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# A survey of trace element distribution in tissues of the dwarf sperm whale (*Kogia sima*) stranded along the South Carolina coast from 1990–2011



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#### A R T I C L E I N F O

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### ABSTRACT

Few studies report trace elements in dwarf sperm whale (*Kogia sima*). As high trophic level predators, marine mammals are exposed through diet to environmental contaminants including metals from anthropogenic sources. Inputs of Hg, Pb, and Cd are of particular concern due to toxicity and potential for atmospheric dispersion and subsequent biomagnification. Liver and kidney tissues of stranded *K. sima* from coastal South Carolina, USA, were analyzed for 22 trace elements. Age-related correlations with tissue concentrations were found for some metals. Mean molar ratio of Hg:Se varied with age with higher ratios found in adult males. Maximum concentrations of Cd and Hg in both tissues exceeded historical FDA levels of concern, but none exceeded the minimum 100 µg/g Hg threshold for hepatic damage. Tissue concentrations of some metals associated with contamination were low, suggesting that anthropogenic input may not be a significant source of some metals for these pelagic marine mammals.

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The dwarf sperm whale (*Kogia sima*) is generally found living over the continental shelf and slope adjacent to tropical and temperate ocean coasts (Rice, 1998 and McAlpine, 2009). They appear to feed primarily on deep-water cephalopods, as well as other prey types, including fish and crustaceans (Aguiar dos Santos and Haimovici, 2001; Jefferson et al., 1993; McAlpine, 2009). Adult male dwarf sperm whales generally weigh between 135 and 272 kg and may reach lengths of up to 270 cm. Adult females may be slightly smaller than males (Plön, 2004).

Dwarf sperm whales (*K. sima*) are the third most frequently stranded marine mammal in South Carolina, USA and usually strand as either single animals or mother–calf/juvenile pairs (Coastal Carolina University, 2014). Between 1990 and 2011, twelve dwarf sperm whales stranded along the South Carolina coast. Because of difficulty in positively distinguishing the dwarf sperm whale at sea, much of current knowledge about *K. sima* is based on stranded individuals or those taken by fisheries (Caldwell and Caldwell, 1989). The International Union for Conservation of Nature (IUCN) classifies *K. sima* as a "data deficient species" on its Red List of Threatened Species; there are insufficient data to make an assessment of its risk of extinction (Taylor et al., 2012).

In addition to uncertainty in regard to the status of dwarf sperm whale populations, there is concern for their health (Taylor et al., 2007 and Ross, 2006). Due to their nearshore distribution, *K. sima* may be

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susceptible to human activities and pollution (Culik, 2011), including the ingestion of marine debris, potential for ship strikes, and fish net entanglement. Unexplained strandings in the Gulf of Mexico and the Atlantic coast of Florida have warranted further concern about the population (Waring et al., 2006). Exposure to pollutants can result in oxidative stress which has been linked to the development of disease. Stranded Kogiids have shown degenerative heart disease, immune system deficiencies, and heavy parasite infestations (Culik, 2011; Bossart et al., 2007; Bossart, 2011).

Increased human activity in recent decades has accelerated inputs of contaminants, including metals, to the marine environment. As a long-lived apex predator, *K. sima* may act as an indicator of marine pollution with the potential to accumulate significant quantities of contaminants including metals. Heavy metals are well known environmental pollutants that accumulate in the bodies of odontocetes and have potential to constitute a toxicological risk for the species (Caurant et al., 1996; Endo et al., 2002; Haraguchi et al., 2000; Simmonds et al., 2002; Stavros et al., 2011). Seawater enrichment with heavy metals from natural occurrence or from anthropogenic impact may lead to an increase of metal burdens entering marine food chains (Fernandez et al., 2007). The impact of metal contamination is not limited to coastal waters; elevated concentrations of heavy metals (Co, Cr, and Ni) have been reported in a cephalopod (*Nautilus macromphalus*) that inhabits depths of several hundred meters (Bustamante et al., 2000).

Although metals generally occur at low concentrations in the oceans, marine organisms bioaccumulate trace elements with significant increase of metal burdens through the food web, especially toxic elements such as Hg or Cd (Gerpe et al., 2006; Meador et al., 1999). In

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odontocentes, Cd has been known to accumulate in the internal organs (Honda et al., 1983; Endo et al., 2002; Gerpe et al., 2006; Holsbeek et al., 1998) and bind to metallothioneins (Das et al., 2000). Although Hg has a high affinity for metallothioneins, only a small amount of total Hg has been shown to be bound to metallothioneins in marine mammals (Caurant et al., 1996; Wagemann et al., 1998; Holsbeek et al., 1998).

Marine mammals are principally exposed to methylHg through diet. The Hg present in fish and squid is methylated (Caurant et al., 1996; Das et al., 2000; Gerpe et al., 2006), but the majority of Hg accumulated in marine mammal internal organs is inorganic mercury (Wagemann et al., 1998 and Cardellicchio et al., 2002). Demethylation of methylHg, followed by the formation of a less toxic Hg-Se complex, is thought to occur in cetacean livers as a protective physiological mechanism (Das et al., 2000 and Endo et al., 2004). An imbalance of Hg and Se can lead to oxidative stress that can impair protein function, damage DNA, and damage membrane lipids leading to onset of disease (Arteel and Sies, 2001). Increasing molar ratios of Hg:Se with increasing Hg and increasing age have been documented in dolphins and correlated with the progression of heart disease in adult *Kogia breviceps* males (Itano et al., 1984; Bryan et al., 2012).

To date, few studies have reported metal concentrations in *Kogiid* tissues. The aim of the present study was to examine the distribution of major and minor trace elements in the liver and kidney of *K. sima*. Results are contrasted among organ type, age class, size, and gender to provide information on heavy metal concentrations in a top marine predator. Because Se is recognized to decrease toxicity of Hg, molar ratios of Hg:Se are compared for gender and age in liver samples.

Stranded dwarf sperm whales, *K. sima*, were collected along the South Carolina coast from 1990 – 2011 by staff from the National Oceanic and Atmospheric Administration's (NOAA) Center for Coastal Environmental Health and Biomolecular Research laboratory in Charleston, SC, using established marine mammal necropsy protocols (Geraci and Lounsbury, 2005). Animals were either euthanized (code 1) or freshly dead (code 2) to reduce post-mortem tissue degradation; they were either stranded alone or in cow-calf pairs (Fig. 1).

For the present study, neonates are considered to be <105 cm; with juveniles representing the next size class up to the median length at attainment of sexual maturity by gender. Based on the study of dwarf

sperm whales off southern Africa, which found the age at maturity to be five years of age (Plön, 2004); median adult lengths are considered to be 197 cm for males and 215 cm for females. In this study, a female stranded with its presumed calf had a length of 212 cm, so the lower limit for adult females was adjusted to 212 cm. For age class comparisons, neonates were grouped with juveniles. In the laboratory, necropsies were performed, life history data were collected (Table 1), and the kidney and liver were removed and frozen at - 80 °C until subsampling for trace element analysis.

Subsamples (~10 g) of liver or kidney tissue were homogenized and stored in pre-cleaned polypropylene containers at -80 °C until processing for analysis. Homogenized tissue samples were prepared for inductively coupled plasma mass spectrometry (ICP-MS) analysis by microwave-assisted digestion in PTFE pressurized vessels with ultrapure nitric acid followed by ultrapure 30% H<sub>2</sub>O<sub>2</sub>. Resulting solutions were diluted with Millipore deionized water prior to trace element analysis (EPA Method 3052, 1996). For total Hg determination, tissue samples were weighed directly into nickel boats for analysis.

An additional portion (~2.5 g) of each homogenate was dried to estimate the dry fraction. The dry fraction of each tissue sample was determined gravimetrically with an analytical balance after drying for 48 h in an 80 °C oven. Average moisture content of tissues was 78.1  $\pm$  1.6% for the kidney (range = 76.2–80.9%) and 70.0  $\pm$  5.2% for liver (range = 61.3–79.0%).

