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Concentrations and relative compositions of metallic elements differ between predatory squid and filter-feeding sardine from the Indian and South Atlantic oceans

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Highlights

- First assessment of metal concentrations in sardine and squid from South Africa
- Concentrations differed between organisms from the South Atlantic and Indian Oceans
- A number of metals occurred at higher concentrations in the predatory squid
- 'Fingerprint' analyses indicate possible stock discrimination for sardine and squid
- No mean concentrations exceeded recommended human intake limits

Key words: South Atlantic Ocean; Indian Ocean; muscle tissue; cadmium; mercury; lead.

Abstract

Although metallic elements occur naturally, they can occur or accumulate in organisms at levels toxic to the organism and/or their consumers. Concentrations of twenty-nine metallic elements in muscle tissue from sardine *Sardinops sagax* and chokka squid *Loligo reynaudii* from South Atlantic and Indian Ocean waters off South Africa were established, for the first time, using inductively-coupled plasma mass spectrometry. Chokka showed significantly higher ($p < 0.05$) concentrations of B, Cr, Zn, As, Se, Rb, Sr, Cd, and Tl and significantly lower concentrations of V, Mn, Ti, and Mo compared to sardine. There were also significant differences in some metallic elements between the two oceans. Multivariate analyses indicated possible population structure of both species, suggesting that these analyses may be useful as a stock discrimination tool. Only two sardine samples contained quantifiable Hg. Based on South African estimated daily intake, total hazard quotient, and European Union limits for Hg, Cd, and Pb, we consider tissues from sardine and chokka in South African waters to be safe for human consumption.

1. Introduction

The aquatic ecosystem is both a receiver and a reservoir for pollutants such as metals and persistent organic pollutants (Bouwman et al., 2015; Newman and Watling, 2007; Smita Achary et al., 2017). The uptake of pollutants by aquatic biota occurs through a dissolved state in water flowing over the body and gills, the organism's diet, or combinations thereof (Fernandez et al., 2014). Metallic elements occur in the environment naturally, or elevated above natural background levels due to pollution from mining, industry, and agriculture (du Preez et al., 2018; Greenfield et al., 2011; Nel et al., 2015; O'Donoghue and Marshall, 2003; Wepener and Degger, 2012). Fish and cephalopods are good bio-indicators of metallic elements because they occupy many trophic levels, can accumulate pollutants over long lifespans, and in some cases, exhibit severe effects (Jiang et al., 2018; Mziray and Kimirei, 2016; Viera et al., 2011). Organisms at higher trophic levels also tend to accumulate higher concentrations of pollutants, potentially making them more susceptible to the effects of excess pollutants such as metals (Fernandez et al., 2014), and passing them on to yet higher trophic levels.

South Africa is bordered by two oceans; the Indian Ocean on the east and south coasts, and the South Atlantic Ocean on the west coast, with these two oceans adjoining in the region of Cape Agulhas (20°E; Hutchings et al., 2009, Fig 1.). The upwelling of cold, nutrient-rich water onto the west coast shelf in the austral spring and summer and due to south easterly winds makes these waters in the South Atlantic Ocean highly productive. The south coast is impacted by the warm Agulhas Current at the shelf edge, shows shelf-edge and coastal upwelling, and is characterised by both easterly and westerly winds. Shelf waters are stratified in summer and mixed in winter. Circulation patterns are complex but create a clockwise eddy that circulates around a sub-surface cool ridge and acts as a retention area for phytoplankton and zooplankton (Hutchings et al., 2009), and likely also nutrients and metals.

The sardine *Sardinops sagax* is an economically and ecologically important fish (Beckley and van der Lingen, 1999) for the South African small pelagic fishery. Annual catches of sardines since 1990 ranged between 51,000 and 374,000 metric tons, and it is mainly canned for human consumption, pet food, and bait (DAFF, 2016). Sardines are prey to many predators such as Cape fur seals *Arctocephalus pusillus*, sea birds, and squids (Bouwman et al., 2015; Connan et al., 2017; Huisamen et al., 2012). Chokka or the Cape Hope squid *Loligo reynaudii* also supports a commercial fishery for human consumption (mostly export) and bait. Chokka are caught primarily with jigging from deck boats, and as by-catch in demersal trawls. Annual catches fluctuated between 2,700 and 13,300 metric tons between 2003 and 2015 (DAFF, 2016).

The South African sardine is primarily an indiscriminate filter feeder, feeding mostly on phytoplankton, zooplankton, and fish eggs (van der Lingen, 2002), making the sardine a primary and secondary consumer. Chokka are opportunistic predators during all life stages, with juveniles favouring crustaceans and adults feeding mostly on small pelagic fish and other cephalopods (Augustyn et al., 1994; Lipinski, 1992; Sauer and Lipinski, 1991). Because chokka feed on small pelagic fish as part of their diet, they occupy a higher trophic level than do sardines, as shown by stable isotope analyses; chokka had higher nitrogen stable isotope ratios ($\delta^{15}\text{N}$; an index of trophic level) (mean 13.8, trophic level 4.08) than did sardines (mean 11.1, trophic level 3.0; van der Lingen and Miller, 2011). While sardines would be exposed to and potentially accumulate metals via uptake from both water and ingestion of filtered food particles, chokka squid would be exposed to metals in water and

metals accumulated by their prey (likely including sardines), potentially resulting in higher body burdens. However, physiologically important elements may be regulated to stay within physiological limits, resulting in narrower concentration variations than in elements that are not so regulated (Emsley, 2003).

