels of As can be offloaded by females through lactation, as seen in the PFS milk samples. Since SASL females are lactating when samples are collected, As concentrations may be lower in serum even though females may be exposed to higher As concentrations than males year-round.

Adult male SASL vibrissae and serum were collected in 2013 (n=4), 2014 (n=4), and 2015 (n=9). Concentrations of Mn, Hg, and Se varied significantly in male vibrissae (Figure 12). Concentrations of Hg and Se in the vibrissae were significantly higher in 2013 (4.60, 2.46 μg/g, respectively) than 2015 (2.55 μg/g, $F(2) = 6.840$, $p = 0.008$; 1.82 μg/g, $F(2) = 6.795$, $p = 0.009$, respectively). Manganese concentrations from 2014 (0.10 μg/g) were significantly lower than concentrations from 2015 (0.29 μg/g; $X^2(2) = 9.294$, $p = 0.01$). Male serum significantly differed between years for Al and Mn (Figure 13). Aluminum concentrations from 2013 (2.90 μg/g) were significantly lower than 2015 (6.31 μg/g; $X^2(2) = 10.206$, $p = 0.006$). Manganese serum concentrations from 2014 (0.01 μg/g) were significantly lower than 2015 (0.06 μg/g; $X^2(2) = 10.187$, $p = 0.006$).

Male SASL vibrissae represent an average of 8 years in 2013 and 5.5 years in 2014 and 2015. Sample collection for SASL occurred in February; therefore, 2015 samples do not include the extreme El Niño. However, the largest SSTA difference during this study period occurred from June 2013 (-1.91 SSTA) to June 2014 (1.54 SSTA). This dramatic SST increase is reflected in 2015 vibrissae samples and is likely linked to the significantly lower Hg and Se and higher Mn concentrations in 2015. The significant increase of Al and Mn in 2015 serum samples were also likely caused by the rapid transition from a strong La Niña to a strong El Niño in one year.

Adult female SASL vibrissae and serum were collected in 2017 (n=6) and 2018 (n=8). Vibrissae concentrations from 2017 were significantly higher than 2018 for Cd (0.67, 0.38 μg/g, respectively; $p = 0.004$), Co (0.018, 0.016 μg/g, respectively; $p = 0.03$), Mn (0.28, 0.23 μg/g, respectively; $p = 0.01$), and V (0.12, 0.09 μg/g, respectively; $p = 0.03$). Female vibrissae concentrations from 2017 were significantly lower than 2018 for As (0.37, 0.54 μg/g, respectively; $p = 0.03$) and Cu (14.72, 15.58 μg/g, respectively; $p = 0.01$) (Figure 14). Female serum concentrations from 2017 were significantly higher than 2018 for As (0.04, 0.02 μg/g,

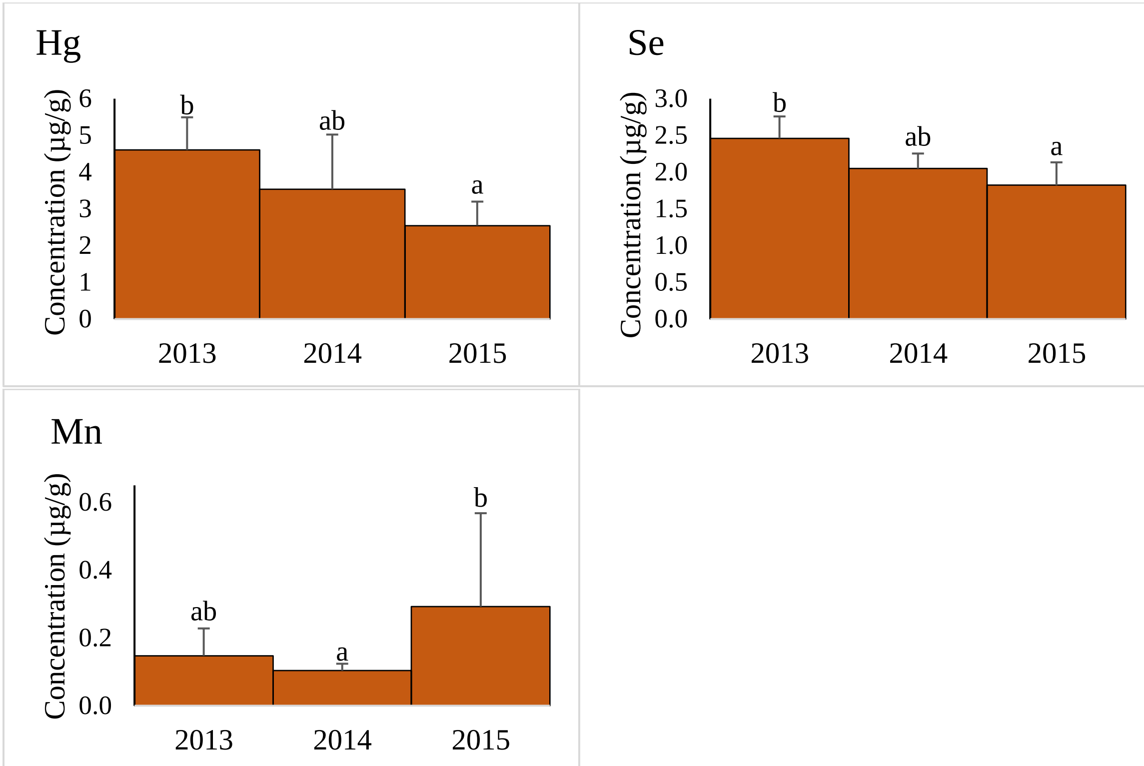

Figure 12. Mean vibrissae concentrations (µg/g) for trace elements that significantly differed between years in South American sea lion males. For each element, years with the same letter are not significantly different from each other. Error bars correspond to standard deviation.

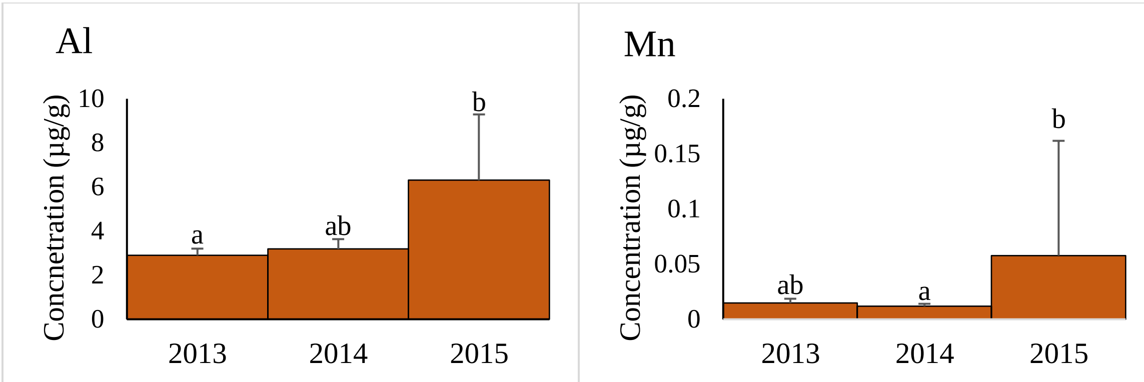

Figure 13. Mean serum concentrations (µg/g) for trace elements that significantly differed between years in South American sea lion male. For each element, years with the same letter are not significantly different from each other. Error bars correspond to standard deviation.

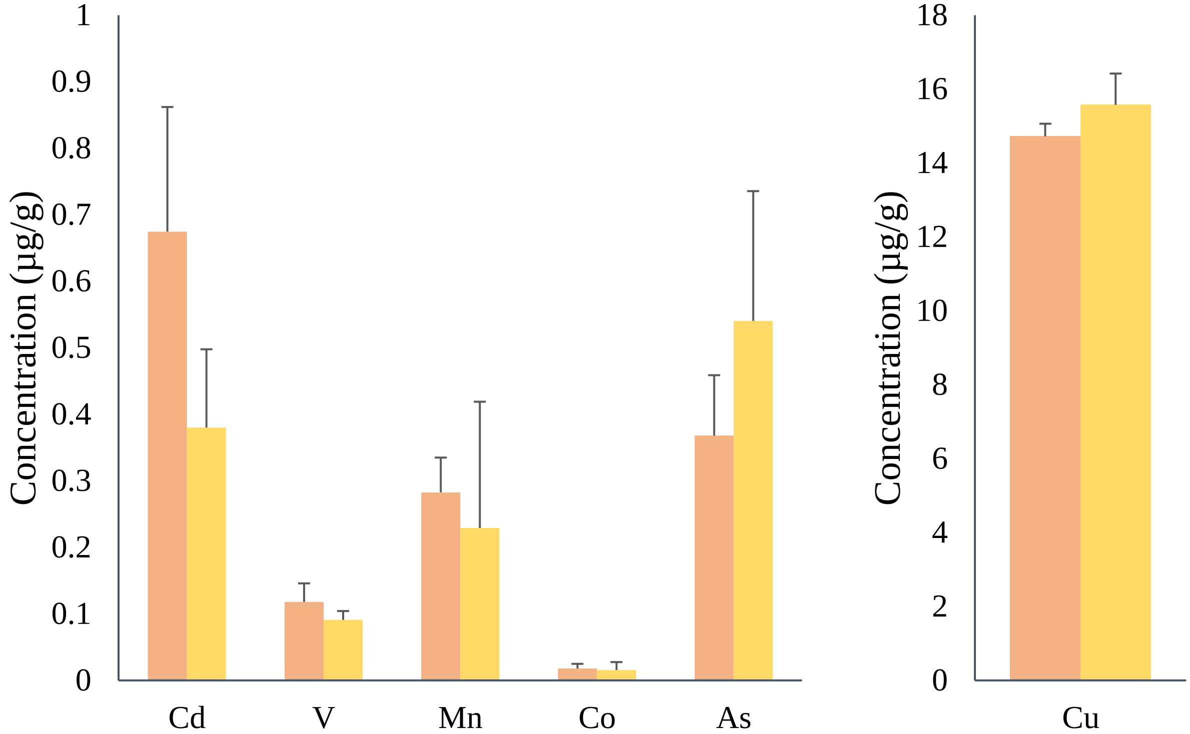

Figure 14. Mean vibrissae concentrations (µg/g) for trace elements that significantly differed between 2017 (orange) and 2018 (yellow) in South American sea lion females. Error bars correspond to standard deviation.

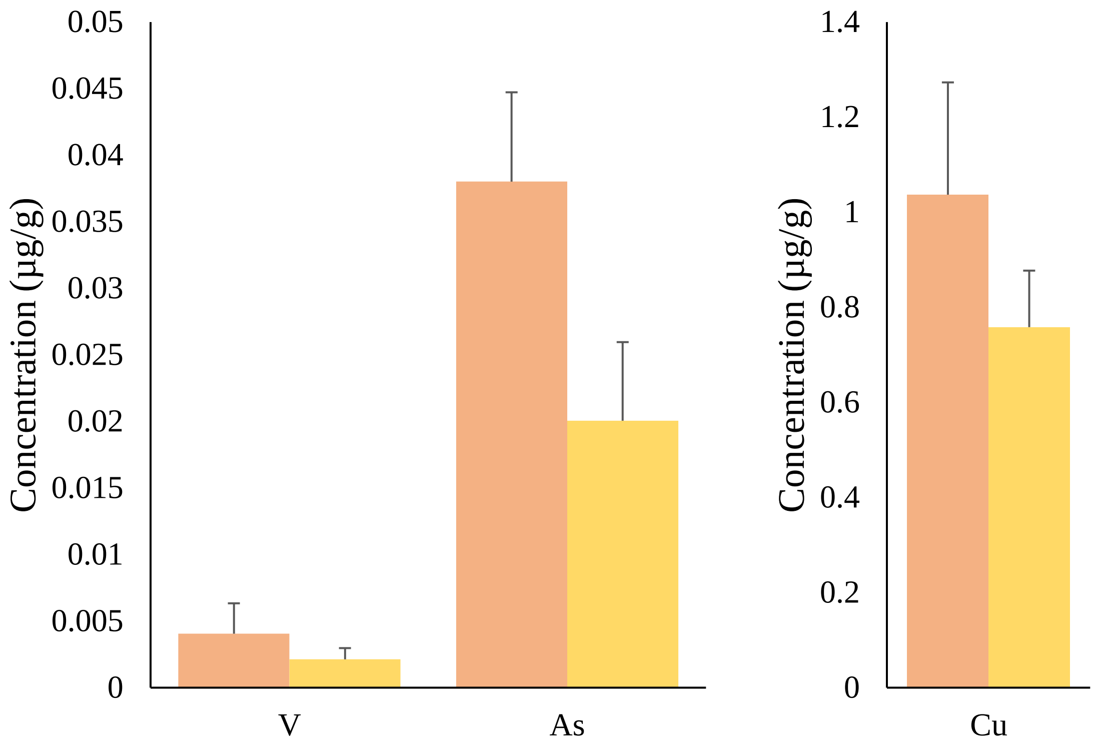

Figure 15. Mean serum concentrations (µg/g) for trace elements that significantly differed between 2017 (orange) and 2018 (yellow) in South American sea lion females. Error bars correspond to standard deviation.

respectively; $p<0.001$), Cu (1.04, 0.76 μg/g, respectively; $p = 0.004$), and V (0.004, 0.002 μg/g, respectively; $p = 0.02$; Figure 15).

Female vibrissae samples represent an average of 5.5 years. The 2018 samples were collected in April, two months later into the breeding and pupping season than in 2017. This could impact contaminant concentrations and potentially explain differences in trace elements in serum. Element concentrations can change in dam blood during lactation which may have influenced SASL serum concentrations in 2018 (Habran et al., 2011, 2013). The increase in As in SASL female vibrissae was also seen in PFS and discussed in the previous section. An increase in Cu vibrissae concentrations was seen in PFS females from 2015 to 2019 and may be linked to agricultural runoff as females tend to forage closer to the rookery year-round.

3.5. Peruvian pinniped species differences

Adult PFS vibrissae concentrations across all years and both sexes were significantly higher than SASL concentrations for Co, Cu, Mn, Sn, and Zn ($p = 0.03$, $p<0.001$, $p<0.001$, $p = 0.006$, $p<0.001$, respectively). PFS vibrissae concentrations across all years and both sexes were significantly lower than SASL for As, Cd, Ni, Se, and V ($p = 0.03$, $p<0.001$, $p<0.001$, $p<0.001$, $p<0.001$, respectively). Across all years and both sexes, PFS serum concentrations were significantly higher than SASL concentrations for As and Cd ($p<0.001$, $p = 0.03$, respectively), while PFS concentrations were significantly lower than SASL for Co, Fe, and Se ($p<0.001$, $p = 0.01$, $p<0.001$, respectively). Mean element concentrations for both species and sample types are presented in Table 4.

Two-sample t-tests and Mann-Whitney Wilcoxon tests determined differences between species for vibrissae and serum. Adult PFS male vibrissae concentrations were significantly higher than SASL male vibrissae concentrations for As (0.22, 0.15 μg/g, respectively; $p = 0.01$), Cu (18.20, 14.10 μg/g, respectively; $p<0.001$), Sn (2.20, 0.56 μg/g, respectively; $p = 0.001$), and Zn (167.1, 126.4 μg/g, respectively; $p<0.001$). PFS male vibrissae concentrations were significantly lower than SASL male concentrations for Cd (0.27, 1.31 μg/g, respectively; $p<0.001$), Ni (0.21, 0.47 μg/g, respectively; $p<0.001$), Se (1.16, 2.03 μg/g, respectively; $p<0.001$), and V (0.02, 0.16 μg/g, respectively; $p<0.001$; Figure 16). PFS male serum concentrations were significantly higher than SASL male serum concentrations for As (0.09, 0.05 μg/g, respectively; $p<0.001$) and Cu (1.02, 0.85 μg/g, respectively; $p = 0.01$). PFS male

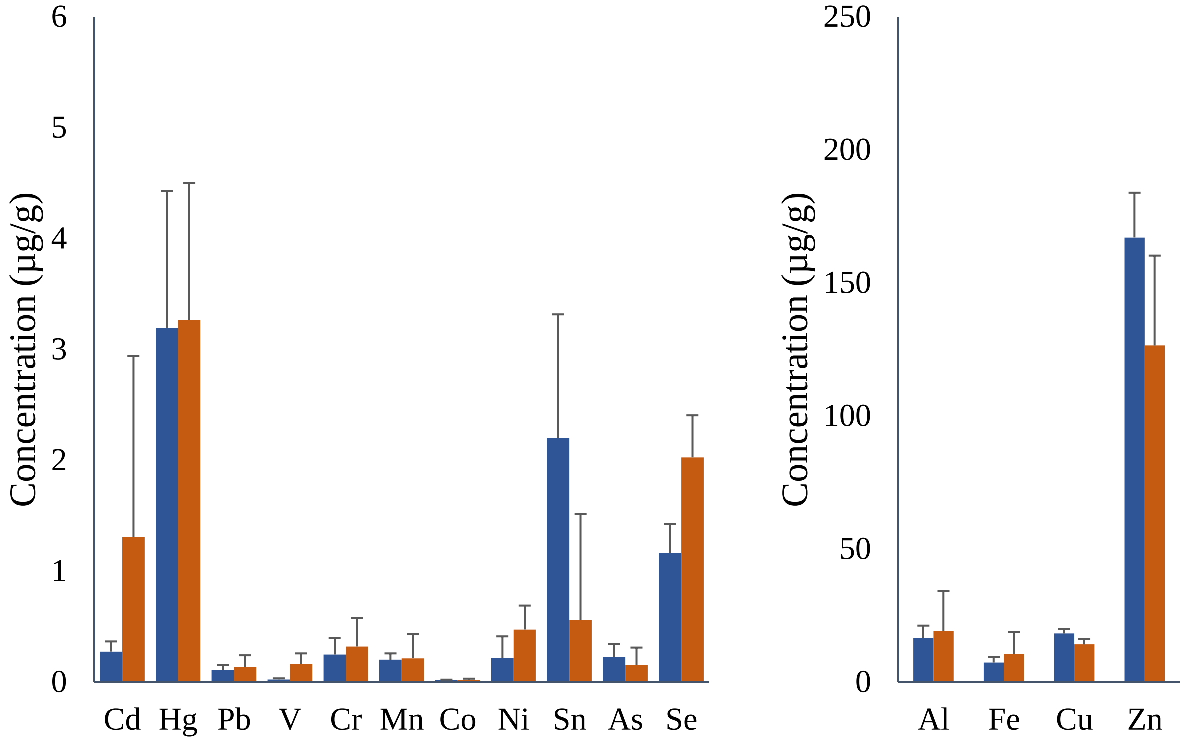

Figure 16. Mean vibrissae trace element concentrations (µg/g) for adult Peruvian fur seal males (blue) and South American sea lion males (orange). Error bars correspond to standard deviation.