A Perkin Elmer Sciex ELAN® 6100 Inductively Coupled Plasma Mass Spectrometer with an AS-91 autosampler (Perkin Elmer, Inc., Waltham, MA) was used to measure the following 39 isotopes of 22 elements: <sup>107</sup>Ag, <sup>109</sup>Ag, <sup>27</sup>Al, <sup>75</sup>As, <sup>136</sup>Ba, <sup>137</sup>Ba, <sup>9</sup>Be, <sup>111</sup>Cd, <sup>112</sup>Cd, <sup>114</sup>Cd, <sup>59</sup>Co, <sup>52</sup>Cr, <sup>53</sup>Cr, <sup>63</sup>Cu, <sup>65</sup>Cu, <sup>54</sup>Fe, <sup>57</sup>Fe, <sup>6</sup>Li, <sup>7</sup>Li, <sup>55</sup>Mn, <sup>60</sup>Ni, <sup>206</sup>Pb, <sup>207</sup>Pb, <sup>208</sup>Pb, <sup>121</sup>Sb, <sup>123</sup>Sb, <sup>77</sup>Se, <sup>82</sup>Se, <sup>117</sup>Sn, <sup>119</sup>Sn, <sup>120</sup>Sn, <sup>203</sup>Tl, <sup>205</sup>Tl, <sup>235</sup>U, <sup>238</sup>U, <sup>51</sup>V, <sup>64</sup>Zn, <sup>66</sup>Zn, and <sup>68</sup>Zn in all samples. Reported values are the average of listed isotopes for an element. A multiple element internal standard (<sup>45</sup>Sc, <sup>72</sup>Ge, <sup>103</sup>Rh, <sup>175</sup>Lu) was added to each sample and calibration standard. Standard solutions were purchased from High Purity Standards (Charleston, SC). Samples were diluted as necessary for bracketing by calibration curves. Quality assurance for ICP-MS data included analysis of duplicate samples, reagent blanks, standard reference material, NIST SRM 1566b (NIST, Gaithersburg, MD), and Trace Metals in Drinking



Fig. 1. Dwarf sperm whale stranding locations along the South Carolina coast from 1990–2011 labeled with NOAA sample number.

Table 1				
Comparison	of collection	data fo	r individual	K. sima

NOAA number	Stranding date	Latitude	Longitude	Condition code	Length (cm)	Age class	Gender
11-451	07/22/98	32.8004	-79.7407	1	97	Neonate <sup>a</sup>	М
11-444	03/11/97	32.7572	-79.8404	1	102	Neonate <sup>b</sup>	F
11-445	12/07/98	33.6565	- 78.9188	2	121	Juvenile <sup>b</sup>	F
11-449	05/01/09	33.8112	-78.6891	1	164	Juvenile	М
11-440	12/03/90	N/A	N/A	1	199	Adult <sup>a</sup>	Μ
11-450	02/03/11	32.7813	-79.7928	2	203	Adult	Μ
11-448	11/02/01	32.7608	-79.8350	2	207	Adult	М
11-447	09/02/98	32.1058	-80.8230	1	209	Adult	М
11-443	03/11/97	32.7572	-79.8404	1	212	Adult <sup>b</sup>	F
11-441	02/28/93	32.6602	-79.9254	2	218	Adult	Μ
11-446	12/07/98	33.6566	-78.9185	1	218	Adult <sup>a,b</sup>	F
11-442	03/10/96	32.3250	-80.4666	2	233	Adult	М

<sup>a</sup> No kidney sample available for analysis; analyzed only liver.

<sup>b</sup> Mother–calf pair stranded together.

Water (TMDW), a certified reference material (High Purity Standards, Charleston, SC). Recoveries for all elements in the reference materials ranged from 83–117%, averaging 101  $\pm$  10%; calculated detection limits ranged from 0.001–0.030 µg/g.

A direct mercury analyzer, the DMA-80 (Milestone Inc., Shelton, CT), was used to determine the mass fraction of total Hg by pyrolytic decomposition of the sample, catalytic reduction to elemental Hg, trapping on a gold amalgamator, with Hg thermally desorbed and Hg atomic absorbance measured at 254 nm. Subsamples of homogenized tissues were accurately weighed into nickel boats for mercury analysis. The instrument was calibrated with the certified reference material, DORM-2 (National Research Council, Canada). Quality assurance evaluation included blanks, duplicates and the certified reference materials, DOLT-3 and NIST SRM 1566b. Recovery of Hg ranged from 94% to 105%, averaging 100  $\pm$  2%; calculated instrument limit of detection is 0.01 µg/g.

Descriptive statistics were calculated on a wet weight basis using SAS v.9.1.3 (SAS Institute Inc., Cary, NC) and Microsoft Excel (Redmond, WA). Samples with values less than the method detection limit were reported as zero. Analysis of variance (ANOVA) and multiple linear regression were used to analyze the relationship of trace element concentrations with the factors of age class and gender. Tukey honestly significant difference (HSD) tests and least squares (LS) mean plots were performed on statistically significant (p < 0.05) data to determine how the means varied within a factor.

Seven of the twelve study animals were classified as code 1; the remainder were code 2. Both genders were studied. There were more males, as well as a higher percentage of adult males. The only adult females that stranded were found with their presumed calves. Ages ranged from neonate to sexually mature adult; two individuals were classified as juvenile and two as neonates (Plön, 2004). Neonates were grouped with juveniles for statistical analysis. Total length of animals studied ranged from 97–233 cm.

Measurable concentrations of all elements studied were found in *K. sima* tissues, with the exception of Be, Tl, and U; Ag was not detected in the kidney. There were few samples of either tissue type with measurable Li. Lead concentrations were near the limit of detection, and Sn was not detected in juvenile and neonate liver. The most abundant element detected in either tissue was Fe, followed by Cu in the liver and Zn in the kidney. Average values for Fe were  $192 \pm 15.7 \,\mu$ g/g in the kidney and  $633 \pm 60 \,\mu$ g/g in the liver. Values for Al, Cd, Hg, Mn, Se, and V ranged from 1–10  $\mu$ g/g; concentration of Ag, As, Cr, Sb, and Sn were less than 1.0  $\mu$ g/g. Elements detected in trace amounts (<0.1  $\mu$ g/g) were Ba, Co, Li, Ni, Pb, and Sn.

Metals are typically heterogeneously distributed among tissues (Gerpe et al., 2006; Honda et al., 1983; Lahaye et al., 2007; Stavros et al., 2011; Zhou et al., 2001). A single factor ANOVA showed that in general, the liver had higher concentrations than the kidney for the following elements: Ag, Cr, Cu, Fe, Hg, Mn, Pb, and Sn; Sb was higher in the kidney. When only paired data are examined, differences by tissue type

for Cu and Sb are not significant. Average element concentrations for all animals on a wet weight basis for the two tissues studied are shown in Table 2.

Differences in metal concentration due to age class were found (Tables 3a and 3b). Age-related accumulation of heavy metals is likely related to their cephalopod diet. Both the kidney and liver were found

Table 2

Element concentrations ( $\mu$ g/g wet wt.) in kidney and liver tissues from *Kogia sima* stranded along the South Carolina coast (mean  $\pm$  standard error and range).

Element	Kidney	Liver
	(n = 9)	(n = 12)
Ag <sup>a</sup>	n.d.	$0.945 \pm 0.320$
-		(0.264 - 4.03)
Al	$5.72 \pm 1.38$	$5.30 \pm 1.45$
	(2.22-15.9)	(0.544-19.3)
As	$0.801 \pm 0.074$	$0.640 \pm 0.098$
	(0.530-1.25)	(0.297 - 1.25)
Ba	$0.043 \pm 0.004$	$0.039 \pm 0.004$
	(0.031-0.063)	(0.019-0.065)
Cd	$6.90 \pm 2.36$	$4.40 \pm 1.66$
	(0.014-22.5)	(0.002-18.6)
Со	$0.040 \pm 0.002$	$0.047\pm0.006$
	(0.031-0.050)	(0.031 - 0.084)
Cr <sup>a</sup>	$0.308 \pm 0.017$	$0.389 \pm 0.020$
	(0.255-0.390)	(0.271-0.495)
Cu <sup>a</sup>	$2.20\pm0.104$	$45.0\pm17.0$
	(1.67-2.57)	(1.67-157)
Fe <sup>a</sup>	$192 \pm 15.7$	$633 \pm 60.2$
	(122-263)	(155-1,016)
Hg <sup>a</sup>	$2.86 \pm 1.07$	$6.25 \pm 1.86$
	(0.176-10.2)	(0.210-17.9)
Li	$0.021 \pm 0.008$	$0.018\pm0.006$
	(0.000-0.051)	(0.000-0.049)
Mn <sup>a</sup>	$0.667 \pm 0.040$	$1.79\pm0.177$
	(0.545-0.883)	(0.889-3.11)
Ni	$0.037 \pm 0.007$	$0.030\pm0.004$
	(0.021-0.088)	(0.016-0.066)
Pb <sup>a</sup>	$0.008\pm0.001$	$0.013\pm0.002$
	(0.000-0.011)	(0.000 - 0.024)
Sb <sup>b</sup>	$0.182 \pm 0.005$	$0.167\pm0.004$
	(0.160-0.206)	(0.146-0.191)
Se	$8.16 \pm 0.881$	$9.61 \pm 1.29$
	(3.77–11.6)	(3.57-20.1)
Sn <sup>a</sup>	$0.036 \pm 0.003$	$0.148\pm0.043$
	(0.025-0.050)	(0.000-0.392)
V	$2.67 \pm 0.781$	$2.34\pm0.510$
	(0.571-8.45)	(0.243-6.08)
Zn	$14.5 \pm 0.859$	$16.1\pm1.56$
	(12.4–19.5)	(9.76-26.1)

n.d. = non-detected.