The aim of this study was to establish metallic element concentrations and patterns in sardine and chokka muscle tissues from the South Atlantic and Indian Ocean coasts of South Africa. We compare the concentrations within and between species from the same ocean, and compare within species between the two oceans. We also assess levels of three major toxic metals (cadmium (Cd), lead (Pb) and mercury (Hg)) for human consumer safety.

2. Methods and Materials

2.1. Sardine and chokka collection sites

Fig. 1. Map of sardine and chokka sample collection sites.

Sardine and chokka samples were received from the South African Department of Agriculture, Forestry, and Fisheries (DAFF). The sardine samples (SCS1 and SCS2; bottom depths 39 m and 68 m, respectively) were sourced from commercial catches (Figure 1) in March 2017. Sardine standard length ranged from 150-195 mm, while mass ranged from 51-120 g. One of the chokka samples (CCS1, bottom depth 162 m) was sourced from a commercial catch made in the Indian Ocean in November 2017. The other two chokka samples (CCS2 and CCS3, bottom depths 192 m and 145 m, respectively) were sourced from demersal trawls conducted during a research survey off the west coast in February 2017. Chokka total length ranged from 160-320 mm, and mass ranged from 45-504 g.

Fish and chokka were chilled on ice after capture. Whole samples were selected randomly for analyses, and then frozen. The sardine and chokka samples were couriered frozen from Cape Town and Port Elizabeth to the laboratory at the North-West University (NWU) in Potchefstroom, South Africa, where they were received frozen and stored in -20°C freezers pending analysis.

2.2. Dissection of sardine and chokka

We thawed sardine and chokka samples at room temperature until they were in workable condition (still firm). Sardine muscle tissue and chokka mantle (without skin) samples were taken and weighed to obtain wet mass (approximately 10 g) from both dorso-lateral sides of the fish and squid, and transferred to 50 ml high-density polypropylene centrifuge tubes. The weighed samples were first frozen and then freeze-dried for three days at 8 kPa and -50 °C. The freeze-dried samples were then weighed to obtain dry mass (approximately 2 g).

2.3. Analyses of sardine and chokka

Freeze-dried samples were analysed by Eco-Analytica at the North-West University (NWU). Accurately weighed tissue samples were dissolved in concentrated nitric acid, and microwave-digested with an Ethos UP microwave unit, as per the United States Environmental Protection Agency method 3051A. The sample and acid were placed in a fluorocarbon polymer vessel, sealed, and heat-digested in the microwave unit for 35 minutes.

A standard reference material (SRM) (ERM-CE278K – marine mussel tissue) was used as quality control (QC) with the same digestion protocol. We analysed the microwave-digested solutions using an Agilent 7500ce, inductively-coupled-plasma mass-spectrometer (ICP-MS), optimised with an aqueous solution containing cerium (Ce), lithium (Li), ytterbium (Y), and thallium (Tl) (1 µg/L) to reduce interference ($\leq 1.5\%$). Forward power was 1550 W, plasma gas flow was set at 15 l/min, the nebuliser gas flow was 1.2 l/min, and the sampling depth in the container was at 8 mm. We quantified twenty-nine elements.

For external calibration, we used ULTRASPEC-certified mixed multi-element standard solutions (De Bruyn Spectroscopic Solutions). Full calibration sets and QC-check standards were run. The QC check standard was a calibration standard of midrange concentration. Detection limits for each element analysed are indicated in table S1. Data are expressed as mg/kg dry mass (dm). Wet-mass based concentrations were calculated (mg/kg wm, see section 2.2) for comparisons with intake limits.

2.4. Statistical analysis

We tested data for normality using the Shapiro-Wilks normality test (GraphPad Prism 7.04; www.graphpad.com). Data that were not normally distributed were log-transformed. We used two-tailed t-tests to compare mean metal concentrations between the same species from different oceans, and between species from the same ocean. We used Kruskal-Wallis (unpaired, non-parametric, one-way ANOVA) to compare concentrations between the three chokka collection sites, using Dunn's test to correct for multiple comparisons.

For multivariate analyses, we used nonmetric-multidimensional-scaling (NMS) to ordinate the metal concentrations for species and collection sites (MjM Software PC-ORD version 7.03; www.pcord.com). The data were relativized per element to obtain proportional

elemental compositions per sample (or 'fingerprints'). Four axes were allowed. We selected Gower-ignore-0 as the distance measure. The maximum number of iterations allowed was 200. Fifty runs of real data were used with random starting configurations. Monte Carlo tests were then performed with randomised data, also using 50 runs. We used convex hulls to visualise relative elemental compositions of species and collection sites.