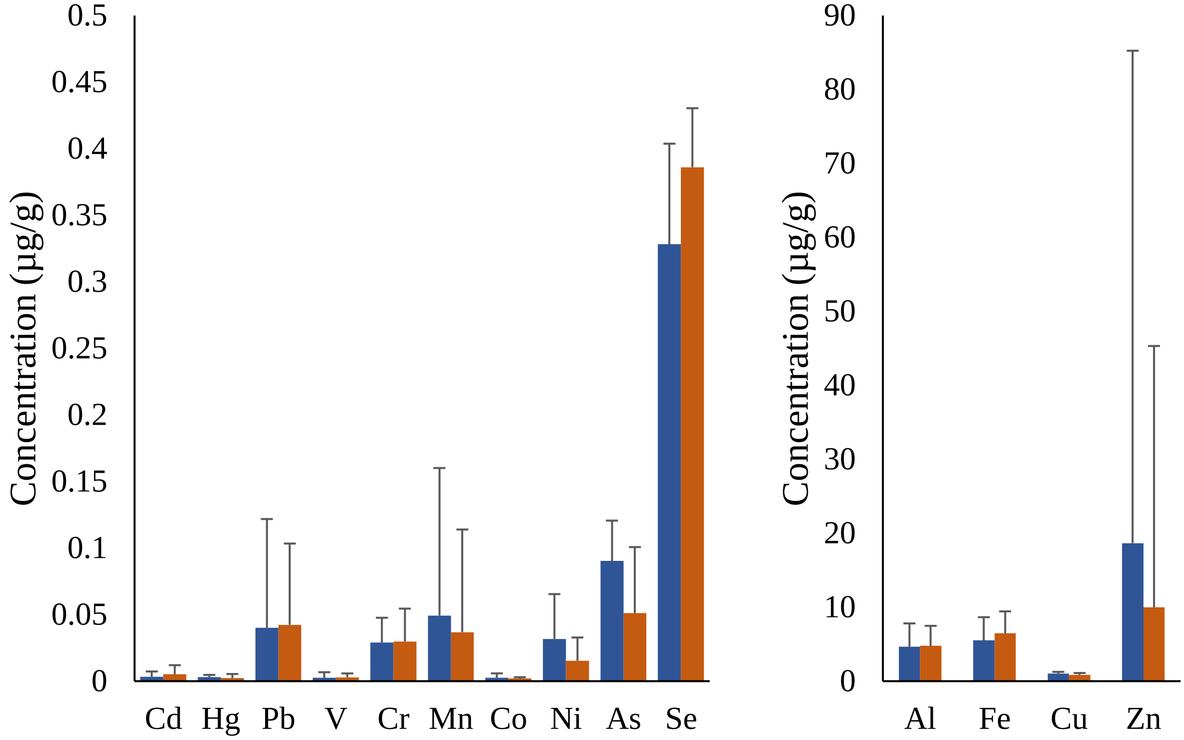

Figure 17. Mean serum trace element concentrations (µg/g) for adult Peruvian fur seal males (blue) and South American sea lion males (orange). Error bars correspond to standard deviation. Tin was not analyzed.

serum concentrations were significantly lower than SASL male concentrations for Se (0.33, 0.39 μg/g, respectively; $p = 0.005$; Figure 17).

Adult PFS female vibrissae concentrations were significantly higher than SASL female vibrissae concentrations for Cu (20.74, 15.21 μg/g, respectively; $p<0.001$), Mn (0.37, 0.25 μg/g, respectively; $p = 0.02$), Hg (1.93, 1.18 μg/g, respectively; $p<0.001$), and Zn (189.1, 168.4 μg/g, respectively; $p = 0.01$). PFS female vibrissae concentrations were significantly lower than SASL female concentrations for As (0.17, 0.47 μg/g, respectively; $p<0.001$), Cd (0.23, 0.51 μg/g, respectively; $p<0.001$), Se (1.02, 1.86 μg/g, respectively; $p<0.001$), and V (0.04, 0.10 μg/g, respectively; $p<0.001$; Figure 18). PFS female serum concentrations were significantly higher than SASL female concentrations for As (0.06, 0.03 μg/g, respectively; $p<0.001$) and Cd (0.009, 0.001 μg/g, respectively; $p<0.001$). PFS female serum concentrations were significantly lower than SASL female concentrations for Co (0.001, 0.004 μg/g, respectively; $p = 0.004$) and Ni (0.01, 0.02 μg/g, respectively; $p = 0.006$; Figure 19). Tin was not analyzed for male or female serum and Hg was not analyzed for female serum due to insufficient sample size.

Peruvian fur seal As and Cd concentrations were lower than SASL in vibrissae, but higher than SASL in serum. Previous studies have found higher Cd concentrations in South American fur seal blood and teeth compared to SASL in Uruguay (Polizzi et al., 2017; De María et al., 2020). Although SASL males sampled were younger than PFS males, SASL males had an average Cd vibrissae concentration (1.31 μg/g) almost five times higher than PFS male vibrissae (0.27 μg/g) and three times higher than SASL female vibrissae (0.51 μg/g). Male SASL vibrissae represent approximately six years while PFS male vibrissae represent approximately four years and SASL female vibrissae represent an average of 5 years. Vibrissae length may partially explain the substantial difference in Cd concentrations; however, the diet of SASL males is likely different than fur seals and SASL females. Young SASL males may be foraging on prey high in Cd such as squid (Gerpe et al., 2000). Both PFS and SASL prey of cephalopods, but the accumulation of trace elements in cephalopods varies greatly among species. Squid are known to accumulate high concentrations of Cd, but some species of octopus are known to contain relatively low concentrations of Cd and higher concentrations of Cu (Gerpe et al., 2000). Peruvian fur seal vibrissae had higher Cu and Zn concentrations than SASL vibrissae. Peruvian fur seals tend to feed on more small, pelagic fish than SASL, which may contribute to their elevated Zn concentrations. Moreno-Sierra et al. (2016) examined trace metals of prey species

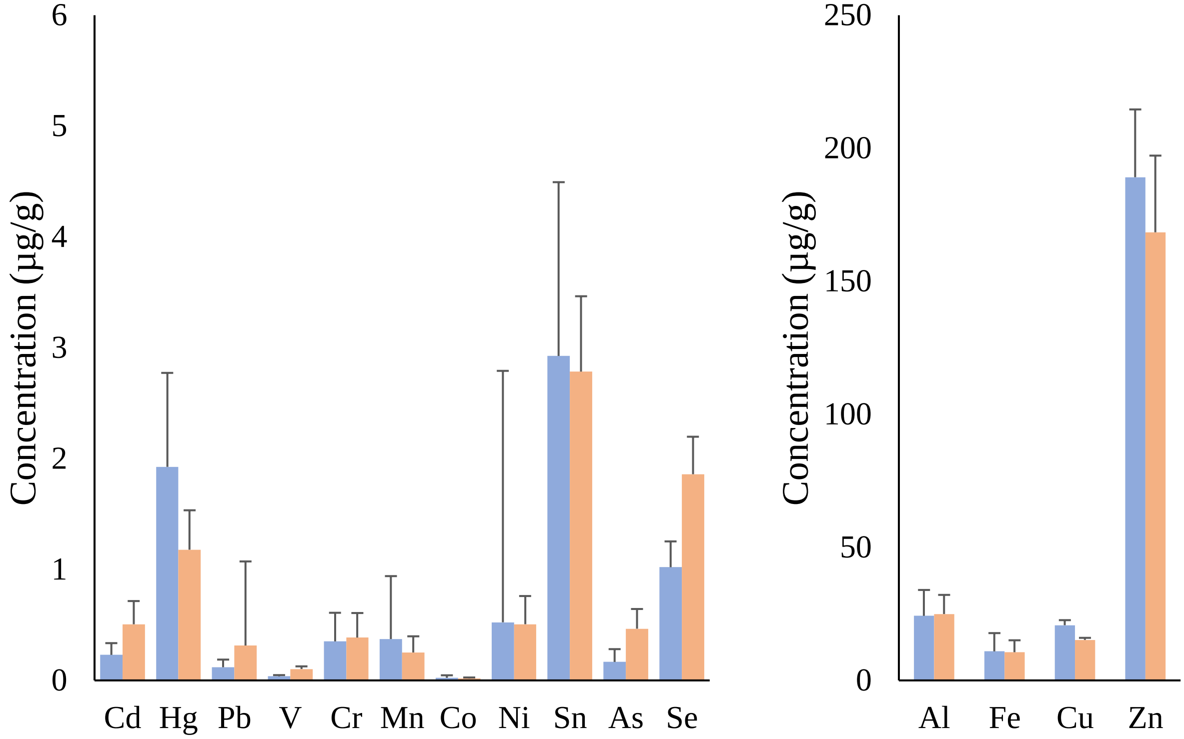

Figure 18. Mean vibrissae trace element concentrations (µg/g) for adult Peruvian fur seal females (blue) and South American sea lion females (orange). Error bars correspond to standard deviation.

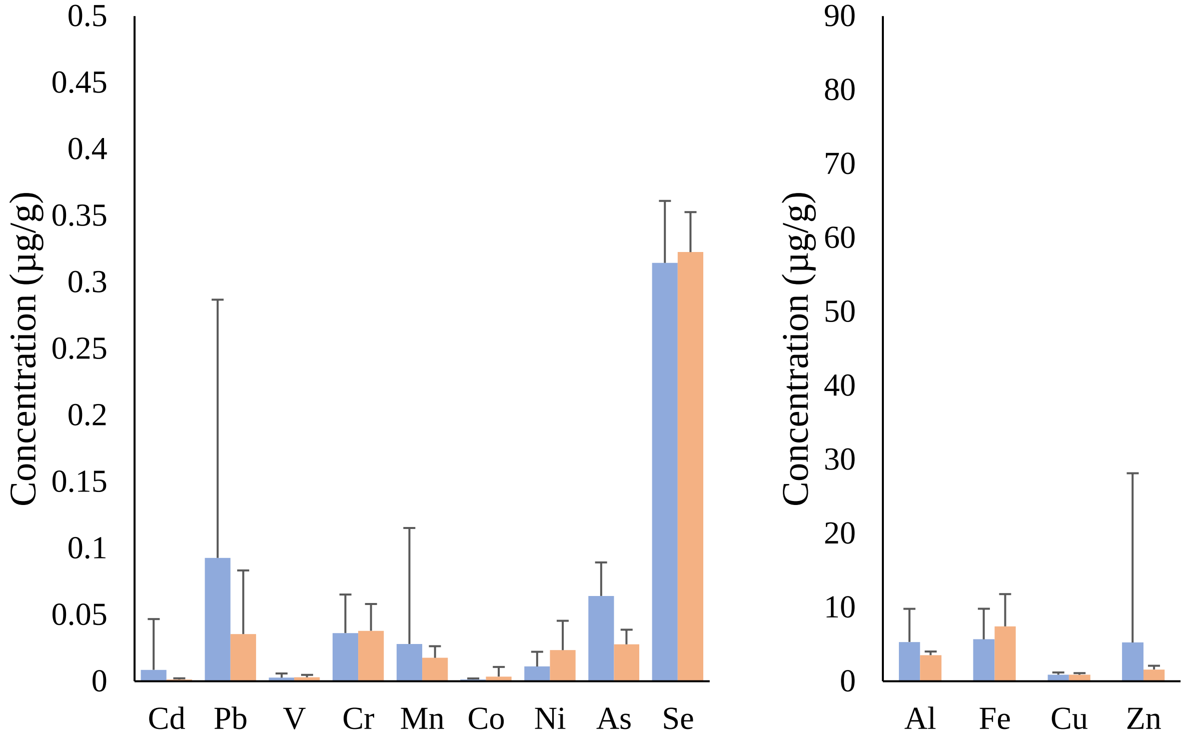

Figure 19. Mean serum trace element concentrations (µg/g) for adult Peruvian fur seal females (blue) and South American sea lion females (orange). Error bars correspond to standard deviation. Mercury and tin were not analyzed.

from stomach contents in sailfish from the eastern Pacific. They found that the small, pelagic fish species from the family Clupeidae were the most concentrated source of Zn in the diet of sailfish.

3.6. Peruvian fur seal dams/pups

Peruvian fur seal dam and pup paired samples were collected in 2009, 2010, 2015, and 2019. Only serum pairs were collected in 2009 (n=11) and 2010 (n=15) and only vibrissae pairs were collected in 2015 (n=6), while both vibrissae and serum pairs were collected in 2019 (n=16 vibrissae, n=14 serum). Mean and median element concentrations for dam and pup paired vibrissae and serum are presented in Table 14. Median element concentrations for 2019 samples, which included dam and pup paired vibrissae and serum as well as milk, are presented in Table 15.

A paired t-test was used to determine significant differences between dam and pup paired serum and vibrissae (Figure 20 and Figure 21). Dam serum had significantly higher concentrations than pup serum for As ($p<0.001$), Cd ($p<0.001$), Cu ($p<0.001$), and Se ($p<0.001$). Pup serum was collected within one week of birth and thus mainly reflects concentrations during gestation where pup and dam serum would be the most similar. A significant positive correlation was found between dam and pup serum for As ($T = 533$, $\tau = 0.37$, $p<0.001$), Pb ($T = 499$, $\tau = 0.28$, $p = 0.01$), and Ni ($T = 294$, $\tau = 0.26$, $p = 0.04$) while Al showed a negative correlation ($T = 292$, $\tau = -0.25$, $p = 0.02$). There were no pairs where both dam and pup serum concentrations were above the detection limit for Hg and Sn; therefore, Hg and Sn were not analyzed.

Dam serum concentrations were significantly lower than pup vibrissae concentrations for all elements (Figure 22). Vanadium was significantly negatively correlated between dam serum and pup vibrissae ($S = 2538$, $\rho = -0.43$, $p = 0.045$). Dam vibrissae concentrations were significantly higher than pup vibrissae for Cu ($p = 0.02$), Hg ($p<0.001$), Sn ($p = 0.01$), and Zn ($p = 0.001$). Dam vibrissae had significantly lower concentrations than pup vibrissae for Al ($p<0.001$), As ($p<0.001$), Cd ($p = 0.008$), Cr ($p = 0.02$), Co ($p<0.001$), Fe ($p<0.001$), Pb ($p<0.001$), Mn ($p<0.001$), Ni ($p<0.001$), Se ($p<0.001$), and V ($p<0.001$). Pup vibrissae concentrations were significantly higher than pup serum concentrations for all elements (Figure 23). Lead concentrations were significantly correlated between pup vibrissae and serum ($S = 168$, $\rho = 0.63$, $p = 0.02$).

While there are no reports in the literature for when vibrissae develop in utero in otariids, in gray seals vibrissae begin to grow 2-3 months into active gestation, resulting in 6-7 months of

Table 14. Trace element concentrations of Peruvian fur seal dam and pup paired vibrissae and serum. Data presented as mean (median) ± standard deviation (μg/g). N/A = not available.

Element	Sample Type	Dams	Pups
Al	Vibrissae	20.50 (19.82) ± 5.382	159.7 (145.5) ± 54.62
	Serum	5.524 (3.650) ± 3.773	4.502 (3.472) ± 2.659
As	Vibrissae	0.225 (0.231) ± 0.090	0.438 (0.401) ± 0.184
	Serum	0.056 (0.054) ± 0.017	0.042 (0.040) ± 0.011
Cd	Vibrissae	0.215 (0.183) ± 0.078	0.604 (0.487) ± 0.755
	Serum	0.012 (0.003) ± 0.051	0.002 (0.001) ± 0.001
Cr	Vibrissae	0.241 (0.188) ± 0.146	0.431 (0.264) ± 0.390
	Serum	0.034 (0.027) ± 0.027	0.037 (0.025) ± 0.037
Co	Vibrissae	0.021 (0.015) ± 0.025	0.040 (0.035) ± 0.028
	Serum	0.001 (0.001) ± 0.001	0.002 (0.001) ± 0.004
Cu	Vibrissae	20.98 (20.82) ± 2.048	19.50 (18.65) ± 4.009
	Serum	0.892 (0.850) ± 0.355	0.587 (0.565) ± 0.175
Fe	Vibrissae	10.73 (7.969) ± 9.367	25.28 (21.85) ± 11.59
	Serum	6.155 (5.080) ± 4.680	6.534 (6.302) ± 3.157
Pb	Vibrissae	0.116 (0.084) ± 0.097	0.574 (0.207) ± 1.561
	Serum	0.062 (0.040) ± 0.057	0.052 (0.043) ± 0.041
Mn	Vibrissae	0.475 (0.242) ± 0.842	0.707 (0.641) ± 0.281
	Serum	0.037 (0.012) ± 0.117	0.024 (0.016) ± 0.052
Hg	Vibrissae	2.128 (2.077) ± 0.426	1.465 (1.561) ± 0.397
	Serum	0.003 (0.002) ± 0.005	0.018 (0.019) ± 0.007
Ni	Vibrissae	0.156 (0.155) ± 0.069	0.387 (0.372) ± 0.133
	Serum	0.010 (0.008) ± 0.010	0.010 (0.009) ± 0.008
Se	Vibrissae	1.122 (1.095) ± 0.264	3.973 (3.910) ± 1.027
	Serum	0.322 (0.320) ± 0.054	0.135 (0.133) ± 0.019
Sn	Vibrissae	1.623 (2.168) ± 1.415	0.143 (0.022) ± 0.427
	Serum	N/A	N/A
V	Vibrissae	0.035 (0.036) ± 0.008	0.068 (0.062) ± 0.024
	Serum	0.003 (0.002) ± 0.004	0.003 (0.003) ± 0.002
Zn	Vibrissae	188.8 (188.7) ± 25.09	162.9 (164.4) ± 23.60
	Serum	6.049 (1.261) ± 29.43	6.001 (1.292) ± 29.26

Table 15. Peruvian fur seal dam and pup median concentrations (μg/g) for 2019 vibrissae, serum, and milk.

	n	Al	As	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Ni	Se	Sn	V	Zn
Vibrissae																
Dam	*16*	18.89	0.25	0.17	0.15	0.01	21.62	7.97	0.09	0.24	2.11	0.13	1.15	0.02	0.04	188.9
Pup	*16*	147.9	0.41	0.29	0.25	0.03	20.79	21.03	0.20	0.66	1.72	0.40	4.25	0.02	0.05	169.9
Serum																
Dam	*16*	3.99	0.05	0.003	0.03	0.001	0.85	2.44	0.08	0.01	0.003*	0.01	0.31	N/D	0.002	1.18
Pup	*14*	3.75	0.04	0.002	0.02	0.001	0.57	7.24	0.05	0.02	N/D	0.01	0.15	N/D	0.002	1.24
Milk																
Dam	*11*	3.75	0.56	0.001*	0.03	0.002	2.62	1.50	0.02	0.03	0.02	0.01	0.49	N/D	0.001	8.95

*Only detected in one sample.

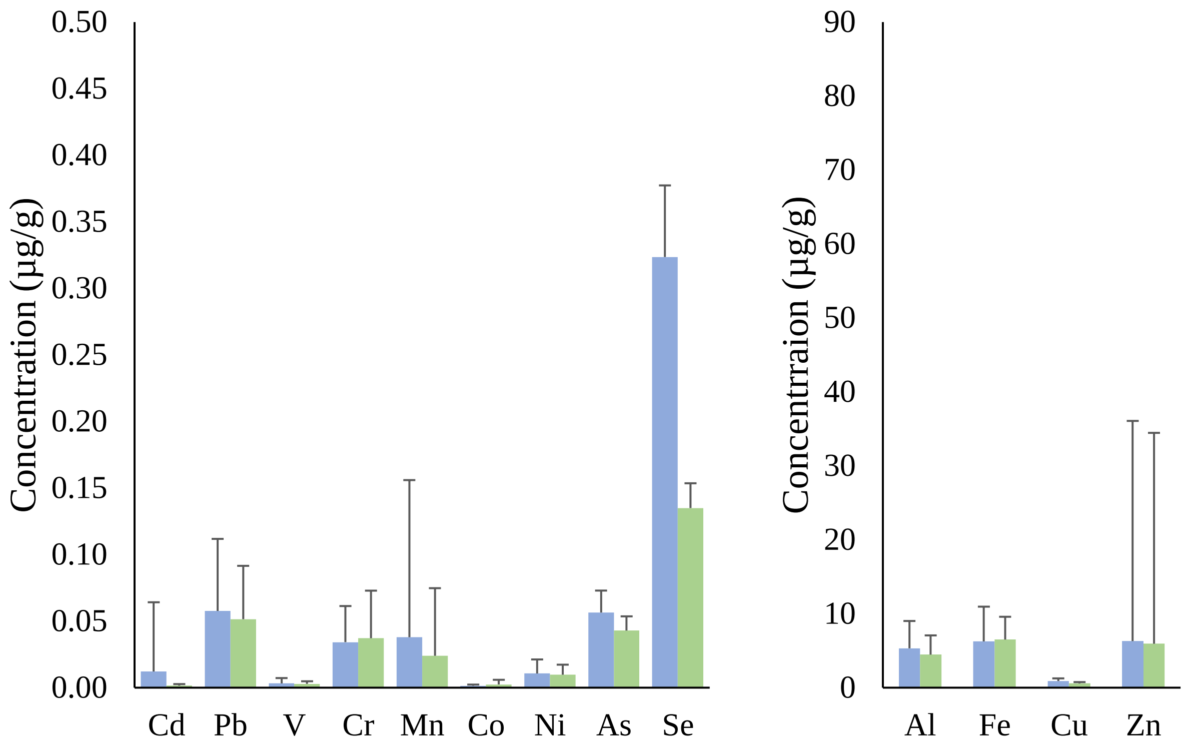

Figure 20. Mean serum trace element concentrations (µg/g) for Peruvian fur seal dams (blue) and pups (green). Error bars correspond to standard deviation. Mercury and tin were not analyzed.