<sup>a</sup> Indicates liver value significantly greater than kidney.

<sup>b</sup> Indicates kidney value greater than liver.

#### Table 3a

Element concentrations ( $\mu$ g/g wet wt.) in adult and juvenile kidney from stranded *K. sima* (mean  $\pm$  standard error and range).

#### Table 3b

Element concentrations ( $\mu$ g/g wet wt.) in adult and juvenile liver from stranded *K. sima* (mean  $\pm$  standard error and range).

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Analyte	Adult	Juvenile	A
Ag         n.d.         n.d.         A           Al $4.29 \pm 0.654$ $8.56 \pm 3.83$ (2.22 - 6.22) $(3.08 - 15.9)$ A           As <sup>a</sup> $0.897 \pm 0.083$ $0.610 \pm 0.069$ (0.657 - 1.25) $(0.530 - 0.746)$ A           Ba $0.046 \pm 0.006$ $0.039 \pm 0.004$ (0.031 - 0.063) $(0.011 - 0.045)$ B           Cd <sup>a</sup> $9.91 \pm 2.80$ $0.877 \pm 0.822$ (3.47 - 22.5) $(0.014 - 2.52)$ C           Co <sup>a</sup> $0.043 \pm 0.003$ $0.034 \pm 0.002$ (0.035 - 0.050) $(0.031 - 0.039)$ C           Cr $0.306 \pm 0.018$ $0.312 \pm 0.040$ (0.255 - 0.390)         C           Cu $2.11 \pm 0.137$ $2.38 \pm 0.109$ (1.57 - 2.57)         (2.17 - 2.51)         C           Cu $2.11 \pm 0.137$ $2.38 \pm 0.109$ (1.43 - 12.2)         (1.75 - 2.50)         C           Hg <sup>a</sup> $4.18 \pm 1.30$ $0.219 \pm 0.027$ (1.43 - 10.2)         (1.76 - 0.269)         F           Li $0.022 \pm 0.010$ $0.017 \pm 0.017$ (0.024 - 0.088)         N           Mn $0.626 \pm 0.027$ $0.749 \pm 0.104$ (0.024 -		(n = 6)	(n = 3)	
Al $4.29 \pm 0.654$ $8.56 \pm 3.83$ (2.22 - 6.22)       (3.08 - 15.9)       A         As <sup>a</sup> 0.897 $\pm$ 0.083       0.610 $\pm$ 0.069       A         Ba       0.046 $\pm$ 0.006       0.039 $\pm$ 0.004       A         Ba       0.046 $\pm$ 0.006       0.039 $\pm$ 0.004       B         Cd <sup>a</sup> 9.91 $\pm$ 2.80       0.877 $\pm$ 0.822       C         (3.47 - 22.5)       (0.014 - 2.52)       C       C         Co <sup>a</sup> 0.043 $\pm$ 0.003       0.034 $\pm$ 0.002       C         (0.035 - 0.050)       (0.031 - 0.039)       C       C         (1.45 - 0.03)       (0.25 - 0.390)       C       C       C         (1.47 - 2.57)       (2.17 - 2.51)       C       C       C       A         (1.43 - 10.2)       (0.176 - 0.269)       F       Hg <sup>a</sup> (1.48 + 1.30       D219 $\pm$ 0.027       C       C         (1.43 - 10.2)       (0.176 - 0.269)       F	Ag	n.d.	n.d.	A
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Al	$4.29 \pm 0.654$	$8.56 \pm 3.83$	
As <sup>a</sup> $0.897 \pm 0.083$ $0.610 \pm 0.069$ (0.657 - 1.25)       (0.530 - 0.746)       A         Ba $0.046 \pm 0.006$ $0.031 \pm 0.004$ A         (0.031 - 0.063)       (0.031 - 0.045)       B         Cd <sup>a</sup> 9.91 ± 2.80 $0.877 \pm 0.822$ C         (3.47 - 22.5)       (0.014 - 2.52)       CC       CC         (0.035 - 0.050)       (0.031 - 0.039)       CC       C         (0.263 - 0.379)       (0.255 - 0.390)       CC       CU       2.11 ± 0.137       2.38 ± 0.109       CC         Cu       2.11 ± 0.137       2.38 ± 0.109       CC       CU       C1.67 - 2.57)       C.17 - 2.51)       CC         Fe       2.04 ± 18.1       167 ± 2.83       C       C134 - 263)       C122 - 220)       FE         Hg <sup>a</sup> 4.18 ± 1.30       0.219 ± 0.027       C       C       C       CO		(2.22 – 6.22)	(3.08 – 15.9)	A
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	As <sup>a</sup>	$0.897 \pm 0.083$	$0.610 \pm 0.069$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(0.657 – 1.25)	(0.530 – 0.746)	A
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ba	$0.046\pm0.006$	$0.039 \pm 0.004$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(0.031 - 0.063)	(0.031 - 0.045)	В
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cd <sup>a</sup>	$9.91 \pm 2.80$	$0.877 \pm 0.822$	
$\begin{array}{ccccc} {\rm Co}^{\rm a} & 0.043 \pm 0.003 & 0.034 \pm 0.002 & (0.035 - 0.050) & (0.031 - 0.039) & {\rm CO} & (0.036 \pm 0.018 & 0.312 \pm 0.040) & (0.263 - 0.379) & (0.255 - 0.390) & {\rm CO} & (0.263 - 0.379) & (0.255 - 0.390) & {\rm CO} & (1.67 - 2.57) & (2.17 - 2.51) & {\rm CO} & (1.67 - 2.57) & (2.17 - 2.51) & {\rm CO} & (1.67 - 2.57) & (2.17 - 2.51) & {\rm CO} & (1.43 - 263) & (122 - 220) & {\rm F} & (1.43 - 10.2) & (0.176 - 0.269) & {\rm F} & (1.43 - 10.2) & (0.176 - 0.269) & {\rm F} & (1.43 - 10.2) & (0.176 - 0.269) & {\rm F} & (0.000 - 0.049) & (0.000 - 0.051) & {\rm L} & (0.000 - 0.049) & (0.000 - 0.051) & {\rm L} & (0.000 - 0.049) & (0.000 - 0.051) & {\rm L} & (0.022 \pm 0.010 & 0.017 \pm 0.017 & (0.000 - 0.049) & (0.002 - 0.088) & {\rm N} & (0.023 - 0.040) & (0.021 - 0.088) & {\rm N} & (0.023 - 0.040) & (0.021 - 0.088) & {\rm N} & (0.008 - 0.011) & (0.000 - 0.009) & {\rm P} & {\rm Sb} & 0.184 \pm 0.006 & 0.177 \pm 0.006 & (0.166 - 0.188) & {\rm Sc} & (0.160 - 0.206) & (0.166 - 0.188) & {\rm Sc} & (0.166 - 0.206) & (0.166 - 0.188) & {\rm Sc} & (0.25 - 0.050) & (0.029 - 0.031) & {\rm Sc} & (0.025 - 0.050) & (0.029 - 0.031) & {\rm Sc} & (0.571 - 2.93) & (1.88 - 8.5) & {\rm V} & 1.89 \pm 0.366 & 4.25 \pm 2.19 & {\rm Co} & (1.27 - 13.6) & {\rm Z} & {\rm Co} & {\rm Co}$		(3.47 – 22.5)	(0.014 – 2.52)	C