3. Results

3.1 Concentrations

We analysed 18 sardines and 15 chokka from the South Atlantic, and 12 sardines and ten chokka from the Indian Ocean. Recoveries of certified elements were within 20% of SRM certified values. Beryllium, Ni, Ag, Bi and Au were below detection limits in sardine muscle. Beryllium, Ni, Au and Bi were below detection limits in chokka muscle. Summary results of the 14 elements that had significantly different concentrations in the same species between oceans are presented in Table 1. Summarised data for all elements analysed per species and sample site are presented in Table S1.

3.2. Concentration differences between sardines from different oceans

Significant differences (un-paired, two-way t-tests; $p < 0.05$) were found between sardines from the two different oceans for mean concentrations of B, V, Cr, As, Se, Rb, Mo, Cd, and Ti (Table 1; Figures 2 and 3). Boron, V, Cr, Se, Mo, Cd, As, and Ti had significantly ($p < 0.05$) higher mean concentrations in sardines from the South Atlantic Ocean with only Rb showing significantly higher concentrations in fish from the Indian Ocean. Titanium, Mn, Zn, Co, and Sr mean concentrations were not significantly different between sardines from the two oceans (Figures 2 and 3).

3.3. Concentration differences between chokka from different oceans

We found significant differences (un-paired, two-way t-tests; $p < 0.05$) in mean concentrations between chokka from the Indian and South Atlantic oceans for Ti, V, Mn, Rb, and Sr. Chokka from the Indian Ocean had significantly higher mean concentrations of V, Rb, Mn, and Sr (Figures 2 and 3). Boron, Cr, Co, Zn, As, Se, Mo, Cd, and Ti showed no mean concentration differences between samples from the South Atlantic and Indian oceans.

3.4. Concentration differences between sardines and chokka per ocean

In both oceans, sardines had significantly (un-paired, two-way t-tests; $p < 0.05$) higher mean concentrations compared with chokka for V, Co, and Mo, and for Mn for the Atlantic Ocean only. Chokka had significantly higher (un-paired, two-way t-tests; $p < 0.05$) concentrations than sardines for B, Ti, Cr, Zn, As, Se, Rb, Sr, Cd, and Ti (Figures 2 and 3) in both oceans.

3.5. Multivariate analyses of relative elemental compositions of sardine and chokka per collection site

Two dimensions were needed to ordinate the relative elemental compositions in sardine muscle, with a final stress of 11.7, and a final instability of 0.00017, reached after 30 iterations (Figure 4). According to Clarke's rule of thumb (McCune and Grace, 2002), a final

stress between 10 and 20 presents a usable picture for interpretation. Sardine sample site 1 (SCS1, Indian Ocean) had a convex hull that did not overlap with SCS2 from the South Atlantic Ocean. SCS1 was characterised by higher relative proportions of Th, Sb, Pt, and Pb, while SCS2 was characterised by higher relative proportions of B, Ti, Mo, Cd, and V.

Three dimensions were needed to ordinate the relative elemental compositions in chokka muscle tissue, of which we show only two (Figure 5). The third dimension explained 21.8% of the variability. The final stress was 9.89, and the final instability was < 0.0001 , reached after 54 iterations. According to Clarke's rule of thumb (McCune and Grace, 2002), a final stress between 5 and 10 presents a good ordination with little risk of deriving false inferences. The chokka collection sites had distinctly different profiles, with especially CCS1 characterised by higher relative proportions of Mn, U, and V.

Table 1: Concentrations (mg/kg dm) of metallic elements in muscle tissue that had significantly different ($p < 0.05$) concentrations according to species and catch site.

Element	Organism	Indian Ocean			Atlantic Ocean		
		N	Mean	SD	N	Mean	SD
B	Sardine	8	0.73	0.82	18	1.5	0.67
B	Chokka	10	5.2	2.8	15	5.5	1.1
Ti	Sardine	12	18	2.7	18	17	2.3
Ti	Chokka	10	21	1.2	15	23	2.1
V	Sardine	12	0.29	0.17	18	2.0	0.96
V	Chokka	10	0.12	0.078	15	0.039	0.028
Cr	Sardine	12	0.61	0.064	18	0.66	0.069
Cr	Chokka	10	1.6	0.21	15	1.6	0.18
Mn	Sardine	12	2.2	1.0	18	2.3	0.93
Mn	Chokka	10	2.6	1.3	15	1.1	0.16
Co	Sardine	12	0.078	0.032	18	0.083	0.036
Co	Chokka	10	0.027	0.0064	15	0.022	0.011
Zn	Sardine	12	27	13	18	21	4.0
Zn	Chokka	10	46	3.1	15	47	2.4
As	Sardine	12	2.7	0.60	18	4.1	0.95
As	Chokka	10	17	6.1	15	17	2.7
Se	Sardine	12	1.2	0.17	18	1.6	0.28
Se	Chokka	10	2.8	0.63	15	2.8	0.35
Rb	Sardine	12	3.6	0.26	18	3.1	0.25
Rb	Chokka	10	11	0.82	15	8.4	1.2
Sr	Sardine	12	5.1	2.9	18	5.7	1.7
Sr	Chokka	10	15	2.5	15	13	2.0
Mo	Sardine	12	0.056	0.025	18	0.49	0.22
Mo	Chokka	10	0.034	0.0079	15	0.038	0.011
Cd	Sardine	12	0.18	0.13	18	0.30	0.17
Cd	Chokka	10	1.8	1.3	15	2.7	2.2
Tl	Sardine	12	0.034	0.028	17	0.11	0.022
Tl	Chokka	10	0.21	0.085	14	0.21	0.044