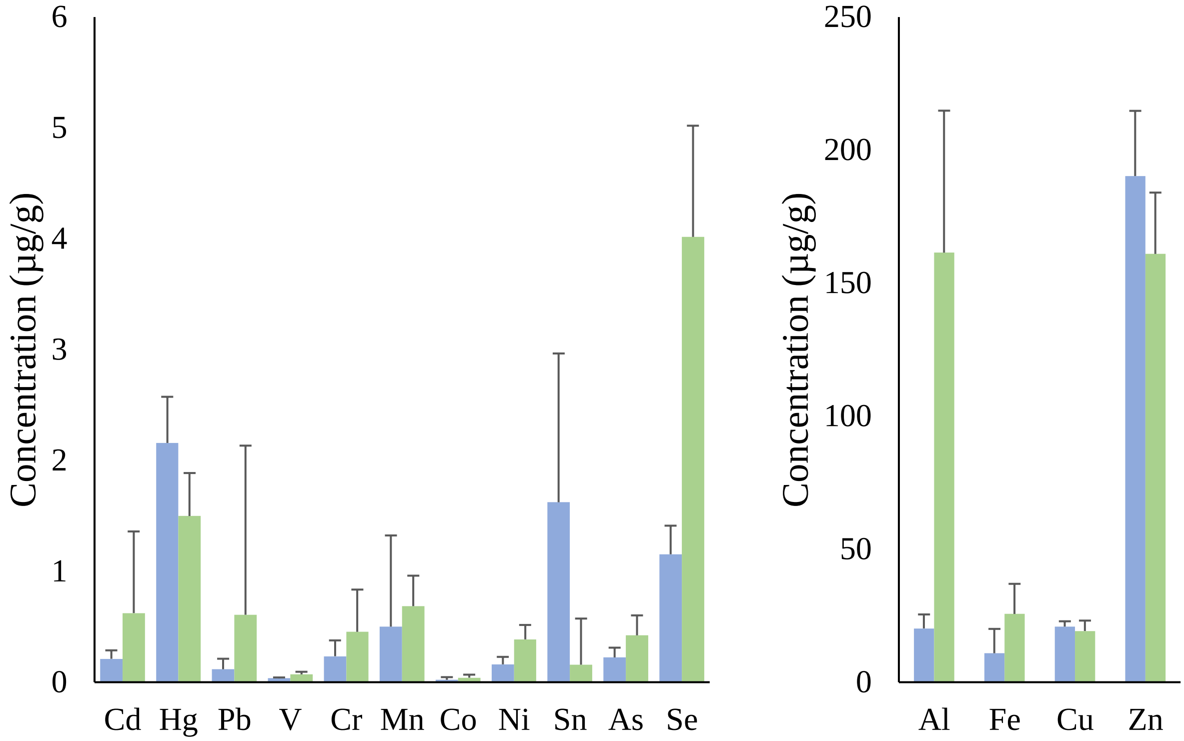

Figure 21. Mean vibrissae trace element concentrations (µg/g) for Peruvian fur seal dams (blue) and pups (green). Error bars correspond to standard deviation.

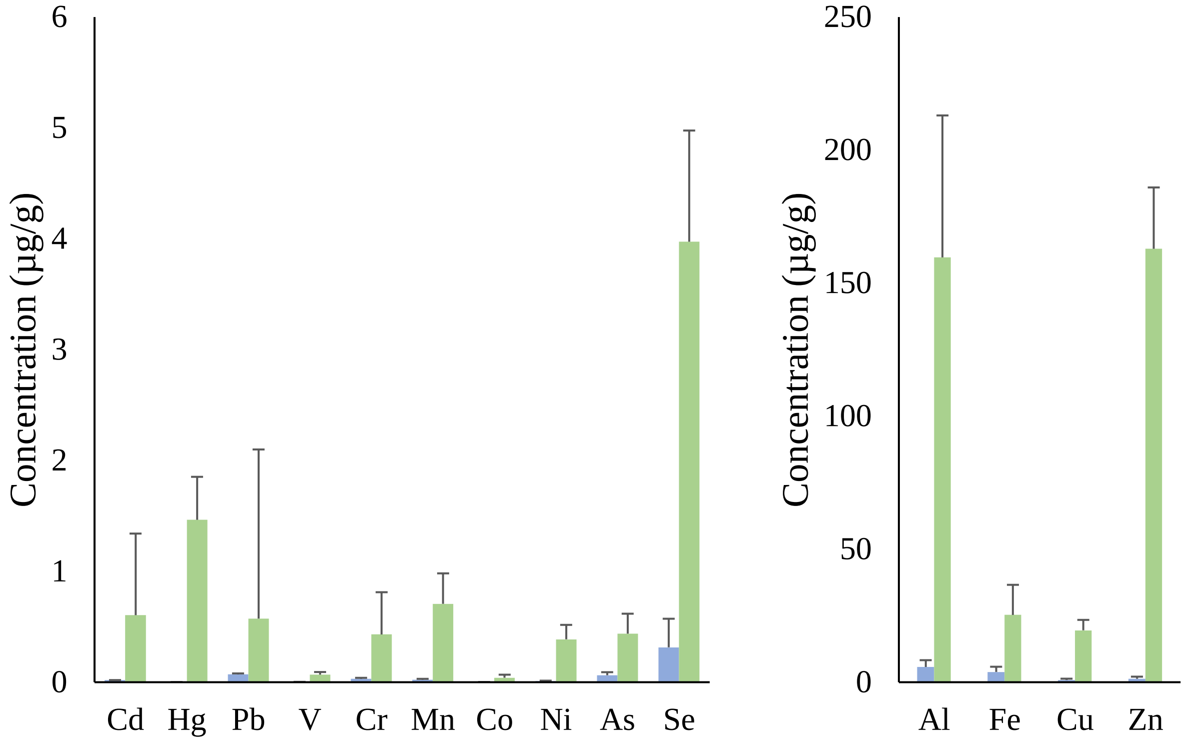

Figure 22. Mean trace element concentrations (µg/g) for Peruvian fur seal dam serum (light blue) and pup vibrissae (light green). Error bars correspond to standard deviation. Tin was not analyzed.

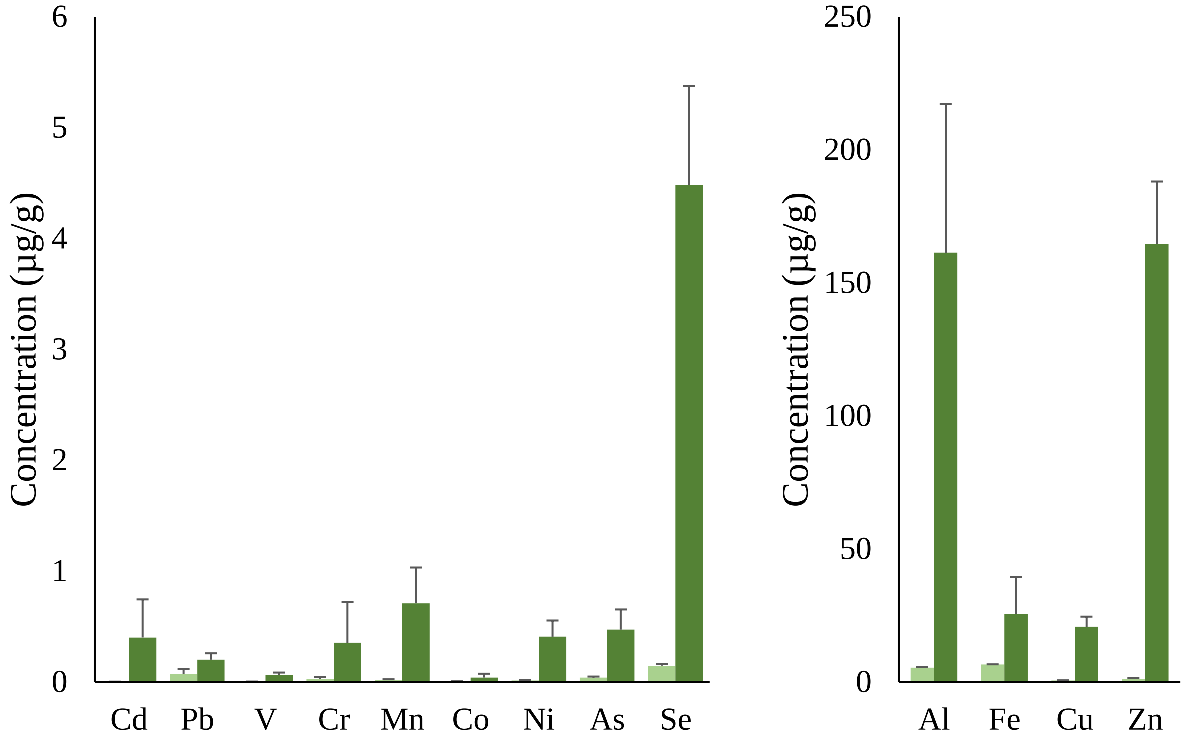

Figure 23. Mean trace element concentrations (µg/g) for Peruvian fur seal pup serum (light green) and vibrissae (dark green). Error bars correspond to standard deviation. Mercury and tin were not analyzed.

active vibrissae growth in utero (Hewer et al. 1968; Lerner et al. 2018). The gestation period for PFS last 11 months including a 2-3 month diapause, followed by active gestation. Fetuses begin to develop vibrissae approximately 2 months after early embryo gestation and vibrissae continue to grow for 6-7 months in utero (K. Colegrove & M. Adkesson, personal communication). Pups were sampled within one week of their birth; therefore, the majority of the pup vibrissa reflect gestational transfer from the dam. Although pup vibrissae only reflect 6-7 months of growth while dam vibrissae contain approximately 3.5 years of growth, pup vibrissae had significantly higher concentrations of 11 of the 15 elements analyzed. This suggests that dams offload contaminants to pups and that pups can effectively offload contaminants via vibrissae at a young age. The extremely high Al, Cd, Pb, and Se concentrations in pup vibrissae compared to dam vibrissae suggests that these elements transferred from dam to pup are released from maternal body stores and may indicate high concentrations in dam body tissues.

Habran et al. (2013) examined whole blood in dam and pup paired gray seals and found higher Cu and Se in dam blood compared to pup blood. The authors also determined element concentrations in dam fur and pup lanugo. Their findings were similar to the current study with Cu, Hg, and Zn concentrations higher in dams, but also showed dams had higher Cd, Cr, Fe, Pb, Ni, Se, and V than pups. Average Cu concentrations were much higher in PFS dam and pup vibrissae (20.9, 19.3 µg/g, respectively) compared to dam fur and lanugo in gray seals from Scotland (4.2, 2.8 µg/g, respectively, Scotland; Habran et al., 2013). However, mean Hg concentrations were much lower in PFS dam and pup vibrissae (2.2, 1.5 µg/g, respectively) than in gray seal fur and lanugo (7.7, 4.6 µg/g, respectively, Scotland; Habran et al., 2013) and northern fur seal dam and pup fur (4.87, 7.84 µg/g, respectively, Alaska; Beckmen et al., 2002). Mercury and Cd are mainly transferred from dam to pup during gestation with little transfer during lactation (Habran et al., 2013; Grajewska et al., 2019). This is confirmed for PFS through the undetected and low concentrations of Hg and Cd found in milk and higher Hg and Cd concentrations in pup vibrissae grown in the last 6-7 months of gestation. Lead was positively correlated between dam and pup serum (τ=0.28) and pup vibrissae and pup serum (ρ=0.63). Similar correlations for Pb in dam and pup whole blood (ρ=0.63) and pup lanugo and blood (ρ=0.5) were found in gray seals (Habran et al., 2013).

Trace element concentrations for milk are summarized in Table 5. Milk samples were collected in 2011 (n=16), 2015 (n=3), and 2019 (n=11). Iron and V milk concentrations in 2011 were significantly higher than 2019 concentrations (4.40, 2.73 μg/g, $F(2) = 0.276$, $p = 0.04$; 0.005, 0.002 μg/g, $F(2) = 1.014$, $p<0.001$, respectively). Milk concentrations for Se in 2011 (0.27 μg/g) were significantly lower than 2019 concentrations (0.47 μg/g, $F(2) = 0.135$, $p<0.001$; Figure 24).

There is a clear increase in As, Cu, Se, and Zn concentrations for milk across the years sampled. Average milk Zn concentrations (10.30 μg/g) are only slightly higher than concentrations found in gray (7.3 μg/g, Scotland; Habran et al., 2013) and harp seals (6 μg/g, Gulf of Saint Lawrence; Wagemann et al., 1988), but average Cu concentrations (2.24 μg/g) are four times higher than gray (0.45 μg/g, Scotland; Habran et al., 2013) and harp seals (0.54 μg/g, Gulf of Saint Lawrence, Wagemann et al., 1988). Elevated Cu and Zn concentrations may be due to Cu mining dust and waste and should be monitored. There was an extreme El Niño in 2015 but since there were only three samples available that year it is difficult to determine if El Niño conditions significantly affected maternal transfer of trace element concentrations via milk. If dams forage success decreases during El Niño due to less abundant prey, dams may remobilize adipose stores, in turn remobilizing and increasing lactational transfer of contaminants. Although SASL milk samples were not available, the high concentrations of As in SASL females suggest that their milk could also contains high As levels and should be monitored.

Peruvian fur seal milk concentrations were significantly higher than dam serum concentrations for As (0.42, 0.05 μg/g, respectively; $p<0.001$), Cd (0.028, 0.003 μg/g, respectively; $p = 0.01$), Co (0.003, 0.001 μg/g, respectively; $p<0.001$), Cu (2.24, 0.82 μg/g, respectively; $p<0.001$), Mn (0.05, 0.01 μg/g, respectively; $p<0.001$), Ni (0.01, 0.04 μg/g, respectively; $p<0.01$), Se (0.36, 0.31 μg/g, respectively; $p = 0.02$), and Zn (10.68, 1.47 μg/g, respectively; $p<0.001$). Iron milk concentrations were significantly lower than dam serum concentrations (3.63, 4.29 μg/g, respectively; $p = 0.03$; Figure 25). Selenium and V concentrations were significantly positively correlated between dam serum and milk ($S = 1866$, $\rho = 0.43$, $p = 0.03$; $S = 1716$, $\rho = 0.48$, $p = 0.01$, respectively).

Milk concentrations were significantly higher than pup serum concentrations for As (0.48, 0.04 μg/g, respectively; $p<0.001$), Cu (2.95, 0.65 μg/g, respectively; $p<0.001$), Se (0.49, 0.15 μg/g, respectively; $p<0.001$), and Zn (15.54, 1.21 μg/g, respectively; $p = 0.002$). Iron milk concentrations were significantly lower than pup serum (2.73, 7.50 μg/g, respectively; $p<0.001$; Figure 26). Pup serum and vibrissae Pb were both significantly negatively correlated with milk

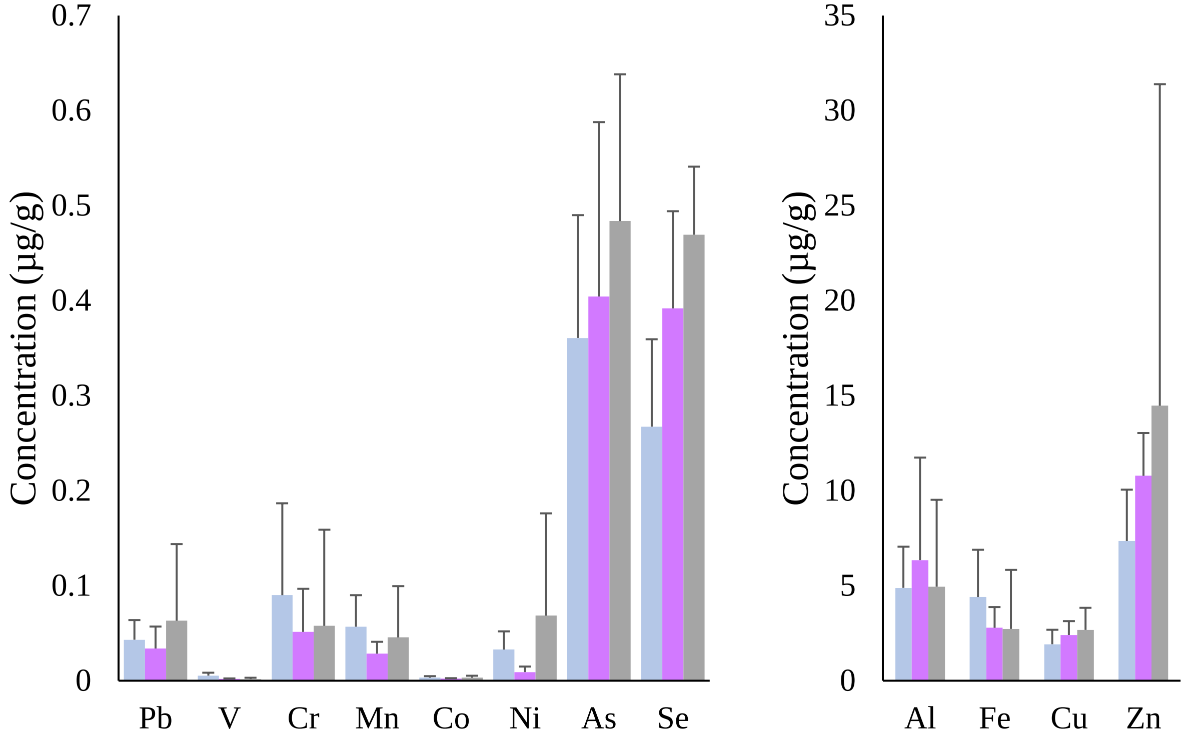

Figure 24. Mean Peruvian fur seal milk trace element concentrations (µg/g) for 2011 (blue), 2015 (purple), and 2019 (gray). Error bars correspond to standard deviation. Cadmium, mercury, and tin were not analyzed.