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Co <sup>a</sup>	$0.043 \pm 0.003$	$0.034\pm0.002$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(0.035 - 0.050)	(0.031 - 0.039)	C
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cr	$0.306 \pm 0.018$	$0.312 \pm 0.040$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(0.263 - 0.379)	(0.255 - 0.390)	C
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cu	$2.11 \pm 0.137$	$2.38\pm0.109$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(1.67 – 2.57)	(2.17 – 2.51)	C
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe	$204 \pm 18.1$	$167 \pm 28.8$	
$\begin{array}{ccccccc} Hg^a & 4.18 \pm 1.30 & 0.219 \pm 0.027 \\ & (1.43 - 10.2) & (0.176 - 0.269) & H \\ Ii & 0.022 \pm 0.010 & 0.017 \pm 0.017 \\ & (0.000 - 0.049) & (0.000 - 0.051) & L \\ & (0.000 - 0.049) & (0.000 - 0.051) & L \\ Mn & 0.626 \pm 0.027 & 0.749 \pm 0.104 \\ & (0.545 - 0.727) & (0.545 - 0.883) & M \\ & (0.032 \pm 0.003 & 0.049 \pm 0.020 \\ & (0.023 - 0.040) & (0.021 - 0.088) & M \\ Pb & 0.010 \pm 0.001 & 0.005 \pm 0.003 \\ & (0.008 - 0.011) & (0.000 - 0.009) & P \\ Sb & 0.184 \pm 0.006 & 0.177 \pm 0.006 \\ & (0.160 - 0.206) & (0.166 - 0.188) & S \\ & (0.25 - 11.6) & (3.77 - 10.2) & S \\ Sr & 0.039 \pm 0.004 & 0.030 \pm 0.001 \\ & (0.025 - 0.050) & (0.029 - 0.031) & S \\ V & 1.89 \pm 0.366 & 4.25 \pm 2.19 \\ & (0.571 - 2.93) & (108 - 8.45) & V \\ Zn & 15.2 \pm 1.21 & 13.1 \pm 0.265 \\ & (12.4 - 19.5) & (12.7 - 13.6) & Z \end{array}$		(134 – 263)	(122 – 220)	F
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Hg <sup>a</sup>	$4.18 \pm 1.30$	$0.219 \pm 0.027$	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		(1.43 – 10.2)	(0.176 - 0.269)	H
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Li	$0.022 \pm 0.010$	$0.017 \pm 0.017$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(0.000 - 0.049)	(0.000 - 0.051)	L
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mn	$0.626 \pm 0.027$	$0.749 \pm 0.104$	
$\begin{array}{cccccccc} {\sf Ni} & 0.032 \pm 0.003 & 0.049 \pm 0.020 \\ & (0.023 - 0.040) & (0.021 - 0.088) & {\sf N} \\ {\sf Pb} & 0.010 \pm 0.001 & 0.005 \pm 0.003 & {\sf P} \\ & (0.008 - 0.011) & (0.000 - 0.009) & {\sf P} \\ {\sf Sb} & 0.184 \pm 0.006 & 0.177 \pm 0.006 & {\sf O} \\ & (0.160 - 0.206) & (0.166 - 0.188) & {\sf S} \\ & (0.160 - 0.206) & (0.166 - 0.188) & {\sf S} \\ {\sf Se} & 9.02 \pm 0.822 & 6.43 \pm 1.92 & {\sf O} \\ & (6.25 - 11.6) & (3.77 - 10.2) & {\sf S} \\ & (0.025 - 0.050) & (0.029 - 0.031) & {\sf S} \\ {\sf V} & 1.89 \pm 0.366 & 4.25 \pm 2.19 & {\sf O} \\ & (0.571 - 2.93) & (1.08 - 8.45) & {\sf V} \\ {\sf Zn} & 15.2 \pm 1.21 & 13.1 \pm 0.265 & {\sf O} \\ & (12.4 - 19.5) & (12.7 - 13.6) & {\sf Z} \end{array}$		(0.545 – 0.727)	(0.545 - 0.883)	Ν
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ni	$0.032 \pm 0.003$	$0.049 \pm 0.020$	
$\begin{array}{ccccccc} Pb & 0.010 \pm 0.001 & 0.005 \pm 0.003 \\ & (0.008 - 0.011) & (0.000 - 0.009) & P \\ Sb & 0.184 \pm 0.006 & 0.177 \pm 0.006 \\ & (0.160 - 0.206) & (0.166 - 0.188) & S \\ Se & 9.02 \pm 0.822 & 6.43 \pm 1.92 \\ & (6.25 - 11.6) & (3.77 - 10.2) & S \\ Sn & 0.039 \pm 0.004 & 0.030 \pm 0.001 \\ & (0.025 - 0.050) & (0.029 - 0.031) & S \\ V & 1.89 \pm 0.366 & 4.25 \pm 2.19 \\ & (0.571 - 2.93) & (108 - 8.45) & V \\ Zn & 15.2 \pm 1.21 & 13.1 \pm 0.265 \\ & (12.4 - 19.5) & (12.7 - 13.6) & Z \end{array}$		(0.023 - 0.040)	(0.021 - 0.088)	Ν
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Pb	$0.010\pm0.001$	$0.005 \pm 0.003$	
$\begin{array}{cccccccc} {\rm Sb} & 0.184 \pm 0.006 & 0.177 \pm 0.006 \\ & (0.160 - 0.206) & (0.166 - 0.188) & {\rm S} \\ {\rm Se} & 9.02 \pm 0.822 & 6.43 \pm 1.92 \\ & (6.25 - 11.6) & (3.77 - 10.2) & {\rm S} \\ {\rm Sn} & 0.039 \pm 0.004 & 0.030 \pm 0.001 \\ & (0.025 - 0.050) & (0.029 - 0.031) & {\rm S} \\ {\rm V} & 1.89 \pm 0.366 & 4.25 \pm 2.19 \\ & (0.571 - 2.93) & (1.08 - 8.45) & {\rm V} \\ {\rm Zn} & 15.2 \pm 1.21 & 13.1 \pm 0.265 \\ & (12.4 - 19.5) & (12.7 - 13.6) & {\rm Z} \end{array}$		(0.008 - 0.011)	(0.000 - 0.009)	Р
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb	$0.184\pm0.006$	$0.177 \pm 0.006$	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		(0.160 - 0.206)	(0.166 - 0.188)	S
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Se	$9.02\pm0.822$	$6.43 \pm 1.92$	
$\begin{array}{cccc} Sn & 0.039 \pm 0.004 & 0.030 \pm 0.001 \\ & & & & & & & & & & & & & & & & & & $		(6.25 – 11.6)	(3.77 – 10.2)	S
$\begin{array}{cccc} (0.025-0.050) & (0.029-0.031) & S\\ V & 1.89\pm 0.366 & 4.25\pm 2.19 & \\ & (0.571-2.93) & (1.08-8.45) & V\\ Zn & 15.2\pm 1.21 & 13.1\pm 0.265 & \\ & (12.4-19.5) & (12.7-13.6) & Z \end{array}$	Sn	$0.039 \pm 0.004$	$0.030 \pm 0.001$	
$ \begin{array}{cccc} V & 1.89 \pm 0.366 & 4.25 \pm 2.19 \\ & (0.571 - 2.93) & (1.08 - 8.45) & V \\ Zn & 15.2 \pm 1.21 & 13.1 \pm 0.265 \\ & (12.4 - 19.5) & (12.7 - 13.6) & Z \\ \end{array} $		(0.025 - 0.050)	(0.029 - 0.031)	S
$\begin{array}{cccc} (0.571-2.93) & (1.08-8.45) & V\\ Zn & 15.2\pm1.21 & 13.1\pm0.265 & \\ (12.4-19.5) & (12.7-13.6) & Z\end{array}$	V	$1.89 \pm 0.366$	$4.25 \pm 2.19$	
Zn $15.2 \pm 1.21$ $13.1 \pm 0.265$ (12.4 - 19.5) (12.7 - 13.6) Z		(0.571 – 2.93)	(1.08 - 8.45)	ν
(12.4 – 19.5) (12.7 – 13.6) Z	Zn	$15.2 \pm 1.21$	$13.1 \pm 0.265$	
(		(12.4 – 19.5)	(12.7 – 13.6)	Z