ANOVAs for the three chokka collection sites indicated significantly (Kruskal-Wallis, one-way ANOVA; $p < 0.05$) higher median concentrations of V, Mn, Rb, and Sr in CCS1. Significantly (Kruskal-Wallis, one-way ANOVA; $p < 0.05$) higher concentrations of Ti were found in CCS2 and CCS3. Other mean elemental concentrations were not significantly different between the chokka collection sites.

Fig. 2. Scatterplots and results of two-way, unpaired t-tests between logical pairs for elements that showed significant differences: Between sardines (red symbols) from each ocean, between chokka (blue symbols) from each ocean, and between sardines and chokka from the same ocean. Means and standard deviations are indicated. SAO = South Atlantic Ocean; IO = Indian Ocean.

Fig. 3. Scatterplots and results of two-way, unpaired, t-tests between logical pairs for elements that showed significant differences: Between sardines (red symbols) from each ocean, between chokka from each ocean, and between sardines and chokka from the same ocean. Means and standard deviations are indicated. SAO = South Atlantic Ocean; IO = Indian Ocean.

Fig. 4. Nonmetric multidimensional scaled (NMS) ordination of relativized metal concentrations (using Gower- ignore-0 as distance measure) for sardine muscle tissue.

Fig. 5. Nonmetric multidimensional scaled (NMS) ordination of relativized metal concentrations (using Gower- ignore-0 as distance measure) for chokka mantle tissue.

4. Discussion

4.1. Concentration differences between sardines from different oceans

Oceanographic conditions along the South African coast vary substantially both in time and space (Hutchings et al., 2009; Hampton et al., 2018) influencing the occurrence and numbers even of such widespread species as the sardine. Human activities may also influence the occurrence of various species, as will be discussed in section 4.3.

We found that sardine muscle tissue had significantly higher mean concentrations of Mo, Cd, Ti, B, V, Cr, As, and Se in the South Atlantic Ocean compared with the Indian Ocean, while the reverse was true for Rb (Figures 2 and 3). Metallic element concentrations in organisms can be influenced by age, sex, size, feeding habits, and habitats (Griboff et al., 2018). For instance, B occurs at higher concentrations in zooplankton than in phytoplankton (EPA, 1998).

SCS2 was in the South Atlantic Ocean, which is known for upwelling events during austral spring and summer (Hutchings et al., 2009). Upwelling is known to increase metallic elements (especially Cd) in water (Jiang et al., 2017) which can then be incorporated into fish muscle tissue and otoliths. This seasonal upwelling would result in increased plankton and hence more food for sardines (Bode et al., 2018). Since plankton take up metallic elements effectively from their environment (Sanders and Riedel, 1998), sardines at SCS2 may be exposed to higher concentrations via plankton compared with sardines from SCS1.

Sardines are primarily indiscriminate filter feeders. While phytoplankton is the most commonly-ingested prey, zooplankton provides most of the fish's sustenance in both the South Atlantic and Indian oceans (van der Lingen, 2002). Spatial variability in sardine diet is apparent, with phytoplankton and smaller zooplankton more important in the South Atlantic Ocean (van der Lingen, 2002; Idris et al., 2016). This difference in diet, and spatial differences in natural background concentrations arising from different oceanographic conditions and anthropogenic sources, may explain the differences in sardine muscle metallic concentrations between collection sites. Similar background concentrations (Newman and Watling, 2007) or physiological regulation (Emsley, 2003) may explain the lack of significant differences of other elements.

4.2. Concentration differences between chokka from different oceans

Significant differences were found for V, Mn, Rb, Sr and, Ti between chokka collection sites (Table 2). Vanadium, Mn, Rb, and Sr had significantly ($p < 0.05$) higher concentrations in the Indian Ocean, and Ti had a significantly ($p < 0.05$) higher concentration in the South Atlantic Ocean. As mentioned in section 4.1, the species included in this study are exposed to an ever-changing environment in the oceans around South Africa, and we show clear mean concentration differences. Apart from the natural background levels, the geographic distribution of anthropogenic sources (discussed in 4.3) of elements probably also explains the differences found.