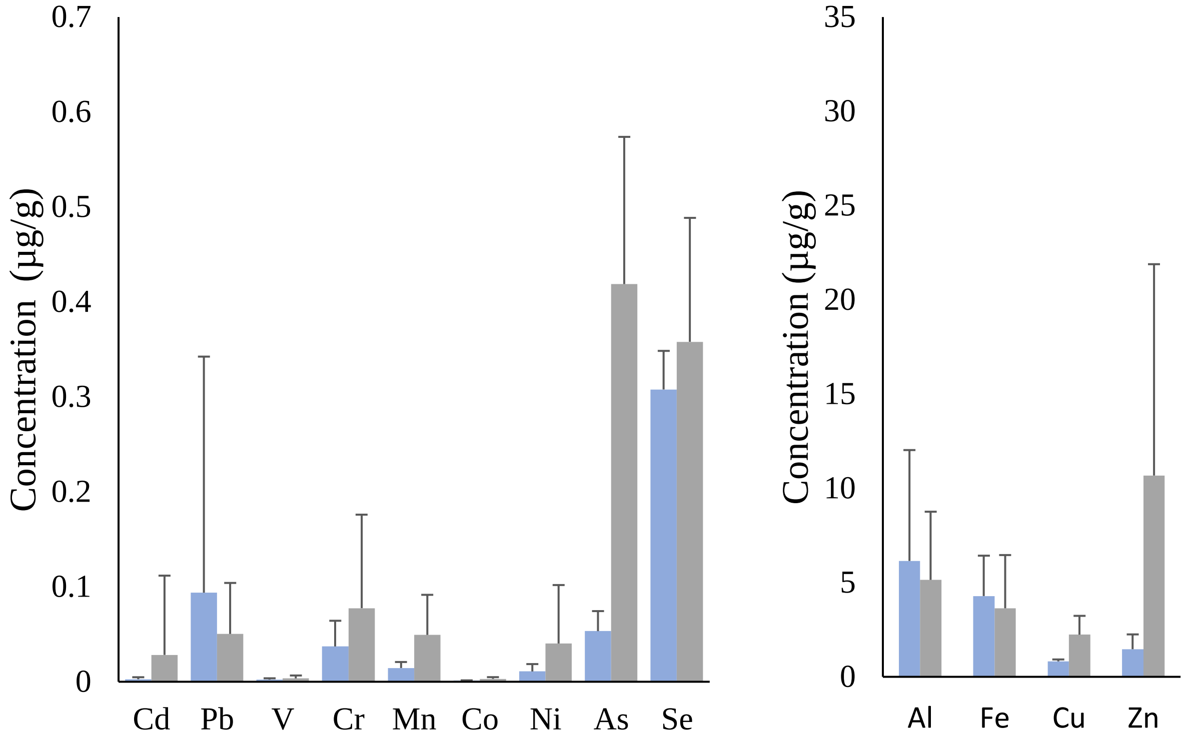

Figure 25. Mean trace element concentrations (µg/g) for Peruvian fur seal dam serum (blue) and milk (gray). Error bars correspond to standard deviation. Mercury and tin were not analyzed.

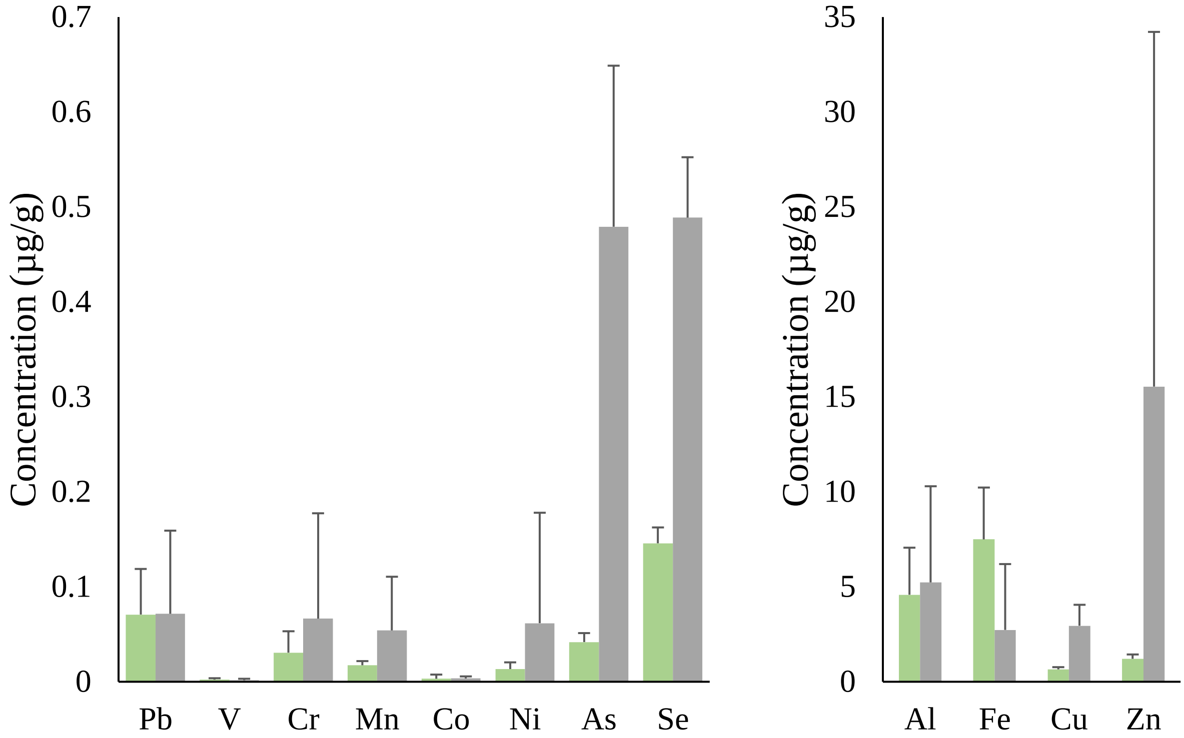

Figure 26. Mean trace element concentrations (µg/g) for Peruvian fur seal pup serum (green) and milk (gray). Error bars correspond to standard deviation. Cadmium, mercury, and tin were not analyzed.

(S = 208, ρ = -0.73, p = 0.03; S = 704, ρ = -0.55, p = 0.04, respectively). Cadmium, Hg, and Sn were not analyzed for milk concentrations by year and milk versus pup serum.

Milk concentrations were higher than both dam and pup serum for As, Cu, Se, and Zn. In gray seals, milk had higher concentrations than dam and pup blood for Zn, but not for Cu or Se (Habran et al., 2013). Lead was positively correlated between pup serum and vibrissae, but negative correlations were seen for Pb between pup serum and milk (ρ=-0.73) and pup vibrissae and milk (ρ=-0.55). This may indicate that Pb is mainly transferred to the pup during gestation with little transfer through lactation. Habran et al. (2013) found a positive relationship between Pb, V, Ni, and Cr in gray seal milk. Similar relationships were seen in this study between Ni and V (ρ=0.464), Cr and V (ρ=0.642), Cr and Ni (ρ=0.546), and Cr and Pb (ρ=0.669). This indicates that these elements follow similar pathways in milk development.

3.7. Comparison to published data

Concentrations of essential and non-essential elements in the vibrissae of PFS and SASL in the present study are presented in Tables 16 and 17, along with published reference values from the fur of other pinniped species and the feathers of Humboldt penguins from PSJ. Aluminum concentrations in adult PFS and SASL vibrissae in the present study (22.08, 21.80 µg/g, respectively) were more than twice as high as fur Al concentrations in leopard and Weddell seals from Antarctica (8.87, 9.13 µg/g, respectively; Gray et al., 2008). Concentrations of Al in human hair range from 0.1 to 36 µg/g; however, Al concentrations over 8 µg/g have been linked to developmental disorders in children (Krewski et al., 2007; Blaurock-Busch et al., 2012). Human hair and pinniped fur reflect a shorter time frame of a few months to a year compared to vibrissae that reflect approximately 4 to 5 years of exposure. This may partially explain the high concentrations in vibrissae compared to human hair and fur.

Humboldt penguin feathers collected from PSJ also contained a high average Al concentration (67 µg/g) suggesting elevated bioavailable Al is present near PSJ. Since Al is the most abundant metal in the earth’s crust, local mining activities may release Al into the environment (ATSDR, 2008). Potential Al toxicity is especially concerning in PFS pups with an average Al concentration in vibrissae of 159.7 µg/g, as Al toxicity can affect bone growth and development (Jaishankar et al., 2014). Additionally, the levels in PFS pup vibrissae reflect only a short period of in utero development and one to two weeks of lactation, suggesting substantial maternal offloading of Al to the pups.

Table 16. Essential trace element concentrations in vibrissae of Peruvian fur seal and South American sea lion in the present study, reference values reported from the fur of other pinniped species, and reference values from the feathers of Humboldt penguins from Punta San Juan, Peru. Data presented as mean ± standard deviation in µg/g. BDL = below detection limit, - = not analyzed.

Species	**Age Class**	**Sample Type**	**Cr**	**Co**	**Cu**	**Fe**	**Mn**	**Ni**	**Se**	**V**	**Zn**
Peruvian fur seal[1]	Adult	Vibrissae	0.32 ± 0.24	0.02 ± 0.02	20.03 ± 2.17	9.90 ± 6.14	0.33 ± 0.49	0.44 ± 1.93	1.06 ± 0.25	0.03 ± 0.01	183.0 ± 25.31
	Pup	Vibrissae	0.43 ± 0.39	0.04 ± 0.03	19.50 ± 4.01	25.28 ± 11.59	0.71 ± 0.28	0.39 ± 0.13	3.97 ± 1.03	0.07 ± 0.02	162.9 ± 23.60
South American sea lion[1]	Adult	Vibrissae	0.35 ± 0.24	0.02 ± 0.01	14.60 ± 1.74	10.58 ± 6.73	0.23 ± 0.19	0.49 ± 0.23	1.95 ± 0.37	0.13 ± 0.08	145.4 ± 37.69
Weddell seal[2]	Adult	Fur	5.87 ± 0.47	0.04 ± 0.04	15.1 ± 13.2	73.9 ± 16.4	1.15 ± 0.41	3.52 ± 0.76	3.12 ± 0.93	4.22 ± 0.65	137 ± 14.3
Leopard seal[2]	Adult	Fur	3.81 ± 0.64	BDL	3.37 (3.03-3.75) *	73.1 (70.3-76.0) *	1.36 (1.28-1.45) *	1.35 (1.17-1.57) *	2.95 ± 1.41	1.82 (1.62-2.04) *	103 (97.7-108) *
Baikal seal[3]	-	Fur	0.94 ± 0.88	0.059 ± 0.048	5.37 ± 1.97	-	1.81 ± 0.91	-	2.3 ± 0.7	1.0 ± 0.8	105 ± 13
Caspian seal[3]	-	Fur	1.2 ± 1.4	0.18 ± 0.14	33.8 ± 59.7	-	1.75 ± 1.55	-	2.3 ± 1.9	0.71 ± 0.39	98.1 ± 26.4
Northern fur seal[3]	-	Fur	0.74 ± 0.25	0.041 ± 0.018	6.13 ± 1.79	-	0.349 ± 0.295	-	6.1 ± 2.0	3.1 ± 1.0	186 ± 55
Gray seal[4]	Adult	Fur	0.24 ± 0.06	-	4.2 ± 1.1	87 ± 56	-	1.29 ± 0.37	4.1 ± 1.2	2.36 ± 0.63	101 ± 9
	Pup	Lanugo	0.05 ± 0.01	-	2.8 ± 0.2	9 ± 4	-	0.18 ± 0.04	2.9 ± 0.5	0.09 ± 0.12	122 ± 13

Humboldt penguin[5]	Adult	Feather	BDL (<5)	BDL (<5)	10.5 ± 6.6	304 ± 206	5.7 ± 3.9	BDL (<5)	BDL (<5)	BDL (<5)	48 ± 9

*Presented in geometric mean and 95% confidence interval.
[1]Present Study (Punta San Juan, Peru)
[2]Gray et al., 2008 (Antarctica)
[3]Ikemoto et al., 2004c (Baikal seal: Russia, Caspian seal: Caspian Sea, norther fur seal: Japan)
[4]Habran et al., 2013 (Scotland)
[5]Adkesson et al., 2019 (Punta San Juan, Peru)

Table 17. Non-essential trace element concentrations in vibrissae of Peruvian fur seal and South American sea lion in the present study, reference values reported from the fur of other pinniped species, and reference values from the feathers of Humboldt penguins from Punta San Juan, Peru. Data presented as mean ± standard deviation in μg/g. BDL = below detection limit, - = not analyzed.

Species	Age Class	Sample Type	Al	As	Cd	Pb	Hg	Sn
Peruvian fur seal[1]	Adult	Vibrissae	22.08 ± 9.29	0.19 ± 0.12	0.24 ± 0.10	0.12 ± 0.06	2.28 ± 1.12	2.70 ± 1.47
	Pup	Vibrissae	159.7 ± 54.62	0.44 ± 0.18	0.60 ± 0.76	0.57 ± 1.56	1.47 ± 0.40	0.14 ± 0.43
South American sea lion[1]	Adult	Vibrissae	21.80 ± 12.26	0.29 ± 0.23	0.95 ± 1.27	0.22 ± 0.51	2.32 ± 1.41	1.71 ± 1.39
Weddell seal[2]	Adult	Fur	9.13 ± 4.69	2.51 ± 2.11	2.81 ± 0.58	1.29 ± 1.12	5.60 ± 1.43	1.36 ± 1.78
Leopard seal[2]	Adult	Fur	7.62 ± 4.73	1.63 ± 0.73	1.12 (0.87-1.42) *	0.06 ± 0.10	0.06 ± 0.10	BDL
Baikal seal[3]	-	Fur	-	-	0.094 ± 0.065	13.4 ± 15.3	3.6 ± 1.7	-
Caspian seal[3]	-	Fur	-	-	0.394 ± 0.352	3.53 ± 2.14	1.6 ± 0.9	-
Northern fur seal[3]	-	Fur	-	-	0.635 ± 0.245	7.68 ± 5.60	4.9 ± 1.1	-
Gray seal[4]	Adult	Fur	-	-	0.27 ± 0.07	2.2 ± 1.5	7.7 ± 5.3	-
	Pup	Lanugo	-	-	0.02 ± 0.01	0.64 ± 0.51	4.6 ± 2.3	-
Humboldt penguin[5]	Adult	Feather	67 ± 90	5.0 ± 0.2	BDL (<5)	BDL (<5)	2.21 ± 0.27	-

*Presented in geometric mean and 95% confidence interval.
[1]Present Study (Punta San Juan, Peru)
[2]Gray et al., 2008 (Antarctica)
[3]Ikemoto et al., 2004c (Baikal seal: Russia, Caspian seal: Caspian Sea, norther fur seal: Japan)
[4]Habran et al., 2013 (Scotland)
[5]Adkesson et al., 2019 (Punta San Juan, Peru)

In human hair, As concentrations between 0.1 and 0.5 μg/g indicates chronic As exposure (Ratnaike, 2003). All vibrissae from female SASL contained As concentrations over 0.1 μg/g, with approximately 29% exceeding 0.5 μg/g. In PFS females, 41% had vibrissae As concentrations over 0.1 μg/g, but all 2019 female samples exceeded 0.1 μg/g. For males, 47% of SASL males and 84% of PFS male vibrissae contained As concentrations over 0.1 μg/g. All vibrissae samples in the last four years of this study (2016 to 2019) exceeded As concentrations of 0.1 μg/g, indicating chronic and possibly increasing As exposure in pinnipeds at PSJ.

Average vibrissae Hg concentrations in adult PFS and SASL (2.28, 2.32 μg/g, respectively) were similar to fur concentrations in the Baikal seal (3.6 μg/g; Ikemoto et al., 2004c) and Caspian seal (1.6 μg/g; Ikemoto et al., 2004c), and lower than human hair in populations that regularly consume fish (5 to 15 μg/g; Dietz et al., 2011). Clinical signs of Hg toxicity are associated with fur concentrations exceeding 30 μg/g in wild mammals; however, biochemical alterations have been documented in polar bears with fur Hg concentrations of 5.4 μg/g (Dietz et al., 2011). Two males, one PFS and one SASL, contained vibrissae concentrations over 5.4 μg/g (5.43, 5.46 μg/g, respectively). Although Hg toxicity thresholds are not clear for pinniped species, these values raise concern for Peruvian pinnipeds and population monitoring for signs of toxicity should continue.

Adult vibrissae Fe concentrations were more than seven times lower than fur concentrations found in other pinnipeds. Adult vibrissae had average Fe concentrations of approximately 10 μg/g. Fur Fe concentrations below 30 ppm indicate Fe deficiency in dogs, while fur concentrations between 20 to 40 ppm indicate Fe deficiency in cattle (Puls, 1988). Low Fe concentrations in Peruvian pinniped vibrissae may be worth investigating further as Fe deficiency can lead to improper growth and reduce immune response (Valko et al., 2005). However, no evidence of deficiency or associated anemia has been noted in blood analysis.

Reference values for Cd in human hair differ geographically ranging from 0.03 μg/g to 0.61 μg/g (Rahimzadeh et al., 2017). The average concentration for Cd in vibrissae was 0.24 μg/g and 0.95 μg/g for PFS and SASL adults, respectively indicating little concern for further investigation.

Concentrations of Cr in human hair range from 0.17 to 0.99 μg/g (Liang et al., 2017). Vibrissae average concentrations in PFS and SASL were 0.32 and 0.35 μg/g, respectively.

Chromium vibrissae concentrations were in the range of human hair concentrations and may not be a concern worth investigating further.

The reference level for Pb in human hair from Egypt was 6.82 µg/g (Mortada et al., 2001), while concentrations in Peruvian pinnipeds averaged 0.12 and 0.22 µg/g for PFS and SASL, respectively. This is an order of magnitude lower than human hair and Pb is therefore likely not a toxicity concern. Vibrissae concentrations for Co, Cu, Se, and Zn were within normal ranges for fur in various domestic animals including cattle, dogs, and horses, indicating little concern for toxicity (Puls, 1988).

Essential and non-essential trace element concentrations in serum of PFS and SASL in the present study, other pinniped species, and Humboldt penguins from PSJ are presented in Tables 18 and 19. Peruvian pinniped serum concentrations for Al, Pb, Mn, and Zn were at least three times greater than concentrations found in leopard and Weddell seals from eastern Antarctica (Gray et al., 2008). Aluminum concentrations in serum of Humboldt penguins from PSJ was also an order of magnitude higher than in leopard and Weddell seals (Gray et al., 2008; Adkesson et al., 2019). Similar to Al in vibrissae, high serum concentrations in all three species from PSJ indicates elevated bioavailable Al in this ecosystem. Normal concentrations of Al in human serum are between 1 to 3 µg/L (~0.001 to 0.003 µg/g; ATSDR, 2008). Aluminum serum concentrations in adult PFS and SASL were three orders of magnitude higher (5.19, 4.21 µg/g, respectively) than normal human levels.

Lead serum concentrations were at least an order of magnitude higher than serum concentrations for leopard and Weddell seals (Table 19). Peruvian fur seal and SASL adult Pb serum concentrations (0.08, 0.04 µg/g, respectively) were also an order of magnitude higher than whole blood concentrations for bottlenose dolphins in Florida (0.003 µg/g; Bryan et al., 2007). In many species, whole blood Pb concentrations exceeding 0.35 µg/g indicates Pb poisoning (Blakley, 2013). In humans, serum Pb concentrations represent between 0.24% and 0.70% of whole blood Pb concentrations (Hernández-Avila et al., 1998; Manton et al., 2001). Whole blood Pb concentrations for Peruvian pinnipeds were estimated using the linear relationship described by Manton et al. (2001), yielding estimated average whole blood Pb concentrations of 33.07 µg/g for PFS adults, 24.78 µg/g for PFS pups, and 16.47 µg/g for SASL adults. These results suggest that Peruvian pinnipeds either have extremely high Pb concentrations (two orders of magnitude higher than known toxicity thresholds in other mammals) or the linear relationship established

Table 18. Essential trace element concentrations in serum of Peruvian fur seal and South American sea lion in the present study, reference values reported from serum of other pinniped species, and reference values from serum of Humboldt penguins from Punta San Juan, Peru. Data presented as mean ± standard deviation in µg/g. BDL = below detection limit.