$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Analyte	Adult Juvenile	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	-	(n = 8) (n =	
No $(0.315-4.03)$ $(0.264-0.377)$ Al $6.31 \pm 1.99$ $3.26 \pm 1.65$ $(2.50-19.3)$ $(0.544-8.07)$ As $0.611 \pm 0.115$ $0.698 \pm 0.207$ $(0.297-1.12)$ $(0.356-1.25)$ $Ba^a$ $0.046 \pm 0.004$ $0.026 \pm 0.002$ $(0.029-0.065)$ $(0.019-0.029)$ $Cd^a$ $6.55 \pm 2.12$ $0.106 \pm 0.093$ $(0.513-18.6)$ $(0.002-0.384)$ $Co^a$ $0.054 \pm 0.007$ $0.032 \pm 0.001$ $(0.033-0.084)$ $(0.031-0.035)$ $Cr$ $0.414 \pm 0.022$ $0.339 \pm 0.027$ $(0.352-0.495)$ $(0.271-0.388)$ $Cu$ $17.2 \pm 10.7$ $101 \pm 33.0$ $(1.67-90.2)$ $(10.5-157)$ $Fe$ $714 \pm 55.3$ $473 \pm 113$ $(572-1.016)$ $(155-679)$ $Hg^a$ $9.17 \pm 2.12$ $0.415 \pm 0.097$ $(1.31-17.9)$ $(0.210-0.623)$ $Li$ $0.016 \pm 0.008$ $0.021 \pm 0.012$ $(0.000-0.049)$ $(0.000-0.047)$ Mn $1.82 \pm 0.249$ $1.74 \pm 0.235$ $(0.020-0.666)$ $(0.016-0.039)$ $Pb^a$ $0.016 \pm 0.002$ $0.007 \pm 0.002$ $(0.009-0.024)$ $(0.000-0.09)$ Sb $0.171 \pm 0.004$ $0.160 \pm 0.006$ $(0.156-0.191)$ $(0.166-0.176)$ Se $11.0 \pm 1.55$ $6.74 \pm 1.70$ $(3.98-20.1)$ $(3.57-11.4)$ Sn <sup>a</sup> $0.221 \pm 0.044$ $0.000 \pm 0.0006$	Ag	$1.27 \pm 0.442$	$0.296 \pm 0.027$
Al $6.31 \pm 1.99$ $3.26 \pm 1.65$ As $0.611 \pm 0.115$ $0.698 \pm 0.207$ $0.250-19.3$ $0.544-8.07$ As $0.611 \pm 0.115$ $0.698 \pm 0.207$ $0.297-1.12$ $0.356-1.25$ $Ba^a$ $0.046 \pm 0.004$ $0.026 \pm 0.002$ $0.029-0.065$ $(0.019-0.029)$ $Cd^a$ $6.55 \pm 2.12$ $0.106 \pm 0.093$ $(0.513-18.6)$ $(0.002-0.384)$ $Co^a$ $0.054 \pm 0.007$ $0.322 \pm 0.001$ $(0.33-0.084)$ $(0.031-0.035)$ $Cr$ $0.414 \pm 0.022$ $0.339 \pm 0.027$ $(0.352-0.495)$ $(0.271-0.388)$ $Cu$ $17.2 \pm 10.7$ $101 \pm 33.0$ $(1.67-90.2)$ $(10.5-157)$ $Fe$ $714 \pm 55.3$ $473 \pm 113$ $(572-1.016)$ $(155-679)$ $Hg^a$ $9.17 \pm 2.12$ $0.415 \pm 0.097$ $(1.31-17.9)$ $(0.210-0.623)$ Li $0.016 \pm 0.008$ $0.021 \pm 0.012$ $(0.000-0.049)$ $(0.000-0.047)$ Mn $1.82 \pm 0.249$ $1.74 \pm 0.235$ $(0.020-0.666)$ $(0.016-0.039)$ $Pb^a$ $0.016 \pm 0.002$ $0.007 \pm 0.002$ $(0.009-0.024)$ $(0.000-0.009)$ Sb $0.171 \pm 0.004$ $0.160 \pm 0.006$ $(0.156-0.191)$ $(0.166-0.176)$ Se $11.0 \pm 1.55$ $6.74 \pm 1.70$ $(3.98-20.1)$ $(3.57-11.4)$ Sn <sup>a</sup> $0.221 \pm 0.044$ $0.000 \pm 0.0006$		(0.315-4.03)	(0.264-0.377)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Al	6.31 + 1.99	3.26 + 1.65
As $0.611 \pm 0.115$ $0.698 \pm 0.207$ $(0.297-1.12)$ $(0.356-1.25)$ $Ba^a$ $0.046 \pm 0.004$ $0.026 \pm 0.002$ $(0.029-0.065)$ $(0.019-0.029)$ $Cd^a$ $6.55 \pm 2.12$ $0.106 \pm 0.093$ $(0.513-18.6)$ $(0.002-0.384)$ $Co^a$ $0.054 \pm 0.007$ $0.332 \pm 0.001$ $(0.033-0.084)$ $(0.031-0.035)$ $Cr$ $0.414 \pm 0.022$ $0.339 \pm 0.027$ $(0.352-0.495)$ $(0.271-0.388)$ $Cu$ $17.2 \pm 10.7$ $101 \pm 33.0$ $(1.67-90.2)$ $(10.5-157)$ $Fe$ $714 \pm 55.3$ $473 \pm 113$ $(572-1.016)$ $(155-679)$ $Hg^a$ $9.17 \pm 2.12$ $0.415 \pm 0.097$ $(1.31-17.9)$ $(0.210-0.623)$ $Li$ $0.016 \pm 0.008$ $0.021 \pm 0.012$ $(0.000-0.049)$ $(0.000-0.047)$ Mn $1.82 \pm 0.249$ $1.74 \pm 0.235$ $(0.289-3.11)$ $(1.38-2.43)$ Ni $0.032 \pm 0.005$ $0.025 \pm 0.005$ $(0.020-0.66)$ $(0.016-0.039)$ $Pb^a$ $0.016 \pm 0.002$ $0.007 \pm 0.002$ $(0.009-0.024)$ $(0.000-0.09)$ Sb $0.171 \pm 0.004$ $0.160 \pm 0.006$ $(0.156-0.191)$ $(0.146-0.176)$ Se $11.0 \pm 1.55$ $6.74 \pm 1.70$ $(3.98-20.1)$ $(3.57-11.4)$ Sn <sup>a</sup> $0.221 \pm 0.044$ $0.000 \pm 0.000$		(2.50–19.3)	(0.544 - 8.07)
$\begin{array}{c cccc} & (0.297-1.12) & (0.356-1.25) \\ Ba^a & 0.046 \pm 0.004 & 0.026 \pm 0.002 \\ & (0.029-0.065) & (0.019-0.029) \\ Cd^a & 6.55 \pm 2.12 & 0.106 \pm 0.093 \\ & (0.513-18.6) & (0.002-0.384) \\ Co^a & 0.054 \pm 0.007 & 0.032 \pm 0.001 \\ & (0.033-0.084) & (0.031-0.035) \\ Cr & 0.414 \pm 0.022 & 0.339 \pm 0.027 \\ & (0.352-0.495) & (0.271-0.388) \\ Cu & 17.2 \pm 10.7 & 101 \pm 33.0 \\ & (1.67-90.2) & (10.5-157) \\ Fe & 714 \pm 55.3 & 473 \pm 113 \\ & (572-1.016) & (155-679) \\ Hg^a & 9.17 \pm 2.12 & 0.415 \pm 0.097 \\ & (1.31-17.9) & (0.210-0.623) \\ Li & 0.016 \pm 0.008 & 0.021 \pm 0.012 \\ & (0.000-0.049) & (0.000-0.047) \\ Mn & 1.82 \pm 0.249 & 1.74 \pm 0.235 \\ & (0.889-3.11) & (1.38-2.43) \\ Ni & 0.032 \pm 0.005 & 0.025 \pm 0.005 \\ & (0.020-0.666) & (0.016-0.039) \\ Pb^a & 0.016 \pm 0.002 & 0.007 \pm 0.002 \\ & (0.009-0.024) & (0.000-0.049) \\ Sb & 0.171 \pm 0.004 & 0.160 \pm 0.006 \\ & (0.156-0.191) & (0.146-0.176) \\ Se & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ & (3.98-20.1) & (3.57-11.4) \\ Sn^a & 0.221 \pm 0.044 & 0.000 \pm 0.000 \\ \end{array}$	As	$0.611 \pm 0.115$	$0.698 \pm 0.207$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(0.297-1.12)	(0.356-1.25)
$\begin{array}{c c} (0.029-0.065) & (0.019-0.029) \\ \hline Cd^a & 6.55 \pm 2.12 & 0.106 \pm 0.093 \\ (0.513-18.6) & (0.002-0.384) \\ \hline Co^a & 0.054 \pm 0.007 & 0.032 \pm 0.001 \\ (0.033-0.084) & (0.031-0.035) \\ \hline Cr & 0.414 \pm 0.022 & 0.339 \pm 0.027 \\ (0.352-0.495) & (0.271-0.388) \\ \hline Cu & 17.2 \pm 10.7 & 101 \pm 33.0 \\ (1.67-90.2) & (10.5-157) \\ \hline Fe & 714 \pm 55.3 & 473 \pm 113 \\ (572-1.016) & (155-679) \\ \hline Hg^a & 9.17 \pm 2.12 & 0.415 \pm 0.097 \\ (1.31-17.9) & (0.210-0.623) \\ \hline Li & 0.016 \pm 0.008 & 0.021 \pm 0.012 \\ (0.000-0.049) & (0.000-0.047) \\ Mn & 1.82 \pm 0.249 & 1.74 \pm 0.235 \\ (0.889-3.11) & (1.38-2.43) \\ \hline Ni & 0.032 \pm 0.005 & 0.025 \pm 0.005 \\ (0.020-0.666) & (0.016-0.039) \\ \hline Pb^a & 0.016 \pm 0.002 & 0.007 \pm 0.002 \\ (0.009-0.024) & (0.000-0.009) \\ \hline Sb & 0.171 \pm 0.004 & (0.160 \pm 0.006 \\ (0.156-0.191) & (0.146-0.176) \\ \hline Se & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ (3.98-20.1) & (3.57-11.4) \\ \hline Sn^a & 0.221 \pm 0.041 \\ \hline \end{array}$	Ba <sup>a</sup>	$0.046 \pm 0.004$	$0.026 \pm 0.002$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(0.029-0.065)	(0.019 - 0.029)