4.3. Possible sources

4.3.1. Geological background

The predominant geology of the land mass close to the catch sites is dominated by the Cape Supergroup that can be subdivided into three groups the Table Mountain Group, the Bokkeveld Group, and the Witteberg Group (Shone and Booth, 2005). These groups are mostly made up sedimentary rocks containing quartz and quartz arenites (Shone and Booth, 2005). These groups would mostly contribute Si, Na, Ca, and Al to the surrounding waters as these elements are the most abundant minerals found in quartz (Klein and Philpotts, 2013). The fairly uniform geology of the mainland does not provide an explanation for the differences in metal concentrations found in this study.

4.3.2. Anthropogenic sources

Natural processes are not the only factor that affect the elemental composition of the world's oceans. South Africa is a mineral-rich country (V, Mn, and Ti [DMR, 2008, 2013]) and a high proportion of her income is derived by the mining and processing of metals (Minerals Council of South Africa, 2018). Metals from combustion, consumer products, and other sources (Table 2) can enter rivers and eventually oceans through run-off and atmospheric deposition (AMAP, 2005; Odiyo, et al., 2005; Dallas and Day, 2004; Fatoki and Mathabatha, 2001). Terrestrial and freshwater pollution, which is widely reported in South Africa (Wepener and Degger, 2012; O'Donoghue and Marshall, 2003), could therefore have affected the concentrations found in our study.

For instance, the Port Elizabeth and Kouga harbours and associated estuaries are potential sources of metals to the Indian Ocean from industries and ore loading (Nel et al., 2015; Fig. 1). Hence, we expected higher metallic element concentrations at the nearby sardine and chokka collection sites, which, indeed, we found for Pb in sardines from SCS1 (Table S1).

Table 2. Possible anthropogenic sources of metals that were significantly different between sites and species in oceans.

Metallic elements	Possible anthropogenic sources	References
B	Combustion of coal and biomass, soap, fertilizer, and flame retardants	Park and Schlesinger, 2002.
Ti	Mining, manufacturing of paints, fiber, and cosmetics	Reimann and de Caritat, 1998
V	Mining and the combustion of petroleum and coal	Schelsinger et al., 2017
Cr	Electroplating, paint, agriculture, combustion of fossil fuels and waste	He et al., 2005, Mzimela et al., 2014
Mn	Mining, dry cell batteries, and animal feed	Richir and Gobert, 2016
Zn	Agriculture (pesticide), wastewater, and galvanic industry	Neff, 2002, van Aswegen et al., 2019
As	Timber treatment, agriculture(pesticide) and burning of fossil fuels	Tchonwou et al., 2012, Lesch and Bouwman., 2018
Se	Mining, agriculture and combustion of fossil fuel	Wen and Carignan, 2007
Mo	Mining and agricultural runoff	Reimann and de Caritat, 1998
Cd	Batteries, paints, agricultural runoff, mining and the combustion of fossil fuels	Yuan et al., 2019
Tl	Mining and coal combustion	Karbowska, 2016

Although naturally occurring in the ocean, Cd, As, Tl, Mo, and Se can be anthropogenically increased by mining and industry (Karbowska, 2016; Kehrig et al., 2013; Oremland and Stolz, 2003; Satarug et al., 2003). These elements occurred at higher concentrations in sardines collected in the South Atlantic, and Cd was also higher for chokka there compared to the Indian Ocean. Although upwelling could have caused the higher concentrations, this does not dismiss the possible contribution from anthropogenic sources.

Large deposits of Mn are found in the North Cape (west coast) (DMR, 2013) which could have affected the concentrations found in our study. However, this was not the case as significantly higher concentrations of Mn were found in chokka from the Indian Ocean (CCS1). This could be due to the influence of Mn nodules found in the mid-Indian Ocean (Bollman et al., 2010).

Our data therefore indicate that the concentrations found in our study cannot be attributed to either natural background or anthropogenic activity as major sources, but rather a combination of these two, the relative contributions of which we do not know. Indications of relative contributions may be needed when comparing anthropogenic and natural halogenated organic compounds with metals in marine organisms from the two oceans (Aznar-Alemany et al., 2019; Bouwman et al., 2015; Van Aswegen et al., 2019; Wu et al., 2019).

4.4. Differences in concentrations between sardine and chokka

We found significantly higher ($p < 0.001$) concentrations of B, Ti, Cr, Zn, As, Se, Rb, Sr, Cd, and Tl in chokka when compared with sardines (Figures 2 and 3), suggesting accumulation in chokka from their prey. Loliginid species are believed to accumulate most of their metallic elements via the trophic pathway (Penicaud, 2017). Other prey items are likely to reflect similar local conditions, contributing towards consistently higher concentrations and accumulation in chokka, despite inter-ocean differences. However, sardines had significantly ($p < 0.001$) higher concentrations of Mn, Mo, V, and Co than chokka, suggesting physiological regulation by either or both. A contributing explanation could be that Co and V accumulate in the brachial heart of loliginid species (Penicaud, 2017) and may cause these elements to be lower in the muscle tissue.