Species	**Age Class**	**Cr**	**Co**	**Cu**	**Fe**	**Mn**	**Ni**	**Se**	**V**	**Zn**
Peruvian fur seal [1]	Adult	0.035 ± 0.027	0.002 ± 0.002	0.91 ± 0.30	5.64 ± 3.95	0.03 ± 0.09	0.015 ± 0.020	0.32 ± 0.05	0.003 ± 0.003	7.93 ± 36.01
	Pup	0.037 ± 0.037	0.002 ± 0.004	0.58 ± 0.18	6.53 ± 3.16	0.02 ± 0.05	0.010 ± 0.008	0.14 ± 0.02	0.003 ± 0.002	6.00 ± 29.26
South American sea lion[1]	Adult	0.034 ± 0.023	0.003 ± 0.005	0.86 ± 0.24	6.90 ± 3.63	0.03 ± 0.06	0.019 ± 0.020	0.36 ± 0.05	0.003 ± 0.002	6.20 ± 26.16
Weddell seal[2]	Adult	0.37 ± 0.04	<0.001	0.36 ± 0.18	3.33 ± 0.76	<0.001	BDL	0.23 ± 0.08	0.10 ± 0.01	0.36 ± 0.05
Leopard seal[2]	Adult	0.22 ± 0.02	BDL	0.60 ± 0.29	3.83 ± 1.71	<0.005	0.01 ± 0	0.59 ± 0.15	0.06 ± 0	0.48 ± 0.12
Humboldt penguin[3]	Adult	BDL (<0.5)	BDL (<0.5)	BDL (<0.5)	21.8 ± 6.9	BDL (<1)	BDL (<0.5)	BDL (<0.5)	BDL (<0.5)	0.57 ± 0.12

[1]Present Study (Punta San Juan, Peru)
[2]Gray et al., 2008 (Antarctica)
[3]Adkesson et al., 2019 (Punta San Juan, Peru)

Table 19. Non-essential trace element concentrations in serum of Peruvian fur seal and South American sea lion in the present study, reference values reported from serum of other pinniped species, and reference values from serum of Humboldt penguins from Punta San Juan, Peru. Data presented as mean ± standard deviation in µg/g. BDL = below detection limit, - = not analyzed.

Species	**Age Class**	**Al**	**As**	**Cd**	**Pb**	**Hg**	**Sn**
Peruvian fur seal[1]	Adult	5.19 ± 4.24	0.069 ± 0.028	0.008 ± 0.034	0.08 ± 0.18	0.003 ± 0.003	0.41 ± 0.50
	Pup	4.50 ± 2.66	0.042 ± 0.011	0.002 ± 0.001	0.06 ± 0.04	0.018 ± 0.007	BDL (<0.001)
South American sea lion[1]	Adult	4.21 ± 2.10	0.041 ± 0.039	0.003 ± 0.005	0.04 ± 0.06	0.002 ± 0.003	BDL (<0.001)
Weddell seal[2]	Adult	0.08 ± 0.20	0.05 ± 0.02	<0.001	<0.001	0.01 ± 0.01	BDL
Leopard seal[2]	Adult	0.25 ± 0.09	0.07 ± 0.02	<0.005	<0.005	<0.005	-
Humboldt penguin[3]	Adult	2.14 ± 0.61	BDL (<0.5)	BDL (<0.5)	BDL (<0.5)	0.0024 ± 0.001	-

[1]Present Study (Punta San Juan, Peru)
[2]Gray et al., 2008 (Antarctica)
[3]Adkesson et al., 2019 (Punta San Juan, Peru)

for humans does not hold true for these species. These estimated whole blood Pb concentrations are also two orders of magnitude higher than PFS and SASL adult vibrissae concentrations (0.12 and 0.22 μg/g, respectively). Further work is needed to evaluate these findings. Peruvian pinniped whole blood samples should be monitored for potential signs of Pb toxicity.

The normal range for serum Mn in humans is 0.5 to 1.2 μg/L (0.0005 to 0.0012 μg/g; Crossgrove and Zheng, 2004). This is an order of magnitude lower than Mn concentrations determined in these Peruvian pinnipeds (0.03 μg/g) and indicates potential risk of Mn toxicity. Although average Zn serum concentrations appear much higher in Peruvian pinnipeds compared to other species (Table 18), median concentrations were much lower; 1.24 μg/g for PFS adults, 1.45 μg/g for SASL adults, and 1.29 μg/g for PFS pups. These median concentrations are only slightly above the normal range for serum Zn in humans according to Mayo Clinic Laboratories, 0.66 to 1.10 μg/mL (μg/g) and therefore may not be a concern worth investigating further.

Copper and Hg serum concentrations were within the range of reference values for humans (Cu: 0.08 to 1.75 μg/g, Hg: 0.002 to 0.006 μg/g). Concentrations of As, Fe, and Se were slightly above reference values for humans (As: 0.0017 to 0.015 μg/g, Fe: 0.75 to 1.5 μg/g, Se: 0.046 to 0.143 μg/g), but within the same order of magnitude (Iyengar and Woittiez, 1988). Cadmium, Cr, Co, and Ni serum concentrations in PFS and SASL were one order of magnitude higher than reference values for humans, and therefore may be a concern worth further investigation (Iyengar and Woittiez, 1988). The normal range for Cr in human serum is 0.0001 to 0.002 μg/g, while Cr concentrations in Peruvian pinnipeds were 0.035 and 0.034 μg/g for PFS and SASL adults, respectively. Serum levels of Cd are estimated to be as low as 0.0001 μg/g since most Cd is bound to red blood cells, and serum concentrations for PFS and SASL adults were 0.008 and 0.003 μg/g, respectively (Iyengar and Woittiez, 1988). Serum Co concentrations in PFS and SASL adults were 0.002 to 0.003 μg/g, respectively, while the serum reference range of Co in humans is 0.0001 to 0.0004 μg/g. The normal range for Ni in human serum is 0.0026 to 0.0075 μg/g (Iyengar and Woittiez, 1988). Average serum concentrations for Ni in PFS and SASL were 0.015 and 0.019 μg/g, respectively.

Essential and non-essential trace element concentrations in milk of PFS in the present study and those reported in the literature for other pinniped species are presented in Tables 20 and 21. Peruvian fur seal milk concentrations of Cu (2.24 μg/g) are nearly five times higher than gray seals (0.45 μg/g, Scotland; Habran et al., 2013) and harp seals (0.54 μg/g, Gulf of Saint

Table 20. Essential trace element concentrations in milk of Peruvian fur seal in the present study and reference values reported from milk of other pinniped species. Data presented as mean ± standard deviation in µg/g. - = not analyzed.

Species	Cr	Co	Cu	Fe	Mn	Ni	Se	V	Zn
Peruvian fur seal[1]	0.07 ± 0.09	0.003 ± 0.002	2.24 ± 0.97	3.63 ± 2.71	0.05 ± 0.04	0.04 ± 0.06	0.35 ± 0.13	0.0037 ± 0.0030	10.30 ± 10.69
Gray seal[2]	0.004 ± 0.003	-	0.45 ± 0.06	24 ± 7	-	0.030 ± 0.017	0.9 ± 0.4	0.004 ± 0.004	7.3 ± 1.0
Harp seal[3]	-	-	0.54 ± 0.076	-	-	-	0.14 ± 0.10	-	6 ± 1.5

[1]Present Study (Punta San Juan, Peru)
[2]Habran et al., 2013 (Scotland)
[3]Wagemann et al., 1988 (Gulf of Saint Lawrence)

Table 21. Non-essential trace element concentrations in milk of Peruvian fur seal in the present study and reference values reported from milk of other pinniped species. Data presented as mean ± standard deviation in µg/g. BDL = below detection limit, - = not analyzed.

Species	Al	As	Cd	Pb	Hg	Sn
Peruvian fur seal[1]	5.05 ± 3.44	0.41 ± 0.15	0.025 ± 0.075	0.05 ± 0.05	0.129 ± 0.409	0.05 ± 0.02
Gray seal[2]	-	-	BDL	0.022 ± 0.027	0.012 ± 0.004	-
Harp seal[3]	-	-	0.057 ± 0.023	-	0.0065 ± 0.0026	-

[1]Present Study (Punta San Juan, Peru)
[2]Habran et al., 2013 (Scotland)
[3]Wagemann et al., 1988 (Gulf of Saint Lawrence)

Lawrence; Wagemann et al., 1988). High Cu concentrations were also seen in vibrissae and serum compared to other pinniped species. Increased bioavailable Cu may be caused by the local Cu mine or leeching from naturally rich Cu deposits. Although milk Cu concentrations are higher than those reported in other pinnipeds, they are similar to World Health Organization (WHO) guidelines for drinking water (2.0 µg/g) and likely pose little risk for toxicity.

Although there are no reported values in the literature for Al in pinniped milk, the average concentration in PFS milk, 5.05 µg/g, is quite high compared to Al concentrations in human breast milk. Aluminum concentrations in breast milk range from 15 to 30 µg/L (~0.015 to 0.030 µg/g), although much higher concentrations of up to 700 µg/L (0.7 µg/g) have been detected in infant formulas (Fanni et al., 2014). The Food and Drug Association (FDA) recommend concentrations of Al in drinking water do not exceed 0.2 mg/L (0.2 µg/g), which is an order of magnitude lower than the PFS milk concentrations and therefore may warrant further investigation (FDA, 2020a).

No evidence exists in the literature that As concentrations have been assessed for pinniped milk. However, As has been detected in other mammalian milk including cows and humans (Chandra Sekhar et al., 2003; Bansa et al., 2017; Hameed et al., 2019). Chandra Sekhar et al. (2003) found elevated average As concentrations (up to 0.33 µg/g) in cattle fed contaminated grass compared to the control (0.02 µg/g). The authors did not indicate any signs of toxicity or disease in the cattle with high milk As concentrations. Bansa et al. (2017) examined As in breast milk of women from mining communities in Ghana and found a geometric mean As concentration of 0.027 µg/g (27.5 µg/L), which is more than 2.5 times higher than WHO limit for drinking water (10 µg/L; WHO, 2011). The FDA recommends As concentrations do not exceed 100 ppb (0.1 µg/g) in infant rice cereals (FDA, 2020b). All milk samples in the present study contained As concentrations above the WHO limit for drinking water and the FDA suggested limit for infant rice cereals indicating As contamination in Peruvian pinnipeds.

Milk concentrations of Cr in PFS (0.07 µg/g) were almost 20 times higher than concentrations determined in gray seals (0.004 µg/g, Scotland; Habran et al., 2013). However, PFS milk Cr is similar to WHO guidelines for drinking water of 0.05 µg/g and suggest little concern for toxicity (WHO, 2011). Manganese, Ni, and Zn milk concentrations were also similar to or below WHO guidelines for water (Mn: 0.05 µg/g, Ni: 0.07 µg/g, Zn: 5.0 µg/g; WHO, 2011). Iron concentrations in PFS milk (3.63 μg/g) were much lower than concentrations measured in gray seals (24 μg/g; Habran et al., 2013); however, they are within the normal range for Fe in cow milk (0.2 to 6.3 μg/g; Puls, 1988) and may not be a concern worth investigating further.

The average Hg concentration in PFS milk was high (0.13 μg/g), but the median concentration was 0.004 μg/g which is lower than the WHO guideline for water of 0.006 μg/g (WHO, 2011). The average milk concentration for Pb, 0.05 μg/g, was slightly higher than WHO water guidelines (0.01 μg/g) and therefore should continue to be monitored. Milk concentrations of Cd (0.025 μg/g) and Se (0.35 μg/g) were an order of magnitude higher than WHO guidelines for water (Cd: 0.003 μg/g, Se: 0.04 μg/g; WHO, 2011), but similar to other pinniped milk concentrations. Signs of Cd toxicity have not been observed in marine mammals despite relatively high Cd concentrations compared to humans indicating that marine mammals may have a higher Cd toxicity threshold (Das et al., 2003).

4. Conclusion

Punta San Juan, Peru is home to many economically and ecologically important species that are subject to natural and anthropogenic impacts. Peruvian fur seals and South American sea lions are apex predators and sentinel species in this ecosystem. All 15 trace elements (Al, As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Ni, Se, Sn, V, and Zn) were detected in Peruvian pinniped vibrissae, serum, and milk samples. Since vibrissae accumulate elements over several years, trace element concentrations were found to be 2 to 20 times higher in vibrissae than serum. Vibrissae provide an ideal offloading route since they are not metabolically active and can store contaminants without risk of remobilization. Milk contained the highest As concentrations among the three tissues, potentially due to mobilization of arsenic from adipose stores. Since milk is the main source of nutrition for growing pups, high As concentrations are of great concern for the health of the pup. Arsenic concentrations in SASL female vibrissae were twice as high as PFS and three times higher than SASL male vibrissae. Although SASL milk was not available for this study, it is speculated that As concentrations would be as high or higher than PFS milk and is a concern for SASL pups. All female SASL vibrissae contained As concentrations within the range for chronic exposure in humans (0.1 to 0.5 μg; Ratnaike, 2003). Vibrissae concentrations in the last 4 years of this study (2016 to 2019) also exceeded As concentrations of 0.1 μg/g indicating chronic and potentially increasing exposure to As in Peruvian pinnipeds.

Male SASL contained Cd vibrissae concentrations 5x higher than PFS males (2x higher than SASL females) indicating potential foraging differences between species. Young male SASL likely forage on more prey high in Cd, such as squid, than SASL females and PFS (Gerpe et al., 2000). Female vibrissae contained higher concentrations of Al, Cu, Mn, Sn, and Zn and lower concentrations of Cd and Hg than males. Females may accumulate less Cd and Hg than males by offloading these contaminants to their pups via gestation and lactation. This is evident in PFS as pup vibrissae grown in utero had higher Cd concentrations than dam vibrissae.

Since usually only one species or sex was collected each year, it is difficult to compare concentrations over years. An increase in vibrissae As concentrations was seen in PFS males and females and SASL females. This may indicate increasing bioavailable As due to expanding Cu mining and agricultural runoff. The main anthropogenic source of As is Cu smelting. There is a Cu smelting facility south of PSJ on the coast of Ilo, Peru. The Humboldt Current may carry contaminants from the Cu smelting facility north to Peruvian pinniped foraging grounds. Once released into the environment, As is taken up in the food web and bioaccumulates in marine mammals. Average Hg concentrations approached thresholds associated with toxicity and should be monitored carefully over time.

All 15 elements were detected in PFS milk and pup vibrissae indicating gestational and lactational transfer of all elements from the dam to the pup. Aluminum and As showed potential toxicity in PFS milk and should be monitored as they may affect proper growth and development in pups. Pup vibrissae had significantly higher concentrations than dam vibrissae for 11 of the 15 elements analyzed. Pup vibrissae grow for the last 6-7 months of gestation and represent gestational transfer from the dam. High pup vibrissae concentrations indicate that dams may be offloading high levels of trace elements during gestation.

This study was the first to identify trace elements in Peruvian pinniped at Punta San Juan, Peru. Little information existed previously on trace element concentrations in otariids, especially for vibrissae and milk. The results of this study provide important information on general element concentrations in Peruvian pinniped and maternal offloading in PFS. High concentrations of Al, As, and Pb indicate the need for continued monitoring of these species for potential signs of toxicity, as well as further evaluation of the linear agreement between Pb concentrations in serum and whole blood. Segmented analysis of vibrissae in future studies can provide a better understanding of how contaminant concentrations vary over months or years.

Determining trace element concentrations in prey species is also necessary to understand potential sources of contamination. Increased local mining along with waste and agricultural runoff may be negatively affecting the marine environment leading to the bioaccumulation of contaminants in high trophic level species such as pinnipeds. These data will be shared with the national protected areas service (SERNANP) to be included in future management and conservation plans.

Literature Cited

Adkesson, M.J., Levengood, J.M., Scott, J.W., Schaeffer, D.J., Langan, J.N., Cárdenas-Alayza, S., de la Puente, S., Majluf, P., Yi, S., 2018. Assessment of polychlorinated biphenyls, organochlorine pesticides, and polybrominated diphenyl ethers in the blood of Humboldt penguins (*Spheniscus humboldti*) from the Punta San Juan Marine Protected Area, Peru. Journal of Wildlife Diseases 54, 304-314. https://doi.org/10.7589/2016-12-270

Adkesson, M.J., Levengood, J.M., Scott, J.W., Schaeffer, D.J., Panno, B., Langan, J.N., Cárdenas-Alayza, S. and James-Yi, S., 2019. Analysis of toxic and essential elements in the blood and feathers of Humboldt penguins (*Spheniscus humboldti*) at Punta San Juan, Peru. Journal of Wildlife Diseases 55, 438-443. https://doi.org/10.7589/2018-03-081

Andrade, S., Carlini, A.R., Vodopivez, C., Poljak, S., 2007. Heavy metals in molted fur of the southern elephant seal *Mirounga leonina*. Marine Pollution Bulletin 54, 602-605. https://doi.org/10.1016/j.marpolbul.2006.12.006

Arias-Schreiber, M., 2000. Los lobos marinos y su relación con la abundancia de la anchoveta peruana durante 1979-2000. Boletin Instituto del Mar del Peru 19, 133-138.

Arias-Schreiber, M., 2003. Prey spectrum and feeding behaviour of two sympatric pinnipeds (*Arctocephalus australis* and *Otaria flavescens*) in relation to the 1997–98 ENSO in southern Peru. Master's Thesis. University of Bremen, Germany.

Arnould, J.P., Hindell, M.A., 1999. The composition of Australian fur seal (*Arctocephalus pusillus doriferus*) milk throughout lactation. Physiological and Biochemical Zoology 72, 605-612. https://doi.org/10.1086/316702

ATSDR (Agency for Toxic Substances and Disease Registry), 2005. Toxicological profile for Tin. U.S. Department of Health and Human Services.

ATSDR (Agency for Toxic Substances and Disease Registry), 2008. Toxicological profile for aluminum. U.S. Department of Health and Human Services.

Bakun, A., Black, B.A., Bograd, S.J., Garcia-Reyes, M., Miller, A.J., Rykaczewski, R.R., Sydeman, W.J., 2015. Anticipated effects of climate change on coastal upwelling ecosystems. Current Climate Change Reports 1, 85-93. https://doi.org/10.1007/s40641-015-0008-4

Bakun, A., Weeks, S.J., 2008. The marine ecosystem off Peru: What are the secrets of its fishery productivity and what might its future hold? Progress in Oceanography 79, 290-299. https://doi.org/10.1016/j.pocean.2008.10.027

Bansa, D.K., Awua, A.K., Boatin, R., Adom, T., Brown-Appiah, E.C., Amewosina, K.K., Diaba, A., Datoghe, D., Okwabi, W., 2017. Cross-sectional assessment of infants' exposure to toxic metals through breast milk in a prospective cohort study of mining communities in Ghana. BMC Public Health 17, 1-12. https://doi.org/10.1186/s12889-017-4403-8

Baraj, B., Niencheski, L., Windom, H., Hermanns, L., 2009. Trace metal concentration in liver, kidney and heart in South American fur seal (*Arctocephalus australis*) from southern Brazil. Marine Pollution Bulletin 12, 1948-1952. https://doi.org/10.1016/j.marpolbul.2009.07.026

Barber, R., Kogelschatz, J., 1990. Nutrients and productivity during the 1982/83 El Niño. Elsevier Oceanography Series 52, 21-53. https://doi.org/10.1016/S0422-9894(08)70032-1

Barbosa, A.P.M., Méndez-Fernandez, P., Dias, P.S., Santos, M.C.O., Taniguchi, S., Montone, R.C., 2018. Transplacental transfer of persistent organic pollutants in La Plata dolphins (*Pontoporia blainvillei*; Cetartiodactyla, Pontoporiidae). Science of the Total Environment 631, 239-245. https://doi.org/10.1016/j.scitotenv.2018.02.325

Barceloux, D.G., Barceloux, D., 1999. Cobalt. Journal of Toxicology: Clinical Toxicology 37, 201-216. https://doi.org/10.1081/CLT-100102420

Barth, J.A., Menge, B.A., Lubchenco, J., Chan, F., Bane, J.M., Kirincich, A.R., McManus, M.A., Nielsen, K.J., Pierce, S.D. and Washburn, L., 2007. Delayed upwelling alters nearshore coastal ocean ecosystems in the northern California current. Proceedings of the National Academy of Sciences 104, 3719-3724. https://doi.org/10.1073/pnas.0700462104

Bearhop, S., Hilton, G.M., Votier, S.C., Waldron, S., 2004. Stable isotope ratios indicate that body condition in migrating passerines is influenced by winter habitat. Proceedings of the Royal Society of London. Series B: Biological Sciences 271, S215-S218. https://doi.org/10.1098/rsbl.2003.0129

Beckmen, K.B., Duffy, L.K., Zhang, X., Pitcher, K.W., 2002. Mercury concentrations in the fur of Steller sea lions and northern fur seals from Alaska. Marine Pollution Bulletin 44, 1130-1135. https://doi.org/10.1016/S0025-326X(02)00167-4

Bedoya-Perales, N.S., Pumi, G., Talamini, E. and Padula, A.D., 2018. The quinoa boom in Peru: Will land competition threaten sustainability in one of the cradles of agriculture? Land Use Policy 79, 475-480. https://doi.org/10.1016/j.landusepol.2018.08.039

Berglund, M., Lind, B., Björnberg, K.A., Palm, B., Einarsson, Ö., Vahter, M., 2005. Inter-individual variations of human mercury exposure biomarkers: a cross-sectional assessment. Environmental Health 4, 1-11. https://doi.org/10.1186/1476-069X-4-20

Berry, M.J., Ralston, N.V., 2008. Mercury toxicity and the mitigating role of selenium. EcoHealth 5, 456-459. https://doi.org/10.1007/s10393-008-0204-y

Berta, A., Churchill, M., 2012. Pinniped taxonomy: review of currently recognized species and subspecies, and evidence used for their description. Mammal Review 42, 207-234. https://doi.org/10.1111/j.1365-2907.2011.00193.x

Blakley, B. 2013. Overview of Lead Poisoning. Merck Manual. https://www.merckvetmanual.com/toxicology/lead-poisoning/overview-of-lead-poisoning

Blaurock-Busch, E., Amin, O.R., Dessoki, H.H., Rabah, T., 2012. Toxic metals and essential elements in hair and severity of symptoms among children with autism. Maedica 7, 38-48.