$\begin{array}{cccc} (0.513-18.6) & (0.002-0.384) \\ (0.032-0.084) & (0.032\pm 0.001 \\ (0.033-0.084) & (0.031-0.035) \\ (0.031-0.035) & (0.031-0.035) \\ (0.0352-0.495) & (0.271-0.388) \\ (0.0352-0.495) & (0.271-0.388) \\ (0.0352-0.495) & (0.271-0.388) \\ (0.0352-0.495) & (0.271-0.388) \\ (0.05-157) \\ Fe & 714\pm 55.3 & 473\pm 113 \\ (572-1.016) & (155-679) \\ Hg^a & 9.17\pm 2.12 & 0.415\pm 0.097 \\ (1.31-17.9) & (0.210-0.623) \\ Ii & 0.016\pm 0.008 & 0.021\pm 0.012 \\ (0.000-0.049) & (0.000-0.047) \\ Mn & 1.82\pm 0.249 & 1.74\pm 0.235 \\ (0.889-3.11) & (138-2.43) \\ Ni & 0.032\pm 0.005 & 0.025\pm 0.005 \\ (0.020-0.066) & (0.016-0.039) \\ Pb^a & 0.016\pm 0.002 & 0.007\pm 0.002 \\ (0.009-0.024) & (0.000-0.099) \\ Sb & 0.171\pm 0.004 & 0.160\pm 0.006 \\ (0.156-0.191) & (0.146-0.176) \\ Se & 11.0\pm 1.55 & 6.74\pm 1.70 \\ (3.98-20.1) & (3.57-11.4) \\ Sn^a & 0.221\pm 0.044 & 0.000\pm 0.0001 \\ \end{array}$	Cd <sup>a</sup>	$6.55 \pm 2.12$	$0.106 \pm 0.093$
$\begin{array}{cccc} {\rm Co}^{\rm a} & 0.054 \pm 0.007 & 0.032 \pm 0.001 \\ & (0.033-0.084) & (0.031-0.035) \\ {\rm Cr} & 0.414 \pm 0.022 & 0.339 \pm 0.027 \\ & (0.352-0.495) & (0.271-0.388) \\ {\rm Cu} & 17.2 \pm 10.7 & 101 \pm 33.0 \\ & (1.67-90.2) & (10.5-157) \\ {\rm Fe} & 714 \pm 55.3 & 473 \pm 113 \\ & (572-1.016) & (155-679) \\ {\rm Hg}^{\rm a} & 9.17 \pm 2.12 & 0.415 \pm 0.097 \\ & (1.31-17.9) & (0.210-0.623) \\ {\rm Li} & 0.016 \pm 0.008 & 0.021 \pm 0.012 \\ & (0.000-0.049) & (0.000-0.047) \\ {\rm Mn} & 1.82 \pm 0.249 & 1.74 \pm 0.235 \\ & (0.889-3.11) & (1.38-2.43) \\ {\rm Ni} & 0.032 \pm 0.005 & 0.025 \pm 0.005 \\ & (0.020-0.066) & (0.016-0.039) \\ {\rm Pb}^{\rm a} & 0.016 \pm 0.002 & 0.007 \pm 0.002 \\ & (0.009-0.024) & (0.000-0.009) \\ {\rm Sb} & 0.171 \pm 0.004 & 0.160 \pm 0.006 \\ & (0.156-0.191) & (0.146-0.176) \\ {\rm Se} & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ & (3.98-20.1) & (3.57-11.4) \\ {\rm Sn}^{\rm a} & 0.221 \pm 0.041 & 0.0005 \\ \end{array}$		(0.513-18.6)	(0.002 - 0.384)
$\begin{array}{cccc} (0.033-0.084) & (0.031-0.035) \\ (0.031-0.035) & (0.031-0.035) \\ (0.352-0.495) & (0.271-0.388) \\ (0.271-0.388) \\ (0.271-0.388) \\ (0.271-0.388) \\ (0.271-0.388) \\ (0.271-0.388) \\ (1.67-90.2) & (10.5-157) \\ Fe & (1.67-90.2) & (10.5-157) \\ Hg^a & 9.17\pm2.12 & 0.415\pm0.097 \\ & (1.31-17.9) & (0.210-0.623) \\ Ii & 0.016\pm0.008 & 0.021\pm0.012 \\ & (0.000-0.049) & (0.000-0.047) \\ Mn & 1.82\pm0.249 & 1.74\pm0.235 \\ & (0.889-3.11) & (1.38-2.43) \\ Ni & 0.032\pm0.005 & 0.025\pm0.005 \\ & (0.020-0.066) & (0.016-0.039) \\ Pb^a & 0.016\pm0.002 & 0.007\pm0.002 \\ & (0.009-0.024) & (0.000-0.09) \\ Sb & 0.171\pm0.004 & 0.160\pm0.006 \\ & (0.156-0.191) & (0.146-0.176) \\ Se & 11.0\pm1.55 & 6.74\pm1.70 \\ & (3.98-20.1) & (3.57-11.4) \\ Sn^a & 0.221\pm0.044 & 0.000\pm0.0001 \\ \end{array}$	Co <sup>a</sup>	$0.054 \pm 0.007$	$0.032\pm0.001$
$\begin{array}{cccc} {\rm Cr} & 0.414 \pm 0.022 & 0.339 \pm 0.027 \\ & (0.352-0.495) & (0.271-0.388) \\ {\rm Cu} & 17.2 \pm 10.7 & 101 \pm 33.0 \\ & (1.67-90.2) & (10.5-157) \\ {\rm Fe} & 714 \pm 55.3 & 473 \pm 113 \\ & (572-1.016) & (155-679) \\ {\rm Hg}^{\rm a} & 9.17 \pm 2.12 & 0.415 \pm 0.097 \\ & (1.31-17.9) & (0.210-0.623) \\ {\rm Li} & 0.016 \pm 0.008 & 0.021 \pm 0.012 \\ & (0.000-0.049) & (0.000-0.047) \\ {\rm Mn} & 1.82 \pm 0.249 & 1.74 \pm 0.235 \\ & (0.889-3.11) & (1.38-2.43) \\ {\rm Ni} & 0.032 \pm 0.005 & 0.025 \pm 0.005 \\ & (0.020-0.666) & (0.016-0.039) \\ {\rm Pb}^{\rm a} & 0.016 \pm 0.002 & 0.007 \pm 0.002 \\ & (0.009-0.024) & (0.000-0.09) \\ {\rm Sb} & 0.171 \pm 0.004 & 0.160 \pm 0.006 \\ & (0.156-0.191) & (0.146-0.176) \\ {\rm Se} & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ & (3.98-20.1) & (3.57-11.4) \\ {\rm Sn}^{\rm a} & 0.221 \pm 0.044 & 0.000 \pm 0.0001 \\ \end{array}$		(0.033-0.084)	(0.031-0.035)
$\begin{array}{c cccc} (0.352-0.495) & (0.271-0.388) \\ (0.271-0.388) \\ (1.72\pm10.7 & 101\pm3.0 \\ (1.67-90.2) & (10.5-157) \\ \hline Fe & 714\pm55.3 & 473\pm113 \\ (572-1.016) & (155-679) \\ \hline Hg^a & 9.17\pm2.12 & 0.415\pm0.097 \\ (1.31-17.9) & (0.210-0.623) \\ \hline Li & 0.016\pm0.008 & 0.021\pm0.012 \\ (0.000-0.049) & (0.000-0.047) \\ \hline Mn & 1.82\pm0.249 & 1.74\pm0.235 \\ (0.889-3.11) & (1.38-2.43) \\ \hline Ni & 0.032\pm0.005 & 0.025\pm0.005 \\ (0.020-0.666) & (0.016-0.039) \\ \hline Pb^a & 0.016\pm0.002 & 0.007\pm0.002 \\ (0.009-0.024) & (0.000-0.009) \\ \hline Sb & 0.171\pm0.004 & (0.160\pm0.006 \\ (0.156-0.191) & (0.146-0.176) \\ \hline Se & 11.0\pm1.55 & 6.74\pm1.70 \\ (3.98-20.1) & (3.57-11.4) \\ \hline Sn^a & 0.221\pm0.044 & 0.0005 \\ \hline \end{array}$	Cr	$0.414 \pm 0.022$	$0.339 \pm 0.027$
$\begin{array}{cccc} {\rm Cu} & 17.2 \pm 10.7 & 101 \pm 33.0 \\ & (1.67 - 90.2) & (10.5 - 157) \\ {\rm Fe} & 714 \pm 55.3 & 473 \pm 113 \\ & (572 - 1.016) & (155 - 679) \\ {\rm Hg}^{\rm a} & 9.17 \pm 2.12 & 0.415 \pm 0.097 \\ & (1.31 - 17.9) & (0.210 - 0.623) \\ {\rm Li} & 0.016 \pm 0.008 & 0.021 \pm 0.012 \\ & (0.000 - 0.049) & (0.000 - 0.047) \\ {\rm Mn} & 1.82 \pm 0.249 & 1.74 \pm 0.235 \\ & (0.889 - 3.11) & (1.38 - 2.43) \\ {\rm Ni} & 0.032 \pm 0.005 & 0.025 \pm 0.005 \\ & (0.020 - 0.666) & (0.016 - 0.039) \\ {\rm Pb}^{\rm a} & 0.016 \pm 0.002 & 0.007 \pm 0.002 \\ & (0.009 - 0.024) & (0.100 - 0.009) \\ {\rm Sb} & 0.171 \pm 0.004 & 0.160 \pm 0.006 \\ & (0.156 - 0.191) & (0.146 - 0.176) \\ {\rm Se} & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ & (3.98 - 20.1) & (3.57 - 11.4) \\ {\rm Sn}^{\rm a} & 0.221 \pm 0.044 & 0.000 \pm 0.0006 \\ \end{array}$		(0.352-0.495)	(0.271-0.388)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cu	$17.2 \pm 10.7$	$101\pm33.0$