Manganese is incorporated into loliginid eggs (Penicaud, 2017) suggesting a possible reason why Mn concentrations were lower in the chokka mantle tissue as these samples were caught in the austral summer when chokka lay their eggs. Chokka could also incorporate these elements into the gladius – this, however, has not been tested before. Different tissues should be analysed in the future as loliginids build up stores of metallic elements in the brachial heart and the digestive gland (Penicaud, 2017). This information could be crucial in understanding the accumulation of metallic elements in squids in general.

No study has been done on the relationship of metallic elements in muscle tissue between sardine and any squid in the Southern Hemisphere. Comparison with studies from elsewhere indicates similarities and differences (Table 3). Rubidium has been found at higher concentrations in higher trophic levels in aquatic ecosystems (Campbell et al., 2005a, b). Zinc has been shown to accumulate through trophic levels by several studies, some using stable isotope analyses (Campbell et al., 2005b; Chen et al., 2000; Quinn et al., 2003; Trevizani et al., 2018; Tu et al., 2012). Lower concentrations in higher trophic levels have been found for Mn (Griboff et al., 2018; Hao et al., 2013).

On the other hand, and contrary to our findings, other studies found lower concentrations in higher trophic levels for Zn (Besser et al., 2001; Jara-Marini et al., 2009; Borrell et al.,

2016), Cd (Guo et al., 2016; Campbell et al., 2005b), Cr (Revenga et al., 2012), and As (Trevizani et al., 2018; Chen et al., 2000). Differences in food web structure, and probably differences in the physiologies of molluscs (chokka) and vertebrates (sardine), where invertebrate molluscs feed on vertebrates, are likely contributory factors. Little information is available about the possible accumulation B, Ti, Se and, Sr; more research on the trophic differences of these elements is required.

Our data are not directly comparable with the findings of others, as different trophic systems may react to metallic elements in different ways. Analysing more samples, more species from more trophic levels (e.g., plankton, sharks, and tuna) from more sites, and increasing the number of samples from different trophic levels within the same systems (the Indian and South Atlantic oceans in this case) would be needed for clarification.

4.5. Multivariate analyses of relative elemental compositions of sardine and chokka per collection site

Clear ‘fingerprint’ differences in metallic element compositions were seen between the two sardine sites (Figure 4). These differences can be attributed to many factors mentioned in section 4.1 and 4.3. Although we only had two sardine sampling sites, our data supports the hypothesis of multiple sardine stocks off South Africa. Multiple stocks are also implied by other studies that compared morphometric, meristic, genetic, and parasite load characteristics of sardines from the west, south, and east coasts (Groenewald et al., 2019; Idris et al., 2016; Teske et al., 2018; van der Lingen et al., 2015; Weston et al., 2015). A recent study (Hampton et al., 2018) showed that otolith microchemistry of South African sardine juveniles differed between collection sites in the same ocean - most of the compositional differences were site specific and varied annually. Our study had a smaller sample size and only two collection sites and could not indicate if these differences were gradual (supporting a single stock assumption) or discontinuous (indicating multiple stocks) along the coast of South Africa. Larger samples sizes and more collection sites would confirm and be able to track different stocks using muscle tissue elemental concentrations as an easy alternative to otolith microchemistry, morphometrics, and parasite composition, or complement these methods.

Chokka collection sites had relative elemental composition profiles that did not overlap (Figure 5), and ANOVAs and t-tests showed that only a few elements (V, Mn, Rb, Ti) differed in mean concentration between the collection sites. These differences in compositions could be explained by different prey at the different collection sites, as prey is a crucial pathway of metallic elements in loliginids. Although spatial differences in metallic element compositions in chokka were not as large as those seen in sardines, the non-overlapping compositions (Figure 5) between chokka collection sites supports the hypothesis of multiple stocks in this species. Chokka from around southern Africa appear to be genetically uniform (Shaw et al., 2010) but show significant morphometric diversity (van der Vyver et al., 2015), leading to the hypothesis that chokka off southern Africa is a large and mobile metapopulation, that comprises three main geographic groups, two of which are off South Africa (Lipinski et al., 2016). Again, data from more samples from more sites would be needed to confirm this.

4.6. Comparisons with similar studies

We selected three well-known toxic metals that are regularly reported in literature (Cd, Pb, Hg) and compared our findings with other studies (Table 3). Studies were chosen with similar taxa as this is the first time metallic elemental data is presented for *Loligo reynaudii*, and only the third study published on *Sardinops sagax*. *Loligo vulgaris* was chosen as the species to compare to chokka as *L. reynaudii* was previously classified as a subspecies of *L. vulgaris*. *Sardina pilchardus* was chosen as another comparative species for sardine because of its similar feeding habits as *Sardinops sagax* (Garrido and van der Lingen, 2014). Sardines from the South Atlantic Ocean (SCS2) and Indian Ocean (SCS1) collection sites had the second and third highest Cd, and third and second highest Pb concentrations of the studies that were compared. Only two of our sardine samples had quantifiable Hg, and these values were the lowest of all the studies we compared. Cadmium concentrations in chokka were the highest, and Hg the second highest, when compared with other studies, indicating either a high natural background, pollution, or both.