Borrell, A., 1993. PCB and DDT in blubber of cetaceans from the northeastern north Atlantic. Marine Pollution Bulletin 26, 146-151. https://doi.org/10.1016/0025-326X(93)90125-4

Borrell, A., Bloch, D., Desportes, G., 1995. Age trends and reproductive transfer of organochlorine compounds in long-finned pilot whales from the Faroe Islands. Environmental Pollution 88, 283-292. https://doi.org/10.1016/0269-7491(95)93441-2

Brookens, T.J., Harvey, J.T., O'Hara, T.M., 2007. Trace element concentrations in the Pacific harbor seal (*Phoca vitulina richardii*) in central and northern California. Science of the Total Environment 372, 676-692. https://doi.org/10.1016/j.scitotenv.2006.10.006

Brown, T., Ross, P., Reimer, K., 2016. Transplacental transfer of polychlorinated biphenyls, polybrominated diphenylethers, and organochlorine pesticides in ringed seals (*Pusa hispida*). Archives of Environmental Contamination and Toxicology 70, 20-27. https://doi.org/10.1007/s00244-015-0191-2

Bryan, C.E., Christopher, S.J., Balmer, B.C., Wells, R.S., 2007. Establishing baseline levels of trace elements in blood and skin of bottlenose dolphins in Sarasota Bay, Florida: implications for non-invasive monitoring. Science of the Total Environment 388, 325-342. https://doi.org/10.1016/j.scitotenv.2007.07.046

Byrd, J.T., Andreae, M.O., 1986. Concentrations and fluxes of tin in aerosols and rain. Atmospheric Environment 20, 931-939. https://doi.org/10.1016/0004-6981(86)90277-5

Cámara, F., Amaro, M.A., Barberá, R., Clemente, G., 2005. Bioaccessibility of minerals in school meals: Comparison between dialysis and solubility methods. Food Chemistry 92, 481-489. https://doi.org/10.1016/j.foodchem.2004.08.009

Campagna, C., 1985. The breeding cycle of the southern sea lion, *Otaria Byronia*. Marine Mammal Science 1, 210-218. https://doi.org/10.1111/j.1748-7692.1985.tb00010.x

Campagna, C., Boeuf, B.J.L., 1988. Reproductive behaviour of southern sea lions. Behaviour 104, 233-261. https://doi.org/10.1163/156853988X00539

Campagna, C., Werner, R., Karesh, W., Marín, M.R., Koontz, F., Cook, R., Koontz, C., 2001. Movements and location at sea of South American sea lions (*Otaria flavescens*). Journal of Zoology 255, 205-220. https://doi.org/10.1017/S0952836901001285

Cappozzo, H.L., Perrin, W. F. 2009. South American sea lion *Otaria flavescens*. In: Perrin, W.F, Wüsig, B., Thewissen, J.G.M. (Eds.), Encyclopedia of Marine Mammals. Academic Press. 1076-1079.

Cárdenas-Alayza, S., 2012. Prey abundance and population dynamics of South American fur seals (*Arctocephalus australis*) in Peru. Master's Thesis. University of British Columbia.

Cárdenas-Alayza S, Cardeña-Mormontoy MA., 2012. The Punta San Juan project– protecting one of the world's largest colonies of Humboldt penguins. The Penguin TAG Conservation Newsletter 16, 10-15.

Cárdenas-Alayza, S., Crespo, E., Oliveira, L. 2016a. *Otaria byronia*. The IUCN Red List of Threatened Species. http://dx.doi.org/10.2305/IUCN.UK.2016-1.RLTS.T41665A61948292.en

Cárdenas-Alayza, S., Oliveira, L., Crespo, E. 2016b. *Arctocephalus australis*. The IUCN Red List of Threatened Species 2016. http://dx.doi.org/10.2305/IUCN.UK.2016-1.RLTS.T2055A45223529.en

Cárdenas-Alayza, S., Oliveira, L. 2016. *Arctocephalus australis* Peruvian/Northern Chilean subpopulation. The IUCN Red List of Threatened Species 2016. http://dx.doi.org/10.2305/IUCN.UK.2016-1.RLTS.T72050476A72050985.en.

Castellini, J.M., Rea, L.D., Lieske, C.L., Beckmen, K.B., Fadely, B.S., Maniscalco, J.M., O'Hara, T.M., 2012. Mercury concentrations in hair from neonatal and juvenile Steller sea lions (*Eumetopias jubatus*): Implications based on age and region in this northern Pacific marine sentinel piscivore. EcoHealth 9, 267-277. https://doi.org/10.1007/s10393-012-0784-4

Castilla, J., Correa, J., 1997. Copper tailing impacts in coastal ecosystems of northern Chile: from species to community responses, in: Moore M, Imray P, Dameron C, Callan P, Langley A, Mangas S (Eds.), Copper National Environmental Health Forum Monographs, Metal Series, Brisbane. 71-80.

Cempel, M., Nikel, G., 2006. Nickel: A review of its sources and environmental toxicology. Polish Journal of Environmental Studies 15, 375-382.

Chandra Sekhar, K., Chary, N.S., Kamala, C.T., Rao, J.V., Balaram, V., Anjaneyulu, Y., 2003. Risk assessment and pathway study of arsenic in industrially contaminated sites of Hyderabad: a case study. Environment International 29, 601-611. https://doi.org/10.1016/S0160-4120(03)00017-5

Chavez, F.P., Ryan, J., Lluch-Cota, S.E., Ñiquen, M., 2003. From anchovies to sardines and back: multidecadal change in the Pacific Ocean. Science 299, 217-221. https://doi.org/10.1126/science.1075880

Committee on Taxonomy. 2014. List of marine mammal species and subspecies. Society for Marine Mammalogy. Available at https://www.marinemammalscience.org.

Cossaboon, J.M., Ganguli, P.M., Flegal, A.R., 2015. Mercury offloaded in northern elephant seal hair affects coastal seawater surrounding rookery. Proceedings of the National Academy of Sciences 112, 12058-12062. https://doi.org/10.1073/pnas.1506520112

Councell, T.B., Duckenfield, K.U., Landa, E.R., Callender, E., 2004. Tire-wear particles as a source of zinc to the environment. Environmental Science and Technology, 38, 4206-4214. https://doi.org/10.1021/es034631f

Crossgrove, J. and Zheng, W., 2004. Manganese toxicity upon overexposure. NMR in Biomedicine: An International Journal Devoted to the Development and Application of Magnetic Resonance In Vivo 178, 544-553. https://doi.org/10.1002/nbm.931

Darimont, C.T., Reimchen, T.E., 2002. Intra-hair stable isotope analysis implies seasonal shift to salmon in gray wolf diet. Canadian Journal of Zoology 80, 1638-1642. https://doi.org/10.1139/z02-149

Das, K., Debacker, V., Pillet, S., Bouquegneau, J., 2003. Heavy metals in marine mammals, In: Vos J.G., B.G., Fournier, M., O'Shea, T., (Eds.), Toxicology of Marine Mammals., 1st ed. Taylor and Francis Publishers, London. 135-154. https://doi.org/10.1201/9780203165577

De Guise, S., Martineau, D., Béland, P, Fournier, M., 1995. Possible mechanisms of action of environmental contaminants on St. Lawrence beluga whales (*Delphinapterus leucas*). Environmental Health Perspectives, 103, 73-77. https://doi.org/10.1289/ehp.95103s473

De María, M., Szteren, D., García-Alonso, J., de Rezende, C.E., Gonçalves, R.A., Godoy, J.M. and Barboza, F.R., 2021. Historic variation of trace elements in pinnipeds with spatially segregated trophic habits reveals differences in exposure to pollution. Science of the Total Environment 750, 141296. https://doi.org/10.1016/j.scitotenv.2020.141296

Dietz, R., Riget, F., Born, E., 2000. An assessment of selenium to mercury in Greenland marine animals. Science of the Total Environment 245, 15-24. https://doi.org/10.1016/S0048-9697(99)00430-1

Drago, M., Cardona, L., Crespo, E., Aguilar, A., 2009. Ontogenic dietary changes in South American sea lions. Journal of Zoology 279, 251-261. https://doi.org/10.1111/j.1469-7998.2009.00613.x

Edwards, M.R., 2018. Peruvian pinnipeds as archivists of ENSO effects. Master's Thesis. Nova Southeastern University.

Ehresman, D.J., Froehlich, J.W., Olsen, G.W., Chang, S.-C., Butenhoff, J.L., 2007. Comparison of human whole blood, plasma, and serum matrices for the determination of perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and other fluorochemicals. Environmental Research 103, 176-184. https://doi.org/10.1016/j.envres.2006.06.008

Eisler, R. 1987. Mercury hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish and Wildlife Service Biological Report 85(1.10).

El Khalil, H., El Hamiani, O., Bitton, G., Ouazzani, N., Boularbah, A., 2008. Heavy metal contamination from mining sites in south Morocco: Monitoring metal content and toxicity of soil runoff and groundwater. Environmental Monitoring and Assessment 136, 147-160. https://doi.org/10.1007/s10661-007-9671-9

Elorriaga-Verplancken, F., Aurioles-Gamboa, D., 2008. Trace metal concentrations in the hair of *Zalophus californianus* pups and their relation to feeding habits. Biological Trace Element Research 126, 148-164. https://doi.org/10.1007/s12011-008-8186-8

Endo, T., Kimura, O., Hisamichi, Y., Minoshima, Y., Haraguchi, K., Kakumoto, C., Kobayashi, M., 2006. Distribution of total mercury, methyl mercury and selenium in pod of killer whales (*Orcinus Orca*) stranded in the northern area of Japan: comparison of mature females with calves. Environmental Pollution 144, 145-150. https://doi.org/10.1016/j.envpol.2005.12.035

Espinoza-Morriberón, D., Echevin, V., Colas, F., Tam, J., Ledesma, J., Vásquez, L., Graco, M., 2017. Impacts of El Niño events on the Peruvian upwelling system productivity. Journal of Geophysical Research: Oceans 122, 5423-5444. https://doi.org/10.1002/2016JC012439

Fanni, D., Ambu, R., Gerosa, C., Nemolato, S., Iacovidou, N., Van Eyken, P., Fanos, V., Zaffanello, M., Faa, G., 2014. Aluminum exposure and toxicity in neonates: a practical guide to halt aluminum overload in the prenatal and perinatal periods. World Journal of Pediatrics 10, 101-107. https://doi.org/10.1007/s12519-014-0477-x

FAO. 2020. The State of World Fisheries and Aquaculture 2020. Sustainability in action. Rome. https://doi.org/10.4060/ca9229en

FDA, Departement of Health and Human Services. 2020a. 21 C.F.R. § 165.110. https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/cfrsearch.cfm?fr=165.110

FDA, Department of Health and Human Services, 2020b. Inorganic Arsenic in Rice Cereals for Infants: Action Level Guidance for Industry. https://www.fda.gov/media/97234/download

Ferdinando, P.M., 2019. Assessment of Heavy Metals in Subsistence-Harvested Alaskan Marine Mammal Body Tissues and Vibrissae. Master's Thesis. Nova Southeastern University.

Fernández-Martínez, A., Charlet, L., 2009. Selenium environmental cycling and bioavailability: a structural chemist point of view. Reviews in Environmental Science and Bio/Technology 8, 81-110. https://doi.org/10.1007/s11157-009-9145-3

Finley, J.W., Davis, C.D., 1999. Manganese deficiency and toxicity: are high or low dietary amounts of manganese cause for concern? Biofactors 10, 15-24.

Fire, S.E., Adkesson, M.J., Wang, Z., Jankowski, G., Cárdenas-Alayza, S. and Broadwater, M., 2017. Peruvian fur seals (*Arctocephalus australis ssp.*) and South American sea lions (*Otaria byronia*) in Peru are exposed to the harmful algal toxins domoic acid and okadaic acid. Marine Mammal Science 33, 630-644. https://doi.org/10.1111/mms.12371

Flemming, C.A., Trevors, J.T., 1989. Copper toxicity and chemistry in the environment: a review. Water, Air, and Soil Pollution 44, 143-158. https://doi.org/10.1007/BF00228784

Flora, S., Mittal, M., Mehta, A., 2008. Heavy metal induced oxidative stress & its possible reversal by chelation therapy. Indian Journal of Medical Research 128, 501-523.

Fosmire, G.J., 1990. Zinc toxicity. The American Journal of Clinical Nutrition 51, 225-227. https://doi.org/10.1093/ajcn/51.2.225

Fossi, M., Marsili, L., Junin, M., Castello, H., Lorenzani, J., Casini, S., Savelli, C., Leonzio, C., 1997. Use of nondestructive biomarkers and residue analysis to assess the health status of endangered species of pinnipeds in the south-west Atlantic. Marine Pollution Bulletin 34, 157-162. https://doi.org/10.1016/S0025-326X(96)00073-2

Fossi, M.C., Panti, C., 2017. Sentinel Species of Marine Ecosystems. Oxford Research Encyclopedia of Environmental Science. https://doi.org/10.1093/acrefore/9780199389414.013.110

Gabrielsen, K.M., Villanger, G.D., Lie, E., Karimi, M., Lydersen, C., Kovacs, K.M., Jenssen, B.M., 2011. Levels and patterns of hydroxylated polychlorinated biphenyls (OH-PCBs) and their associations with thyroid hormones in hooded seal (*Cystophora cristata*) mother–pup pairs. Aquatic Toxicology 105, 482-491. https://doi.org/10.1016/j.aquatox.2011.08.003

Gehara, M.C.M., 2009. Filogeografia do leão-marinho-do-sul, *Otaria flavescens* Shaw 1800, Faculdade de Biociências. Dissertação. Pontifícia Universidade Católica do Rio Grande do Sul.

Georges, J.-Y., Groscolas, R., Guinet, C., Robin, J.-P., 2001. Milking strategy in subantarctic fur seals *Arctocephalus tropicalis* breeding on Amsterdam Island: evidence from changes in milk composition. Physiological and Biochemical Zoology 74, 548-559.

Gerpe, M.S., De Moreno, J.E.A., Moreno, V.J., Patat, M.L., 2000. Cadmium, zinc and copper accumulation in the squid *Illex argentinus* from the Southwest Atlantic Ocean. Marine Biology 136, 1039-1044. https://doi.org/10.1007/s002270000308

Gerpe, M., Rodríguez, D., Moreno, V., Bastida, R., Aizpún J., 2007. Copper, zinc, cadmium, and mercury in southern sea lions (*Otaria flavescens*) from Argentina. Aquatic Mammals 33, 223. https://doi.org/10.1578/AM.33.2.2007.223

Ginter, C.C., DeWitt, T.J., Fish, F.E., Marshall, C.D., 2012. Fused traditional and geometric morphometrics demonstrate pinniped whisker diversity. PLOS ONE 7. https://doi.org/10.1371/journal.pone.0034481

Godwin, C.M., Zehnpfennig, J.R. and Learman, D.R., 2020. Biotic and abiotic mechanisms of manganese (II) oxidation in Lake Erie. Frontiers in Environmental Science 8. https://doi.org/10.3389/fenvs.2020.00057

Grajewska, A., Falkowska, L., Saniewska, D. and Pawliczka, I., 2019. Changes in total mercury, methylmercury, and selenium blood levels during different life history stages of the Baltic gray seal (*Halichoerus grypus grypus*). Science of The Total Environment 676, 268-277. https://doi.org/10.1016/j.scitotenv.2019.04.204

Gray, R., Canfield, P. and Rogers, T., 2008. Trace element analysis in the serum and hair of Antarctic leopard seal, *Hydrurga leptonyx*, and Weddell seal, *Leptonychotes weddellii*. Science of the Total Environment 399, 202-215. https://doi.org/10.1016/j.scitotenv.2008.03.039

Grazuleviciene, R., Nadisauskiene, R., Buinauskiene, J., Grazulevicius, T., 2009. Effects of elevated levels of manganese and iron in drinking water on birth outcomes. Polish Journal of Environmental Studies 18, 819-825.

Greig, D.J., Ylitalo, G.M., Hall, A.J., Fauquier, D.A., Gulland, F.M., 2007. Transplacental transfer of organochlorines in California sea lions (*Zalophus californianus*). Environmental Toxicology and Chemistry: An International Journal 26, 37-44. https://doi.org/10.1897/05-609R.1

Grønnestad, R., Villanger, G.D., Polder, A., Kovacs, K.M., Lydersen, C., Jenssen, B.M., Borgå, K., 2017. Maternal transfer of perfluoroalkyl substances in hooded seals. Environmental Toxicology and Chemistry 36, 763-770. https://doi.org/10.1002/etc.3623

Guillamet, E., Creus, A., Ponti, J., Sabbioni, E., Fortaner, S., Marcos, R., 2004. In vitro DNA damage by arsenic compounds in a human lymphoblastoid cell line (TK6) assessed by the alkaline comet assay. Mutagenesis 19, 129-135. https://doi.org/10.1093/mutage/geh005

Gupta, N., Gaurav, S.S., Kumar, A., 2013. Molecular basis of aluminium toxicity in plants: a review. American Journal of Plant Sciences 4, 21-37. http://dx.doi.org/10.4236/ajps.2013.4.12A3004

Habran, S., Debier, C., Crocker, D.E., Houser, D.S., Das, K., 2011. Blood dynamics of mercury and selenium in northern elephant seals during the lactation period. Environmental Pollution 159, 2523-2529. https://doi.org/10.1016/j.envpol.2011.06.019

Habran, S., Pomeroy, P.P., Debier, C., Das, K., 2013. Changes in trace elements during lactation in a marine top predator, the gray seal. Aquatic Toxicology 126, 455-466. https://doi.org/10.1016/j.aquatox.2012.08.011

Hameed, A., Akhtara, S., Amjada, A., Naeema, I., Tariqa, M., 2019. Comparative assessment of arsenic contamination in raw milk, infant formulas and breast milk. Journal of Dairy & Veterinary Sciences 13, 555851. http://doi.org/10.19080/JDVS.2019.13.555851

Harcourt, R., 1993. Individual variation in predation on fur seals by southern sea lions (*Otaria byronia*) in Peru. Canadian Journal of Zoology 71, 1908-1911. https://doi.org/10.1139/z93-273

Heileman, S., Guevara, R., Chavez, F., Bertrand, A., Soldi, H., 2009. XVII-56 Humboldt Current: LME# 13. The UNEP large marine ecosystem report: A perspective on changing conditions in LMEs of the world's regional seas, 749-762.