$\begin{array}{ccccc} {\rm Fe} & & 714 \pm 55.3 & 473 \pm 113 \\ & & (572-1.016) & (155-679) \\ {\rm Hg}^{a} & & 9.17 \pm 2.12 & 0.415 \pm 0.097 \\ & & (1.31-17.9) & (0.210-0.623) \\ {\rm Li} & & 0.016 \pm 0.008 & 0.021 \pm 0.012 \\ & & (0.000-0.049) & (0.000-0.047) \\ {\rm Mn} & & 1.82 \pm 0.249 & 1.74 \pm 0.235 \\ & & (0.889-3.11) & (1.38-2.43) \\ {\rm Ni} & & 0.032 \pm 0.005 & 0.025 \pm 0.005 \\ & & (0.020-0.066) & (0.016-0.039) \\ {\rm Pb}^{a} & & 0.016 \pm 0.002 & 0.007 \pm 0.002 \\ & & (0.009-0.024) & (0.000-0.009) \\ {\rm Sb} & & 0.171 \pm 0.004 & 0.160 \pm 0.0006 \\ & & (0.156-0.191) & (0.146-0.176) \\ {\rm Se} & & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ & & (3.98-20.1) & (3.57-11.4) \\ {\rm Sn}^{a} & & 0.221 \pm 0.044 & 0.000 \pm 0.0001 \\ \end{array}$		(1.67–90.2)	(10.5-157)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe	$714 \pm 55.3$	$473 \pm 113$
$\begin{array}{cccc} Hg^a & 9.17 \pm 2.12 & 0.415 \pm 0.097 \\ (1.31 - 17.9) & (0.210 - 0.623) \\ Li & 0.016 \pm 0.008 & 0.021 \pm 0.012 \\ (0.000 - 0.049) & (0.000 - 0.047) \\ Mn & 1.82 \pm 0.249 & 1.74 \pm 0.235 \\ (0.889 - 3.11) & (1.38 - 2.43) \\ Ni & 0.032 \pm 0.005 & 0.025 \pm 0.005 \\ (0.020 - 0.066) & (0.016 - 0.039) \\ Pb^a & 0.016 \pm 0.002 & 0.007 \pm 0.002 \\ (0.009 - 0.024) & (0.000 - 0.009) \\ Sb & 0.171 \pm 0.004 & 0.160 \pm 0.006 \\ (0.156 - 0.191) & (0.146 - 0.176) \\ Se & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ (3.98 - 20.1) & (3.57 - 11.4) \\ Sn^a & 0.221 \pm 0.044 & 0.000 \pm 0.000 \\ \end{array}$		(572-1.016)	(155-679)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Hg <sup>a</sup>	$9.17\pm2.12$	$0.415\pm0.097$
$ \begin{array}{ccccc} \text{Li} & 0.016 \pm 0.008 & 0.021 \pm 0.012 \\ & (0.000-0.049) & (0.000-0.047) \\ \text{Mn} & 1.82 \pm 0.249 & 1.74 \pm 0.235 \\ & (0.889-3.11) & (1.38-2.43) \\ \text{Ni} & 0.032 \pm 0.005 & 0.025 \pm 0.005 \\ & (0.020-0.066) & (0.016-0.039) \\ \text{Pb}^{a} & 0.016 \pm 0.002 & 0.007 \pm 0.002 \\ & (0.009-0.024) & (0.000-0.009) \\ \text{Sb} & 0.171 \pm 0.004 & 0.160 \pm 0.006 \\ & (0.156-0.191) & (0.146-0.176) \\ \text{Se} & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ & (3.98-20.1) & (3.57-11.4) \\ \text{Sn}^{a} & 0.221 \pm 0.044 & 0.000 \pm 0.000 \\ \end{array} $		(1.31–17.9)	(0.210-0.623)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Li	$0.016 \pm 0.008$	$0.021\pm0.012$
$\begin{array}{cccc} Mn & 1.82 \pm 0.249 & 1.74 \pm 0.235 \\ (0.889 - 3.11) & (1.38 - 2.43) \\ Ni & 0.032 \pm 0.005 & 0.025 \pm 0.005 \\ (0.020 - 0.066) & (0.016 - 0.039) \\ Pb^a & 0.016 \pm 0.002 & 0.007 \pm 0.002 \\ (0.009 - 0.024) & (0.000 - 0.009) \\ Sb & 0.171 \pm 0.004 & 0.160 \pm 0.006 \\ (0.156 - 0.191) & (0.146 - 0.176) \\ Se & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ (3.98 - 20.1) & (3.57 - 11.4) \\ Sn^a & 0.221 \pm 0.044 & 0.000 \pm 0.000 \\ \end{array}$		(0.000-0.049)	(0.000-0.047)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mn	$1.82 \pm 0.249$	$1.74 \pm 0.235$
$ \begin{array}{cccc} Ni & 0.032 \pm 0.005 & 0.025 \pm 0.005 \\ & (0.020-0.066) & (0.016-0.039) \\ Pb^a & 0.016 \pm 0.002 & 0.007 \pm 0.002 \\ & (0.009-0.024) & (0.000-0.009) \\ Sb & 0.171 \pm 0.004 & 0.160 \pm 0.006 \\ & (0.156-0.191) & (0.146-0.176) \\ Se & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ & (3.98-20.1) & (3.57-11.4) \\ Sn^a & 0.221 \pm 0.044 & 0.000 \pm 0.000 \\ \end{array} $		(0.889-3.11)	(1.38-2.43)
$\begin{array}{cccc} (0.020-0.066) & (0.016-0.039) \\ (0.016\pm0.002 & 0.007\pm0.002 \\ (0.009-0.024) & (0.000-0.009) \\ \text{Sb} & 0.171\pm0.004 & 0.160\pm0.006 \\ (0.156-0.191) & (0.146-0.176) \\ \text{Se} & 11.0\pm1.55 & 6.74\pm1.70 \\ (3.98-20.1) & (3.57-11.4) \\ \text{Sn}^{a} & 0.221\pm0.044 & 0.000\pm0.000 \\ \end{array}$	Ni	$0.032 \pm 0.005$	$0.025 \pm 0.005$
$ \begin{array}{cccc} Pb^a & 0.016 \pm 0.002 & 0.007 \pm 0.002 \\ (0.009-0.024) & (0.000-0.009) \\ Sb & 0.171 \pm 0.004 & 0.160 \pm 0.006 \\ (0.156-0.191) & (0.146-0.176) \\ Se & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ (3.98-20.1) & (3.57-11.4) \\ Sn^a & 0.221 \pm 0.044 & 0.000 \pm 0.000 \\ \end{array} $		(0.020-0.066)	(0.016-0.039)
$\begin{array}{cccc} (0.009-0.024) & (0.000-0.009) \\ \text{Sb} & 0.171 \pm 0.004 & 0.160 \pm 0.006 \\ & (0.156-0.191) & (0.146-0.176) \\ \text{Se} & 11.0 \pm 1.55 & 6.74 \pm 1.70 \\ & (3.98-20.1) & (3.57-11.4) \\ \text{Sn}^{a} & 0.221 \pm 0.044 & 0.000 \pm 0.000 \\ \end{array}$	Pb <sup>a</sup>	$0.016 \pm 0.002$	$0.007\pm0.002$
Sb $0.171 \pm 0.004$ $0.160 \pm 0.006$ $(0.156-0.191)$ $(0.146-0.176)$ Se $11.0 \pm 1.55$ $6.74 \pm 1.70$ $(3.98-20.1)$ $(3.57-11.4)$ Sn <sup>a</sup> $0.221 \pm 0.044$ $0.000 \pm 0.000$		(0.009-0.024)	(0.000 - 0.009)
$(0.156-0.191)$ $(0.146-0.176)$ Se $11.0 \pm 1.55$ $6.74 \pm 1.70$ $(3.98-20.1)$ $(3.57-11.4)$ Sn <sup>a</sup> $0.221 \pm 0.044$ $0.000 \pm 0.000$	Sb	$0.171 \pm 0.004$	$0.160 \pm 0.006$
Se $11.0 \pm 1.55$ $6.74 \pm 1.70$ $(3.98-20.1)$ $(3.57-11.4)$ Sn <sup>a</sup> $0.221 \pm 0.044$ $0.000 \pm 0.000$	-	(0.156-0.191)	(0.146-0.176)
$\begin{array}{ccc} (3.98-20.1) & (3.57-11.4) \\ \text{Sn}^{a} & 0.221 \pm 0.044 & 0.000 \pm 0.000 \\ (0.000 \pm 0.000) & (0.000 \pm 0.000) \end{array}$	Se	$11.0 \pm 1.55$	$6.74 \pm 1.70$
$Sn^{a}$ 0.221 ± 0.044 0.000 ± 0.000		(3.98–20.1)	(3.57–11.4)
	Snª	$0.221 \pm 0.044$	$0.000 \pm 0.000$
(0.029–0.392) (0.000–0.000)		(0.029-0.392)	(0.000-0.000)
V $2.64 \pm 0.624$ $1.75 \pm 0.932$	V	$2.64 \pm 0.624$	$1.75 \pm 0.932$
(0.858-6.08) (0.243-4.47)	-	(0.858-6.08)	(0.243-4.47)
$\ln \frac{1}{12} \pm \frac{19}{12} = \frac{14.3 \pm 2.68}{12.2}$	Zn	$1/.1 \pm 1.97$	$14.3 \pm 2.68$
(9./0-20.1) (10.2-21.8)		(9.76-26.1)	(10.2-21.8)