Table 3 Global comparison of Hg, Pb and Cd (mg/kg wm) in sardine (*Sardina pilchardus* and *Sardinops sagax*) and chokka (*Loligo vulgaris* and *L. reynaudii*) with limits set by the European Union (EU) and the South African government for these metals.

Species	Location	Cd	Pb	Hg	Reference
<i>Sardina pilchardus</i>	Adriatic Sea	0.02	0.03	0.07	Storeli (2008)
<i>Sardina pilchardus</i>	North Atlantic Ocean	0.024	0.076	0.084	Chahid et al. (2014)
<i>Sardina pilchardus</i>	Atlantic Ocean	0.0064	0.03	0.019	Viera et al. (2011)
<i>Sardina pilchardus</i>	Mediterranean Sea	0.002-0.1	0.01-0.08	0.07-0.09	Falco et al. (2006)
<i>Sardinops sagax</i>	Bass Strait (Australia)	0.096	0.013	0.034	Finger et al. (2017)
<i>Sardinops sagax</i>	Bass Strait (Australia)	0.018	0.034	0.034	Finger et al. (2017)
<i>Sardinops sagax</i>	Arabian Gulf	0.037	0.005	<LOQ	Tawfik (2013)
<i>Sardinops sagax</i>	Indian Ocean (SCS1)	0.052	0.052	0.0049	This study
<i>Sardinops sagax</i>	South Atlantic Ocean (SCS2)	0.078	0.044	0.00057	This study
EU limits (Sardine)		0.25	0.3	0.5	EU (2006; 2014)
RSA limits (Sardine)		1	0.5	0.5	South Africa (1997)
<i>Loligo vulgaris</i>	Adriatic Sea	0.26	0.03	0.02	Storeli (2008)
<i>Loligo vulgaris</i>	Mediterranean Sea	0.05-0.15	0.01-0.01	0.02-0.03	Falco et al. (2006)
<i>Loligo vulgaris</i>	Pacific Ocean	0.29	0.04	<LOQ	Sangiuliano et al. (2017)
<i>Loligo vulgaris</i>	Mediterranean Sea	0.3	0.05	0.11	Storeli (2010)
<i>Loligo reynaudii</i>	Indian Ocean (CCS1)	0.38	0.04	0.03	This study
<i>Loligo reynaudii</i>	South Atlantic Ocean (CCS2)	0.72	0.036	0.056	This study
<i>Loligo reynaudii</i>	South Atlantic Ocean (CCS3)	0.66	0.04	0.05	This study
EU limits (Chokka)		1	1	0.5	EU, 2006; EU, 2014
RSA limits (Chokka)		3	4	0.5	South Africa, 1997

4.7. Seafood safety

Metal concentrations found in muscle tissue of sardine and chokka did not exceed the limits (despite marginal exceedances for Cd in two chokka samples) set by both the European Union (EU) and the South African government (Table 3) for Pb, Hg and Cd. No

other elements have similar standards except for Sn, but this is for canned fish only, hence not applicable here.

Estimated daily intakes (EDIs) and total hazard quotients (THQs) were calculated according to the formulae used by Beheary and El-Matary (2018). The average mass and lifespan of a South African resident was selected at 70 kg and 72.7 years, respectively. The daily intake of sardine was estimated to be 0.0006 kg/day, and the chokka daily intake was estimated to be at 0.00018 kg/day for South African residents (WWF, 2014). The THQ values (Table 4) were all orders of magnitude below the quotient of unity and would thus pose no threat to consumers based on our assumptions. For Cd, Pb, and Hg, sardine and chokka should be considered safe for human consumption and export, but more samples from more locations would add weight to our findings.

Table 4: Estimated daily intakes (EDIs) and total hazard quotients (THQs) for cadmium, lead and mercury measured in sardine and chokka from each catch site.

Catch sites	Cd EDI	Cd THQ	Pb EDI	Pb THQ	Hg EDI	Hg THQ
SCS1	0.0000043	0.0043	0.0000043	0.0012	0.00000040	0.00013
SCS2	0.0000064	0.0064	0.0000036	0.0010	0.000000047	0.000016
CCS1	0.00000094	0.00094	0.0000001	0.000029	0.000000074	0.000047
CCS2	0.0000018	0.0018	0.000000074	0.000021	0.00000014	0.00004
CCS3	0.0000016	0.0016	0.0000001	0.000029	0.00000012	0.028

5. Conclusions

Globally, marine fish and cephalopods are important food sources and are ecologically important. This is the first study to report on the metallic element composition in sardine muscle and chokka mantle tissues from the African coast, with previous studies only done on Hg in seafood in South African supermarkets (Bosch et al., 2016).