Hernández-Avila, M., Smith, D., Meneses, F., Sanin, L.H., Hu, H., 1998. The influence of bone and blood lead on plasma lead levels in environmentally exposed adults. Environmental Health Perspectives 106, 473-477. https://doi.org/10.1289/ehp.106-1533211

Hewer, H.R. and Backhouse, K.M., 1968. Embryology and foetal growth of the gray seal, *Halichoerus grypus*. Journal of Zoology 155, 507-533.

Hirons, A.C., Schell, D.M., St. Aubin, D.J., 2001. Growth rates of vibrissae of harbor seals (*Phoca vitulina*) and Steller sea lions (*Eumetopias jubatus*). Canadian Journal of Zoology 79, 1053-1061. https://doi.org/10.1139/z01-055

Hoch, M., 2001. Organotin compounds in the environment—an overview. Applied geochemistry 16, 719-743. https://doi.org/10.1016/S0883-2927(00)00067-6

Hoguet, J., Keller, J.M., Reiner, J.L., Kucklick, J.R., Bryan, C.E., Moors, A.J., Pugh, R.S., Becker, P.R., 2013. Spatial and temporal trends of persistent organic pollutants and mercury in beluga whales (*Delphinapterus leucas*) from Alaska. Science of the Total Environment 449, 285-294. https://doi.org/10.1016/j.scitotenv.2013.01.072

Holmgren, M., Scheffer, M., Ezcurra, E., Gutiérrez, J.R., Mohren, G.M., 2001. El Niño effects on the dynamics of terrestrial ecosystems. Trends in Ecology & Evolution 16, 89-94. https://doi.org/10.1016/S0169-5347(00)02052-8

Hunter, P., 2008. A toxic brew we cannot live without. EMBO Reports 9, 15-18. https://doi.org/10.1038/sj.embor.7401148

Hyvärinen, H., Sipilä, T., 1984. Heavy metals and high pup mortality in the Saimaa ringed seal population in eastern Finland. Marine Pollution Bulletin 15, 335-337. https://doi.org/10.1016/0025-326X(84)90490-9

Ikemoto, T., Kunito, T., Anan, Y., Tanaka, H., Baba, N., Miyazaki, N., Tanabe, S., 2004a. Association of heavy metals with metallothionein and other proteins in hepatic cytosol of marine mammals and seabirds. Environmental Toxicology and Chemistry 23, 2008-2016. https://doi.org/10.1897/03-456

Ikemoto, T., Kunito, T., Tanaka, H., Baba, N., Miyazaki, N., Tanabe, S., 2004b. Detoxification mechanism of heavy metals in marine mammals and seabirds: Interaction of selenium with mercury, silver, copper, zinc, and cadmium in liver. Archives of Environmental Contamination and Toxicology 47, 402-413. https://doi.org/10.1007/s00244-004-3188-9

Ikemoto, T., Kunito, T., Watanabe, I., Yasunaga, G., Baba, N., Miyazaki, N., Petrov, E.A. and Tanabe, S., 2004c. Comparison of trace element accumulation in Baikal seals (*Pusa sibirica*), Caspian seals (*Pusa caspica*) and northern fur seals (*Callorhinus ursinus*). Environmental Pollution 127, 83-97. https://doi.org/10.1016/S0269-7491(03)00251-3

IMARPE. 2006. Censo Nacional de Lobo Chusco (*Otaria flavescens*) 2006. Unidad de Investigación de Depredadores Superiores. Informe Interno.

IMARPE. 2014. Anuario Científico y Tecnológico. IMARPE Vol. 13, 2014.

Irfan, M., Hayat, S., Ahmad, A., Alyemeni, M.N., 2013. Soil cadmium enrichment: Allocation and plant physiological manifestations. Saudi Journal of Biological Sciences 20, 1-10. https://doi.org/10.1016/j.sjbs.2012.11.004

Irwandi, J., Farida, O., 2009. Mineral and heavy metal contents of marine fin fish in Langkawi Island, Malaysia. International Food Research Journal 16, 105-112.

Iyengar, V. and Woittiez, J., 1988. Trace elements in human clinical specimens: evaluation of literature data to identify reference values. Clinical chemistry 34, 474-481.

Jacox, M.G., Hazen, E.L., Zaba, K.D., Rudnick, D.L., Edwards, C.A., Moore, A.M., Bograd, S.J., 2016. Impacts of the 2015–2016 El Niño on the California Current System: Early assessment and comparison to past events. Geophysical Research Letters 43, 7072-7080. https://doi.org/10.1002/2016GL069716

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., Beeregowda, K.N., 2014. Toxicity, mechanism and health effects of some heavy metals. Interdisciplinary Toxicology 7, 60-72. http://doi.org/10.2478/intox-2014-0009

Jakimska, A., Konieczka, P., Skóra, K., Namieśnik, J., 2011a. Bioaccumulation of metals in tissues of marine animals, Part I: The role and impact of heavy metals on organisms. Polish Journal of Environmental Studies 20, 1117-1125.

Jakimska, A., Konieczka, P., Skóra, K., Namieśnik, J., 2011b. Bioaccumulation of metals in tissues of marine animals, Part II: Metal concentrations in animal tissues. Polish Journal of Environmental Studies 20, 1127-1146.

Jankowski, G., Adkesson, M.J., Saliki, J.T., Cárdenas-Alayza, S., Majluf, P., 2015. Survey for infectious disease in the South American fur seal (*Arctocephalus australis*) population at Punta San Juan, Peru. Journal of Zoo and Wildlife Medicine 46, 246-254. https://doi.org/10.1638/2014-0120.1

Jefferson, T.A., Leatherwood, S., Webber, M.A., 1993. Marine mammals of the world, In: Carpenter, K.E., Sommer, C., Bogusch, A., Agnalt, A.L. (Eds.), Food and Agriculture Organization of the United Nations. 232-247.

Kannan, K., Guruge, K.S., Thomas, N.J., Tanabe, S., Giesy, J.P., 1998. Butyltin residues in southern sea otters (*Enhydra lutris nereis*) found dead along California coastal waters. Environmental Science & Technology 32, 1169-1175. https://doi.org/10.1021/es970914u

Kannan, K., Senthilkumar, K., Loganathan, B.G., Takahashi, S., Odell, D.K., Tanabe, S., 1997. Elevated accumulation of tributyltin and its breakdown products in bottlenose dolphins (*Tursiops truncatus*) found stranded along the US Atlantic and Gulf coasts. Environmental Science & Technology 31, 296-301. https://doi.org/10.1021/es960657d

Karstensen, J., Ulloa, O., 2009. Peru–Chile Current System, In: Steele, J.H. (Ed.), Encyclopedia of Ocean Sciences (Second Edition). Academic Press, Oxford. 385-392.

Kelleher, C., 2016. Vibrissae growth rates and foraging and migration patterns for juvenile male northern fur seals (*Callorhinus ursinus*) from St. Paul Island, Alaska determined with stable isotope analysis. Master of Science Thesis, University of California, San Diego.

Kim, G.B., Lee, J.S., Tanabe, S., Iwata, H., Tatsukawa, R., Shimazaki, K., 1996. Specific accumulation and distribution of butyltin compounds in various organs and tissues of the Steller sea lion (*Eumetopias jubatus*): comparison with organochlorine accumulation pattern. Marine Pollution Bulletin 32, 558-563. https://doi.org/10.1016/0025-326X(96)84576-0

Koen Alonso, M., Crespo, E.A., Pedraza, S.N., Garcia, N.A., Coscarella, M.A., 2000. Food habits of the South American sea lion, *Otaria flavescens*, off Patagonia, Argentina. Fishery Bulletin 98, 250-263.

Kozlowski, H., Janicka-Klos, A., Brasun, J., Gaggelli, E., Valensin, D., Valensin, G., 2009. Copper, iron, and zinc ions homeostasis and their role in neurodegenerative disorders (metal uptake, transport, distribution and regulation). Coordination Chemistry Reviews 253, 2665-2685. https://doi.org/10.1016/j.ccr.2009.05.011

Krejpcio, Z., 2001. Essentiality of chromium for human nutrition and health. Polish Journal of Environmental Studies 10, 399-404.

Krewski, D., Yokel, R.A., Nieboer, E., Borchelt, D., Cohen, J., Harry, J., Kacew, S., Lindsay, J., Mahfouz, A.M., Rondeau, V., 2007. Human health risk assessment for aluminium, aluminium oxide, and aluminium hydroxide. Journal of Toxicology and Environmental Health, Part B 10, 1-269. https://doi.org/10.1080/10937400701597766

Laker, M., 1982. On determining trace element levels in man: the uses of blood and hair. The Lancet 320, 260-262. https://doi.org/10.1016/S0140-6736(82)90336-1

Lehnert, K., Desforges, J.-P., Das, K., Siebert, U., 2018. Chapter 10 - Ecotoxicological biomarkers and accumulation of contaminants in pinnipeds, In: Fossi, M.C., Panti, C. (Eds.), Marine Mammal Ecotoxicology. Academic Press. 261-289.

Lerner, J.E., Ono, K., Hernandez, K.M., Runstadler, J.A., Puryear, W.B. and Polito, M.J., 2018. Evaluating the use of stable isotope analysis to infer the feeding ecology of a growing US gray seal (*Halichoerus grypus*) population. PloS One 13, e0192241. https://doi.org/10.1371/journal.pone.0192241

Levi, M., Hjelm, C., Harari, F., Vahter, M., 2018. ICP-MS measurement of toxic and essential elements in human breast milk. A comparison of alkali dilution and acid digestion sample preparation methods. Clinical Biochemistry 53, 81-87. https://doi.org/10.1016/j.clinbiochem.2017.12.003

Levy, B.S., Nassetta, W.J., 2003. Neurologic effects of manganese in humans: a review. International Journal of Occupational and Environmental Health 9, 153-163. https://doi.org/10.1179/oeh.2003.9.2.153

Leyssens, L., Vinck, B., Van Der Straeten, C., Wuyts, F., Maes, L., 2017. Cobalt toxicity in humans—A review of the potential sources and systemic health effects. Toxicology 387, 43-56. http://dx.doi.org/10.1016/j.tox.2017.05.015

Liang, G., Pan, L. and Liu, X., 2017. Assessment of typical heavy metals in human hair of different age groups and foodstuffs in Beijing, China. International journal of environmental research and public health 14, 914. https://doi.org/10.3390/ijerph14080914

Mackey, E.A., Becker, P.R., Demiralp, R., Greenberg, R.R., Koster, B., Wise, S.A., 1996. Bioaccumulation of vanadium and other trace metals in livers of Alaskan cetaceans and pinnipeds. Archives of Environmental Contamination and Toxicology 30, 503-512. https://doi.org/10.1007/BF00213402

Majluf P., 1984. South American fur seal *Arctocaphalus australis*, in Peru. In: Croxall J, Gentry R (Ed.), Status, biology and ecology of fur seals: Proceedings of an international symposium and workshop. NOAA Technical Report, Cambridge, England. 33-36.

Majluf, P., 1987. Reproductive ecology of female South American fur seals at Punta San Juan, Peru. Ph.D. Thesis. University of Cambridge.

Majluf, P., Trillmich, F., 1981. Distribution and abundance of sea lions (*Otaria byronia*) and fur seals (*Arctocephalus australis*) in Peru. Zeitschrift für Säugetierkunde 46, 384-393.

Manton, W.I., Rothenberg, S.J., Manalo, M., 2001. The lead content of blood serum. Environmental research 86, 263-273. https://doi.org/10.1006/enrs.2001.4271

Marcovecchio, J.E., Gerpe, M.S., Bastida, R.O., Rodríguez, D.H., Morón, S., 1994. Environmental contamination and marine mammals in coastal waters from Argentina: an overview. Science of the Total Environment 154, 141-151. https://doi.org/10.1016/0048-9697(94)90084-1

Marcovecchio, J.E., Gerpe, M.S., Moreno, V.J., Bastida, R.O., Rodríguez, D.H., 1991. Organ and tissues distribution of total mercury in the South American fur seal, *Arctocephalus australis.* In: Farmer, J.G. (Ed.), Heavy Metals in the Environment: 8th International Conference. Edinburgh, 16-20 September 1991. UK, CEP Consultant Ltd. 364-368.

Martin, S., Griswold, W., 2009. Human health effects of heavy metals. Environmental Science and Technology Briefs for Citizens 15, 1-6.

Matschullat, J., 2000. Arsenic in the geosphere—a review. Science of the Total Environment 249, 297-312. https://doi.org/10.1016/S0048-9697(99)00524-0

Mayer, D.R., Kosmus, W., Pogglitsch, H., Beyer, W., 1993. Essential trace elements in humans. Biological Trace Element Research 37, 27-38. https://doi.org/10.1007/BF02789399

McHuron, E.A., Harvey, J.T., Castellini, J.M., Stricker, C.A., O'Hara, T.M., 2014. Selenium and mercury concentrations in harbor seals (*Phoca vitulina*) from central California: Health implications in an urbanized estuary. Marine Pollution Bulletin 83, 48-57. https://doi.org/10.1016/j.marpolbul.2014.04.031

Molina, O., Olivari, J., Pietrobelli, C., 2016. Global value chains in the Peruvian mining sector. Inter-American Development Bank. 6-8.

Moreno-Sierra, D., Bergés-Tiznado, M.E., Márquez-Farías, F., Torres-Rojas, Y.E., Ruelas-Inzunza, J.R., Páez-Osuna, F., 2016. Trace metals in target tissues and stomach contents of the top predator sailfish *Istiophorus platypterus* from the Eastern Pacific: concentrations and contrasting behavior of biomagnification. Environmental Science and Pollution Research 23, 23791-23803. https://doi.org/10.1007/s11356-016-7551-y

Mortada, W.I., Sobh, M.A., El-Defrawy, M.M., Farahat, S.E., 2002. Reference intervals of cadmium, lead, and mercury in blood, urine, hair, and nails among residents in Mansoura city, Nile delta, Egypt. Environmental research 90, 104-110. https://doi.org/10.1006/enrs.2002.4396

Najeeb, U., Ahmad, W., Zia, M.H., Zaffar, M., Zhou, W., 2017. Enhancing the lead phytostabilization in wetland plant *Juncus effusus* L. through somaclonal manipulation and EDTA enrichment. Arabian Journal of Chemistry 10, S3310-S3317. https://doi.org/10.1016/j.arabjc.2014.01.009

Neff, J.M., 1997. Ecotoxicology of arsenic in the marine environment. Environmental Toxicology and Chemistry: An International Journal 16, 917-927. https://doi.org/10.1002/etc.5620160511

Nielsen, F.H., 2000. Importance of making dietary recommendations for elements designated as nutritionally beneficial, pharmacologically beneficial, or conditionally essential. The Journal of Trace Elements in Experimental Medicine 13, 113-129. https://doi.org/10.1002/(SICI)1520-670X(2000)13:1<113::AID-JTRA13>3.0.CO;2-D

Nielsen, F.H., 1998. Ultratrace elements in nutrition: current knowledge and speculation. The Journal of Trace Elements in Experimental Medicine: The Official Publication of the International Society for Trace Element Research in Humans 11, 251-274. https://doi.org/10.1002/(SICI)1520-670X(1998)11:2/3<251::AID-JTRA15>3.0.CO;2-Q

Nielsen, F.H., Sandstead, H.H., 1974. Are nickel, vanadium, silicon, fluorine, and tin essential for man? A review. The American journal of clinical nutrition 27, 515-520. https://doi.org/10.1093/ajcn/27.5.515

Nriagu, J.O., 1989. A global assessment of natural sources of atmospheric trace metals. Nature 338, 47-49. https://doi.org/10.1038/338047a0

Nriagu, J., 2007. Zinc toxicity in humans. School of Public Health, University of Michigan. 1-7.

Oliveira, L.R., 2011. Vulnerability of South American pinnipeds under El Niño Southern Oscillation events. In: Casalegno, S. (Ed.), Global Warming Impacts-Case Studies on the Economy, Human Health, and on Urban and Natural Environments. InTech, Croatia. 237-252.

Oliveira, L.R., Brownell Jr., R.L., 2014. Taxonomic status of two subspecies of South American fur seals: *Arctocephalus australis australis* vs. *A. a. gracilis*. Marine Mammal Science 30, 1258-1263. https://doi.org/10.1111/mms.12098

Olushola Sunday, A., Abdullahi Alafara, B., Godwin Oladele, O., 2012. Toxicity and speciation analysis of organotin compounds. Chemical Speciation & Bioavailability 24, 216-226. https://doi.org/10.3184/095422912X13491962881734

Pacyna, E.G., Pacyna, J.M., Fudala, J., Strzelecka-Jastrzab, E., Hlawiczka, S., Panasiuk, D., Nitter, S., Pregger, T., Pfeiffer, H., Friedrich, R., 2007. Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. Atmospheric Environment 41, 8557-8566. https://doi.org/10.1016/j.atmosenv.2007.07.040

Papp, L.V., Lu, J., Holmgren, A., Khanna, K.K., 2007. From selenium to selenoproteins: synthesis, identity, and their role in human health. Antioxidants & Redox Signaling 9, 775-806. https://doi.org/10.1089/ars.2007.1528

Patrick, L., 2002. Mercury toxicity and antioxidants: part I: role of glutathione and alpha-lipoic acid in the treatment of mercury toxicity. (Mercury Toxicity). Alternative Medicine Review 7, 456-472.

Paredes, R., Arias-Schreiber, M., 1999. Dieta del lobo fino (*Arctocephalus australis*) y lobo chusco (*Otaria byronia*) en la costa peruana durante Mayo y Junio de 1999. Report for Subdirección de Investigaciones en Mamíferos Marinos. Instituto del Mar del Perú, Callao, Perú.

Peña, N., Moreno, V., Marcovecchio, J., Pérez, A., 1988. Total mercury, cadmium and lead distribution in tissues of the southern sea lion (*Otaria flavescens*) in the ecosystem of Mar del Plata, Argentina, In: Seeliger U., de Lacerda L.D., S.R. Patchineelam (Eds.), Metals in Coastal Environments of Latin America. Springer, Berlin, Heidelberg. 140-146. https://doi.org/10.1007/978-3-642-71483-2_15

Pennington, J.T., Mahoney, K.L., Kuwahara, V.S., Kolber, D.D., Calienes, R., Chavez, F.P., 2006. Primary production in the eastern tropical Pacific: A review. Progress in Oceanography 69, 285-317. https://doi.org/10.1016/j.pocean.2006.03.012

Peterson, S.H., Ackerman, J.T., Crocker, D.E., Costa, D.P., 2018. Foraging and fasting can influence contaminant concentrations in animals: an example with mercury contamination in a free-ranging marine mammal. Proceedings of the Royal Society B: Biological Sciences 285, 20172782. https://doi.org/10.1098/rspb.2017.2782

Pinedo, M., 1990. Ocorrência de pinípedes na costa brasileira. Gracia de Orla Série Zoologia 15, 37-48.

Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R.B., Friedli, H.R., Leaner, J., Mason, R., Mukherjee, A.B., Stracher, G.B., Streets, D., 2010. Global mercury emissions to the atmosphere from anthropogenic and natural sources. Atmospheric Chemistry and Physics 10, 5951-5964. http://doi.org/10.5194/acp-10-5951-2010

Polizzi, P., Romero, M.B., Boudet, L.C., de León, A.P., Medici, S., Costas, A., Rodríguez, D. and Gerpe, M., 2017. Blood cadmium and metallothionein concentrations in females of two sympatric pinnipeds species. Marine pollution bulletin 122, 446-449. https://doi.org/10.1016/j.marpolbul.2017.05.049

Ponce de León, A, Pin, O.D., 2006. Distribución, reproducción y alimentación del lobo fino *Arctocephalus australis* y del león marino *Otaria flavescens* en Uruguay. In: Menafra R, Rodríguez-Gallego L, Scarabino F, Conde D (Eds.), Bases para la conservación y el manejo de la costa uruguaya. Vida Silvestre Uruguay, Montevideo. 305–313.