n.d. = non-detected.

<sup>a</sup> Indicates adult value significantly greater than juvenile value.

to have higher Cd, Co, and Hg concentrations for adults. Additionally, adults had higher liver values for Ba, Pb, and Sn, and in adult kidney, As was higher.

When gender was considered (a higher percentage of immature animals were female) without regard for age, males generally had greater values in the kidney and liver for Fe. Male kidney samples also had higher concentrations for As, Li, and Se; male liver samples had higher concentrations of Al, Cr, Ni, and V. Female kidney samples had greater values for Mn and Cu. Concentration of Cd was higher for adult female kidney followed by liver.

Total animal length was positively correlated with Hg and Pb tissue concentrations. A linear trend with increasing concentration was also seen for Ba, Co, Fe, and Sn in the liver and Cd and Mn in the kidney. A negative correlation with length was observed for Cu in the liver. The strength of the relationships were rather weak (R<sup>2</sup> range: 0.45–0.73).

Analysis of the inter-elemental relationship between Hg and Se showed a strong positive correlation ( $R^2 = 0.79$ ) (Fig. 2). Selenium concentrations did not differ significantly among dwarf sperm whales in either tissue examined. Mercury values were highest for adults regardless of gender. Liver values exceeded kidney; adults had greater Hg:Se liver molar ratios than younger age classes. All individuals had Hg:Se molar ratios of less than 1:1, indicating an excess of Se. A molar excess of Se is considered to be protective against Hg toxicity (Ralston and Raymond, 2010).

Element concentrations for *K. sima* from the present study were compared with data reported for the more commonly stranded, similar size odontocete, the bottlenose dolphin (*Tursiops truncatus*). These

Indicates adult value significantly greater than juvenile.

animals had stranded along the South Carolina coast during 2000 – 2008 (Stavros et al., 2011). Average values of all elements analyzed for liver in *K. sima* are within an order of magnitude of those reported for *T. truncatus* liver. Although the ranges for Hg values for these two species overlap, average and maximum values for *T. truncatus* [34.3  $\pm$  58.9 µg/g (0.977–205)] exceed those for *K. sima* [6.25  $\pm$  1.86 µg/g (0.210–17.9)].

A lack of fundamental information on trace elements in *K. sima* warrants collection of baseline information on the type and concentration of elements in dwarf sperm whale tissues to establish benchmark comparisons, since bioaccumulation and toxicological effects may be species related. Establishing databases on contaminants in marine mammals can contribute to the understanding of their role in mortality events. With a high trophic level and long life span, marine mammals can be considered sentinels for monitoring spatial and temporal trends of contaminants and environmental health.

Limited information is available to assess the toxicological implications of metal concentrations in marine mammals. In some countries, humans consume cetacean products despite the health risk associated with Hg levels (Endo et al., 2002). In comparison with the US Food and Drug Administration (FDA) historical levels of concern for seafood (LOCs), As, Cr, Ni, and Pb concentrations were well below those levels for all animals studied (FDA, 1993a, 1993c, 1993d, and 1993e). However, Hg concentrations for all adult animals for both tissues exceeded the FDA LOC of  $1.0 \,\mu$ g/g (FDA, 1996), and most adult animals had Cd concentrations in both the kidney and liver exceeding the FDA LOC of  $3 \,\mu$ g/g (FDA, 1993b). Other studies of odontocetes have found Hg and Cd



Fig. 2. Relationship between Hg molar mass and Hg:Se molar ratio in livers of dwarf sperm whales, partitioned as a function of gender and age class.

concentrations 1–2 orders of magnitude higher in the liver and kidney in comparison with muscle tissue (Cardellicchio et al., 2000).

None of the stranded animals exceeded the minimum 100  $\mu$ g/g Hg threshold for hepatotoxicity in marine mammals (Wagemann and Muir, 1984). Data from the present study were also compared with immunotoxic thresholds for Hg (10  $\mu$ g/g) and Cd (20  $\mu$ g/g) shown to alter the functional activity of leukocytes in *T. truncatus* (Camara Pellisso et al., 2008). The Hg concentration for half of adult livers and one adult kidney exceeded the threshold, and one adult kidney exceeded the threshold, and cd exposure may suppress immunity and could be a contributing factor in health outcomes and susceptibility to disease in *K. sima*.

The present study provides data on baseline ranges of trace element concentrations in the tissues of stranded *K. sima* along the South Carolina coast. Trace element concentrations are within the range reported for another commonly stranded odontocete, which also showed age-related accumulation of Cd and Hg. Our results show a range of baseline metal concentrations in dwarf sperm whale kidney and liver that can occur in different age classes for both genders. Further studies are needed to assess the ecotoxicological hazard associated with the presence of trace elements in dwarf sperm whale tissues.

#### 1. NOAA disclaimer

The scientific results and conclusions, as well as any opinions expressed herein, are those of the author(s) and do not necessarily reflect the views of NOAA or the Department of Commerce. The mention of any commercial product is not meant as an endorsement by the Agency or Department.

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