Different sites showed considerable differences in metallic element composition for sardines and chokka. Due to different oceanographic conditions around South Africa, with upwelling substantially more important on the west coast, the background concentrations of metals may vary, resulting in variable metal concentrations in fish and squid.

Although based on only two collection sites, metallic element concentration differences did not contradict a multiple stock assumption for sardine. Although spatial differences in chokka metallic element composition were not as marked as in sardine, our data also support a multiple stock hypothesis for chokka. Metallic elements could therefore be investigated as a stock discrimination tool for both of these species. Boron Cr, Zn, As, Se, Rb, Sr, Cd, and, Ti had significantly higher ($p < 0.0001$) concentrations in chokka than sardines, indicating possible accumulation by chokka. Vanadium, Mn, Ti, and, Mo concentrations were significantly lower ($p < 0.0001$) in chokka than sardines, indicating physiological regulation of these elements in chokka.

Chokka and sardines from South Africa, although based on a limited sample size, can be considered safe for human consumption in terms of the concentrations of Pb, Hg, and Cd. We recommend that future studies of the metallic element composition of South African marine biota increase the number of species from different trophic levels, increase the number of sites, and use larger sample sizes to investigate trophic level interactions and the utility of this method as a stock discrimination tool for fisheries management.

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Further reading

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Table S1.

Mean concentrations of metallic elements in sardine (SCS) and chokka (CCS) muscle tissue per site (mg/kg dry mass) with the detection limit of each element analysed. Elements not mentioned in text are presented for archival purposes.

		SCS1		SCS2		CCS1		CCS2		CCS3	
	LOD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
B	0.0025	0.73	0.82	1.5	0.67	5.2	2.8	5.7	1.7	5.5	0.76
Mg	0.00003	1800	230	2100	220	3900	400	3400	270	3900	580
Al	0.0018	7.4	4.5	9.5	5.8	4.1	1.7	3.3	2.5	3.9	3.2
P	0.00094	11000	1800	11000	1400	12000	600	1300	1400	12000	800
K	0.0034	22000	2400	19000	2400	17000	1100	16000	1400	16000	900
Ti	0.000041	18	2.7	17	2.3	21	1.2	23	2.8	23	1.8
V	0.000029	0.30	0.17	2.0	0.96	0.10	0.077	0.020	0.0042	0.048	0.031
Cr	0.00089	0.61	0.064	0.66	0.069	1.6	0.21	1.6	0.10	1.6	0.22
Mn	0.000016	2.2	1.0	2.3	0.93	2.6	1.3	1.0	0.19	1.0	0.15
Fe	0.0011	50	10	53	12	10	1.3	8.0	2.7	9.0	1.8
Co	0.000008	0.079	0.032	0.083	0.036	0.027	0.0060	0.013	0.0039	0.026	0.010
Cu	0.000012	3.5	0.68	3.2	0.41	20	8.9	21	7.9	15	3.2
Zn	0.000076	27	13	21	4.2	46	3.1	46	1.9	48	2.4
As	0.000012	2.7	0.55	4.1	0.95	17	6.1	13	2.1	17	2.1
Se	0.00011	1.2	0.17	1.6	0.28	2.8	0.63	2.8	0.53	2.7	0.25
Rb	0.0000023	3.6	0.26	3.1	0.25	11	0.82	8.0	0.76	9.0	1.4
Sr	0.0000056	5.0	2.8	5.7	1.7	15	2.5	11	2.1	13	1.6
Mo	0.0000023	0.056	0.025	0.49	0.22	5.2	2.8	5.7	1.7	5.4	0.76
Pd	0.00000098	0.010	0.015	0.0020	0.0024	0.011	0.0021	0.0079	0.0024	0.012	0.0066
Ag	0.0000098	<LOQ	<LOQ	<LOQ	<LOQ	0.40	0.34	0.65	0.32	0.41	0.15
Cd	0.000032	0.18	0.13	0.30	0.17	1.8	1.3	1.6	0.70	3.3	2.5
Sb	0.0000040	0.0040	0.0020	0.0048	0.0040	0.0090	0.0029	0.0062	0.0011	0.0068	0.0017
Ba	0.000021	0.42	0.19	0.68	0.25	0.16	0.052	0.014	0.024	0.17	0.063

Pt	0.0000062	0.0040	0.0042	0.0012	0.0017	0.011	0.0072	0.011	0.0056	0.0074	0.0052
Hg	0.0000085	0.0049	0.061	0.00057	0.0065	0.15	0.12	0.28	0.27	0.025	0.081
Tl	0.0000093	0.026	0.0065	0.11	0.022	0.21	0.044	0.17	0.036	0.21	0.086
Pb	0.0000013	0.20	0.22	0.17	0.10	0.20	0.042	0.18	0.032	0.20	0.081
Th	0.0000023	0.0080	0.0098	0.0086	0.0067	0.0040	0.0011	0.0031	0.0012	0.0032	0.0014
U	0.0000011	0.0060	0.0054	0.0061	0.0033	0.0066	0.0041	0.0023	0.0019	0.0052	0.0017