Puls, R., 1988. Mineral levels in animal health: Diagnostic data. Sherpa International, Canada. 5-152.

Rahimzadeh, M.R., Rahimzadeh, M.R., Kazemi, S., Moghadamnia, A.A., 2017. Cadmium toxicity and treatment: An update. Caspian journal of internal medicine 8, 135. https://doi.org/10.22088/cjim.8.3.135

Ramirez, M., Massolo, S., Frache, R., Correa, J.A., 2005. Metal speciation and environmental impact on sandy beaches due to El Salvador copper mine, Chile. Marine Pollution Bulletin 50, 62-72. https://doi.org/10.1016/j.marpolbul.2004.08.010

Ratnaike, R.N., 2003. Acute and chronic arsenic toxicity. Postgraduate medical journal 79, 391-396. http://dx.doi.org/10.1136/pmj.79.933.391

Rea, L.D., Castellini, J.M., Correa, L., Fadely, B.S., O'Hara, T.M., 2013. Maternal Steller sea lion diets elevate fetal mercury concentrations in an area of population decline. Science of the Total Environment 454, 277-282. https://doi.org/10.1016/j.scitotenv.2013.02.095

Rey-Crespo, F., Miranda, M. and López-Alonso, M., 2013. Essential trace and toxic element concentrations in organic and conventional milk in NW Spain. Food and Chemical Toxicology 55, 513-518. https://doi.org/10.1016/j.fct.2013.01.040

Ridgway, S., Reddy, M., 1995. Residue levels of several organochlorines in *Tursiops truncatus* milk collected at varied stages of lactation. Marine Pollution Bulletin 30, 609-614. https://doi.org/10.1016/0025-326X(95)00020-N

Riedman, M., 1990. The Pinnipeds: Seals, sea lions, and walruses. University of California Press. 439.

Rosas-Hernández, M.P., Hernández-Camacho, C.J., González-Rodríguez, E., Aurioles-Gamboa, D., 2018. Vibrissa growth rate in California sea lions based on environmental and isotopic oscillations. PLOS ONE 13, 1-14. https://doi.org/10.1371/journal.pone.0204641

Rosas, F.C., Pinedo, M.C., Marmontel, M., Haimovici, M., 1994. Seasonal movements of the South American sea lion (*Otaria flavescens*, Shaw) off the Rio Grande do Sul coast, Brazil. Mammalia 58, 51-60. https://doi.org/10.1515/mamm.1994.58.1.51

Rosen, B.P., Liu, Z., 2009. Transport pathways for arsenic and selenium: A mini review. Environment International 35, 512-515. https://doi.org/10.1016/j.envint.2008.07.023

Ross, P.S., Ellis, G., Ikonomou, M., Barrett-Lennard, L., Addison, R., 2000. High PCB concentrations in free-ranging Pacific killer whales, *Orcinus orca*: effects of age, sex and dietary preference. Marine Pollution Bulletin 40, 504-515. https://doi.org/10.1016/S0025-326X(99)00233-7

Rubino, F.M., 2015. Toxicity of glutathione-binding metals: a review of targets and mechanisms. Toxics 31, 20-62. https://doi.org/10.3390/toxics3010020

Saeki, K., Nakajima, M., Noda, K., Loughlin, T., Baba, N., Kiyota, M., Tatsukawa, R., Calkins, D., 1999. Vanadium accumulation in pinnipeds. Archives of Environmental Contamination and Toxicology 36, 81-86. https://doi.org/10.1007/s002449900445

Sarmiento-Devia, R., Sepúlveda, M., Pavez, G., Valdés, J., Canto, A., Orellana, M., Oliva, D., 2020. Diet composition of an opportunistic predator from an upwelling area in the Southeastern Pacific. Austral Ecology 45, 1145-1155. https://doi.org/10.1111/aec.12944

Scheuhammer, A., 1991. Effects of acidification on the availability of toxic metals and calcium to wild birds and mammals. Environmental Pollution 71, 329-375. https://doi.org/10.1016/0269-7491(91)90036-V

Schiffer, S., Liber, K., 2017. Toxicity of aqueous vanadium to zooplankton and phytoplankton species of relevance to the athabasca oil sands region. Ecotoxicology and environmental safety 137, 1-11. https://doi.org/10.1016/j.ecoenv.2016.10.040

Schlesinger, W.H., Klein, E.M., Vengosh, A., 2017. Global biogeochemical cycle of vanadium. Proceedings of the National Academy of Sciences 114, E11092-E11100. https://doi.org/10.1073/pnas.1715500114

Schoffman, H., Lis, H., Shaked, Y., Keren, N., 2016. Iron–nutrient interactions within phytoplankton. Frontiers in Plant Science 7, 1223. https://doi.org/10.3389/fpls.2016.01223

Sepúlveda, M.S., Ochoa-Acuña, H., Sundlof, S.F., 1997. Heavy metal concentrations in Juan Fernández fur seals (*Arctocephalus philippii*). Marine Pollution Bulletin 34, 663-665. https://doi.org/10.1016/S0025-326X(97)00054-4

Sepúlveda, M., Olea, D., Carrasco, P., Santos-Carvallo, M., Castillo, J., Quiñones, R.A., 2014. Latitudinal variation in local productivity influences body condition of South American sea lion pups. Aquatic Biology 23, 39-47. https://doi.org/10.3354/ab00604

Sharma, B., Singh, S., Siddiqi, N.J., 2014. Biomedical implications of heavy metals induced imbalances in redox systems. BioMed Research International 2014, 1-26. http://dx.doi.org/10.1155/2014/640754

Simonsen, L.O., Harbak, H., Bennekou, P., 2012. Cobalt metabolism and toxicology—a brief update. Science of the Total Environment 432, 210-215. http://doi.org/10.1016/j.scitotenv.2012.06.009

Singh, N., Kumar, D., Sahu, A.P., 2007. Arsenic in the environment: Effects on human health and possible prevention. Journal of Environmental Biology 28, 359.

Soto, K.H., Trites, A.W., Arias-Schreiber, M., 2004. The effects of prey availability on pup mortality and the timing of birth of South American sea lions (*Otaria flavescens*) in Peru. Journal of Zoology 264, 419-428. https://doi.org/10.1017/S0952836904005965

Soto, K.H., Trites, A.W., Arias-Schreiber, M., 2006. Changes in diet and maternal attendance of South American sea lions indicate changes in the marine environment and prey abundance. Marine Ecology Progress Series 312, 277-290. http://doi.org/10.3354/meps312277

Stauber, J.L., Andrade, S., Ramirez, M., Adams, M., Correa, J.A., 2005. Copper bioavailability in a coastal environment of northern Chile: Comparison of bioassay and analytical speciation approaches. Marine Pollution Bulletin 50, 1363-1372. https://doi.org/10.1016/j.marpolbul.2005.05.008

Sun, H.-J., Rathinasabapathi, B., Wu, B., Luo, J., Pu, L.-P., Ma, L.Q., 2014. Arsenic and selenium toxicity and their interactive effects in humans. Environment International 69, 148-158. http://dx.doi.org/10.1016/j.envint.2014.04.019

Tanabe, S., 1999. Butyltin contamination in marine mammals–a review. Marine Pollution Bulletin 39, 62-72. https://doi.org/10.1016/S0025-326X(99)00064-8

Taylor, M.H., Wolff, M., Mendo, J., Yamashiro, C., 2008. Changes in trophic flow structure of Independence Bay (Peru) over an ENSO cycle. Progress in Oceanography 79, 336-351. https://doi.org/10.1016/j.pocean.2008.10.006

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J., 2012. Heavy metal toxicity and the environment, Molecular, Clinical and Environmental Toxicology. Springer, pp. 133-164. https://doi.org/10.1007/978-3-7643-8340-4_6

Trillmich, F., 1990. The behavioral ecology of maternal effort in fur seals and sea lions. Behaviour 114, 3-20. https://doi.org/10.1163/156853990X00022

Trillmich, F., Kooyman, G.L., Majluf, P., Sanchez-Grinan, M., 1986. Attendance and diving behavior of South American fur seals during El Niño in 1983. In: Gentry, R.L., Kooyman, G.L. (Eds.), Fur Seals: Maternal Strategies on Land and at Sea. Princeton University Press. 153-167.

Trumbo, P., Yates, A.A., Schlicker, S., Poos, M., 2001. Dietary reference intakes: Vitamin A, vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium, and zinc. Journal of the Academy of Nutrition and Dietetics 101, 294. http://doi.org/10.1016/S0002-8223(01)00078-5

Valdés, J., Castillo, A., 2014. Assessment of environmental quality of marine sediments in the bay system Caldera (27°S), Chile. Latin American Journal of Aquatic Research 42, 497-513.

Vales, D.G., Cardona, L., García, N.A., Zenteno, L., Crespo, E.A., 2015. Ontogenetic dietary changes in male South American fur seals *Arctocephalus australis* in Patagonia. Marine Ecology Progress Series 525, 245-260. https://doi.org/10.3354/meps11214

Valko, M.M.H.C.M., Morris, H., Cronin, M.T.D., 2005. Metals, toxicity and oxidative stress. Current Medicinal Chemistry 12, 1161-1208. https://doi.org/10.2174/0929867053764635

Vargas, G., Pantoja, S., Rutllant, J.A., Lange, C.B., Ortlieb, L., 2007. Enhancement of coastal upwelling and interdecadal ENSO-like variability in the Peru-Chile Current since late 19th century. Geophysical Research Letters 34, 1-6. https://doi.org/10.1029/2006GL028812

Vaz-Ferreira, R., 1978. South American sea lion, Mammals in the Seas: Report. Food & Agriculture Org., p. 9.

Vedamati, J., Chan, C. and Moffett, J.W., 2015. Distribution of dissolved manganese in the Peruvian Upwelling and Oxygen Minimum Zone. Geochimica et Cosmochimica Acta 156, 222-240. https://doi.org/10.1016/j.gca.2014.10.026

Villanueva, R., Jordán, R., Burd, A., 1969. Informe sobre el estudio de comportamiento de cardúmenes de anchoveta, Serie de lnformes Especiales Nº IM-45. IMARPE.

Visschedijk, A., Pacyna, J., Pulles, T., Zandveld, P., Denier van der Gon, H., 2004. Coordinated European particulate matter emission inventory program (CEPMEIP), Proceedings of the PM emission inventories scientific workshop, Lago Maggiore, Italy, pp. 163-174.

Volesky, B., 1990. Removal and recovery of heavy metals by biosorption. Taylor & Francis, Quebec Canada, pp. 7-43.

Wagemann, R., 1989. Comparison of heavy metals in two groups of ringed seals (*Phoca hispida*) from the Canadian Arctic. Canadian Journal of Fisheries and Aquatic Sciences 46, 1558-1563. https://doi.org/10.1139/f89-198

Wagemann, R., Stewart, R., Lockhart, W., Stewart, B., Povoledo, M., 1988. Trace metals and methyl mercury: associations and transfer in harp seal (*Phoca groenlandica*) mothers and their pups. Marine Mammal Science 4, 339-355. https://doi.org/10.1111/j.1748-7692.1988.tb00542.x

Waluda, C.M., Yamashiro, C., Rodhouse, P.G., 2006. Influence of the ENSO cycle on the light-fishery for *Dosidicus gigas* in the Peru current: An analysis of remotely sensed data. Fisheries Research 79, 56-63. https://doi.org/10.1016/j.fishres.2006.02.017

Wang, T., Müller, D.B. and Graedel, T.E., 2007. Forging the anthropogenic iron cycle. Environmental Science & Technology 41, 5120-5129. https://doi.org/10.1021/es062761t

Wenzel, C., Adelung, D., Kruse, H., Wassermann, O., 1993. Trace metal accumulation in hair and skin of the harbour seal, *Phoca vitulina*. Marine Pollution Bulletin 26, 152-155. https://doi.org/10.1016/0025-326X(93)90126-5

World Health Organization (WHO), 2011. Guidelines for drinking-water quality, fourth edition. Chapter 12: Chemical fact sheets. 307-442.

Zhang, H., Feng, X., Chan, H.M., Larssen, T., 2014. New insights into traditional health risk assessments of mercury exposure: implications of selenium. Environmental Science & Technology 48, 1206-1212. http://dx.doi.org/10.1021/es4051082

Zuta, S., Rivera, T., Bustamante, A., 1978. Hydrologic aspects of the main upwelling areas off Peru, Upwelling ecosystems. Springer, pp. 235-257.

Appendix

Appendix Table 1. Concentrations of essential trace elements in South American fur seal and sea lion tissues from the present study and those reported in the literature. PSJ = Punta San Juan, Peru, BDL = below detection limit, - = not analyzed.

Species	Location	Age Class	Tissue	Cr	Co	Cu	Fe	Mn	Ni	Se	V	Zn
Peruvian fur seal	PSJ[1]	Adult	Vibrissae	0.32 ± 0.24	0.02 ± 0.02	20.03 ± 2.17	9.90 ± 6.14	0.33 ± 0.49	0.44 ± 1.93	1.06 ± 0.25	0.03 ± 0.01	183 ± 25.31
		Pup		0.43 ± 0.39	0.04 ± 0.03	19.50 ± 4.01	25.28 ± 11.59	0.71 ± 0.28	0.39 ± 0.13	3.97 ± 1.03	0.07 ± 0.02	163 ± 23.60
		Adult	Serum	0.04 ± 0.03	0.002 ± 0.002	0.91 ± 0.30	5.64 ± 3.95	0.03 ± 0.09	0.02 ± 0.02	0.32 ± 0.05	0.003 ± 0.003	7.93 ± 36.01
		Pup		0.04 ± 0.04	0.002 ± 0.004	0.59 ± 0.18	6.53 ± 3.16	0.02 ± 0.05	0.01 ± 0.01	0.14 ± 0.02	0.003 ± 0.002	6.00 ± 29.26
		Adult	Milk	0.07 ± 0.09	0.003 ± 0.002	2.24 ± 0.97	3.63 ± 2.71	0.05 ± 0.04	0.04 ± 0.06	0.35 ± 0.13	0.004 ± 0.003	10.30 ± 10.69
South American fur seal	Argentina[2]	-	Muscle	-	-	1.7 ± 0.1	-	-	-	-	-	28.2 ± 15.4
			Liver	-	-	12.2 ± 2.0	-	-	-	-	-	56.5 ± 11.0
			Kidney	-	-	3.9 ± 0.9	-	-	-	-	-	44.2 ± 8.2
	Uruguay[3]	Pup	Muscle	-	-	1.05 ± 0.10	-	-	-	-	-	10.66 ± 1.66
			Liver	-	-	9.07 ± 1.07	-	-	-	-	-	15.56 ± 2.56
			Kidney	-	-	2.66 ± 0.46	-	-	-	-	-	13.51 ± 2.06

	Brazil[4]	Immature	Heart	0.58 ± 0.11	-	3.29 ± 0.60	117.99 ±16.6	BDL	0.13 ± 0.02	-	-	26.62 ± 3.5
			Kidney	0.56 ± 0.12	-	4.55 ± 1.11	93.27 ± 19.4	0.88 ± 0.25	0.12 ± 0.01	-	-	65.21 ± 19.4
			Liver	1.53 ± 032	-	7.48 ± 3.39	293.64 ± 71.2	7.35 ± 2.29	0.13 ± 0.02	-	-	88.24 ± 35.1
South American sea lion	PSJ[1]	Adult	Vibrissae	0.35 ± 0.24	0.02 ± 0.01	14.60 ± 1.74	10.58 ± 6.73	0.23 ± 0.19	0.49 ± 0.23	1.95 ± 0.37	0.13 ± 0.08	145 ± 37.69
			Serum	0.03 ± 0.02	0.003 ± 0.005	0.86 ± 0.24	6.90 ± 3.63	0.03 ± 0.06	0.02 ± 0.02	0.36 ± 0.05	0.003 ± 0.002	6.20 ± 26.16
	Argentina[5]	Adult*	Muscle	-	-	0.83 ± 0.50	-	-	-	-	-	7.74 ± 5.74
			Liver	-	-	1.26 ± 0.57	-	-	-	-	-	8.31 ± 9.05
			Kidney	-	-	0.92 ± 0.57	-	-	-	-	-	6.45 ± 7.47

*Samples included 3 adults and 1 juvenile.

[1] Present Study

[2] Marcovecchio et al., 1994

[3] Gerpe et al., 2009

[4] Baraj et al., 2009

[5] Gerpe et al., 2007

Appendix Table 2. Concentrations of non-essential trace elements in South American fur seal and sea lion tissues from the present study and those reported in the literature. PSJ = Punta San Juan, Peru, BDL = below detection limit, - = not analyzed.

Species	Location	Age Class	Tissue	Al	As	Cd	Pb	Hg	Sn
Peruvian fur seal	PSJ[1]	Adult	Vibrissae	22.08 ± 9.29	0.19 ± 0.12	0.24 ± 0.10	0.12 ± 0.06	2.28 ± 1.12	2.70 ± 1.47
		Pup		159.7 ± 54.62	0.44 ± 0.18	0.60 ± 0.76	0.57 ± 1.56	1.47 ± 0.40	0.14 ± 0.43
		Adult	Serum	5.19 ± 4.24	0.07 ± 0.03	0.008 ± 0.03	0.08 ± 0.18	0.003 ± 0.003	0.41 ± 0.50
		Pup		4.50 ± 2.66	0.04 ± 0.01	0.002 ± 0.001	0.05 ± 0.04	0.02 ± 0.01	-
		Adult	Milk	5.05 ± 3.44	0.41 ± 0.15	0.03 ± 0.08	0.05 ± 0.05	0.13 ± 0.41	0.05 ± 0.02
South American fur seal	Argentina[2]	-	Muscle	-	-	0.4 ± 0.1	-	0.8 ± 0.3	-
			Liver	-	-	34.5 ± 17.1	-	33.7 ± 11.7	-
			Kidney	-	-	48.15 ± 24.1	-	0.9 ± 0.2	-
	Uruguay[3]	Pup	Muscle	-	-	0.06 ± 0.06	-	0.11 ± 0.12	-
			Liver	-	-	0.05 ± 0.03	-	0.49 ± 0.07	-
			Kidney	-	-	0.06 ± 0.04	-	0.29 ± 0.07	-
	Brazil[4]	Immature	Heart	-	-	0.40 ± 0.32	0.12 ± 0.02	0.19 ± 0.27	-
			Kidney	-	-	13.38 ± 18.71	0.15 ± 0.04	0.59 ± 0.59	-
			Liver	-	-	8.69 ± 12.24	0.17 ± 0.07	10.13 ± 18.51	-
South American sea lion	PSJ[1]	Adult	Vibrissae	21.80 ± 12.26	0.294 ± 0.228	0.945 ± 1.267	0.215 ± 0.514	2.322 ± 1.409	1.713 ± 1.394
			Serum	4.211 ± 2.100	0.041 ± 0.039	0.003 ± 0.005	0.039 ± 0.055	0.002 ± 0.003	BDL (<0.001)
	Argentina[5]	Adult*	Muscle	-	-	0.12 ± 0.21	-	1.42 ± 0.53	-

	Liver	-	-	0.63 ± 0.47	-	33.90 ± 10.09	-
	Kidney	-	-	2.16 ± 2.39	-	0.75 ± 0.47	-

*Samples included 3 adults and 1 juvenile.

[1]Present Study

[2] Marcovecchio et al., 1994

[3] Gerpe et al., 2009

[4]Baraj et al., 2009

[5] Gerpe et al., 2007